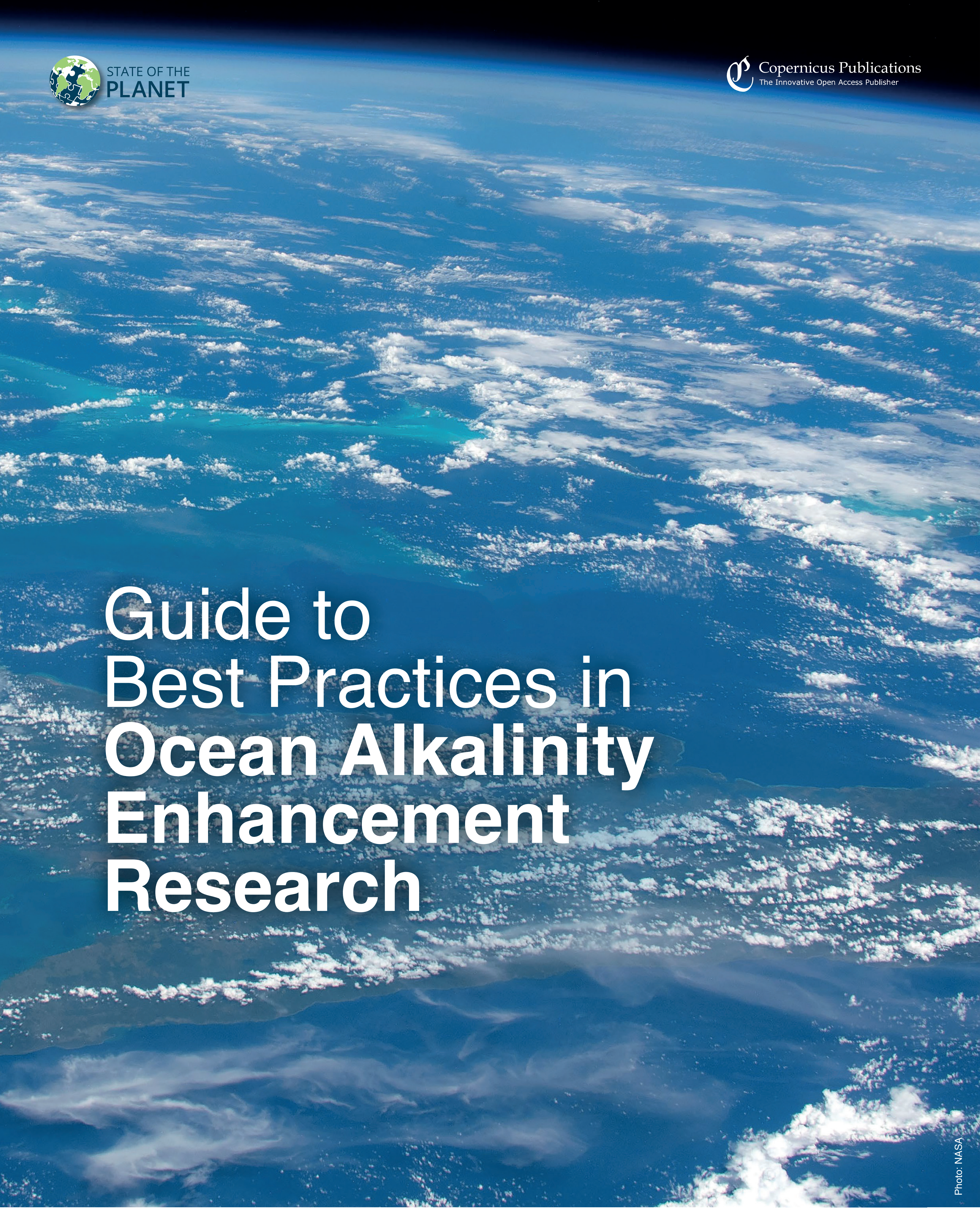

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STATE OF THE PLANET

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Guide to Best Practices in **Ocean Alkalinity Enhancement Research**

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About the Best Practices in Ocean Alkalinity Enhancement Research

Ocean alkalinity enhancement (OAE) is a marine carbon dioxide removal (CDR) approach. Publicly funded research projects have begun, and philanthropic funding and start-ups are collectively pushing the field forward. This rapid progress in research activities has created an urgent need to learn if and how OAE can work at scale. The Best Practices Guide to OAE research contains 7 topics broken down into 13 chapters that compare and synthesise previously published methods and offer guidance for future research.

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Editorial

A key objective of the Paris Agreement is to limit global warming to well below 2 °C and pursue efforts to limit such warming to 1.5 °C. All scenarios assessed by the Intergovernmental Panel on Climate Change (IPCC) compatible with this goal require the removal of a substantial amount of carbon dioxide (CO_2) on the order of 100–1000 Gt CO_2 over the 21st century, already reaching annual removal rates at the gigatonne scale within a decade (IPCC, 2018). Ocean alkalinity enhancement (OAE) is a marine carbon dioxide removal (mCDR) approach that, based on theoretical studies, might have the potential to deliver a significant portion of the required CO_2 removal. Publicly funded research projects have begun, and more projects receiving philanthropic funding as well as start-ups are emerging. Together they are accelerating the scientific understanding of OAE and pushing the field forward. Increasing research activities, as well as the urgency to learn if and how OAE can work at a larger scale well before the middle of the century, have created the need for a "best-practice guide" to OAE research. The present "Guide to Best Practices in Ocean Alkalinity Enhancement Research" (OAE Guide 23) was developed through a bottom-up community initiative, led by Jean-Pierre Gattuso; funded by the ClimateWorks Foundation; and coordinated by an international steering committee comprised of six scientists led by the scientific coordinator, Andreas Oschlies. The OAE Guide 23 underwent an open and transparent review process, where all referee comments and author responses are publicly available, and public comments were welcome throughout the process via a discussion forum provided by the publisher.

Importantly, the OAE Guide 23 is for research and not for implementation of OAE. It does not endorse any OAE approach or encourage or support public and private OAE initiatives. The OAE Guide 23 addresses seven topics, broken down into 13 papers (or chapters). These papers compare and synthesize previously published methods and offer guidance for future research with the aim to

- speed up knowledge generation and sharing;
- ensure that resources for research are used most effectively;
- ensure research is conducted responsibly and transparently;
- ensure comparability of experimental results, measurements, and modelling approaches;
- facilitate synthesis work across different OAE research efforts;
- facilitate an informed public debate on OAE; and
- facilitate the development of responsible governance and of monitoring, reporting, and verification (MRV).

The first three papers introduce the role of OAE as a carbon dioxide removal (CDR) option (Oschlies et al.), provide a background on the seawater carbonate system (Schulz et al.), and present a discussion of the best available knowledge regarding OAE research approaches (Eisaman et al.). Then, best practices for experimental design (Dupont & Metian) as well as laboratory (Iglesias-Rodríguez et al.), field (Cyronak et al.), and pelagic and benthic mesocosm (Riebesell et al.) experiments are covered as well as natural analogues (Subhas et al.) and modelling considerations (Fennel et al.). The final four chapters address legal (Steenkamp & Webb) and social recommendations for OAE research, innovation, and public engagement (Satterfield et al.); considerations about monitoring, reporting, and verification (MRV) (Ho et al.); and data reporting and sharing (Jiang et al.). Each chapter concludes with a list of key recommendations.

A word of caution on the title of the document is in order: “best practices” are defined as being commercial or professional procedures that are accepted or prescribed as correct or most effective. However, the topic of OAE is so new and evolving rapidly that the OAE research community is not yet experienced enough to have developed best practices by that definition. Thus, the best practices presented herein represent a first attempt to offer recommendations for OAE research by the scientific community at this point. We are hopeful that future iterations of the OAE Guide will include advanced best practices. In the meantime, we encourage researchers of well-done OAE studies to report not only the results of experiments deemed successful, but also any negative or neutral results. We also encourage the provision of a repository for planned experiments through a “lessons learned” discussion forum that will ensure that the field continues to move forward and is not slowed down by a lack of reporting of such work. To ensure full transparency of author affiliations involved in the OAE Guide 23, all authors have signed a conflict-of-interest declaration form, which can be found in the supplementary files (https://sp.copernicus.org/articles/sp-oae2023-ci-summary.zip).

We hope that the OAE Guide 23 will help to accelerate learning about OAE, ensure that OAE research is conducted responsibly and efficiently, and enhance transparency and sharing of new information regarding the possible applicability of OAE as a CDR measure.

Key messages box

- We recommend transparent sharing of all results of all experiments, irrespective of whether experimental outcomes are considered “positive” (e.g. affirmative of the experimenters’ prior assumptions), “negative”, or “neutral”. This includes full transparency of OAE research that provides additional complications for and/or roadblocks to OAE implementation (Oschlies et al).

- Calcium carbonate ($CaCO_3$) will precipitate in seawater when the saturation state is beyond certain thresholds; hence, it is recommended to filter carbonate chemistry samples to remove any $CaCO_3$ as interfering with certain measurements, as well as prevent $CaCO_3$ precipitation when stored (Schulz et al.).

- OAE shows promise as a potential CDR solution, and pilot projects and research activities have begun to demonstrate its feasibility in relevant environments. Continued collaboration among scientists, engineers, and policymakers will be crucial in optimizing these technologies. To maximize the effectiveness of OAE, it is critical to consider location-specific or regionally specific constraints to select appropriate application sites (Eisaman et al.).

- The impact of the deployment of OAE on marine life is poorly understood. Changes in alkalinity alone or in combination with other key trace elements co-released during implementation have the potential to negatively impact marine ecosystems. This cannot be resolved using a single approach, and a combination of monitoring, modelling, laboratory, natural, and field experiments is required (Dupont & Metian).

- Natural gradients in alkalinity exist across a range of temporal and spatial scales. These systems provide natural analogues to OAE and can be studied to explore interactions and feedbacks between alkalinity cycling and other Earth system processes, without the need for field trial permitting. They may also serve as technological test beds for emerging MRV methodologies (Subhas et al.).

- Identifying upper limits of alkalinity with respect to effects on physico-chemical (e.g. removal of alkalinity via secondary mineral precipitation, precipitation of nutrients, and alterations in metal availability, pH) and biological (e.g. shifts in organism physiology and population composition) properties is a critical step for upscaling experiments and planning field deployments. It is recommended to test the interactive effects of alkalinity and other parameters (e.g. temperature) in traditional and portable lab experiments and establish time frames to explore acclimation to abrupt alkalinization versus longer-term adaptation (Iglesias-Rodríguez et al.).

- An essential prerequisite for the implementation of OAE applications is their environmental safety, ensuring that ecosystem health and ecosystem services are not at risk. By combining realism and biological complexity with controllability and replication, mesocosm experiments provide an ideal OAE test bed and a critical stepping stone towards field applications (Riebesell et al.).

- Early field experiments will help create the scientific framework needed to scale operational OAE safely and responsibly. Collaboration, transparency, data sharing, and transdisciplinary teams are important for maximizing the return on investment during open experimentation in natural systems. Due to the potential ecological consequences and societal perceptions of field experiments, we recommend active engagement with the public, local communities, and other stakeholders from an early stage (Cyronak et al.).

- A range of modelling tools and analysis methods are available for OAE research to address questions ranging from microscales to global scales; however, each of these tools and methods has limitations and caveats that model users and users of model-generated outputs need to be aware of. We recommend transparent, accessible, and comprehensive sharing of model assumptions, input parameters, code, and output to facilitate universal assessments, intercomparisons, and identification of shortcomings and gaps that require further development (Fennel et al.).

- As OAE research shifts from laboratory to field research, domestic legislation will be required to regulate the conduct of both public and private researchers and their affiliated institutions. In doing so, domestic legislation must account for the minimum rules and standards that may be required under international law. Countries and their relevant authorities should, therefore, stay abreast of developments under relevant international agreements such as the London Protocol, especially as this relates to the emergence of international laws possibly tailored to OAE research (Steenkamp & Webb).

- To ensure that OAE research is responsible (is attentive to societal priorities) and successful (does not prematurely engender widespread social rejection), it will be critical to understand known patterns of when and why new technologies are seen as risky and to adapt social science methods to anticipate primary concerns and/or develop decision-specific protocols (e.g. impact and benefit agreements or similar planning and operation conditions). Methods range from early scoping of public thinking through to representative views across regions. All methods need to be attentive to the full scale and life cycle of OAE including the volume and source of materials and infrastructure needed to realize these (Satterfield et al.).

- Comprehensive, reproducible, and transparent MRV is essential for the responsible development and deployment of OAE as a CDR technology. Observational approaches can be used to monitor the delivery of alkalinity to seawater, monitor for secondary precipitation, and assess ecosystem changes, but they may not be able to detect small changes in alkalinity over time. Numerical simulations will be required to comprehensively quantify the carbon removal potential of OAE and assess the risks of unintended consequences. Therefore, the development of fit-for-purpose models and careful validation against observational data will be critical for MRV (Ho et al.).

- Data management is a core component of OAE research. It helps bridge the gap between OAE observations and the subsequent research and decision support. It is also an integral part of MRV, to help quantify carbon removal for carbon credit accounting. This guide outlines the requisite metadata templates, data standards, and controlled vocabularies for OAE research. Furthermore, care has been taken to ensure that these new templates, standards, and vocabularies are compatible with the needs of ocean acidification research (Jiang et al.).

Angela Stevenson, Andreas Oschlies, and Jean-Pierre Gattuso

Glossary of terms

Box of recommended terminology

Term	Abbreviation	Synonyms	Definition	Reference, if applicable
Carbon budget			Refers to two concepts in the literature: (i) an assessment of carbon cycle sources and sinks on a global level, through the synthesis of evidence for fossil fuel and cement emissions, emissions and removals associated with land use and land-use change, ocean and natural land sources and sinks of CO_2, and the resulting change in atmospheric CO_2 concentration, collectively referred to as the global carbon budget; (ii) the maximum amount of cumulative net global anthropogenic CO_2 emissions that would result in limiting global warming to a given level with a given probability, taking into account the effect of other anthropogenic climate forcers, collectively referred to as the total carbon budget when expressed starting from the pre-industrial period and as the remaining carbon budget when expressed from a recent specified date.	IPCC (2022)
Carbon dioxide removal	CDR	Negative emission technologies (NETs, if applied to CO_2 only)	Human activities that lead to a net removal of CO_2 from the atmosphere, either by increasing the removal of CO_2 from the atmosphere or by reducing the emissions of CO_2 from natural sources to the atmosphere, and that durably store the removed carbon away from the atmosphere.	OAE Guide 23
Carbon footprint			Measure of the exclusive total amount of emissions of carbon dioxide (CO_2) that is directly and indirectly caused by an activity or is accumulated over the lifecycle stages of a product.	Wiedmann & Minx (2008)
Carbon sequestration			The process of storing carbon in a carbon pool. It is a naturally occurring process, but it can also be enhanced or achieved with technology. The timescale of storage is climatically relevant and often described via “durability” or “permanence”.	IPCC (2022)
Direct air capture with carbon Storage	DACCS	Direct air capture and storage (DACS)	Engineered physico-chemical process by which CO_2 is captured directly from the ambient air, with subsequent storage.	OAE Guide 23

Term	Abbreviation	Synonyms	Definition	Reference, if applicable
Durability			The amount of time CO_2 is being sequestered and prevented from being released into the atmosphere through natural processes or human activities. Some protocols and registries for CDR use 100 years as a time span for classifying CO_2 sequestration as durable, while others may require a longer time frame, such as 1000 years, to ensure that the carbon removal is considered durable. Sometimes, the term "permanent" is used, while we recommend using "durability" instead.	OAE Guide 23
Enhanced weathering			A proposed method to increase the natural rate of removal of CO_2 from the atmosphere using silicate and carbonate rocks. The active surface area of these minerals is increased by grinding before they are actively added to soil, beaches, or the open ocean, the latter overlapping with the concept of OAE.	IPCC (2022)
Leakage			The term is used in two contexts: (i) it describes the physical release of CO_2 back to the atmosphere from the reservoir that is used to store CO_2 removed from the atmosphere via CDR and (ii) it describes the situation that may occur if, for reasons of costs related to climate policies, businesses were to transfer production to other countries with less strict emission constraints. This could lead to an increase in their total emissions.	OAE Guide 23
Marine carbon dioxide removal	mCDR	Ocean CDR	CDR approaches in which CO_2 is (i) removed from the atmosphere directly to the ocean or (ii) retained in the ocean where it otherwise would naturally degas to the atmosphere. For example, enhanced rock weathering on land is terrestrial CDR resulting in the transfer of dissolved inorganic carbon to the ocean but is not mCDR because the CO_2 removal from the atmosphere happens on land, and only the alkaline, carbon-rich products of such weathering are eventually stored in the ocean. On the other hand, macroalgae farming and harvesting with subsequent carbon storage on land or in geological reservoirs is marine CDR because the CO_2 removal from the atmosphere happens across the sea surface.	OAE Guide 23
Mitigation (of climate change)			A human intervention to reduce emissions or enhance the sinks of greenhouse gases.	IPCC (2022)

Term	Abbreviation	Synonyms	Definition	Reference, if applicable
Monitoring, reporting, and verification	MRV	Measuring, reporting, and verification	The process of accurately measuring, reporting, and verifying the amount of atmospheric CO_2 removal and durability of its storage by CDR techniques. MRV is a critical component of assessing the performance and impact of these CDR methods and ensuring transparency and accountability in their implementation.	OAE Guide 23
Negative emissions technologies	NETs	CDR (for CO_2)	Engineered approaches that increase the removal of CO_2 or other greenhouse gases from the atmosphere or reduce the emissions of CO_2 from natural sources to the atmosphere and that durably sequester the removed carbon away from the atmosphere.	OAE Guide 23
Net-zero CO_2 emissions		Carbon neutrality	Condition in which anthropogenic CO_2 emissions are balanced by anthropogenic CO_2 removals over a specified period. (Note that carbon neutrality and net-zero CO_2 emissions are overlapping concepts. The concepts can be applied at global or sub-global scales (e.g. regional, national, and sub-national). At a global scale, the terms carbon neutrality and net-zero CO_2 emissions are equivalent. At sub-global scales, the term net-zero CO_2 emissions is generally applied to emissions and removals under direct control or territorial responsibility of the reporting entity, while carbon neutrality generally includes emissions and removals within and beyond the direct control or territorial responsibility of the reporting entity. Accounting rules specified by greenhouse gas (GHG) programmes or schemes can have a significant influence on the quantification of relevant CO_2 emissions and removals.)	IPCC (2022)
Net-zero greenhouse gas emissions		Net zero	Net-zero greenhouse gas emissions, such as called for in the Paris Agreement, describe the balancing of sources and sinks of all anthropogenic greenhouse gases. How this is achieved depends on the metric used to compare the different greenhouse gases, which all have different lifetimes in the atmosphere. A metric is not provided in the Paris Agreement. UNFCCC and IPCC generally use the 100-year warming potential to compute CO_2 equivalents, CO_2 eq., and then require net-zero CO_2 eq. This would lead to zero additional radiative forcing on a 100-year timescale. Zero additional radiative forcing by net-zero greenhouse gases can only be achieved on all timescales when each individual greenhouse gas reaches net-zero anthropogenic emissions.	OAE Guide 23

Term	Abbreviation	Synonyms	Definition	Reference, if applicable
Ocean alkalinity enhancement	OAE	Alkalinity enhancement, ocean alkalinization	A proposed marine carbon dioxide removal (CDR) method that involves deposition of CO_2-reactive (i) alkaline minerals or (ii) chemical bases or (iii) their dissociation products into ocean surface waters that contact the atmosphere. This increases surface ocean total alkalinity, decreasing partial pressure of CO_2 in the surface ocean such that either the CO_2 flux from the atmosphere to the ocean is intensified or the CO_2 flux from the ocean to the atmosphere is lessened. OAE can help to elevate pH and ameliorate ocean acidification.Alkalinity enhancement that results from the addition of non-CO_2-reactive alkalinity to the ocean (e.g. alkalinity that is already equilibrated with atmospheric CO_2 prior to entering the ocean such as runoff from soil-enhanced weathering whose alkaline, C-rich products drain to the ocean) is not marine CDR and therefore not considered OAE here, as carbon dioxide removal is achieved before alkalinity and carbon enter the ocean.	IPCC (2022)
Permanence			See preferred term "durability".	
Reporting			The process of formal reporting of assessment results to the UNFCCC, according to predetermined formats and established standards, especially the Intergovernmental Panel on Climate Change (IPCC) Guidelines and GPG (Good Practice Guidance).	UN-REDD (2009 in IPCC, 2022)
Residual emissions			Thoseemissions (of greenhouse gases or, if specified, CO_2) that remain after efforts to eliminate such emissions have been implemented. For example, even with a concerted effort to eliminate all emissions, industries such as agriculture and cement production are likely to continue releasing greenhouse gases into the atmosphere. The quantity of residual emissions depends on societal choices, norms, values, and interests. Typical estimates of residual greenhouse gas emissions for the mid-century range from around 10% to 20% of today's emissions.	OAE Guide 23
Scalability			The property of a system to handle a growing amount of work.	OAE Guide 23
Sequestration potential		Mitigation potential	The quantity of greenhouse gases that could be removed from the atmosphere by anthropogenic enhancement of sinks and stored in a pool for a climate-relevant period of time.	Modified from IPCC (2022)

Term	Abbreviation	Synonyms	Definition	Reference, if applicable
Sink			“Any process, activity or mechanism which removes a greenhouse gas . . . from the atmosphere” and thus encompasses both natural and more technological or engineered removal approaches.	UNFCCC (in Oschlies et al., 2023)

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STATE OF THE PLANET

Climate targets, carbon dioxide removal, and the potential role of ocean alkalinity enhancement

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Abstract. The Paris Agreement to limit global warming to well below 2 °C requires the ambitious reduction in greenhouse gas emissions and the balancing of remaining emissions through carbon sinks (i.e., the deployment of carbon dioxide removal or CDR). While ambitious climate mitigation scenarios until now primarily consider land-based CDR methods, there is growing concern about their potential to deliver sufficient CDR, and marine CDR options are receiving more and more interest. Based on idealized theoretical studies, ocean alkalinity enhancement (OAE) appears as a promising marine CDR method. However, the knowledge base is insufficient for a robust assessment of its practical feasibility, of its side effects, social and governance aspects, and monitoring and verification issues. A number of research efforts aims to improve this in a timely manner. We provide an overview on the current situation of developing OAE as a marine CDR method and describe the history that has led to the creation of the OAE research best practices guide.

1 Climate goals and the need for carbon dioxide removal

A key finding of climate research in recent decades is that the increase in global mean surface air temperature since the beginning of industrialization is proportional to cumulative emissions of carbon dioxide (CO_2), which is the major anthropogenic greenhouse gas (Matthews et al., 2009). The Paris Agreement's goal of limiting global warming to well below 2 °C, and ideally 1.5 °C above preindustrial levels (UNFCCC, 2015), can thus be converted to a remaining carbon budget that, for current global emissions, will be used up in a few years for the 1.5 °C target and about 2 decades for the 2 °C target (United Nations Environmental Programme, 2022). The Paris Agreement thus explicitly demands ambitious reductions in anthropogenic greenhouse gas emissions and the balancing of hard-to-abate emissions through carbon sinks in the second-half of the 21st century (UNFCCC, 2015). The balance to be achieved is also called net zero and is a qualitatively new element compared to previous climate protection agreements.

Arresting global warming will require net-zero CO_2 emissions. Non-CO_2 greenhouse gases (GHGs), in particular ni-

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trous oxide and methane, also contribute to current warming. However, because their lifetime in the atmosphere is considerably shorter than that of CO_2, arresting global warming does not require net-zero emissions for non-CO_2 GHGs (Allen et al., 2022). Nevertheless, increases in non-CO_2 GHG emissions may lead to further temperature rise, whereas a decrease in non-CO_2 GHG emissions will relatively quickly reduce atmospheric concentrations of the respective non-CO_2 GHG and thus radiative forcing and global warming. In order to achieve the long-term temperature goal, parties to the Paris Agreement agreed to reach global peaking of GHG emissions as soon as possible, to undertake rapid reductions thereafter, and to achieve a balance, i.e., net zero, between anthropogenic emissions by sources and removals by sinks of greenhouse gases in the second-half of this century. The Paris Agreement adopts the United Nations Framework Convention on Climate Change (UNFCCC) definition of "sink", which refers to "any process, activity or mechanism which removes a greenhouse gas … from the atmosphere" and thus encompasses both ecosystem-based and more technological or engineered removal approaches. Presently, no viable method exists for large-scale removal of non-CO_2 GHGs. Therefore, carbon dioxide removal will likely have to balance not only hard-to-abate residual emissions of CO_2, e.g., from cement production, waste incineration, aviation, and maritime transport, but also emissions of non-CO_2 GHGs, in particular from agriculture.

The amount of these residual emissions needs to be politically and socially viable. In principle, all hard-to-abate emissions are technically avoidable, e.g., by switching from fossil to renewable energy, by capturing and safely storing CO_2 from process emissions (e.g., cement production using renewable energy), or by avoiding the processes that lead to emissions. Particularly in the agricultural sector, avoiding all emissions appears impossible without critical societal impacts; rice production and the raising of livestock are associated with methane production, and any use of nitrogen fertilizer is associated with nitrous oxide production, and both of these are potent non-CO_2 greenhouse gases. The exact amount of residual emissions is thus largely an issue of economic and social costs and society's ambition to avoid emissions. Which emissions are deemed unavoidable also vary across historical and political contexts and are influenced by claims as to what is regarded as legitimately possible (Lund et al., 2023). Ultimately, decisions about the amount of residual emissions depend on values, norms, and interests. Current scenarios assume that, by mid-century, residual emissions will amount to between 10 % and 20 % of today's emissions (i.e., about 6 to 12 $\mathrm{Gt\,CO_2e\,yr^{-1}}$ globally), where CO_2e includes the CO_2 equivalents of non-CO_2 GHGs that are estimated to contribute half to two-thirds of the residual emissions (Buck et al., 2023).

Current global carbon dioxide removal (CDR) has been estimated to be near 2 $\mathrm{Gt\,CO_2\,yr^{-1}}$ almost exclusively by the conventional management of land, primarily forest management (Grassi et al., 2021), afforestation, and reforestation and with only 0.002 $\mathrm{Gt\,CO_2\,yr^{-1}}$ by novel CDR schemes comprising bioenergy with carbon capture and storage (BECCS), direct air capture with carbon storage (DACCS), enhanced weathering, and marine CDR, also sometime called ocean CDR, including ocean alkalinity enhancement (OAE) as a subcategory (Smith et al., 2023). According to the *State of Carbon Dioxide Removal* report (Smith et al., 2023), the deployment of novel CDR approaches will have to increase by 3 orders of magnitude by mid-century in order to reach net-zero emissions, even in the most ambitious emission reduction scenarios. Note that many scenarios used in the recent Intergovernmental Panel on Climate Change Sixth Assessment Report (IPCC, 2022) assume that emissions turn net negative after having reached net zero (Fig. 1), which would allow a net cooling and is also deemed necessary for so-called temperature overshoot scenarios (Geden and Löschel, 2017) that receive more attention the longer it takes to drastically reduce emissions. It is, however, currently unclear how to best incentivize and govern net negative emissions.

While the current climate goal of the UNFCCC is to limit the temperature rise to 2 or 1.5 °C relative to preindustrial levels, one could also envisage climate targets that aim to reduce global temperatures further toward preindustrial levels – and much faster than the tens to hundreds of millennia that planetary feedbacks would take to do so (Archer et al., 2009). Should humanity aim for a faster restoration of the planetary thermal balance to preindustrial times, then CDR would be a prime mechanism, with the deployment required being well beyond the current net-zero targets.

2 CDR approaches and the role the ocean could play

Traditionally, the focus of CDR has been on land-based methods such as reforestation and afforestation or BECCS. While these approaches certainly have some potential, there are unresolved issues related to land use competition and associated political and societal feasibility challenges, and it is currently unclear if and how their combined deployment will be possible at scales sufficient to meet the net-zero target by mid-century (The Land Gap Report, Dooley et al., 2022). It is thus unlikely that such terrestrial-ecosystem-based solutions alone will be sufficient to achieve net zero (Smith et al., 2023), and therefore, novel approaches will also have to be applied to a considerable extent. None of these is ready for large-scale deployment today. Transparent research into the efficacy, risks, and benefits of different approaches is urgently needed, and the societal debate on what counts as residual emissions and whether and how to deploy different CDR approaches must begin quickly so that appropriate processes can be developed in time, well-informed decisions can be made about research, development, and deployment, and mechanisms can be devised to regulate such use responsi-

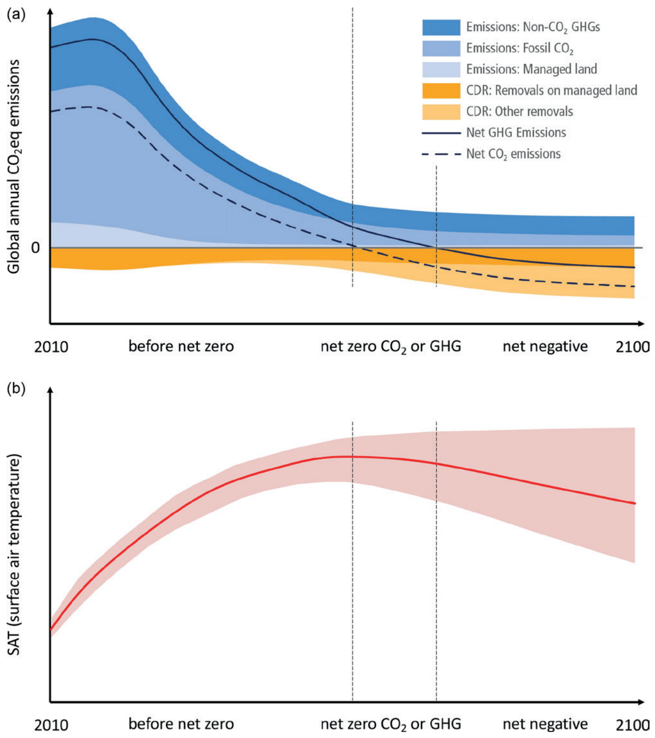

Figure 1. **(a)** The role of CO_2 removal (CDR) in a stylized pathway of ambitious climate. Dark orange illustrates the CO_2 removals from land management, and light orange illustrates removal from other CDR methods, including ocean-based methods. Note that net-zero CO_2 is reached well before net-zero greenhouse gas (GHG), and the amount of CDR required for net-zero CO_2 can be substantially smaller than the amount of CDR required for non-zero GHG. Any contribution of ocean alkalinity enhancement would be included in light orange (CDR: other removals). This panel **(a)** has been modified from IPCC (2022, Cross-Chapter Box 8, Fig. 2). **(b)** The corresponding global surface air temperature, with shading indicating a typical uncertainty range.

bly. Importantly, deployment at a scale of hundreds to thousands of megatons of CO_2 per year could compete with other societal demands for land, water, and energy (Lawrence et al., 2018). Marine CDR has the potential to reduce the need for land and freshwater resources. Large-scale marine CDR approaches, however, may struggle to achieve public acceptance (Bertram and Merk, 2020; Nawaz et al., 2023).

Marine CDR options are receiving more and more interest, acknowledging that the ocean has already absorbed more than a quarter of the anthropogenic CO_2 emissions and would, on timescales of thousands to hundreds of thousands of years, take up most of the remaining emissions (Archer and Brovkin, 2008), as it has done with natural high-CO_2 excursions in the Earth's geological past. The ocean holds more than 50 times as much carbon (primarily in the form of dissolved inorganic carbon) as the preindustrial atmosphere and about 20 times as much as the carbon stored in global terrestrial plants and soils (Carlson et al., 2001). Its theoretical carbon storage potential appears large when compared to the atmospheric and terrestrial carbon pools. However, increasing the oceanic carbon pool will affect the marine environment and may put additional pressure on marine ecosystems. The current level of scientific understanding of marine CDR is low, and more research is required to comprehensively assess the diverse portfolio of proposed options (e.g., NASEM, 2021). A particular challenge for marine CDR concerns the monitoring and verification of any CDR-induced carbon fluxes and carbon storage, which is essential for reliable and honest carbon crediting (Boyd et al., 2023). The detection and attribution of CDR signals is particularly difficult, due to the large natural marine carbon pool that already contains a considerable anthropogenic signal. The high temporal and spatial variability in these signals, as well as the temporal and spatial decoupling of air–sea CO_2 fluxes and carbon storage in the interior ocean, pose specific challenges to the detection and attribution of CDR. The determination of a baseline, the additional carbon sequestered beyond the baseline, and the quantification of carbon storage durability will likely be associated with considerable uncertainties. A key aspect of monitoring, reporting, and verification (MRV) is the development of transparent schemes that allow a reliable determination of CDR and of consequent impacts on the carbon cycle, and hence climate, as well as the association of carbon credits with individual CDR activities.

Currently considered marine CDR approaches include (1) biological methods, such as photosynthetic carbon fixation by microalgae, macrophytes (e.g., seaweeds), or mangrove trees and the subsequent storage of carbon in the deep ocean or in coastal sediments; and (2) abiotic methods that aim to alter the carbonate chemistry of seawater in a way that enhances the air–sea flux of CO_2 and subsequently stores atmospheric carbon as dissolved inorganic carbon in seawater. Hybrid biological, physical, and/or chemical marine CDR approaches are also considered (artificial upwelling or downwelling, marine BECCS, bio-enhanced alkalinity generation, hybrid ocean–geochemical approaches, etc.). Among marine CDR methods investigated, abiotic approaches have been assessed as being those with the lowest knowledge base and highest efficacy (Gattuso et al., 2018; NASEM, 2021). Improving their knowledge base therefore appears critical, and we focus here on the ocean alkalinity enhancement.

3 Ocean alkalinity enhancement

Ocean alkalinity enhancement is a marine CDR concept with high theoretical sequestration potential in the range of 3 to 30 Gt CO_2 yr^{-1} (Köhler et al., 2013; Renforth and Henderson, 2017; Feng et al., 2017), for which a number of technical deployment approaches has been suggested (Fig. 2). Alkalinity, which is the excess of proton acceptors over donors, is a chemical concept that largely determines the storage capacity for CO_2 in seawater. OAE aims to enhance alkalinity by adding alkaline material to the surface ocean or by removing acid from seawater via electrochemistry. Alkalinity enhancement results in the consumption of protons, which is a corresponding increase in the pH, results in a decrease in the partial pressure of CO_2 in seawater. If applied to the surface ocean, and depending on the initial air–sea CO_2 gradient, it would promote CO_2 uptake from – or lessen CO_2 release to – the atmosphere, in both cases leading to a net reduction in atmospheric CO_2 at the expense of an increase in the oceanic pool of dissolved inorganic carbon. The atmospheric CO_2 absorbed via OAE-induced air–sea gas exchange is essentially stored in the form of dissolved bicarbonate and carbonate ions that do not exchange with the atmosphere.

When applied to the surface ocean, OAE can rely on air–sea gas exchange to at least partially restore the OAE-induced decrease in the partial pressure of CO_2. Air–sea gas equilibration of CO_2 can take months to years (Jones et al., 2014) and may pose specific challenges to MRV (He and Tyka, 2023). However, along the path to equilibration, air–sea CO_2 fluxes approach zero and would, for otherwise constant environmental conditions, follow an inverse exponential function for which a disproportionate share of the total CO_2 flux occurs at the beginning of the equilibration period. The complex impacts of mixing and transport of water masses in reality make direct observations of the CO_2 influx unfeasible. Numerical models may be required for reliable quantification of air–sea gas exchange, but their skill has yet to be demonstrated (Bach et al., 2023). OAE can also be applied by adding alkalinity to chemical reactors upstream that could at least partially pre-equilibrate the alkalized seawater with additional CO_2 taken either from ambient air or from CO_2 waste streams. If CO_2 is taken from waste streams, then this would, technically, correspond to emissions avoidance and not CDR. Also, if this CO_2 were taken from ambient air via, e.g., direct air capture facilities or bioenergy plants, then CDR would be termed according to the process that removes additional CO_2 from the atmosphere and not the process that provides terminal carbon storage. OAE applied to chemical reactors or to the surface ocean qualifies as marine CDR if it leads to a net removal of CO_2 from the atmosphere, either by increasing the flux of CO_2 from the atmosphere to the ocean or by reducing the emissions of CO_2 from the ocean to the atmosphere. Hybrid schemes that combine emission reduction by dissolving minerals with acidic CO_2 waste streams in chemical reactors to generate dissolved alkaline solutions to be added into the ocean for subsequent marine CDR can also be envisaged.

OAE was positioned in the “concept stage” cluster of a recent assessment of ocean-based measures for climate action (Gattuso et al., 2021). This cluster was defined for measures with potentially very high effectiveness but with feasibility and cost-effectiveness levels which have yet to be demonstrated. The assessment highlighted the urgent need to improve knowledge on concept stage measures because the full implementation of proven measures runs the risk of falling short of providing enough of a cost-effective CDR capacity. The attractive aspects of OAE compared to many other methods, in particular those that store carbon in biomass, are its potential to reduce ocean acidification at least locally (Albright et al., 2016) and the theoretical durability of storage over several tens to hundreds of thousands of years. An effective leakage of CO_2, either via enhanced CO_2 flux back to the atmosphere or by reduced CO_2 uptake from the atmosphere compared to a baseline scenario, can result from enhanced formation and reduced dissolution of carbonate minerals in the water column or at the sea floor. Possible leakage effects via the impacts of OAE on pelagic calcifiers are uncertain (Bach et al., 2019), and feedbacks via changes in the dissolution and preservation of carbonates on the sea floor operate on timescales of hundreds to thousands of years (e.g., Gehlen et al., 2008). While there is little indication that leakage is a major concern for OAE on shorter than centennial timescales, a quantitative assessment of leakage across the spectrum of timescales is lacking. Frequently mentioned drawbacks of OAE are (i) the amount and the quality of alkaline material that is needed (whether mined in the case of mineral-based approaches or generated from waste brine in electrochemical approaches) and the energy required (whether mining, grinding, and transport for mineral-based approaches or the source of electricity for electrochemical approaches); and (ii) the difficulty of reliably quantifying CDR (MRV). Regarding point (i), all known CDR methods require, at climate-relevant scales, the movement of large amounts of matter. In addition to abundant carbonate and silicate minerals, a number of industrial waste products or artificial minerals can also be considered to be alkalinity sources (Renforth, 2019; Caserini et al., 2022). Employing these for OAE would require proper accounting for any CO_2 emitted in their production (e.g., $Ca(OH)_2$ or $Mg(OH)_2$ produced through the calcination of $CaCO_3$ or $MgCO_3$, respectively). Overall, there is no shortage of alkaline materials on the planet (Caserini et al., 2022). Regarding point (ii), MRV is indeed a challenge and is addressed by Ho et al. (2023, this Guide).

So far, the CDR potential of OAE has essentially been inferred from modeling and techno-economic studies (Kheshgi, 1995; Harvey, 2008), including spatially resolved global or regional models (e.g., Ilyina et al., 2013; Keller et al., 2014; Hauck et al., 2016; Wang et al., 2023). Such models employ simplified representations of marine biogeochemistry, rudimentary descriptions of marine ecosystems, and typically simulate OAE as being the addition, often instantaneously, of pure alkalinity or of olivine minerals consisting of silicate, iron, and alkalinity. Such studies can provide large-scale estimates of the theoretical CDR potential of OAE. Small-scale experimental studies can complement this with insight into realizable effectiveness of alkalinity addition and with the investigation of impacts that cannot be predicted from simplified modeled systems, such as environmental side-effects. The first experimental studies have

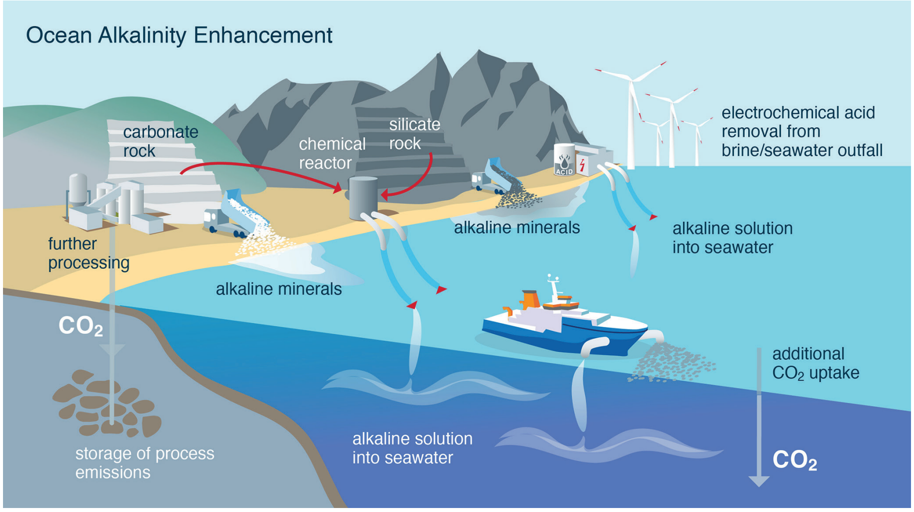

Figure 2. Illustration of the various methods that have been proposed as ocean alkalinity enhancement measures to achieve carbon dioxide removal.

started only recently and have already generated novel insight into issues regarding the actual delivery of alkalinity, in particular the risk of calcium carbonate precipitation that may negate intended CDR effects (Fuhr et al., 2022; Moras et al., 2022; Hartmann et al., 2023), and ecological impacts (Ferderer et al., 2022), and further research efforts are underway. Some information on the biogeochemical and ecological impacts of OAE might be gained from experimental work on ocean acidification that has been carried out during recent decades. Indeed, a first OAE field experiment was carried out in the context of ocean acidification research. It used alkalinity addition to demonstrate that ocean acidification is detrimental to coral reef calcification and that alkalinity addition can alleviate some effects of ocean acidification (Albright et al., 2016). Insight into the possible impacts of OAE on marine organisms can be gained from research by the shellfish industry investigating the utility of so-called sweetening of the water through addition of mainly soda ash (Na_2CO_3), a practice utilized in shellfish hatcheries for decades, and also in the academic and industrial fields of river liming, which dissolved primarily $CaCO_3$ and dolomite in higher-latitude watersheds to offset the effects of acid rain in the 1960s and 1970s but is still practiced today in Canada and some Scandinavian countries, among other places (Mant et al., 2013).

Still, crucial knowledge gaps exist. Issues to be researched include the method of alkalinity addition, the alkaline materials to be used, and their processing, the key attributes of ideal locations for deployment, the CDR potential that can be realized on given timescales, the durability of the carbon storage, biogeochemical, and ecological co-benefits and risks, as well as MRV and the economic, legal, social, and ethical aspects of OAE. Of particular relevance for OAE and most other marine CDR methods is the regulatory perspective at international level. This is required to govern activities affecting the ocean as part of the global commons.

The very few (fewer than 10, according to the authors' knowledge) field trials that have been carried out so far, or are being discussed in the year 2023, have the potential to take up a few tonnes of CO_2 per trial. For the various OAE approaches, technology-readiness levels (TRLs) are relatively low and are generally rated as being 1–2 by Smith et al. (2023), 3–4 for specific approaches (Foteinis et al., 2022), and possibly approaching 5–6 for methods with the first field trials in preparation or underway (see Eisaman et al., 2023, this Guide). Scaling up the CO_2 uptake by several orders of magnitude to many millions of tonnes per year or possibly even a billions of tonnes per year by mid-century is extremely ambitious. It would require all instruments, measures, and policies put in place that can advance every option forward from its current readiness level. In their *State of Carbon Dioxide Removal* report, Smith et al. (2023) estimated that so-called novel CDR methods, which include OAE, would need to be scaled up about by a factor 30 by 2030 and a factor of 1300 by mid-century in order to meet the demand expected for reaching promised climate goals. Required average annual OAE growth rates will have to be around 50 %, which is extremely ambitious compared to, for example, an average of 9 % annual increase in the global capacity of renewable energy (IRENA, 2021). Whether or not CDR and OAE specifically can be scaled up sufficiently by mid-century will depend on progress over the next decade, which Smith et al. (2023) call the "novel CDR's formative years". A possible advantage of most OAE methods is that, technologically, they appear relatively simple and rely, to a substantial degree, on technology that exists already for processing different mineral resources at annual rates similar to those that may be required by OAE by mid-century. A possible roadblock for rapidly scaling up OAE may be a lack of public acceptance (Bertram and Merk, 2020; Nawaz et al., 2023).

In addition to technological challenges and acceptability issues that would need to be resolved, appropriate governance schemes will be needed if OAE is to be deployed at climatically relevant scales (GESAMP, 2019; Boettcher et al., 2021). The 2013 amendment to the London Protocol offers an approach for governing marine CDR, with a focus on ocean fertilization, but would need to be developed further with regards to OAE (see Steenkamp and Webb, 2023, this Guide). Interactions between OAE and other ocean-based activities will also need to be considered (e.g., via marine spatial planning), and any climate-relevant OAE deployment would require new or significantly expanded climate policies and financing schemes. The inclusion of OAE in carbon markets will require the establishment of robust MRV procedures.

All of these issues need to be resolved before OAE can be implemented at a large scale. Achieving this by mid-century is challenging but not impossible. Research is urgently required on all aspects that are addressed in the various papers of this volume.

4 Motivation for developing a best practices guide

Given the urgency of establishing a portfolio of CDR options, a rapid improvement of our understanding of the carbon storage potential and of the co-benefits and risks of OAE is needed. This requires responsible, efficient, and transparent scientific research in order to generate new and reliable information, allowing for rapid sharing, testing, and synthesis of the results. With the first publicly funded research projects having started in several countries, philanthropy funding a number of research projects to accelerate the scientific progress, and start-ups working on enhancing technological readiness and developing scalable methodologies, this has motivated us to develop a best practice guide for OAE research.

The papers included in this guide describe current knowledge on the strengths and weaknesses of different OAE approaches, scientific uncertainties, biological and ecological impacts, knowledge gaps, and research needs. Recommendations for the experimental setup of a laboratory, pelagic and benthic mesocosms, and field experiments, as well as for modeling approaches, are provided. The guide also discusses the legal context in which research occurs and offers recommendations for responsible research and innovation, public engagement, data reporting and sharing, MRV, and attribution.

The best practice guide aims at fostering intercomparison and synthesis efforts of different studies evaluating the potential, effectiveness, and durability of OAE. This will help to improve knowledge sharing and information gain and thereby speed up scientific progress at a time when robust information about OAE as a carbon dioxide removal option is urgently needed to enable society to define and design appropriate actions to reach agreed climate goals.

This research field is in its infancy and is rapidly evolving. The broader legal and social contexts in which research occur are also undergoing change. What we designate as best practice in this guide today may not be considered the best practice in the future. As such, our guide comprises our current understanding of OAE, but it is critical that users remain up to date with respect to the literature published after publication of the OAE guide. There will almost certainly be improvements in protocols as the field develops, and everyone is invited to contribute to this process.

5 Development of this best practice guide

Best practice guides have proven useful when new areas of research open up, often bringing together scientists from different fields and with different methodological backgrounds. One example is the *Guide to best practices in ocean acidification research and data reporting* (Riebesell et al., 2010), in which the project lead, Jean-Pierre Gattuso, the scientific coordinator, Andreas Oschlies, and a number of authors of this guide were involved. The ocean acidification guide had an enormous catalytic effect in growing the field of ocean acidification research by lowering the barrier to entry and making the comparison of different studies and the generation of synthesis products more straightforward. The expectation is that the present guide on OAE research will have a similar impact on the OAE community and ocean CDR field at large and also provide guidelines for ensuring that OAE research is conducted responsibly and most efficiently for the public good.

In summer 2022, Jean-Pierre Gattuso and Andreas Oschlies sent a proposal to the ClimateWorks Foundation with a request for funding to produce a detailed guide that outlines all the relevant approaches available for researching ocean alkalinity enhancement as a carbon dioxide removal method. The requested funding for a part-time project manager, a 3 d in-person workshop of the chapter lead authors, and costs for the production, publication, and printing of the guide (a total sum of USD 170 000) was approved. A steering committee, consisting of the authors of the present paper, was established and had several online meetings to develop outline and a conflict-of-interest form that all authors would have to sign in order to ensure transparency, best scientific knowledge, and the absence of conflicts of interest. Lead authors for each paper of the guide were chosen by the steering committee based on experience, scholarship, and diversity. In consultation with the steering committee, all lead authors then chose the co-leads and additional authors of their respective papers.

In early 2023, a 3 d in-person workshop of the steering committee and lead authors took place in Villefranche-sur-Mer, France. All paper outlines were discussed, gaps identified, and the timeline agreed upon. The lead authors were responsible for developing their papers, with support from the scientific project manager. A public website (https://oae-best-practice.carbondioxide-removal.eu, last access: 26 October 2023) with a list of papers and lead authors was set up and advertised via social media and the CDR news stream (https://www.carbondioxide-removal.eu, last access: 26 October 2023). An internal review was initiated in May 2023. All papers were submitted to *State of the Planet* in order to allow for public review and to ensure that the *OAE Guide 23* provides state-of-the-art information.

Key recommendations

- Research on ocean alkalinity enhancement should consider and, whenever appropriate, follow the best practices lined out in the *OAE Guide 23*.
- Results of all experiments should be shared transparently, irrespective of whether experimental outcomes are considered positive (e.g., affirmative of the experimenters' prior assumptions), negative, or neutral. This includes full transparency with respect to OAE research that provides additional complications and/or roadblocks to OAE implementation.
- We recommend establishing a public registry for OAE field experiments, where all field experiments should be registered before the experiment is carried out.
- Researchers on OAE should help to further develop and improve the best practices outlined here and eventually strive for an update of the *OAE Guide 23* in the future.

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Seawater carbonate chemistry considerations for ocean alkalinity enhancement research: theory, measurements, and calculations

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Abstract. Ocean alkalinity enhancement (OAE) is a proposed marine carbon dioxide removal (mCDR) approach that has the potential for large-scale uptake of significant amounts of atmospheric carbon dioxide (CO_2). Removing anthropogenic legacy CO_2 will be required to stabilise global surface temperatures below the 1.5–2 °C Paris Agreement target of 2015. In this chapter we describe the impacts of various OAE feedstocks on seawater carbonate chemistry, as well as pitfalls that need to be avoided during sampling, storage, and measurement of the four main carbonate chemistry parameters, i.e. dissolved inorganic carbon (DIC), total alkalinity (TA), pH, and CO_2 fugacity ($f\mathrm{CO_2}$). Finally, we also discuss considerations in regard to calculating carbonate chemistry speciation from two measured parameters. Key findings are that (1) theoretical CO_2 uptake potential (global mean of 0.84 mol of CO_2 per mole of TA added) based on carbonate chemistry calculations is probably secondary in determining the oceanic region in which OAE would be best; (2) carbonate chemistry sampling is recommended to involve gentle pressure filtration to remove calcium carbonate ($CaCO_3$) that might have been precipitated upon TA increase as it would otherwise interfere with a number of analyses; (3) samples for DIC and TA can be stabilised to avoid the risk of secondary $CaCO_3$ precipitation during sample storage; and (4) some OAE feedstocks require additional adjustments to carbonate chemistry speciation calculations using available programs and routines, for instance if seawater magnesium or calcium concentrations are modified.

1 Seawater carbonate chemistry revisited

In the following sections the basic concepts of the seawater carbonate system are laid out, together with definitions of the key parameters.

1.1 Acid–base parameters and equilibrium chemistry

The acid–base equilibrium chemistry of seawater has been described in the *Guide to Best Practices for Ocean CO_2 Measurements* (Dickson et al., 2007) and the carbonate chemistry chapter in the *Guide to Best Practices for Ocean Acidification Research and Data Reporting* (Dickson, 2010). These publications are open-access and provide practical guidance related to studying the carbon dioxide system in seawater. They describe tested approaches for measuring the four main parameters that are commonly used to constrain seawater acid–base chemistry and provide recommended values for the various equilibrium constants (as functions of salinity and temperature and at 1 atm total pressure). Another key resource, although not open-access, is the book *CO_2 in seawater: Equilibrium, Isotopes, Kinetics* (Zeebe and Wolf-Gladrow, 2001), which offers comprehensive theoretical knowledge on all aspects relevant for carbonate-chemistry-related research, including ocean alkalinity enhancement (OAE).

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The marine carbonate system can be constrained by knowing next to temperature, salinity, and pressure two carbonate chemistry parameters (Zeebe and Wolf-Gladrow, 2001). Additional data such as silicic acid or phosphate concentrations might also be required, although these have typically limited influence on carbonate chemistry speciation. Four carbonate chemistry parameters are commonly measured (carbonate ion concentration measurements are less common). These are

- DIC – the total dissolved-inorganic-carbon (expressed as an amount content of carbon atoms, i.e. moles per kilogramme of seawater) in a sample of seawater (Eq. 1);
- TA – the total alkalinity (expressed as an amount content of hydrogen ions that is equivalent to the bases – defined relative to a specified equivalence point) in a sample of seawater (Eq. 2);
- pH_T – a measure of the amount content of *total* hydrogen ions in a sample of seawater (Eq. 3);
- fCO_2 – the fugacity of carbon dioxide in air that is in solubility equilibrium with a sample of seawater (Eq. 4).

$$\mathrm{DIC} = \left[\mathrm{CO_2}^*\right] + \left[\mathrm{HCO_3^-}\right] + \left[\mathrm{CO_3^{2-}}\right], \tag{1}$$

with $[CO_2^*]$ denoting the sum of dissolved $[CO_2]$ and $[H_2CO_3]$.

$$\begin{aligned}\mathrm{TA} = {} & \left[\mathrm{HCO_3}^-\right] + 2\left[\mathrm{CO_3^{2-}}\right] + \left[\mathrm{B(OH)_4^-}\right] + \left[\mathrm{OH^-}\right] \\ & + \left[\mathrm{HPO_4^{2-}}\right] + 2\left[\mathrm{PO_4^{3-}}\right] + \left[\mathrm{H_3SiO_4^-}\right] + [\mathrm{NH_3}] \\ & + \left[\mathrm{HS^-}\right] - \left[\mathrm{H^+}\right]_\mathrm{F} - \left[\mathrm{HSO_4}^-\right] - [\mathrm{HF}] - [\mathrm{H_3PO_4}] \\ & + \ldots - \ldots,\end{aligned} \tag{2}$$

with the last two terms denoting minor contributions of additional proton acceptors and donors.

$$\mathrm{pH_T} = \left[\mathrm{H^+}\right]_\mathrm{F} + \left[\mathrm{HSO_4}^-\right], \tag{3}$$

with $[H^+]_F$ describing the free hydrogen ion concentration.

$$f\mathrm{CO_2} = K_0\left[\mathrm{CO_2}^*\right], \tag{4}$$

with K_0 denoting the temperature- and salinity-dependent carbon dioxide solubility, or Henry's law constant. Another important carbonate chemistry concept is that of the calcium carbonate ($CaCO_3$) saturation state (Eq. 5).

$$\Omega = \frac{\left[\mathrm{Ca^{2+}}\right]\left[\mathrm{CO_3^{2-}}\right]}{K_\mathrm{sp}}, \tag{5}$$

with K_{sp} describing the temperature-, salinity-, and pressure-dependent solubility product of a particular calcium carbonate morphotype such as calcite or aragonite and $[Ca^{2+}]$ and $[CO_3^{2-}]$ being respective in situ concentrations. When Ω is above 1 $CaCO_3$ precipitation is thermodynamically favoured, while below 1 it is its dissolution.

The equilibrium constants for the amount contents of the various constituents of the acid–base equilibria in a sample of seawater are essentially dependent on the major ion composition of the seawater (usually approximated by the salinity); the temperature of the seawater; and the total pressure, i.e. water depth. Hence if salinity, temperature, or pressure of a seawater sample changes, the various equilibrium constants will necessarily change. Thus, the pH_T and fCO_2 of the seawater will change as a consequence, and it is important to note the salinity, temperature, and pressure at which the measurements were made. For TA and DIC this is not a problem. The individual amount contents of unionised dissolved carbon dioxide, bicarbonate ion, and carbonate ion each change as salinity, temperature, and/or pressure changes, but their total sum does not (the number of carbon atoms that are in an inorganic form is conserved). Of course, this assumes that any redox reactions involving carbon do not occur on the relatively short timescales appropriate to the changes in salinity, temperature, or pressure. The same applies to the sum of the individual TA components.

Any two of the five measurable parameters (DIC, TA, pH_T, fCO_2, and CO_3^{2-}) can – in principle – be used together with salinity, temperature, and pressure (defining suitable equilibrium constants) to calculate the state of the carbon dioxide acid–base system in a seawater sample. The parenthetic note "in principle" is an acknowledgement that – as a consequence of errors in the measurements of these parameters and in the measurement of the associated equilibrium constants – the results from using alternate pairs of parameters will likely not be identical (Orr et al., 2018). When total alkalinity is used as a measured parameter, it implicitly incorporates all other acid–base equilibria occurring within the sample of seawater, i.e. in addition to the inorganic CO_2 system (Eq. 2). This is relatively straightforward if the total amount content of each acid–base system present has been measured directly, can be calculated from sample salinity, or can safely be neglected. For each acid–base system considered, the acid-dissociation constants also need to be known. A useful consequence of the TA definition is that TA does not change when CO_2 is in- or outgassing. However, there is a growing awareness that the presence of organic acids and bases in seawater can complicate the use of total alkalinity as a measurable parameter (see e.g. Fong and Dickson, 2019). The contribution of such species to total alkalinity is usually neglected, especially for open-ocean seawater samples.

1.2 Deffeyes diagrams

Deffeyes (1965) published a detailed description of how to use contour diagrams plotting individual seawater CO_2 system properties as a function of total alkalinity and total dissolved inorganic carbon for seawater of a specified salinity and at a particular temperature (and pressure). Insofar as this chapter is aimed at studies of ocean alkalinity enhancement, we feel such diagrams may be useful to help visualise the compositional changes that are involved in such processes.

When an alkaline agent such as sodium hydroxide (NaOH) is used to increase total alkalinity, such addition does not change total dissolved inorganic carbon (the vertical red line, Fig. 1). Alternatively, alkalinity could be added as a soluble inorganic carbonate salt (e.g. ikaite, $CaCO_3 \cdot 6H_2O$, or Na_2CO_3). Both would increase TA and DIC at a ratio of 2 : 1 (blue line, Fig. 1). As that modified water sample then equilibrates with the atmosphere, e.g. takes up CO_2 from the air, DIC increases. It is straightforward to assess the potential of 1 kg of an alkalinity-enhanced seawater to remove CO_2 from the atmosphere. It is equivalent to the change in DIC after re-equilibration to the initial $f\mathrm{CO_2}$ prior to the alkalinity addition (horizontally moving from the tip of the alkaline agent arrow to the initial $f\mathrm{CO_2}$). This concept takes into account that marine carbon dioxide removal (mCDR) also includes scenarios in which an oceanic CO_2 source is reduced. Similar diagrams can be drawn to assess the impact of various TA additions on Ω or pH (Fig. 1b, c).

1.3 OAE impacts on seawater and potential secondary $CaCO_3$ precipitation

As mentioned above, ocean alkalinity can be increased by various means (see also Eisaman et al., 2023, this Guide). First, there are multiple minerals found in natural rocks which release TA upon dissolution in seawater. Dissolution kinetics depend on how finely the minerals have been milled as well as on the mineral itself (e.g. Anbeek, 1992). For instance, olivine, a magnesium/iron silicate – $(Mg,Fe)_2SiO_4$, dissolves relatively slowly (for the purpose of OAE), on the order of weeks to months, and appears to have a relatively low solubility (Monserrat et al., 2017; Flipkens et al., 2023). On the other end of the spectrum, brucite ($Mg(OH)_2$) dissolution rates can be on the order of hours (Moras et al., 2023a). Another way to increase oceanic TA is to add it in "liquid" or aqueous form, i.e. hydroxide ions – OH^-, which can be produced electrochemically from seawater (e.g. Rau et al., 2013, but also see Eisaman et al., 2023, this Guide).

Whichever the approach, once alkalinity is increased it raises pH, shifting carbonate chemistry speciation towards lower aqueous carbon dioxide ($[CO_2]$) and higher carbonate ion concentrations ($[CO_3^{2-}]$), as well as saturation states for various calcium carbonate ($CaCO_3$) morphotypes such as calcite (Ω_{calc}) and aragonite (Ω_{arag}). In this context, saturation states can be considered critical thresholds, and depending on the application there are levels that should not be exceeded for extended periods of time. Avoiding critical saturation thresholds is important because $CaCO_3$ will precipitate inorganically through a number of mechanisms at higher Ω values. Such secondary precipitation should be avoided as it reduces the oceanic uptake capacity for atmospheric CO_2 and can even lead to runaway $CaCO_3$ precipitation, where more TA is removed than had been added, reducing typical CO_2 uptake potential by a factor of 8 (Fuhr et al., 2022; Moras et al., 2022).

In seawater there are three mechanisms for inorganic $CaCO_3$ precipitation: (1) homogeneously – in the absence of any soluble or particulate surfaces; (2) pseudo-homogeneously – in the presence of particulate or colloidal organics; and (3) heterogeneously – in the presence of solid mineral phases (Marion et al., 2009). The critical Ω threshold beyond which $CaCO_3$ formation would occur is highest for homogeneous and lowest for heterogeneous precipitation, with pseudo-homogeneous in between (Morse et al., 2007). In a natural setting, homogeneous precipitation is unlikely, as seawater is hardly void of organic or inorganic particles and/or colloids. For pseudo-homogeneous $CaCO_3$ precipitation, the critical Ω_{arag} threshold is about 12.3 at a salinity of 35 and 20 °C (Marion et al., 2009). For heterogeneous precipitation, it depends on the so-called lattice compatibility between $CaCO_3$ and the mineral surfaces it precipitates onto. For instance, the mineral $CaCO_3$ has a perfect lattice compatibility, meaning that any existing pre-cursors will lead to precipitation at Ω above 1 (Zhong and Mucci, 1989). The rate of precipitation exponentially increases with Ω, about 5-fold for a doubling in saturation state. In contrast, other mineral surfaces have lower lattice compatibilities; for instance $CaCO_3$ precipitation was observed for CaO and $Ca(OH)_2$ above an Ω of 7, while for $Mg(OH)_2$ rates appeared to be even further reduced (Moras et al., 2022, 2023a). Critical Ω thresholds are also influenced by grain size, salinity, and dissolved-organic-matter concentrations (Simkiss, 1964; Chave and Suess, 1970; Moras et al., 2023a) and most likely temperature as well.

The risk of secondary precipitation is particularly high when TA has been increased, but atmospheric CO_2 has not yet entered the ocean; i.e. Ω is still high. However, there is also the possibility of equilibrating seawater with respect to atmospheric CO_2 during TA addition, which would reduce the possibility of secondary $CaCO_3$ precipitation as Ω would be much lower for the same amount of TA added (Bach et al., 2019). Likewise, dilution of TA enhanced with unperturbed seawater has been shown to effectively slow/stop secondary precipitation due to a reduction in Ω (Moras et al., 2022).

1.4 TA additions and critical Ω thresholds in the surface ocean

From a practical OAE standpoint, there will always be an Ω that one will try not to go beyond for extended periods of time to minimise potential secondary $CaCO_3$ precipitation. How much TA can be added therefore depends on initial in situ seawater Ω. Globally, both surface ocean Ω_{arag} and Ω_{calc} are highly correlated, at least on larger scales, with temperature and salinity. On smaller scales, there is also a biological component, i.e. photosynthesis increasing Ω and respiration

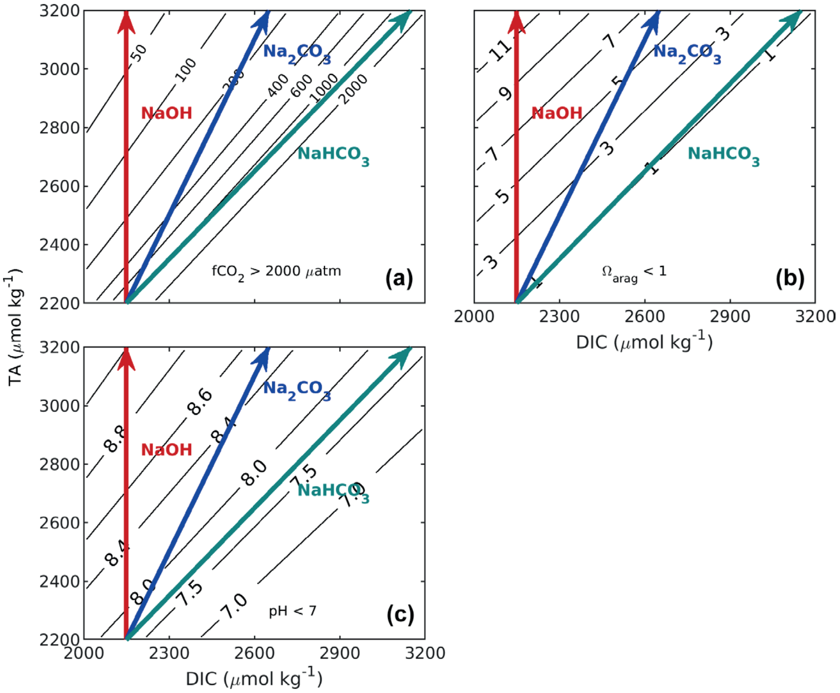

Figure 1. Implications of changes in C_T and A_T on the properties of undersaturated seawater appropriate to the California Current region ($S = 33.5$, $t = 10\,°C$, $A_T = 2200\,\mu mol\,kg^{-1}$, $C_T = 2150\,\mu mol\,kg^{-1}$). Panel **(a)** shows $f(CO_2)$, **(b)** shows aragonite saturation state (Ω_{arag}), and **(c)** shows pH_T. Calculations were carried out with the MATLAB version of CO2SYS (van Heuven et al., 2011) using the stoichiometric dissociation constants for carbonic acid from Sulpis et al. (2020), for sulfuric acid by Dickson et al. (1990), and for total boron from Uppström (1974). The red line indicates the effect of adding NaOH, the blue line indicates the effect of adding Na_2CO_3, and the teal line indicates the effect of adding $NaHCO_3$. If a different initial seawater is chosen, this whole grouping (red, blue, and teal lines) can be translated (moved without any distortion or rotation) so that its initial position is elsewhere in these figures.

decreasing it. Impacts of temperature and salinity changes on carbonate chemistry speciation are 2-fold. While there is a direct effect of temperature on carbonate chemistry speciation, the bigger impact on Ω stems from the higher CO_2 solubility in low-temperature waters. The resulting higher $[CO_2]$ and lower TA/DIC at atmospheric equilibrium leads to a shift towards lower $[CO_3^{2-}]$, and hence Ω. This is because $[CO_3^{2-}]$ is approximately equal to the difference between carbonate alkalinity (CA) and DIC in the ocean (Schulz and Maher, 2023). This largely explains the latitudinal gradient of surface ocean Ω (Jiang et al., 2015). Additionally, the temperature sensibility of the stoichiometric calcium carbonate solubility product (K_{sp}) also contributes to the latitudinal Ω gradient (Mucci, 1983).

When it comes to salinity, there is also a direct effect, but the major driver is that in oceanic waters DIC and TA scale with salinity (mostly driven by water evaporation and precipitation), meaning that they will be significantly reduced at lower salinities. And for a similar oceanic pH at equilibrium with atmospheric CO_2, reducing salinity and DIC, for instance 5-fold, will reduce $[CO_3^{2-}]$ by a similar amount. In turn, this will reduce Ω, together with the salinity-related reductions in $[Ca^{2+}]$ at lower salinities. Globally, sea surface temperatures are highest in the tropics and subtropics and decrease towards higher latitudes (Fig. 2a). Similarly, there is a tendency towards higher salinity at low latitudes and lower salinities at high latitudes (Fig. 2b). In concert, this leads to increasing Ω from polar to tropical waters. For instance, while there are polar regions in which Ω_{arag} is close to 1 on an annual basis, in large parts of the tropical surface ocean Ω_{arag} can be close to 4 (Fig. 2c). Finally, as mentioned earlier, there are also biological drivers of sea surface Ω, for which a good indicator is CO_2 fugacity. Higher-than-current atmospheric pressures of ~425 µatm are indicative of respiratory CO_2 generation, reducing Ω, while pressures below are typically driven by photosynthetic CO_2 fixation, increasing Ω. This modulating effect of biology on temperature- and salinity-driven global surface ocean Ω distributions can be seen by the upwelling of CO_2-enriched deep waters in the tropical Pacific, where elevated fCO_2 results in lower Ω_{arag} (Fig. 2c, d). Altogether, this determines how much TA can be added before a critical Ω threshold is reached. Assuming that Ω should not surpass a threshold of 5 to avoid secondary $CaCO_3$ precipitation (Moras et al., 2022), 5-times-higher TA additions would be possible at high in comparison to low latitudes (Fig. 2e).

The amount of atmospheric CO_2 that can be taken up for a certain TA increase depends on the uptake factor η_{CO_2}

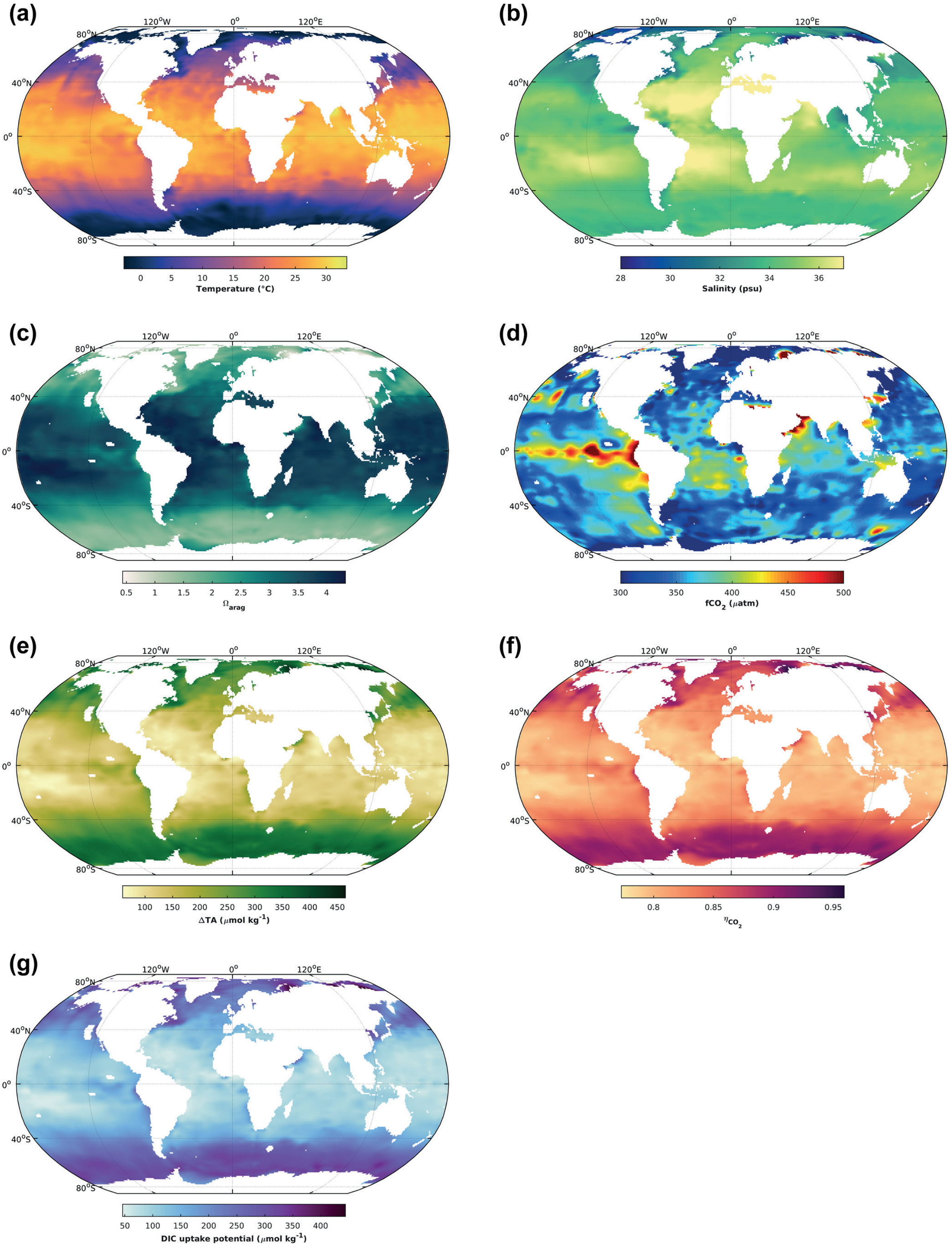

Figure 2. The 1 × 1° GLODAP climatology (Lauvset et al., 2016) for surface ocean (upper 30 m) temperature **(a)**, salinity **(b)**, aragonite saturation state **(c)**, and fCO_2 **(d)**. The latter two variables were calculated from GLODAP dissolved inorganic carbon and total alkalinity using the stoichiometric dissociation constants for carbonic acid from Sulpis et al. (2020), for sulfuric acid from Dickson et al. (1990), and for total boron from Uppström (1974). Finally, the concentration by which total alkalinity can be increased in order to reach an aragonite saturation state of 5, ΔTA **(e)**; the CO_2 uptake factor η_{CO_2} **(f)**; and the resulting increase in DIC by uptake of atmospheric CO_2 upon air–sea equilibration **(g)**. For details see text.

(Humphreys et al., 2018; Tyka et al., 2022). It denotes the molar ratio of the concomitant DIC increase relative to the amount of TA added upon establishing initial seawater $f\mathrm{CO_2}$ by air–sea gas exchange. It is mainly determined by sea surface temperatures, with minor effects of salinity and biology. It ranges between 0.77 and 0.96, with higher values at lower temperatures closer to the poles (Fig. 2f). The resulting DIC uptake potential for global surface waters, for a critical Ω threshold of 5, ranges between only 50 and up to 400 µmol kg^{-1}, being higher at high and lower at low latitudes (Fig. 1g). It is noted though that the $\mathrm{CO_2}$ uptake factor plays only a minor role, and most differences in regional $\mathrm{CO_2}$ uptake potential are driven by the amount of TA that can be added before a critical Ω threshold is reached and/or the amount of time a water parcel stays in contact with the atmosphere (see next section). The uptake factor can be empirically estimated using available carbonate chemistry calculation tools or calculated analytically, for which there are also dedicated routines available (Humphreys et al., 2018).

1.5 Cautionary note on apparent trends in regional differences for atmospheric $\mathrm{CO_2}$ uptake

When looking at the distribution of global DIC uptake potential calculated for a specific OAE application (Ω threshold), there appears to be a general trend for higher uptake at high and lower at low latitudes. However, that only applies to the open ocean, as coastal areas are not included in the underlying Global Ocean Data Analysis Project (GLODAP) climatology. And there, the situation is likely to be quite different, as these areas are heavily impacted by terrestrial influences such as freshwater input but also anthropogenic disturbances such as nutrient runoff, which affects biological processes, and hence the $\mathrm{CO_2}$ uptake potential (see above), in particular as biological activity can be orders of magnitude higher than in the open ocean. Additionally, seasonal changes to carbonate chemistry speciation, which can be quite large, are also not captured.

Furthermore, it is only an uptake potential, and the realised increase in DIC critically depends on regional gas transfer velocities, i.e. how quickly atmospheric $\mathrm{CO_2}$ is equilibrating with the surface ocean and for how long the surface water with increased TA is in contact with the atmosphere before eventually being subducted. There are regions with relatively quick $\mathrm{CO_2}$ equilibration and surface waters remaining in contact with the atmosphere on the relevant timescales, meaning that about a year after the TA increase ∼ 80 %–100 % of the $\mathrm{CO_2}$ uptake potential could be realised (He and Tyka, 2023). In contrast, there are regions with either quite slow equilibration and/or where significant portions of TA-enriched surface waters lose contact with the atmosphere for relatively long times, e.g. regions of deep water formation. Here, the realised $\mathrm{CO_2}$ uptake potential might only be 50 % or less after a couple of decades (He and Tyka, 2023).

Finally, a water mass that has received a TA addition might change its physical properties such as temperature, for instance when moving from high to low latitudes. As such $\eta_{\mathrm{CO_2}}$ decreases along the trajectory, meaning that the $\mathrm{CO_2}$ uptake potential declines. Hence, instead of using $\eta_{\mathrm{CO_2}}$ at the site of TA addition to estimate its DIC uptake potential, it appears more appropriate to use a global mean of 0.84.

Last but not least, it is advisable to not treat $\eta_{\mathrm{CO_2}}$ or the DIC uptake potential as a measure of OAE efficiency. The latter should be assessed in two steps, i.e. first how much of a stable TA increase can be achieved, accounting for potential $\mathrm{CaCO_3}$ precipitation, as well as potentially shifting natural TA source/sink terms, for instance in sediments (Bach, 2023), and secondly, how much of DIC is actually then taken up given a particular air–sea gas exchange and exposure time. Such an approach takes into account the quite different timescales of TA and DIC increases.

2 Sampling and storage of TA-enriched water

Sampling of discrete DIC, TA, pH, and $f\mathrm{CO_2}$ should generally follow protocols described in Standard Operating Procedure (SOP) 1 by Dickson et al. (2007). One caveat, however, is that these protocols were developed for common oceanic carbonate chemistry conditions. Here, we discuss additional measures for sampling and sample storage that may be necessary for carbonate chemistry conditions specific to OAE (i.e. high TA, high pH, and high Ω). We acknowledge that many of the procedures described below are based on anecdotal evidence and need to be further scrutinised with increasing maturation of OAE research and ongoing improvements of this guide.

2.1 Specific problems to consider

In general, there are 4 processes that can alter carbonate chemistry conditions in a sample during its collection and storage. These are

1. modifications via air–sample gas exchange (sampling)
2. modifications via biological activity such as respiration (storage)
3. modifications via the precipitation of $\mathrm{CaCO_3}$ (storage)
4. modifications via diffusion of $\mathrm{CO_2}$ into or out of sampling container walls (storage).

These four processes affect carbonate chemistry parameters differently, and the effect size also depends to a large degree on the sample itself (Table 1). Sampling and storage procedures that describe how to deal with processes 1 and 2 can be found in SOP 1 by Dickson et al. (2007), such as how samples should be collected and stored, including thorough instructions of what materials are recommended to be used and how they should be prepared.

Table 1. Direction of change in a measured carbonate chemistry parameter due to various processes (NC denotes no change). Note that for process 1 the direction depends on whether the sample is over- or undersaturated with respect to atmospheric CO_2. For process 4 the direction depends on whether CO_2 is diffusing from the walls into the sample or vice versa. Also, the direction of TA change in process 2 depends on which form of inorganic nutrients are being released during organic matter remineralisation.

	Air–sample CO_2 exchange (process 1)	Respiration/ remineralisation (process 2)	$CaCO_3$ precipitation (process 3)	Absorption and diffusion of CO_2 to/from walls (process 4)
TA	NC	$+/-$	$-$	NC
DIC	$+/-$	$+$	$-$	$-/+$
pH	$-/+$	$-$	$-$	$+/-$
$f\mathrm{CO_2}$	$+/-$	$+$	$+$	$-/+$
$[\mathrm{CO_3^{2-}}]$	$-/+$	$-$	$-$	$+/-$

$CaCO_3$ precipitation (process 3) has received less attention in SOP 1. This is because $CaCO_3$ precipitation is very slow under most natural seawater carbonate chemistry conditions and is therefore not considered to affect carbonate chemistry conditions during sampling and storage of such waters. However, $CaCO_3$ precipitation accelerates exponentially the further Ω deviates from 1 (Zhong and Mucci, 1989). Extreme Ω values which are much higher than what is commonly observed in the oceans will be frequently encountered in OAE research. Indeed, Subhas et al. (2022) experienced this problem in their OAE experiments, where TA and DIC concentrations in the OAE treatment samples declined during sample storage due to $CaCO_3$ precipitation. The precipitation of $CaCO_3$ reduces TA and DIC at a 2 : 1 molar ratio, also changing carbonate chemistry speciation (Fig. 3). As discussed above, precipitation rates critically depend on Ω but are also influenced by the presence of organic/inorganic particles as precipitation nuclei (Zhong and Mucci, 1989; Marion et al., 2009; Moras et al., 2022; Fuhr et al., 2022), the Mg concentration (Moras et al., 2023a), or the concentration of dissolved organic carbon (DOC; e.g. Chave and Suess, 1970; Pan et al., 2021; Moras et al., 2023a). Since precipitation is usually difficult to predict in terms of how long a sample might be stable, it is advisable to treat the sample in such a way that the potential problem of precipitation is minimised/mitigated.

In the following we describe procedures to avoid changes in carbonate chemistry conditions upon sampling and storage of DIC, TA, pH, and $f\mathrm{CO_2}$.

2.2 General sampling considerations: filtration

It is advisable to filter carbonate chemistry samples upon their collection to remove particles. In oceanography, the cut-off between what is considered to be dissolved or particulate has been operationally defined by passing or being retained on a GF/F filter (Whatman glass fibre grade F). Such a filter has a nominal pore size of 0.7 µm, but smaller pore sizes, for instance 0.2 µm, which would remove bacteria at the same time and theoretically produce a sterile sample, have also worked in the past. Filtration has multiple benefits and might even be required:

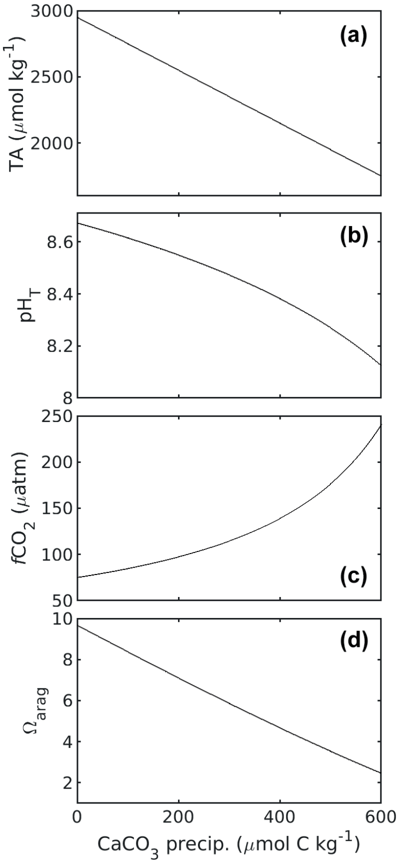

Figure 3. Changes in TA **(a)**, $\mathrm{pH_T}$ **(b)**, $f\mathrm{CO_2}$ **(c)**, and Ω_{arag} **(d)** in response to $CaCO_3$ precipitation, i.e. DIC removal. Carbonate chemistry calculations for a salinity of 35 at 20 °C were as described in the caption of Fig. 1. Starting TA and DIC were 2950 and 2100 µmol kg^{-1}. Please note that for 1 mol of $CaCO_3$ precipitated, 1 mol of DIC is consumed.

1. Particles can serve as precipitation nuclei, which catalyse $CaCO_3$ precipitation during storage. Removing par-

ticles via filtration will therefore help to reduce the risks of secondary precipitation.

2. Removing particles will be necessary if $CaCO_3$ precipitation has already occurred in situ to not interfere with the measurements. This is because typical analytical procedures to measure DIC and TA rely on acidifying the seawater sample during analysis, meaning that any $CaCO_3$ present would re-dissolve and be measured as additional DIC and TA.

3. Filtration of the sample is also useful to remove substrate for biological breakdown and organisms that respire organic carbon. Respiration has limited influence on TA but strongly affects DIC, pH, $f\mathrm{CO_2}$, and $[\mathrm{CO_3^{2-}}]$ (Table 1). However, for samples intended to be stored longer than a few days, sterile filtration is not recommended but instead fixation with mercuric chloride ($HgCl_2$; Dickson et al., 2007).

Filtration can have negative side effects that need to be considered and mitigated. Most obviously, filtration requires additional sampling gear, which introduces contamination risks. Thus, all filtration gear must be prepared appropriately following SOP 1 in Dickson et al. (2007). The most critical issue is that filtration increases the risk of air–sample CO_2 gas exchange. This risk can be reduced when the sample is handled by gentle pressure filtration (as opposed to vacuum filtration, which is prone to gas exchange, i.e. CO_2 degassing) in a closed system. For example, the sample could be pumped via a peristaltic pump using Tygon tubing (relatively impermeable for CO_2) through a membrane filter directly into the sampling bottle, filling it from bottom to top with significant overflow (Dickson et al., 2007; Schulz et al., 2017). Alternatively, the sample could be filled into a syringe (again, potential air–water gas exchange has to be minimised) and filtered through a syringe filter, again from bottom to top with overflow. CO_2 gas exchange would change DIC and hence is also a problem for pH, $f\mathrm{CO_2}$, and $[\mathrm{CO_3^{2-}}]$ samples, which would also change. While TA samples are not affected by air–sample CO_2 gas exchange, they are sensitive to evaporation, so prolonged exposure to the atmosphere must also be avoided.

2.3 General storage considerations

Samples for DIC, TA, pH, $f\mathrm{CO_2}$, and $[\mathrm{CO_3^{2-}}]$ should be prepared for storage and stored as described in SOP 1 in Dickson et al. (2007). If these samples have relatively high Ω values (as a rule of thumb $\Omega_{\mathrm{arag}} > 12$ for filtered and $\Omega_{\mathrm{arag}} > 5$ for unfiltered samples), they most likely require additional measures to avoid changes through $CaCO_3$ precipitation that could eventually occur during storage.

We reiterate that much of what is described below, while appearing to be logical, remains to be tested and validated in dedicated laboratory studies. Thus, care must be taken when adopting these preliminary recommendations.

2.3.1 Preparing DIC samples for storage

DIC changes with $CaCO_3$ precipitation at a 1 : 1 molar ratio (Fig. 3). Eventual $CaCO_3$ precipitation can be avoided by adding a strong acid (e.g. hydrochloric acid – HCl) to the sample, although precautions have to be taken (see below). HCl reduces TA and hence Ω. Such addition also decreases pH and increases $f\mathrm{CO_2}$ in the sample but leaves DIC concentrations untouched. Increasing sample $f\mathrm{CO_2}$ might, however, be a problem; if acid is added in excess to the added TA, $f\mathrm{CO_2}$ will eventually rise above atmospheric levels and increase the risk of outgassing, which would decrease DIC.

Hence, to mitigate CO_2 outgassing it is advisable to dose the HCl additions to just compensate the TA addition, bringing Ω down to typical seawater levels, i.e. $\Omega_{\mathrm{arag}} \sim 2$. Also, prior to full mixing, there might be localised high $f\mathrm{CO_2}$ microenvironments; hence exposure of the sample to air after acidification should be avoided, for instance by closing the lid. Again, equilibrated OAE samples most likely do not require such an acidification step (see Sect. 2.3.1).

To reduce sample dilution, it is recommended to use strong acids (e.g. HCl) at relatively high concentrations. The dilution of the DIC sample with HCl will need to be considered to calculate the DIC concentration of the undiluted sample.

2.3.2 Preparing TA samples for storage

TA changes due to $CaCO_3$ precipitation occur at a 2 : 1 molar ratio (Fig. 3a). $CaCO_3$ precipitation, due to initially high Ω, can be avoided by briefly bubbling the TA sample with pure CO_2 gas. CO_2 decreases Ω and pH and increases DIC and $f\mathrm{CO_2}$ but leaves TA unaffected (note that CO_2 is not part of the TA definition; Eq. 2). The approach was tested with 120 mL of seawater sample, where high-purity CO_2 gas (4.5, i.e. 99.995 %) was bubbled via Tygon tubing through a clean 1 mL pipette tip into the sample for 10 s (Lenc et al., 2023). The CO_2 flow rate was not determined but adjusted so that the bubbling did not lead to spillover in the 125 mL sample bottle. Measured pH declined from initially ~ 8.7 to well below 6 within 10 s so that Ω_{arag} went from ~ 9.5 to much below 1. Under these conditions, TA loss through $CaCO_3$ precipitation is impossible. It is noted that bringing the pH down to pH levels prior to the TA addition, i.e. around 8, would have reduced Ω_{arag} sufficiently (< 5) to avoid $CaCO_3$ precipitation during sample storage if the sample had been filtered.

However, there are several aspects to consider when employing this sample fixation approach. First, impurities in the CO_2 gas could contaminate the TA sample. Particle impurities can be avoided by using filters. Gas impurities (e.g. NH_3) will be more difficult to remove so that it is important to use high-purity gases and test for potential TA impurities. Second, bubbling with dry CO_2 gas directly leads to evaporation of water, increasing TA. It is unclear at this stage how relevant this problem is for a short bubble burst, but it could be avoided by saturating the CO_2 gas stream with H_2O before bubbling the sample, as for example described in Moras et al. (2023b).

Finally, atmosphere-equilibrated OAE samples which have Ω levels below the critical thresholds described above should not require CO_2 bubbling. However, it is advised to actually calculate expected sample Ω from estimates of TA and DIC prior to storage.

2.3.3 Samples for pH and fCO_2

Samples for pH and fCO_2 cannot be stabilised with any of the methods described above. The addition of HCl or CO_2 would alter the carbonate chemistry speciation, including pH and fCO_2. There may be methods to reduce $CaCO_3$ precipitation via the addition of certain inhibitors such as DOC, but such methods would need to be developed. Thus, the recommendation for pH and fCO_2 of samples with high Ω is to measure them immediately after collection.

3 Carbonate chemistry measurements of TA-enriched water

Concerning measurements of carbonate chemistry parameters, there are different needs depending on scientific research questions. Two levels of uncertainty have been proposed, one being able to detect relatively small carbonate chemistry speciation changes in "climate" signals and the other being able to monitor shorter-term or spatial variability, which can be considerably larger, termed "weather" signals (Newton et al., 2015).

Being able to resolve climate signals requires measurement uncertainties equal to or better than $2\,\mu mol\,kg^{-1}$ for DIC and TA, 0.003 for pH, and 0.5 % for CO_2 fugacity. In comparison, for weather signals, values better than $10\,\mu mol\,kg^{-1}$ for DIC and TA, 0.02 for pH, and 2.5 % for fCO_2 are sufficient (Newton et al., 2015).

Concerning OAE, both thresholds could be aimed for depending on the application. For example, if it is to monitor initial TA changes upon an alkalinity addition, which can be on the order of several hundred micromoles per kilogramme of seawater, then aiming to resolve such a weather signal with an uncertainty of better than $10\,\mu mol\,kg^{-1}$ is probably sufficient. However, once this signal becomes diluted and to monitor CO_2 ingassing and DIC increase over timescales of months, an uncertainty for climate signals must be aimed for. In fact, depending on dilution, this might even not be enough, highlighting the fact that monitoring, reporting, and verification (MRV), i.e. determining how many carbon credits can be assigned to a certain OAE effort in the end, are likely to require modelling (Fennel et al., 2023, this Guide; Ho et al., 2023, this Guide).

In any case, a first step before measuring any carbonate chemistry sample would be to assess the accuracy (how far off measurements are with respect to certified reference materials) and precision (what the standard deviation of replicate measurements is) of one's instrumentation, allowing estimation of the overall uncertainty for each parameter in question. Another important point to consider is that OAE samples can be far off the concentrations of typical certified reference material, meaning that checking for linearity can be important (see below for details).

Finally, for any measurements described below, the starting point should be the *Guide to Best Practices of ocean CO_2 Measurements* (Dickson et al., 2007). Hence, with the exception of fCO_2, below we mostly refer to discrete, not in situ, measurements, although the following recommendations should also be considered for the latter.

3.1 Measuring DIC

Acknowledging that OAE samples for DIC can be prone to air–sample gas exchange, if the right precautions are taken during sampling and storage (see Sect. 2.3.1), they should be straightforward to measure. This is because DIC concentrations in a "non-equilibrated" OAE sample will be the same as for untreated seawater samples. However, in samples equilibrated with the atmosphere DIC can be several hundred micromoles higher than typical seawater samples or certified reference material, meaning that the linearity of the measurement instrument and procedure has to be ascertained.

Linearity can be checked for by preparing and measuring Na_2CO_3 (ultrapure and dried at 280 °C for 2 h) solutions of increasing DIC in Milli-Q water (ideally prepared from a concentrated stock solution), covering the required concentration range and comparing the fractional offset of measured against theoretical concentrations for each measurement point (Fig. 4). If the fraction does not change with concentration, the system response is linear, and a "one-point calibration" against a certified reference material will be sufficient. Using $NaHCO_3$ to create a DIC gradient is not ideal as it is not available in ultrapure form, and without further modifications it would create high-fCO_2 samples, which would need additional precautions because of potential CO_2 degassing (note that ΔfCO_2 is much higher for $NaHCO_3$ than for Na_2CO_3 samples).

Finally, it is again emphasised that sample filtration prior to measurement is most likely a crucial step to first stabilise the sample in terms of reducing the potential for $CaCO_3$ precipitation and second to remove any $CaCO_3$ that would have precipitated prior to sampling as it would interfere with the DIC measurement (see Sect. 2.2 for details).

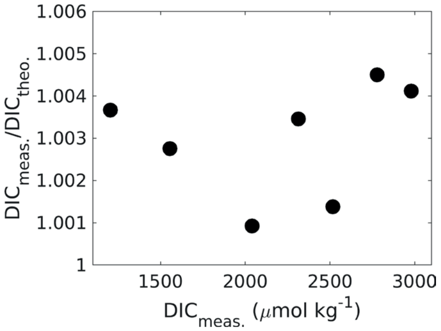

Figure 4. Measured DIC concentrations versus the ratio of measured-to-theoretical DIC, showing that DIC is measured between ∼ 0.1 % and 0.4 % higher than theoretically predicted from self-prepared Na_2CO_3 solutions without an obvious trend across the DIC range. If the instrument response were not linear, this ratio would change with concentration changes. When linear, the mean ratio of measured-to-theoretical DIC allows for correcting measured concentrations for any accuracy bias.

3.2 Measuring TA

When it comes to measuring TA, samples are likely to be enriched in comparison to the typical surface ocean. Hence, checking for linearity of the instrument set-up like in the case of DIC is important. Again, this can be done by preparing suitable calibration standards, covering the required concentration range. However, unlike for relatively straightforward DIC measurements, this requires interpreting pH titration data on the basis of chemical acid–base equilibria in a well-defined ion matrix, called seawater (precisely defining the zero level of protons). Hence, simply using Na_2CO_3 or $NaHCO_3$ in Milli-Q water is not the ideal option. Instead, to cover the higher TA range, suitable amounts of $NaHCO_3$ could be added to seawater (Na_2CO_3 is not advisable as it is quite alkaline and might induce some sort of carbonate precipitation, impacting TA). If the TA range also requires concentrations lower than typical seawater, for instance for samples that had seen substantial amounts of $CaCO_3$ precipitation, then this can be easily achieved by diluting natural seawater with Milli-Q water (weight by weight) and taking the change in salinity into account. Again, checking for changes in the ratio of measured-to-theoretical TA along the measured TA gradient will tell if the measurement system is linear, like for DIC (compare Fig. 4).

A last thing to consider is that high-TA samples can need considerably more titrant if the molarity of the acid is not increased. Under certain circumstances this can lead to nonlinearities, e.g. if the dosing unit needs calibration. Finally, as for DIC it is important that no $CaCO_3$ is present in the sample; hence an additional filtration step during sampling might be required.

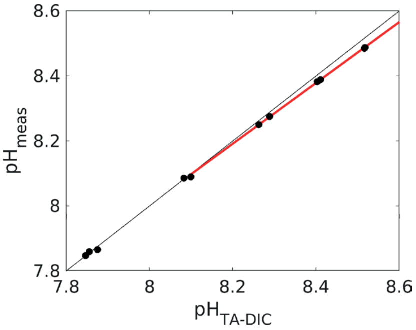

Figure 5. Calculated (from measured DIC and TA; see caption of Fig. 1 for details) vs. measured pH (total scale) using an unpurified batch of mCP. The red line denotes a linear fit through the data above a pH of 8.1.

3.3 Measuring pH

If pH is measured by a glass electrode, following the recommendations in Dickson et al. (2007), there should be no additional precautions required for OAE samples, whether they are of high TA and pH or high TA and DIC, hence typical seawater pH. Also, any $CaCO_3$ that has precipitated prior to sampling will not interfere with the measurements (potentiometric pH only). However, if $CaCO_3$ has precipitated post-sampling, this will have decreased the pH, and an erroneous reading will be made. Concerning accuracy, potentiometric pH measurements can be less accurate than spectrophotometric pH measurements (Bockmon and Dickson, 2015).

For spectrophotometric measurements, one key element is the working range of the pH dye being used. It has been suggested that for sulfonephthalein indicator dyes it is between 1 pH unit below and above the indicator's pK_2 (see Hudson-Heck et al., 2021, and references therein). The latter is the pH for which the concentration of the double-unprotonated form of the dye is equal to that of the single-protonated one (Byrne et al., 1988). The two most commonly used pH dyes for seawater are meta-cresol purple (mCP) and thymol blue (TB), with pK_2 of ∼ 8.0 and ∼ 8.5, respectively, at a temperature of 25 °C and a salinity of 35, although there are a number of studies that have extended the salinity and temperature range (see Hudson-Heck et al., 2021, and references therein). That would suggest that seawater pH ranging from 7 to 9.5 could be measured at high accuracy and precision. However, in practice accuracy can be influenced by dye impurities, and their effect can even be dependent on pH. Hence, when unpurified dyes are used, it is highly recommended to check for the proper working range.

Indeed, we have found the working range to be significantly reduced for an unpurified mCP batch, for which we compared measured pH with calculated pH from measured DIC and TA (Fig. 5). And while a pH deviation of 0.03 pH units at a pH of 8.5 might not seem much, it corresponds to an offset of about 30 μmol kg^{-1} in DIC or TA if this

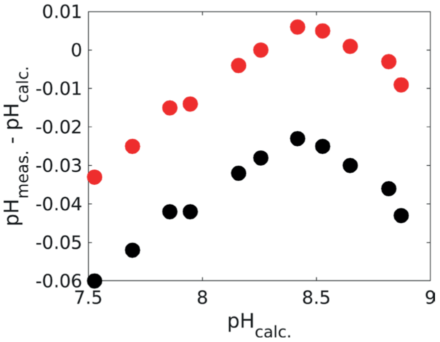

Figure 6. Calculated pH (from measured DIC and TA) versus the difference between measured and calculated pH (total scale). The black dots are values prior to the impurity correction and the red ones after (see text for details).

pH measurement were used for carbonate chemistry calculations without correction, which is clearly way above both the weather and climate thresholds.

Another option for applying corrections is by direct means without the need for ancillary TA and DIC measurements (although they are recommended to check whether corrections are actually working within the desired pH range, which is actually quite important, as we see below). For that purpose, the absorbance ratios obtained with an unpurified dye need to be corrected. While the actual procedure is beyond the scope of this chapter, the reader is referred to detailed instructions in Douglas and Byrne (2017) for mCP and Hudson-Heck et al. (2021) for TB. Again, for the uncorrected pH measurements we found a considerable offset of up to 0.06 pH units (Fig. 6), corresponding to a $\sim 60\,\mu\text{mol kg}^{-1}$ inaccuracy in TA or DIC if this pH measurement were used for carbonate chemistry calculations. Furthermore, the pH error is smallest around pK_2 and increases below and above. While the impurity correction does fix the error close to pK_2, the observed trend remains. The fact that there is some sort of optimum curve behaviour around pK_2 points to an issue with the dye, rather than with measurements of DIC and TA. Hence, two separate linear corrections similar to the one with mCP (Fig. 4) could be applied. Alternatively, purified dyes could be sourced (e.g. Takeshita et al. 2021).

Finally, as for potentiometric pH measurements the starting point for setting up spectrophotometric pH should be Dickson et al. (2007).

3.4 Measuring $f\text{CO}_2$

For $f\text{CO}_2$ measurements, air is being equilibrated with seawater, either via a CO_2-permeable membrane or in a so-called showerhead equilibrator. As for potentiometric pH, any CaCO_3 in suspension will not affect $f\text{CO}_2$ measurements if precipitated pre-sampling. The only difference to typical seawater measurements is that $f\text{CO}_2$ can be relatively low for "un-equilibrated" OAE, e.g. below 100 µatm for a TA addition of $\sim 500\,\mu\text{mol kg}^{-1}$. Hence, full equilibration of seawater with the air to be measured might take a bit longer. Other than that, we do not see any particular issues, other than the generic problems with potential CaCO_3 precipitation if samples are stored (Sect. 2.3).

4 Carbonate chemistry calculations

Carbonate chemistry calculations in an OAE context from two measured parameters can require additional considerations. One is that particular OAE applications change not only TA or eventually DIC but also the major ion composition of seawater. For instance, for calcium-based OAE, with for instance calcium oxide or hydroxide (CaO and Ca(OH)_2), for each mole of TA half a mole of Ca^{2+} will be added. This is the same for magnesium-based OAE, for instance with Mg(OH)_2 or olivine (forsterite). For example, increasing TA by $500\,\mu\text{mol kg}^{-1}$ would increase both calcium and magnesium ion concentrations by $250\,\mu\text{mol kg}^{-1}$, i.e. by 2.5 % and 0.5 %, respectively, over seawater background levels at a salinity of 35.

For calcium-based OAE this means that calculations of calcium carbonate saturation states have to factor in the increase in the calcium-to-salinity ratio. In other words, using standard settings in various carbonate chemistry speciation calculation programs, e.g. CO2SYS, seacarb, and PyCO2SYS (for an overview see Orr et al., 2015), which derive calcium ion concentrations from salinity, will result in wrongly calculated saturation states. Hence, they would need to be calculated in a separate step from calculated carbonate ion and actual calcium concentrations (e.g. Moras et al., 2022), the programs being adapted or special functions used (for instance available for seacarb).

Furthermore, making changes to the matrix of the major ions in seawater also affects acid–base equilibria, i.e. stoichiometric dissociation constants such as for carbonic acid. Hence, one may also need to apply corrections to K_1 and K_2 for carbonic acid (Ben-Yakoov and Goldhaber, 1972), which then can be used to calculate carbonate chemistry speciation, either by hand (Zeebe and Wolf-Gladrow, 2001) or by adapting available programs. Furthermore, the solubility product of calcium carbonate, K_{sp}, needs to be corrected, which can be achieved by using the specific magnesium-to-calcium ratio in a seawater sample (Tyrell and Zeebe, 2004). Finally, the effects of major (and minor) ion composition changes on carbonate chemistry speciation can also be assessed by Pitzer modelling (for an overview see Turner et al., 2016), and there have been several programs and functions made available by the Scientific Committee on Oceanic Research (SCOR) Working Group 145, MARCHEMSPEC: Chemical Speciation Modelling in Seawater to Meet 21st Century Needs (http://marchemspec.org/, last access: 6 November 2023).

Key recommendations

Calcium carbonate ($CaCO_3$) will precipitate in seawater when the saturation state is beyond certain thresholds (critically depending on the presence of organic matter or mineral precursors, among others). Hence, when it comes to determining carbonate chemistry speciation for samples with significantly increased total alkalinity (TA) at regular dissolved-inorganic-carbon (DIC) concentrations, $CaCO_3$ that has precipitated prior to sampling has to be removed for most measurements (TA, DIC, spectrophotometric pH) as it interferes with the analytical procedures. Gentle pressure filtration, avoiding gas exchange of the sample with air, is recommended. Furthermore, if samples are to be stored prior to analysis, $CaCO_3$ precipitation needs to be prevented, which can be achieved for TA (lowering the calcium carbonate saturation state by brief sparging with CO_2) and DIC (acidifying the sample to reduce TA to natural pre-OAE conditions). Samples for $f CO_2$ and pH cannot be stabilised and should therefore not be stored. Any sample that has been stored should be checked visually for potential $CaCO_3$ precipitation on container walls or in suspension. For carbonate chemistry speciation calculations from two measured parameters, if experimental treatments have changed the Mg^{2+}-to-Ca^{2+} ratio in seawater this should be considered by applying corrections to stoichiometric equilibrium constants. Also, experimental changes to Ca^{2+} concentrations mean that readily available calculation routines will report a wrong $CaCO_3$ saturation state as simply related to salinity. Again, corrections have to be made.

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Assessing the technical aspects of ocean-alkalinity-enhancement approaches

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Abstract. Ocean alkalinity enhancement (OAE) is an emerging strategy that aims to mitigate climate change by increasing the alkalinity of seawater. This approach involves increasing the alkalinity of the ocean to enhance its capacity to absorb and store carbon dioxide (CO_2) from the atmosphere. This chapter presents an overview of the technical aspects associated with the full range of OAE methods being pursued and discusses implications for undertaking research on these approaches. Various methods have been developed to implement OAE, including the direct injection of alkaline liquid into the surface ocean; dispersal of alkaline particles from ships, platforms, or pipes; the addition of minerals to coastal environments; and the electrochemical removal of acid from seawater. Each method has its advantages and challenges, such as scalability, cost effectiveness, and potential environmental impacts. The choice of technique may depend on factors such as regional oceanographic conditions, alkalinity source availability, and engineering feasibility. This chapter considers electrochemical methods, the accelerated weathering of limestone, ocean liming, the creation of hydrated carbonates, and the addition of minerals to coastal environments. In each case, the technical aspects of the technologies are considered, and implications for best-practice research are drawn. The environmental and social impacts of OAE will likely depend on the specific technology and the local context in which it is deployed. Therefore, it is essential that the technical feasibility of OAE is undertaken in parallel with, and informed by, wider impact assessments. While OAE shows promise as a potential climate change mitigation strategy, it is essential to acknowledge its limitations and uncertainties. Further research and development are needed to understand the long-term effects, optimize techniques, and address potential unintended consequences. OAE should be viewed as complementary to extensive emission reductions, and its feasibility may be improved if it is operated using energy and supply chains with minimal CO_2 emissions.

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1 Introduction

1.1 Overview of ocean-alkalinity-enhancement approaches

The oceans could be artificially alkalized by the addition of alkali (sodium, Na, or potassium, K) and alkaline (magnesium, Mg, or calcium, Ca) silicates, carbonates, oxides, and hydroxides, often as solids, but also in dissolved, aqueous form. The suite of technologies that aim to achieve this is referred to as ocean alkalinity enhancement (OAE). Figure 1 provides a comparative overview of some of the most widely considered OAE approaches.

Approximately $0.25\,\mathrm{Gt\,yr^{-1}}$ of carbon is removed from the atmosphere due to weathering of silicate rocks on land (Hartmann et al., 2009). The products of this natural process (e.g., Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, CO_3^{2-}, H_4SiO_4) are transferred via rivers and groundwaters to the ocean, where they can durably reside for thousands of years (Renforth and Campbell, 2021). This natural process can be enhanced by first mining and grinding the Mg- and Ca-rich silicate rocks such as basalt and peridotite into fine powders and then adding them to the ocean (Rigopoulos et al., 2018; Köhler et al., 2013; Fakhraee et al., 2023). However, for full dissolution of silicate minerals at the ocean surface, very small particles are needed ($<10\,\mu m$), and as such, the grinding energy to achieve this can be prohibitive (Hangx and Spiers, 2009; Strefler et al., 2018). Instead, larger grains ($<100\,\mu m$) can be applied to coastal zones (Montserrat et al., 2017), where waves and tides have been suggested to help break down the particles and accelerate dissolution in seawater in close contact with the atmosphere in a process known as coastal enhanced weathering (CEW) (Sects. 6 and 7). Although these larger particles dissolve more slowly, they have a lower initial environmental footprint and could be integrated into coastal management schemes such as beach nourishment (Foteinis et al., 2023).

Carbonate rocks, such as limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), are sometimes proposed as an alternative to silicate rocks for OAE due to their faster dissolution in water. However, the surface ocean waters are supersaturated with respect to calcite and aragonite almost everywhere (Orr et al., 2005), implying that limestone is unlikely to dissolve. One solution is to allow the $CaCO_3$ to sink to deeper water, where it is undersaturated (Harvey, 2008), but the significant delay in making contact with the atmosphere and technical challenges limit this approach. Another solution is to convert the limestone to a more soluble form (i.e., calcium bicarbonate: $Ca(HCO_3)_{2(aq)}$) by first dissolving it in a reactor with a high partial pressure of CO_2 (pCO_2) (Rau and Caldeira, 1999). This approach is termed accelerated weathering of limestone (AWL) (Sect. 3). Potential improvements to AWL include systems such as buffered AWL, whereby alkaline minerals (e.g., hydrated lime, $Ca(OH)_2$) are added to buffer the unreacted CO_2 before being discharged to seawater (Caserini et al., 2021a). Calcium bicarbonate solutions for OAE may also be produced electrochemically (Rau, 2008). For these approaches to be meaningful for CDR (carbon dioxide removal), the concentrated CO_2 used in the process must come from the atmosphere (or the surface ocean), via direct air capture (DAC), or from biomass combustion or metabolism.

Alternatively, limestone could be used to create more reactive materials such as lime (CaO) or $Ca(OH)_2$, which dissolve rapidly in the ocean surface – a process referred to as ocean liming (OL) (Kheshgi, 1995) (Sect. 4). Other fast-dissolving solids have been suggested as liming agents, including brucite ($Mg(OH)_2$) (Renforth and Kruger, 2013) and sodium carbonate ("soda ash", Na_2CO_3) (Kheshgi, 1995). However, CaO could be mass-produced by the mining, grinding, and then calcining of limestone, potentially using the pre-existing spare capacity of the cement industry (Renforth et al., 2013). The CO_2 produced in the calcination step can be stored geologically or even utilized and the CaO, or most likely the $Ca(OH)_2$, transported and spread to the oceans. Nevertheless, open questions remain, particularly around the effect of localized pH increase on the marine ecosystems in the wake of the delivery vessels (Caserini et al., 2021b; He and Tyka, 2023) or pipes, while the potential runaway $CaCO_3$ precipitation could lower the CO_2 sequestration efficiency of the approach (Moras et al., 2022).

Alternative pathways are being explored to cost-effectively hydrate minerals and use them as reactive alkaline feedstocks (Sect. 5). Ikaite is one example of a hydrated calcium carbonate mineral which is not supersaturated in the ocean, making it potentially viable for OAE (Renforth et al., 2022). In general, hydration of carbonates has the potential to be less energy-intensive than calcination of limestone while offering comparable alkalinity enhancement to lime and slaked lime.

Aqueous salt solutions such as seawater and brines (e.g., desalination wastes and geological fluids) could potentially provide an abundant source of alkalinity through their electrochemical processing to produce aqueous $NaOH_{(aq)}$ or other hydroxides, which can be used for near-instant OAE and CO_2 drawdown (Sect. 2). There are two main methods of electrochemically generating alkalinity from aqueous salt solutions: electrolysis and electrodialysis. Electrolysis (Willauer et al., 2014) produces high-concentration (approximately 26 wt %) $NaOH_{(aq)}$, along with significant quantities of $H_{2(g)}$ and $Cl_{2(g)}$, which must be used within existing energy or product markets or safely stored through reaction with silicate rocks. Electrodialysis (Eisaman et al., 2012) produces lower-concentration $NaOH_{(aq)}$ (approximately 4 wt %) along with $HCl_{(aq)}$ and negligible amounts of $H_{2(g)}$ and $O_{2(g)}$ that are vented. Electrodialysis has a lower theoretical voltage drop than electrolysis per mole of alkalinity generated because it relies on enhancing water dissociation and the subsequent separation of H^+ and OH^- ions across ion exchange membranes, while electrolysis employs the splitting of water at an electrode surface (Kumar et al.,

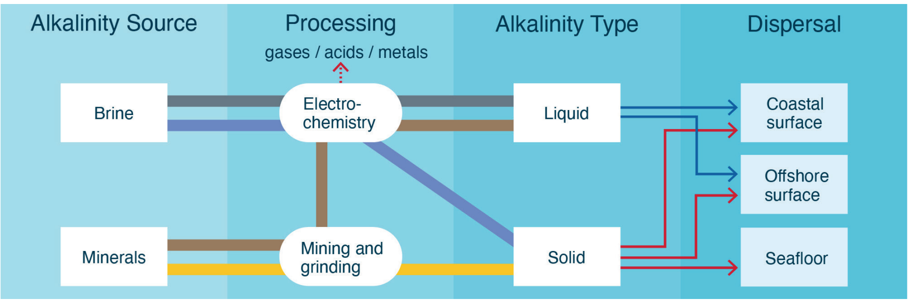


Figure 1. Categorization of different OAE approaches by alkalinity source, processing method, alkalinity type, and dispersal location. Each pathway color represents a unique approach. Dispersal location options are determined by alkalinity type. Liquid alkalinity will likely be dispersed on the coast due to its relatively low value of alkalinity per unit volume and mass, whereas solid alkalinity could be dispersed nearshore, offshore, or directly on the seafloor (in shallow water, e.g., <100 m depth).

2021). That said, electrodialysis produces lower concentrations of $NaOH_{(aq)}$ than electrolysis. In electrolysis $H_{2(g)}$ can be burned for energy or utilized, but the $Cl_{2(g)}$ can be difficult to dispose of and is a potential environmental hazard. In electrodialysis, a use or neutralization pathway must be found for the dilute $HCl_{(aq)}$, for example, by neutralization upon contact with abundant sources of mineral alkalinity.

Even though OAE approaches have the potential to remove atmospheric CO_2 at the scale of gigatonnes per year, they are also responsible for carbon and other emissions during their life cycle. For example, nitrogen-containing explosives (Tovex) that are typically used for mining can impact eutrophication (Foteinis et al., 2022), whereas nickel (Ni) release from olivine dissolution could contribute to aquatic toxicity (Foteinis et al., 2023), although low solubility or co-precipitation with secondary minerals may limit the impact (Guo et al., 2022). Therefore, for sustainable and scalable OAE the life cycle environmental impacts of each approach should be considered and accounted for via life cycle assessment (LCA), rather than simply relying on carbon balances alone. By doing so, not only is the net carbon dioxide equivalent (CO_2 eq.) removal quantified, avoided emissions and tradeoffs with other environmental impacts are also identified. For consistent and meaningful LCAs for OAE, standardized guidelines are required, since the relevant ISO standards (ISO 14040 and 14044) only provide generic guidance that is not technology- or sector-specific. For this reason, the LCA should be specially tailored to OAE applications. Previous work on LCA best practices for similar sectors, such as those for direct air capture and storage (DACS) (Cooney, 2022), and for the wider CDR sector (Terlouw et al., 2021) can serve as a useful starting point.

1.2 OAE technology readiness level

Technology readiness levels (TRLs), developed by NASA in the 1970s, are an estimate of technological maturity. TRLs are based on a scale from 1 to 9, with 9 being the most mature technology (Heder, 2017). Research institutes tend to focus on TRLs 1 to 4, while the private sector focuses on TRLs 7 to 9. Several OAE approaches lie between TRLs 4 to 7, sometimes called the “Valley of Death”, where neither research institutes nor the private sector prioritizes investment.

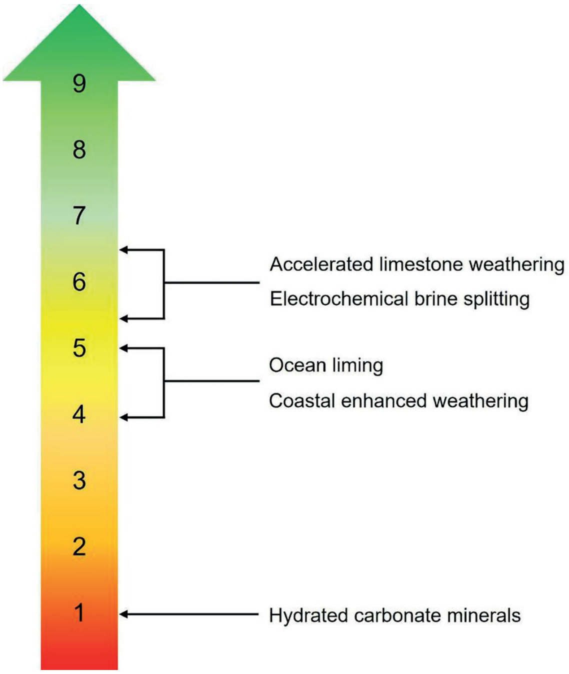


Figure 2. Technology readiness levels (TRLs) for different ocean-alkalinity-enhancement approaches: (1) basic principles observed, (2) technology concept formulated, (3) experimental proof of concept, (4) technology validated in laboratory environment, (5) technology validated in a relevant environment, (6) technology demonstrated in a relevant environment, (7) system prototype demonstration in an operational environment, (8) actual system completed and qualified, (9) actual system proven in an operational environment.

The TRL of OAE approaches is summarized in Fig. 2. A feasibility case study for an AWL system attached to a coastal power plant in Taiwan (Chou et al., 2015) and most recently a pilot-scale AWL reactor for flue gas separation

(Kirchner et al., 2020b) suggests TRL 5–6. Electrochemical brine splitting has a similar TRL of around 6, with several start-up companies in the process of deploying pilot demonstrations. CEW has a lower TRL of between 4 and 5 and is currently undergoing (at the time of submission) field trials in Southampton, New York, to prove its efficacy. There are still significant challenges to scaling up the approach, particularly surrounding monitoring, reporting, and verification (e.g., Rau et al., 2022; see Ho et al., 2023, this Guide) and potential ecosystem effects (Bach et al., 2019), as well as logistical challenges around mining, grinding, and transporting enough alkaline material from land to distribute in the marine environment, which would require massive infrastructure and long supply chains (Renforth et al., 2013). Previously, OL was assigned a TRL of 3 to 4 (McLaren, 2012) but can now be considered to have advanced to a TRL of 4 to 5 after recent (May 2022) field trials in Florida (Voosen, 2022). Finally, the production and application of hydrated carbonate minerals such as ikaite has a TRL of 1 (Renforth et al., 2022).

Overall, while OAE may have great potential for CDR, there are still many unanswered questions about the long-term ecological impacts and the feasibility of implementing these techniques on a large scale. As such, further research and development is needed to increase the TRLs of these approaches and to determine which, if any, other approaches should be scaled up. The ocean is a heterogeneous system, and field tests are required across a variety of oceanic conditions, e.g., temperatures, upwelling velocities, seawater chemistries, and biological profiles. A research program designed to accelerate technology development and demonstration of pilot-scale facilities will also need to assess any potential ecological impacts and governance issues.

2 Electrochemical production of alkalinity for OAE

2.1 Technical summary – chloride brines

Aqueous brine (for example, $NaCl_{(aq)}$) represents an abundant source from which aqueous alkalinity (for example $NaOH_{(aq)}$) can be generated using electrochemistry. In these approaches, the alkalinity is in the form of hydroxide ions ultimately derived from the water in the brine stream, with the dissolved brine ions (for example Na^+ and Cl^-) providing the conductivity and charge balance needed for the process.

The two primary electrochemical processes used to generate alkalinity from brine are electrolysis (O'Brien et al., 2005, pp. 31–34) and electrodialysis (Strathmann, 2011, pp. 163–167), as shown in Fig. 3. Electrolysis generates higher-concentration alkalinity than electrodialysis but requires a higher electrical potential per mole of alkalinity to do so.

This is because electrolysis uses more energy-intensive *water splitting* at electrodes to generate the alkalinity, while electrodialysis uses *enhanced water dissociation* at the junction of the bipolar membranes, combined with ion-selective separation. While the primary by-products from electrolytic alkalinity generation are Cl_2 and H_2 gases, the primary by-product from electrodialytic alkalinity generation is aqueous acid, for example $HCl_{(aq)}$.

The electrolytic generation of alkalinity from an NaCl solution (see Fig. 4) is essentially the well-known chlor-alkali process (O'Brien et al., 2005, pp. 31–34), where aqueous brine (approximately 26 wt %) and NaOH (approximately 28 wt %) are converted into less concentrated brine (approximately 24 wt %), more concentrated NaOH (approximately 30 wt %), hydrogen gas (H_2), and chlorine gas (Cl_2) (Kumar et al., 2021). The development of efficient and durable oxygen-selective electrodes is critical to making seawater electrolysis more feasible (La Plante et al., 2023).

The electrodialytic generation of alkalinity from an NaCl brine typically uses three-chamber bipolar membrane electrodialysis (BPMED) (Strathmann, 2011, pp. 163–167; Fig. 5 herein). In this process, aqueous brine (approximately 3.5 wt %–5 wt %), HCl (approximately 2 wt %), and NaOH (approximately 2 wt %) are converted into less concentrated brine (approximately 2 wt %–3.5 wt %), more concentrated HCl (approximately 3 wt %–4 wt %), and more concentrated NaOH (approximately 3 wt %–4 wt %). Hydrogen gas (H_2) and oxygen gas (O_2) are created at the end electrodes, but in contrast to electrolysis, because there are typically 50–200 membrane triplets between each pair of electrodes, the rate of H_2 and O_2 gas generation relative to the rate of NaOH production is negligible, reduced by a factor of the inverse number of cell triplets relative to electrolysis. In practice the H_2 and O_2 gases generated during electrodialysis are combined and vented. The $HCl_{(aq)}$ generated in this process is used on land in processes that result in the neutralization of the acid, for example in the neutralization of alkaline waste ponds found at sand and gravel operations. Scaling to gigatonnes of CO_2 per year will require larger-scale uses of the acid such as the pretreatment of silicate rocks to enhance the kinetics and capacity of CO_2 mineralization (Guy and Schott, 1989; Pollyea and Rimstidt, 2017).

Once the alkalinity is generated, it must be dispersed into the ocean. An advantage of aqueous hydroxides such as $NaOH_{(aq)}$ is that the rate at which the alkalinity source is *added* to the ocean is equal to the rate at which alkalinity is actually *delivered* to the ocean. In contrast, with solid forms of alkalinity such as crushed minerals, the relationship between rate of alkalinity source *added* and the rate at which this potential alkalinity is *delivered* to the ocean depends on the dissolution kinetics of the solid. From a molecular point of view, since the Na^+ and OH^- ions came from the seawater itself, the net effect of the process is simply the removal of acid in the form of H^+ and Cl^- ions.

Once the alkalinity has been delivered to the ocean, the response of the ocean and atmosphere is governed by two timescales: an immediate timescale that corresponds to the response of the carbonate chemistry of the ocean (Reac-

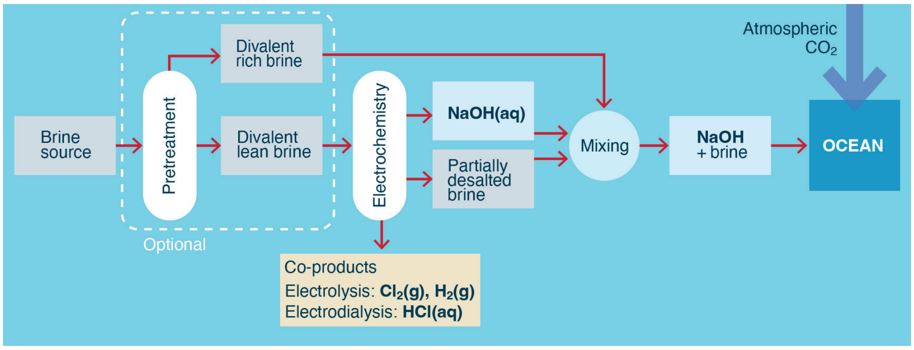


Figure 3. Process flow for the electrochemical conversion of aqueous chloride brine into alkalinity. Both pretreatment and the separation of brine into divalent-rich and divalent-lean streams are optional and are not performed in all processes.

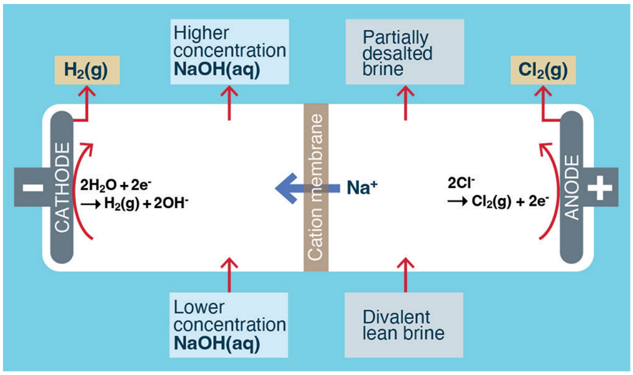


Figure 4. Typical process flow for the electrolytic conversion of aqueous NaCl-rich brine into alkalinity using the chlor-alkali membrane process. A chlor-alkali diaphragm process also exists but is not shown (Kumar et al., 2021).

tion R1),

$$OH^- + CO_{2(aq)} \rightarrow HCO_3^- \tag{R1a}$$

$$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}, \tag{R1b}$$

and a slower timescale of weeks to >100 years (He and Tyka, 2023) that corresponds the re-equilibration of CO_2 in the air and surface ocean via air–sea gas exchange (Reaction R2),

$$CO_{2(air)} \rightarrow CO_{2(aq)} \tag{R2a}$$

$$CO_{2(aq)} + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-. \tag{R2b}$$

The net reaction described by Reactions (R1) and (R2) once equilibrium has been reached is (Reaction R3)

$$OH^- + aCO_{2(aq)} \rightarrow bHCO_3^- + cCO_3^{2-} + dOH^- + eH_2O, \tag{R3}$$

where coefficients a–e are molar ratios relative to the added OH^- (added alkalinity), $a = b + c$ (carbon mass balance), and $b + 2c + d = 1$ (charge balance). For example, modeling in CO_2SYS (Lewis and Wallace, 1998) shows $a = 0.827$, $b = 0.742$, $c = 0.086$, $d = 0.086$, and $e = 0.095$ in seawater at an equilibrium pH of 8.1, $S = 35$ ppt, $T = 20\,°C$, and $P = 1$ bar. These ratios are sensitive to the preceding seawater variables; previously reported values for the ratio of moles of removed CO_2 to moles of added alkalinity (a coefficients) range from 0.75 to more than 0.85 (Tyka et al., 2022; He and Tyka, 2023; Renforth and Henderson, 2017; Wang et al., 2023; Schulz et al., 2023).

As shown in Reaction (R1), on fast timescales, the addition of alkalinity decreases the dissolved CO_2 concentration, putting the surface ocean pCO_2 out of equilibrium with atmospheric pCO_2. On slower timescales of weeks to months for Reaction (R2), equilibrium is re-established as CO_2 from the atmosphere replenishes the CO_2 deficit in the surface ocean. The combined result of these two processes is the net removal of CO_2 from the atmosphere and storage as oceanic bicarbonate and carbonate ions.

Upon dispersal to the ocean, the added alkalinity is increasingly diluted as it moves away from the point of addition. This results in a mixing zone centered at the point of alkalinity addition where the increase in pH and total alkalinity (TA) is largest. The ratio of the rate of alkalinity addition to the rate of dilution must be kept sufficiently low to avoid the precipitation of $Mg(OH)_2$ (which can result in an undesired increase in turbidity) or $CaCO_3$ (which reduces the efficiency of OAE for CO_2 removal) within the mixing zone (Hartmann et al., 2023). Due to this constraint and the permitted limits in the mixing zone for parameters such as pH and turbidity, in practice the pH of aqueous alkalinity may need to be reduced prior to dispersal. For example, prior to release into the ocean, the alkalinity could be mixed with the partially desalted brine stream from which the alkalinity was generated.

To reduce the need for dilution, the alkalinity may first be contacted with CO_2 in air to decrease the pH by converting some of the hydroxide (OH^-) into carbonate (CO_3^{2-}) (Stolaroff et al., 2008). This has the added advantage that all the CO_2 captured in this way is measurable and verifiable through direct measurement. This effectively provides a tuneable knob to perform “partial direct air capture” (DAC)

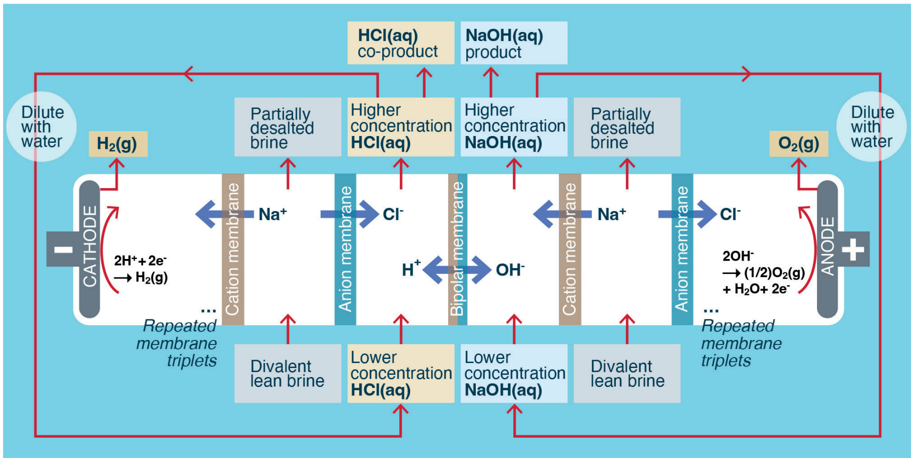


Figure 5. Typical process flow for the electrodialytic conversion of aqueous brine into alkalinity.

to the degree required to reach the target pH, at which point it can be diluted to the pH required by permitting, and the remainder of the CO_2 removal can occur via OAE once it is dispersed into the ocean. The advantage of this use of DAC as a "partial pre-equilibration" for OAE compared to standard DAC, is that when used as a preparation step for OAE, no energy needs to be applied to release the CO_2 as a pure gas. As an example, if one generates approximately 4 % $NaOH_{(aq)}$ using electrodialysis, partial DAC can be used to bring the pH into the range of 11–12, at which point it can be blended with waste brine to the final pH suitable for ocean delivery.

Rather than partial DAC and dilution, aqueous alkalinity may be directly delivered to the ocean at higher concentrations as long as natural or engineered dilution rates in the mixing zone avoid unwanted precipitation and stay within permitted bounds. Alternatively, when discharged within permitted turbidity limits, more slowly dissolving forms of particulate alkalinity such as $Mg(OH)_{2(s)}$ could be used to distribute the added alkalinity more evenly in space and time (Fakhraee et al., 2023).

A process that is very related to OAE using chloride brines is "indirect ocean capture", or IOC (de Lannoy et al., 2018; Eisaman et al., 2018; Eisaman, 2020), also referred to as "direct ocean capture", "direct ocean removal" (DOR), or "CO_2 removal from ocean water" (Kim et al., 2023). This approach employs *alkalinity cycling* to remove CO_2 from the ocean, but *without a net increase in ocean alkalinity* or DIC (total dissolved inorganic carbon). Because the net alkalinity is not enhanced in this process, it should not be labeled as OAE. In one version of this approach, electrodialysis is first used to generate $HCl_{(aq)}$ and $NaOH_{(aq)}$ from brine streams containing $NaCl_{(aq)}$. The acid is used to acidify seawater, decreasing its pH and alkalinity and shifting all its DIC to dissolved CO_2 gas, which is then vacuum-stripped out of the seawater (de Lannoy et al., 2018; Eisaman et al., 2018). The alkaline base is then added to the now decarbonized seawater to restore its lost alkalinity, resulting in CO_2 moving from the air to the seawater to restore equilibrium, thereby replacing the vacuum-stripped CO_2. At a high level, this approach uses the ocean as a pump, in contrast to OAE, which uses the ocean as a sponge. In a second version of this approach, the $NaOH_{(aq)}$ is added to seawater to remove CO_2 as $CaCO_{3(s)}$, with additional $NaOH_{(aq)}$ then added to restore this lost alkalinity and draw CO_2 from the air to replace the removed CO_2 (de Lannoy et al., 2018; Eisaman et al., 2018). The precipitation of $CaCO_{3(s)}$ reduces alkalinity (resulting either in lower efficiency of CO_2 removal per unit of added alkalinity in the case of OAE or a release of CO_2 in cases where the precipitation occurs in the absence of an alkalinity addition), making this second version relatively inefficient from a CO_2 removal perspective, but this may be pursued if other considerations such as ease of verification outweigh this inefficiency. A third version of this approach relies primarily on the precipitation of $Mg(OH)_2$, in addition to the precipitation of some $CaCO_{3,}$ and prevents release of CO_2 in the process of $CaCO_3$ precipitation by generating alkalinity at a sufficiently high rate to keep the pH at a constant target value (La Plante et al., 2021, 2023).

2.2 Technical summary – non-chloride brines and minerals

In addition to the production of alkalinity from chloride salts discussed above, hydroxides can also be electrochemically produced from non-chloride salt solutions such as Na, K, Ca, or Mg sulfates, nitrates, or carbonates. One disadvantage of such an approach is that such salts are much less naturally abundant or less soluble than chloride salts, though they can be present in waste streams. However, as is described in this paper, they can be produced from mineral sources of metal cations and recycled anions. Because of electrochemical issues with nitrate salts and because carbonate salts present

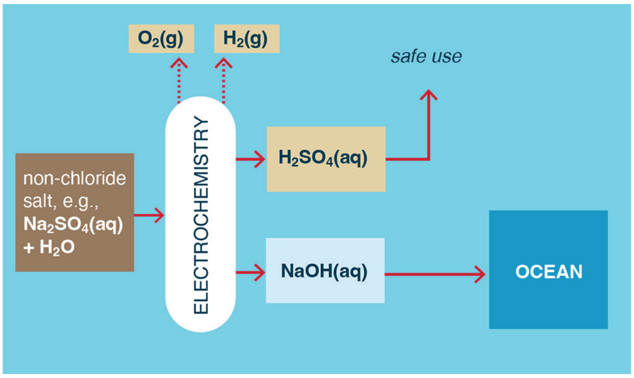


Figure 6. Example of a non-chloride metal salt used to electrochemically produce an acid; a metal hydroxide; and, in the case of electrolysis, H_2 and O_2.

more limited net carbonation potential and often have less solubility, the focus here is on metal sulfate salts.

In the case of $Na_2SO_{4(aq)}$, such solutions can be electrolyzed or electrodialyzed to produce H_2SO_4 (sulfuric acid) at the anode and NaOH at the cathode. In electrolysis, H_2 and O_2 (rather than Cl_2) are also produced at the cathode and anode, respectively (Fig. 6).

While the NaOH can be used for OAE CDR as described above, uses of the acid at the production scales required for globally significant OAE must be identified. Such acids (including the hydrochloric acid described in the previous section) can be reacted with alkaline minerals to produce more neutral metal salts and water (La Plante et al., 2023). For example, the reaction of sulfuric acid with the silicate mineral forsterite (Mg_2SiO_4) yields $MgSO_4$, SiO_2, and H_2O (Reaction R4):

$$Mg_2SiO_4 + 2H_2SO_4 \rightarrow 2MgSO_4 + SiO_2 + 2H_2O. \qquad \text{(R4)}$$

As suggested by House et al. (2007) such metal salts produced from the preceding reaction are in theory benign and could be added to the ocean. However, most silicate minerals contain multiple metals that upon acidification yield metal salts such as Mg, Ca, Fe, Ni, Co, and Na sulfates or chlorides in solution. While at least some of these metal salts will have limited solubility in alkaline seawater, their disposal in the ocean would be problematic due to potential biological effects (see Sect. 4). One alternative is to take advantage of the differences in the reduction in metal solubility as pH rises to selectively remove the less soluble metals as solid metal hydroxides, such as $Fe(OH)_2$, $Ni(OH)_2$, and $Co(OH)_2$, as is commonly done in metal extraction from rocks (Hamilton et al., 2020). Some of the produced NaOH could be used to facilitate pH elevation of the metal salt solution, and the resulting valuable metal precipitates can be harvested for further refining. The remaining, more soluble metal salts, e.g., $MgSO_4$, $CaSO_4$, and Na_2SO_4, could then provide a more benign way to dispose of the products of acid neutralization.

However, such schemes (e.g., Rau et al., 2013) require loss of SO_4^{2-} (or Cl^- in the case of HCl use), and thus a continuous supply of (expensive) sulfate would be required. To overcome this challenge, the sulfate can be recycled first as an acid and then as a metal sulfate and back again (Lammers et al., 2023). For example, a monovalent salt solution, e.g., Na_2SO_4, can be electrolyzed or electrodialyzed to generate H_2SO_4 that is again used to leach metal salts from minerals, but where the NaOH produced in the catholyte is used exclusively to precipitate less soluble polyvalent metals as metal hydroxides (Fig. 7), with the then-reformed $Na_2SO_{4(aq)}$ recycled as brine/electrolyte. In this way Na_2SO_4 is (largely) conserved, and the metal hydroxide precipitates could then be used as an alkalinity source for OAE if they are at least partially soluble in seawater.

Another alternative is to use dissolved metal sulfates produced from the mineral/acid leaching directly as electrolyte/brine in cells where the subsequent precipitation of metal hydroxide inside the cell is avoided or otherwise accommodated (Fig. 8). This could include continually harvesting, for example, $Mg(OH)_2$ or $Ca(OH)_2$ precipitated on or near the cathode (Pan et al., 2020; Sano et al., 2018) and/or using diaphragms (Kelland et al., 2022) or membrane-less cells (Talabi et al., 2017) to avoid membrane fouling by precipitates. Compared to the process in Fig. 7, this method more directly generates hydroxides from mineral sources and water.

2.3 Considerations for best research practices

In this section, we highlight key parts of the brine-to-alkalinity OAE process where the application of best practices is especially critical to performing reproducible research.

2.3.1 Brine treatment

The aqueous brine source input into the electrochemical unit for the generation of alkalinity is often seawater, reverse osmosis concentration (ROC), or some other brine stream that also contains the divalent cations Ca^{2+} and Mg^{2+}. Because the electromechanical systems used for this purpose have compartments with high pH values (>13), care must be taken to avoid the precipitation of solid $Mg(OH)_2$ and/or $CaCO_3$ within the electrochemical unit, as this can lead to increasing voltages, current shunting, and increased hydraulic pressure. Some combination of pretreatment to decrease the concentration of divalent cations and periodic, acidic clean-in-place flushing can avoid this problem. Examples of pretreatment methods include but are not limited to ion exchange and the use of precipitation softening via $NaOH_{(aq)}$ addition.

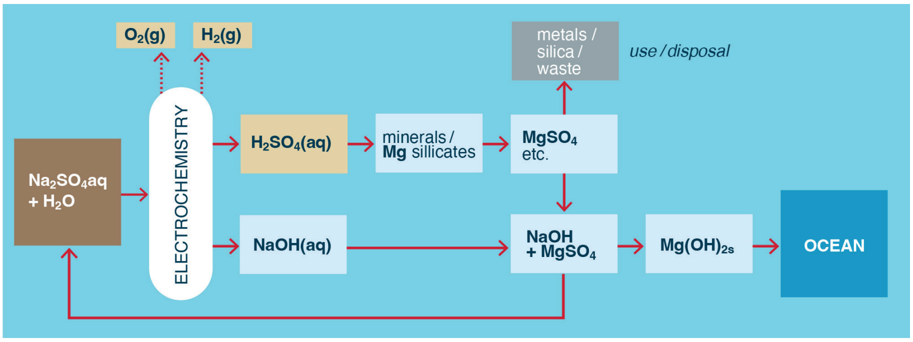


Figure 7. Example of the indirect production of solid, polyvalent metal hydroxides from minerals and water using electrodialysis or electrolysis of a monovalent salt. H_2 and O_2 are also produced.

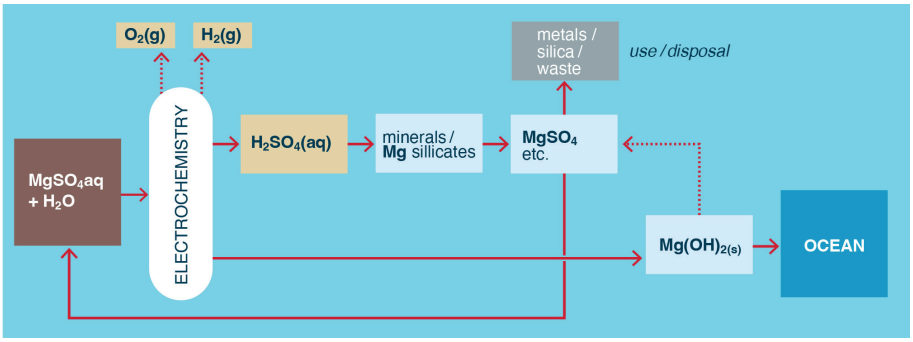


Figure 8. Example of the direct use of metal salts acid-leached from minerals in the electrochemical production of alkalinity for OAE.

2.3.2 Alkalinity generation

In practice, the generated alkalinity may have a more complex ionic composition than the simplified description provided above, depending on the input brine composition and the properties of the electrochemical system such as membrane permittivity and selectivity. For example, because seawater contains K^+ ions and because cation exchange membranes allow K^+ and Na^+ transport, the alkalinity generated from the electrodialytic processing of seawater will not be pure $NaOH_{(aq)}$ but will also contain some fraction of $KOH_{(aq)}$. This means that in-line measurement proxies for the generated alkalinity such as conductivity and pH should be calibrated by offline measurements such as TA titrations and inductively coupled mass spectrometry (ICP-MS). Sampling ports built into the electrochemical system are recommended for this purpose.

2.3.3 Aqueous alkalinity dispersal

As previously mentioned, the ratio of the rate of alkalinity addition to the rate of dilution must be kept low to avoid the precipitation of $Mg(OH)_2$ or $CaCO_3$ within the mixing zone. The carbonate chemistry and turbidity should be continuously monitored near the point of dispersal. Precipitation will manifest as a decrease in TA and increase in turbidity (see Sect. 4).

2.3.4 Energy cost, CO_2 emissions, and economics

In order for research on electrochemical OAE to be relevant to CDR performed at globally relevant scales, it is necessary to document or estimate the energy use, CO_2 emissions, capital costs, and operating costs that are incurred in small-scale systems, and particularly how these would scale for larger systems. These are essential for making informed decisions regarding future RD&D allocations and ultimately decisions about when and where the most cost-effective methods might be deployed.

2.3.5 Environmental and societal impacts and benefits

So as to better inform decision makers, researchers must assess how land, air, ocean, and societal systems might be affected by electrochemical OAE. This includes the environmental and societal consideration of (i) land and resource use such as mineral–salt–brine–water extraction, transportation, processing, and refining; (ii) the footprint of the facility and its operation; and (iii) the downstream impacts/benefits of the products. Researchers should aim to produce a comprehensive budget of all fluxes across the system boundaries (inputs and outputs of energy and matter) to enable this assessment (see Sect. 5).

3 Accelerated weathering of limestone as an OAE strategy

3.1 Technical summary

In a process called accelerated weathering of limestone (AWL), calcium carbonate (derived from carbonate-bearing rocks, e.g., limestone) can be spontaneously carbonated in the presence of elevated $p\mathrm{CO_2}$ and seawater to form predominantly calcium and bicarbonate ions in seawater (Rau and Caldeira, 1999) via the reaction (Reaction R5)

$$\mathrm{CaCO_{3(s)}} + a\mathrm{CO_{2(aq)}} + b\mathrm{H_2O} \rightarrow \mathrm{Ca^{2+}} + c\mathrm{HCO_3^-} + d\mathrm{CO_3^{2-}} + e\mathrm{OH^-}, \qquad \text{(R5)}$$

where the molar quantities relative to $\mathrm{CaCO_3}$ are approximately $a = 0.65$, $b = 0.74$, $c = 1.48$, $d = 0.17$, and $e = 0.18$ when re-equilibrated with typical seawater at pH 8.1 and at a $p\mathrm{CO_2} = 420\,\mu\mathrm{atm}$. The preceding quantities are halved when expressed in units of moles per mole of alkalinity since 1 mol of $\mathrm{CaCO_3}$ = 2 mol alkalinity. This implies a maximum tonnes of $\mathrm{CO_2}$ removal per tonne of $\mathrm{CaCO_3}$ of about 0.29 or a minimum requirement of about 3.5 t of $\mathrm{CaCO_3}$ per tonne of $\mathrm{CO_2}$ captured and stored.

While AWL is an OAE scheme, given the requirement of elevated $\mathrm{CO_2}$ to spontaneously drive Reaction (R5), it has been more widely considered to be a $\mathrm{CO_2}$ emissions reduction technology, analogous to CCS (carbon capture and storage), at coastally located, fossil-fueled power plants (Rau and Caldeira, 1999; Caldeira and Rau, 2000; Rau et al., 2007; Langer et al., 2009; Rau 2011; Haas et al., 2014; Chou et al., 2015, Kirchner et al., 2020a, b; Caserini et al., 2021a; Xing et al., 2022). However, this approach can be relevant to CDR if the concentrated $\mathrm{CO_2}$ used is from (i) emissions from biomass respiration, energy (electricity) production, gasification, or fermentation; (ii) direct air capture; (iii) natural emissions from hydrothermal or geothermal activity; or (iv) possibly natural or artificial upwelling of deep seawater whose $p\mathrm{CO_2}$ is high enough and a $\mathrm{CaCO_3}$ saturation state low enough to facilitate $\mathrm{CaCO_3}$ dissolution.

The $\mathrm{CO_2}$ must be of sufficient concentration so that when equilibrated with water or seawater, $\mathrm{CaCO_3}$ undersaturation in the solution is effected, and the reaction can spontaneously proceed. Calculations using $\mathrm{CO_2SYS}$ (Lewis and Wallace, 1998) suggest that surface seawater equilibrated with a $p\mathrm{CO_2}$ greater than about 2500 µatm is required for $\mathrm{CaCO_3}$ undersaturation to occur and for the reaction to spontaneously proceed. Sufficiently elevated $p\mathrm{CO_2}$ drives down solution pH and thus $[\mathrm{CO_3^{2-}}]$ to achieve a $\mathrm{CaCO_3}$ saturation state that is corrosive to $\mathrm{CaCO_{3\mathit{s}}}$. The higher the $p\mathrm{CO_2}$, the lower the pH, $[\mathrm{CO_3^{2-}}]$, and $\mathrm{CaCO_3}$ saturation state (Ω_{cal}) and hence the faster the kinetics of the reaction, the greater the areal and volumetric reaction rates achieved, and the higher the DIC concentration attained. Experiments have shown reaction rates ranging from about 10^{-7} to $10^{-5}\,\mathrm{mol\,m^{-2}}$ of mineral surface per second. Since volumetric reaction rates are sensitive to carbonate mineral surface area per reaction volume, the interplay among carbonate particle size, seawater and gas contacting, and flow rates dictates reactor design, size, and performance (Rau 2011; Kirchner et al., 2020a; Xing et al., 2022).

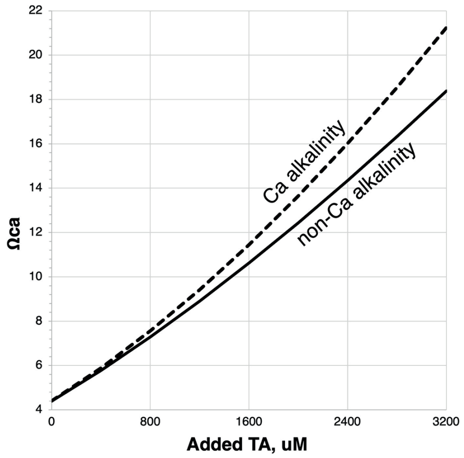


Figure 9. Ωca (the saturation state of calcite) response to calcium-based vs. non-calcium-based alkalinity added to seawater initially containing 2350 µM total alkalinity (TA) and equilibrated with a $p\mathrm{CO_2}$ of 420 µatm. Modeled using $\mathrm{CO_2SYS}$ (Lewis and Wallace, 1998) modified to account for variable $[\mathrm{Ca^{2+}}]$.

Once the calcium bicarbonate+carbonate ions are formed and discharged into the ocean it is presumed that the longevity and security of the storage will be equivalent to that of the existing alkaline C in the ocean, on the order of 100 000 years (Middelburg et al., 2020). This assumes that the AWL Reaction (R5) will not be reversed prematurely by enhanced biotic or abiotic $\mathrm{CaCO_3}$ precipitation. Biotic calcification in some marine taxa has been shown to increase with increasing alkalinity and rising calcium carbonate saturation state, Ω_{cal} (Renforth and Henderson 2017; Gore et al., 2019). Note that calcium carbonate saturation state will be more sensitive to the addition of Ca (bi)carbonate than non-Ca alkalinity since both $\mathrm{Ca^{2+}}$ and $\mathrm{CO_3^{2-}}$ are being added: $\Omega_{\mathrm{cal}} = [\mathrm{Ca^{2+}}]\ [\mathrm{CO_3^{2-}}]/\mathrm{K_{sp}}$, where $\mathrm{K_{sp}}$ is a temperature-, salinity-, and pressure-sensitive solubility constant for calcite. Thus, on a per-mole basis, the threshold for carbonate precipitation will be more rapidly reached with calcium-based alkalinity addition relative to the addition of other forms of dissolved metal (bi)carbonates (Fig. 9).

An additional feature that will further promote carbonate precipitation is the degassing of the excess $\mathrm{CO_2}$ from the carbonated solution once exposed to air. This in effect removes acid from the carbonated solution, raising pH, $[\mathrm{CO_3^{2-}}]$, and Ω_{cal}. An example of the chemical sequence of events in car-

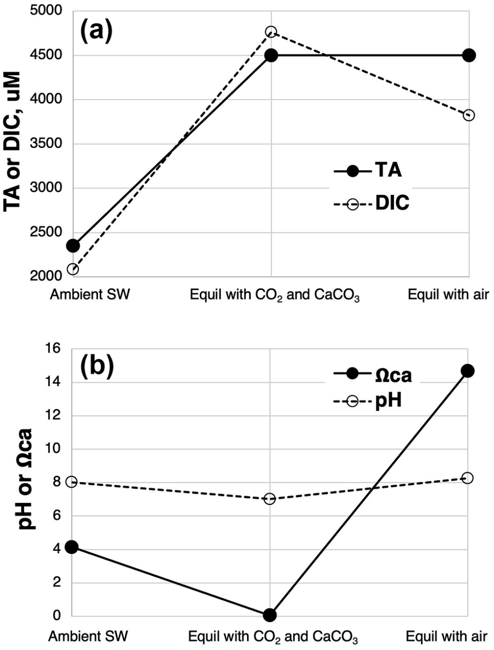


Figure 10. Example of the chemical progression of AWL starting first with representative, ambient seawater at $p\mathrm{CO_2} = 420$ µatm, followed by equilibration with $CaCO_3$s and a $p\mathrm{CO_2}$ of 10 000 µatm as well as re-equilibration with air $p\mathrm{CO_2} = 420$ µatm. **(a)** DIC: total dissolved inorganic carbon; TA: total alkalinity. **(b)** Ωca: the saturation state of calcite. Modeled using CO_2SYS (Lewis and Wallace, 1998; modified to account for variable [Ca^{2+}]).

bonating seawater using AWL and then re-equilibrating the carbonated seawater with air is shown in Fig. 10.

Here the net addition of 2150 µM of dissolved calcium (bi)carbonate in equilibrium with an excess of $CaCO_3$s and a $p\mathrm{CO_2}$ of 10 000 µtams yields a transfer of carbon from the gas to seawater of 2679 µM, about 310 µM of which is in the form of $CO_{2(aq)}$. If this solution was then added to the surface ocean and allowed to re-equilibrate with air $p\mathrm{CO_2} = 420$ µatm, pH would rise above that of the initial seawater (by about 0.24 units), and stored carbon would decline from its high value following carbonation by about 35 %, resulting in a net C storage from the AWL process of 1739 µM C (Fig. 10a). In a full-scale facility, Kirchner et al. (2020b) modeled a 50 % loss of captured carbon following an AWL discharge. The percentage of captured CO_2 lost will very much depend on the $p\mathrm{CO_2}$ of the gas used as well as the degree of chemical equilibration achieved among gas, carbonate, and seawater. Use of high CO_2 and its equilibration with seawater, but with incomplete equilibration with carbonate minerals, will result in an AWL discharge solution with high DIC largely as $CO_{2(aq)}$, but with relatively little additional alkaline C formed (little long-term C storage).

Upon equilibration with air, the loss of excess CO_2 from the above alkalinized seawater forces a rise in Ω_{cal} to 14.5 in the above example (Fig. 10b). This is >3× higher than the initial ambient seawater and could cause spontaneous $CaCO_3$ precipitation from seawater. However, such an effect is likely countered by the rapid dilution of the carbonated solution with ambient seawater relative to the slow kinetics of $CaCO_3$ precipitation (Fig. 7 in He and Tyka, 2023). As long as dilution occurs faster than $CaCO_{3(s)}$ formation, $CaCO_{3(s)}$ precipitation and alkalinity loss can be avoided (He and Tyka, 2023).

The limitations of this approach in the context of OAE CDR include the need for a concentrated non-fossil CO_2 source in close proximity to seawater and carbonate minerals. Potential mineral carbonate sources include globally abundant limestone as well as less abundant dolomite and magnesite. Waste marine shell material or carbonate sands can also be considered, especially because aragonitic shell material should be more soluble than calcite (e.g., limestone) and because this aragonite dissolution simply speeds up the natural return of its marine-derived constituents to seawater. Proximity to the ocean is also a requirement for both the water used for carbonation and for discharge and storage of the carbonated, alkalized seawater. Also, considering a possible upper limit of only about 25 mg C (92 mg CO_2) stably stored per liter of seawater, significant pumping of seawater to facilitate gas/carbonate contacting and conversion must occur. Mining, processing, and transportation of >3.5 t $CaCO_3$ t^{-1} CDR also need to be considered, as do the size and capital and operating costs of the seawater–CO_2–carbonate contactor. For one AWL design, Xing et al. (2022) estimate an energy cost of 5.7–8.2 GJ and a land requirement of 7.1–13.1 m^2 per tonne of CO_2 captured and stored after allowing for degassing of the carbonated seawater following discharge in the ocean.

Advantages of the process include (i) spontaneous, exothermic conversion and long-term storage of CO_2; (ii) potential restoration of ocean pH; (iii) relative ease of verifying CDR by carbonating alkalinity prior to release and quantifying the increase in carbon concentration in solution prior to release rather than having to verify CDR occurring in the ocean; and (iv) providing a relatively simple, low-tech, widely applicable approach to OAE at coastal sites.

In sum, considering the global abundance of concentrated CO_2 waste streams, calcium carbonate mineral resources (including massive waste piles; Langer et al., 2009), and the reactivity of these minerals in elevated $CO_{2(aq)}$ solutions, AWL seems to be an effective way to perform relatively safe, low-cost, low-tech OAE at scale, especially considering that it is routinely used at small scales to alkalinize saltwater aquaria (Huntington, 2002) and considering that such spontaneous rock–water–CO_2 reactions provide the primary source of alkalinity naturally present in the global ocean (Middelburg et al., 2020). Its use in CDR is, however, more restricted considering that the CO_2 used must be concentrated above that in air in order to make the CDR rate relevant on human timescales. Further research is needed to better determine the desirability, effectiveness, and capacity of AWL.

3.2 Considerations for best research practices

3.2.1 Purity of feedstocks

Any impurities in the feed CO_2 or carbonate mineral have the potential to be released with the discharge of the carbonated seawater. The quantity and impacts of these impurities need to be measured to assess the potential for downstream environmental impact as well as reduction in reactivity per mass of mineral. For example, Kirchner et al. (2020a) found measurable trace metal concentrations in their discharge originating from the limestone used, but all concentrations they considered were "below levels of environmental concern". Only slightly elevated NO_3^- was observed in the discharge seawater that originated from the NO_x from the flue gas processed. This study explored the dissolution of limestone in seawater driven by high CO_2 from a point source of fossil fuel combustion emissions rather than concentrated from the atmosphere, and it should be noted that these two cases may not have the same impurities.

3.2.2 Monitoring, reporting, and verification

Because AWL carbonation likely occurs before addition to the ocean, the quantity of carbon captured and converted for long-term storage can in theory be easily quantified as an increase in seawater DIC at point of discharge. This is especially true if the carbonated seawater is equilibrated with air prior to release to the ocean so that excess dissolved CO_2 (that will ultimately be lost from seawater once released) is not counted as sequestered carbon (Fig. 2). Otherwise, the net CO_2 removed and stored can be measured/calculated by either (i) bubbling with air a subsample of the freshly carbonated seawater and measuring its DIC upon air equilibration (e.g., indicated by attaining a stable pH higher than the initially carbonated solution) or (ii) calculating DIC in air-equilibrated discharge by measuring temperature, salinity, pH, DIC, and TA of the freshly carbonated seawater and then modeling its DIC at ambient air $p\mathrm{CO}_2$. In each case the proportional difference in DIC before and after air equilibration must be subtracted from the DIC of the carbonated seawater to yield long-term, gross carbon removed. Net carbon removal is obtained by subtracting all anthropogenic CO_2 emissions incurred in the performance of AWL from gross CDR: gross CDR − emissions = net CDR. Emissions includes those associated with carbonate extraction, processing and transportation; energy usage in water pumping and other operating activities; and infrastructure and maintenance of the system.

3.2.3 Economics

Estimating the possible economics of AWL systems at scale is essential for making informed decisions on future R&D. It requires extrapolating/modeling the costs measured or inferred at research scales. It is therefore important to record carbonate purity, energy usage, and efficiency as well as volumetric reaction rates, water pumping requirements, etc. so as to better estimate costs and performance at scale.

3.2.4 Environmental and social impacts

As in all OAE, the upstream and downstream environmental and social impacts of AWL must be considered at research and larger scales. In particular the impacts of the following must be considered.

i. *Increased carbonate mineral extraction and processing.* However, it should be kept in mind that limestone mining and processing has resulted in massive waste piles of carbonate material whose use could actually benefit land reclamation (Langer et al., 2009).

ii. *Seawater pumping, screening, and carbonation, which can impact resident biota (CEC, 2005).* When possible, it is best to utilize existing seawater pumping (such as for power plant condenser cooling) to avoid additional cost/impacts of new pumping. If the CO_2 used for carbonation is hot (e.g., from exhaust from a biomass energy plant) this will warm the seawater, potentially affecting downstream biota.

iii. *The purity of the carbonate minerals used*. In particular, this refers to the presence of any trace constituents that could have environmental consequences downstream (Sect. 4). Likewise, the purity and temperature of the CO_2 used must be considered in evaluating downstream impacts.

iv. *The societal consequences of AWL activities*. This includes those associated with the upstream increased carbonate mineral extraction, processing, and transportation; the footprint of the AWL operation on land; and any impacts occurring downstream in the ocean (see Sect. 5).

4 Ocean liming

4.1 Technical summary

Ocean liming is the process of adding lime (CaO) or hydrated lime ($Ca(OH)_2$) to the surface ocean (Kheshgi, 1995; Renforth et al., 2013), the dissolution of which increases seawater alkalinity (Reactions R6 and R7; Kheshgi, 1995). Lime is conventionally manufactured through the calcination of limestone at >800 °C (Reaction R8) using fossil fuels and is used in a range of industries including steelmaking, paper manufacturing, construction, and agriculture.

$$CaO_{(s)} + 2CO_{2(aq)} + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \quad (R6)$$

$$Ca(OH)_{2(s)} + 2CO_{2(aq)} \rightarrow Ca^{2+} + 2HCO_3^- \quad (R7)$$

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad (R8)$$

First proposed for OAE (Kheshgi, 1995), the CO_2 produced from the kiln (from limestone decomposition and fossil fuel use) must be captured and stored for the technology to result in a net CO_2 removal (Fig. 11). However, energy requirements (<6 GJ per tonne of CO_2) and the cost (USD 70–160 per tonne of CO_2) of ocean liming are consistent with other engineered CDR approaches (Renforth et al., 2013). Others have shown that the integration of biomass and hydrogen energy vectors may improve the process carbon balance and cost feasibility (Caserini et al., 2019).

Kiln technologies for CaO (often referred to as "burned lime" or "quicklime") production are diverse and include upright or inclined shafts, rotating shafts, and parallel or contraflow introduction of fuel and feedstock. The selection of kiln type depends on the product material characteristics, quality of the limestone feedstock, local market demand, fuel type and availability, and finance availability (European Commission, 2013).

Limestone decomposes at high temperature by solid-state diffusion of CO_2 through the material. The resulting CaO retains the overall volume of the initial calcite but with increased internal porosity (Fischer, 1955). As such it is possible to create lump lime (larger particles of lime produced from similarly sized feedstock limestone).

Powdered $Ca(OH)_2$ is produced by adding a stoichiometric volume of water to CaO ("hydration"; if excess water is used this is referred to as "slaking"; Reaction R9). This hydration reaction is exothermic, resulting in the breakdown of CaO to a fine powder of $Ca(OH)_2$. This is thought to be via a topochemical mechanism (Gartner, 2018), which produces $Ca(OH)_2$ particles around 2–5 µm (Yakymechko et al., 2020); these particles often form larger aggregates of 30–40 µm bound together by weak van der Waals forces (Yakymechko et al., 2020). They are also more porous than CaO, resulting in a higher specific surface area (Moropoulou et al., 2001). There is some literature to suggest that the size of the particle may be controlled by the slaking temperature, (e.g., steam slaking Pesce et al., 2023). Furthermore, the fast reaction rates resulting from small particle size and high surface area are useful in most traditional applications but may not be appropriate for ocean liming (see below):

$$CaO_{(s)} + H_2O \rightarrow Ca(OH)_{2(s)}. \quad (R9)$$

Provided that the CCS is in place to capture the CO_2 emissions from limestone decomposition during calcination, OL can be carbon-negative even when current technology and not fully decarbonized energy is used. Specifically, an LCA on OL (Foteinis et al., 2022) revealed that the main environmental hotspots of the process were limestone calcination, where fossil fuel is consumed for heat generation, followed by CCS, which is energy intensive, while mining, hydration, and ocean spreading affected the environment impact to a much lesser extent. The LCA results were also sensitive to transportation means and distance (although carbonate sedimentary rocks are widely distributed; Fig. 12) and particularly to the kiln technology and fuel type during calcination. When the best available technology is used, along with renewable electricity to drive the process (e.g., calcination using plasma torches), OL's environmental performance is optimized. If the low-grade heat generated during hydration is also recovered and used for district heating, then avoided emissions could also be realized, which can be larger than the process life cycle emissions. In this sense, not only the full amount of CDR is credited to OL, but avoided emissions are also achieved (Foteinis et al., 2022).

It is possible to create magnesium oxides and hydroxides, through either the calcination of magnesium carbonates (McQueen et al., 2020) or extraction from magnesium silicates (Renforth and Kruger, 2013). While the calcination temperature and energy of magnesite is substantially lower than that of calcite, global reserves are approximately ~ 10 Gt (McQueen et al., 2020), which suggests that their exploitation at scale for ocean liming may be limited. Renforth and Kruger explore the coupling of mineral carbonation and ocean liming, in which Mg is extracted from abundant silicate minerals through carbonation and then calcined to produce magnesium oxide/hydroxide materials (Fig. 13).

Processes have been suggested for the extraction of Mg from silicate minerals and the creation of $Mg(OH)_2$ for the purpose of capturing carbon dioxide from flue gases (Madeddu et al., 2015; Nduagu et al., 2012) but may be suitable for OAE as well. Nduagu et al. (2012) suggest a multi-step process in which serpentinite (a Mg-rich rock) is heated at 400 °C, with solid ammonium sulfate creating a solid magnesium sulfate and silica and evolving ammonia and water as gas. The silica can be leached by washing the solid product with water, after which bringing the ammonia gas back into contact with the Mg sulfate creates high-pH conditions under which $Mg(OH)_2$ can precipitate. An alternative approach (Madeddu et al., 2015) heats solids of NaOH and an olivine-rich rock at 180 °C, forming $Mg(OH)_2$ and a Na silicate. Both approaches propose using the $Mg(OH)_2$ for direct reaction with flue gas, and no work has explored their potential for OAE.

4.2 Considerations for best research practices

4.2.1 Lime/hydrated lime production

Lime can be easily created for small-scale laboratory experiments by calcining limestone (or laboratory grade calcium carbonate) in a furnace at 900 °C. It is possible to sinter lime at temperatures >1100 °C, which would result in a lower reactivity. While sintering is often undesirable for commercial

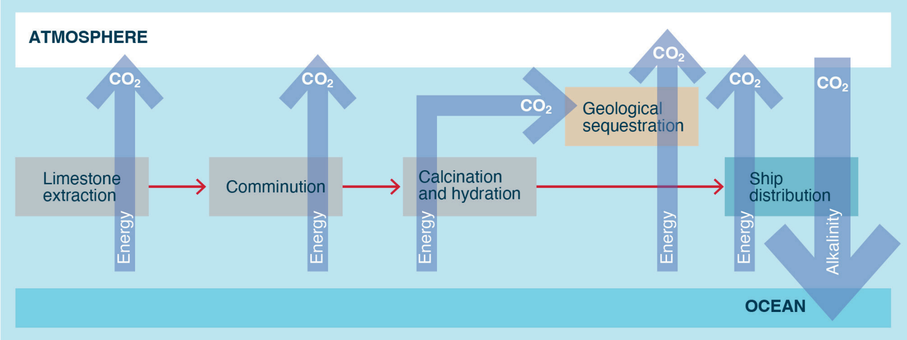


Figure 11. A simplified process flow diagram of ocean liming (Renforth et al., 2013).

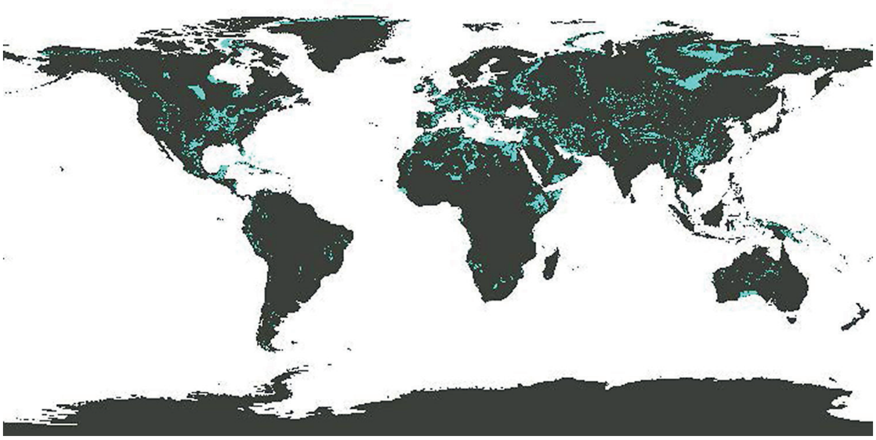


Figure 12. Global distribution of carbonate sedimentary deposits (Hartmann and Moosdorf, 2012; map adapted from Renforth et al., 2022).

lime, the effect may be useful for OAE to reduce particle dissolution rate and prevent oversaturation of carbonate minerals in seawater. Lime products can also be sourced from commercial suppliers. The reaction of burnt lime (CaO) with water is highly exothermic, and its fire safety risk should be considered when storing or using in the laboratory.

4.2.2 Carbonation prior to experimentation

Lime and hydrated lime readily react with atmospheric CO_2 and should thus be produced or sourced as near to the start of the experimental work as possible. The materials can be stored in airtight and/or desiccated containers to minimize carbonation. However, it is difficult (if not impossible) to limit carbonation, and it will certainly be present within commercially sourced material. Carbonate content should be measured (e.g., through mass loss on ignition) before the experiment.

4.2.3 Reactivity and spontaneous precipitation in seawater

Commercially sourced hydrated lime has been manufactured for applications in which high reactivity is desirable. Hartmann et al. (2023) have shown that additions of these particles ($0.7\,\mathrm{mg\,Ca(OH)_2} : 1\,\mathrm{g}$ seawater) may result in spontaneous precipitation of carbonate minerals. Caserini et al. (2021b) modeled an initial particle density of approximately $80\,\mathrm{mg\,Ca(OH)_2} : 1\,\mathrm{g}$ seawater, diluting to $<0.6\,\mathrm{mg\,Ca(OH)_2} : 1\,\mathrm{g}$ seawater (assuming a $10\,\mathrm{kg\,s^{-1}}$ addition through a single discharge nozzle in the wake of a ship) within about 30 s. Experiments that add hydrated lime to solution should use an initial concentration $<0.7\,\mathrm{mg\,Ca(OH)_2}$ assessing particle dissolution across a 10^2–10^4 min range of dilution.

5 Hydrated-carbonate-mineral formation

5.1 Technical summary

There are several hydrated carbonate minerals such as ikaite, monohydrocalcite, nesquehonite, hydromagnesite, and amorphous calcium carbonate that are undersaturated in the surface ocean and are thermodynamically likely to dissolve and increase alkalinity when added to seawater (Table 1). The occurrence of these minerals and a method for their industrial production is presented below.

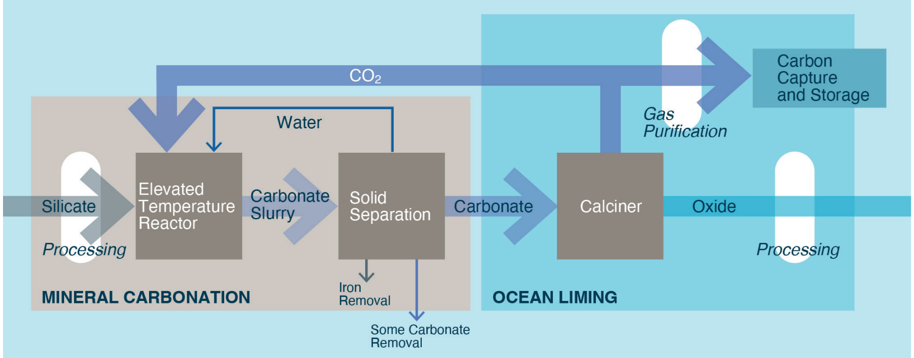


Figure 13. A coupled mineral carbonation ocean liming system proposed by Renforth and Kruger (2013).

Table 1. A summary of potential hydrated carbonate minerals for ocean alkalinity enhancement (see Renforth et al., 2022).

Hydrated carbonate mineral	Chemical formula	Reported occurrence	Gibbs free energy of hydration reaction from unhydrated forms* (kJ mol^{-1})	Gibbs free energy of dissolution reaction in seawater* (410 ppm @ 25 °C) (kJ mol^{-1})
Monohydrocalcite (MHC)	$CaCO_3$ H_2O	Formation of MHC requires magnesium in the solution in spite of the incompatibility of magnesium in the MHC structure. Monohydrocalcite has been observed in air conditioning systems and in moonmilk deposits in caves; both probably formed from spray of carbonate-rich fluids.	4.0	−2.4
Ikaite	$CaCO_3$ $6H_2O$	Naturally occurring, metastable hydrated calcium carbonate mineral that forms in cold (<15 °C), alkaline, nutrient-rich waters.	10.2	−8.9
Nesquehonite	$MgCO_3$ $3H_2O$	The magnesium trihydrate carbonate nesquehonite readily precipitates from solutions of magnesium bicarbonate at room temperature.	17.1	−11.5
Hydromagnesite	$Mg_5(CO_3)_4$ $(OH)_2$ $5H_2O$	Hydromagnesite is an abundant naturally occurring magnesium hydroxyl carbonate (e.g., Königsberger et al., 1999; Russell et al., 1999; Edwards et al., 2005) that constitutes a large and potentially reactive sink for C.	16.9	−28.9
Hydrated amorphous calcium carbonate (ACC)	$CaCO_3$ xH_2O	ACC is unstable under normal conditions and is found naturally in taxa as wide-ranging as sea urchins, corals, mollusks, and foraminifera.	–	–
Calcite	$CaCO_3$	Naturally abundant in limestone.	–	1.6
Magnesite	$MgCO_3$	Accessory mineral in limestone, alteration product in weathering of ultrabasic rock.	–	5.7

* Negative values denote an exothermic/spontaneous reaction.

Ikaite ($CaCO_3 \cdot 6H_2O$) precipitates from aqueous solutions close to freezing conditions (Boch et al., 2015) in a narrow temperature range below ca. 4–8 °C and depending on ionic strength down to negative temperature values (e.g., in highly saline solutions down to −8 °C; Hu et al., 2014; Papadimitriou et al., 2014). Alternatively, elevated-pressure conditions (>3 kbar at 25 °C) facilitate the crystallization of ikaite (Marland, 1975; Shahar et al., 2005). The solubility of ikaite is higher compared to the anhydrous calcium carbonate polymorphs calcite, aragonite, and vaterite (Brečević et al., 1993; Marion, 2001). Dissolved compounds such as magnesium, phosphate, sulfate, and organic molecules that inhibit the formation of anhydrous calcium carbonates favor the nucleation of ikaite (Brooks et al., 1950; Bischoff et al., 1993). Outside these restricted environments ikaite dehydrates and disintegrates rapidly (within minutes to weeks), preferentially into more stable carbonate minerals and water (Mikkelsen et al., 1999). In some cases, calcite pseudomorphs after ikaite might persist ("glendonite"; Greinert and Derkachev, 2004).

Monohydrocalcite (MHC: $CaCO_3 \cdot H_2O$) is a rare mineral in geological settings (Nishiyama et al., 2013) but is frequently associated with other calcium and magnesium carbonate minerals, such as calcite, aragonite, lansfordite, and nesquehonite (Nishiyama et al., 2013). Monohydrocalcite has been observed in air conditioning systems (Nishiyama et al., 2013), in "moonmilk" deposits in caves (Nishiyama et al., 2013), and in beach sands formed from algal spume (Nishiyama et al., 2013). It has been reported as a significant component of the decomposition of ikaite in the towers of the Ikka Fjord, West Greenland (Nishiyama et al., 2013). Both laboratory studies and natural observations have indicated that the formation of MHC requires the presence of magnesium in the solution (Nishiyama et al., 2013), possibly forming via a Mg-rich amorphous precursor (Nishiyama et al., 2013).

The magnesium carbonate mineral nesquehonite ($MgCO_3 \cdot 3H_2O$) precipitates at room temperature from supersaturated solutions rich in magnesium and bicarbonate (Hopkinson et al., 2008). It is metastable and transforms into hydromagnesite under ambient conditions (e.g., Kazakov et al., 1959), which may be responsible for some naturally occurring hydromagnesite (Davies and Bubela, 1973). Mafic and ultramafic mining wastes, by virtue of their high calcium and magnesium content, are prone to forming numerous carbonate species upon contact with atmospheric CO_2 depending on the environmental conditions that prevail at the stockpiles, but metastable nesquehonite was reported to be the dominant magnesium carbonate forming under ambient conditions (Zarandi et al., 2017). Upon rising the temperature above 50 °C, nesquehonite evolves into thermodynamically more stable products with lower $CO_2 : Mg$ ratios (Zarandi et al., 2017).

Hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) is a naturally occurring hydrated magnesium carbonate (e.g., Königsberger et al., 1999). At the Woodsreef Asbestos Mine, New South Wales, Australia, weathering of ultramafic mine waste sequesters significant amounts of CO_2 in hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) (Oskierski et al., 2021). Mineralization of CO_2 in aboveground, sub-aerially stored tailings is driven by the infiltration of rainwater dissolving Mg from bedrock minerals present in the tailings (Oskierski et al., 2021). Complete dissolution of source minerals, or formation of Mg-poor products during weathering, is expected to transfer Mg into solution without significant alteration of the Mg isotopic composition (Oskierski et al., 2021). The main mineral sources of Mg in the tailings (silicate, oxide/hydroxide, and carbonate minerals) are isotopically distinct, and the Mg isotopic composition of fluids and thus of the precipitating hydromagnesite reflects both isotopic composition of source minerals and precipitation of Mg-rich secondary phases (Oskierski et al., 2021). The consistent enrichment and depletion of ^{26}Mg in secondary silicates and carbonates, respectively, underpins the use of the presented hydromagnesite and fluid Mg isotopic compositions as a tracer of Mg sources and pathways during CO_2 mineralization in ultramafic rocks (Oskierski et al., 2021).

Amorphous calcium carbonate (ACC) is unstable under normal conditions and is found naturally in taxa as wide-ranging as sea urchins, corals, mollusks, and foraminifera. It is usually found as a monohydrate, holding the chemical formula $CaCO_3 \cdot H_2O$; however, it can also exist in a dehydrated state, $CaCO_3$ (Rodriguez-Blanco et al., 2011). ACC was first reported over 100 years ago, when a non-diffraction pattern of calcium carbonate was discovered by Herman Sturcke, exhibiting its poorly ordered nature (Rodriguez-Blanco et al., 2011). The structure and chemistry of ACC is complex, with several forms of ACC classified according to their water content, local order, and mode of formation (e.g., abiotic vs. biogenic). A key variable is the amount of structural water. Hydrated ACC can contain up to ∼1.6 mol of water per mole of $CaCO_3$, yet several less hydrated and even anhydrous forms of ACC have been described (Rodriguez-Blanco et al., 2011; Bots et al., 2012).

Hydrated carbonate minerals are relatively rare and thus insufficient to meet the demand of a scaled up OAE industry. As such, they would need to be created. Renforth et al. (2022) suggest a process by which limestone is dissolved in water in an elevated CO_2 pressure reactor (∼ 2 bar). The water is then degassed in lower-pressure reactors (∼ 20 mbar) under vacuum to evolve/recycle the gaseous CO_2 and create conditions under which carbonate minerals are likely to precipitate from the solution (Fig. 14). If the precipitation environment is cooled or in the presence of calcite precipitation inhibitors, then Renforth et al. (2022) suggest that ikaite will form.

There are several benefits for considering hydrated-carbonate-mineral addition for OAE. The chemical energy imparted into lime or hydrated lime during production is released during its dissolution and carbonation in the surface ocean. This energy is impossible to recover. The production of hydrated carbonates requires considerably less energy.

5.2 Considerations for best research practices

5.2.1 Summary of method of precipitating hydrated carbonates

The multistep pressure system for its mass production (Fig. 14) may not be convenient or necessary for all laboratory studies that may want to consider the impact of ikaite dissolution on seawater biogeochemistry. Existing methods for precipitating hydrated carbonates involve the reaction of an alkaline liquid (usually NaOH or Na_2CO_3) with calcium or magnesium chloride (e.g., Lennie et al., 2004). It is not yet clear if characteristics of these materials differ from those that might be produced from a pressure swing system.

5.2.2 Stability of hydrated carbonates

The feasibility of using hydrated minerals for OAE requires the produced mineral to remain stable for sufficient time to be

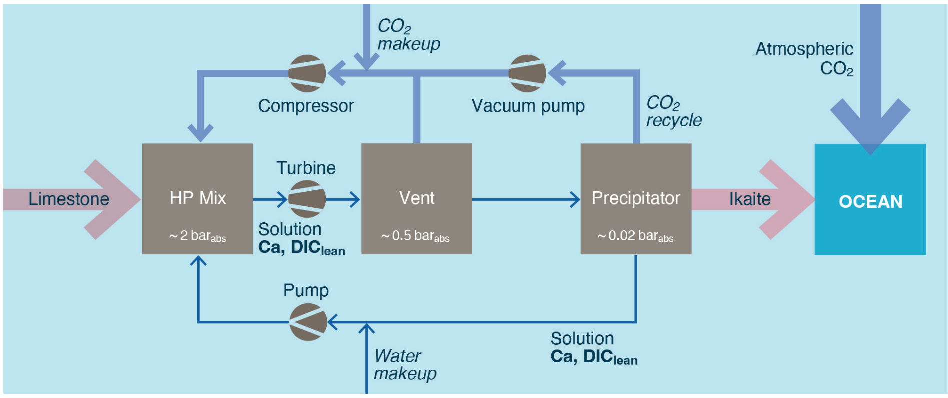


Figure 14. A CO_2 pressure swing process for creating a hydrated carbonate (adapted from Renforth et al., 2022).

added to the ocean and dissolve. Similarly, experiments performed using hydrated minerals should have sufficient confidence that the materials added to seawater have not converted to more stable anhydrous polymorphs. If these minerals were to transform into calcite or magnesite before addition it could result in a reduction in alkalinity by seeding additional carbonate precipitation. Experimental work suggests that synthetic ikaite can be stable for days at low temperature and that it increases alkalinity when dissolved in seawater (Renforth et al., 2022).

5.2.3 Methods of detection

Hydrated carbonate minerals are identifiable by several techniques including Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), electron probe X-ray microanalysis (EPMA), and scanning electron microscopy (SEM).

Raman spectroscopy is a non-destructive method that requires little or no sample preparation. Moreover, all the bands related to carbonates in the mid-infrared region have characteristic positions which make it easy to differentiate from other minerals. Raman analyses of carbonates have long been used in mineralogical and geochemical research (see Kim et al., 2021, and references therein).

FTIR is rapid (a few minutes per sample), does not require hazardous chemicals, has a small sample requirement (~ 1 mg), and produces several distinguishable carbonate bands in its spectrum. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a form of FTIR with additional advantages compared to transmission FTIR. DRIFTS does not require sample dilution in infrared transparent material, thus reducing sample preparation time; its sample-holding microcells allow for fixed volumes; and the sample is recoverable after analysis. DRIFTS is a method that has been used for identifying and quantifying calcite and dolomite in natural sediments. Few studies have used spectroscopic techniques to quantify carbonate in non-carbonate geological matrices (Bruckman and Wriessnig, 2013; Du et al., 2014; Tatzber et al., 2007).

XRD is the most commonly used tool for identification of major minerals. In addition to qualitative analysis, quantitative XRD is possible because the peak intensities of a given mineral in the diffractogram are proportional to the weight percent of that particular mineral in the sample. However, peak intensities are also a function of the mineral's absorption coefficient, particle size, degree of crystallinity, and the preferred orientation of the sample; this means that compared to qualitative analysis quantitative XRD requires more specialized expertise to produce accurate results.

6 Mineral addition to pelagic coastal environments

6.1 Technical summary

Using the ocean's surface waters (which refers to the mixed layer) for mineral addition to increase ocean alkalinity has been the focus of interest of numerous research projects (Renforth and Henderson, 2017), starting with exploring suitable minerals to achieve increased alkalinity while investigating potential side effects on marine life and ecosystems. An obvious problem for the community of researchers involved in OAE has been identifying and generating the particle type and size required to allow for dissolution, classically considered to be smaller than 63 µm (Hangx and Spiers, 2009). However, while this particle size is comparably easy and energy-efficient to produce, residence times in the water column would for most minerals be too short to allow for dissolution, and particles would sink out too rapidly. To avoid mineral loss via sinking, particle sizes of <1µm would be required (Köhler et al., 2013), which are difficult to produce in a climate-neutral manner, and their application might be harmful for humans, leading to respiratory problems (e.g., Doelman et al., 1990). One way to work with bigger grain sizes is to turn to coastal systems, where particles would sink to the seafloor and be transported back into the water column by natural turbulence, allowing for increased dissolution over time.

Classically, silica minerals such as olivine (forsterite or fayalite) and carbonate sedimentary rock such as limestone and dolostone (dolomite) have been suggested to increase alkalinity in an efficient way (Renforth and Henderson, 2017). However, large-scale experiments are still a rarity (see also Riebesell et al., 2023, this Guide and Cyronak et al., 2023, this Guide). Other possible minerals for this purpose are basalt or serpentine. When choosing minerals, an ambition should be to ensure availability near the application location to reduce the carbon footprint, thus limiting the choice of mineral and again emphasizing the advantage of coastal applications as compared to open-ocean applications.

Another concern when applying alkaline minerals is the stability of alkalinity due to possible formation of carbonate phases. This results from the ocean's supersaturation in calcite and aragonite (Sarmiento and Gruber, 2006). If an increase in alkalinity is introduced along with an increase in carbonate ion concentrations, the supersaturation would increase even more, which has been suggested to lead to solid carbonate precipitation (Fuhr et al., 2021; Moras et al., 2022; Hartmann et al., 2023). This, in turn, would decrease surface alkalinity, causing an effect opposite to the desired one, whereby the decrease in alkalinity would depend on the mineral used. One proposed solution to address this challenge is the application of CO_2-equilibrated alkaline solutions to minimize the risk of losing alkalinity due to carbonate phase formation.

Open-ocean and water column silicate mineral applications have the potential to increase both the chemical and the biological carbon pump. Here, the biological carbon pump was of interest due to its potential to remove CO_2 on a timescale of several thousands of years (Longhurst et al., 1995; Petit et al., 1999; McNeil et al., 2003). The line of reasoning was often based on Earth's historical considerations, with cold periods in Earth history having been related to increased photosynthetic activity by phytoplankton (Kirschvink, 1992; Penman and Rooney, 2019). However, recent studies suggest that mineral additions can, in addition to benefits, also pose risks to marine life, including primary producers (Bach et al., 2019; Guo et al., 2022). This effect is likely related to the increased concentrations of trace metals enriched in the minerals of choice. Earlier dissolution experiments with olivine have shown that an increase in alkalinity of about $100\,\mu mol\,L^{-1}$ led to an increase of $\sim 3\,\mu mol\,Ni\,L^{-1}$ due to non-stoichiometric dissolution of the heterogeneous material; this equals approximately 3 times the natural concentration in seawater (Montserrat et al., 2017), within the toxic range for many eukaryotic microalgae (Glass and Dupont, 2017). Other trace metals present in alkaline minerals, including Cu, Cd, Cr, or other heavy metals, might impose further ecotoxicological effects, depending on their concentration in the minerals transferred to the water column or sediment (Simkin and Smith, 1970; Beerling, 2017). Anthropogenic materials including from mining or cement production could also contain a variety of trace metals at concentrations yet to be determined, which might become particularly problematic to organisms of higher trophic levels in which they accumulate (Garai et al., 2021).

It is essential to consider whether the added minerals remain in the water column and impact the growth of the vital primary producers in the food web. Another important consideration is whether adding alkaline minerals impacts the local communities in the treated area and leads to any changes. Moreover, a possible change in the local communities might see the appearance of organisms that release other greenhouse gases, potentially offsetting the sequestration achieved through the treatment.

Careful considerations have to be undertaken in order to ensure safe minimum standards. One important aspect is that field applications cannot exceed environmental quality standards (EQSs; European Commission, 2017). EQSs define the threshold concentration of potentially harmful toxic metals, like nickel and chromium. The impact of minerals enriched in those trace metals on biodiversity and ecosystem function is difficult to study, as minerals are not necessarily homogeneous and contain similar trace metal concentrations. Trace metal concentrations, however, may limit the amount of mineral addition, especially of olivine-rich rocks, that can be deployed in marine habitats (e.g., Flipkens et al., 2021). The potential difficulty arising from introducing toxic compounds would vary strongly depending on the respective ecosystem's tolerance to those compounds. Coastal environments can have limitations, especially with regard to sediments, which already have a (natural) background in trace metals and accumulate trace metals over time (see Sect. 6.2). Furthermore, seawater pH should be kept within a natural seawater range ($pH \leq 8.2$; Pedersen and Hansen, 2003). Even though phytoplankton can be adapted to a wide range of pH, the growth rates of a majority of species can be influenced significantly (Hinga, 2002; Penman and Rooney, 2019). In addition, a $pH > 9.5$ can promote the precipitation of aragonite, as well as brucite together with phosphorus and silicate (Hartmann et al., 2023). On the other hand, depending on the deployed material, specific plankton groups might benefit from, for example, iron additions (Boyd et al., 2000).

To scrutinize the effect of OAE as a tool to mitigate climate change, it is necessary to also investigate the impact of mineral addition, pH, and alkalinity changes on non-CO_2 greenhouse gas production. Two important greenhouse gases are methane and nitrous oxide, with warming potentials of approximately 70 and 300 times that of CO_2, respectively (Bange, 2006a). While the ocean is a minor source of methane to the atmosphere, it contributes about one-third of nitrous oxide emissions to the atmosphere (Bange, 2006), making it critical to understand any potential impacts of OAE on its formation. N_2O is chiefly produced biologically, with the microbes producing it known to be sensitive to changes in pH (Thomsen et al., 1994; Seeländer, 2023); however, so far, the few available studies indicate a reduction in N_2O production if pH and alkalinity are increased.

When considering the technical challenges within the pelagic environment for OAE, one of the primary considerations is how to effectively measure the CO_2 offsets generated from techniques that utilize the pelagic environment; therefore a standardization of MRV (measurement, reporting, and verification) is a necessity to secure procedures that ensure the accuracy and precision of measurements (see also Ho et al., 2023, this Guide). Within that, a reliable and well-established analysis technique for determining relevant parameters (e.g., alkalinity) is required to ensure the accuracy and comparability of data. Ecosystem diversity in pelagic environments will vary according to the location because of the biological, chemical, and physical parameters due to, for example, ocean currents, temperatures, and wind. Therefore, considerations from many disciplines are essential to explore the complexity.

To carry out coastal pelagic OAE research an understanding of benthic–pelagic coupling is required to assess the impact on benthic systems and ecosystems and to be able to maximize the use of this coupling for OAE. Further, it is critical to assess the local and regional biodiversity by means of meta-omics, flow cytometry, or similar high-resolution methods for microbial life to then understand what thresholds for trace metal additions would introduce toxic effects as defined in Bach et al. (2019) and references therein. For macro-life forms, targeted ecotoxicological assessments are required to avoid damage to, and heavy metal accumulation in, top predators and to establish robust thresholds.

6.2 Considerations for best research practices

Application of particles is challenging (see also Sect. 7.2), as small sizes are required to assure water column dissolution, but larger particles ($\sim 63\,\mu m$) can be used if the goal is to achieve OAE in both the benthic and pelagic parts of a coastal system, where resuspension of particles can be useful to achieve mixing. However, any particle addition might lead to shadowing, thus impacting photosynthetic organisms in the pelagic and benthic realm, requiring a thorough understanding of both benthic and pelagic primary production to avoid harming the basis of the ecosystem. In addition, mechanical stress can be imposed on benthic organisms by adding particles; data, however, are limited here and will have to be gathered for every system individually.

While those effects will vary largely for each ecosystem, trace metal toxicity can be avoided. Before particles are added, we recommend a thorough analysis of the major elements in the mineral of choice to quantify the effect of mineral addition on the total alkalinity change potentially obtained in the system but also to define the upper limit of additions with respect to trace metal toxicity. For some organisms, including pelagic primary producers, thresholds are available from the literature; however, to understand the impact of trace metal toxicity on complex food webs testing before application should be carried out in mesocosms and benthocosms containing assemblages or subsets of the natural communities present in the ecosystem of choice. At a minimum, key species should be tested individually for their trace metal (and pH) tolerance to avoid damage to biodiversity.

7 Addition to the coastal seafloor

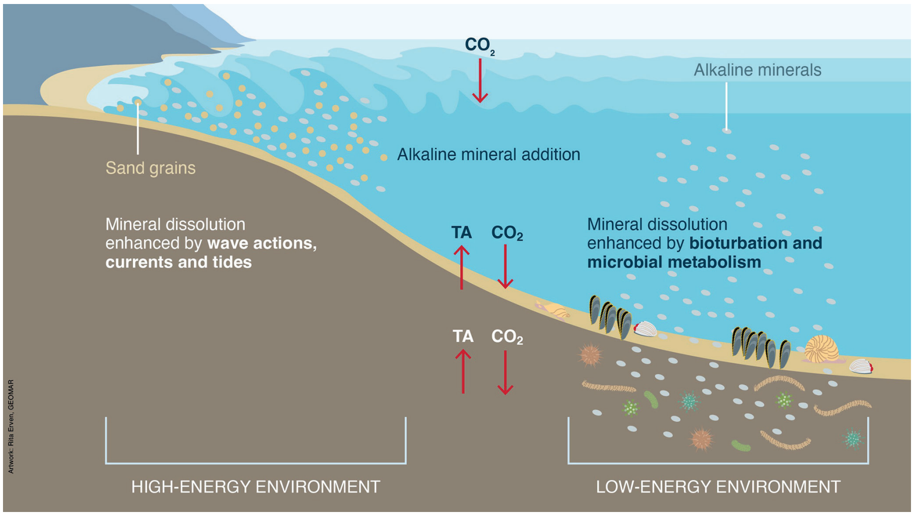
7.1 Technical summary

Continental shelves comprise only about 7 % of the global surface ocean, yet they account for up to 30 % of the oceanic primary production (Gattuso et al., 1998) and between 10 % and 25 % of the present-day CO_2 uptake (Regnier et al., 2013). Shelves are also important areas for cation and TA turnover related to detrital mineral dissolution and authigenic carbonate and clay precipitation (e.g., Linke et al., 1994; Jeandel et al., 2011; Jeandel and Oelkers, 2015; Torres et al., 2020). Assuming an ice-free surface area of continental shelf seas of $22 \times 10^6\,km^2$, natural carbon uptake in coastal waters has been estimated to be $-0.19\,Pg\,C\,yr^{-1}$, showing the importance of shelves as a natural global sink of atmospheric CO_2 (Laruelle et al., 2014, 2018).

The addition of ground minerals to the shelf seafloor may enhance this uptake even further and as such are candidate locations for OAE. Large-scale mineral application would be logistically convenient, using excavators either directly on the beach or from small vessels or barges in offshore shallow waters. Several companies and initiatives already take advantage of this relatively easy CDR implementation and study the effectiveness of mineral dissolution in the field.

The most obvious advantage of adding particulate minerals to the seafloor compared to the water column is the required grain size. Compared to water column deployment, for which the required grain sizes are $<1\mu m$ in order to avoid rapid sinking (Hauck et al., 2016), the optimum grain sizes needed for seafloor deployment are proposed to range between 0.2 and 1.4 mm (Schuiling and de Boer, 2010, 2011; Strefler et al., 2018), which is economically attractive. However, these recommendations lack thorough experimental testing, both in the laboratory and in the field.

Further, the choice of grain size depends on the region of deployment. Two potential coastal regions for mineral addition are low- and high-energy environments (modified after Meysman and Montserrat, 2017) (Fig. 15). High-energy environments are characterized by extensive water mass movement, such as surf zones, thereby providing a natural grinding mechanism, allowing larger, less costly grain sizes to be used (Flipkens et al., 2023). In contrast, low-energy environments require the addition of smaller grain sizes (~ 20 to $100\,\mu m$) as a higher surface area maximizes mineral dissolution (Oelkers et al., 2018). In this environment, mineral dissolution is enhanced by biota through bioturbation and mi-



Artwork: Rita Erven, GEOMAR

Figure 15. High- and low-energy environments with different regional advantages favoring mineral dissolution.

crobial metabolism (Meysman and Montserrat, 2017). These two distinct environments are discussed below with respect to their advantages and disadvantages.

7.1.1 High-energy environments

These environments are located along the coastal surf zone or the shallow shelf, where wave action, currents, and tidal activity lead to natural mineral erosion. The required grain sizes can be relatively large (millimeter-scale) for this environment, given that the constant movement naturally grinds the minerals, continuously exposing fresh reactive mineral surfaces and enhancing dissolution. Given that alkalinity enhancement directly occurs close to the air–sea interface in these well-mixed shallow water settings, the impact on atmospheric CO_2 uptake is immediate.

Detection of mineral dissolution and alkalinity production in these high-energy environments is challenging due to rapid mixing, dilution, and dispersal of solutes. Minerals may also be transported along- and offshore away from their deployment location. This requires carefully designed field experiments to assess the efficiency of this OAE approach with regard to CO_2 drawdown (see Sect. 7.2 and Cyronak et al., 2023, this Guide). Furthermore, these factors hamper accurate evaluation concerning MRV for commercial carbon removal purchases (see Ho et al., 2023, this Guide). An advantage of mineral dissolution in coastal surface sediments is the lower risk of secondary mineral formation. In an open environment, supersaturation levels potentially triggering carbonate or phyllosilicate precipitation in conjunction with other relevant factors (e.g., pH, DIC, TA) are more unlikely to be attained. CO_2 consumption may therefore be more efficient compared to low-energy environments. See Table 2 for a summary of advantages and disadvantages for mineral deployment in high-energy environments.

7.1.2 Low-energy environments

Shelf environments comprise the waters below the wave base down to 200 m that are not significantly affected by normal wave action. The continental slope and deep seafloor are not considered here given that the exchange of bottom waters with surface ocean waters may be too slow to be relevant for near-term CO_2 reduction strategies (Smith et al., 2023).

The shelf sediment is mostly sand and mud (Schulz and Zabel, 2006), providing an ideal environment for mineral dissolution by taking advantage of the “benthic weathering engine” (Meysman and Montserrat, 2017). Here, two mechanisms can be distinguished that potentially accelerate mineral dissolution, that is, microbial metabolism and bioturbation by macro-organisms.

The degradation of organic matter by microbial activity in fine-grained sediment creates a unique microenvironment that may be conducive to dissolution of some types of minerals. The microbial degradation of organic matter by aerobic and, in particular, anaerobic remineralization pathways (e.g., denitrification, iron and manganese reduction, and sulfate reduction) leads to an accumulation of reduced forms of S, N, Fe, and Mn in both the dissolved and particulate phases. If these compounds are exposed to oxygen or nitrate at the sediment surface they can be oxidized rapidly, leading to a local decrease in pH to <6. Under these conditions, carbonate dissolution may take place if pore fluids become undersaturated with respect to the dissolving mineral phase (Jahnke and Jahnke, 2000). Silicate dissolution strongly depends on the mineral type, whereby Mg-silicate dissolution (e.g., olivine) is enhanced at low pH and aluminosilicates at high pH (Oelkers et al., 2018, and references therein). Mineral dissolution may be facilitated or even enhanced through the action of electrogenic cable bacteria that can oxidize S by shuttling electrons from subsurface anaerobic sediments to

Table 2. Advantages and disadvantages of coastal marine mineral addition on the continental shelf (low-energy environment) compared to the surf zone (high-energy environment).

	Low-energy environment (continental shelves)	High-energy environment (surf zone)
Mineral dissolution	Enhanced by metabolic processes Bioturbation	Wave actions, tides and currents
Mineral size	Medium (micrometer range)	Large (millimeter range)
Grinding	Mechanically, on land	In situ by wave actions, water movement
Risk of secondary mineral formation	High, due to saturation levels in pore fluids	Low, due to dilution by ambient seawater
Background rain rate of detrital minerals	High risk of fast alkaline mineral burial POC; high rates may enhance mineral dissolution	Low impact
Risk of mineral relocation	Medium; strong bottom currents may transport minerals to offshore depocenters	High; transport by wave action and currents out of turbulent zone
TA detection	Challenged by water depths – logistical difficulties Large seawater alkalinity background	High dilution factors with seawater Turbulent waters, impacting stationary sensor systems
Air–sea exchange	Enhanced by benthic–pelagic coupling Enhanced by currents, upwelling	Instantaneous

the oxic surface layer (Meysman et al., 2019). However, cable bacteria are not thought to be highly active in bioturbated sediments, such that their potential impact on alkalinity enhancement by mineral dissolution may not be quantitatively significant at the regional scale.

The effect of burrowing by large macro-organisms, known as bioturbation, enhances mineral incorporation into the sediment matrix and, consequently, brings the minerals in contact with the acidic pore fluids and enhances benthic–pelagic exchange (Neumann et al., 2021). Additionally, the digestive systems of macro-organisms, with their high enzymatic activity, low pH, mechanical abrasion, and digestion, have been shown to increase silicate and carbonate dissolution (Cadée, 1976; Volkenborn et al., 2009). However, this process is poorly understood, and its significance for mineral dissolution is unknown at regional scales.

A large drawback of the low-energy benthic environment for OAE is the high probability of secondary mineral precipitation. Formation of authigenic carbonates or phyllosilicates releases CO_2 (e.g., Wallmann et al., 2008; Torres et al., 2020) and directly counteracts the envisioned TA release and CO_2 uptake by mineral addition. Authigenic aluminosilicate formation was recently found to be a large Si sink in the global marine Si cycle, releasing CO_2 and consuming TA (e.g., Wallmann et al., 2008; Rahman et al., 2017; Tréguer et al., 2021) on timescales of weeks to months, that is, much faster than previously considered (10^3 years) and impacting element cycles on human timescales (Geilert et al., 2023). Authigenic, inorganic carbonate precipitation at the sediment–water interface or within the sediment column is triggered by alkalinity production from anaerobic microbially mediated reactions (Sun and Turchyn, 2014) and can also be caused by silicate dissolution, buffering the potential pH drop induced by methanogenesis and by that creating carbonate-saturated environments (Torres et al., 2020). In the context of mineral addition to increase ocean alkalinity, these secondary mineral formations may play a major role in the net CO_2 sequestration efficiency, as recently shown in laboratory experimental studies (Fuhr et al., 2021; Moras et al., 2022; Hartmann et al., 2023). Further research is required to identify the probability and impact of secondary mineral formation on net CO_2 turnover with respect to OAE (Table 2 and Sect. 7.2). The results from laboratory studies though (Fuhr et al., 2021; Moras et al., 2022; Hartmann et al., 2023) are still debatable with regards to their transferability to the open ocean, where secondary mineral saturation states are reached less easily. Mesocosm studies might offer a solution here (Riebesell et al., 2023, this Guide), in which open-ocean conditions can be simulated more realistically, and the triggering factors for secondary mineral formation can be identified (see also Sect. 7.2).

As in the high-energy shallow environments, detection of mineral addition in deeper and fine-grained coastal waters (50–200 m) can be difficult. The deployment of autonomous instruments on the seafloor, such as benthic chambers, can be used to measure fluxes of alkalinity and other dissolved compounds to/from the seafloor. Depending on the nature of the sediment and the carbon degradation rates, benthic chambers can typically detect O_2 consumption and nutrient release on timescales of 1–2 d of continuous deployment in shelf environments (Sommer et al., 2016). However, the attribution of mineral dissolution to changes in alkalinity is challenging, particularly against the large seawater alkalinity background. Only in the most reactive coastal settings such as upwelling areas can alkalinity fluxes be determined accurately (Ilyina et al., 2013; Dale et al., 2015). The development and incorporation of high-precision pH and $p\mathrm{CO}_2$ sensors may provide a solution to detecting small changes in CO_2 and alkalinity fluxes due to mineral dissolution. To our knowledge, the suitability of benthic chambers with respect to detection of OAE at the seafloor still requires field testing.

For both high- and low-energy environments, the risk exists that the alkaline minerals will not remain at the site of deployment, due to seabed erosion by either wave action and currents, transport, or burial. In areas where there are strong bottom currents, fine-grained minerals can be eroded and transported. These minerals are then ultimately delivered to regional depocenters in deeper basins in shallow coastal seas such as the Baltic Sea (e.g., Wallmann et al., 2022) or to the continental slopes on open margins (e.g., Anderson et al., 1994). Once deposited in deep waters, they are removed from the shallow regions, where the benthic–pelagic water mass exchange is rapid.

A final point for consideration is the sedimentation rate. On the one hand, high particulate organic carbon (POC) sedimentation rates are desirable to guarantee high rates of organic matter degradation and low-pH pore fluids necessary for enhanced mineral dissolution. On the other hand, high sedimentation rates of detrital minerals or low POC sedimentation rates may be counterproductive, leading to rapid burial of OAE minerals below the dissolution zone. These factors need to be factored into the cost–benefit analysis of envisaged OAE mineral deployment in low-energy environments.

7.2 Considerations for best research practices

7.2.1 Quantity of deployed mineral

As the effects on the ecosystem by local alkalinity enhancement are still the subject of current investigation, care should be taken when adding minerals to the seafloor. The risk of smothering flora and sessile organisms and clogging of burrows with mineral particles can be minimized by avoiding large deposits in the target area. It is currently unknown whether locally enhanced TA increases in sediment pore fluids driven by oversupply of minerals might be detrimental to certain organisms or produce a shift in the microbial community, potentially affecting mineral dissolution rates. Therefore, dispersed mineral distribution is desirable by, for example, sprinkler systems. Post-deployment channeling of minerals to depocenters by bottom currents might be unavoidable for fine-grained particles. To avoid an accumulation of undissolved minerals on the seafloor, potentially negatively affecting marine ecosystems, care must be taken in assessing the quantity added. An upper limit of long-term mineral addition may be scaled to the local annual POC rain rate depending on the stoichiometry of CO_2 sequestration by the relevant mineral if the CO_2 released from carbon respiration is quantitatively consumed by benthic weathering. This also assumes that mineral dissolution is tightly coupled to the remineralization of organic matter, which is unlikely to be universally the case. This question is currently being addressed in benthic mesocosm experiments (see Riebesell et al., 2023, this Guide) and still requires verification in field trials. For mafic minerals such as olivine, further unwanted side effects may arise due to release of heavy metals that may be toxic to marine organisms at higher concentrations (e.g., Ni). Testing the potential accumulation of metals in locally sourced sediment cores amended with minerals under laboratory conditions is recommended.

7.2.2 Secondary precipitates

The precipitation of secondary minerals either as discrete grains or on the surface of the added alkaline mineral, decreasing its effective surface area, will hamper the efficiency of CO_2 removal. Especially in the case of secondary silicate precipitation, many unknowns remain concerning the controlling factors of formation. Identification of reaction pathways and rates will require highly precise monitoring either of the solid or the fluid phase. Analyses of the fluid phase are challenged by the large background seawater concentrations of chemical tracers, though distinct changes in pore fluid chemistry (e.g., K, Li, Mg) and/or the application of stable-isotope tracers (e.g., Si, B, Li, K) have the potential to identify secondary mineral precipitation. Analyses of the solid phase can identify secondary minerals as well, by either bulk rock quantification techniques (e.g., XRD), in situ mineral analyses (e.g., Campbell et al., 2023), and/or sequential leaching procedures; however, it remains a challenge to identify if the precipitates are of marine or terrestrial origin. For a reliable quantification of secondary mineral formation in the context of OAE, repeated sampling of solid and fluid phases at regular intervals needs to be conducted to assess element turnover and thus CO_2 sequestration.

7.2.3 Methods of detection

Arguably the biggest challenge is to quantify and monitor CO_2 sequestration related to mineral addition on the seafloor. In low-energy deeper waters, the use of benthic chambers is an option to monitor the carbonate system over discrete time intervals. However, artifacts such as changing redox conditions within the chamber due to oxygen depletion need to be considered and, if possible, compensated for in situ. Regular sampling is also needed. In the shallow and easily accessible high-energy environment, regular water sampling is unlikely to detect alkalinity increase or CO_2 drawdown in this highly diluted and well-mixed environment. Long-term monitoring using autonomous chemical sensor platforms for detection of changes in pH, pCO_2, and TA (Sonnichsen et al., 2023) is an option but highly challenging due to large fluctuations over timescales ranging from hours to years. Keeping track of the mass of mineral gains over time may yield more robust results.

8 Conclusions

OAE as a potential solution to combat ocean acidification and remove CO_2 from the air continues to show great promise. OAE's unique potential among CDR approaches to compensate for CO_2 degassing from the ocean resulting from large-scale atmospheric CO_2 removal makes it an especially valuable approach worthy of continued pursuit. This chapter delves into technical aspects of the various technologies and considerations for best practices in their research and development. Although challenges remain, such as cost effectiveness and minimizing environmental impacts, pilot projects have begun to demonstrate the feasibility of deploying various OAE techniques in relevant operational environments. Continued innovation and collaboration among scientists, engineers, and policymakers will be crucial in refining these technologies further. While initial experiments have been successful on a smaller scale, significant challenges lie in deploying these techniques on a global level. Addressing logistical complexities, ensuring proper monitoring and regulation, and securing necessary funding are imperative for successful scaling. Additionally, considering regional variations and selecting appropriate sites for implementation will be vital for maximizing the efficiency and effectiveness of OAE projects. The identification and implementation of best practices are essential for the success of OAE initiatives. Conducting comprehensive environmental impact assessments, employing adaptive management strategies, and promoting transparency and public engagement are crucial steps in ensuring responsible deployment. Learning from past experiences, both positive and negative, will help refine the methodologies and minimize any unintended consequences. It is crucial to approach this strategy with careful consideration, ensuring technology readiness, addressing scaling challenges, and implementing best practices.

Recommendations for research on technical aspects of OAE

- OAE shows promise as a potential CDR solution, and pilot projects and research activities have begun to demonstrate its feasibility in relevant environments. Continued collaboration among scientists, engineers, and policymakers will be crucial in optimizing these technologies. To maximize the effectiveness of OAE, it is critical to consider location or regionally specific constraints to select appropriate application sites for specific OAE approaches.
- Conducting comprehensive environmental impact assessments, employing adaptive management strategies, and promoting transparency and public engagement are crucial steps in ensuring responsible deployment of OAE.
- Excessive accumulation of undissolved minerals on the seafloor, potentially harming marine organisms, should be avoided; assuming that benthic mineral dissolution is coupled to organic matter remineralization, the POC rain rate can be used as an upper limit of the amount of mineral addition.
- The potential formation of secondary minerals, either carbonates or silicates, which can reduce the net CO_2 sequestration efficiency of an OAE approach, needs to be monitored on a regular basis by thorough chemical analyses of the involved fluid and/or solid phases.
- Technology readiness levels for the different OAE measures need to be increased in laboratory experiments and in field studies, also to identify potential "tipping points" for organism viability and the ecosystem in general.

Appendix A: Definitions and common abbreviations

AWL	Accelerated weathering of limestone
CDR	Carbon dioxide removal
CCS	Carbon capture and storage, specifically where CO_2 is concentrated from waste streams
DIC	Total dissolved inorganic carbon
LCA	Life cycle analysis
MRV	Monitoring, reporting, and verification
OAE	Ocean alkalinity enhancement
Ω_{cal}	Calcium carbonate (calcite) saturation state
pCO_2	Partial pressure of CO_{2g}
pH	Negative logarithm of the hydrogen ion activity, a measure of acidity
TA	Total alkalinity
XRD	X-ray diffraction

Data availability. No data sets were used in this article.

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General considerations for experimental research on ocean alkalinity enhancement

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Abstract. Ocean alkalinity enhancement (OAE) is proposed as an approach to capture carbon by adding alkaline substances to seawater to enhance the ocean's natural carbon sink. These substances include minerals, such as olivine, or artificial substances, such as lime or some industrial byproducts. Deployment of OAE will lead to complex and dynamic changes in the seawater carbonate chemistry, and in some cases the addition of other compounds and impurities from the minerals. While OAE alters the carbonate chemistry in a very different way, much can be learned from the abundant literature on ocean acidification documenting the impact of changes in the carbonate chemistry on marine life from genes to ecosystems. A vast majority of the experimental work was performed by manipulating the concentration of carbon dioxide in seawater under constant alkalinity (TA) to simulate near-future ocean acidification. Understanding the impact of changes in alkalinity on marine species and the ecosystem is less understood. In the context of OAE, it is critical to resolve such impacts, alone or in combination with other compounds and impurities from the minerals to be co-released during implementation, to ensure that any field manipulation does not translate into damaging biological effects. As for other environmental drivers, this will require an understanding across all the levels of biological organizations from species to ecosystems over relevant time exposure considering the method of deployment (e.g., dilution, repeated exposure) and factors such as local adaptation. Such complex questions cannot be resolved using a single approach, and a combination of monitoring, modeling, laboratory, natural (i.e., proxies or analogs), and field experiments will be required. This chapter summarizes some key general considerations for experimental design. It also compares strengths and weaknesses of the different approaches. We will also consider best practices relevant to OAE such as the need to properly monitor and consider the addition of trace elements and byproducts, as well as potential interactions with other naturally occurring drivers.

1 Identifying a relevant question

A pre-requisite to the selection of a given research approach or strategy is to define a clear question. For a safe and efficient implementation of ocean alkalinity enhancement (OAE) one needs to answer several key questions, including those given below.

- What are the best implementation methods to optimize efficiency and minimize risks?
- Is the implementation of OAE safe for marine species and ecosystems?

These questions are too big and complex to be resolved by a single experiment or approach. Fully addressing these would require a large-scale involvement of the scientific community and strong international and multi-disciplinary collaboration. Specifically, in order to fully understand and project the ecological consequences of OAE, a suite of mechanistic based models will need to be developed and connected across all levels of biological organization from species to ecosystem. For example, the dynamic energy budget provides a framework to synthesize complex physiological responses and processes at the organism level and allows us to project how key traits (e.g., growth, metabolism, reproduction) respond to environmental changes (Kooijman, 2001). At community and ecosystem levels, data are needed on the response of key ecological traits and processes that structure communities, such as predator–prey relationships, competition, habitat provision, and facilitation. This will require a wide range of different mechanistic experiments that when combined through parameterization of models will provide the holistic view required for forecasting. These models can then be tested against the response in the "real" world, helping validate the model's underlying parameterization and assumptions.

Exposure to elevated alkalinity at different rates and intensity, potentially combined with the other elements such as silicate, calcium, magnesium, and trace metals (e.g., iron, nickel, cobalt, chromium), would expose natural ecosystems to conditions that strongly deviate from the present range of natural variability and thus has the potential to drive negative effects. At present, these impacts are poorly understood. Understanding the impact of multiple environmental changes (alkalinity and the consequence for the carbonate chemistry, as well as other elements) on key marine ecosystems requires research at the crossroad between physiology, ecology, and evolution. As a comparison, after more than 2 decades of research on ocean acidification and the publication of more than 10 000 scientific articles, we are still lacking the full mechanistic understanding that would allow us to bridge chemical and biological changes and the forecasting ability required for science-based management (Cooley et al., 2022).

Regarding the urgency of the climate crisis and the limited resources, it is critical to quickly identify the key subquestions that need to be urgently answered to provide informed guidance to if, how, where, and when OAE should be implemented. These priorities should be identified in the spirit of the United Nation Decade of Ocean Science for Sustainable Development (The science we need for the ocean we want) and focus on the trade-off between the desirable level of understanding to take informed decisions, the time needed to collect such data, and how these data and decisions can lead to concrete actions. Each question can organically translate into a research strategy and the selection of the appropriate approach(es), species and ecosystems, or experimental designs (see Sect. 3).

Examples of key sub-questions to resolve the potential impacts of OAE on marine ecosystems include the following examples.

- What is the best material (e.g., mineral) for a safe implementation of OAE?
- What is the safest deployment method for the surrounding ecosystems?
- What makes a species or an ecosystem sensitive to OAE?

Resolving these questions would allow us to identify the best sites and methods for safe implementation but would require a complex experimental strategy combining laboratory studies, e.g., identifying thresholds for key parameters such as alkalinity or trace element concentrations, resolving the combined effect of multiple drivers, and developing a mechanistic understanding of how species and ecosystem resilience (the inherent ability to absorb various disturbances and reorganize while undergoing state changes to maintain critical functions) to OAE links to factors such as present natural variability, taxonomy, physiology, life-history strategies, trophic levels, and field experimentation, including in mesocosms, to validate mechanistic models. That will require work across the whole range of sizes and complexities and the breaking down of these complex questions into smaller manageable ones within a strategy.

Additionally, it is important to remember that the implementation of OAE will also involve large-scale industrial activity in marine systems. The impacts of these will be additional to the direct chemical changes and any associated additional stressors with the transport and addition of the alkalinity to the marine system should also be considered.

2 Comparison of the different research approaches

Every scientific manipulation experiment, either in the field or in the laboratory, is an abstraction of reality. While best practices, in terms of experimental design, measurements, or monitoring of environmental conditions, are well established (see Riebesell et al., 2011, in the context of ocean acidification), the outcome of any scientific study is strongly dependent on experimental choices (e.g., tested scenarios, duration, level of biological organization, selected species or population) These are often resulting from a compromise between the requested design to test a given hypothesis and practical constraints and limitations. Understanding the impact of OAE on marine ecosystems is a complex question that can be broken down into multiple hypotheses. For each hypothesis, a strong scientific strategy involving multiple approaches and/or experiments is needed. In this section, we will briefly describe and highlight the strengths and limitations of each approach (Fig. 1).

2.1 Laboratory experiments (see Iglesias-Rodriguez et al., 2023, this Guide, for more information and references)

Chemical changes associated with OAE deployment can be easily simulated in laboratory experiments. These includes

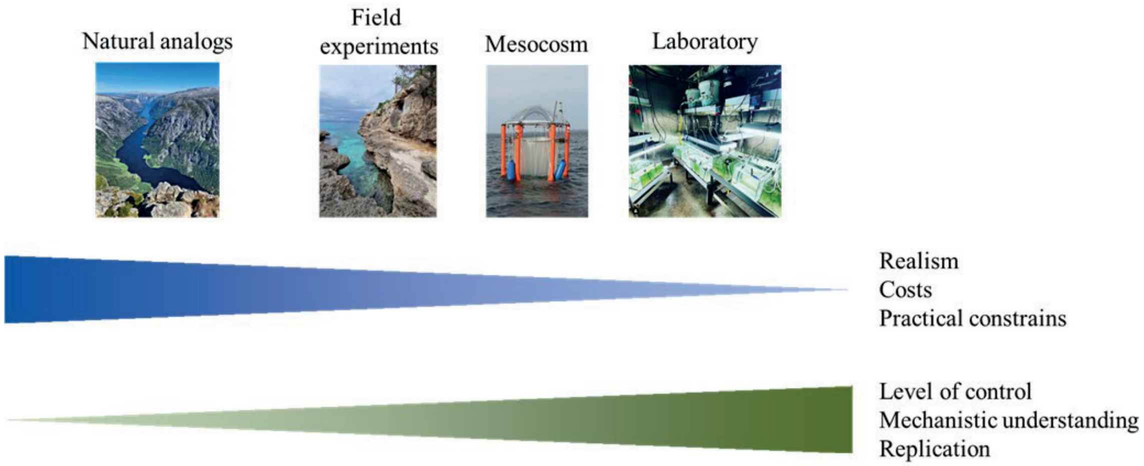

Figure 1. Simplified version of the strengths and limitations of different complementary research approaches. While the level of environmental and ecological realism decreases from natural analogs to laboratory experiments, field-based approaches face other complexities: high costs, legal and practical constraints, lower control and attribution to the tested parameters, and a lower level of replication. The selection of an approach should be based on the question, and most questions requires a strategy combining multiple approaches.

manipulation of alkalinity and/or concentration of the various other compounds or impurities. Different concentrations and dynamic of exposure (e.g., constant vs. fluctuating concentration simulating a dilution or single vs. repeated exposure) can be compared in single- or multiple-driver experimental designs. Laboratory experiments are classically used as a tool to test hypotheses and attribute biological changes to tested variables beyond the correlative approach often used for field observations and manipulations. A wide variety of approaches exist, allowing for small- to large-sized experimental units (from mL to m^3, depending on the model), single and multiple species or life history stages, and short- or long-term exposure, and provide adapted options to work with organisms from bacteria to fish.

- *Strengths*. Experiments in the laboratory offer a wide range of options and have the potential for the highest level of control in the tested parameters (e.g., physicochemistry, food concentration, species composition, density) As such, laboratory experiments, in combination with other approaches, are the best alternative to build a mechanistic understanding of the biological impacts of OAE. While not without limitations, some experimental setups allow for a high level of replication and to test complex questions highly relevant in the context of OAE including the following examples. (What is the biological impact of combined effect of increased alkalinity with trace elements? What is the biological impact of repeated exposures?). As for any experimentation on living organisms, there are some ethical and sometimes legal aspects associated with biological experimentation. However, those are much easier to resolve than with field approaches.

- *Limitations*. While complex laboratory experiments can have some degree of ecological realism, they cannot fully replicate the complexity of a natural ecosystem. For example, it can be highly challenging to include natural variability for all relevant physicochemical parameters (seasonal or associated with OAE deployment) or incorporate the full complexity of an ecosystem. As such, mechanistic models developed from laboratory experiments need to be validated in more realistic settings (e.g., field experiments).

2.2 Mesocosm experiments (see Riebesell et al., 2023, this Guide, for more information and references)

As for laboratory experiments, manipulations in alkalinity and/or other compounds released during OAE deployments can be performed using mesocosms to achieve a greater level of ecological realism. Mesocosms are generally large-scale enclosed bodies of water, with (benthic) or without (pelagic mesocosms) sediments, including biological communities and related processes that can be experimentally manipulated. Depending on the tested communities, the size can vary between 1 L and several cubic meters of seawater.

- *Strengths*. Mesocosm experiments can partially compensate for the limitations of laboratory-based experiments. They sit between laboratory and field experiments and can be used to evaluate the impact of the tested parameter(s) at the ecological level. Working in a closed system minimizes the public concerns and legal requirement when compared to field trials (GESAMP, 2019).

- *Limitations*. While mesocosms allow for a certain level of controls of the environment, some physicochemical parameters follow natural variability, limiting their ability to attribute the observed effects directly to the tested parameter(s). The size and complexity of mesocosms can also limit the number of replicates and thus their ability to detect significant effects. When limitation occurs in term of replication, either in mesocosm or laboratory experiments, an alternative is to replicate by repeating the same experiment multiple times. However, this can introduce unwanted variability as some biological processes vary between days, seasons, and years and decreasing the probability of detecting significant effects. Some other limitations include unnatural mixing and turbulence (pelagic mesocosms) or unnatural water flows (benthic mecososms) as well as limitation inherent to a closed system.

2.3 Field experiments (see Cyronak et al., 2023, this Guide, for more information and references)

Open-system field experiments consist of a direct manipulation (e.g., addition of alkalinity) in a natural system. This approach can be used to simulate an OAE deployment at realistic spatial scale.

- *Strengths*. This approach allows the evaluation of the potential impacts at the ecosystem level in the real world while other environmental parameters naturally fluctuate.

- *Limitations*. Several logistical (e.g., access) and legal challenges (e.g., permit, public acceptance) can be associated with field experiments. Similarly to mesocosm experiments, the cost of the ecological realism is the complexity in attributing the observed effect to the given treatment. It is complicated by the difficulty of truly replicating the experiment and identifying controls. However, this can be partly resolved by substituting space for time and replicating the experiment in time if no strong year-to-year variability is observed.

2.4 Natural analogs (see Subhas et al., 2023, this Guide, for more information and references)

As for other physicochemical parameters, alkalinity is not constant across the ocean. The natural variability in alkalinity is linked to cycling of carbon dioxide, calcium carbonate, and other minerals. As a consequence, some locations have conditions that can be used as “natural analogs” to OAE deployments. Natural analog sites present environments that resemble the conditions of an OAE implementation and can then be used as a test bed for both sensor deployments and collection of data on feasibility at scale and potential impacts on key species and ecosystems. These include glacial fjords and runoff into the marine system, seafloor weathering of basalts, sites where artificial materials are added to the marine system, river plumes and deltas, and many others (Subhas et al., 2023).

- *Strengths*. Natural analogs provide the opportunity to work in the field at the ecosystem level and provide a test bed for the interpretation and validation of data collected in laboratory and field experiments and models. Different types of analogs can be used to address different space and time processes (Fig. 2 in Subhas et al., 2023) from hours at the deployment site to decades at the global level. Observations of natural analogs also have some practical advantages as they can be less costly than experimental approaches (e.g., mesocosms), logistically risky, and do not require complex permits to implement (e.g., field manipulation).

- *Limitations*. OAE analogs have the same constraints as any natural analog for other environmental parameters. While working in the field provides opportunities for the collection of data at a higher level of complexity, it lacks the control over the tested variable, making it difficult to attribute any observed effect to one or several parameters, and it does not necessarily account for the presence of impurities or the dynamics of exposure associated with some OAE deployments. While some statistical options are available to disentangle the individual effects of the different environmental parameters (e.g., multivariate and regression analyses), a full attribution is not possible as many nonlinear processes and complex interactions are unavoidable when ecology and multiple stressors are involved. This can be partly solved by incorporating mechanistic understanding and theoretical frameworks coming from more controlled laboratory and field studies. Other limitations include the difficulty of replication and identification of control sites. Natural analogs are also open systems with mobile species flowing through the ecosystem and introducing confounding factors and noise in the collected data.

2.5 Modeling considerations (see Fennel et al., 2023, this Guide, for more information and references)

The complex scientific questions associated with OAE will require a combination of approaches to develop the needed mechanistic understanding and field validation. Models are critical tools to bridge the different approaches, generate testable hypotheses, upscale from local to global aspects, and forecast the outcome of different intervention strategies. Developing a fully parameterized model simulating the complexity of the biological response to OAE is extremely challenging. Changes associated with OAE deployment can drive direct effects of each individual driver, including impacts of alkalinity, magnesium, and calcium ions on the calcification or toxic or stimulating effects of trace elements such as iron ions. These can become even more complex and unpredictable when in combination and including the dynamic

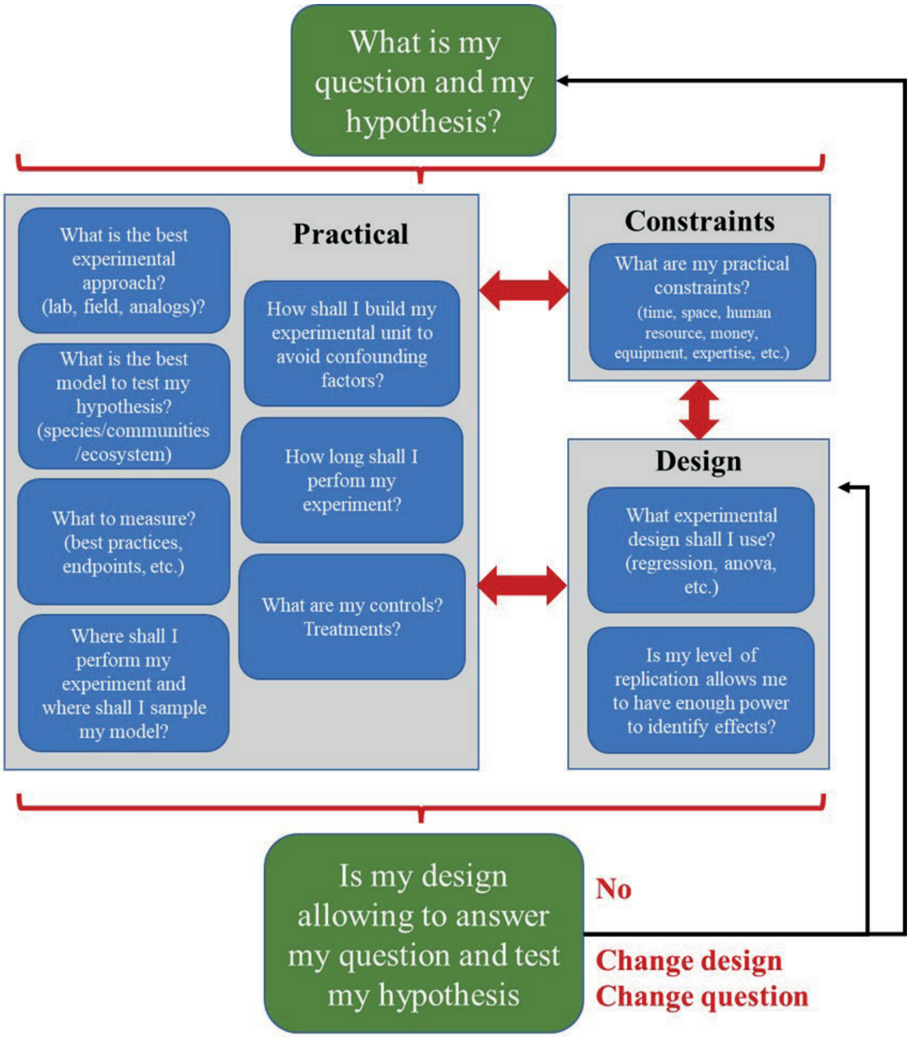

Figure 2. Flowchart guiding decisions for the design of experiments evaluating the impact of OAE. First, start with a question and a hypothesis. The design of the experiment is an array of decisions at the crossroad between constraints (e.g., time, space), experimental choices (e.g., tested biological model, duration), and analytic approaches (e.g., regression, ANOVA). When the final design is fixed, ensure that it would allow for answering the initial question. If not, correct your design or, if this is not possible, change your question.

of exposure. Indirect effects include impacts on the environment properties such as seawater turbidity modulating the propagation of light or cascading ecological processes. A more realistic approach is to use the toolkit of existing models for a fit-for-purpose modelisation associated with specific questions. For example, dynamic energy budget (DEB) is one of the most comprehensive frameworks for bioenergetics, and models based on this theory have been extensively applied to understand the effects of environmental changes, including the ecological consequences (Kooijman, 2001). Ecotoxicological models such as a mechanistically based model can be used to resolve the combined effects of the multiple changes associated with OAE deployment (Schäfer and Piggott, 2018).

3 Best practices: from a scientific question to an experimental strategy

A full consideration of best practices for experimental design is beyond the scope of this chapter. We will summarize some key general and OAE-specific considerations while designing an experimental strategy or experiment. Adapting the famous quote by George Box, we can say that essentially all experiments are wrong, but some are useful (Field et al., 2015). Each research approach is associated with its own set of strengths and limitations (Fig. 1) that, combined with practical and technical constraints, such as time, space, human resources, money, or expertise, lead to decisions that limit experiments that are wrong but that some are useful in terms of the potential of the collected data to answer some complex questions. The full picture can only come from a combination of different approaches and experimental decisions (e.g., Quinn and Keough, 2002).

There are, however, some general best practices that should be followed, including the importance of defining proper controls, monitoring the physicochemical parameters following established procedures, including calibration and use of reference materials, using the appropriate level of true replication, and following best practices for the measured endpoints (e.g., Riebesell et al., 2011).

Following best practices optimizes the chance to identify the impact of a given environmental change. Variability is the rule in any biological data and can have different sources: technical (e.g., quality of the method used for the manipulation of a parameter or the measurement of an endpoint), experimental noise (e.g., confounding factors), and biologically relevance (e.g., genetic diversity or driven by the manipulated parameter). Each experiment should be designed to minimize unwanted variability. This includes randomization of the experimental units, proper training of the person(s) taking care of the experiments, or measuring the endpoints, etc.

For each question and associated experimental design, one must take the following decisions (Fig. 2).

- *What is my model organism or ecosystem?*
  One approach is to follow the Krogh's principle. For such a large number of problems there will be some model of choice (or a few such models) through which it can be most conveniently studied. A given species can be selected for its life history trait, longevity, physiology, phylogenetic position, sensitivity to the tested parameter, or role in the ecosystem. For example, to study the potential for genetic adaptation to OAE, a species with short generation time would be most appropriate. Model species may be considered when specific techniques are needed (e.g., functional genetics). Additional factors also need to be considered, including size, life history stage, age, weight, sex. Different ecosystems, numbers of trophic levels, and levels of complexity (among other factors) can also be considered.

- *Where should I sample or perform the experiment?*
  As a consequence of local adaptation, species and ecosystems evolved different strategies to cope with different locations and environments. For example, different populations of the same species can have contrasting sensitivity to the same changes in the carbonate chemistry (Vargas et al., 2022). In the context of OAE, the physical environment can also influence dilution rates of the alkalinity or the trace elements, the distribution of the particles, or the water turbidity, and the chemistry can also impact the dissolution of the used minerals and modulate other drivers or combined effects. The biological characteristics can also influence the potential sensitivity to changes (e.g., natural variability, redundancy, endangered species).

- *How do I design my experimental unit?*
  To avoid introducing confounding factors, it is critical that the design of the experimental unit (e.g., aquarium, mesocosm) fits the tested species, community, or ecosystem. This includes using the right volume of water, realistic density of biological models, open vs. flow-through design, density of food, water used, aeration, currents, and other physicochemical parameters.

- *How long should I conduct my experiment or observations for?*
  Based on the question, different durations should be considered to ensure that the observed effect can truly be representative of the treatment. For example, this can be short-term, chronic, or dynamic depending on the tested OAE scenario.

- *What is the general experimental design?*
  Two general experimental approaches can be used: the replicated scenario "ANOVA" approach and the gradient "regression" approach (Fig. 3). There are pros and cons to both approaches. The regression approach allows us to identify nonlinear processes, resolve performance curves, and identify potential thresholds. However, there is the risk of not being able to properly analyze the collected data if no obvious trend is present. It is also possible to combine both approaches using a collapsed design (Boyd et al., 2018).

- *Do I have the proper control(s) and treatment(s) to test my hypothesis?*
  All research approaches should consider the proper controls taking into account the present natural variability at the relevant spatiotemporal scale as well as conditions in the context of the implementation of OAE. The treatments can mimic a deployment of OAE and cover a wide range of alkalinity (e.g., 1500 to 4000 $\mu\mathrm{mol\,kg^{-1}}$) and other parameters for a more mechanistic approach. The concentrations of alkalinity and trace elements are not the only parameters to consider, as the duration and dynamic of exposure can strongly vary depending on the implementation method. The selection of the experimental approach (laboratory, mesocosm, field, natural analog) and design is highly dependent on the question and will directly inform the selection of treatment(s). The OAE dynamics of deployment over space and time are subjected to a variety of physical forcings. The plume dispersal will be influenced by currents, eddies, seabed topography, and other physical characteristics (Subhas et al., 2023), as well as additional variability from repeated deployments. Any understanding of the biological response to OAE will then need to consider aspects beyond any sensitivity thresholds for alkalinity

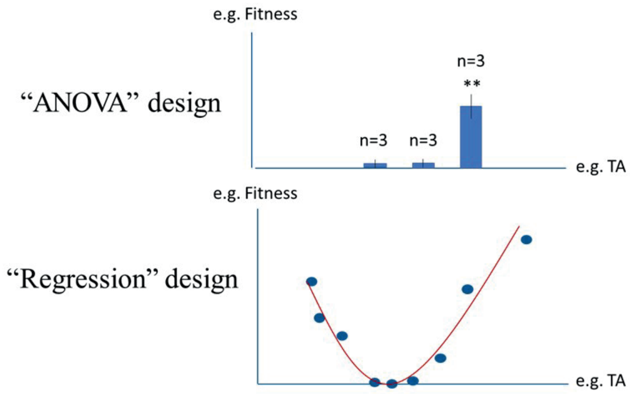

Figure 3. Illustration of two complementary experimental approaches using the same level of replication.

and trace elements and include the dynamic of exposure. Exposure will vary from immediate "shock" responses at the periphery of a plume to longer-term acclimated responses in ecosystems that may sit directly in the outfall of a plume (Subhas et al., 2023). Some experimental methods may be more adapted to simulate such complex dynamics (e.g., field experiments) as they would require complex technologies and high levels of control and monitoring in a closed-systems laboratory or mesocosm experiments. Such complex questions can only be answered through the combination of multiple experimental approaches and a strong communication between fields.

- *What to measure?*
  A wide variety of parameters and methods are available to evaluate biological impacts, including indicators of biodiversity, ecosystem health, and individual fitness. A rule of thumb is to use an endpoint that is as close as possible to the process under evaluation. For example, transcriptomic is often used to infer on organismal physiology while there is very poor correlation between these two endpoints (Feder and Walser, 2005). Ultimately, it is critical to evaluate the potential biological impact of OAE deployment on ecosystem functioning. This will require measuring the impacts at several trophic levels and include the higher trophic levels. Evaluating the potential ecological impacts is also critical to build trust with local communities. In April 2023, 300 protesters gathered to voice their concerns regarding an OAE deployment in St Ives Bay and called for greater scientific scrutiny. Specifically, they worried about the impact on the local environment and in particular on the grey seal population. Seals are benthic feeders that could directly and indirectly be impacted by the heavy metals released (Weeks, 2023).

4 Best practices: specificities to OAE

4.1 Manipulation of alkalinity (see Eisaman et al., 2023, this Guide, for more information and references)

The desire to increase the alkalinity of aquatic environments is not new and predates the concept of OAE. For example, aquaculture farmers are using liming agents or sodium bicarbonate to restore pond alkalinity to increase photosynthesis and fish production and to better buffer production water against possible pH changes over time. The so-called "liming" has been used through various materials or chemicals applied in ponds such as agricultural limestone, alkaline slag, agricultural gypsum (calcium sulfate), calcium chloride, slaked lime, quicklime, and lime liquor. While all these compounds mainly neutralize soil acidity before the filling with water, some are more convenient or more effective than others (Boyd and Tucker, 1998). On a smaller scale, aquarists who farm ornamental marine life such as fish, crustaceans, and corals also carefully monitor seawater alkalinity. They use different methods to activate calcium and alkalinity, such as additional water changes, kalkwasser (lime water), "balling", and devices such as calcium reactors containing alkaline material that can produce high-alkalinity liquid upstream of the aquarium (Goemans, 2012).

In the context of OAE, different methods of manipulating alkalinity are proposed. Two main options are generally considered:

- the addition of ground alkaline material or in situ enhanced weathering,
- pre-dissolution of alkaline materials or agents prior to pouring the resulting liquid into studied waters.

These can be directly used in experiments, while a more controlled manipulation of the chemistry (alkalinity and other substances) can be used to resolve the mechanisms and modes of action.

When alkaline materials are used, other compounds or impurities can also be released, such as silicate, calcium, magnesium and various trace metals (e.g., iron, nickel, cobalt, chromium). The main elements released through the use of lime, olivine, or magnesite are magnesium and calcium ions, along with minor elements like iron and trace elements, that occur at relatively low concentrations in seawater. However, their levels could be sufficient to affect marine organisms (e.g., Hauck et al., 2016; Moore et al., 2013). Therefore, the seawater contamination by the compounds and impurities inherent to alkaline materials has to be properly monitored and included in impact studies.

4.2 Monitoring compounds and impurities

There are many analytical methods available for measuring trace metals or other elements. The full process of collecting samples and analyzing dissolved trace elements is time-consuming and complex. The existence of multiple chemical forms (speciation) and specialized procedures for different elements due to speciation effects and contamination means that such analytical work has to be coordinated with specialized laboratories and chemists. One of the major challenges in determining trace metals is indeed preventing contamination of environmental water samples during sampling and analysis (Benoit et al., 1997). Nevertheless, there are some good procedures available online validated by experts to collect and handle samples for dissolved trace elements analysis (e.g., GEOTRACES, 2017; Noble et al., 2020). Among the different research methods discussed in this section, the survey of dissolved trace metals or other elements inherent in alkaline substances in seawater is easier to plan and to realize in laboratory experiments than in the field as the collection and handling of the samples is more straightforward and the risk of contaminating samples is much lower.

An exhaustive list of analytical equipment available to analyze all possible compounds and pollutants released into the ocean from each candidate alkaline material is outside the scope of this paper. The most suitable approach may be to combine a seawater preconcentration system (automated, such as seaFAST, or non-automated; Hirata et al., 2000; Wuttig et al., 2019) with inductively coupled plasma mass spectrometry (ICP-MS). There are exceptions for some elements, but this approach works for most elements expected to be released. Furthermore, the use of passive samplers has the advantage of better temporal and spatial resolution of marine pollution risks compared to discrete samples (Schintu et al., 2014; samples have then subsequently been analyzed in laboratories).

4.3 Combined effects of increased alkalinity and compounds and impurities inherent to alkaline materials

Many questions remain to be answered to fully address the potential ecological impacts of OAE and understanding the combined effects of increased alkalinity with other compounds and impurities is a tremendous challenge. Such questions require specific best practices and strategies (Boyd et al., 2018; IOC UNESCO, 2022). Parameters of the carbonate chemistry and other dissolved elements are very likely to have different modes of actions and functional changes at the cellular and physiological level. Changes in environmental parameters with different modes of action can lead to complex interactions between these parameters, making it difficult to project their combined impacts. Changes in the seawater chemistry can also directly affect the chemical form and bioavailability of a given element (Millero et al., 2009). Resolving these interactions requires a combination of mechanistic studies, modeling, and complex multi-stressor experiments.

When considering chemicals such as metals as potential stressors, two different aspects need to be considered. One is the dose-specific effects on the organism, and the other is the complexity of maintaining constant realistic metal exposures in the laboratory.

The relationship between organismal metal exposure and internal dose or adverse effects is nonlinear and depends on the metal studied and the organism selected. The accumulation and storage of bioavailable metals varies widely among aquatic organisms and is element specific. In addition, several metals, such as Co, Fe, Mn, and Zn, are essential for the metabolism of organisms and have optimal concentrations in their tissues (the optimal contents vary from species to species). Therefore, depletion or excess of these elements in an organism can have deleterious effects on the organism (e.g., Forstner and Wittmann, 1983), and some high concentrations may also be beneficial to the organism at certain levels.

From a technical point of view, exposing organisms in microcosms or mesocosms to specific levels of dissolved metals (or mixtures of metals) is more difficult than in field experiments. Indeed, the exposure has to be ideally maintained at a certain level in order to provide a more meaningful risk assessment, but at the same time it will not fully mirror the reality of the exposure environment due to fluctuations. Furthermore, there is a high likelihood in the microcosm that the presence of organisms with the ability to bioaccumulate metals will decrease exposure levels; repeated doses or flow-through systems will be required to keep the concentration constant.

Nickel may be one of the most important trace metal pollutants in olivine-based ocean alkalization, but there are other potential bioavailable trace metals (such as Cr, Cu, or Cd; Bach et al., 2019), which all can be bioaccumulated to a certain extent (Metian et al., 2007; Hédouin et al., 2010; Eisler, 2009). There is a large body of literature detailing the toxicity, sub-toxic concentration, or bioaccumulation potential of many of the compounds released by OAE in marine organisms (e.g., the compendium edited by Eisler is one of the most comprehensive sources of information; most elements have an extremely wide range of species from protozoa to vertebrates; Eisler, 2009, 2010). However, the effects of some elements found in rocks have not been studied or are poorly reported (e.g., zirconium).

5 Key recommendations for experimental research relevant to OAE

Resolving the biological impacts of complex and dynamic changes in carbonate chemistry and other compounds and impurities associated with OAE will require a scientific strategy combining different experimental approaches, methods, and collaboration between disciplines. To successfully develop and implement such scientific strategies, we provide the following key recommendations.

- Identify key scientific questions, sub-questions, and associated testable hypotheses.
- For each sub-question, select the most appropriate experimental approach or combination of approaches (laboratory experiments, mesocosms, field experiments, natural analogs, models), locations, biological models, level of biological organization, duration, controls, measured parameters, etc.
- Follow general experimental best practices for experimental design (e.g., replication, analyses)
- Take advantage of existing best practices for each specific field involved (e.g., multiple stressors experiments, manipulation and measurements of the carbonate chemistry and/or impurities).

Data availability. No data sets were used in this article.

Author contributions. SD and MM designed the structure of this manuscript, wrote the initial draft, and performed the needed revisions.

Competing interests. Competing interests are declared in a summary for the entire volume at: https://sp.copernicus.org/articles/sp-oae2023-ci-summary.zip.

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Laboratory experiments in ocean alkalinity enhancement research

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Abstract. Recent concern about the consequences of continuing increases in atmospheric CO_2 as a key heat-trapping agent (Wuebbles et al., 2017; Masson-Delmotte et al., 2021) has prompted ocean experts to come together to discuss how to provide science-based solutions. Ocean alkalinity enhancement (OAE) is being considered not only as an ocean carbon dioxide removal (CDR) approach but also as a potential way to mitigate ocean acidification. Over the last 2 decades, inter-laboratory comparisons have proven valuable in evaluating the reliability of methodologies associated with sampling and analysis of carbonate chemistry parameters, which have been routinely used in ocean acidification research. Given the complexity of processes and mechanisms related to ecosystem responses to OAE, consolidating protocols to ensure compatibility across studies is fundamental for synthesis and upscaling analysis. This chapter provides an overview of best practice in OAE laboratory experimentation and facilitates awareness of the importance of applying standardized methods to promote data re-use, inter-lab comparisons, meta-analysis and transparency. This chapter provides the reader with the tools to (1) identify the criteria to achieve the best laboratory practice and experimental design, (2) provide guidance on the selection of response variables for various purposes (physiological, biogeochemical, ecological, evolutionary) for inter-lab comparisons, (3) offer recommendation for a minimum set of variables that should be sampled and propose additional variables critical for different types of synthesis and upscaling, and (4) identify protocols for standardized measurements of response variables. Key recommendations include ensuring reproducibility through appropriate experimental design and replication, assessing alkalinity thresholds for secondary precipitates for each experimental approach and condition, using recommended targets of alkalinity (3000–4000 $\mu\mathrm{mol\,kg^{-1}}$) and levels exceeding these concentrations to mimic responses at the site of deployment/non-equilibrium and to use intermediate alkalinity levels to identify potential nonlinear responses, and establishing the appropriate experimental design to address questions at specific levels of organization (chemical, physiological, molecular) and assuming different scenarios (e.g., mimicking impacts at the site of deployment in a non-equilibrated system versus steady-state scenarios in an equilibrated system).

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1 Introduction

Laboratory studies need to be reproducible, consistent and transparent (Box 1) to provide the scientific community and regulators with useful information to move the field forward and facilitate the development of safe guidelines. Based on numerous modeling studies, ocean alkalinity enhancement (OAE) appears to be a promising ocean carbon dioxide removal (CDR) approach, with the likely beneficial side effect of mitigating ocean acidification (Burt et al., 2021; Hartmann et al., 2023; NASEM, 2022; Wang et al., 2023). Laboratory experiments are urgently needed to determine the CDR potential of various OAE methods as well as OAE impacts at various levels of biological organization (ecological, physiological, biochemical, molecular). The emerging empirical studies offer insight while revealing gaps in our knowledge of the mechanisms governing OAE and its effect on marine biota (e.g., Ferderer et al., 2022; Gately et al., 2023; Yang et al., 2023). For example, the conditions preventing or limiting the formation of secondary precipitates and the pros and cons of various alkali are still under debate. Given that empirical work on OAE is still in its infancy and that some of the assumptions based on modeling studies remain untested, this chapter is an evolving document that will be updated as the OAE community continues to release results.

Laboratory manipulations allow making observations in a highly controlled environment using model species or subsets of populations (selected species or populations). Results are generally considered highly reproducible (Box 1) and therefore laboratory manipulations are viewed as a necessary step to either generate hypotheses to test in the field or vice versa, when field experimentation is an option. Under the latter, field observations guide the laboratory experiments to validate field results in well-known systems and under tightly controlled conditions.

A number of approaches – batch, semi-continuous and continuous cultures – have been used to address diverse OAE settings (e.g., at the point of deployment, under steady-state conditions, air- versus non-air-equilibrated seawater) and various biological scenarios (specific stages of growth, life cycle and abrupt/short-term versus long-term responses to manipulations). In some cases, specific stages during the life cycle of organisms can be selected (for example, larval versus adult stage, sexual versus asexual phase). Time series laboratory experiments are less restricted than mesocosm experiments with regards to the duration of experiments because they tend to be "cleaner", with relatively low bacterial numbers and generally without biologically confounding factors (viruses, predation, competition for resources, etc.). Therefore, the cause–effect relationships are easier to elucidate as conditions and organisms can be tested in relative isolation, and there is the possibility of extensive replication.

The main limitation of laboratory experiments is that the dynamic phenomena occurring in the natural environment cannot be captured in the laboratory and, therefore, results may not be applicable to real life scenarios. For example, in laboratory experiments the influence of mixing processes, conditions governing particle flocculation or the linkage to higher levels of biological organization (e.g., predation) are difficult to discern (see Forbes and Calow, 2002; Martin et al., 2014). Portable lab experiments, such as deck incubations aboard research vessels or outdoor incubations, with some influence from the local environment (e.g., diurnal alterations of light, water flow through from the coast to maintain in situ temperature) as well as community-level mesocosm experiments, are the conduit to field manipulations. These large-scale community experimental tanks address the importance of the physico-chemical conditions, space, density-dependent effects, biotic interactions and the complexity of natural environments in their response to OAE manipulations/buffering, or boosting, and the direct effects of environmental stress on organisms (Paiva et al., 2021).

This chapter provides best-practice guidelines in OAE laboratory experimentation and offers recommendations to enable data re-use, inter-lab comparisons and transparency. We offer recommendations regarding (1) the criteria to achieve the best laboratory practice and experimental design; (2) the selection of response variables for various purposes (physiological, biogeochemical, ecological, evolutionary) for inter-lab comparisons; (3) a minimum set of variables that should be sampled and additional variables critical for different types of synthesis and upscaling; and (4) protocols for standardized measurements of response variables.

2 Lessons learned from ocean acidification research

The rich insights obtained into ocean acidification research are key to supporting OAE studies. However, as crucial as it is to follow guidelines when designing laboratory experiments, it is equally important to acknowledge that there may be potential confounders and challenges that may not be accounted for in the guidelines. Being able to conduct quantitative laboratory intercomparisons, including interspecies comparisons, will be critically dependent on identifying recommendations regarding experimental design, sample collection and data analysis. Important considerations include the source of alkalinity, rate of alkalinity addition, testing of air-CO_2-equilibrated versus non-equilibrated seawater, and the effect of ancillary variables (e.g., temperature) in multifactorial experiments which are known to yield complex and variable results (e.g., see the interactive effects of ocean acidification and warming – Harvey et al., 2013). The guidelines provided in this chapter should significantly improve the quality and impact of the OAE research, which is required to meet the identified societal need for research on OAE and other types of ocean CDR (NASEM, 2022).

- ***Reproducibility***. From the emerging OAE research (e.g., regarding the formation of secondary precipitates - see Montserrat et al., 2017 versus Fuhr et al., 2022; and Moras et al., 2022) and the ocean acidification literature (e.g., see Ridgwell et al., 2009), we have learned that similar approaches can lead to conflicting and unresolved outcomes. Without appropriate reporting of sample collection, methodology and data processing, it is challenging to re-analyze the data and reconcile the discrepancies. As the field emerges and evolves, reevaluating early experiments and possibly re-analyzing results with updated protocols will be required.
- ***Defining inclusion and exclusion criteria.*** In order to reduce confounding covariates, attention must be paid to factors affecting flocculation; aggregation of particles (e.g., possibly impacted by dissolved organic matter increases after phytoplankton blooms); fluctuations in temperature, which affect mineral dissolution and precipitation rates; and biological and physiological properties, including stage during the life cycle, trophic state and seasonality, that affect the susceptibility of organisms to OAE (e.g., see Vandamme et al., 2015; Subhas et al., 2022).
- ***Establishing experimental controls.*** In OAE experimental designs, controls must be appropriately selected. These could include seawater without added alkalinity, seawater ± nutrients/food, treatments with and without the organisms tested. When mineral dissolution is too slow, an alternative analog that reproduces the basic chemistry is encouraged (for example, the use of salts and alkali; e.g., $CaCl_2$ and Na_2CO_3 to mimic the effect of limestone-based mineral dissolution). Controls could also contain an alternative form of alkalinity that alters the seawater carbonate chemistry solely, without adding carbon or trace metals (e.g., NaOH).
- ***Basic biological responses.*** Studies on organisms' physiological responses (e.g., growth, respiration, size, reproduction, photosynthesis and calcification) are recommended. These responses can be measured directly, for example, as uptake rates of solutes using traditional assays, mass spectrometric methods for indirect assessment of changes in elements, or molecular responses using markers of functional processes. Rates of growth and calcification can also be measured by changes in dry mass or buoyant mass in many types of organisms, especially in macroinvertebrates and macroalgae (see Dodge et al., 1984; Davis, 1989; Sanders et al., 2018). For organisms that undergo development one must determine which stage of development (e.g., larval vs. adult, vegetative vs. gamete stage) to target. Also, when altering more than one parameter, particular attention must be paid to potential confounding effects. Multifactorial experiments can be used to explore the weight of each parameter.

Box 1. Criteria for best laboratory practice.

An exploration of procedures, patterns and challenges associated with ocean acidification research has offered ideas on how to design rigorous and reproducible laboratory experiments that enable measuring and monitoring carbonate chemistry shifts and biological responses to ocean acidification (Cornwall and Hurd, 2016). Cornwall and Hurd (2016) reported that 95 % of the experimental work between 1993 and 2014 had interdependent treatment replicates or lacked replication in clearly defined treatments or did not report sufficient methodological detail. More broadly, results from Wernberg et al. (2012) from marine climate change experiments between 2000 and 2009 reported that ∼ 49 % of the experiments had identifiable issues with their experimental procedures, and 91 % of the experiments reported showed a lack of treatment replication or pseudo-replication. Amongst the studies, 9 % included extreme/unrealistic treatments of temperature or pH far beyond worst-case scenario projections (Wernberg et al., 2012), although "extreme" pH/alkalinity conditions may prove useful to define thresholds of tolerance and upper limits of alkalinity enhancement and to understand underlying physiological mechanisms of acclimation to alkalinization. While the urgent need for field trials requires careful consideration of treatment levels, in order to maximize the insight gained from OAE experiments, testing conditions outside the year 2100 IPCC CO_2 emission scenarios are encouraged. These conditions outside worst-case scenario projections will further our knowledge on the mechanisms governing biological (e.g., shell production) and abiotic (e.g., particle aggregation, secondary precipitation) responses to applied chemical CDR.

Like in ocean acidification research, careful attention should be given to the advantages and disadvantages that concern the choices of dissolved inorganic carbon species to be measured and to how error propagation will affect the calculated parameters (Martz et al., 2015). Moreover, dissolved organic matter (DOM) is known to contribute to alkalinity (Kim and Lee, 2009; Koeve et al., 2010), although the presence of strong acidic groups in organic matter can decrease net alkalinity (Hu, 2020; Middelburg et al., 2020). Depending on the type of system under investigation, attention should be paid to whether to apply titration alkalinity (typically used in ocean studies) versus the charge balance approach (often used in freshwater systems, with high concentrations of dissolved organic matter) (see Middelburg et al., 2020). Results from ocean acidification mesocosm experiments focused on phytoplankton revealed that nutrient-limited communities appeared to be more responsive to changing carbonate chemistry than those having access to high inorganic nutrient concentrations (see Paul et al., 2015; Sala et al., 2016; Bach et al., 2016). These observations indicate that trophic state might play a role in the susceptibility of organisms to the changes in carbonate chemistry driven by alkalinization. Also, competition between species has been found to be altered under various carbonate chemistry conditions (see Kroeker et al., 2013a), which merits a focus on experiments that address preferential selection of taxonomic groups under different alkalinity conditions. Although applying nutrient-limiting conditions is experimentally challenging, understanding how species succession and community composition might respond to alkalinization could in part be addressed in a laboratory context.

While it is fairly straightforward to determine how individual changes in parameters influence chemical and biological responses, understanding the impacts of multiple parameters (e.g., increased alkalinity and warming, increased alkalinity and resource availability, such as nutrients, light or prey) can be challenging as they can interact in complex ways. Indeed, ocean acidification research has revealed antagonistic, synergistic and additive responses when studying ocean acidification and warming (Byrne and Przeslawski, 2013; Kroeker et al., 2013b; Harvey et al., 2013; Pistevos et al., 2017). Identifying tipping points and interactive effects when other parameters (e.g., temperature) are altered in seawater, in addition to alkalinity, is critical given the capacity of these parameters to drive (otherwise unpredictable) shifts in species abundances, biodiversity and community composition, physiological outputs, survival, and reproduction (Crain et al., 2008; Darling and Côté, 2008; Galic et al., 2018).

3 Seawater media preparation and manipulation of carbonate chemistry

The different steps in experimental design are outlined in Table 1. The process starts with natural or artificially made seawater with or without nutrient additions. One must consider whether adding nutrients/food/prey is required; for example, whether exploring OAE impacts is intended in conjunction with specific scenarios, e.g., nutrient fertilization, specific stages of growth or population development, and the extent to which nutrient additions or any other basic manipulation of the environmental conditions might impact the interpretation of results. For OAE manipulations where sterilization is required for the experimental setup, autoclaving is discouraged given the alterations in carbonate chemistry, including the loss of CO_2, leading to a decrease in dissolved inorganic carbon and alterations in alkalinity (increase with increasing salinity/decrease with precipitation of carbonate) triggered by autoclaving. Instead, filter sterilization of seawater through small-pore-size filters (e.g., 0.22 µm filters) is required to remove particles and most bacteria and produce the stock media where different manipulations are applied to create different alkalinity treatments.

There are several approaches to simulating the addition of alkalinity that capture different components of any manipulation experiment. The first approach could be testing the impact of the instantaneous addition of alkalinity to seawater to mimic the impact on seawater chemistry and ecosystems at the point of deployment. The second involves aeration and equilibration with the atmosphere to explore the physicochemical response to a steady-state/equilibrated scenario. In the latter instance, the medium is aliquoted out to the experimental vessels/tanks where aeration is applied to promote air equilibration. Monitoring carbonate chemistry through time enables determining when the equilibration of seawater with air occurs.

3.1 Sources of alkalinity

As yet, it is unclear what the optimal method or source of alkalinity enhancement may be in order to simulate the desired chemistry in seawater media. Proposed sources of alkalinity include silicate minerals (olivine, basalt), brucite, limestone and its derivatives (quicklime and portlandite), NaOH, and mine tailings (NASEM, 2022; Nawaz et al., 2023). Given the slow dissolution kinetics of the minerals, generating alkaline solutions artificially is acceptable. For example, Gately et al. (2023) simulated alkalinity enhancement via a limestone-inspired solution by adding Na_2CO_3 and $CaCl_2$ or its hydrated form ($CaCl_2H_4O_2$) to seawater. Adding Na_2CO_3 raises total alkalinity (TA) and dissolved inorganic carbon (DIC) at a 2 : 1 ratio, with 2 mol of TA added by two conservative Na^+ ions in Na_2CO_3 and 1 mol DIC added by CO_3^{2-}. $CaCl_2$ does not raise alkalinity because it adds equal amounts of positive and negative conservative charge to the solution from Ca^{2+} and $2 \times Cl^-$. However, it does raise the calcium in solution and therefore the saturation state of the seawater with respect to $CaCO_3$.

Many possibilities for solid or liquid alkalinity additions are being considered (see OAE Guide 23, Chap. 3). While adding minerals as precursors of alkalinity can provide a source of potentially beneficial nutrients (e.g., silicate, iron, magnesium) (Hartmann et al., 2023), the possible toxic effect of metals leached out of minerals, an example being nickel (Ni) leached from olivine (Montserrat et al., 2017), is of concern. The use of NaOH is currently gaining attention given that its environmental footprint is perceived as smaller than the mining of alkaline minerals, which necessitate an expan-

Table 1. Experimental considerations for OAE experimentation. Medium preparation: the seawater can be obtained from coastal or open-ocean sites. Filtered seawater or, when appropriate (e.g., when growing autotrophic organisms), seawater supplemented with nutrients, for example, using $f/2$ or variations of $f/2$ media (see Guillard and Ryther, 1962), will be used for growing organisms. Seawater media can also be prepared from artificial recipes (e.g., Aquil medium; Morel et al., 1979) when specific compounds or elements need to be altered in seawater. Media must be sterilized by filtration rather than through autoclaving, and nutrients can be added, typically from stock solutions. When possible, moderate aeration should be applied. Types of alkali include adding pulverized mineral directly to the media and promoting dissolution physically (e.g., by stirring); dissolving the mineral separately and filtering out any particles remaining in the media before experimentation; dissolving salts to mimic the chemistry of the dissolved alkali (e.g., to mimic limestone dissolution and dissolve $CaCl_2$ and $NaCO_3$, which result in higher dissolution rates); and adding liquid alkali such as NaOH. Establishing time series prior to the experiment to determine time frames regarding the length of experiment, frequency of sampling, etc., is recommended. Experimental design: in addition to optimizing reproducibility by designing enough replication and testing the reproducibility of the method, researchers should remain engaged with respect to protocols and experimental design to avoid artifacts and undesirable side effects of the methodology. When possible, ensure the equilibration of seawater gases with air and define experimental time frames to test impacts under conditions representative of the site of deployment (where limited gas exchange occurs) and those representative of steady-state/equilibrated conditions. Although most laboratory experiments address short-term impacts, chronic effects can be tested in long-term incubations. Sampling and analysis: the parameters to be considered should allow inter-lab comparisons, address functional properties of organisms (e.g., calcification, silicification, particulate organic carbon) and fulfill needs to improve model parameterizations. It is important to establish well-defined time windows for sampling as well as the frequency of sampling to capture the physical, chemical and biological properties of the studied system. It is advisable to limit the time of sample storage to minimize observations that might confound the interpretation of results (e.g., reverse weathering during storage). Stock solutions (e.g., nutrient and alkalinity solutions) must be stored in the appropriate vessels to avoid contamination from leachates coming out of the vessel itself (e.g., silicate contamination from solutions stored in borosilicate containers). Detection limits and accuracy and precision should be offered for each protocol.

Medium preparation	Experimental design	Sampling and analysis
Natural/artificial seawater Filter sterilization (e.g., 0.22 µm): ± nutrient addition, ± aeration. Type of alkalinity treatment: – pulverized mineral, – pre-dissolved mineral, – dissolved salts, – liquid alkali. Pre-equilibrated vs. non-equilibrated seawater with air phase: – carbonate chemistry, – flocculation/aggregation, – biology.	Best actions to maximize confidence: – within-study replication and pseudo-replication, – coordinated networks (teams sharing progress to decide on best protocols). Preliminary time series of TA and carbonate chemistry: – define experimental time frames, – assess TA upper limits, – expand the upper limits to address impacts at site of deployment. Abrupt vs. chronic biology impacts: – short-term tests (acclimation), – long-term experiments (adaptation).	Criteria for key parameters: – inter-lab comparisons, – functional properties, – model parameterization. Sampling frequency and timing: – select time window for sampling, – identify sampling frequency that captures key chemical, physical or biological features. Limit storage to minimize artifacts Identify and report key analytical parameters affecting error: – detection limits, – measurement accuracy/precision, – identify any impact of experimental design on uncertainties.

sion of mining operations, transportation and industrial processing, which are energetically costly and can lead to air pollution. Additionally, the amount of Na added to seawater is very small relative to the large background of NaCl in seawater.

The addition of NaOH and other forms of alkalinity to seawater cause initial spikes in pH and a drop in aqueous CO_2 that can be balanced to a steady state via bubbling with air (Table 1). Determining abiotic and biotic responses to the initial spikes in pH and drops in CO_2 is an important step in addition to understanding responses under steady-state conditions. It may be that large manipulations of alkalinity are needed to elicit a measurable and reproducible response, and the required alkalinity concentrations will be refined with more detailed modeling but, based on current information, proposed targets for alkalinity manipulations are 3000–4000 $\mu mol\,kg^{-1}$ (Renforth and Henderson, 2017). The concentration of alkalinity (~ 4000 and $\sim 3000\,\mu mol\,kg^{-1}$) expected at locations in the ocean where alkalinity is initially added is the concentration of alkalinity expected once ocean circulation has dispersed the alkalinity over a larger area (Renforth and Henderson, 2017). Alkalinity thresholds for the formation of precipitates will need to be determined for each experimental approach and condition. It is, however, recommended that researchers consider using alkalinities exceeding the recommended targets and utilize intermediate treatments (e.g., 2000, 4000, 7000 $\mu atm\,kg^{-1}$ seawater) rather than just low/high treatments, in order to identify potential nonlinear and even parabolic responses. This approach has led to important and unexpected outcomes in ocean acidification research (e.g., Ries et al., 2009).

3.2 Impacts of impurities/metal leachates

An important consideration in OAE studies is the impact of metals leached from dissolving minerals and their ecotoxicological potential on marine organisms. For example, although some elements (e.g., Fe and Mg) leached out of minerals could be beneficial micronutrients, the potentially toxic effect of metals such as nickel (Ni) (Montserrat et al., 2017), leached from olivine, is of concern. Diverse responses have, however, been reported with respect to Ni, and it appears that some cyanobacteria rely on Ni more than other photosynthetic organisms (see Dupont et al., 2008, 2010; Ho, 2013). A recent laboratory study testing olivine leachates (containing Si, Ni, Mg, Fe, Cr and Co) in phytoplankton revealed either positive or neutral physiological short-term responses in all treatments (Hutchins et al., 2023). However, one should consider the role of long-term experiments to examine organismal and population adaptation of metal exposure as well as potential bioaccumulation and biomagnification impacts in consumers.

Another important consideration is the effect of pH on metal speciation as pH and a change in the concentration of OH^- and CO_3^{2-} ions can affect the solubility, adsorption, toxicity and rates of redox processes of metals in seawater thus altering the interactions of metals with marine organisms (Millero et al., 2009). When dissolving minerals in seawater, one must consider non-stoichiometry and incomplete dissolution, perhaps as a result of dissolution of impurities, precipitation of secondary minerals, or preferential leaching of elements from the mineral surface (Brantley et al., 2008; NASEM, 2022). The formation of secondary precipitates has been observed in several studies exploring the dissolution of olivine (Fuhr et al., 2022) and limestone derivatives (Moras et al., 2022; Gately et al., 2023; Hartmann et al., 2023). Using an alkaline solution rather than reactive alkaline particles has been recommended to reduce carbonate precipitation unless seawater critical supersaturation levels are exceeded (Hartmann et al., 2023). In addition, runaway $CaCO_3$ precipitation, a condition where more alkalinity is removed than initially added, reduces the OAE CO_2 uptake efficiency. More complex precipitates containing Fe, Si and P were observed in a study using a limestone-inspired OAE approach revealing that mineral precipitation caused by seawater alkalinization can also remove inorganic nutrients from solution (Gately et al., 2023).

Maintaining alkalinity following OAE is critically dependent on the carbonate saturation state, its temporal evolution and particle surface processes (Hartmann et al., 2023). To minimize the loss of alkalinity and maximize alkalinity enhancement, Hartmann et al. (2023) propose the application of an alkaline solution in CO_2 equilibrium with the atmosphere and/or solutions with tested saturation levels to prevent a further increase in supersaturation and the precipitation of carbonate "to avoid loss of alkalinity". A separate reservoir where alkaline solutions have been prepared is desirable for testing the upper limits of alkalinity addition and identifying saturation thresholds to minimize precipitation.

4 Experimental design

4.1 Experimental replication

Replication is important to determine if results are reproducible, although one must consider that when results are so dependent on precise experimental conditions that replicability is needed for reproducibility, the result may be unique and potentially less relevant than a phenomenon that can be reproduced by a variety of independent, non-identical approaches (see Casadevall and Fang, 2010). A number of experimental designs can be used to achieve adequate statistical replication (Fig. 1). For example, simple replication involves experimental units (each of the replicates) per treatment where all the conditions are manipulated independently but in the same way for that treatment and where responses to the treatment are measured (defined by Hurlbert (2009) as the "evaluation unit") and each experimental unit can be regarded as independent. In temporal replication, multiple measurements are made through time (temporal trends) on the same experimental unit. Sacrificial replication involves the use of multiple sampling times per treatment (for example, a time series) and multiple experimental units at the time of sampling. Each approach has distinct strengths and limitations, and the choice of the approach depends on the scientific questions and the extent of the risk of error propagation. For example, one might choose sacrificial replication for certain chemical manipulations that require sampling from vessels with comparable volumes but choose instead temporal replication for monitoring the evolution of a microbial culture or the physiology of fish over time under certain alkalinity conditions.

4.2 Preliminary experiments

In addition to testing the biological responses to abrupt enhanced alkalinity, marine organisms can be exposed to enhanced alkalinity conditions after the equilibration of seawater pCO_2 with that in the air phase following alkalinity addition. Ideally, aeration should be maintained to ensure O_2 levels required by marine animals and also maintain stable pCO_2 levels in the alkalinity perturbation experiments. Depending on the organism tested (a few organisms do not tolerate aeration in tanks), aeration might or might not remain for the duration of the experiment (Table 1). The vessels used in OAE experiments might not be traditional tanks used in aquaria but rather any type of container adequate for different types of organisms (e.g., culture flasks for bacteria, conical flasks, carboys for phytoplankton, open tanks for echin-

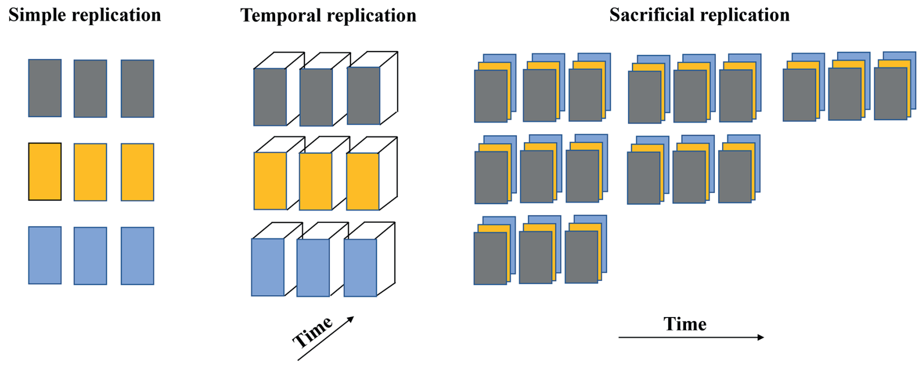

Figure 1. Examples of experimental laboratory design with regards to replication. Each treatment, represented by a color, contains experimental units (replicates). Each experimental unit is treated as an independent experiment except in the sacrificial replication approach, where each replicate is treated statistically as an experimental unit.

oderms and fish) with air lines to introduce aeration into the media. When running multifactorial experiments (e.g., temperature and alkalinity), designing an analysis plan and concrete experimental questions to interrogate can help determine the sample size and minimum number of treatments.

An analogy to OAE is the use of lime soda and other alkali to combat acid rain, which has caused deleterious changes in freshwater ecosystems for more than half a century in northern Europe and North America. To reverse some of these' changes a number of governmental and nongovernmental teams have applied lime and other neutralizing compounds to streams, rivers, lakes and catchments in the most affected or most ecologically valuable regions (see Clair and Hindar, 2005). Another example is the effects of seawater buffering mainly by the addition of Na_2CO_3 addition utilized by the commercial shellfish industry (e.g., Ragg et al., 2019), which showed a broad improvement in larval health compared to undersaturated waters.

Standardizing technical details in protocols, sampling, sample processing and analyses is crucial to control for variation introduced by reagents, sample storage and other factors. The collection and curation of metadata associated with each sample are critical for data interpretation, inter-lab comparison and drawing conclusions to move forward with planning field deployments for research purposes. For studies involving more than one level of biological organization, i.e., grazing experiments and competition experiments, particular attention should be paid to designing adequate controls.

The effects of OAE and its interactions with other parameters might differ depending on the duration of the experiments. Indeed, in ocean acidification studies, compensatory metabolic pathways appear to take longer to become established, depending on factors such as the exposure history (Calosi et al., 2013) and phase of the life cycle (Hettinger et al., 2012). In a study testing ocean acidification and warming, biological effects were not detectable in the short term but were instead manifested over time (Godbold and Solan, 2013). It was suggested that species responses to seasonal variations in environmental conditions might explain these differences that, depending upon timing, can either exacerbate or buffer the long-term directional effects of climatic forcing (Godbold and Solan, 2013).

4.3 Recommended minimum set of variables to report

To improve comparability between future work, we recommend a minimum set of variables with the understanding that more variables might be added as new results emerge (Table 2). We recommend measuring and reporting at least the following variables (shown in bold in Table 2).

- At least alkalinity and one more parameter of the carbonate system must be measured to calculate key carbonate chemistry parameters including bicarbonate and carbonate ions, CO_2, pH, and the saturation state of $CaCO_3$ polymorphs. This information is critical to determine chemical alterations in the dissolved inorganic carbon system as a result of alkalinization.
- Resource availability (e.g., prey, dissolved inorganic nutrients, light) are needed to monitor the growth conditions.
- Particulate organic carbon (POC), nitrogen (PON) and phosphorous (POP) are required to learn about trends in biomass production and stoichiometry.
- Basic physiological properties (respiration, photosynthesis) should be measured to inform biogeochemical models and learn about biologically mediated fluxes of elements.
- Some functional group-specific properties, particularly those involving mineral precipitation (calcification, silicification) and those with environmental effects (e.g., toxin production) and with climate-relevant impacts (nitrogen fixation/denitrification) in context-specific cases must be measured.

- The size of offspring and fecundity rates can be used as indicators of trans-generational plasticity and adaptation to alkalinization.

Other variables are important in the exploration of specific questions such as the following: how does seawater alkalinization affect biodiversity, how does metal bioavailability change under increased pH and what is the role of organic alkalinity in coastal systems? The variables and protocols listed in this chapter are not exhaustive and only provides a proxy sample largely based on the literature on climate impacts on marine systems and ocean acidification.

4.4 Type of experiments

Laboratory experiments can be designed to both address short-term responses and to explore the longer-term adaptation to chronic exposure to enhanced alkalinity conditions. Filtered natural seawater should be used, when possible, in incubations unless artificial seawater is required (for example, when studying the effect of metal concentrations). Short-term manipulations involve the use of batch, semi-continuous and continuous incubation experiments. In *batch incubation experiments*, all resources are provided at the beginning of the incubation, without further addition, and sampling takes place during a short time period (hours, days, weeks). Only gases and alkali can be added during the course of the experiment. When biological processes are measured, a phase during the life cycle (e.g., larva/adult, vegetative cells/gametes) or growth (healthy, exponentially growing/resource-limited, stationary growing organisms/senescent organisms) is typically targeted. Sampling is conducted until the nutrients are consumed and beyond that if decaying populations are the focus of the investigation.

Given that resources (light, nutrients) are the limiting factor in batch incubation experiments, the organisms are in the exponential growth phase for a limited time period. To expand sampling and replication during the exponential growth phase, resupply of nutrients using a *semi-continuous culturing* approach can prevent food/nutrients from becoming a limiting factor. When the studied organism is phototrophic, one must ensure subculturing (microbial cultures) or appropriate arrangement or organisms to prevent light limitation. The advantage of semi-continuous culturing is that it allows investigating trends over extended time periods, increasing replication and higher yield. Generally, the resource is added manually or pumped from the nutrient supply vessel into the culture vessel during exponential growth or when specific conditions are met (e.g., when a certain biomass concentration is reached).

In *continuous cultures*, the rate of the addition of nutrients is controlled to maintain steady-state cell growth. This system is known as chemostat, where, typically, a volume of culture medium is added and the same volume is removed from the growing culture. A challenge with this type of "bioreactors" is that, over long time periods, they can be more susceptible to microbial contamination and long-term phenotypic and genotypic variance in the cultures (Reusch, 2014).

Portable incubation experiments that simulate regional in situ alkalinity deployments are an important step in understanding seawater alkalinization and its impact on marine organisms prior to field testing. This type of incubation experiments, which simulate alkalinity additions under diverse local in situ parameters (e.g., temperature, irradiance, nutrients), can be accomplished using portable incubators on board research vessels (i.e., deck incubations) or outdoors, at coastal research facilities (Fig. 2).

When studying photosynthetic organisms, high-quality light filters should be attached to the acrylic tank to adjust photosynthetically active radiation (PAR) within the incubator (e.g., Fig. 2). To maintain in situ seawater temperatures, an inflow port can supply seawater to the incubator. Effort should be taken to ensure movement of seawater quickly through the incubator to maintain a uniform temperature.

When collecting natural seawater, one must consider how biological interactions (e.g., grazing) could confound results and filter accordingly. Unlike laboratory experiment, which allow for seawater–air-phase CO_2 equilibration, portable incubation experiments require instantaneous alkalinity additions; thus, careful consideration should be given to the method of alkalinity addition used. When adding liquid alkalinity, e.g., solutions (e.g., 1 M) of NaOH one must consider that flocculation commonly occurs upon alkalinity addition (Subhas et al., 2022). Adding pulverized minerals directly to the treatment vessels is another option, although this method may yield incomplete dissolution or slow dissolution (e.g., Fuhr et al., 2022) with undesirable effects including secondary precipitation, particle aggregation and detrimental biological impacts (NASEM, 2022). Some researchers have opted for mimicking mineral dissolution instead (see Gately et al., 2023). As in the traditional laboratory experiments described above, vessels within the incubator should ideally be aerated during experimentation. In addition to chemical and biological parameters, PAR and temperature data should be collected throughout the experimental time frame through discrete sampling or semi-continuously using sensors and data loggers. The best practices outlined in Box 1 should be adhered to when planning portable incubation experiments. Effort should be taken to position the incubator in a way that avoids confounding factors such as light contamination (e.g., from the ship).

5 Sampling and analysis

Technical variability amongst experimental methods ranging from sampling and sample processing can propagate through the various steps before analysis; for example, chemical analysis and molecular work/sequencing can be error-prone (e.g., Catlett et al., 2020). The use of blanks every

Table 2. Examples of responses to ocean alkalinity enhancement to be measured in experimental manipulation studies. Knowledge need: M – medium; H – high. Measurement mode: MM – manual mode; S – sensor; SD – sensor in development. A minimum variable set is highlighted in bold. Selected references are provided as examples of protocols.

Type of response	Variable	Knowledge need	Measurement mode	Protocol reference
Chemical and environmental	**Carbonate chemistry parameters** $\{[\mathbf{HCO_3^-}], [\mathbf{CO_3^{2-}}], [\mathbf{CO_2}], \boldsymbol{p}\mathbf{CO_2}, \boldsymbol{\Omega}\}$	H	MM, S, SD	Dickson (2010), Bockmon and Dickson (2015)
	Dissolved organic matter	M	MM	Marañón et al. (2004), Sharp et al. (1995)
	Dissolved inorganic nutrients	H	MM	Worsfold et al. (2013)
	Resource availability (prey, light)	H	MM, S	Lawrence et al. (2017)
	Particulate organic matter (C, N, P)	H	MM	Verardo et al. (1990), Hilton et al. (1986), Pujo-Pay and Raimbault (1994), Fu et al. (2008)
	Trace metals (in solution and in aggregates)	M	MM	Guo et al. (2022), Hutchins et al. (2023)
	Biologically and biogeochemically relevant elements (e.g., Si, Mg : Ca)	M	MM	Brzezinski (1985), de Nooijer et al. (2017)
Physiological	**Basic physiology (respiration, photosynthesis, growth rates; morphometric measurements)**	H	MM, S	Iglesias-Rodriguez et al. (2008), Kelly et al. (2013), Farrell et al. (2009)
	Some functional group-specific physiology (e.g., calcification, silicification, nitrification/denitrification, toxin production)	H	MM, S	Cohen et al. (2017), DeCarlo et al. (2019)
	Physiological stress, e.g., heat shock proteins, oxidative stress-related proteins, photosynthetic stress (shifts in quantum yield), morphological alterations (e.g., cyst formation)	M	MM	O'Donnell et al. (2009), Moya et al. (2015), Trimborn et al. (2017)
	Incidence of pathogens and disease	H	MM	Asplund et al. (2014)
Reproduction	Spawning success	M	MM	Liu et al. (2011)
	Size of offspring	M	MM	Cao et al. (2018), Johnson (2022), Albright et al. (2010)
	Sperm motility	M	MM	Esposito et al. (2020), Havenhand et al. (2008)
	Epigenetic analysis	M	MM	Li et al. (2018), Lee et al. (2022)
	Fecundity	M	MM	Maranhão and Marques (2003), Thor and Dupont (2015)
	Hatching success	M	MM	Saigusa (1992)
Species interactions	Competition for resources	M	MM	Connell et al. (2013), Guo et al. (2022)
	Predation and species interactions	M	MM	Greatorex and Knights (2023), Bacus and Kelley (2023), Mitchell et al. (2023)
	Synergistic/antagonistic effects of other environmental parameters	M	MM, S	Gerhard et al. (2023), Khalil et al. (2023)

Figure 2. **(a, b)** Portable incubator with blue filters to adjust photosynthetically active radiation (PAR). A scalar PAR sensor (LI-COR) can be observed within the incubator (**a**, right side). **(c)** Laboratory experiment using aeration and sacrificial replication. Images were taken by James Gately **(a, c)** and Sylvia Kim (**b**).

time sampling is conducted is essential for detecting contamination originating from the experiment itself or from the adjacent environment (e.g., exogenous sources such as surface contamination, flagellates in droplets through aeration). When possible, several barriers to contamination are recommended (e.g., filters at various points of aeration). Additionally, for samples (other than those preserved for analysis of alkalinity, dissolved inorganic carbon analysis or pH) that are kept for further analyses, contaminants that grow during shipping or while samples are being stored can sometimes be reduced by freezing at −80 °C, when possible, or by using the appropriate preservatives when storing at ambient temperature is required (e.g., ethanol, paraformaldehyde, glutaraldehyde). Attention should be paid to the material of vessels where samples and solutions are stored; for example, avoid borosilicate bottles to store nutrients or alkalinity solutions as silicate can be leached into solution.

Establishing time series prior to the experiment to determine time frames regarding the appropriate length of the experiment and frequency of sampling is recommended. It is important to establish well-defined time windows for sampling as well as frequency of sampling to capture physical, chemical and biological properties of the studied system. It is advisable to limit the time of sample storage to minimize observations that might confound the interpretation of results (e.g., reverse weathering during storage) (Subhas et al., 2022).

5.1 Criteria for key parameters

For the most part, laboratory experiments are aimed at elucidating the physiological performance and biogeochemical responses of organisms (rather than communities) to physical or chemical alterations in the environment, although conclusions about responses in ecological fitness could be drawn from laboratory experiments (Table 2). Importantly, environmental change can affect species differently and interactions between species that are sensitive to environmental change can function as ecological leverage points through which modest changes in abiotic conditions are amplified into large changes in marine ecosystems (see Kroeker and Sanford, 2022). These interactions can be measured as competition, predation and symbiotic relationships (mutualism, commensalism and parasitism) that can vary along environmental gradients that cause stress (Stachowick, 2001; Bruno et al., 2003; Ma et al., 2023).

Criteria for selection of species should include whether the organism is amenable to laboratory experimentation, the amount of background knowledge on the organism's physiology and biogeochemistry, ecological importance of the organism, and local and global impacts. Considerations when selecting organisms should also include geographic origin (e.g., temperate/tropical/polar) and ecosystem type (e.g., benthic vs. pelagic). Special attention should be paid to those species that (1) significantly impact or respond biogeochemically to chemical changes caused by alkalinity addition (e.g., possibly calcifiers, photosynthetic organisms), (2) keystone organisms (e.g., corals, salmon, sea stars, toxin-producing phytoplankton), and (3) organisms/functional groups of known vulnerability to climate change (corals, urchins).

Calcium-carbonate-producing organisms are particularly interesting because of their known sensitivity to changes in carbonate chemistry and because any alteration in their abundance or calcification rates could have implications in the CDR potential of alkalinization. The mineralogical composition of carbonate-containing organisms might possibly be affected by alkalinization. For example, recent meta-analysis of studies exploring the effects of the carbonate chemistry shifts caused by ocean acidification revealed effects on shell state, development and growth rate (Figuerola et al., 2021). Biomineralization studies should explore species-specific responses driven by mineralogical composition (calcite, aragonitic, high/low Mg calcite) of their tests, shells and skeletons. Environmental and biological control on calcification, particularly any changes in the Mg content in calcite driven by the use of brucite and other minerals potentially adding Mg to calcite, must be reported, as calcite with a high Mg content is less stable in aqueous solutions (Ries et al., 2016). Empirical studies have shown that the Mg / Ca ratio of Mg-calcite-producing organisms generally varies proportionally with seawater Mg / Ca (e.g., Ries, 2004, 2006), and therefore particular attention should be paid to the Mg content (and solubility) of biomineralized calcite. The addition to proposed Ca- and Mg-containing minerals – $Ca(OH)_2$ (slaked lime), $Mg(OH)_2$ (brucite), $CaCO_3$ (limestone) or $(Mg,Ca)CO_3$ (dolomite) – will alter the Mg / Ca ratio of the seawater. An extensive body of literature reports biogenic and abiotic precipitation of low-Mg calcite when seawater Mg / Ca falls within the calcite stability field (seawater molar Mg / Ca < 2) and the biogenic and abiogenic precipitation of aragonite and high-Mg calcite when seawater Mg / Ca falls within the aragonite stability field (seawater molar Mg / Ca > 2) (Ries, 2010). Thus, modification of local seawater Mg / Ca ratios by OAE has the potential to favor aragonite and high-Mg calcite organisms if seawater Mg / Ca is increased and low-Mg calcite organisms if seawater Mg / Ca is decreased. This is an important area of future OAE research.

Central to OAE laboratory experimentation is our ability to measure any possible stress induced by alkalinization and learn about underlying mechanisms behind acclimation to the chemical alterations of seawater caused by OAE. This can be achieved by measuring basic functions (growth rates, size, reproductive success); sensitivities to alkalinization might be organism-specific and possibly trophic-level-specific (e.g., Voigt et al., 2003; Gilman et al., 2010), although most laboratory experiments do not address the complexity of trophic interactions. Similarly, measuring adaptation and diversity in acclimation between and within related organisms is a challenge, and the ocean acidification literature has revealed how important it is to pay attention to diversity of responses (see Kroeker et al., 2010).

Stress is often measured as a reduction in organismal performance or fitness caused by environmental change (Schulte, 2014). In addition to these general physiological or behavioral responses, markers of stress such as oxidative stress are often used. For example, it is well established that the production of reactive oxygen species (ROS) can increase due to environmental stress including ocean acidification (Lesser, 2006; Lushchak, 2011). Many biomarkers are commonly used for studying oxidative stress in marine organisms (Cailleaud et al., 2007; Vehmaa et al., 2013), and an increase in ROS and superoxide dismutase and catalase activities has been reported in marine animals under stress (von Weissenberg et al., 2022). Heat shock proteins (HSPs) are also used as molecular markers of stress because of their abundance, high sensitivity to stress and ubiquitous expression (Gross, 2004). Among all HSPs, HSP70s are the most studied as a strong up-regulation of HSP70 production has been demonstrated broadly with the exception of *Hydra oligactis* (Bosch et al., 1988) and some Antarctic animals (La Terza et al., 2001; Place and Hofmann, 2005).

5.2 Measurements of nutrient uptake rates

The uptake rate of carbon and other nutrients that results in the observed standing stocks of particulate matter involves many physiological processes that are sensitive to changes in inorganic carbon chemistry and pH (Matsumoto et al., 2020). Chemical changes following the addition of alkalinity might alter physiological processes that represent sources (calcification, respiration) and sinks (photosynthesis) of CO_2. One should also pay attention to the reciprocal interactions between these physiological processes and the chemically altered environment as even minor changes in biological processes or in the balance between them can have implications for the CDR potential and biodiversity.

One of the most unknown effects of OAE is the fate of biological fixation rates of different elements (e.g., carbon and N_2 fixation rates). Such rates are measured in batch cultures and bioassay (mixed natural community) incubation experiments (LaRoche et al., 2010). While the objective of culture experiments is to understand the effect of environmental parameters on the elemental uptake by particular species in a lab, bioassay experiments have to deal with a rather complex species interaction in the field or after subsampling of mesocosms in a lab (Hutchins et al., 2007; Paul et al., 2016). Labeled/enriched ($\sim 99\,\%$) stable isotope tracers represents the most used method for rate estimation these days. The rate calculation is based on isotopic mass balance equation (Montoya et al., 1996):

$$\text{C or N}_2 \text{ fixation rate } = \frac{[\text{POM}]}{t}\left(\frac{A_\text{f}-A_0}{A_\text{e}-A_0}\right), \tag{1}$$

where [POM] is the concentration of element of interest (C or N) at the end of the incubation. Likewise, $A_\text{f} = \text{atom}\,\%$ in POM at the end of incubation, $A_0 = \text{atom}\,\%$ in POM at the start of the incubation, t is time of incubation and A_e is the isotopic enrichment in the dissolved form after the tracer addition at the start of the incubation.

This equation/method is sensitive to analytical protocols in routine incubations (White et al., 2020) and might be even more sensitive in OAE incubations due to the issue of gas equilibration in tightly capped bottles. While the C substrate-based incubations are supposedly straightforward, N_2 gas incubations face the challenge of under-equilibration leading to underestimation of rates. But OAE incubations can produce larger errors in the C fixation estimates as well. This is because $NaHCO_3$ is generally used as a C substrate. To estimate ^{13}C isotopic enrichment after tracer addition (term in Eq. 1), a DIC value is normally assumed (as it does not change much at a given region). But OAE is expected to increase (or fluctuate) DIC during the experimental period, and thus a measured DIC value should be used in the enrichment factor calculation. Likewise, the ^{14}C method, which is widely used for marine primary production and calcification rate measurements due to its sensitivity (Nielsen, 1952), also requires treatment-specific determination of DIC concentrations. Likewise, slow dissolution of N_2 gas poses a challenge to accurately estimating isotopic enrichment factor (A_e), and it is advisable to measure this term.

Although the analytical precision of C and N isotopes is of the order of sub-per-mil levels, many times the low reported rates ($< 0.1\,\text{nmol N L}^{-1}\,\text{d}^{-1}$) are questionable (Gradoville et al., 2017). Therefore, the detection limit of rate measurements and its proper reporting is a major concern. To overcome this, following the propagation of analytical and statistical errors in each term of mass balance equation (1), Gradoville et al. (2017) have proposed to report minimal quantifiable rates (MQRs) and the limit of detection (LOD) in triplicate samples. We ought to follow these protocols in the rates measured in OAE. In addition, we must make sure to sample/filter sufficient water to achieve 35 µg N and 150 µg C in the sample for reliable mass spectrometric measurements.

6 Conclusions and recommendations

The field of OAE faces a great diversity of challenges given the continuously evolving experimental approaches and emerging data availability that will undoubtedly provide new information and ideas to optimize best practice in laboratory experimentation. This chapter highlights the need for attention to the design, sampling, performance and analysis of laboratory procedures used in OAE laboratory experiments. The criteria we present to achieve best practice in laboratory experimentation and design focus on reproducibility, factors affecting CDR potential and organism health (e.g., alkalinity conditions leading to flocculation, aggregation), establishing suitable experimental controls, and identifying the appropriate level of biological organization (physiological, molecular) to study biotic responses to OAE. Key response variables providing information on alterations in seawater chemistry following alkalinization, growth of organisms/biomass buildup/reproductive success and biogeochemically relevant properties (e.g., photosynthesis, respiration, calcification) under elevated alkalinity conditions should be measured and reported. The main recommendations include the following:

- Ensure reproducibility through appropriate experimental design and replication.
- Determine alkalinity thresholds for the formation of precipitates for each experimental approach and condition.
- In addition to the proposed alkalinity target values of 3000–4000 $\mu\text{mol kg}^{-1}$ (Renforth and Henderson, 2017), use concentrations exceeding these recommended values to mimic responses at the site of deployment/non-equilibrium and use intermediate alkalinity levels to identify potential nonlinear responses.
- Establish an appropriate experimental design to address questions at specific levels of organization (chemical,

physiological, molecular) and assuming different scenarios (e.g., mimicking impacts at the site of deployment in a non-equilibrated system versus steady-state scenarios in an equilibrated system).

Given the emerging nature of ocean alkalinity enhancement as a research field, this chapter will evolve to update guidelines as more results become publicly available. Frequent assessments of knowledge acquired from emerging and future studies and a review of best practices are needed to keep the OAE community engaged and forward-thinking.

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Mesocosm experiments in ocean alkalinity enhancement research

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Abstract. An essential prerequisite for the implementation of ocean alkalinity enhancement (OAE) applications is their environmental safety. Only if it can be ensured that ecosystem health and ecosystem services are not at risk will the implementation of OAE move forward. Public opinion on OAE strategies will depend first and foremost on reliable evidence that no harm will be done to marine ecosystems, and licensing authorities will demand measurable criteria against which environmental sustainability can be determined. In this context mesocosm experiments represent a highly valuable tool in determining the safe operating space of OAE applications. By combining biological complexity with controllability and replication, they provide an ideal OAE test bed and a critical stepping stone towards field applications. Mesocosm approaches can also be helpful in testing the efficacy, efficiency and permanence of OAE applications. This chapter outlines strengths and weaknesses of mesocosm approaches, illustrates mesocosm facilities and suitable experimental designs presently employed in OAE research, describes critical steps in mesocosm operation, and discusses possible approaches for alkalinity manipulation and monitoring. Building on a general treatise on each of these aspects, the chapter describes pelagic and benthic mesocosm approaches separately, given their inherent differences. The chapter concludes with recommendations for best practices in OAE-related mesocosm research.

Preface. The authors would like to emphasize that this chapter does not intend to cover all aspects of mesocosm experimentation in its full breadth, but rather it tries to address aspects specific to research on ocean alkalinity enhancement (OAE) or aspects we consider important to reiterate here. For a more comprehensive presentation of recommendations and guidelines on mesocosm experiments the reader is referred to Chapter 6 of the *Guide for Best Practices on Ocean Acidification Research and Data Reporting* (Riebesell et al., 2010) and references therein as well as Stewart et al. (2013).

Although the general approach to mesocosm experiments is straightforward and basically involves enclosing a body of water with or without sediment in order to monitor responses of the enclosed communities and related processes to the manipulated perturbation over an extended period of time, the specifics of conducting such experiments can vary considerably. These include factors such as the materials, design and location of the enclosures (e.g., fixed structures on land or flexible wall enclosures in situ) as well as the procedures for mesocosm filling, operation, mixing and sampling. While the dimensions of the experimental enclosures can range from less than 1 m^3 to > 1000 m^3 depending on the requirements of the experiment, we here adopt the classification set out by the SCOR Working Group 85 (1991): microcosms (less than 1 m^3), mesocosms (between 1 and 1000 m^3) and macrocosms (more than 1000 m^3). We note that benthic experimental enclosures can have different size categories.

1 Placing mesocosms in the context of OAE research

Mesocosm experiments provide an essential bridge between the tightly controlled but poorly realistic laboratory culture experiments and the complexity of natural systems. This is

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particularly important for possible OAE implementations, in order to achieve a sound understanding of the entire process of the proposed OAE strategies, from the dissolution kinetics and effectiveness of the alkalinization technique to the potential environmental impacts, risks and co-benefits. This knowledge is crucial prior to any form of OAE application to safeguard the protection of marine ecosystems functioning, biodiversity and related ecosystem services. Moreover, should OAE prove to be a viable approach for marine carbon dioxide removal (mCDR), it will also be crucial to achieve social acceptance for potential OAE implementations. Also in this context mesocosm experiments can serve as a useful tool for proof of concept, the results of which can play an important role in the public discourse about the risks and benefits of mCDR implementation.

Functional redundancy and species richness in ecosystems allow for some degree of resistance to withstand disturbances and resilience to recover once a disturbance has ended or dissipated. To determine the actual ecological impacts of OAE it is essential, therefore, to test suggested applications at the community/ecosystem level. Doing this in field trials, however, poses serious difficulties, given the hydrographic complexity of most marine systems, with lateral advection (currents, tides), vertical flow (convection, up- and downwelling) and wave-driven mixing. Determining dose–response relationships for environmental impacts is extremely challenging under such conditions. Mesocosm experiments, on the other hand, enable the combination of biological complexity needed for testing resistance and resilience of communities/ecosystems in their natural setting and seasonal succession (in a single experiment where succession occurs on short timescales, e.g., a phytoplankton bloom, or multiple experiments in different seasons using the exact same experimental setup) with a reasonable degree of control and replication and hence the statistical power to reach reliable conclusions. At the same time, they allow testing the chemical kinetics of mineral dissolution and secondary carbonate precipitation, thereby providing vital information on the efficacy of the suggested OAE applications in a natural setting under a range of environmental conditions (salinity, temperature, carbonate chemistry, inorganic nutrient concentrations, dissolved and particulate organic carbon concentrations etc.). Testing them in mesocosm enclosures has the additional benefit of minimizing public concern and regulatory requirements when compared to field trials.

Environmental impacts of OAE will be scale- and context-dependent in terms of the physical (e.g., timescales of mixing and CO_2 equilibration, point source vs. diluted release), chemical (e.g., amount/type of alkaline substance, impurities), and biological characteristics (e.g., seasonal succession and related ecosystem vulnerability). Biological impacts are determined by exposure time and dose, ranging from acute shock responses on transient and local scales at point sources to chronic effects associated with possible transitions of ecosystem structure and performance at the regional and long-term scale. Key research questions which can be addressed adequately through mesocosm experiments are the following:

- What is the safe operating space for OAE applications with respect to possible impacts on marine ecosystems functioning, biodiversity and ecosystem services?
- How could OAE be implemented to reduce the risk of inadvertent negative environmental effects and maximize co-benefits?
- Which biological indicators can serve as early warning signals or proxies for OAE environmental impacts?
- How do different OAE approaches perform in terms of efficiency (e.g., mineral dissolution, CO_2 uptake) and permanency (e.g., secondary precipitation)?
- Which application sites are most appropriate for which OAE approach?

2 Strengths and weaknesses of mesocosm experimentation

Mesocosm experiments offer a salient advantage over laboratory-based investigations, as they allow a realistic replication of natural communities. Multiple trophic levels can be confined under natural environmental conditions over a long period of time in a self-sustaining manner. Thereby, the same community can be sampled repeatedly over time. Furthermore, these experiments permit straightforward validation in the context of field research. Mesocosms, in essence, are closer to representing natural ecosystems characterized by carefully defined dimensions and monitored conditions and processes. To ensure realistic ecological boundary conditions, mesocosm experiments should be exposed to meteorological conditions resembling those of the target environment. Notably, the logistical flexibility of mesocosms affords researchers the opportunity to conduct investigations beyond the geographical confines of the environment under investigation. Consequently, mesocosms provide an invaluable avenue for the controlled study of specific environments and the impact of controlled manipulations therein. Given the diverse range of natural processes encountered in mesocosm experiments, external influences may be challenging to control, necessitating a robust monitoring strategy to achieve statistical power by either treatment replication or treatment gradients. Moreover, mesocosm experiments provide extensive multidisciplinary datasets that allow for a high degree of scientific integration and interdisciplinary collaboration. These datasets are valuable for parameterization and assessment of marine ecosystems and biogeochemical models.

While mesocosm experiments can be considered the preferred tool for the assessment of environmental impacts of

OAE applications, they have several weaknesses that need to be considered when interpreting the data and extrapolating the results to the real world. These weaknesses include unnatural mixing and turbulence (in pelagic mesocosm), unnatural flow of bottom water across the sediment (in benthic mesocosms), wall effects and the growth of periphyton and other organisms on the mesocosm walls, spatial heterogeneity in the enclosed sediments, and the related difficulties in obtaining representative samples. The larger and more expensive the enclosures become, the more difficult it becomes to have a sufficient number of replicates in a replicated design or treatments in a gradient design. The fact that even the largest mesocosms enclose truncated communities (i.e., exclude higher trophic levels and highly migratory organisms) makes it difficult to adequately represent the responses of organisms with longer life cycles and the associated impacts on the food web. Another drawback of mesocosm experiments is their limited duration, due to the gradual diversion from their natural counterparts, e.g., due to community shifts, nutrient depletion and the consequent progressive loss of biological realism. The increasing variability between mesocosms in this process makes it increasingly difficult to identify treatment effects with statistical significance.

3 Experimental design

The primary purpose of a mesocosm experiment is to obtain “near-natural” conditions, that is to say, keeping the abiotic and biotic factors as close to the environment as possible in order to maximize the realism of the tested conditions. In general, timescale is related to mesocosm volume: the shorter the time needed for a controlled experiment, the smaller the enclosure size. Careful consideration should be given to the experimental design to adequately address the specific research questions and account for ecosystem- and site-specific characteristics as well as seasonal variability. The choice of the experimental configuration includes the three key dimensions of time, space and biological complexity, along with the required level of replication. Preference should be given to mimic the natural seasonal succession rather than provoking out-of-season events, e.g., triggering phytoplankton blooms through nutrient addition.

Considering the often limited number of experimental units, a critical consideration concerns the level of replication (Kreyling et al., 2018). The choice is between two basic approaches: (1) replicated ($n \geq 3$) treatments, with limited treatment levels (e.g., Riebesell et al., 2007) and (2) a gradient approach with a larger number of non-replicated treatment levels (e.g., Taucher et al., 2017). The statistical power of the two options, using ANOVA statistics for the replicated design and regression statistics for the gradient design, is similar for the small number of experimental units typically available in mesocosm studies (Havenhand et al., 2010). If large within-treatment variation is expected, e.g., due to strong environmental variability or spatial heterogeneity, the replicated approach is recommended. In fact, strong within-treatment variability can easily mask subtle treatment effects. An important advantage of the gradient approach, on the other hand, is that it enables the identification of non-linearities, thresholds and tipping points in biological responses to OAE applications, relevant information for model parameterizations in terms of community functional responses. Knowledge about thresholds and possible tipping points is crucial also in the context of regulatory considerations for OAE implementation.

3.1 Pelagic mesocosms

When aiming to investigate OAE applications in the free water column, pelagic mesocosms are the research tool of choice. Among the various proposed strategies, ocean liming in the wake of ships would consist of sparging high-alkalinity fluids or mineral particles within the surface layer in offshore settings. In this scenario, any chemical perturbation is expected to affect in the first instance the pelagic domain and the planktic component of the marine ecosystem. Also OAE applications at fixed locations with a discharge of alkalinity-enriched water into coastal waters, e.g., desalination plants or sewage treatment plants, are best simulated in pelagic mesocosms. A suitable simulation of OAE approaches in which the alkalizing mineral is released in particulate form should ideally have the dissolution rate of the particles known in advance. If the rate is fast enough to ensure complete dissolution in the water column, pelagic mesocosms are well suited. In cases where the dissolution rate is slow compared to the particle sinking rate and particles sink to the seabed before dissolving, the experimental design may require a benthic component.

A missing component in all closed-system mesocosm experiments is the dilution through mixing with non-perturbed waters. Switching to an open system, where the enclosed water is partially replaced by non-alkalized water, places much greater demands on monitoring and complicates the interpretation of the observed responses, to the extent that it may be impossible to establish a reliable dose–response relationship. This experimental artifact is exacerbated when repeated additions of alkalinity are applied. Incorporating naturally occurring dilution in the experimental design can be done by applying the OAE treatment to only part of the enclosed water column and allowing for gradual mixing with the untreated water. The time until mixing can be controlled by stratifying the water column through a salinity gradient (adding fresh water into the upper layer or brine into the bottom layer, whereby the salinity change should be at a low enough level not to cause a biological response, e.g., a few tens of a salinity unit) or via a temperature stratification. Break-off of the stratification can be gradual or abrupt through active mixing. Parallel sampling of the OAE treated and untreated wa-

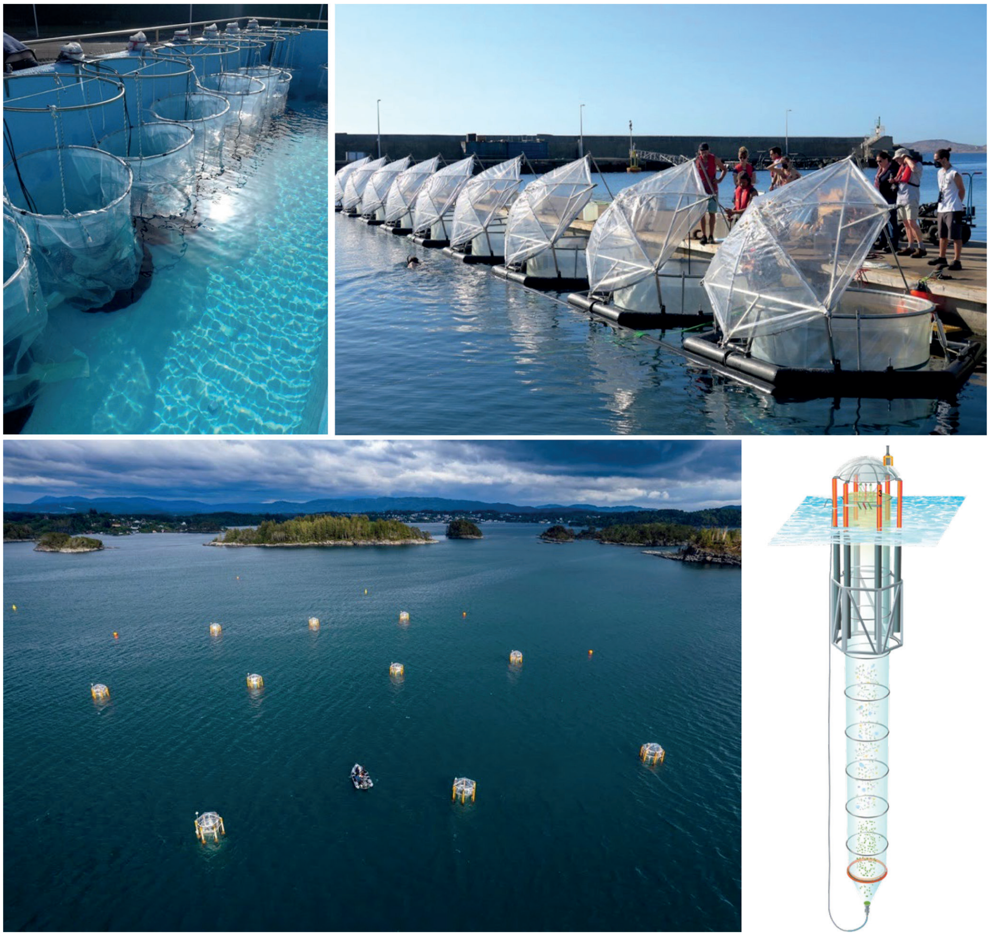

Figure 1. Pelagic mesocosm facilities currently used in OAE research. Top left: land-based mesocosms (1 m^3) at the University of Vigo, Spain. Top right: in situ on-shore mesocosms (10 m^3) operated by GEOMAR, here employed on Gran Canaria, Spain. Bottom left: Kiel Off-Shore Mesocosms for Ocean Simulations (KOSMOS), here employed in the Raunefjord, Norway. Bottom right: sketch of a KOSMOS mesocosm unit (55 m^3). Image sources: (top left) Daniela Basso, University of Milano-Bicocca; (top right) Ulf Riebesell, GEOMAR; (bottom left) Uli Kunz; (bottom right) Rita Erven, GEOMAR.

ter bodies can provide insights about the compensating effect of dilution.

There is a wide range of enclosure volumes and structures used in pelagic mesocosm experimentation (Fig. 1). Among the various available solutions, the most obvious difference is the placement of the mesocosm: (1) stable, permanent structures on land or (2) floating bags in the water. All materials that come into contact with the enclosed water/sediment must be chemically inert; i.e., they must not leach or actively absorb any substances. Some technical details of the mesocosm design can markedly affect some abiotic factors, such as thermal characteristics, light conditions or mixing intensity of the enclosed water column. Most pelagic mesocosm enclosures are made of transparent material supported by a minimal rigid framework, with the intent to keep light conditions as in nature. Most materials, however, change the spectrum of the transmitted light; for example they are not transparent for UV light. As enclosure depth is often lower than the mixed-layer depth of the natural environment, natural light conditions are not well represented in mesocosms, with light intensities averaged over the mesocosm depth often higher than those averaged over the mixed-layer depth.

3.2 Benthic mesocosms

Benthic mesocosm experiments offer the unique chance to study OAE-mineral addition to the seafloor in a controlled setup. In comparison to experiments in laboratory settings, often small in scale with respect to mineral weathering, benthic mesocosms are more likely to mimic natural seafloor conditions and allow the coupling of biogeochemical processes at larger spatial and temporal scales. Key research questions on seabed alkalinization to be addressed in benthic mesocosm experiments include the following:

1. What are alkaline mineral dissolution rates under mesocosm conditions?

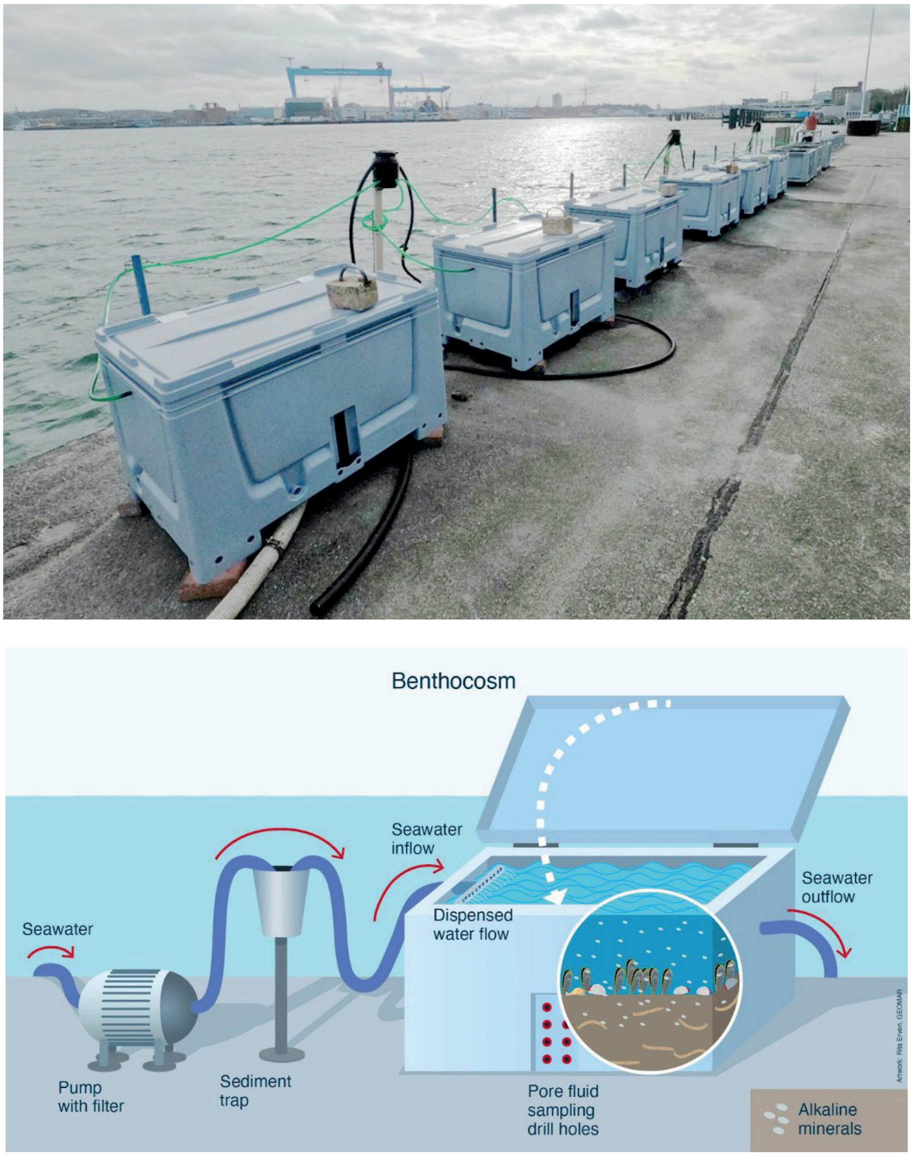

Figure 2. Top: benthic mesocosm units currently (2022–2023) installed at the Kieler Förde, Germany. Bottom: sketch of the experimental setup for the benthic mesocosms shown in top picture. Image sources: (top) Sonja Geilert; (bottom) Rita Erven, GEOMAR.

2. Do secondary minerals form that may compromise the net CO_2 sequestration efficiency of this method?

3. How are microbial communities and macrofauna affected by mineral dissolution?

4. Is there a release and accumulation of heavy metals related to addition of silicate-based minerals and how does their toxicity affect the community/ecosystem?

Continuous water flow system. In this setup, a continuous flow of ambient seawater, preferably bottom water, over the sediment (Fig. 2), likely best resembles natural seafloor conditions. It is recommended to remove larger debris that could obstruct the water supply using a sediment trap (Fig. 2) whilst allowing small particulate matter to enter the mesocosms. The supply of particulate matter is essential to sustain natural microbial metabolism in the sediments and to provide food for filter-feeding macrofauna that colonize the sediment surface within a short period of weeks to months (Fig. 2). A relatively high flow rate is required (between 5000 to 10 000 $\mathrm{L\,d^{-1}}$) to keep the seawater well oxygenated and guarantee the survival of fauna and for maintaining the natural microbial communities as closely as possible to in situ conditions. With this setup, the bottom water should be monitored to trace seasonal changes in physical and chemical properties of the incoming seawater.

Water circulation approach. The benthic mesocosm setup with a seawater circulation approach consists of two tanks

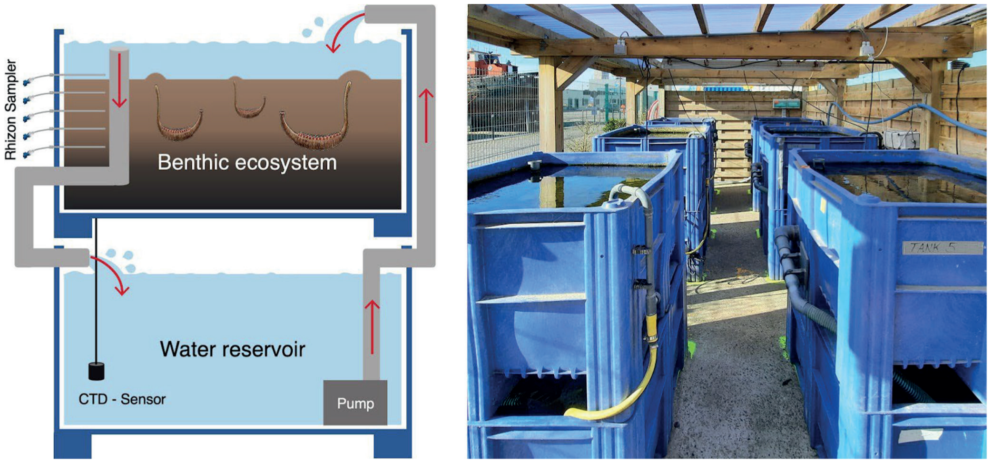

Figure 3. In the benthic mesocosms at the University of Antwerp the dissolution kinetics of silicate minerals and the impacts on the benthic fauna in coastal environments have been monitored since 2019. The system comprises 20 units with two stacked tanks: the upper tank houses the benthic ecosystem, and the lower tank functions as a water reservoir. Natural sediment of 40 sediment heights with a mean grain size of 123 µm (3.0 ϕ) was collected from an intertidal sand flat in the Oosterschelde (the Netherlands) and mixed with olivine sand of similar grain size. Water from the Eastern Scheldt Estuary (salinity 32–35) is used to conduct flux sessions of 5 weeks (weekly sampling). At the end of each session, the total volume of water in each unit ($\sim$ 500 L) is renewed (drawing: Astrid Hylén (UAnt); photo: Matthias Kreuzburg, https://www.coastal-carbon.eu/, last access: 7 November 2023, Geobiology, University of Antwerp).

stacked on top of each other, with the upper tank housing the benthic ecosystem with sediments and organisms and the lower tank functioning as a seawater reservoir from which water is pumped into the upper tank (Fig. 3). Thus, a constant flow of water is generated through the water in- and outflow, and the height of the water column in the upper tank can be controlled by the vertical positioning of the outflow. The tanks for the benthic mesocosms have a volume of approximately 1 m^2 and are situated outdoors and exposed to natural temperature fluctuations.

Based on the water circulation approach, the closed system allows for the detection and accumulation of weathering products and to focus on a specific process or reaction, such as the dissolution kinetics of silicate minerals in the case of the University of Antwerp study (Fig. 3). After a defined time span (flux session) the total amount of water is replaced and accumulation of weathering products starts again from initial values. In terms of this experiment design, ≥ 3 replicates of benthic mesocosms are crucial to ensure that results are statistically significant and can be generalized to the broader ecosystem being studied (e.g., Wadden Sea).

The total experiment duration as well as the sampling strategy is defined by the research questions, and longer experiments may be necessary to capture seasonal or long-term trends in the system. The use of natural sediment and the inclusion of a dominant bioturbating organism (e.g., *Arenicola marina*) in benthic mesocosm experiments is a crucial step toward making the experimental setup more representative of real-world conditions. However, it is important to emphasize that the choice of sediment type and benthic organisms should be aligned with the specific research objectives and questions being addressed.

In OAE studies involving benthic mesocosms, various types of sediments can be considered, ranging from fine-grained sediments to rocky substrates. The selection of sediment type should be guided by factors such as the local environmental conditions, the availability of sediment types that reflect the targeted ecosystem and the specific geochemical interactions being investigated. For studies related to carbonate dissolution and alkalinity enhancement as given above, fine-grained or sandy sediments are most suitable, given their potential to facilitate mineral dissolution and subsequent alkalinity release.

Similarly, the choice of benthic organisms should be tailored to the research objectives. While many benthic organisms can be tested in mesocosms, it is important to consider the life history, behavior and ecological role of the selected species (Bach et al., 2019; Flipkens et al., 2021). For instance, if the experiment spans a year and aims to study the recruitment and life cycle of benthic organisms that have a pelagic phase, careful planning is required. Monitoring larval settlement, growth and interactions with the sediment during their benthic phase becomes integral to such investigations.

As an illustrative example, consider an OAE study targeting the enhancement of carbonate precipitation through the addition of alkalinity. In a coastal setting, sandy sediments rich in carbonate minerals might be chosen, given their potential for mineral dissolution and subsequent bicarbonate formation. Benthic organisms like filter-feeding mollusks and burrowing polychaetes could be tested to assess their responses to altered alkalinity levels.

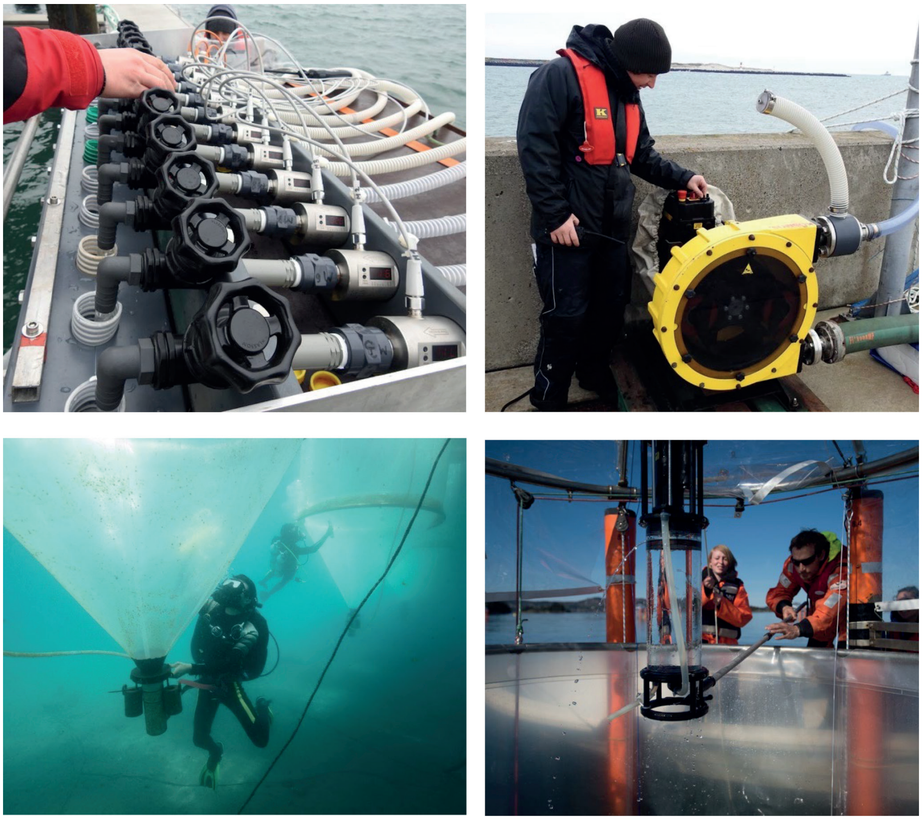

Figure 4. Upper left: distributor control system enabling parallel filling of all mesocosms. Upper right: peristaltic pump ensuring smooth flow of source water during filling of the mesocosms, keeping damage to fragile organisms at a minimum. Lower left: sediment traps forming the bottom of in situ mesocosm enclosures. Lower right: programmable water sampler, enabling depth-integrated water samples over the entire mesocosm depth (or parts thereof) (photo sources: (upper left and upper right) Ulf Riebesell; (lower left) Michael Sswat; (lower right) Solvin Zankl).

Finally, the water circulation approach should be carefully designed to ensure consistency in water flow rates and initial seawater chemistry. Sedimentation in the water reservoir tank has to be prevented to avoid secondary sediment surfaces, and a continuous monitoring system (salinity, temperature) is recommended to estimate evaporation rates. In addition, regular sampling of environmental conditions (humidity, $p\mathrm{CO}_2$) as well as carbonate system parameters and nutrients can ensure that the experiment proceeds as planned and that the results are reliable.

4 Mesocosm operation: filling, sampling, wall cleaning

Filling of the mesocosms is a delicate process that, if not done with care, can jeopardize the entire experiment. A key aspect is to ensure identical starting conditions, both for the abiotic and biotic conditions in all mesocosms. Between-mesocosm differences in baseline conditions can cause divergence of the enclosed communities and severely hamper the detection of treatment effects. As the filling often represents a major perturbation itself, some time of equilibration may be needed before applying the treatment manipulation and starting the actual experiment. The time for equilibration may differ for pelagic and benthic habitats as well between different ecosystems and seasons. Adequate monitoring during this pre-manipulation phase can determine when a new steady state is reached and confirm whether all mesocosms have similar starting conditions. Key parameters for which equal starting conditions among mesocosms need to be ensured include temperature, salinity, inorganic nutrient concentrations, the carbonate chemistry (pH, $p\mathrm{CO}_2$, dissolved inorganic carbon, DIC, and total alkalinity, TA) dissolved and particulate organic matter concentrations, community composition and diversity, and standing stocks of the dominant taxonomic groups across trophic levels.

Another critical aspect of mesocosm operation is taking representative samples. The enclosed water bodies and sediments typically show spatial heterogeneity (vertical gradients in the water column and sediments, patchiness in the distribution of larger organisms). The spatial variability of the target variables of the enclosed system should be determined prior to deciding on the best sampling strategy. Sampling bias related to vertical gradients, e.g., water column nutrient concentration and phytoplankton biomass, can be overcome by taking depth-integrated water samples (Fig. 4). Some species may even perform diurnal vertical migration, which also should be accounted for in the sampling strategy.

Mesocosm enclosures are always associated with additional surfaces, the mesocosm walls, that are not present in the natural environment. The smaller the mesocosms, the larger the additional surface area relative to the enclosed volume. Free surfaces are generally subject to rapid biofilm formation, followed by colonization of larger organisms. The associated microbial community can significantly influence water column processes, which is of particular concern in pelagic mesocosms. To minimize such wall effects, cleaning of the mesocosm walls can be useful. Specific to OAE mesocosm experimentation is that under conditions where the water column is highly oversaturated with respect to calcium carbonate, mesocosm walls can provide free surfaces for secondary precipitation of carbonates. Under these circumstances, wall cleaning can scrape off these carbonates, creating additional precipitation nuclei in the water column. If wall cleaning is continued under these circumstances, possible effects caused by this, e.g., enhancement of secondary precipitation in the water column and increased ballasting of particulate matter, should be seen as artifacts and interpreted as such. If wall cleaning is discontinued and the biofilm on the walls grows to a significant biomass compared to the suspended biomass, this may limit the duration of the experiment. The decision for or against wall cleaning must be made on a case-by-case basis and depends, among other things, on the severity of wall growth, the duration of the experiment and the specific research questions to be investigated.

4.1 Pelagic mesocosms

Different techniques have been employed for filling pelagic mesocosms, including (1) direct pumping from the sea in cases where mesocosms are placed in situ or close to natural waters, (2) collection in tanks when source waters need to be transported over some distance and subsequent pumping from the tanks into the mesocosm, and (3) lowering a flexible bag like a curtain over an undisturbed water column. In all cases care should be taken to fill the mesocosms with identical source waters. Considering that water masses may change over the filling procedure, this can best be achieved by filling the mesocosms in parallel through a distributor system (Fig. 4). Likewise, if several tanks are needed to obtain the required source water volume, the water of each tank should be distributed evenly into all mesocosm units. The source water should be representative of the targeted ecosystem. This concerns the depth at which the source water is collected and, when diurnally vertically migrating organisms are present, the time of day. When pumping is applied some damage to fragile organisms, e.g., gelatinous zooplankton, is unavoidable. It is therefore recommended to use pumps that ensure a smooth flow of pumped water, e.g., peristaltic pumps (Fig. 4). To prevent large and rare organisms from entering and being unevenly distributed in the mesocosms, some screening can be applied at the intake of the pumping hose.

As mentioned above a typical artifact of mesocosm enclosures is the reduced level or absence of turbulence. In mesocosms with solid wall structures it may be useful to apply some form of mixing of the water column, considering that turbulence (including its absence) is known to strongly affect the plankton community composition and succession. In floating enclosures with flexible walls some turbulence is induced by surface wave action, below surface water movement and variability in water currents, but the vorticity of the enclosed water is still always much reduced compared to that of the natural environment. Somewhat related to the mixing regime is another potential artifact in mesocosms where settling particulate matter is continuously resuspended from the bottom. Resuspension of degrading organic matter, which under natural conditions would sink out of the upper mixed layer, exaggerates the heterotrophic processes in the system. Collecting and removing the sedimented matter in cone-shaped sediment traps which form the bottom of the mesocosms can avoid this problem (Fig. 4).

4.2 Benthic mesocosms

A particular challenge in benthic mesocosm experiments concerns the filling with sediment from the seafloor. Depending on the size of the tanks and the sediment height, it may be necessary to transfer several hundreds of kilograms of sediment from the seafloor to the tanks. Near-intact sediments (undisturbed vertical stratification) may be collected relatively easily in sub-tidal areas. At sea, undisturbed sediments may be retrieved using a box corer or similar device, although this may be a tedious exercise involving multiple deployments of the coring equipment. Large amounts of sediment can be gathered relatively easily and quickly using a sediment grab, but disturbance of the sediment matrix is inevitable, and longer equilibration times for the sediment geochemistry to stabilize will be required before experiments can be started. In any case, benthic communities within mesocosms may be altered from those in natural ecosystems, and a sound understanding of the equilibration period is crucial to allow for changes in benthic communities and the establishment of a new steady state within the benthic mesocosm. This equilibration period should be determined based on the specific conditions of the mesocosm experiment, including the number of replicates, environmental parameters and the selected organisms. Adequate monitoring and sampling during the equilibration period are essential to ensure that the experimental conditions have stabilized and the ecosystem has reached a new steady state, which in turn increases material and labor requirements. Robust control units are crucial in benthic mesocosm experiments and should ideally consist of the same number of replicates as the treatment group to ensure that any observed changes are due to the experimental treatments rather than natural variability. Sampling and monitoring should be in the same manner as the treatment group.

5 Alkalinity manipulation and monitoring

Different minerals, waste materials and electrochemical products have been suggested as feedstock for ocean alkalinity enhancement (for a comprehensive introduction to potential source materials, see Eisaman et al., 2023, this Guide). Most source materials do not come as pure alkalinity but rather contain other substances, such as silicate, calcium, magnesium and various trace metals (e.g., iron, nickel, cobalt, chromium). OAE can be achieved by addition in dissolved form, which requires dissolution of the feedstock before its release into the sea, or in particulate form, after grinding of the feedstock, with the grain size being one important factor determining the dissolution rate. OAE can further be conducted in a CO_2-equilibrated mode, which involves some form of active injection of CO_2 into the alkalinity-enriched source water prior to its release, or in a non-equilibrated mode, which relies on air–sea gas exchange to provide the additional CO_2 that the alkalinized seawater can absorb. In the case of the latter it is important to keep in mind that the timescales for CO_2 equilibration are on the order of months and can only occur as long as the alkalinized seawater is in contact with the atmosphere (see Schulz et al., 2023, this Guide, for further details).

Taken together, this results in a wide range of possible application scenarios, not all of which can be tested with the same scrutiny in mesocosm experiments due to the high financial and personnel costs involved. Hence, it is important to focus on those OAE application scenarios which are most likely to be implemented. As the field of OAE R&D is developing rapidly and dynamically, there will likely be changes in what is considered the most suitable OAE application approaches, in terms of cost, efficiency, environmental safety, friendliness in terms of monitoring, verification and reporting (MRV), technological readiness, and the regulatory requirements for their implementation. Mesocosm research in this field should maintain sufficient flexibility to respond to those changes and aim for testing “real-world” scenarios of OAE applications. On the other hand, because the results obtained from mesocosm studies will likely be context-specific (depending on, e.g., ecosystem type, time of year, latitudinal location, hydrographic setting) and depend on the mesocosm setup and operation itself, it takes multiple such studies for a given OAE approach to reach robust conclusions about its environmental safety. To facilitate inter-comparison between results, it would be favorable to use standardized mesocosms and follow common protocols for mesocosm experimentation.

From an experimental perspective, there is a trade-off between testing pure alkalinity enhancement and feedstocks which involve the release of other biologically active components. While the latter is more in line with real-world applications, it complicates the interpretation of the observed responses due to confounding factors and limits the extrapolation of the findings, considering that the stoichiometric composition differs between feedstocks. As the field is currently still at an early stage and considering that the number of mesocosm studies will likely be small due to their high costs, it seems beneficial to first establish a basic understanding of alkalinity effects in isolation, before turning to more feedstock-specific testing. This being said, we note that the above-mentioned confounding effects may actually be the intended research question or that the focus may be on a specific feedstock likely to be utilized widely. In general, we recommend designing mesocosm experiments with a more generic approach first and addressing feedstock-specific in smaller-scale laboratory-based experiments.

5.1 Pelagic mesocosms

Alkalinity manipulations in pelagic mesocosms are fairly straightforward when done in dissolved form. Dissolving the alkaline feedstock in freshwater or deionized water prevents secondary carbonate precipitation during preparation of the concentrated solution (we note that the use of freshwater for feedstock dissolution may not be practical for large-scale implementation of OAE). To avoid confounding effects of the freshwater addition on the mesocosm community, the volume should be kept to a minimum. Using source materials with a high solubility in water, such as $NaHCO_3$, Na_2CO_3, $Ca(OH)_2$ or NaOH, enables highly concentrated alkaline source water (Hartmann et al., 2023). To simulate CO_2-equilibrated alkalinization, $NaHCO_3$ and Na_2CO_3 can be combined in appropriate proportions (Subhas et al., 2022); for non-equilibrated alkalinization, carbonate-free source materials such as NaOH and $Ca(OH)_2$ can be used (Moras et al., 2022). To avoid prolonged pH peaks and secondary precipitation during the injection procedure, it needs to be assured that the concentrated solution is mixed in rapidly. One way to achieve a uniform alkalinity enhancement across the water column is to move a distribution device with multiple outlets up and down the mesocosms at a constant speed (Fig. 5). Flocculent precipitates that form directly at the injection site are usually not stable and disappear quickly when further diluted through mixing. Care should be taken to ensure that the added alkalinity is evenly distributed throughout the enclosed water column.

Alkalinity enhancement in particulate form is far less practical. If the particles sink faster than they dissolve, they accumulate on the mesocosm floor or sink directly into the trap in mesocosms with a sediment trap at the bottom. Accumulation and subsequent dissolution at the bottom might lead to highly concentrated alkalinity enrichment, enhancing the

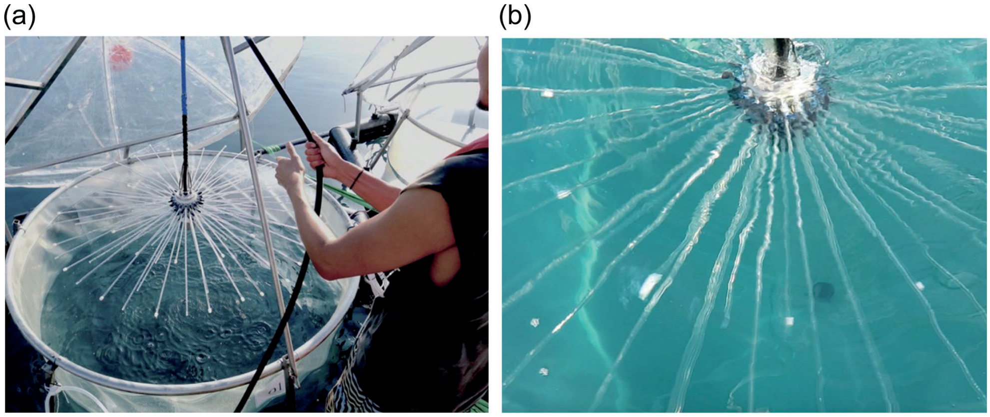

Figure 5. **(a)** Distribution device used for alkalinity addition; by moving it up and down in the water column during alkalinity injection at constant speed, a uniform alkalinity enhancement can be achieved. **(b)** Milky water at the outlet of the injection tubes indicates temporary precipitation, which, however, quickly disappears as the highly concentrated alkalinity solution dilutes. Photo sources: Ulf Riebesell.

risk of secondary precipitation and of strong negative impacts in bottom waters. Alkaline particles sinking into the sediment trap would be lost from the mesocosm enclosure during the next trap sampling. In both cases it would be considered an experimental artifact. It is therefore recommended to use minerals with high dissolution rates (e.g., NaOH, CaO, $Ca(OH)_{2,Mg(OH)2}$) and small grain sizes to ensure dissolution before the mineral particles reach the bottom of the mesocosms (see Eisaman et al., 2023, this Guide, for a detailed description of technical aspects of OAE).

Monitoring of seawater carbonate chemistry in the water column should adhere to the guidelines provided in Schulz et al. (2023, this Guide). High levels of non-equilibrated alkalinization can lead to secondary precipitation, triggering a process termed “runaway precipitation” (Moras et al., 2022; Hartmann et al., 2023), whereby carbonate formation can consume more alkalinity than initially added. It seems that the initiation of this process can occur both in the water column and on the mesocosm walls. As the carbonate crystals grow in size, their sinking velocity increases. When incorporated in organic matter aggregates they serve as ballast, thereby increasing the vertical flux of organic matter. In addition, carbonate crystals could affect mobility and feeding of plankton organisms, with possible adverse effects on food web interactions and trophic transfer. Secondary precipitation also increases seawater turbidity, affecting light attenuation and possibly primary production. Collecting this sinking particulate matter in sediment traps at the bottom of the mesocosms enables the quantification and identification of the precipitates and provides information about the chemical reactions leading to their formation. In mesocosms without integrated sediment traps, simple traps can easily be set up on the bottom and sampled through a tube that reaches the surface.

5.2 Benthic mesocosms

Alkalinity enhancement in the benthic mesocosm approach is achieved by mineral addition, which dissolves in the surface sediment over time. In general, the addition of sedimentary OAE source materials (e.g., siliciclastic minerals, carbonates; Eisaman et al., 2023, this Guide) modifies the grain size distribution of the sediment and thus affects the porosity, permeability and water flow through the sediment. The changing sediment structure can impact living conditions for organisms, as well as the distribution and abundance of organisms living in the sediment and their behavior and ecology. With respect to mineral addition, the grain size selection is important, as a trade-off between grain size and production costs is required (e.g., Hartmann et al., 2013). Previous studies have investigated the relationship between CO_2 sequestration efficiency and grain sizes, and there is a general assumption that small grain sizes reveal higher dissolution rates and CO_2 sequestration rates due to larger reactive surface areas, whereas more grinding energy is required generating a higher CO_2 footprint and lower CO_2 sequestration efficiencies (Köhler et al., 2010; Renforth and Henderson, 2017; Foteinis et al., 2023). Clearly, the CO_2 emissions during production and transport must be significantly lower than the potential CO_2 sequestration of benthic mineral dissolution (see Eisaman et al., 2023, this Guide). The selection of appropriate grain sizes for the addition of alkaline minerals is a critical consideration for experimental studies, particularly in the context of the target environment’s geological setting. From an environmental perspective, it is recommended to choose comparable grain sizes that are stable under in situ hydrodynamic conditions. For highly dynamic ecosystems such as the Wadden Sea, estuaries and wave-dominated coastal areas, a range of grain sizes from fine to coarse sand (0.075 to 2 mm) may be appropriate for experimental approaches. However, in low-dynamic systems such as lagoons, enclosed

Figure 6. Left: pore fluid sampling using rhizons. Right: benthic incubation chamber to assess alkalinity enhancement with respect to mineral dissolution in benthic mesocosm experiments. Photo sources: (left) Sonja Geilert; (right) Michael Fuhr, GEOMAR.

bays or shelf regions, grain sizes from silt to very fine sand (< 0.075 mm) can be considered for investigation. This approach would also help to ensure that the sedimentary structure and settings for organisms in the mesocosms are representative of the natural conditions of the target environment.

It may be practical to interrupt the water circulation system during mineral deployment in order to allow sedimentation of the suspended matter. To achieve a uniform alkalinity enhancement in the benthic mesocosms, minerals should be evenly distributed. To induce a measurable effect on alkalinity changes in the envisioned experimental time, grain sizes smaller than 1 mm are desirable (Strefler et al., 2018). The addition to the marine environment could best be achieved through a mixture of natural seawater, marine sediments and OAE source materials. This may ensure a more uniform distribution and reduce the purity of industrially produced OAE source materials, which are poor in nutrients and microbial organisms. Thus, this approach is also recommended for the addition of silicates to benthic mesocosms. By using a mixture, the potential effects of silicate addition can be more accurately evaluated because the experimental conditions are more similar to those in the natural environment.

For calcium carbonate, it may be reasonable to use the annual flux of particulate organic matter to the seafloor as an upper estimate of the required mineral to be added. The underlying assumption here is that the added mineral can completely neutralize the natural CO_2 produced from organic matter degradation. However, this assumes that mineral dissolution efficiency is close to 100 %, which may not be the case if it is mixed below the undersaturated layers. Adding minerals in large excess risks clogging the surface layer and creating a physical barrier against effective benthic–pelagic coupling of solute fluxes. Finding the optimal mineral dosage to achieve a balance between dissolution efficiency and dissolution rate would likely be specific to the local environmental characteristics and require testing at each potential mineral addition site. For silicate minerals (e.g., olivine), the upper limit of mineral addition per square meter will also depend on the trace metal concentrations (Flipkens et al., 2021). Based on the variation in Ni content of marine sediments (prior to the addition of olivine), this implies that the allowable range for the addition of olivine is between 0.059 and 1.4 kg m^2 of seafloor without posing a risk to benthic biota. This threshold is based on Environmental Quality Standards (EQS), which are derived from metal toxicity data using methods such as species sensitivity distributions (SSDs). They provide threshold metal concentrations in seawater or sediment that are considered protective for the aquatic environment and are used by industries, governments and environmental agencies to guide regulations. So far, these guidelines have been only appropriate to specific regions and environments and may need to be re-evaluated for broader use in OAE applications.

Monitoring of mineral dissolution will be determined by the experimental design. A major drawback of a high throughflow is that rapid dilution and flushing of geochemical tracers emitted from the sediment compromises the analytical detection of dissolving alkaline minerals in the overlying water and the reliable assessment of the effectiveness of the method. In this case, alternative ways of mineral dissolution detection may be required. For instance, alkalinity enhancement may be detectable in pore fluids, which can be extracted using filters (e.g., rhizons) inserted horizontally through holes pre-drilled vertically in the tank (Fig. 6). However, the vertical sampling resolution may be too coarse to detect mineral dissolution close to the sediment surface. Microelectrodes for O_2, pH and H_2S are arguably a better alternative to detect changes in surface geochemistry in the uppermost centimeters after mineral addition. An advantage of the high dilution factors is the potential suppression of secondary mineral formation such as phyllosilicates and/or carbonates, which could reduce the net CO_2 sequestration efficiency of

OAE (Fuhr et al., 2022; Moras et al., 2022; Hartmann et al., 2023). Secondary mineral formation is a common process in marine seafloor sediments, potentially impacting global carbon and element cycles on a global scale, and the controlling factors have not been unambiguously identified to date (e.g., Rahman et al., 2017; Torres et al., 2020; Geilert et al., 2023).

The deployment of benthic incubation chambers within the mesocosms themselves is a non-invasive method for detecting alkalinity release following mineral addition (Fig. 6). These benthic chambers enclose a certain area of the surface sediment and allow the accumulation of alkalinity and other components of interest over time, from which benthic fluxes can be determined. Mineral dissolution rates can be estimated by comparison with control mesocosms where no minerals were artificially added. Fluid sampling can be achieved by hand via suction using connected tubing and syringes. Care is needed to prevent hypoxia or anoxia inside the chambers due to respiration by benthic biota, which may be observable by a blackening of the sediment surface due to precipitation of iron sulfide minerals. Low oxygen levels will result in an interruption to the normal respiration rates of animals causing them to resurface. This may alter natural sediment mixing rates as well as mineral saturation states via changes in biogeochemical turnover rates and pathways in the sediment. Together, these undesired artifacts may be reflected in unrealistic fluxes of alkalinity and other solutes from the sediment. Completely interrupting the water flow to the whole benthic mesocosm in order to detect changes in bottom water alkalinity will only serve to magnify these side effects.

Recommendations

General recommendations include the following:

- Use inert materials for mesocosm hardware (e.g., plastics, stainless steel).
- Select the mesocosm size and experimental duration according to the enclosed community and processes studied.
- Choose the experimental design to maximize the statistical power and report it.
- Maximize similarity in starting conditions between mesocosms during enclosure filling.
- Monitor starting conditions before applying experimental treatment.
- Allow for the natural (e.g., seasonal) succession and avoid out-of-season events.
- Avoid confounding factors and perturbations other than the intended treatments.
- Adapt the sampling frequency to the dynamics of the processes studied.
- Determine spatial heterogeneity and take account of it in the sampling strategy.
- Apply depth-integrated sampling in case of vertical gradients (pelagic mesocosms).
- Minimize wall growth, e.g., by regularly cleaning the walls.

OAE-specific recommendations include the following:

- Test real-world OAE scenarios, focusing on those most likely to be implemented.
- Keep some flexibility to respond to changes in the OAE R&D field.
- Monitor carbonate chemistry with at least two carbonate system parameters and watch out for secondary precipitation.
- Maximize transferability of results by testing generic OAE approaches.
- Take note of the context specificity of the observed ecosystem responses.
- Provide detailed information of the feedstock composition utilized for experimental manipulations.
- Closely monitor signs of potential barriers to OAE implementation (e.g., long-term restructuring of community composition and functioning, decline in ecosystem productivity, proliferation of harmful species, disruption of trophic transfer, changes in elemental cycling).

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Field experiments in ocean alkalinity enhancement research

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Abstract. This chapter focuses on considerations for conducting open-system field experiments in the context of ocean alkalinity enhancement (OAE) research. By conducting experiments in real-world marine and coastal systems, researchers can gain valuable insights into ecological dynamics; biogeochemical cycles; and the safety, efficacy, and scalability of OAE techniques under natural conditions. However, logistical constraints and complex natural dynamics pose challenges. To date, only a limited number of OAE field studies have been conducted, and guidelines for such experiments are still evolving. Due to the fast pace of carbon dioxide removal (CDR) research and development, we advocate for openly sharing data, knowledge, and lessons learned as quickly and efficiently as possible within the broader OAE community and beyond. Considering the potential ecological and societal consequences of field experiments, active engagement with the public and other stakeholders is desirable, while collaboration, data sharing, and transdisciplinary scientific teams can maximize the return on investment. The outcomes of early field experiments are likely to shape the future of OAE research, implementation, and public acceptance, emphasizing the need for transparent and open scientific practices.

1 Introduction

This chapter addresses considerations for conducting open-system field experiments related to ocean alkalinity enhancement (OAE). We define “field experiment” or “field studies” broadly as the addition or manipulation of alkalinity in a natural system that is relevant to OAE, independent of the spatial and temporal scale. We intentionally exclude spatial and temporal scales from our definition to encompass the wide spectrum of OAE methods and approaches. In fact, field experiments are likely to span spatial scales of squared meters (m^2) to hundreds of squared kilometers (km^2) and last from days to years. Field experiments and studies differ from both “field trials” and “field deployments” in their motivation, as both trials and deployments denote the practical application and usage of a specific product, device, or technology. The scientific focus during field trials is likely to be on the efficacy of carbon dioxide removal (CDR) and fine-tuning operational deployment, while field experiments will encompass a broader range of scientific goals and objectives. The nature, logistics, and objectives of field experiments are likely to make them smaller in scale than operational deployments. This will be advantageous, as field experiments that emulate planned OAE trials and deployments will help create the scientific framework needed to scale operational OAE safely and responsibly.

The benefits of conducting experiments in natural systems include observing complex ecological dynamics and impacts at the ecosystem level, understanding the role of biogeochemical cycles and physical processes that cannot be replicated in other settings, and assessing CDR under real-world

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scenarios. The complexity and breadth of some field experiments will necessitate science that transcends disciplinary boundaries, making collaboration a priority. Success in the field faces many challenges due to the inherent complexity of natural systems along with limiting logistical constraints (e.g., permitting, access, social license, infrastructure, life cycle emissions). Despite these challenges, the first OAE field experiments are already underway, many of which are small-scale representations of scalable OAE approaches. There will be much to learn from these early studies, and any knowledge or insights gained should be shared as efficiently and openly as possible within the wider OAE community and beyond.

While some OAE field experiments have been completed or are already in progress, many more are on the horizon. We recommend that three overarching questions be taken into consideration, especially when in the planning stages:

- *What are the main goals of the experiment?*
  Establishing the objectives of a field experiment early in the planning stage will help guide all aspects of the scientific research plan, including site selection, measurement techniques and approaches, data analysis, and measured outcomes. Potential overarching goals of OAE field experiments include demonstrating functionality, efficacy, process, and/or scalability; determining ecological and environmental impacts; developing measurement, reporting, and verification (MRV) protocols; and assessing community engagement. Life cycle assessments (LCAs) may be a critical learning objective for some projects (e.g., Foteinis et al., 2023), especially those that are examining OAE at the scale of operational deployments. This list of overarching goals is not comprehensive, and goals are not necessarily mutually exclusive. For example, larger projects may aim to assess multiple components of an OAE approach, while smaller projects might be highly focused.

- *What is the type of alkalinity perturbation?*
  The type of alkalinity that is added (e.g., aqueous vs. solid, carbonates, hydroxides, oxides, or naturally occurring (ultra)mafic rocks) will ultimately determine many aspects of the scientific research plan. For example, projects adding ground alkaline minerals (e.g., olivine) to the ocean may have different goals and timelines than projects that add aqueous alkalinity (e.g., liquid NaOH) (see Eisaman et al., 2023, this Guide). Priorities for projects adding ground material might include tracking the dissolution of the alkaline material and monitoring the fate of the dissolved alkalinity and its dissolution coproducts (e.g., trace metals), while projects adding aqueous alkalinity will likely be more concerned with the latter. Other important experimental considerations that will be driven by the type of alkalinity perturbation include the concentration of added alkalinity, duration of additions, dilution and advection at the field site, residence time, air–sea equilibration, co-deployed tracers, sampling scheme, and environmental side effects. These and other research considerations are discussed in more detail below.

- *What are the permitting constraints and wider social implications?*
  Addressing the appropriate regulatory requirements is essential before any field experiment can move forward. Permitting requirements will be influenced by the study location, type of alkalinity perturbation, spatial scale, and duration. The use of existing infrastructure (e.g., wastewater discharge sites) and environmental projects (e.g., beach renourishment) may offer ways to facilitate alkalinity perturbations under existing regulatory frameworks. Community engagement and outreach are other areas that will be important to address, especially when the alkalinity perturbation is large and uncontained. Ideally, local communities should be engaged at the earliest possible stage since social license to operate is critical for the success of CDR projects (Nawaz et al., 2023). For a more detailed discussion of legal and social issues, see Steenkamp and Webb (2023, this Guide) and Satterfield et al. (2023, this Guide).

With these overarching questions in mind, we discuss considerations for OAE field experiments in more detail below.

2 Research methods

2.1 Types of alkalinity addition

Field experiments of OAE present many challenges. One of the biggest obstacles to success is tracking alkalinity added to an open system. Methods for adding alkalinity can be divided into two general approaches: (1) in situ or coastal enhanced weathering from the addition of ground alkaline minerals and rocks with the expectation they will dissolve directly in seawater and (2) aqueous alkalinity additions or the addition of "pre-dissolved" alkalinity to seawater that can be generated in numerous ways including through dissolution reactors and electrochemical techniques (Eisaman et al., 2023, this Guide). Tracking the added alkalinity, and subsequent CDR, under each approach comes with its own unique set of challenges and considerations.

Adding ground minerals and rocks to an open system presents two distinct scientific challenges. First, for alkalinity to be considered additional, it needs to be attributed to the dissolution of the solid material. This can be accomplished through a range of techniques including measuring the loss of mass of the added material or using geochemical tracers in the receiving waters. Determining dissolution kinetics in situ will be particularly important, and they are likely to vary between different deployment environments and strategies (e.g., coastal vs. open ocean). For example, the chemistry (e.g., salinity, pH, temperature) of the waters where the mineral is added could vary significantly depending on the environment (e.g., beach face, estuary, continental shelf). Chemical (e.g., seawater conditions, such as salinity, $p\text{CO}_2$, and silica concentrations) and physical (e.g., grain size and surface area of the added material) conditions will be critical in determining dissolution rates (Rimstidt et al., 2012; Montserrat et al., 2017; Fuhr et al., 2022). Physical abrasion through wave action and currents is also likely to be an important control on dissolution (Flipkens et al., 2023). Field experiments will help translate dissolution kinetics from laboratory and mesocosm experiments to natural systems, which is not often straightforward due to complicated biogeochemical processes that are hard to replicate ex situ (Morse et al., 2007).

The second major challenge is common to both solid and aqueous approaches and involves tracking the added alkalinity, which becomes a particularly difficult problem in open-system field experiments where water is freely exchanged. Depending on the objectives of the field deployment, this is likely to be a main scientific concern. However, it is important to note that tracking the added alkalinity does not necessarily equate to observing CDR (i.e., an increase in seawater CO_2 stored as bicarbonate or carbonate). Observing an increase in atmospheric CO_2 stored as seawater dissolved inorganic carbon comes with its own set of challenges that are discussed in depth by Ho et al. (2023, this Guide).

Whether or not the alkalinity is derived from in situ mineral dissolution or direct aqueous additions, for OAE to be successful, atmospheric CO_2 needs to be taken up by seawater, or CO_2 effluxes from seawater to the atmosphere need to be reduced. Therefore, understanding the physical mixing and air–sea gas exchange dynamics of the deployment site will be a factor of interest for many field studies. Incorporating physical mixing models with biogeochemical processes will likely be the end goal of many field experiments focused on MRV (Ho et al., 2023, this Guide; Fennel et al., 2023, this Guide). Choosing sites with minimal mixing of different water masses or with well-defined diffusivities could facilitate tracing released alkalinity and subsequent air–sea CO_2 fluxes. While minimal mixing of different ocean water masses may be desired, higher wind speeds and wave action will increase the rate of air–sea gas exchange and may make CDR easier to measure. Background seawater chemistry will also be important in controlling air–sea gas exchange. For example, sites with naturally lower buffering capacities will see greater changes in CO_2 per unit of added alkalinity (Egleston et al., 2010; Hauck et al., 2016). The release of conservative tracers will likely be useful for field experiments that aim to track the added alkalinity and is discussed in more detail below (Sect. 2.5).

Other experimental considerations related to the type of alkalinity perturbation include the duration and location of alkalinity addition, which will be important for environmental and regulatory considerations. Alkalinity can be added once, in timed doses, or continuously. Aqueous alkalinity could be added directly to seawater, but the rate of this addition will likely be important, especially for avoiding secondary precipitation (Hartmann et al., 2023; Moras et al., 2022; Fuhr et al., 2022). Compared to experiments based on one-time additions of aqueous alkalinity or fast-dissolving solid-phase materials (e.g., Ca(OH)_2), field experiments adding solid minerals with comparatively slow dissolution rates (e.g., olivine) will likely need to consider longer experimental time frames to incorporate the monitoring of mineral dissolution. However, the timescale of each experiment will ultimately depend on the scientific objectives and could last from weeks to years and even decades. Location is another important factor that will influence logistics. For example, amending beach sand with alkaline minerals will present different challenges compared to the addition of alkaline material to outfalls that discharge into the ocean. Based on these and other considerations, each field experiment will require specific spatial and temporal sampling schemes to be developed. These sampling schemes should be planned well in advance of any perturbation and may require preliminary sampling campaigns to fine tune.

2.2 Alkalinity sources

OAE via coastal enhanced weathering can be accomplished using a variety of naturally occurring and human-made rocks and minerals (Table 1). The addition of these rocks and minerals is done after they have been ground to a desired grain size, with many unique application techniques proposed after the initial grinding step (see Eisaman et al., 2023, this Guide). The simplest application is done via sprinkling the ground material on the ocean surface, although this has many disadvantages including sinking and advection of the material before it dissolves (Köhler et al., 2013; Fakharee et al., 2023), although deployment in boat wakes may be viable (Renforth and Henderson, 2017; He and Tyka, 2023). Other application techniques include spreading material in coastal ecosystems such as on beaches, marshes, riverbeds, and estuaries, which have the potential to enhance dissolution through processes such as physical wave action and favorable water chemistry. However, the complex physical and biogeochemical processes that promote enhanced weathering in coastal ecosystems can make field experimentation more complicated by creating strong spatiotemporal modes of variability in water chemistry. To make results more broadly applicable, field experiments should attempt to mimic real-world alkalinity application scenarios such as those described above.

Any field experiments that add ground material to marine ecosystems may consider tracking the fate of that material from the addition site. Experiments could also artificially contain the material using barriers to avoid rapid loss of the ground material via currents; however, this could make the experiment less comparable to real-world OAE deployments. Sampling should extend from the water column into areas where the material is added, including sediments and pore waters.

Table 1. Types of alkalinity sources and considerations for each.

Alkalinity source	Solid/aqueous	Dissolution kinetics	Dissolution coproducts
NaOH	Aqueous	Instantaneous but can induce brucite ($Mg(OH)_2$) precipitation when NaOH elevates $pH > 9$. Brucite re-dissolves relatively quickly in most cases.	Alkalinity, Na^+.
Manufactured and natural Mg-derived alkalinity sources (e.g., brucite)	Solid or aqueous slurry	Relatively fast but a combination of dissolution rates both in the receiving and dosing waters.	Alkalinity, limited amounts of nutrients and trace metals (generally less than silicates), Mg^{2+}.
Silicates (e.g., olivine, basalt, wollastonite)	Solid	Relatively slow dissolution kinetics, but rates are different between silicates.	Alkalinity, silicate, trace metals. Materials need to be individually assessed prior to their use.
Manufactured lime-derived alkalinity sources (e.g., quicklime, ikaite)	Solid or aqueous slurry	Relatively fast but different kinetics between lime products.	Alkalinity, limited amounts of nutrients and trace metals (generally less than silicates), Ca^{2+}. Materials need to be individually assessed prior to their use.
Iron and steel slag	Solid	Components within steel slag that provide alkalinity (e.g., CaO) dissolve relatively fast, but different iron and steel slag contains different amounts.	Alkalinity, Ca^{2+}, Mg^{2+}, silicate, phosphate, and trace metals. Materials need to be individually assessed prior to their use.
Natural and synthetic carbonates (e.g., calcite, aragonite)	Solid	They do not dissolve under common surface ocean carbonate chemistry conditions. Dissolution rates can be higher in microenvironments such as corrosive sediment pore waters, where saturation is low due to respiratory CO_2.	Alkalinity, phosphate in some mined sources, dissolved inorganic carbon.

Likely environmental impacts associated with coastal enhanced weathering come from the physical impacts of adding finely ground material or the chemical release of trace elements and other contaminants. Both processes could have associated risks and/or co-benefits for a range of ecological processes and biogeochemical cycles (Bach et al., 2019). For example, the addition of finely ground material could lead to increased turbidity from the initial addition, subsequent resuspension, or secondary precipitation of particulates in the water column. Additionally, any release of nutrients or heavy metals from the dissolving material could alter primary production or cause harm to biological systems. The bioaccumulation of toxic metals in higher trophic level organisms, especially those of commercial importance, is a widespread concern.

Safety criteria should be put in place that can create a pause in the field experiment or prevent future experiments of the same type from taking place. These guardrails should be developed by the broader OAE community but may include obvious damage or health impacts to ecologically important organisms such as primary producers and keystone species, large and unexpected changes in biogeochemical cycles, and the general deterioration of environmental conditions. Risk–benefit analysis may be particularly useful in determining whether projects can or should move forward and may already be included in regulatory requirements through existing frameworks such as environmental impact assessments.

Aqueous and slurry-based additions of alkalinity provide different benefits and challenges compared to solid forms of alkalinity feedstock. One of the primary benefits of aqueous additions is that the alkalinity has been pre-dissolved, avoiding the often slow dissolution kinetics of minerals and rocks in seawater. Aqueous alkalinity can be generated by two main mechanisms: (1) the dissolution of alkaline rocks and minerals in reactors and (2) electrochemical processes that generate alkalinity by splitting seawater or other brine streams into an acid and base (Eisaman et al., 2023, this Guide). For some materials, such as $Ca(OH)_2$ and $Mg(OH)_2$, dissolution slurries are formed, and a combination of particulate and aqueous alkalinity can be dosed into seawater. Any particulates that are dosed from the slurry need to dissolve, meaning dissolution kinetics in seawater will be critical. However, the dissolution of these materials tends to be much quicker than with rocks and minerals (Table 1). There are important processes that need to be considered when adding aqueous alkalinity, including the unintended precipitation of calcium carbonates due to locally elevated saturation states (Hartmann et al., 2023; Moras et al., 2022).

Field experiments that use aqueous or slurry-based alkalinity additions will need to assess the impacts on seawater chemistry at the source of addition and across a dilution radius. Depending on the type of experiment and magnitude of additions, this dilution radius could extend upwards of kilometers, but the magnitude of the perturbation to carbonate chemistry would become smaller the further away from the alkalinity source (He and Tyka, 2023). The potential environmental impacts from aqueous type alkalinity additions will be similar to those discussed for coastal enhanced weathering but also include extreme localized changes in carbonate chemistry.

2.3 Considerations for site selection

Careful consideration should be given to site selection and experimental design to make sure the study adequately addresses the specific research questions and goals. Some aspects of the field site that will be important include ecosystem- and site-specific characteristics, the prevailing meteorological and oceanographic conditions, and natural spatiotemporal variability. Logistical considerations for site selection include physical access, permitting, availability of electricity, ship time, and consideration of the local community. These considerations will grow with the scale of field experiments and will likely be first-order determinants of where field experiments take place. For example, proximity to a marine institute (for land-based approaches) or access to a research cruise (for open-ocean approaches) may be desirable. Logistics will ultimately determine where operational OAE deployments take place, and early field experiments will help to elucidate important issues including the impacts of life cycle emissions on CDR.

OAE field experimentation requires careful assessment of the field site prior to alkalinity additions to provide foundational knowledge of the site characteristics. Scientific considerations for site selection can be broken down into three categories, the (1) physical, (2) chemical, and (3) biological properties of each site. Important considerations for each category are provided in Box 1. To facilitate baseline assessments and site selection we propose Table 2 as guidance for relevant parameters to measure. We note that this list is broad; however it is not exhaustive, and specific field sites may require the monitoring of different or additional parameters. Furthermore, some of the listed parameters may be more applicable to specific OAE approaches. Preliminary knowledge of the field site will inform both the experimental design and interpretation of data and experimental outcomes. Due to the large investments in cost and time required to collect baseline data, locations with a wealth of pre-existing scientific data may be considered. These baseline data could be available in the peer-reviewed literature and/or from publicly available coastal and open-ocean time series (e.g., Sutton et al., 2019).

2.4 Measurement considerations

What to measure and the type of instrumentation needed will ultimately depend on the site, scale, and goals of each individual experiment and should be considered on a case-by-case basis. For example, depending on the alkalinity source utilized (Table 1), it may (e.g., in the case of olivine) or may not (e.g., in the case of NaOH) be a priority to measure trace metal or nutrient concentrations. In addition to alkalinity type, the experimental scale will also dictate measurement considerations. For example, if the scale of the perturbation is small or the signal is very dilute, environmental impacts will not likely be measurable far from where the perturbation takes place. If there is a large addition of alkalinity, especially in a semi-enclosed system, both environmental impacts and changes in chemistry will be easier to detect. Ultimately, when OAE is done at a larger scale (e.g., millions of moles' alkalinity), it is likely that large changes in seawater chemistry will need to be avoided to reduce environmental impacts and avoid secondary precipitation. This presents an interesting challenge to conducting field experiments, as the dilution of alkalinity and ultimately CO_2 signal will make MRV more challenging (Ho et al., 2023, this Guide).

Seawater carbonate chemistry measurements will be central to most sampling schemes. To cover the appropriate spatial and temporal scales, traditional bottle sampling will likely have to be combined with state-of-the-art in situ sensors (Bushinsky et al., 2019; Briggs et al., 2020; Ho et al., 2023, this Guide). Bushinsky et al. (2019; their Fig. 1) provide a comprehensive overview of the spatiotemporal capabilities of existing carbonate chemistry sensors and platforms, and care should be taken to make sure sensors are appropriate for measurements in seawater. The appropriate methods and protocols for sampling and analysis are outlined in other chapters in this guide (Schulz et al., 2023, this Guide) and in the Guide to Best Practices (Dickson et al., 2007). Some general considerations for field experiments include appropriately characterizing the natural variability that occurs at the field site through space and time. While total alkalinity (TA) titrations should remain a priority, at least two carbonate chemistry parameters (e.g., total alkalinity, dissolved inorganic carbon, pH, or $p\mathrm{CO}_2$) should be measured for each sample. It is important to note that the combination of $p\mathrm{CO}_2$ and pH is not ideal when calculating CO_2 chemistry (e.g., using CO2SYS) due to the elevated errors when combining those parameters in determining the rest of the carbonate chemistry system in seawater (Lee and Millero, 1995). Currently, commercially available autonomous sensors exist for pH and $p\mathrm{CO}_2$, with sensors in development for both TA and dissolve inorganic carbon (DIC; Fassbender et al., 2015; Briggs et al., 2020; Qiu et al., 2023). While autonomous sensors generally have greater uncertainty than bottle samples coupled with laboratory analysis, they will likely play an important role in sampling schemes to help cover adequate spa-

Table 2. Parameters that could be considered in assessing sites for OAE field experiments. Importantly, some parameters summarized below may require a baseline assessment over sufficiently long time frames to cover the intrinsic variability of physical, chemical, and biological parameters in the studied system. For example, baseline assessment of marine food web structure will likely require a prolonged monitoring effort before (and after) the OAE deployment to have a higher chance of detecting OAE-induced effects on marine biota.

Parameter	Rationale	Potential pathway for assessment
Dilution rate	– Exposure risk to alkalinity and mineral dissolution products. – Detectability of OAE-induced chemical changes.	Tracer release experiment (Sect. 2.5).
Turbulence	– Physical energy input to keep ground particles near the sea surface during dissolution.	Microstructure profiler.
Residence time of perturbed patch in surface ocean	– Determination of residence time of an OAE-perturbed patch in the surface to assess whether there is enough time for air–sea equilibration with the atmosphere.	Risk assessment for incomplete air–sea CO_2 exchange (He and Tyka, 2023; Bach et al., 2023).
Transboundary transport	– Determination of whether there is a high risk for OAE-derived chemicals to be transported into sensitive areas (e.g., marine protected areas, other state territories) in high concentrations. May be useful for residence time as well.	– Tracer release experiment – Virtual Lagrangian particle tracking. – Utilizing natural tracers observable via remote sensing (e.g., CDOM (colored dissolved organic matter) or gelbstoff). – Mixed layer depth.
Light penetration	– Determination of light environment to assess to what extent the addition of particulate alkalinity source could impact turbidity.	Light loggers, turbidity, CTD (conductivity, temperature, and depth) casts.
Carbonate chemistry conditions	– Baseline of mean conditions and variability to assess how much change OAE must induce to become detectable. – Determination if OAE-related changes are likely to affect marine organisms.	Dickson et al. (2007) and ocean acidification literature. Schulz et al., (2023, this Guide)
Macronutrients	– Assessment of whether the designated system is prone to macronutrient fertilization via OAE. (Note that not all OAE approaches would introduce macronutrients into the ocean system.)	Standard photometric approaches (Hansen and Koroleff, 1999). Experimental assessment of limiting elements.
Micronutrients	– Assessment of whether the designated system is prone to micronutrient fertilization via OAE. (Note that not all OAE approaches would introduce micronutrients into the ocean system.)	GEOTRACES cookbook (https://www.geotraces.org/methods-cookbook/, last access: 9 November 2023) Experimental assessment of limiting elements.
Marine food web structure	– Assessment of the planktonic and/or benthic food web structure prior to testing an OAE deployment.	There is a whole range of surveying tools that could be applied depending on the size and abundance of organisms. Applied methods could range from OMICS (including eDNA) to optical observations, acoustics, and flow cytometry.
Risk of damaging organisms by adding ground minerals	– Providing knowledge of whether organisms could be physically harmed, for example, through covering them with mineral powder.	Same range of methods as for the food web assessment.
Endangered species	– Clarification if endangered species could be present at the designated field site.	Same range of methods as for the food web assessment. Plane or drone surveys can help to confirm sightings of larger organisms and there may be online resources to be utilized (e.g., WhaleMap). Furthermore, local knowledge should be sought after from the diverse range of stakeholder groups, for example, consultation with indigenous communities, fishermen, local authorities, and environmental agencies.
Foraging/breeding ground	– Clarification if the designated field site is an important breeding/foraging area for migratory organisms.	Same range as for endangered species assessments.

Physics

- What are the expected dilution rates of the added alkalinity?
- What is the site turbulence, and how will this impact alkalinity additions (e.g., keeping particles in suspension)?
- What is the natural light penetration, and what impacts could increases in turbidity have on this?
- What is the residence time of water in the surface ocean or mixed layer, and how does this relate to the estimated air-sea equilibration time?
- What is driving air-sea gas exchange?
- Will changes in turbidity impact the albedo of the experimental site?
- What is the potential for the lateral export and exchange of alkalinity and other materials?
- Is there the potential for physical disturbance (e.g., impacts of alkalinity additions on physical water mass parameters such as density or the physical impacts of adding undissolved minerals to the benthos)?
- Where will the alkalinity signal be most observable (e.g., pore water vs. water column)?

Chemistry

- What are the natural carbonate chemistry conditions?
- What modes of variability (e.g., daily, seasonal, interannual) impact seawater chemistry?
- How will variations in seawater chemistry impact signal to noise?
- How will seawater chemistry impact mineral dissolution rates?
- Is there potential to disturb the natural concentrations of macro- or micronutrients or toxic metals through dissolution by-products?
- How do anthropogenic sources of alkalinity interact with (and potentially modify) natural sources and sinks of alkalinity?

Biology

- What organisms (benthic and pelagic) are present in the study area, and what are their relative sensitivities to fluctuations in seawater carbonate chemistry (if known)?
- Are there culturally or commercially important species present?
- Are there endangered or rare species present? Is the site a nursery and/or nesting ground? Are there keystone species and/or important primary producers present? These considerations will likely be part of the permitting process.
- Are there times of the day or seasons with elevated species or ecosystem sensitivities?
- What are the trophic dynamics in the environment, and how might the food web be impacted (e.g., shifts in predator–prey relationships)? What are the cascading implications for the ecosystem as a whole? Might effects be transferred beyond the study site via migratory species?
- Could particulates (e.g., ground rock) cause physical damage prior to dissolution?

Box 1. Scientific considerations for field experiments.

tial and temporal resolution in naturally variable marine systems.

While monitoring the background variability and subsequent additions of alkalinity will be critical, scientists may also wish to directly measure fluxes of carbon at the field study site (Ho et al., 2023, this Guide). The direct measurement of carbon fluxes can be accomplished via different methods including benthic and floating chambers, eddy covariance and other benthic boundary layer techniques, and mass balances. These techniques have benefits and drawbacks, including having to enclose the natural system (e.g., chambers) and elevated uncertainty that could be outside of the expected changes due to the perturbation (e.g., eddy covariance). Benthic chamber measurements may be particularly important to quantify the dissolution of minerals and rocks added to sediments. Ultimately, any measurements of fluxes due to OAE activities will likely need to be coupled with numerical modeling to estimate the overall drawdown of atmospheric CO_2 (Fennel et al., 2023, this Guide).

Field experiments should be informed by other scientific studies as much as possible (e.g., studies based on laboratory experiments, mesocosm studies, natural analogs, and numerical modeling). While not necessarily directly translatable to natural systems (Edmunds et al., 2016; Page et al., 2022), these types of studies can provide first-order assessments on safety and efficacy, helping to prevent unintended harmful ecological side effects when conducting large-scale perturbations.

Other measurements that may be useful during OAE field experiments are outlined in Table 2. It is important to note that this list is not meant to be exhaustive, and measurement selection will have to be made on a case-by-case basis. Considering the difficulties of tracking water masses in an open system, the next section is a more detailed discussion on tracers for monitoring mixing and dilution of water within the OAE field experiment site. Tracking added alkalinity will be critical to determine the impacts and efficacy of alkalinity enrichments and may be one of the biggest challenges facing OAE field experiments.

2.5 Dual-tracer regression technique

If the goal is to track alkalinity additions and measure their effects on carbon fluxes (i.e., net ecosystem production or air–sea exchange), a dual-tracer regression method can be used (e.g., Albright et al., 2016, 2018). This approach uses the change in ratios between an active tracer (alkalinity) and a passive tracer (dye, artificial gas tracer; Table 3) to assess the fraction of added alkalinity taken up or released by biogeochemical processes in the system. Passive tracers do not affect fluid dynamics and are passively advected by the surrounding flow field. The use of passive tracers, such as dye tracers (e.g., rhodamine, fluorescein) or artificial gas tracers (e.g., SF6, CF3SF5), that do not occur in nature helps eliminate background noise. Additional considerations include how many tracers to use and what information each tracer provides (Table 3).

During a dual-tracer experiment, changes in the active tracer (alkalinity) result from mixing, dilution, and biogeochemical activity, whereas changes in the passive tracer are due solely to mixing and dilution. By comparing the alkalinity-to-dye ratios before (e.g., upstream) and after (e.g., downstream) the water mass interacts with a study area, it is possible to isolate the change in alkalinity that is due to biogeochemical processes such as calcium carbonate precipitation and dissolution (Figs. 1 and 2). This technique is an extension of Friedlander et al. (1986) and may have applications in other areas of research pertinent to marine CDR, such as nutrient or pollution assessments and the uptake of industrial or agricultural waste. The primary experimental criteria for the dual-tracer technique are that the active and passive tracers are added in a fixed ratio and at a fixed rate, in areas where there is a dominant flow direction, dispersion, or dilution.

2.6 Detecting change and the importance of controlled experiments

Separating an experimental "signal" from the background "noise" inherent in natural systems can be challenging, especially in field experiments where replication may not be practical (Carpenter, 1990). Gaining baseline knowledge on the physical, chemical, and biological components of the study site should be a priority. There is often considerable natural variability in marine systems, and especially in coastal systems, due to fluctuations in biological activity, hydrodynamics, seasonal and/or interannual influences, and other factors (Bates et al., 1998; Bates, 2002; Hagens and Middelburg, 2016; Landschützer et al., 2018; Sutton et al., 2019; Kapsenberg and Cyronak, 2019; Torres et al., 2021). Fully characterizing this variability could take many years, which may create significant barriers to experimental progress in the field. Therefore, we recommend that any potential modes of spatiotemporal variability be recognized and evaluated while planning field experiments. For instance, in coastal systems with river and groundwater inputs, it will be important to know the impact that freshwater has on carbonate chemistry.

Where possible, conducting controlled experiments will help to maximize the ratio of signal to noise, thereby improving statistical power to detect experimental effects. The pros and cons of replicating experimental controls in space versus time should be taken into consideration. For many field experiments (and natural analogs; see Subhas et al., 2023, this Guide), sample size will be inherently limited (e.g., one, or few study sites); therefore, conducting controls in time (e.g., every third day) may be the best option. For studies with limited (or no) replication, there are statistical methods that can be used to isolate effects pre- and post-treatment (Carpenter, 1990). Numerical simulations and machine-learning-based network design are potentially valuable tools to optimize observational networks to detect experimental change.

3 Additional considerations

Permitting. Addressing regulatory requirements is critical prior to conducting field experiments. The spatial and temporal scale of the field trial, as well as the specific considerations of the deployment site (e.g., protection status), will determine permitting requirements. Engaging with this process early is advised – for example, understanding who the permit-granting authorities are for a given area and timelines for associated regulatory processes. In some cases, the use of existing infrastructure (e.g., wastewater discharge sites) and environmental projects (e.g., beach renourishment) may offer ways to streamline experiments, although permitting will be governed by existing regulations. For a detailed discussion on legal considerations, see Steenkamp and Webb (2023, this Guide).

Community engagement and social considerations of field experiments. The likelihood of harmful ecological consequences from OAE field experiments remains unclear and will ultimately depend on the technology and temporal and spatial scale of the experiment. Field experiments evaluating CDR approaches carry the risk of unintended consequences and impacts over large spatial scales, so appropriate scaling (e.g., starting small) is necessary (NASEM, 2022). In response to these unknowns, researchers should follow the key components for a code of conduct for marine CDR research, e.g., as outlined by Loomis et al. (2022), which details best practices that encourage responsible research amongst both the public and private sectors.

Table 3. Passive tracers that are available and commonly used for use in field experiments and considerations for each. Additional tracers may be useful that are not listed in this table, including helium 3 and tritium.

Tracer	Type	Pros	Limitations	Lifespan
Rhodamine	Fluorescent dye	Sensor-based, high-frequency (> 4 Hz) detection, platform flexibility, detection from space and/or the sky for surface releases.	Optically degrades and absorbs to particles, not good for longer-term studies, not as good signal to noise/detection limits as inert gas tracers.	Several days to weeks
Fluorescein	Fluorescent dye	Sensor-based, high-frequency (> 4 Hz) detection, platform flexibility, detection from space and/or the sky for surface releases.	Degrades optically – not good for longer-term studies (> 24 h).	< 24 h
SF6	Artificial gas	Inert; capable of being measured at very low concentrations; able to quantify mixing and residence time; good for large-scale ocean tracer release experiments.	Lower-frequency detection and less flexibility with platforms, requires discrete measurement. High global warming potential.	years
Trifluoromethyl sulfur pentafluoride (CF_3SF_5)	Artificial gas	Good for large-scale ocean experiments.	Difficult to obtain, lower-frequency detection and less flexibility with autonomous platforms, requires discrete measurement. High global warming potential.	years

Figure 1. Rhodamine dye flowing over a coral reef flat study site during a study in One Tree Island, Australia (Albright et al., 2016). NaOH was used as an active tracer to raise alkalinity, and rhodamine was used as a passive tracer to account for mixing and dilution. Changes in the alkalinity-to-dye ratios were used to isolate the change in alkalinity flux that was associated with an increase in net community calcification on the reef flat.

Social license to operate is critical for the success of CDR projects, and researchers have an obligation to involve the full community of people (public and stakeholders) who may be impacted by the research (Nawaz et al., 2023; Cooley et al., 2023). Therefore, public outreach is important both before and during field experimentation. The study site will determine the potential for community engagement. Coordinating with local and/or regional organizations who are connected to relevant stakeholders (for example, your local Sea-Grant office if in the United States) will be helpful. For additional discussion on social considerations of OAE field trials, see Satterfield et al. (2023, this Guide).

Collaboration and data/information sharing. Considering the inherent challenges to OAE field experiments (cost,

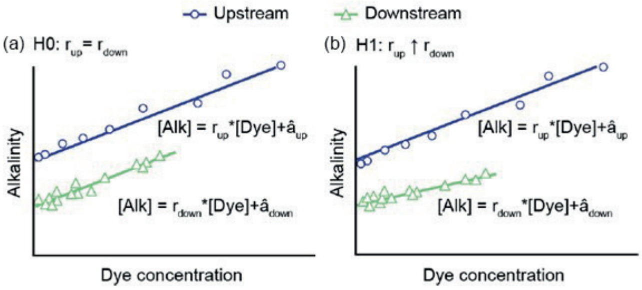

Figure 2. Theoretical representations of the null (H0) and alternative (H1) hypotheses for a dual-tracer regression experiment where NaOH was used as a source of alkalinity and rhodamine dye was used as a passive tracer (from Albright et al., 2016). **(a)** In H0, the benthic community does not take up added alkalinity. Here, the change in alkalinity between the upstream and downstream transects would not be systematically related to the dye concentration, and the ratio of the alkalinity–dye relationship, r, would not be expected to change between the upstream and downstream locations (that is, $r_{\mathrm{up}} = r_{\mathrm{down}}$). **(b)** In H1, an uptake of added alkalinity occurs by the benthic community. Here, areas with more alkalinity (and more dye) change at a different rate than areas with less alkalinity (and less dye), resulting in a change in the alkalinity–dye slope (that is, $r_{\mathrm{up}} > r_{\mathrm{down}}$).

permitting, access, logistics, environmental safety), fostering interdisciplinary and collaborative teams will help ensure the greatest return on investment. Examples of ways to foster collaboration include developing test-bed field sites that are open to participation from diverse stakeholder groups (https://oceanvisions.org/highlevelroadmap/, last access: 14 November 2023), making efforts to include groups who may not traditionally have access to and/or the capacity for field campaigns, and including travel support in grant applications to support external collaborators. Making concerted efforts to share information, resources, and ideas will allow researchers to combine knowledge and resources in ways that might not have been possible when working alone, thereby advancing OAE technology and science at a faster pace. When publishing in peer-reviewed literature, uploading data to publicly available data repositories and publishing in open-access journals following best practices should be prioritized (Jiang et al., 2023, this Guide).

Inclusivity and transparency during OAE field trials are crucial to ensure that knowledge gained is fed back into scientific and other communities efficiently, iteratively informing and refining the next generation of experiments. Some field experiments will mimic plans for real-world OAE deployments and should therefore be done in collaboration with relevant stakeholders across science, industry, policy, and communities. To foster collaboration and technology transfer, we advocate for a centralized platform and/or organization to share data and information in this rapidly evolving field. This might look like a centralized, freely accessible platform for early and/or "real-time" information sharing (i.e., before publication) that can facilitate faster information exchange within the research community (e.g., data sharing, permitting issues). Two existing options that could help fill this gap are the Ocean Acidification Information Exchange (https://www.oainfoexchange.org/index.html, last access: 11 November 2023) and the Ocean Visions community (https://community.oceanvisions.org/dashboard, last access: 11 November 2023). It may prove useful to designate core working groups of experts in various aspects of CDR that investigate specific needs and priorities and work to synthesize and share existing knowledge in the context of field experiments. This approach has been adopted by other scientific disciplines in high-priority, rapidly evolving, and highly collaborative fields, greatly benefiting the scientific community at large (e.g., the Coral Restoration Consortium, https://www.crc.world/, last access: 11 November 2023 – and associated working groups). Coordinating field trials with research groups conducting laboratory and mesocosm experiments, studying natural analogs, and undertaking modeling efforts will help strengthen the interpretation and extrapolation of results.

4 Conclusion and recommendations

Given that few OAE field studies have been conducted to date, there is much to learn from the earliest experiments with respect to experimental design, measurement and monitoring, deployment considerations, environmental impact, and more. Early experiments will only engage with a fraction of the temporal and spatial scales involved in full-scale operational OAE, and longer-term and larger-scale studies will become increasingly important to reveal scale dependencies as the field develops. It is important that marine CDR research is hypothesis-driven, structured, deliberate, and well-planned to best inform future decision-making about OAE techniques and deployments. Careful consideration of the physical, chemical, and biological components of the study area will help inform the experimental approach. The use of baseline studies (both previous and contemporary to the OAE deployment) and controls will help to maximize signal-to-noise ratios and identify experimental effects. The timescale of OAE field experiments should not be underestimated, especially when considering permitting, and the data needed to capture the baseline variability in natural systems.

Considering the urgent timeline required for humanity to meet our climate goals, field experiments need to move forward swiftly yet deliberately. To ensure the success of OAE, diverse perspectives from research, industry, policy, and society must converge, demanding transdisciplinary thinking and a commitment to open and transparent science. Central to this ambitious undertaking are the early field experiments, results from which will ultimately determine the successes and failures of OAE projects and technologies.

Key recommendations

1. Ensure inclusivity and transparency (community engagement, data sharing, etc.) for OAE field experiments to both advance the field as quickly as possible and ensure the field progresses in a socially responsible manner.
2. Assess the potential risks and benefits for any perturbation. Proceed according to a code of conduct and precautionary principles.
3. Develop methods to track signal versus noise in highly variable environments, including robust baseline studies to characterize underlying variability (biological, chemical, physical), and include controlled experiments such as chamber incubations to isolate treatment effects.
4. Consider the logistical constraints and opportunities of field locations.
5. Create test-bed field sites that are open to participation from diverse stakeholder groups.

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Natural analogs to ocean alkalinity enhancement

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Abstract. Ocean alkalinity enhancement (OAE) research can be supplemented by studying the natural alkalinity cycle. In this chapter, we introduce the concept of natural analogs to ocean alkalinity enhancement. We describe Earth system processes relevant to OAE deployment and its measurement, reporting, and verification. We then describe some suitable natural analog locations that could serve as study sites to understand how these processes may interact with OAE. Approaches to examining the geological record are also considered. Practical considerations for establishing a natural analog study are discussed, including geochemical mass balance, choosing a site, establishing a control, choosing a measurement suite and platform, and coordinating with ocean models. We identify rivers and their plumes, glacial fjords, whiting events, and basinal seas with elevated alkalinity as promising candidates for initial natural analog studies. This chapter is not meant to be prescriptive but instead is written to inspire researchers to creatively explore the power of natural analogs to advance our understanding of OAE. Key recommendations include considering appropriate spatial and temporal scales of the study and associated measurement criteria and designing the study with applicable outcomes to OAE research, including implications for deployment and/or monitoring.

1 Introduction

1.1 Alkalinity cycling and a definition of natural analogs for OAE

Despite its residence time of about 100 000 years, there is a vigorous and dynamic alkalinity cycle in the ocean. The spatial and temporal patterns of alkalinity concentrations and fluxes are intimately linked with ocean biogeochemistry. Organic carbon production and remineralization cycles alkalinity through redox processing of oxygen and other electron acceptors (Froelich et al., 1979). Calcium carbonate ($CaCO_3$) production and dissolution consumes and produces alkalinity from the reef (Broecker and Takahashi, 1966; Andersson, 2015) to the ocean basin scale (Emerson et al., 2011; Feely et al., 2002). The inventory of biogenic $CaCO_3$ accumulated in deep-ocean sediments has long been recognized as a source of alkalinity over glacial–interglacial timescales and will likely neutralize a significant fraction of fossil-fuel-derived carbon dioxide (CO_2; Archer et al., 1998). Thus, the alkalinity cycle exerts its own unique influence – through multiple processes and scales – on the ocean's capacity to take up and store atmospheric CO_2.

Many ocean alkalinity enhancement (OAE) approaches are based on established geochemical weathering and acid–base reactions, and deploying these approaches will benefit from an understanding of Earth's natural processing of alkalinity. These processes operate all around us, right now, at climate-relevant scales. The chemical and physical weathering of terrestrial rocks produces alkalinity that is delivered to the ocean via rivers. This input is balanced by global $CaCO_3$ burial in ocean sediments, along with significant contributions from other sedimentary processes such as groundwater discharge and nitrogen and sulfur cycling (Middelburg et al., 2020, and references therein). The $CaCO_3$ cycle buries roughly 36 Tmol alkalinity per year on shelves and along the coasts, and roughly 23 $Tmol\,yr^{-1}$ in the open ocean (Mid-

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delburg et al., 2020). However, open-ocean $CaCO_3$ production of $>100\,\mathrm{Tmol\,yr^{-1}}$ greatly exceeds deep-ocean burial, resulting in the recycling of $\sim 77\,\mathrm{Tmol\,yr^{-1}}$ via $CaCO_3$ dissolution to keep the system at a steady state (Milliman et al., 1999; Berelson et al., 2007; Sulpis et al., 2021). Other mineral reactions, such as silicate weathering and reverse weathering, also produce and consume alkalinity within the ocean system. These alkalinity inputs, outputs, and internal cycles can serve as natural analogs to OAE, providing insight into how OAE deployments would interact with the ocean system and what OAE deployments may look like at the gigaton scale.

Here, we define "natural analogs" as Earth system processes that (1) resemble OAE deployments or (2) can answer open questions about the feasibility, efficacy, and impacts of these deployments. Natural analogs can inform the deployment of OAE at a variety of scales, from small-scale field experiments to the global ocean. Natural analogs may offer test beds for sensor development across alkalinity and carbon gradients, could serve as real-world frameworks for interpreting laboratory and mesocosm experiment results, and could act as validation tools for modelers to study relevant OAE processes. In many cases, natural carbonate chemistry parameters covary with other environmental variables such as temperature, salinity, and nutrients. Identifying alkalinity as the driver of a specific response in these systems can be challenging and must be carefully assessed. This drawback to natural analogs can also be a strength. Demonstrating the effect of alkalinity, in combination with a suite of other stressors or drivers, can be a powerful way to evaluate the downstream impact of OAE deployments, without the need for expensive and time-consuming field trials. Natural analogs, including periods of enhanced ocean alkalinity in the geological past, have the potential to elucidate longer-term, acclimated responses to OAE-relevant conditions.

1.2 The benefits and drawbacks of natural analogs

Natural analogs offer all of the benefits and drawbacks that come with the complexity of Earth systems. They should be viewed as one of many approaches available to OAE researchers. Manipulative experiments may be the most conclusive in terms of demonstrating immediate impact. Laboratory experiments (Iglesias-Rodriguez et al., 2023, this Guide) offer ultimate control over conditions and variables, but their results can be challenging to apply to the real world. Mesocosms (Riebesell et al., 2023, this Guide) are one step up in complexity and benefit from not requiring field trial permits to operate but are costly and limited in their spatial and temporal applications. Field experiments (Cyronak et al., 2023, this Guide) will provide the most information about real-world impacts. However, they require permits and resources that, currently, make them difficult and sometimes prohibitive to execute. In addition, none of these manipulative approaches can provide information on longer-term feedbacks or on large-scale processes. They may not last long enough to document the adaptation of ecosystems to sustained alkalinity inputs. They also may be biased due to the timing and spatial limitations of these experiments, thus missing critical events such as the impact of weather, storms, and turbidity flows. Natural analogs can supplement these manipulative approaches in terms of complexity, scope, and scale. They will not necessarily give "clean" results for alkalinity effects alone; rather, they offer a rich perspective on how OAE may look at scale.

Examples of recent studies of natural analogs in the context of OAE are still limited. However, previous research on ocean acidification (OA) highlights some of the difficulties and complexity associated with natural sites (e.g., Hall-Spencer et al., 2008; Tyrrell et al., 2008; Kroeker et al., 2013; Manzello et al., 2014; reviewed in Rastrick et al., 2018). Relevant examples for OAE may include large river plumes and estuarine systems, where runoff into coastal systems – depending on catchment and underlying bedrock – may create interacting gradients in environmental parameters such as alkalinity, particulate matter, dissolved inorganic carbon (DIC), salinity and/or macronutrients (Raymond and Cole, 2003; McGrath et al., 2016; Gomez et al., 2021), with each of these factors potentially triggering specific species-level or ecosystem responses.

Effects of covarying factors may be large and can wrongfully be attributed to the main variable or process of interest (in this case, alkalinity enhancement). To some degree, targeted site selection can minimize the number of confounding factors. Ideal locations for specific process studies would be sites with distinct spatial and/or temporal gradients in alkalinity and limited fluctuations in other environmental variables (e.g., temperature and salinity, particulate matter, and nutrients).

2 Some defining qualities of natural analogs

2.1 Earth system processes and their relationship to OAE

The delivery of alkalinity to the oceans via OAE will interact with the natural alkalinity cycle in various ways, depending on the approach, scale, and location of deployment. Accordingly, the relationship between OAE and the Earth system processes will be expressed on a variety of spatial and temporal scales. We depict relevant Earth system processes as an oval, with its size and orientation determined by the temporal and spatial scale needed to characterize its influence in the Earth system (Fig. 2). Mineral–fluid reactions, for example, can be studied in the lab at the (sub-)micron scale of the mineral–seawater interface. This oval thus ranges from the bottom-left corner vertically to encompass a wide range of reaction rates at Earth surface conditions. The effect of these reactions on seawater chemistry can occur across a wide range of scales, all of which require water mass transport. For

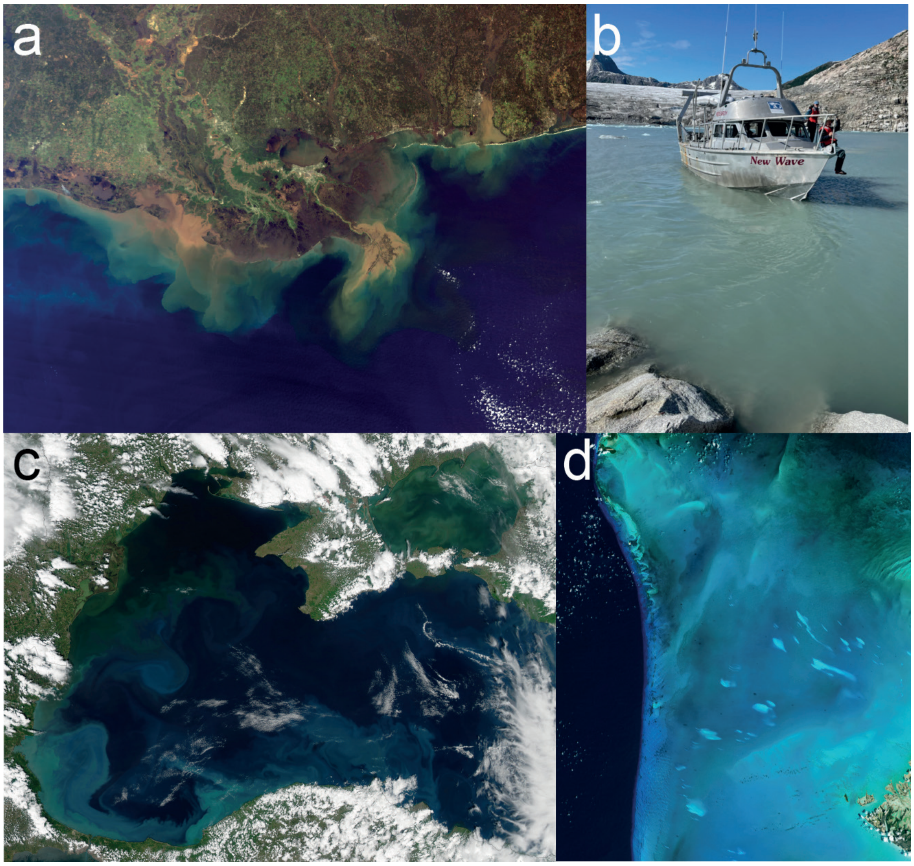

Figure 1. Images of some potential natural analog study sites. **(a)** The Mississippi River plume in the Gulf of Mexico. **(b)** A glacial fjord in Alaska filled with mineral dust. **(c)** Coccolithophore blooms in the Black Sea, as visualized by satellite. **(d)** Whiting events in the Bahamas. Panels **(a)**, **(c)**, and **(d)** are from NASA. Panel **(b)** is from Alex Gagnon.

example, at the platform or reef scale, observations must be made over days, weeks, or months to fully understand calcification budgets. Globally, the alkalinity of the ocean interior is increased through the dissolution of calcite and aragonite in the water column and sediments and the subsequent translation of that signal via ocean circulation.

Earth system processes do not operate in isolation but instead overlap and interact with each other, creating higher-order effects that may generate unexpected and nonlinear responses at a range of spatial and temporal scales (depicted schematically as overlapping ovals that culminate in the gray envelope in Fig. 2). Reactions with minerals could ultimately engage with the carbon cycle and ocean–atmosphere CO_2 fluxes. Particle dynamics could feed back on mineral reaction rates or begin to affect the biological pump, or both. Whether intentional field experiments engage these higher-order effects will depend on their scale in both space and time. The benefit of natural analogs is that these effects are likely already fully coupled with each other. Studying natural analogs of OAE can thus test both the (quasi-) steady-state and transient effects associated with the interactions of these numerous Earth system processes. The large and at-times-undefined scale in both time and space presents a fundamental scale challenge for studying Earth system processes and is a lesson that should be taken to heart by the OAE community. Below we discuss some of these Earth system processes that have direct relevance to OAE.

- *Mineral precipitation and dissolution*. Silicate weathering is the most significant net carbon sink on geological timescales, and relevant dissolution reactions are occurring in many environments around the globe, including marine settings. These reactions are often slow, taking place on the timescale of months to years or even longer. In the context of OAE, mineral dissolution reactions will be limited to the treatment location at which the alkalinity production can be monitored. Because dissolution matrices are often complex (e.g., soils, sediments, and seawater), in situ dissolution rates are often hard to model and interpret. Interrogating real-world dissolution rates of these materials, either suspended in seawater or in sedimentary systems, would place useful constraints on dissolution rates and alkalinity production. Understanding real-world controls on secondary precip-

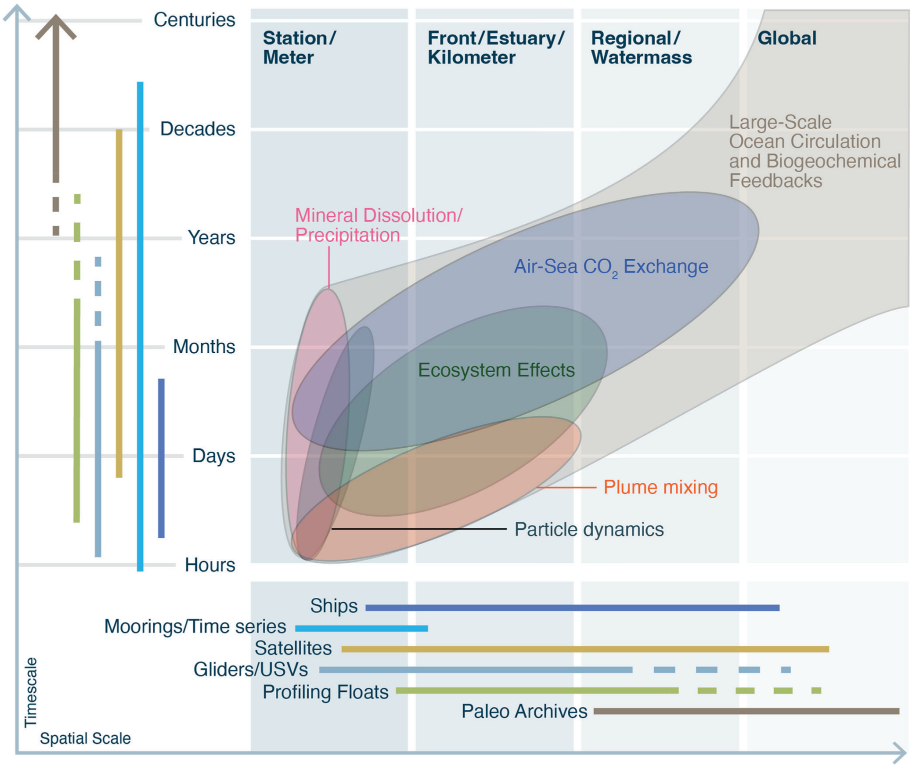

Figure 2. Processes relevant to natural analogs for OAE over a range of length and timescales. Various measurement platforms are shown in the margins, together with their associated operating time and length scales. Studies investigating OAE should match measurement strategies to the appropriate processes being investigated. Figure concept inspired by Chai et al. (2020) and Bushinsky et al. (2019).

itation and subsequent alkalinity consumption will also be critical.

Carbonate minerals are considered to be some of the most reactive on the Earth's surface, and their precipitation and dissolution occurs on faster timescales than most silicate mineral reaction rates. There is a major gap in our understanding of how OAE will interact with the ocean's $CaCO_3$ cycle. In the natural environment, biological and inorganic precipitation are related to a number of complex, interrelated factors. Surface seawater is already supersaturated with respect to most $CaCO_3$ minerals, and $CaCO_3$ precipitation is thought to be kinetically limited (Sun et al., 2015). Temperature, Mg^{2+} and other ionic constituents, dissolved or particulate organic matter, and the in situ biological community all may influence the rate and spatial extent of $CaCO_3$ precipitation. These factors will change both in space and time, meaning that the spatial scale of precipitation is often large and poorly defined.

- *Particle dynamics*. Several OAE approaches involve adding fine-grained material to the ocean surface, and letting it dissolve to produce alkalinity. Currently, our understanding of how the sustained, large-scale addition of particles influence seawater turbidity, flocculation, particle settling velocities, and the marine ecosystem comes from the dredging and dumping literature (Essink, 1999). There may be additional feedbacks associated with mineral dissolution and precipitation reactions within the particle field. These particle dynamics occur on short spatial scales, but small particles could persist for long periods of time in the water column, leading to relatively long exchange timescales for some particle types and chemistries (Bacon and Anderson, 1982).

- *Plume mixing and spreading*. The enhanced-alkalinity seawater plume resulting from an OAE deployment will be subject to a variety of physical forcings and will spread out both horizontally and vertically over time. Plume dispersal will be influenced by currents, eddies, seabed topography, and other physical characteristics. Plumes of solid material will behave differently than plumes of dissolved alkalinity. The plume's dispersal will dilute its alkalinity but will increase its surface area, creating tradeoffs for CO_2 uptake efficiency (He and Tyka, 2023; Wang et al., 2023). Alkalinity will also be lost below the mixed layer due to vertical mixing processes and circulation patterns.

- *Ecosystem effects*. The ecosystem response to OAE is currently unknown (Bach et al., 2019). Responses may be quite variable and will involve both immediate "shock" responses and longer-term acclimated responses. Imagine exposing a marine ecosystem to a dispersing plume of alkalinity. Some parts of that ecosystem may sit directly in the outfall and experience sustained impacts, while others may experience periodic "whiffs" as the periphery of the plume disperses and shifts with water circulation. In the pelagic environment, the ecosystem may move along with the plume.

Whether alkalinity enhancement will stimulate biological calcification, either in open-ocean calcifiers such as coccolithophores or in coastal ecosystems such as coral reefs or shellfish habitats, is an open question. In many cases, OAE will decrease the $p\mathrm{CO_2}$ of seawater, potentially limiting the availability of CO_2 for photosynthesis for some organisms. In the case of solid additions, impurities and other constituents could dissolve along with alkalinity and could begin to interfere with the structure and function of marine ecosystems. How these effects are translated to higher trophic levels, and if there are any direct impacts on higher-trophic-level organisms, is poorly understood.

- *Air–sea CO_2 exchange*. The OAE approach to carbon dioxide removal (CDR) relies on the equilibration of an alkaline seawater parcel with the atmosphere. Air–sea gas exchange is thus a fundamental component of OAE and may play an important role in limiting the timescale of CDR. CO_2 dynamics and equilibration timescales are generally understood and occur on timescales of several weeks to up to a year (Jones et al., 2014). The spatial scale of this equilibration requires the interaction of a water mass with the atmosphere, its physical and chemical characteristics, and wind speeds. It is well understood that increasing the ratio of total alkalinity to dissolved inorganic carbon (TA : DIC) in seawater decreases the partial pressure of CO_2, thus increasing the equilibration timescale of CO_2 uptake from the atmosphere. However, this process has not been investigated in practice. Natural analogs for OAE-induced CO_2 uptake could involve studying air–sea CO_2 fluxes at multiple locations with a range of surface seawater TA : DIC.

- *Large-scale ocean circulation and biogeochemical feedbacks*. Eventually, and especially when considering OAE at gigaton scales, the processes listed above will blend with each other, leading to large-scale feedbacks of the biogeochemical ocean system. These feedbacks will become increasingly large and diffuse, essentially becoming part of the Earth's biogeochemical cycling of alkalinity and carbon. Additionally, large-scale ocean circulation will redistribute alkalinity enhancements throughout the ocean interior. If OAE stimulates biological or inorganic $CaCO_3$ precipitation, alkalinity outputs could fundamentally change at the platform, basin, or global ocean scale. Ecosystem feedbacks, if sustained, could lead to significant reorganization of the biological pump, with implications for the organic carbon cycle and the balance of CO_2 fluxes at the ocean surface.

2.2 A non-exhaustive list of OAE natural analogs

The processes and systems discussed in this chapter are not meant to be prescriptive or limiting. We encourage researchers to think creatively about the problems associated with OAE deployment – whether they be technical or scientific – and find suitable natural systems to study solutions to these problems. Many of the current open questions may be solved or become moot in subsequent years. The natural analog concept can, and should, continue to be applied, even as our knowledge base for OAE grows and evolves over time.

Ideal natural analogs for all of the above processes, and how they will interact with OAE, will typically exist at system boundaries and across defined gradients in carbonate chemistry. For relevance to OAE, it will be important to constrain the interactions between alkalinity and the system in question and ultimately the associated implications for the efficiency, safety, and scalability of OAE.

- *Rivers and their plumes and deltas* (Fig. 1a). There may be opportunities to study natural river chemistries and their associated plume and sediment dynamics in regions with defined, sustained inputs to the marine system. Rivers deliver most of the alkalinity to the ocean, and dedicated surveys of these plumes across a variety of river compositions and plume geometries will provide critical information for large-scale alkalinity enhancement deployments. Deltaic environments may be useful to study the impact of particle loading and sediment–water interactions on the production and removal of alkalinity (Wurgaft et al., 2021). We note that the TA : DIC of rivers is often very close to 1, such that the alkalinity is often assumed to take the form of bicarbonate (Guo et al., 2012; Mu et al., 2023). Thus, riverine systems deliver DIC and TA in roughly equal amounts, limiting the utility of rivers as natural analogs for OAE processes with TA : DIC that is significantly different than unity. Alkalinity concentrations also vary between river systems due to the mineral composition of the drainage basin (e.g., high in the Mississippi and low in the Amazon) and as a function of discharge rates. These variations can be used as comparisons or counterfactuals for natural analog studies.

- *Glacial fjords and runoff into the marine system* (Fig. 1b). The delivery, settling, and reaction of glacial flour in semi-enclosed or restricted basins could be useful for mineral dissolution or precipitation, particle dynamics, and plume evolution. Glaciers grind and dissolve underlying bedrock, creating fine-grained rock material known as glacial flour. This material is often highly reactive, dissolving to produce cations and alkalinity in a wide range of concentrations (Brown, 2002). Mixing of freshwater and seawater has a unique impact on carbonate chemistry (Fransson et al., 2015; Horikawa et al., 2022) and could be linked to the source rock type and meltwater composition, among other factors. Glacial flour dissolution in seawater does not appear to be well-characterized, leaving a potential research avenue for OAE-related dissolution studies. There may be physiological impacts of glacial flour on the marine microbial community (Maselli et al., 2023). Future studies on these glacial systems could inform deployments of fine-grained material for OAE and subsequent environmental monitoring strategies.

- *Basin-scale systems with unique geochemistries and ecologies* (Fig. 1c). The larger the spatial and temporal scale, the larger the natural analog system boundary must become. The advantage of natural analogs is that these large-scale feedbacks can be assessed immediately. The Mediterranean Sea (Geyman et al., 2022), the Red Sea (Steiner et al., 2014), and the Black Sea (Bach and Boyd, 2021) all provide unique high-alkalinity environments that could be compared and contrasted with more open-ocean settings to evaluate large-scale alkalinity and $CaCO_3$ cycling. Perhaps the most relevant question at this scale is evaluating whether basin-wide $CaCO_3$ formation is proportional to surface ocean alkalinity (or the ratio of TA : DIC). Basin-scale systems require large-scale observational capabilities such as repeat-hydrography cruises, observational arrays, and satellite monitoring.

- *The Bahamas carbonate platform and slope (Fig. 1d).* Large plumes of suspended, fine-grained $CaCO_3$ appear regularly in the Bahamas and other marine locations, and their origin remains unclear. These events, known as "whitings", have been studied since the 1930s (Black, 1933) and have been used to investigate the kinetics of $CaCO_3$ precipitation on calcite seeds (Morse et al., 2003). Studying the origin, duration, and extent of whitings would provide insight into how temperature and other seawater properties will interact with OAE to promote the formation of $CaCO_3$ minerals from seawater. Mineral precipitation could either occur directly from seawater (i.e., homogenously) or onto existing mineral seeds (i.e., heterogeneously). Studying whitings and the mechanisms that drive them may help elucidate the role that suspended sediments play in stimulating $CaCO_3$ precipitation (Broecker and Takahashi, 1966).

- *Weathering of rocks on the seafloor*. Since the discovery of hydrothermal vents, the alteration of rocks on the seafloor has been recognized as a major contributor to elemental mass balance in the ocean (Edmond et al., 1979). It is possible that seafloor weathering plays a significant role in controlling seawater calcium and magnesium concentrations, with implications for the marine alkalinity budget (Coogan and Dosso, 2022). Oceanic serpentinite is a common component of the seafloor and contains significant portions of brucite that dissolve when exposed to seawater (Klein et al., 2020). Studying freshly drilled rock sequences could be used to study the precipitation and dissolution of Ca- and Mg-containing metastable minerals in situ. As a complement, studying the alkalinity balance of borehole fluid chemistry could help unpack how alkalinity is created and removed during seafloor weathering (Wheat et al., 2020) and could help constrain the utility of basalts and other naturally occurring feedstocks for OAE.

- *Phytoplankton blooms*. During intense blooms, especially in enclosed or restricted systems, seawater pH can become measurably elevated relative to baseline conditions (Hansen, 2002). These events can be used to investigate potential ecological impacts of elevated pH (Pedersen and Hansen, 2003) and the potential for secondary $CaCO_3$ formation during phytoplankton blooms. These events are not directly caused by alkalinity enhancement, but rather DIC stripping, and thus may be more relevant as a natural analog to direct ocean capture of CO_2. Effects may also be hard to disentangle from nutrient or phytoplankton community dynamics due to vigorous biological activity.

- *Beach locations with unique mineral sand compositions*. Black sand or olivine beaches present unique opportunities to study the integrated, long-term effects of mineral addition. There may also be opportunities to study ongoing beach nourishment projects that, while not strictly natural analogs, could provide systems for study without the need for additional permitting.

- *Wastewater and other anthropogenic outfalls*. Although typically wastewater outfalls are acidic rather than basic, they represent opportunities to study the impacts of altered chemistries on the marine system. Again, these are not strictly "natural" analogs but could provide useful information for the OAE research community.

2.3 Extending OAE to geological timescales

The concept of ocean alkalinity enhancement as a means of carbon sequestration into the ocean is inspired by the conceptual mechanics of the long-term carbon cycle of the Earth system. Any additional output of acidic CO_2 to the ocean–atmosphere system, as derived from, e.g., volcanic outgassing, is thought to be buffered naturally, and therefore stored in the ocean, on an expanding range of timescales by different components of Earth system alkalinity, as follows (Fig. 3):

1. Dissolved carbonate alkalinity (titration of CO_2 with CO_3^{2-} to yield HCO_3^-) redistributes additional carbon between the different carbonate species in a solution (days–years).
2. Deep-ocean $CaCO_3$ sediment (titration of CO_2 with seawater decreases the CO_3^{2-} ion yielding lower carbonate saturation) which drives deep-ocean dissolution and the release of alkalinity from carbonate sediments through the vertical migration of the saturation horizon (7–10 kyr).
3. Alkalinity released from the increased weathering of silicate rocks as a result of elevated temperatures from additional CO_2 in the ocean–atmosphere system (Myr).

2.3.1 Geological measures of ocean alkalinity

Vertical migrations of the carbonate saturation horizon, at least since the advent of pelagic calcifiers ∼ 220 Ma, moderate the deep-ocean alkalinity burial to keep it in balance with the supply of alkalinity to the ocean from the release of cations through continental weathering (e.g., Broecker and Peng, 1987). Consequently, the carbonate compensation depth (CCD), defined as the depth beneath which there is no preserved carbonate in sediments and which moves vertically largely in parallel with the saturation horizon, provides one of the best proxies for ocean alkalinity. Any deepening reflects the increased ocean alkalinity, and vice versa, but not necessarily an increase in weathering inputs to the ocean.

A process of biological carbonate compensation can decouple the CCD from weathering due to environmental triggers which increase the shelf or pelagic carbonate production and burial above the CCD and drive a shallowing, or vice versa (Rickaby et al., 2010; Boudreau et al., 2018). Carbonate Ba/Ca and P/Ca have also been proposed as additional indirect measures of ocean alkalinity (Ingalls et al., 2020; Lea and Boyle, 1989).

2.3.2 Geological targets to study ocean alkalinity enhancement

Over geological history, periods of elevated ocean alkalinity relative to carbon will cause an increase in the deep ocean pH (traced with Boron (B) isotopes in foraminifera; e.g., Foster, 2008) and/or carbonate saturation state. These periods are often defined relative to geological events, such as the Paleocene–Eocene Thermal Maximum (PETM), which corresponds to a very large injection of carbon into the Earth system, resulting in deep-sea ocean acidification and dissolution of deep-sea carbonate. As a response to this pulse of the seafloor alkalinity flux, the carbonate compensation depth overdeepened before restoring its equilibrium (Penman et al., 2016).

Geological periods of enhanced ocean alkalinity are characterized by either an increase in the source of alkalinity to the ocean or a decrease in the sink. The major levers on the global alkalinity budget are those of weathering inputs and $CaCO_3$ burial, but smaller contributors include reverse and submarine weathering and anaerobic processes.

Robust identification of enhanced weathering rates associated with, e.g., elevated temperatures in the geological record could indicate a period of elevated ocean alkalinity due to enhanced alkalinity supply to the ocean. Disentangling weathering intensity from isotopic proxies such as Sr, Os, and Li isotopes is nontrivial. Nonetheless, Earth's weathering thermostat does seem to be triggered to aid recovery after abrupt carbon perturbations when methane and/or CO_2 are added rapidly to the ocean–atmosphere system, e.g., of the Mesozoic (Pogge von Strandman et al., 2013). Furthermore, towards the end of Snowball Earth events when volcanically sourced CO_2 builds in the atmosphere without a weathering sink due to the global ice cover, the post-Snowball-Earth cap carbonates are taken as evidence of an abrupt increase in the global weathering rates during the hothouse aftermath of the Precambrian Snowball events (Hoffman and Schrag, 2000).

Coupled deepening of the CCD with isotopic signals of weathering is likely provide the best measure of the events of ocean alkalinity enhancement. Due to the partitioning of carbonate sediments and alkalinity burial between the shelf and the deep ocean, any periods of lowered eustatic sea level (such as sea level regression, glacial maxima, or ice house periods) which restrict the shelf area for carbonate burial equate to elevated whole-ocean alkalinity. This elevation occurs because the ocean accumulates a greater alkalinity burden from weathering with a reduced shelf sink, potentially with enhanced carbonate alkalinity weathering from the exposed carbonate shelves, until the saturation horizon and CCD deepens. The aftermath of major extinctions involving extinction of biomineralizers, selectively or not, such as the Permo–Triassic, may be subject to enhanced ocean alkalinity in the aftermath as a result of the loss of a major biotic alkalinity sink (Payne et al., 2010; Knoll et al., 2007; Payne et al., 2007). Indeed, immediately prior to the Cambrian explosion of skeletal organisms, both the saturation state and alkalinity are inferred to be highly elevated, based on the evidence of abiotic seafloor precipitation, due to the lack of a major biotic sink of carbonate (Grotzinger and Knoll, 1995).

Events of the burial of organic carbon also perturb the TA : DIC budget by the removal of DIC from the ocean–atmosphere system. Any reduction in the DIC elevates the relative ocean alkalinity (and hence the TA : DIC ratio of the ocean and the deep-sea carbonate ion) and can trigger deepening of the carbonate saturation horizon, as seen during, e.g., the regrowth of the terrestrial biosphere at the end of the Last Glacial Maximum (Berger, 1977). On the deglacial transition, there is a preservation spike in aragonite that produces pteropods in the deep sea, showing the elevated relative alkalinity in response to the removal of carbon from the ocean–atmosphere system by biosphere regrowth.

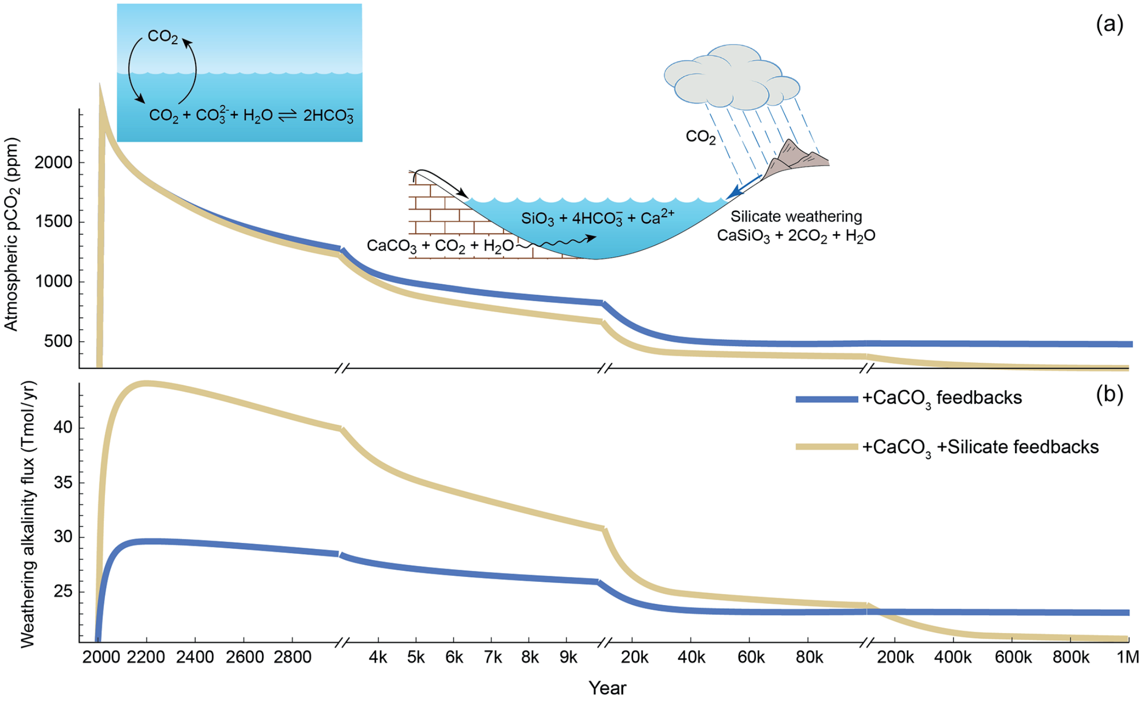

Figure 3. Evolution of **(a)** atmospheric $p\text{CO}_2$ and **(b)** weathering alkalinity flux to the ocean over 1 Myr for a 5000 Gt C emission pulse with terrestrial carbonate (blue) and silicate (tan) weathering feedbacks activated, using Grid ENabled Integrated Earth system modeling (GENIE) with a representation of terrestrial rock weathering. Note the changing timescale (adapted from Colbourn et al., 2015, where the full details of the modeling experiment can be found). After the injection of carbon, $p\text{CO}_2$ initially declines very quickly due to invasion of the ocean and the onset of dissolution of seabed carbonates (a timescale of ~ 1000 years). The slower subsequent decline is due to the action of carbonate weathering occurring first (up to ~ 10 kyr) and then later silicate weathering feedbacks, which reduce the $p\text{CO}_2$ to ~ preperturbation levels after ~ 500 kyr when silicate weathering is active. The difference in the alkalinity inputs in response to the initial injection derives from the feedbacks associated with silicate weathering in GENIE from the land temperature, runoff, and productivity of the terrestrial biosphere.

3 Practical considerations for natural analog studies

The study of natural analogs is related to, but distinct from, basic research into the cycling of alkalinity and carbon through the Earth system. Because many different types of researchers may be approaching OAE and its interactions with the Earth system for the first time, we outline some practical considerations for field observations and the study of natural systems. There are both theoretical and practical constraints with respect to conducting natural analog studies that should be taken into account when determining the scope and scale of a campaign. Many of these concepts are either established in Earth science or, in some cases, are still being actively developed as observational networks evolve and mature.

3.1 A primer on geochemical mass balance

The survey and sampling timescale is important when considering the spatiotemporal scale of one's natural analog (Fig. 2), the duration of the study, and the types of measurements and platforms used. When constructing a geochemical model of a natural system, we typically make the assumption of steady state or, in other words, that the chemical concentrations are not changing with time due to a balance between the inputs and the outputs on the timescale of interest. A steady-state assumption allows researchers to assume that spatial gradients represent a balance of rates or fluxes – in other words, rates are now expressed as a function of space rather than time. As an example, consider a natural analog study that is investigating the removal of alkalinity as river water mixes with ocean water (Figs. 1a, 4). A survey is conducted, with sampling down the river, through the plume, and into the ocean. The river flow is unidirectional and sets up a steady-state gradient between solutes in the river and solutes in the ocean. The total salt content, measured as salinity (S_mix), is a proxy for the fractions of river and ocean water in each sample, and an array can be constructed based on these measurements and the known salinity of the river (S_river) and ocean (S_ocean) endmembers (Boyle et al., 1974):

$$f_\text{river} = \frac{S_\text{mix} - S_\text{ocean}}{S_\text{river} - S_\text{ocean}}, \tag{1a}$$

where f_river is the fraction of river water in the sample. Assuming mixing with an ocean endmember, the sum of the

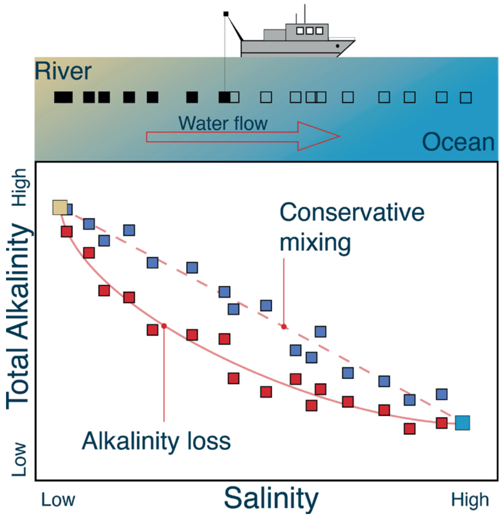

Figure 4. A schematic of a campaign sampling river water (left) out into ocean water (right). Salinity mixes conservatively, and by plotting the total alkalinity (TA) versus salinity, researchers can examine and quantify processes that remove alkalinity from the system as the river flows into the ocean. Conservative mixing is illustrated by the blue points. Nonconservative mixing and alkalinity loss is illustrated by the red points.

river and ocean fractions must equal to 1:

$$f_{\text{river}} + f_{\text{ocean}} = 1, \tag{1b}$$

with f_{ocean} being defined as the fraction of ocean water in the sample. As with salinity, TA and DIC are conservative quantities, meaning that they mix linearly and are not affected by temperature or pressure changes. If no chemical reactions are consuming or producing TA or DIC along the flow path, then the samples will fall on a conservative mixing array, namely

$$\text{TA}_{\text{mix}} = \text{TA}_{\text{river}} f_{\text{river}} + \text{TA}_{\text{ocean}} f_{\text{ocean}}, \tag{1c}$$

where the measured mixture value is a linear combination of the river and ocean endmembers. If the data fall on a straight line between the endmember values for salinity and alkalinity, then the alkalinity is not being produced or consumed in the system (e.g., the blue points in Fig. 4). Any net removal or addition of alkalinity will move the data from this conservative mixing line; i.e., the data will move below it for removal and above it for addition (e.g., the red points in Fig. 4). Critically, the signal of interest must be larger than the scatter in the data to quantitatively establish a reaction process, as illustrated by the scatter of data points in Fig. 4. At steady state, the alkalinity loss can be quantified by multiplying the river flux by the difference between these two curves.

The concepts of steady-state and (non-)conservative mixing are useful frameworks for setting up a study, interpreting the results, and quantifying biogeochemical processes over space and time and can be applied to any water property that mixes linearly. In this river example, DIC–salinity relationships could be used for quantifying carbon uptake and loss due to gas exchange, photosynthesis, and $CaCO_3$ precipitation. While this method can diagnose net changes to TA or DIC budgets due to chemical reactions, the speciation of these quantities may change significantly along the flow path due to the nonlinear nature of the carbonate system. For $p\text{CO}_2$ and pH, mixing relationships are more complicated because they are nonlinear functions of TA and DIC (Schulz et al., 2023, this Guide). One important assumption in this model is that mixing only occurs between two endmembers. If there are more than two endmembers interacting in the study area, then this binary mixing model is not appropriate, and deviations from linearity cannot be equated with chemical reaction. We discuss other methods of analyzing field data in Sect. 3.5.

3.2 Designing a suitable natural analog study

Determining whether a site is a suitable natural analog can be accomplished by asking a series of questions about its relevance to OAE deployment (Eisaman et al., 2023, this Guide) and/or its monitoring, reporting, and verification (MRV; Ho et al., 2023, this Guide; Fig. 5). When considering a candidate site, researchers should ask themselves what qualities make the site relevant to OAE. Relevance can be clearly established through the presence of either enhanced alkalinity and/or solid materials that are producing alkalinity through interaction with seawater. However, other processes such as particle loading and plume mixing may be appropriate, even in the absence of large alkalinity gradients (Fig. 1).

The next consideration is timescale. How fast does the system change, and can alkalinity effects be assessed with an effective sampling strategy? Matching the measurement scheme to the process timescale (Figs. 2, 3) is critical at this stage and should guide the choice of measurement platform(s) used (Sect. 3.3) and the associated measurement suite (Sect. 3.4). Alkalinity effects can only be assessed through to the counterfactual case, in a similar manner to how MRV will be conducted (Ho et al., 2023, this Guide). A control or counterfactual, either in space or in time, should be established and should be quantifiable from the OAE condition (Sect. 3.5). The platform, measurements, and counterfactual conditions will all determine the approach for extracting alkalinity effects from the study location (Sect. 3.5). In some cases, it may be useful to pair field observations with models to contextualize one's results (Sect. 3.6).

In summary, given all of these considerations, it is critical to think through how the results of the study will be synthesized into actionable information about OAE deployment and its MRV. For example, if a feedback on alkalinity is established, is it possible to relate that feedback to alkalinity loading to provide thresholds for OAE deployments or minimum detection limits for MRV? Quantifying efficiencies on CO_2 uptake as a function of alkalinity loading is another example

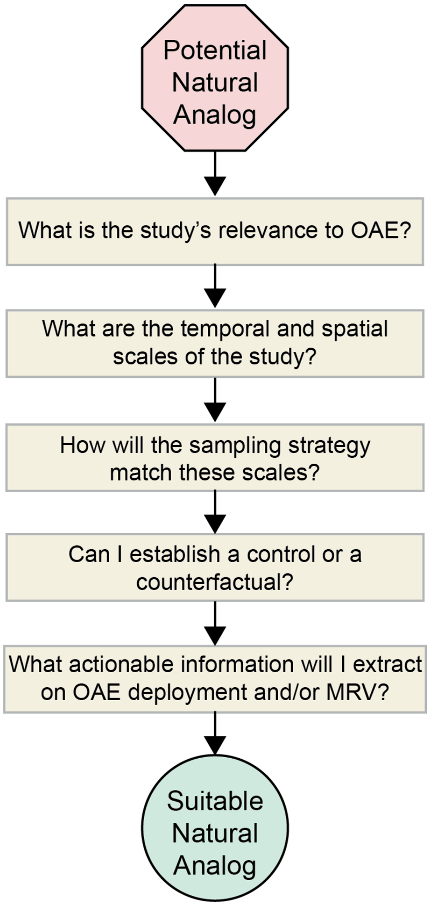

Figure 5. A list of relevant questions for deciding whether the study is suitable as a natural analog.

of a useful outcome from a natural analog. If these questions can be answered, then one has found oneself a natural analog. As shown in Fig. 1, rivers and their plumes, glacial fjords, the Black Sea, and whiting events in the Bahamas immediately stand out as targets for natural analog studies.

3.3 Choice of platform

Once a potential process or site is chosen, it is important to consider what measurements are best suited for the study. Measurements can be conducted either in the lab or in the field, on vessels, or remotely, using autonomous assets (depicted in the margins of Fig. 2). Choosing an appropriate platform and measurement suite will depend on the timescale of the process, access to equipment and instrumentation, and the practicality of the planned operations. Each platform operates within a specific window in both space and time, and these ranges should be considered when planning the field campaign.

- *Research vessels.* These have been part of the oceanographic toolkit for decades, from small boats all the way to 300+ ft (91.3 m) global-class ships. These vessels offer flexibility, a range of built-in scientific instrumentation and equipment, research labs, and well-trained crew. Many research stations around the world operate their own smaller vessels that can be chartered for surveys. They can sample across entire ocean basins but are limited in their temporal coverage to, at most, 2 months of continuous operation.

- *Moorings and time series.* These can be invaluable for studying a specific location over extended periods of time. Time series stations are critical for establishing the ranges of natural variability and can be outfitted with a number of sensors and instruments. However, their applicability to a broader spatial scale is often limited without other regional data or a model for context.

- *Remote sensing.* These instruments can be tasked to investigate ocean surface processes and essentially cover the entire planet. Their timescales are often limited by their orbits and thus cannot provide a very high temporal resolution. Smaller constellations of cube satellites can sometimes be tasked to give a very high (sub-meter) resolution and sometimes multiple transits in a single day, but their spatial scales are limited to coastal areas, and many are never tasked for open-ocean work. Satellites are capable of imaging the surface expression of bloom events (Neukermans et al., 2023) and $CaCO_3$ precipitation features, such as whitings (Yao et al., 2023), as well as other optical properties, such as chlorophyll fluorescence. They could potentially measure alkalinity if proxied by salinity (Priyanka et al., 2022). However, their utility for measuring water chemistry, especially below the surface, is limited.

- *Uncrewed vehicles.* These are becoming an important part of observational networks. Gliders can provide a high spatial resolution, but their operating speeds are often slower than crewed vessels. Depending on the operation, this limitation can be overcome by deploying glider fleets with a suite of intercalibrated sensors. Their operations are also limited by power, either from batteries or access to solar or wind energy. Currently, gliders cannot sample the deep ocean and can also not operate in very shallow or tightly constrained locations due to navigation constraints. Some vehicles can be piloted and reprogrammed on the fly, but many gliders have fixed trajectories that are set upon deployment.

- *Profiling floats.* The floats, such as those used for the Argo and Biogeochemical Argo (BGC-ARGO) programs, have been immensely helpful for establishing state estimates of the global ocean. The integration of biogeochemical sensors is ongoing. However, many profiling floats are limited to the open ocean and cannot operate in coastal or shelf areas with shallow seabeds.

- *Geological archives*. The archives such as sediment cores from drilling programs can be investigated for time periods and geological events that are relevant for OAE.

3.4 Choice of measurement suite

Oceanographic platforms host a unique set of measurements and capabilities and come with tradeoffs between coverage, what one can measure, and how well one can measure it (Table 1; Bushinsky et al., 2019; Chai et al., 2020). Although bottle samples in the lab provide the highest precision and accuracy, they are limited in terms of sample throughput, preservation and shipping, and the need for expensive instrumentation. Underway or pumped systems can provide high-frequency surface data but can clog or foul and need a source water to be pumped through them. They are best suited for research vessels or moorings. In situ sensors can provide very high-frequency data and be deployed on a range of platforms, including gliders and profiling float. However, they must be calibrated, they can drift, and they are currently limited in terms of what parameters they can measure. Remote sensing from satellites has by far the greatest spatial coverage but is limited to the surface layer and by weather. Data are limited to optical measurements and imagery.

The natural variability in the site will be important to balance against one's analytical capabilities. For instance, if an estuary experiences tidal changes of $>100\,\mu\mathrm{mol\,kg^{-1}}$ alkalinity, then it may not be informative to take daily samples without taking tidal cycles into account. In situ sensors with lower precision may not be able to detect small alkalinity enhancements above large natural variations. In addition, it is important to consider which carbonate chemistry variables are ideally suited for the sampling scheme. Alkalinity and DIC are both conservative and can be diagnosed with models, as discussed in Sect. 3.1, but in many cases pH may be more effective as a diagnostic tracer of multiple processes (e.g., alkalinity enhancement and subsequent CO_2 uptake). Combined with its relatively high measurement precision, frequency of measurement, and sensor availability, pH may be an attractive parameter for many early studies, especially if it can be ground-truthed against alkalinity and DIC bottle data.

3.5 Establishing a control

In natural systems, there may not be a "perfect" control condition; instead, establishing relative changes between conditions (spatial, temporal, etc.) may be all one can do. However, these relative changes should be clear and measurable, given the sampling approach one has outlined. Controls can be established both in space and in time. For instance, different beaches, bays, or fjords can exhibit unique water chemistries and rock or sediment types. Setting up a similar survey or measurement scheme in two or more of these locations will yield a data set that can be easily compared and contrasted.

Systems also change over time. For instance, the water chemistry, or river state, can be used to compare geochemical processes when one endmember changes significantly from season to season. As an example, many rivers exhibit different solute concentrations and total water fluxes between the dry and rainy seasons. One season's survey can serve as a control for the second survey, provided that the conditions – and the expected geochemical signatures that result – change significantly on a seasonal basis. These conditions must be established in the context of the spatial and temporal timescales of the process of interest. In addition, similar assumptions for the steady-state nature of the surveys should be verified to ensure that the results can be effectively compared.

3.6 Isolating alkalinity effects in one's data

One of the main challenges when studying natural analogs in the context of OAE arises from potential concurrent effects of various confounding factors (e.g., temperature, salinity, nutrients, light, and other carbonate system parameters) varying in space and/or time along a gradient in TA. For example, alkalinity co-varies strongly with salinity on a global scale (Carter et al., 2014). Regional salinity–TA relationships may be better suited for coastal applications and may deviate significantly from this global relationship due to a number of biogeochemical processes (Hunt et al., 2021). Unequivocally attributing specific biogeochemical or ecosystem responses (e.g., $CaCO_3$ precipitation, species performance, and distribution) to a single environmental variable (e.g., TA) remains challenging. Targeted monitoring combined with statistical tools can help to assess the impact of confounding factors and identify relationships between various covarying factors and specific response variables. The choice of the statistical analysis depends on the particular question of interest and the complexity of the system to be studied.

- Multivariate analyses, such as principal component analysis (PCA), are useful tools to determine the underlying variability in a particular system without necessarily predicting the relationship between a specific dependent and independent variable(s); for example, this can be done to evaluate impacts of hydrography and carbonate chemistry on species performance (Kroeker et al., 2016) or to determine the main drivers of whiting events (Yao et al., 2023).

- Simple and multiple linear regression (MLR) models are common tools to assess the relationship between a particular response variable and the variability in one or more predictor variables; for example, this can be done to study the links between changes in carbonate chemistry (e.g., TA, $p\mathrm{CO}_2$, and $\Omega_{\mathrm{Calcite}}$) and biogeochemical or ecosystem responses (e.g., phytoplankton growth

Table 1. Tradeoffs associated with various measurement approaches.

	Bottle samples	Underway systems	In situ sensors	Remote sensing
Pros	Very high precision or accuracy Well standardized Large range of potential parameters	High frequency Well standardized Real-time data	Very high frequency Can profile Integration on a range of platforms Optical measurements possible	Wide spatial coverage High spatial resolution
Cons	Need for poisoning Requires shore-side lab Transport or shipping costs Lowest temporal resolution	Surface only Need vessel and pumped water Can foul or clog Limited parameters available	Lower precision or accuracy Sensor drift Integration can be challenging Limited parameters available	Limited temporal resolution Must be ground-truthed Surface only Only optical measurements

and calcification; Krumhardt et al., 2016; Silbiger et al., 2017). While general regression models come with clear benefits due to their simplicity, they can be restricting in their application, given the assumption of linearity between dependent and independent variable(s). For example, DIC and TA mix linearly, but pH and $p\mathrm{CO_2}$ do not. The model may thus perform poorly at capturing the complexity within certain data. In addition, regression models are highly sensitive to missing values and outliers, particularly in studies with a small sample size. It is advised to visually inspect the data and verify that the basic assumptions of the model are met before implementing a regression model. For example, graphical tools such as a scatterplot matrix and a bivariate correlation matrix help to verify that the relationships between dependent and independent variables are linear and that independent variables are not highly correlated (e.g., no multicollinearity). Once a model has been implemented, additional useful validation tools may include histograms and normal Q–Q plots to assess the normality or scatterplots to check for the constant variance of the residuals (i.e., homoscedasticity) across observations.

- Extensions to simple linear models may be applied in cases where particular assumptions are violated (e.g., nonlinearity, non-normal distribution, and heteroscedasticity). Possible modifications to the simple linear regression model include (1) generalized linear models (GLMs) for non-normal distributions or (2) generalized additive models (GAMs) for nonlinear relationships. Machine learning approaches (such as neural network models and random forest regressions) are gaining increasing attention for their ability to address nonlinearity, data complexity, and data scarcity and have proven skillful for generating predictive models to assess seasonal and interannual variability in carbonate chemistry across region and global scale (e.g., Bittig et al., 2018; Chen et al., 2019; Gregor and Gruber, 2021).

3.7 Regional modeling for field data validation

Studying natural analogs in the context of OAE has some clear limitations, largely due to the high complexity of the natural system and the difficulty in isolating the effects of TA from other environmental variables. Regional ocean models provide complementary tools that can help to disentangle the effects of confounding factors and determine the underlying mechanisms driving observed patterns in the field. For example, Gomez et al. (2021) implemented a high-resolution ocean–biogeochemical model for the Gulf of Mexico to assess long-term trends in OA progression on a regional scale. By decomposing the carbonate system into individual components (e.g., $p\mathrm{CO_2}$, pH, TA, and Ω_{Ar}), the authors showed that increased riverine alkalinity from the Mississippi River had a strong neutralizing effect on acidification near the river plume, and thus, it may act as a key driver influencing the spatiotemporal variability in the OA.

Regional models provide a verification framework for underlying physical and biogeochemical processes occurring in a system and, as such, can be a valuable tool to test our conceptual understanding of specific processes. Coupled physical–biogeochemical models to evaluate artificial ocean alkalinization on a regional scale are emerging (e.g., Butenschön et al., 2021; Mongin et al., 2021; Wang et al., 2023; see Fennel et al., 2023, this Guide, for details), yet similar modeling exercises applied to validate physical and biogeochemical processes along natural gradients are currently limited. In addition, many models currently lack the ability to model the precipitation and dissolution of carbonate minerals either in these sediments or in the water column, especially for metastable phases such as those found in reef environments. Implementing a regional model, for example, in areas where natural whiting events occur (e.g., Bahama Banks) could be useful to test some of the various proposed mechanisms (e.g., abiotic or biotic calcification and sediment resuspension) leading to the observed accumulation of suspended calcium-rich particles in the water column (e.g., Larson and Mylroie, 2014; Yao et al., 2023). A recent model simulation implemented a point source OAE approach in the Bering Sea to evaluate the efficiency in $\mathrm{CO_2}$ removal associated with a TA addition (Wang et al., 2023), but feedbacks associated with solid $CaCO_3$ cycling are currently missing from these modeling approaches. Similar approaches could give valuable insights when applied to natural analogs, for example, to study the dispersal of an alkaline river plume and associated impacts on pCO$_2$ and carbonate chemistry, porewater alkalinity fluxes, or the interaction of mineral dissolution and circulation in enclosed basins.

In addition to hypothesis testing, models provide a means to increase the spatiotemporal resolution of in situ observations. The coverage of in situ observational data is often spatially and temporally limited due to logistical constraints (e.g., financial constraints and a rare or remote location of the natural analog) and/or natural variability in the system (e.g., seasonality and episodic occurrence), which can make replication challenging. Using ocean models in conjunction with natural (and field) studies allows us to extrapolate spatially and temporally and fill in gaps in field observations.

In turn, models are evaluated with regard to how well observed patterns are reproduced, giving insights into underlying processes and how well these are represented in model parameterization. As such, model simulations rely on underlying assumptions that may not fully reproduce the high complexity and observational pattern of the natural system, in particular with regard to complex biological interactions (e.g., TA loss through carbonate mineral precipitation, trophic interactions, and acclimation). For steady-state systems (e.g., Black Sea), models do not explicitly resolve how the phytoplankton community responds to chronic high-TA exposure. Natural analogs provide an opportunity to study long-term responses and to continue developing modeling tools that are capable of resolving critically important biogeochemical processes.

3.8 Considerations for future natural analogs

Studying natural analogs in the context of OAE is currently to some degree hindered by the availability and quality of oceanographic data. The ongoing expansion of the observational infrastructure, including the deployment of autonomous vehicles such as gliders and BGC-ARGO floats continuously increases data coverage, quality, and availability, making it progressively easier and cheaper to study natural analogs. In situ profiling platforms such as Argo floats are particularly useful for off-shelf regional and basin-scale studies. Autonomous platforms allow the expansion from remotely sensed surface observations (e.g., satellite observations) to high-resolution depth profiles, enabling the study of depth-resolved physical and biogeochemical processes. Recent examples relevant for OAE include the depth-resolved detection of coccolithophores using BGC-ARGO floats (Terrats et al., 2020), increasing the spatial and temporal resolution of ship-based observations and expanding previous satellite-derived estimates to well below the surface layer.

4 Conclusions and key recommendations

The list of natural analogs and targets in the geological record highlighted in this chapter is by no means exclusive, and additional suitable natural sites are likely to be identified as additional questions in the context of OAE arise. Key recommendations for the study of natural analogs include the following:

1. Appropriate consideration must be given to the spatial and temporal scales of the study, with implications for the scale of carbon storage potential represented at the site.

2. The measurement scheme and instrumental toolkit must be matched to the study site in terms of scale, variability, and the signal-to-noise ratio. Models can be used to supplement in situ observations.

3. The study should be designed with outcomes applicable to OAE research, ideally with specific recommendations for deployment and/or monitoring of OAE at the study location or at places with similar Earth system processes.

Natural analogs with potentially different natural gradients, spatiotemporal resolution,s and/or processes that are not accounted for yet in the current surveys may be studied as sensor development and the ability to measure additional parameters evolve. Identifying key biogeochemical processes and ecosystem responses that can be measured and empirically linked to impacts of enhanced alkalinity is crucial in advancing our understanding of potential OAE impacts. Combining natural observational studies with controlled small-scale field manipulation or laboratory experiments will be key for addressing knowledge gaps and questions with regard to specific biogeochemical reactions, spatiotemporal patterns, and species interactions currently emerging from ongoing observational surveys. Importantly, no single approach will be able to resolve the full spatial and temporal extent and complexity of the system, and a combination of approaches (field studies, laboratory experiments, and modeling exercises) will be required to address different physical and biogeochemical processes and levels of complexity.

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Modelling considerations for research on ocean alkalinity enhancement (OAE)

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Abstract. The deliberate increase in ocean alkalinity (referred to as ocean alkalinity enhancement, or OAE) has been proposed as a method for removing CO_2 from the atmosphere. Before OAE can be implemented safely, efficiently, and at scale several research questions have to be addressed, including (1) which alkaline feedstocks are best suited and the doses in which they can be added safely, (2) how net carbon uptake can be measured and verified, and (3) what the potential ecosystem impacts are. These research questions cannot be addressed by direct observation alone but will require skilful and fit-for-purpose models. This article provides an overview of the most relevant modelling tools, including turbulence-, regional-, and global-scale biogeochemical models and techniques including approaches for model validation, data assimilation, and uncertainty estimation. Typical biogeochemical model assumptions and their limitations are discussed in the context of OAE research, which leads to an identification of further development needs to make models more applicable to OAE research questions. A description of typical steps in model validation is followed by proposed minimum criteria for what constitutes a model that is fit for its intended purpose. After providing an overview of approaches for sound integration of models and observations via data assimilation, the application of observing system simulation experiments (OSSEs) for observing system design is described within the context of OAE research. Criteria for model validation and intercomparison studies are presented. The article concludes with a summary of recommendations and potential pitfalls to be avoided.

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1 Introduction

Ocean alkalinity enhancement (OAE) refers to the deliberate increase in ocean alkalinity, which can be realized by either removing acidic substances from or adding alkaline substances to seawater. OAE is receiving increasing attention as a method for removing CO_2 from the atmosphere; such methods are referred to as marine carbon dioxide removal (mCDR) technologies (Renforth and Henderson, 2017). Natural analogues to OAE exist (Subhas et al., 2023, this Guide). An increase in the alkalinity of seawater leads to a repartitioning of its dissolved carbonate species with a shift toward bicarbonate and carbonate ions (Zeebe and Wolf-Gladrow, 2001; Renforth and Henderson, 2017), leading to a reduction in the aqueous CO_2 concentration and thus the partial pressure of CO_2 ($p\mathrm{CO}_2$; Schulz et al., 2023, this Guide). Since exchange of CO_2 between the ocean and atmosphere occurs when the surface ocean $p\mathrm{CO}_2$ is out of equilibrium with that of the atmosphere, a lowering of the ocean's $p\mathrm{CO}_2$ will lead to a net ingassing of atmospheric CO_2 (i.e., an increase in CO_2 uptake by the ocean or a decrease in outgassing due to OAE). This would increase the oceanic and decrease the atmospheric inventories of inorganic carbon; in other words, it would result in mCDR. In contrast to other mCDR technologies, OAE does not exacerbate ocean acidification (Ilyina et al., 2013). In fact, an increase in ocean alkalinity counteracts acidification, and while subsequent net uptake of atmospheric CO_2 largely restores pH to its pre-perturbation value, there is potential for OAE deployment to mitigate acidification impacts near injection sites (Mongin et al., 2021).

Several important research questions should be addressed before implementing OAE as an mCDR technology at scale. These include (1) which alkaline substances are best suited and the doses in which they can be added reliably while avoiding precipitation of calcium carbonate (which would decrease alkalinity and could result in runaway precipitation events); (2) how changes in alkalinity and net carbon uptake can be measured, verified, and reported (referred to as MRV; see Ho et al., 2023, this Guide) to enable meaningful carbon crediting; and (3) what the potential ecosystem impacts are and how harm to ecosystems be can avoided or minimized while maximizing potential benefits. These research questions cannot be addressed by direct observation alone but will require an integration of observations and numerical ocean models across a range of scales. Skilful and fit-for-purpose models will be essential for addressing many OAE research questions, including the MRV challenge, assessment of environmental impacts, and interpretation of natural analogues.

Ocean models are useful for a broad range of purposes, from idealized models for basic hypothesis testing of fundamental principles to realistic models for more applied uses (see primer on ocean biogeochemical models by Fennel et al., 2022). In the context of OAE research, this full range of models is applicable. For example, idealized models of particle–fluid interaction can inform us about dissolution and precipitation kinetics at the scale of particles; realistic local-scale models can inform us about near-field processes in the turbulent environment around injection sites; and larger-scale regional or global ocean models can be used to support observational design for field experiments, to demonstrate possible verification frameworks, and to address questions about global-scale feedbacks on ocean biogeochemistry. A common objective of all these modelling approaches is to realistically simulate the spatiotemporal evolution of the seawater carbon chemistry, including alkalinity and dissolved CO_2, and attribute that evolution to physical, chemical, and biological processes. Models that are suitable for this purpose will provide spatial and temporal context for properties that can be observed (but at much sparser temporal and spatial coverage than a model can provide) as well as estimates of properties and fluxes that cannot be directly observed but may be inferred because of known mechanistic relationships or patterns of correlation. Applications of realistic models rely on them being skilful and accurate, requiring that they include parameterizations of the relevant processes and that they are constrained by observations that contain sufficient meaningful information (what is sufficient depends on the application and research question). Methods for constraining models by observations through a statistically optimal combination of both are available. Application of such methods is referred to as data assimilation and provides the most accurate estimates of biogeochemical properties and fluxes (see Fennel et al., 2022, for fundamentals and code examples).

Model applications for OAE research include the following four general types:

- Hindcasts are model applications where a defined time period in the past was simulated. They can be unconstrained – in the sense that no observations are fed into the model except for initial, boundary, and forcing conditions – or constrained, where observations inform the model state via data assimilation. The latter are also referred to as optimal hindcasts or reanalyses.
- Nowcasts/forecasts are similar to constrained hindcasts but with the simulations carried out up to the present (referred to as nowcasts) or into the future (referred to as forecasts). The latter require assumptions about future forcing and boundary conditions, e.g., from other forecasts or climatologies or assuming persistence.
- Scenarios are unconstrained hindcasts or forecasts where one or more aspects of the model are systematically perturbed to assess the effect of the perturbation; for example, in paired simulations with and without OAE, one would be the realistic case and the other a scenario (also referred to as counterfactual in this case). These can be used to explore even very unlikely situations, which is often required in comprehensive uncertainty and risk assessment.

- Observing system simulation experiments (OSSEs) for observing system design use unconstrained and/or constrained hindcasts to evaluate the benefits of different sampling designs and optimize deployment of observational assets for a defined objective, including tradeoffs between different types of observation platforms.

Successful implementation of models to support OAE research and MRV is challenging because of the general sparseness of relevant biogeochemical observations and the limited lab, mesocosm, and field trial data available to date for model parameterization. Further, models are built at a process level and integrated to reveal behaviour at the emergent scale. As such, models comprise a collective hypothesis of the ocean's physical, biogeochemical, and ecosystem function, but it is important to recognize that model formulations of key processes related to OAE remain uncertain. It may well turn out that parameterizations of the carbonate system, plankton diversity and trophic interactions, small-scale turbulence, submesoscale subduction and restratification processes, and air–sea gas exchange in the current generation of models require improvement to robustly treat OAE-related questions.

The intended scope of this article is to provide an overview of the most relevant modelling tools for OAE research with high-level background information, illustrative examples, and references to more in-depth methodological descriptions and further examples. We aim to provide simple criteria and guidance for researchers on the current state of the art of biogeochemical modelling relevant to OAE research, keeping in mind short-term research goals in support of pilot deployments of OAE and long-term goals such as credible MRV in an ocean affected by large-scale deployment of OAE and possibly other CDR technologies.

2 Modelling approaches

This section provides a brief review of modelling tools available for OAE research with references to more in-depth methodological descriptions and examples, as well as a discussion of which approaches are most applicable to simulating essential processes in different circumstances. The presentation is structured using two complementary organizing principles, the spatial and temporal scales of the problem in Sect. 2.1 and the biogeochemical and ecological complexity represented by different modelling approaches in Sect. 2.2. Section 2 concludes with a summary of suggested future model development efforts in Sect. 2.3.

2.1 Modelling approaches across scales

In the near field, close to the site of an alkalinity increase, an accurate characterization of the spatiotemporal evolution of alkalized waters requires direct representation or parameterization of fluid and particle physics and seawater carbonate chemistry at scales ranging from micrometers to hundreds of metres, spanning turbulent to submesoscale processes (Sect. 2.1.1). In the far field, covering scales from tens of metres to hundreds of kilometres, where the effect of an alkalinity increase depends less on the details of how the alkalinity was added or how the acidity was removed and is instead dominated by ambient environmental processes, local- to regional-scale models are useful for simulating the impact of alkalinity increases, for verifying the intended perturbations in air–sea exchange of CO_2 and in carbonate system variables, and potentially for simulating ecosystem impacts (Sect. 2.1.2). Lastly, investigation of the effects of the global ocean's overturning circulation, impacts on atmospheric CO_2 levels, and Earth system feedbacks resulting from deployment of OAE and other CDR technology at scale requires global modelling approaches (Sect. 2.1.3).

2.1.1 Particle scale to near-field/turbulence scale (micrometre to kilometre scales)

Small-scale modelling approaches cover the range from micrometre-size particles to the turbulent scales and submesoscales in the near field of alkalinity additions. Simulating processes on these scales allows one to address questions about how turbulent mixing dilutes and disperses alkalized water and how it affects the settling, aggregation, disaggregation, precipitation, and dissolution of suspended particles. Near-field modelling has an important role to play in guiding the design of deployment strategies that mitigate environmental impacts and meet future permitting requirements and in supporting monitoring. During the initial dispersion and dilution phase of an alkalinity increase in the near field, the direct impacts on carbonate system variables are greatest, with waters exhibiting the largest elevations in pH and the highest potential for the formation of secondary precipitates. For particulate alkalinity feedstocks, turbulence close to the deployment site affects dissolution and settling rates, increasing dissolution and either accelerating or diminishing the settling of sedimentary particles compared to the Stokes settling speed (Fornari et al., 2016).

Distinct approaches to modelling at these scales involve different levels of parametrization and computational expense, with the relative utility of each approach being dependent on the scientific questions at hand. At the smallest scales, direct numerical simulations (DNSs) are the most computationally expensive and specialized class of fluid modelling, as they resolve flows down to the scales at which flow variances dissipate – typically centimetres or smaller in the ocean. Consequently, computational constraints imply that they cannot be run over domains larger than a few metres. DNSs are thus integrated over idealized physical domains (i.e., they lack realistic bathymetry) and are suited to investigating fundamental physical processes. For example, multiphase DNSs have been used to model the interaction of turbulence with gas bubbles (Farsoiya et al., 2023) and parti-

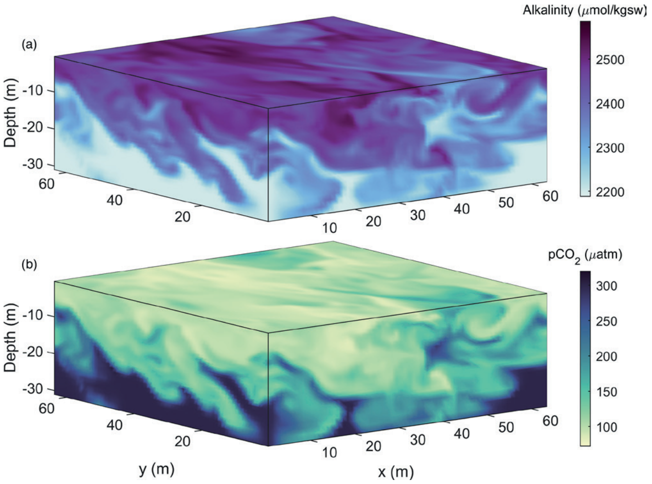

Figure 1. LES of near-surface turbulence coupled to a carbonate system solver. Alkalinity is added at a rate of 4 μmol kg^{-1} m^{-2} s^{-1} for 20 min to the top grid cell at the start of the simulation. Turbulence, generated by surface wind stress and cooling, sets the rate at which it mixes downwards **(a)** along with associated waters of lowered pCO$_2$ **(b)**. Turbulent plumes and eddies lead to inhomogeneities in water properties at scales of tens of metres.

cles (Fornari et al., 2016). Results from such studies provide an important test bed that can be used to develop parameterizations required in lower-resolution models.

A well-established approach to modelling the fluid flow at scales up to about 10 km uses large-eddy simulations (LESs), a class of model that directly solves the unsteady Navier–Stokes equations down to the largest turbulent scales on a high-resolution grid. Such models parameterize turbulence using a subgrid-scale model (e.g., Smagorinsky, 1963). An advantage of these models is their ability to simulate both an alkalized plume and the environmental turbulence into which the plume emerges. Once alkalized waters enter the surface boundary layer, LES models have an established history of simulating turbulence and mixing that is directly relevant to OAE research (e.g., Mensa et al., 2015; Taylor et al., 2020). An example of LESs of near-surface turbulence dispersing surface-deployed alkalinity downwards is illustrated in Fig. 1, where a physical model (Ramadhan et al., 2020) has been coupled to a carbonate solver (Lewis and Wallace, 1998). To date, LESs have rarely been coupled to biogeochemical models due to the computational expenses involved, though their inclusion may be increasingly feasible (Smith et al., 2018; Whitt et al., 2019). As LESs simulate flow physics at scales ranging from 10–10 000 m, they do not explicitly resolve the microscales of fluid motion and chemical reactions at particle scales. Nevertheless, the parameterizations of such processes can be included; for example, Liang et al. (2011) used models of bubble concentration and dissolved gas concentration in LESs to examine the influence of bubbles on air–sea gas exchange.

For alkalized plumes associated with outfalls from, for example, wastewater treatment plants, integral models (that assume plume properties such that the governing equations are simplified) have been developed to examine the initial dilution close to jets and buoyant plumes up to kilometre scales (Jirka et al., 1996). These models are highly configurable, enabling specific diffuser configurations as well as the potential to incorporate sediment-laden plumes with particle settling (Bleninger and Jirka, 2004). Results are commonly accepted for engineering purposes, defining mixing zones, and providing a fast “first look” at diffusion and mixing near an outfall site. However, these models rely on assumptions about the underlying physics of fluid flow (e.g., axisymmetric plumes and simplified entrainment rates) that may not be accurate under general oceanic conditions, and results will not include all effects of irregular bathymetry, finite domain size, or arbitrarily non-uniform ambient conditions. Nevertheless, their simplicity makes them very useful. For example, by combining several simple process models for plume dilution, particle dissolution, and carbon chemistry, Caserini et al. (2021) have simulated the initial dilution of slaked lime Ca(OH)$_2$ particles and alkalinity in a plume behind a moving vessel.

Other methods for modelling at this scale include Reynolds-averaged Navier–Stokes (RANS) and unsteady RANS (URANS), wherein fluctuations against a slowly varying or time mean background are parametrized, often using constant (large-)eddy diffusivities and viscosities. These approaches are often inaccurate at these scales, resulting in simulations that are too diffusive or lacking processes that are of leading-order importance to mixing (Golshan et al., 2017; Chang and Scotti, 2004).

There are multiple, potentially interacting sources of uncertainty to consider when evaluating the uncertainty in the applications described above. Perhaps best understood but still problematic is the uncertainty that arises from the computational intractability of simulating all the relevant scales in the micrometre-to-kilometre range at once, necessitating the different modelling approaches for different scales, with parameterizations to account for unresolved scales and scale interactions. The dissolved carbonate chemistry of seawater is relatively well parameterized (Zeebe and Wolf-Gladrow, 2001), but some modest uncertainties arise from approximations required for computational tractability (Smith et al., 2018). The least understood but potentially dominant source of uncertainty pertains to the representation of the microscale biological, chemical, and physical dynamics of particles, which is an active area of experimental and observational investigation (Subhas et al., 2022; Fuhr et al., 2022; Hartmann et al., 2023). While the explicit multiphase modelling of the particles themselves is computationally costly, an approach wherein the parametrized evolution of inertia-less Lagrangian particles is simulated may provide a fruitful middle ground, providing a mechanism to realistically determine the alkalinity release field associated with the advection, mixing, sinking, and dissolution of reactive mineral particles. These questions about particles apply to those released in OAE deployments as well as particles that precipitate from seawater in part due to OAE deployments and finally the role of ambient biotic and abiotic particles where OAE is deployed.

2.1.2 Local to regional scales (metres to kilometres)

Local- to regional-scale models that range in horizontal resolution from tens of metres to hundreds of kilometres are useful for simulating the impact of alkalinity injections beyond the immediate local area, where conditions do not depend on the details of how the alkalinity was added and instead are determined by regional-scale currents and other process, including the potential for biogenic feedbacks. These models are particularly useful to support OAE field experiments, including planning and observational design as well as analysis, integration, and synthesis of observations, and to facilitate interpretation of observations from natural analogues. Furthermore, local- and regional-scale models will likely prove to be indispensable for quantification of OAE effects in research settings, for guiding assessments of its environmental impacts, and for MRV during the potential implementation of OAE. A skilful model can simulate when and where changes in carbonate chemistry and the ensuing anomalies in air–sea CO_2 exchange occur and provide an estimate of the spatiotemporal extent of the biogeochemical properties affected by OAE.

Regional models have distinct advantages over global models in their ability to resolve the spatial scales on which OAE would be applied both experimentally and operationally and their documented skill in representing coastal and continental shelf processes more accurately (Mongin et al., 2016; Laurent et al., 2021). Examples of regional-model applications in the context of OAE include the recent studies by Mongin et al. (2021) and Wang et al. (2023). Mongin et al. (2021) used a coupled physical–biogeochemical–sediment model tailored to Australia's Great Barrier Reef to investigate the extent to which realistic OAE applied along a shipping line could alleviate anthropogenic ocean acidification on the reef. Wang et al. (2023) used a coupled ice–circulation–biogeochemical model of the Bering Sea to study the efficiency of OAE in coastal Alaska.

Implementation of a regional model in a target domain requires generation of a grid with associated bathymetry, specification of boundary conditions (including atmospheric forcing; information about ocean dynamics along the lateral boundaries of the domain; any fluxes of biogeochemical properties across the air–sea, sediment–water, and land–ocean boundaries; river inputs), and generation of initial conditions within the domain (Fennel et al., 2022). Different circulation models are available for implementation in domains targeted for OAE studies (see, e.g., Table 1 in Fennel et al., 2022), all with distinct strengths and established user communities. Particularly relevant in the context of studying coastal applications of OAE is a model's ability to accurately represent coastal topography, making unstructured grid models and models with terrain-following coordinates particularly attractive. Another feature to be considered is a model's ability to run in two-way nested configurations. In the more widely applied one-way nesting of domains, simulated conditions from a larger-scale model (referred to as the parent model) are used to generate the dynamic lateral boundary conditions of a smaller scale, higher-resolution model (the child model), which runs offline from the parent model. With two-way nesting, both models run simultaneously, and information is exchanged continually along their intersecting boundaries. This allows information generated within the high-resolution child domain (e.g., the spreading distribution of a tracer or alkalinity addition) to be received and propagated by the larger-scale parent model. In this context, model simulations are particularly useful if available in near-real time or in forecast mode. This requires specification of lateral boundary conditions and atmospheric forcing up to the present and into the future. Global $1/12°$ nowcasts and 10 d forecasts of ocean conditions are available from the Copernicus Marine Service (CMEMS, 2023), and atmospheric forcings up to the present and 10 d into the future are available from the European Centre for Medium Range Weather Forecasts (ECMWF, 2023).

One example of a high-resolution local-scale model with two-way nested domains is a framework developed for Bedford Basin in Halifax, Canada (Fig. 2; Laurent et al., 2024). The model framework consists of three nested ROMS models (ROMS is the Regional Ocean Modelling System; Haidvogel et al., 2008; Shchepetkin and McWilliams, 2005). The outermost ROMS domain has a resolution of 900 m and is nested one-way within the data-assimilative GLobal Ocean ReanalYsis and Simulation (GLORYS) reanalysis of physical and biogeochemical properties (Lellouche et al., 2021). Nested within are two models with increasingly higher resolutions of 200 and 60 m. Depending on the scientific objective to be addressed, the models can be run in one-way and two-way nested mode, where two-way nesting is computationally more demanding, and in hindcast or forecast mode. Implementation of dye tracers within the model (Wang et al., 2024) allows one to determine dynamic distribution patterns and residence times.

2.1.3 The global scale

A strength of global ocean models is their capacity to comprehensively represent the global overturning circulation and ocean ventilation. These processes control the timescales over which waters are sequestered in the ocean interior and determine how long surface waters are exposed to the atmosphere and can exchange properties, including CO_2, before being injected back into the ocean interior (Naveira Garabato et al., 2017). Similarly, the large-scale overturning circulation and the patterns associated with ventilation are important to consider in the context of deploying OAE at scale, as

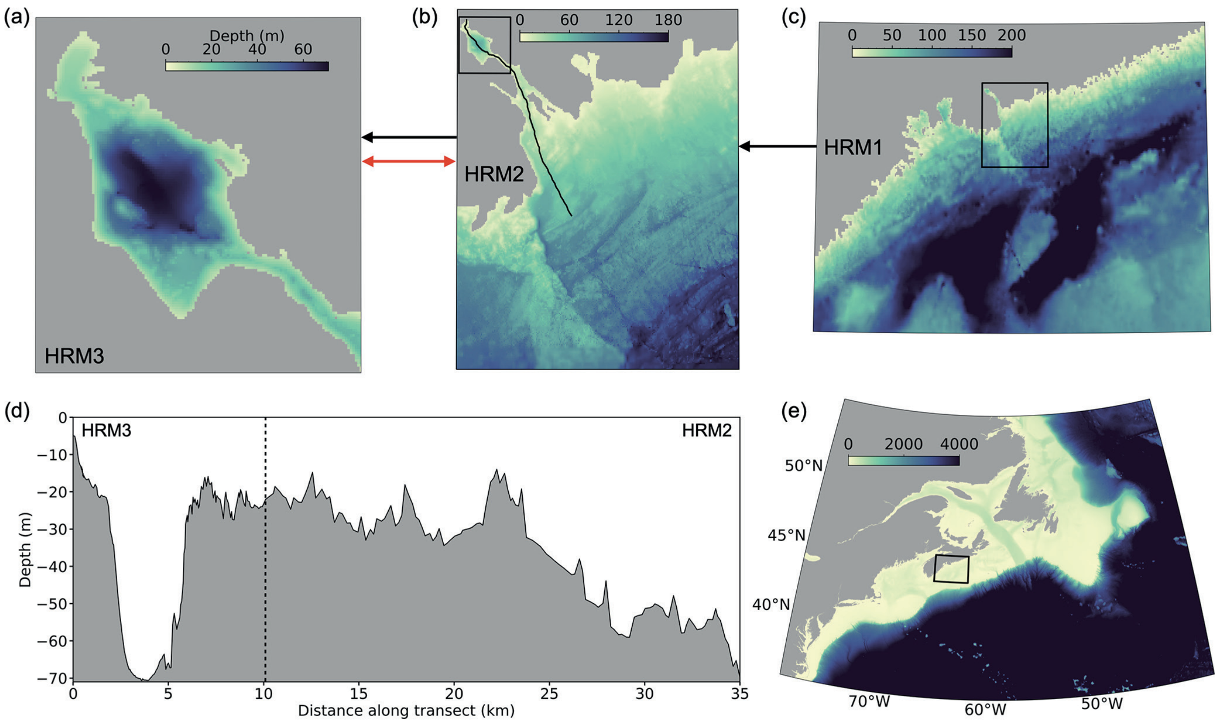

Figure 2. Nested configuration of three ROMS models for the Bedford Basin and the adjacent harbour in Halifax Regional Municipality (HRM). **(a)** The highest-resolution model (HRM3, 60 m) includes the 7 km long and 3 km wide Bedford Basin and The Narrows, a 20 m shallow narrow channel that connects the basin to the outer harbour. **(b)** The larger-scale model (HRM2, 200 m) includes Bedford Basin and Halifax Harbour as well as the adjacent shelf. **(c)** The largest-scale model (HRM3, 900 m) covers the central part of the Scotian Shelf as indicated in **(e)**. **(d)** Bathymetry along a section through HRM3 and HRM2, indicated by the black line in **(b)**. Lateral boundaries of HRM3, HRM2, and HRM1 are shown by black boxes in **(b)**, **(c)**, and **(e)**, respectively. Black arrows indicate the information flow between models in one-way nesting mode. The red arrow indicates that HRM1 and HRM2 can be run simultaneously with bi-directional flow of information (two-way coupled mode).

these patterns exert strong control on the efficiency of OAE at sequestering CO_2 (e.g., Burt et al., 2021).

When global ocean models are dynamically coupled with models of the land biosphere and the atmosphere, they are referred to as Earth system models (ESMs) and can be employed to explore Earth system feedbacks to mCDR. In the case of OAE, the main feedback is the change in atmospheric $p\mathrm{CO}_2$ and air–sea gas exchange that will result when CDR approaches are implemented at scale. While regional models have to be forced by atmospheric CO_2 concentrations, ESMs represent the atmospheric reservoir and are forced by CO_2 emissions into the atmosphere, which then interacts with land and ocean carbon reservoirs. Only the latter approach can account for OAE-induced reductions in the atmospheric CO_2 inventory, which, in turn, would lead to a systematic reduction in air–sea CO_2 fluxes. Regional models and global ocean models that do not explicitly represent the atmospheric CO_2 reservoir and instead are forced by prescribed atmospheric $p\mathrm{CO}_2$ cannot simulate the decline in atmospheric $p\mathrm{CO}_2$ due to OAE. Depending on the alkaline material applied, there may also be feedbacks associated with changes in temperature, albedo, nutrient cycles, and biological responses which can be studied with the help of ESMs.

Another important strength of global models relates to the fact that anomalies in air–sea CO_2 flux generated by OAE deployments will manifest over large spatiotemporal scales because CO_2 equilibrates with the atmosphere via gas exchange slowly. Alkalinity-enhanced waters can be transported far away from injection sites before equilibration is complete (He and Tyka, 2023). Consequently, OAE signals may exit the finite domain of regional models prior to full equilibration with the atmosphere (e.g., Wang et al., 2023). Because global models represent the entire ocean and can be integrated for centuries or longer, they enable full-scale assessments.

A primary challenge for global models, however, is that their horizontal resolution is necessarily limited by computational constraints (see example in Fig. 3). Most of the global ocean models contributing to the Coupled Model Intercomparison Project version 6 (CMIP6), for example, have horizontal resolutions of about 1° or roughly 100 km (Heuzé, 2021) and do not accurately represent biogeochemical processes along ocean margins (Laurent et al., 2021). Model

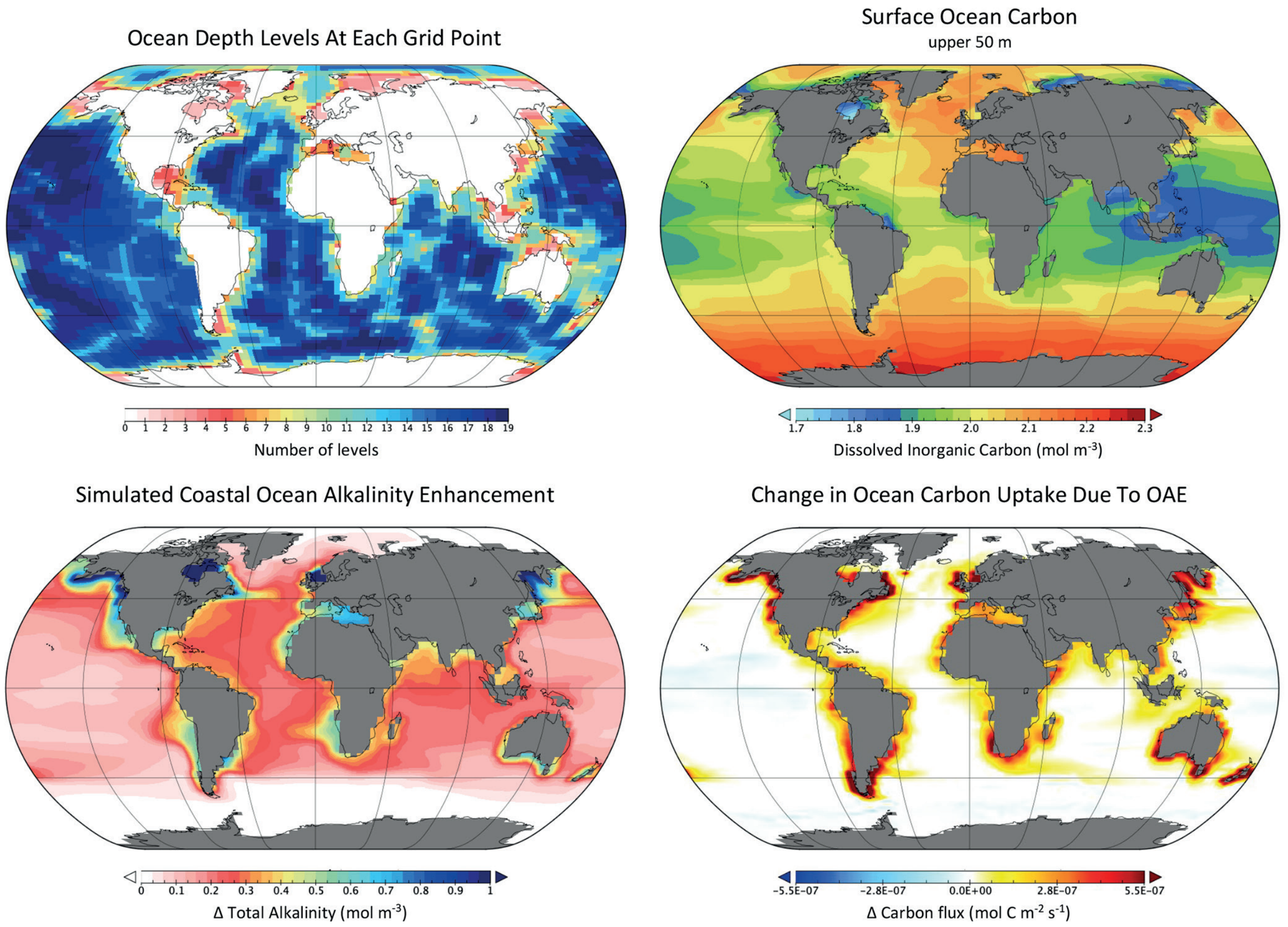

Figure 3. Example of Earth system model properties and output from the University of Victoria Earth System Climate Model (Keller et al., 2012; Mengis et al., 2020) including **(a)** the model bathymetry (depth levels) and **(b)** the simulated present-day dissolved inorganic carbon concentration (mol m^{-3}) averaged over the upper 50 m of the ocean. Panels **(c)** and **(d)** show results from a coastal OAE study by Feng et al. (2017), where the change in upper-ocean alkalinity (upper 50 m) and the air–sea flux of CO_2 are shown relative to the Representative Concentration Pathway (RCP) 8.5 control simulation. The Oliv100_Omega3.4 simulation from Feng et al. (2017) is shown, where 100 µm olivine grains were added to ice-free coastal grid cells in proportion to RCP8.5 CO_2 emissions (i.e., 1 mol of alkalinity per mole of emitted CO_2) until a sea surface aragonite Ω threshold of 3.4 was reached.

grid spacing imposes a limit on the dynamical scales that can be explicitly resolved in the models; this is particularly problematic for coarse-resolution global models because mesoscale eddies – i.e., motions on scales of about 10–100 km – dominate the variability in ocean flows (Stammer, 1997). Since coarse-resolution models cannot resolve mesoscale eddies explicitly, the rectified effects of these phenomena, including their role in transporting buoyancy and biogeochemical tracers, must be approximated with parameterizations (e.g., Gent and McWilliams, 1990).

Notably, the fidelity of the simulated flow in global models, including the imperfect nature of these parameterizations, projects strongly on the model's capacity to accurately simulate ventilation and the associated uptake of transient tracers, such as anthropogenic CO_2 or chlorofluorocarbons (CFCs), from the atmosphere (e.g., Long et al., 2021). Biases in the uptake of transient tracers will also have implications for a model's capacity to faithfully represent the impact of OAE, where the path of alkalinity-enhanced waters parcels in the surface ocean, and their subsequent transport to depth is a key control on the efficiency of carbon removal. Biases in the simulated flow are also an important determinant of the simulated distribution of biogeochemical tracers in the model's mean state. Hinrichs et al. (2023), for example, demonstrate that inaccuracies in the physical redistribution of alkalinity by the flow is a dominant mechanism contributing to biases in the alkalinity distributions simulated by CMIP6 models.

Finally, another important challenge associated with global ocean models is the requirement to represent the entire global ocean ecosystem with a single set of model parameters (e.g., Long et al., 2021; Sauerland et al., 2019). In particular, the biological pump is an important control on the distribution of biogeochemical tracers, including alkalinity and dissolved inorganic carbon (DIC). The magnitude of organic carbon export and the magnitude of biogenic calcium carbonate export are important controls on the distribution of alkalinity and DIC at the ocean surface and in the interior (e.g., Fry et al., 2015). These quantities are a product of ecosystem function and, since the global ocean is characterized by diverse biogeography (e.g., Barton et al., 2013), capturing global variations in the biological pump presents a challenge.

2.1.4 Integration across scales

Choosing the appropriate modelling tool for a given OAE-related question requires clarity about the scale of the problem to be addressed and the objectives of the model application. Approaches for OAE vary significantly with respect to the spatial footprint of alkalinity increase. Proposed methods for spreading alkalinity feedstocks at the surface ocean include the addition of reactive minerals (e.g., CaO, $Ca(OH)_2$, or $Mg(OH)_2$) in ship-propeller washes (e.g., Köhler et al., 2013; Caserini et al., 2021) or using other means (e.g., Gentile et al., 2022) along tracks from commercial or dedicated OAE vessels or through coastal outfalls (e.g., wastewater treatment or power plants); the addition of less-reactive minerals to corrosive or high-weathering environments (e.g., olivine spreading on beaches or mineral addition to riverine discharge; e.g., Montserrat et al., 2017; Foteinis et al., 2023; Mu et al., 2023); and electrochemically generated point sources of alkalinity that are discharged as highly alkaline seawater (e.g., House et al., 2009) from existing facilities (e.g., desalination and wastewater treatment plants), dedicated facilities (e.g., Wang et al., 2023), or an array of smaller infrastructure (e.g., grids of offshore wind turbines). Models for OAE research should represent these footprints of alkalinity increases appropriately for the questions being addressed.

There are research questions that fall relatively neatly into one of the three scale ranges described above in Sect. 2.1.1 to 2.1.3. For example, consideration of the near-field effects of different alkalinity feedstocks (e.g., dissolved versus particles) or analysis of the potential impacts from secondary $CaCO_3$ precipitation due to elevated alkalinity from a point source requires models that resolve the scales of turbulent motion. Examination of the change in air–sea CO_2 flux due to a broad and diffuse alkalinity increase is less demanding on model resolution, and regional-scale models are appropriate for this question. Investigation of Earth system feedbacks requires ESMs. However, there are also many aspects of OAE that require a bridging of scales. For example, when considering different deployment methods like discharge from vessels into the ocean surface boundary layer versus additions made through outfalls via surface or subsurface plumes, modelling requirements vary. In both cases, the resulting biogeochemical response may be affected by dynamics operating in the near field, where conditions are sensitive to the deployment method, and turbulence has to be considered, and the far field, where conditions do not depend on the details of how the alkalinity was added, and the air–sea flux of CO_2 is instead determined by ambient environmental processes. Another example is the challenge that anomalies in air–sea CO_2 flux generated by OAE deployments will manifest over large spatiotemporal scales because CO_2 equilibrates with the atmosphere via gas exchange slowly. Some interplay among the modelling tools described in Sect. 2.1.1 and 2.1.2 is likely going to be required. One straightforward approach would be to parameterize small-scale processes in the larger-scale models.

2.2 The range of biogeochemical realism and complexity

Application of biogeochemical ocean models for the purposes of OAE research and verification requires re-evaluation, and likely further development, of several model assumptions and features related to biogeochemical realism and complexity. For example, the internal sources and sinks of alkalinity are typically not explicitly represented in ocean models; this may become necessary in some circumstances but will be challenging (Sect. 2.2.1). OAE-related perturbations of alkalinity and other carbonate system properties and addition of macro- and micronutrients contained in some alkalinity feedstocks may result in biological and ecosystem responses that current biogeochemical models are not capable of representing but that would be relevant for the assessment of environmental impacts of OAE and the verification of its CDR efficiency (Sect. 2.2.2). Furthermore, depending on the environmental setting, sediments can be sources or sinks of alkalinity; these sediment–water fluxes need to be appropriately considered, including the potential impacts of OAE on their magnitude, in order to obtain complete and trustworthy carbon budgets (Sect. 2.2.3). Other boundary fluxes that require accurate specification are alkalinity inputs from rivers and groundwater (Sect. 2.2.4) and the air–sea flux of CO_2 across the air–sea interface (Sect. 2.2.5).

2.2.1 Representing alkalinity in seawater

Alkalinity is an emergent property that depends on the concentrations of numerous chemical species with distinct internal sources and sinks (Schulz et al., 2023, this Guide; Wolf-Gladrow et al., 2007; Middelburg et al., 2020). Skilful simulation of alkalinity in seawater may require explicit representation of its multiple biotic and abiotic sources and sinks, some of which are difficult to constrain. A major process by which alkalinity is consumed is the production of calcium carbonate. In the water column, this is predominantly a biotic process, performed by calcifiers, although "whiting" events, where calcium carbonate precipitates spontaneously from ambient seawater, can be locally important (e.g., Long et al., 2017).

Models vary in the degree of mechanistic sophistication with which biogenic calcification is represented. For example, some models explicitly resolve calcifiers, such as pelagic coccolithophores (e.g., Krumhardt et al., 2017) and foraminifera (Grigoratou et al., 2022) and, in some cases, also benthic corals, foraminifera, or calcifying higher trophic levels, and thus can mechanistically account for the associated alkalinity consumption. Alternatively, models can parameterize biotic production of carbonate and its subsequent sinking and dissolution, as a fraction of organic matter production combined with an assumed remineralization profile (e.g., Schmittner et al., 2008; Long et al., 2021). Dissolution of carbonate minerals produces alkalinity at the sediment surface and in the water column as carbonate particles sink. This can be represented with first-order abiotic dissolution kinetics with a dependence on the saturation state of ambient water in the water column (e.g., Sulpis et al., 2021); in the sediments (e.g., Emerson and Archer, 1990); or in micro-environments in aggregates or organisms (Barrett et al., 2014) with systematic differences for different crystal structures such as aragonite and calcite (Morse et al., 1980).

Production of alkalinity occurs via uptake of nitrate or nitrite by photoautotrophs, while remineralization consumes alkalinity when happening aerobically but generates alkalinity when occurring anaerobically, e.g., via denitrification (Fennel et al., 2008). Biotic production and consumption of alkalinity is stoichiometrically coupled to the release or uptake of nutrients and carbon, where non-Redfield processes such as nitrogen fixation or denitrification need to be specifically considered in the stoichiometric relationships (Paulmier et al., 2009).

Spontaneous precipitation of carbonate minerals in pelagic environments could occur when seawater is highly oversaturated with respect to carbonate (Moras et al., 2022) but is, to the best of our knowledge, not yet included in ocean models. When simulating OAE approaches that may generate high oversaturation with respect to carbonate, spontaneous precipitation of carbonates needs to be considered, especially when condensation nuclei are present. Appropriate approaches will have to be developed, e.g., using near-field models to mechanistically represent this process and a meta-model approach to develop parameterizations that are suitable for far-field and larger-scale models.

Organic compounds produced within the ocean or originating from land can also act as proton acceptors and contribute to organic alkalinity (e.g., Koeve and Oschlies, 2012; Ko et al., 2016; Middelburg et al., 2020) and will impact the carbonate system, the partial pressure of CO_2, and thus the air–sea CO_2 flux. Commonly, the contribution of organic alkalinity is deemed small enough in oceanic environments to be negligible, but this assumption should be reconsidered in the context of OAE, especially for coastal CDR deployments where the organic contribution to alkalinity is thought to be larger. To the best of our knowledge, models do not account for organic alkalinity. A better quantitative understanding of organic contributions to alkalinity is likely needed to parameterize or mechanistically represent its contribution in models. Similarly, it may be important in the context of mineral OAE deployments to account for local variations in $[Ca^{2+}]$ and $[Mg^{2+}]$ to accurately estimate the $p\mathrm{CO}_2$ anomalies generated by different OAE feedstocks. While these constituents have very long residence times in the ocean and are hence commonly assumed to vary conservatively in proportion to salinity, variations in their relative abundance has an impact on the thermodynamic equilibrium coefficients used to solve seawater carbonate chemistry (Hain et al., 2015).

2.2.2 Representing biological and ecological processes

A key question related to OAE is whether changes in carbonate chemistry induce differential responses in organisms. In the pelagic zone, OAE might shift the phytoplankton community composition, for example, due to distinct physiological sensitivities of different groups (e.g., Ferderer et al., 2022). Further, if OAE is accomplished via rock dissolution, carbonate versus silicate rock may impact the relative balance between phytoplankton functional groups (PFTs) such as calcifiers and diatoms, and changes in Mg and Ca ratios may also influence calcification (Bach et al., 2019). Additionally, ancillary constituents specific to particular feedstocks may have biological activity. Silicate rocks include bioreactive metals such as Fe, a micronutrient with the capacity to stimulate phytoplankton growth, and others that can be toxic when occurring in high concentrations, such as Ni and Cu, and may adversely impact phytoplankton and reduce primary productivity (Bach et al., 2019). The bioreactivity of these metals may be difficult to simulate in models as their dissolved concentrations can be partially mediated by complexation with organic ligands (Guo et al., 2022). Physical impacts of OAE feedstocks may also have important biological impacts through changes in the propagation of light in the surface ocean, and direct exposure to mineral particles may have additional impacts, e.g., on zooplankton through particle ingestion (Harvey, 2008; Fakhraee et al., 2023). Effects of OAE on plankton have the potential to propagate to higher trophic levels through marine food webs as the magnitude and quality of net primary productivity shifts, and trophic energy transfer is altered accordingly.

Simulating this full collection of processes in models is challenging. Dominant modelling paradigms for simulating planktonic ecosystems include PFT- and trait-based models (e.g., Negrete-Garcia et al., 2022). In these systems, physiological sensitivities are parameterized according to transfer functions that modulate rate processes – growth, for instance – on the basis of ambient environmental conditions. Nutrient limitation of growth is often represented using Michaelis–Menten kinetics wherein growth rates decline as nutrient concentrations become limiting. State-of-the-art ESMs represent PFTs with multiple nutrient co-limitation, which is essential to effectively simulate plankton biogeography of the global ocean. Diatoms, for example, are capable of high growth rates, enabling them to outcompete other phytoplankton under high-nutrient conditions, but their range is restricted to high latitudes and upwelling regions where there is sufficient silicate. If OAE were to modulate the concentration of constituents represented by multiple nutrient co-limitation models, it is possible such models could simulate the phytoplankton community response – though it is important to consider whether the models provide representations that are sufficiently robust for the magnitude of OAE-related perturbations. In some cases, models are missing key processes that would be required to mechanistically simulate certain effects. We are aware of no models that represent Ni toxicity, for instance. Including these effects, as well as a capacity to simulate secondary interactions, such as ligand complexation of metals in OAE feedstocks, will require significant investment in empirical experimentation to understand essential rate processes and physiological responses.

Shortcomings in the capacity of models to represent physiological responses to OAE is an important consideration for the ability of models to faithfully represent ecological impacts. Notably, electrochemical OAE techniques present a simpler set of processes to consider than using crushed-rock feedstocks, where ancillary constituents and physical dynamics come into play. For electrochemical OAE, the most likely biological feedback to consider relates to the impacts of changing carbonate chemistry on biogenic rates of calcification or phytoplankton growth rates (Paul and Bach, 2020). It is also possible that carbon limitation of phytoplankton growth (Paul and Bach, 2020; Riebesell et al., 1993) may also be important. Empirical research exploring physiological sensitivities should be used to develop prioritizations of key model processes comprising early targets for implementation. Model documentations should use consistent stoichiometric relations to link alkalinity changes to those of nutrients and carbon (Paulmier et al., 2009) and state the assumptions made about carbonate formation and dissolution.

2.2.3 Representing sediment–water exchanges

The exchange of solutes between the sediments and overlying water influences ocean chemistry, including the properties of the carbonate system (Burdige, 2007). Depending on location and timescale, OAE may affect these exchanges and should be appropriately considered in models. Sediments influence the marine carbonate system primarily through the remineralization of organic matter, which returns DIC to overlying water (and alkalinity if this remineralization occurs anaerobically), and the dissolution of biogenic silicate or carbonate minerals. $CaCO_3$ is of particular importance as its dissolution releases alkalinity, while its burial is an alkalinity sink, and the balance between the two is a key control on the ocean's alkalinity balance over timescales approaching 10^4 years (Middelburg et al., 2020). Furthermore, remineralization and other microbial metabolisms, such as "cable bacteria," can significantly lower pore water pH by several pH units below seawater values (Meysman and Montserrat, 2017). This can drive dissolution of $CaCO_3$ and generate alkalinity in the sediments, even in shallow waters when the overlying water is supersaturated (Rau et al., 2012).

Representing these processes in coastal and shelf sediments (< 200 m) is challenging. Shallow water depths and high productivity result in a significant delivery of organic matter to the sediments that is much larger than in the deep ocean. As a result, the relative importance of sediments in organic matter remineralization is larger, and production of alkalinity by anaerobic metabolisms is more important in these shallow sediments than in the deep ocean (Seitzinger et al., 2006; Jahnke, 2010; Huettel et al., 2014; Chua et al., 2022). In addition, these environments are dynamic, with organic supply and bottom water conditions varying on tidal, seasonal, and interannual timescales. Accounting for the exchange between sediments and overlying water and its variability on tidal, seasonal, and interannual timescales will likely be necessary in regional and global biogeochemical models that aim to simulate alkalinity cycling in coastal and shelf seas, even for relatively short simulation durations of months to years.

The choice of approach to modelling sediments may depend on the sediment type. For example, the mechanisms transporting solutes across the sediment–water interface can be divided into two categories depending on the sediment's grain size. In coarse sediments, i.e., permeable sands, pressure gradients drive flow through the seabed, replenishing sediment oxygen content (Huettel et al., 2014). Organic carbon stores are low, and remineralization was long thought to be primarily aerobic. However, evidence has emerged relatively recently that anaerobic remineralization in sandy sediments is more important than originally thought (Chua et al., 2022, and references therein). Idealized models that represent the three-dimensional sediment structure illustrate the importance of turbulence and oscillatory flows in permeable sediments (see Box 2 in Chua et al., 2022). These models are highly localized and computationally demanding, prohibiting their coupling with ocean biogeochemical models. Thus, permeable sediments are currently not well represented in regional or global ocean biogeochemical models.

In cohesive, fine-grained sediments with low permeability, i.e., muds, transport is limited by diffusion or faunal-mediated mixing and exchange processes, i.e., bioirrigation or bioturbation (Meysman et al., 2006; Aller, 2001). In these environments, detailed multicomponent reactive-transport models of sediment biogeochemistry – so called diagenetic models – can reproduce carbon remineralization rates partitioned between aerobic and anaerobic pathways, precipitation/dissolution reactions between sediment grains and porewaters, and the transport of solutes across the sediment–water interface (Boudreau, 1997; Middelburg et al., 2020). These mechanistic models will be useful for detailed investigations into how perturbations of the carbonate system in seawater overlying the sediments affect their biogeochemistry and for addressing questions about the potential influence of particulate alkalinity feedstocks settling to the seafloor (Montserrat et al., 2017; Meysman and Montserrat, 2017). However, typically these models are one-dimensional and applied to a few representative locations. Coupling fully explicit diagenetic models to three-dimensional ocean biogeochemical models, while conceptually straightforward, is computationally prohibitive. Instead, depth-integrated sediment processes have been implemented as bottom boundary conditions (e.g., Moriarty et al., 2017, 2018; Laurent et al., 2016). For example, Laurent et al. (2016) used a diagenetic model in a "meta-modelling" approach to estimate bottom boundary nutrient fluxes for a regional-scale biogeochemical model. By parameterizing the diagenetic model with detailed geochemical data (porewater profiles and nutrient fluxes) from a few individual locations, then forcing it over a range of expected bottom water conditions, they developed empirical functions relating sediment fluxes to bottom water conditions that could be used to parameterize bottom boundary conditions in the water column model. A similar approach could be used in OAE models to parameterize how sediment biogeochemistry may alter alkalinity fluxes, for example, how redox sensitive processes, such as coupled nitrification–denitrification or sulfate reduction coupled to pyrite burial, both of which may produce alkalinity (Soetaert et al., 2007), may respond to changes in bottom water oxygen or organic matter loading.

When considering the long-term storage of CO_2 in global-scale ESMs, the interactions between sediments and the deep ocean (>1000 m bottom depth) may need to be considered. In this environment most organic matter remineralization occurs in the water column, and the small amount of organic matter reaching the seafloor is remineralized aerobically with little to no release of alkalinity. In this case, sediment remineralization can likely be either ignored or implemented as a reflective boundary condition where the simulated particulate organic carbon (POC) flux to the seafloor is immediately returned as DIC and remineralized nutrients. However, the dissolution or preservation of $CaCO_3$ in deep sediments is critical to controlling deep-water alkalinity and may be important in model simulations that aim to quantify OAE effects on the timescales associated with the large-scale global overturning circulation. $CaCO_3$ solubility increases with pressure and decreasing pH, and $CaCO_3$ eventually becomes undersaturated at depth. The depth at which sinking $CaCO_3$ balances its dissolution is referred to as the carbonate compensation depth (CCD). An increase in bottom water CO_3^{2-} or $CaCO_3$ deposition will deepen the CCD, burying $CaCO_3$, trapping alkalinity, and lowering the alkalinity budget of the ocean. Conversely if $CaCO_3$ rain rate or CO_3^{2-} concentration decreases, the CCD will shoal, and previously buried $CaCO_3$ will dissolve, releasing alkalinity to the deep ocean. CCD compensation therefore opposes any forcing of the deep ocean carbonate system and therefore dampens the rise in CO_2 in the atmosphere but will also counteract any potential OAE solution (see Renforth and Henderson, 2017, for a detailed explanation). Although most $CaCO_3$ dissolution occurs in the sediments, there is no consensus as to the level of detail this needs to be represented in models. Some global models employed to investigate large-scale OAE include calcium carbonate dynamics at the sediment surface (Ilyina et al., 2013); others disregard this process (Keller et al., 2014).

Often global models will parameterize $CaCO_3$ burial as a function of saturation state. Such an approach is effective for resolving CCD dynamics over geological timescales ($\sim 10\,000$ years), but not over the century to millennial timescales of CCD readjustment. Models that fully couple sediment diagenesis can resolve these dynamics (Gehlen et al., 2008), but the computational demand can make them ineffective. One solution is the approach of Boudreau et al. (2010, 2018). By suggesting that $CaCO_3$ dissolution dynamics are controlled by transport of dissolution products across the benthic boundary layer, they were able to derive equations predicting CCD depth and $CaCO_3$ dissolution based on bottom water CO_3^{2-} and $CaCO_3$ rain rate and avoiding a detailed representation of the sediments. These equations, combined with model bathymetry, can parameterize sediment CO_3^{2-} flux as a boundary condition and suitably account for transient sediment $CaCO_3$ dissolution in large-scale ESMs while avoiding the computational demands of a fully coupled ocean circulation–diagenesis model.

2.2.4 Representing river and groundwater fluxes

Regional and global ocean biogeochemical models typically account for river inputs, including their contributions to alkalinity and DIC. In most models this is done by specifying alkalinity and DIC concentrations in imposed riverine freshwater fluxes, although accurate prescription of these concentrations can be challenging. Typically, a combination of direct river measurements where available, output from watershed models (e.g., Seitzinger et al., 2010), and extrapolations of coastal ocean measurements to a freshwater endmember (e.g., Rutherford et al., 2021) is used. Solute inputs from groundwater are typically ignored but could be important locally. In high-resolution coastal domains near urban areas, sewage input may be an additional important source of carbon, nutrients, and alkalinity.

It is important to note that land-based CDR applications may have an important effect on ocean alkalinity dynamics through riverine and groundwater delivery of solutes. Terrestrial OAE equivalents broadly referred to as enhanced rock weathering (ERW) rely on the application of lime or pulverized silicate or carbonate rocks on land and in rivers. These strategies aim to generate CO_2 uptake locally but yield a leaching flux of bicarbonate into freshwater systems and subsequent transport into the coastal ocean. Field trials and some commercial applications are currently underway, most of them with the implicit or explicit assumption that the enhanced delivery of alkalinity will generate carbon removal in the ocean (Köhler et al., 2010; Taylor et al., 2016; Bach et al., 2019). There is a need for coordinated efforts to improve quantification of background riverine fluxes and establish initiatives to effectively track the solute additions from ERW.

2.2.5 Representing air–sea gas exchange

The calculation of air–sea gas exchange is necessary for the quantification of net carbon uptake from OAE in models. Biogeochemical models typically represent this exchange using a bulk relationship that depends on the product of the gas transfer velocity and the effective air–sea concentration difference (Fairall et al., 2000). However, the gas transfer velocity remains highly uncertain and is sensitive to a collection of processes that vary across scales, including sea state, boundary layer turbulence, bubble dynamics, and concentrations of surfactants. The most widely used parameterizations of the gas transfer velocity use empirical fits to observations to construct a functional relation dependent on wind speed only, under the premise that turbulence and bubbles (via the breaking of surface gravity waves) are predominantly determined by wind stress (Wanninkhof, 2014). This neglects processes that could be regionally important such as convection, modification by biological surfactants, rain, and wave–current interactions while vastly simplifying the effects of wave breaking and bubbles. Although different dependencies on wind speed have been proposed (quadratic, cubic, hybrid), parameterizing the gas transfer coefficient as a quadratic function of the 10 m wind speed is the most common (Wanninkhof, 1992, 2014). This relationship is supported by direct measurements of air–sea flux at intermediate wind speeds (3–15 $\mathrm{m\,s^{-1}}$), but at low wind speeds ($< 3\,\mathrm{m\,s^{-1}}$), non-wind effects can have an important impact on gas transfer. At high wind speeds ($> 15\,\mathrm{m\,s^{-1}}$), breaking waves and bubble injection enhance gas exchange for lower-solubility gases such as $\mathrm{CO_2}$ (Bell et al., 2017). Therefore, quadratic fits tend to underestimate the gas exchange at low and high wind speeds (Bell et al., 2017).

More complex air–sea exchange parameterizations account for processes such as bubbles, near-surface gradients, and buoyancy-driven convection (e.g., Liang et al., 2013; Fairall et al., 2000), but they depend upon a wider range of input variables. Other considerations in estimating flux arise from the nonlinear dependence on these variables, e.g., wind speed, which can lead to underestimates when made using daily averages rather than hourly measurements (Bates and Merlivat, 2001).

Notably, the gas transfer velocity (k_w) determines the kinetics of gas exchange, given a perturbation in surface ocean $p\mathrm{CO_2}$ away from equilibrium. The timescale for $\mathrm{CO_2}$ equilibration over the surface mixed layer can be fully quantified using the following expression:

$$\tau_{\text{gas-ex}} = \left(\frac{\partial \mathrm{CO_2}}{\partial \mathrm{DIC}}\right)^{-1} \left(\frac{h}{k_w}\right), \tag{1}$$

where h is the depth of the surface mixed layer, and the partial derivative $\partial\mathrm{CO_2}/\partial\mathrm{DIC}$ captures the thermodynamic state of the carbon system chemistry in seawater, specifically with respect to the amount that dissolved $\mathrm{CO_2}$ changes per unit change in DIC (Sarmiento and Gruber, 2006). This property is related to the buffer capacity and varies in roughly linear proportion to the carbonate ion concentration. The magnitude of $\left(\frac{\partial \mathrm{CO_2}}{\partial \mathrm{DIC}}\right)^{-1}$ is typically about 20, which explains why the equilibration timescale for $\mathrm{CO_2}$ is so long. The contribution of uncertainty in the gas exchange velocity to overall uncertainty in carbon uptake from OAE deployments will depend in part on the circulation regime involved. For example, in situations where alkalinity-enhanced water parcels are retained at the surface for timescales that are significantly longer than $\tau_{\text{gas-ex}}$, full equilibration will occur, and the impact of uncertainty in the gas exchange velocity will have limited influence on the overall uncertainty.

Even though OAE-induced additional air–sea $\mathrm{CO_2}$ fluxes will, even in hypothetical massive deployments, amount to at most a few gigatonnes of $\mathrm{CO_2}$ per year, which is typically not more than 1 % of the atmospheric $\mathrm{CO_2}$ inventory, this subtle difference in the treatment of the atmospheric boundary condition can be significant. Using prescribed atmospheric $p\mathrm{CO_2}$ that is unresponsive to marine CDR-induced air–sea $\mathrm{CO_2}$ fluxes has been shown to overestimate oceanic $\mathrm{CO_2}$ uptake by 2 %, 25 %, 100 %, and more than 500 % on annual, decadal, centennial, and millennial timescales, respectively (Oschlies, 2009). Simulations with prescribed atmospheric $p\mathrm{CO_2}$ need to take such systematic biases into account.

2.3 Model development needs for OAE research

While there is already substantial capacity for simulating ocean biogeochemical dynamics at global to regional scales, the discussion above implicates several areas where additional efforts are required to fully establish a modelling capability suitable for supporting OAE. These fall into four primary areas: (1) supporting multiscale simulations with sufficiently high-fidelity flow fields, (2) faithfully simulating the near-field dynamics associated with alkalinity addition, (3) capturing feedbacks to OAE owing to biological and geochemical responses, and (4) identifying whether there are reduced-complexity modelling approaches that might provide sufficiently robust estimates of the net effects of OAE.

As elucidated above, a primary consideration related to capturing OAE impacts is the fidelity of the simulated flow. Notably, OAE presents a somewhat novel use case requiring an effective multiscale modelling capability. A conceptually straightforward path to improving the representation of ocean circulation and mixing is to increase the resolution of the model grid. However, the computational demand of high-resolution simulations can only be met over more limited-area domains. Since the spatiotemporal footprint of OAE-related perturbations is likely to be large, there will be a need to represent large regions. An argument might be made, however, that the circulation in proximity of an OAE site is most important to capture with high-fidelity. This can be achieved with two-way nested regional models as described in see Sect. 2.1.2 but will require further development to couple in the near-field models described in Sect. 2.1.1. Native grid refinement, e.g., via unstructured grids, is another approach that may be pursued to effectively support OAE research.

The second area of model development relates to the requirement of faithfully representing the dynamics associated with alkalinity addition. Regional to global scales are the most relevant for simulating the air-to-sea exchange of CO_2 ensuing from OAE. It is important, however, to ensure that local processes affecting the mass fluxes and initial dispersal of alkalinity are handled appropriately. As illustrated above, DNSs or LESs (Sect. 2.1.1) can be leveraged to develop parameterizations for larger-scale models, including for crushed-rock feedstocks, where particle dynamics may be important, or techniques involving alkalinity-enhanced streams entering the ocean from outfall pipes. In addition to process fidelity, there are also numerical constraints to consider. For example, advection schemes used in most ocean general circulation models struggle to represent sharp gradients; large mass fluxes of alkalinity into single model grid points are likely to cause advection errors that may contaminate aspects of the model solutions, making interpretation difficult. More specifically, conservative advection schemes can be characterized in terms of their accuracy, monotonicity (i.e., ability to preserve sign), and linearity (i.e., ability to preserve additivity), and there are always tradeoffs to make between these properties. Research may be required to determine which schemes are best suited to the particular challenges associated with representing the advection of OAE signals.

The third area of model development relates to our capacity to fully capture the range of biogeochemical feedback associated with OAE. The class of processes to consider here is potentially large, and many have been touched on in Sect. 2.2.1 to 2.2.3. Precipitation dynamics, specific elemental components of alkalinity, biogenic responses mediated by physiological or ecological sensitivities, impacts and processes controlling the cycling of ancillary constituents, and accurate sediment–water exchange are all areas that merit consideration. Further efforts are required to understand and prioritize these areas of potential development, and, notably, their relative importance is likely to be regionally dependent.

Finally, it is important that models be tailored to address specific questions of relevance. In this context, it may be important to consider how much model complexity is required to capture the effects of perturbations, seeking parsimonious representations that are well supported by empirical constraints and invoking wherever possible a separation of concerns to isolate the factors contributing to uncertainty. For example, there are several near-field considerations that might be addressed using a combination of local observations and ultra-high-resolution modelling tools to generate estimates of alkalinity mass fluxes that are subsequently imposed as forcing in regional- to global-scale models. Another key question is how important it is to comprehensively simulate the mean state to faithfully capture the response to OAE perturbations for the purpose of MRV. For example, if it can be documented that biological feedbacks to OAE are of negligible concern, the core target for simulating OAE effects for MRV may be to capture the cumulative integral of air–sea CO_2 exchange associated with the induced surface ocean pCO_2 anomaly. The mean state of the seawater carbon system is relevant here as the background DIC and alkalinity fields determine the pCO_2 response per unit addition of alkalinity, but fully prognostic calculations of nutrient cycling may not be necessary.

3 Model validation and integration with observations

Whether a model is useful for OAE research depends on how accurately it represents the physical, chemical, and biological processes that are relevant to the specific research question to be addressed. Model validation, the evaluation of a model's performance, and estimation of uncertainties in model output should thus be integral parts of model implementation and application. It is important to note that any model, even after best efforts have been made to improve formulations and conduct the most thorough validation, will deviate from reality. Any model is, by definition, a simplification of the real world, and thus its output will be subject to uncertainties. Deviations of the model state from the real world can be reduced by applying statistical techniques, collectively referred to as data assimilation (DA) methods, that combine models with observations and yield the best possible estimates. The steps typically involved in model implementation and validation and possible integration with observations through data assimilation are shown in Fig. 4. In this section, we summarize the most important observation needs for model validation (Sect. 3.1), briefly describe typical metrics for model validation and articulate a reasonable minimum criterion (Sect. 3.2), give a high-level explanation of approaches for the formal statistical combination of models with observations through parameter optimization and state estimation (Sect. 3.3), and describe approaches for the specification of uncertainty in model outputs (Sect. 3.4).

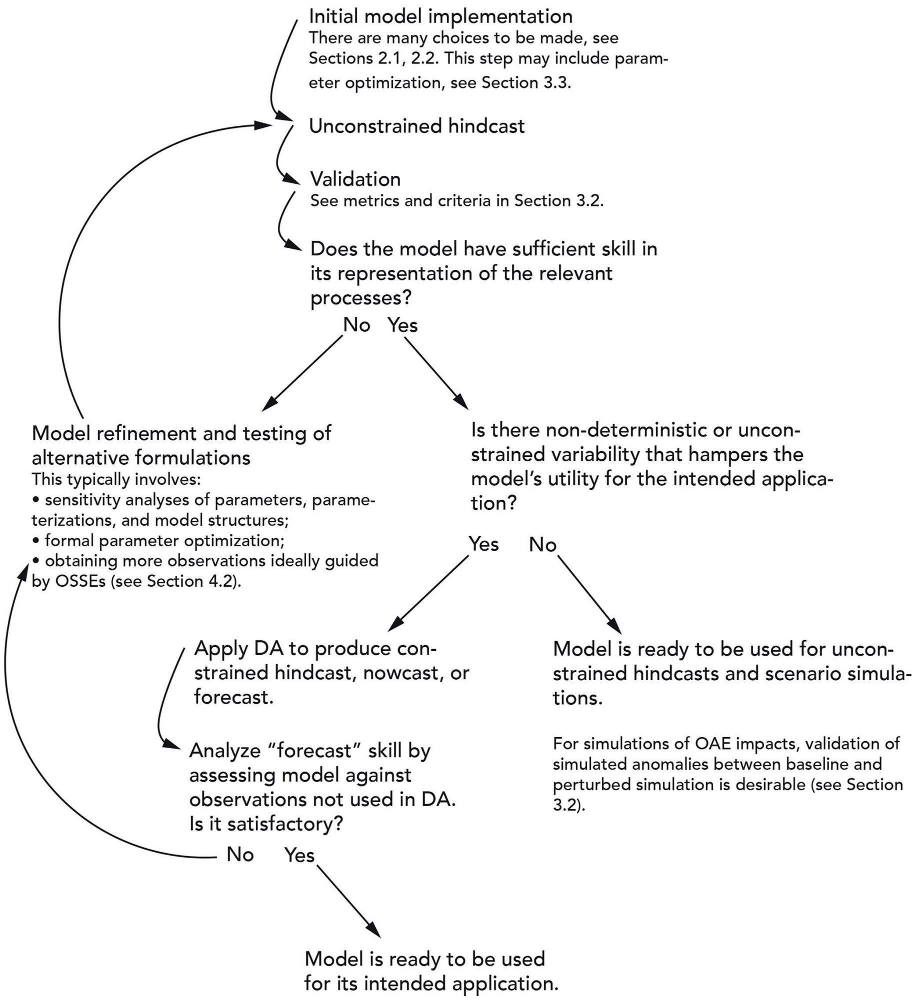

Figure 4. Typical steps in model implementation and validation.

3.1 Observation types for validation

Two fundamental requirements for models to be useful in the context of OAE research are high-fidelity representations of physical transport due to advection and mixing and of biogeochemical effects of OAE and most importantly changes in the inorganic carbon properties.

Observations for validation of the simulated physical transport of alkalized waters include temperature and salinity distributions, direct measurements of currents, surface drifter trajectories, sea surface height observations from satellite altimetry, and estimates of geostrophic flow derived from the latter. Additional metrics relevant for assessing the fidelity of the large-scale overturning circulation in global models include combinations of biogeochemical concentration and transient tracers. For example, oxygen can be useful for identifying large-scale transport pathways, even though it convolutes dynamical and biological information. Particularly valuable for assessing large-scale ocean transport on the timescales relevant for OAE are abiotic transient tracers such as chlorofluorocarbons (CFCs), sulfur hexafluoride (SF_6), and possibly the isotopes ^{39}Ar and ^{14}C. Observational approaches for validation at regional scales include explicit tracer studies for documenting dispersion properties using Rhodamine dye or SF_6.

In addition to the dynamics of the flow, model validation for OAE research requires the assessment of the fidelity of simulated carbonate chemistry variables (e.g., alkalinity, total DIC, pH, $p\mathrm{CO_2}$) and salinity and temperature, which are used to calculate the 13 thermodynamic equilibrium constants and conservative chemical species needed to constrain seawater acid–base chemistry in oxygenated seawater. Depending on the OAE approach and the model application, assessment may also require observed macronutrient (e.g., nitrate, silicate, or phosphate), micronutrient (e.g., Fe), and contaminant (e.g., Ni and Cr) measurements; bulk seawater properties related to biogeochemical cycling (e.g., dissolved organic carbon content, DOC; particulate inorganic carbon, PIC; chlorophyll fluorescence); and biogeochemical rates and fluxes (e.g., net community calcification).

It is not always feasible to obtain the ideal carbonate system observations for model validation. Temperature and salinity can be measured reliably across all ocean depths and, with greater uncertainty and only at the ocean surface, remotely from satellites. The technical capacity for seawater pH measurements is evolving rapidly, and sensors and systems now exist for pH measurements across nearly all depths, though the depth-capable systems require regular recalibration (e.g., Maurer et al., 2021). Similarly, there are numerous ways to observe surface ocean $p\mathrm{CO}_2$ using a variety of crewed, autonomous, and fixed-location platforms (e.g., ship-based, Saildrone, and moored systems). However, interior-ocean $p\mathrm{CO}_2$ observations remain challenging to obtain due to the need for calibration gases and a gas–water interface. Alkalinity titrations are predominantly performed on discrete bottle samples collected by hand, though autonomous titration systems are under development that enable in situ surface time series measurements (Shangguan et al., 2022). Microfluidic in situ alkalinity titrators are also under development that consume less reagent per sample but currently show higher uncertainties than discrete samples (Sonnichsen et al., 2023). Solid-state titrators that generate acid titrant in situ show promise for surface and subsurface alkalinity titrations, but these sensors are still undergoing development and validation (Briggs et al., 2017). DIC observations combine the limitations of current measurement systems for both the $p\mathrm{CO}_2$ and alkalinity, and there are only a handful of automated DIC titration systems rated for surface ocean measurements (e.g., Fassbender et al., 2015; Wang et al., 2015; Ringham, 2022). Theoretically, measurement of two of the carbonate system parameters in combination with temperature and salinity and some additional assumptions allows calculation of the other carbonate system parameters in seawater. Unfortunately, the pair of $p\mathrm{CO}_2$ and pH, which are the most accessible to autonomous measurement among the carbonate system parameters, provide nearly identical information about the system. Thus, the results of the calculations that use this pair have higher uncertainties than other combinations (Dickson and Riley, 1979; Millero, 2007; Cullison Gray et al., 2011; McLaughlin et al., 2015; Raimondi et al., 2019) and are therefore not ideal as a pair for model validation.

3.2 Validation metrics and approach

Validation relies on comparing the model output to observations, often in an iterative loop where the evaluation of a hindcast simulation is followed by model refinements followed in turn by a new hindcast and re-evaluation (Fig. 4 herein; Rothstein et al., 2015). Several evaluation metrics are commonly used (see Box 3 in Fennel et al., 2022). The three most common are the root-mean-square error (RMSE), the bias, and the correlation coefficient. All three are relative measures without any objective criterion that indicates which range of values is acceptable or unacceptable. In contrast, the Z scores, which consider variability within the observational data set, and the so-called model efficiency or model skill, which quantifies whether the model outperforms an observational climatology, are two metrics with built-in criteria as to whether a model's performance is acceptable or not (Fennel et al., 2022). Since no single metric provides a complete picture of a model's skill, multiple complementary metrics should always be used in combination (Stow et al., 2009). Furthermore, different points in space and time and a breadth of variable types should be part of any comprehensive validation because a model may provide accurate estimates for some variables, locations, or times but perform poorly for others (Doney et al., 2009).

For OAE research, validation can be considered to be a two-step challenge. First, it is necessary to validate unperturbed model baselines to gain confidence that the natural variability is represented appropriately and to quantify model uncertainties. One should compare model-simulated spatial fields and time series at strategic locations with appropriate observations to assess the model's skill at representing mean distributions as well as the variability for carbonate chemistry measurements and other relevant properties using several of the complementary quantitative metrics listed above. A model could be considered to be sufficiently validated when mean distributions, their seasonal variability, and the timing and magnitude of events (e.g., blooms, physical disturbances) are accurately represented. As described in Sect. 3.1, insufficient availability of observational constraints on carbonate system parameters presents a major challenge in this regard. In models applied for OAE research, it is particularly important to assess whether they realistically capture the distributions and variability in seawater properties that govern sensitivity of the seawater carbonate system; recent work by Hinrichs et al. (2023) shows that the current representation of alkalinity in state-of-the-art models requires improvements.

The second, even more difficult step is to test whether a model accurately represents alkalinity additions. OAE-related modelling studies thus far have relied on models that are validated only for baseline conditions. These are useful as sensitivity studies. However, validation of a model's ability to accurately represent the perturbations of an alkalinity addition is ultimately needed to address OAE science questions around environmental impacts and MRV. It is likely that the metrics described above for baseline validation are not suitable for this task. Validation should focus on quantifying whether the model accurately captures the anomalies created by OAE. This requires consideration of the spatial footprint and temporal evolution of perturbations and ideally a close integration of experimental, observational, and modelling efforts. For example, a model that is deemed skilful after baseline validation can be used to estimate the appropriate dosage of alkalinity additions, thus ensuring a measurable signal, and guide the observational strategy; subsequent validation may indicate model shortcomings that were not obvious in the baseline validation (e.g., diverging dissipation rates between model and field observations) and prompt model refinement in an iterative loop of model validation, improvement, and renewed experimental assessment (Fig. 4).

It is important to note that even with repeated steps of validation and model improvement, there is going to be a limit to the degree of realism that can be achieved with any model. Any model simulation will be prone to errors and uncertainties. Sources of error include inaccuracies in model inputs, numerical approximation schemes, insufficient process understanding, and inaccurate model parameters and parameterizations.

3.3 Data assimilation

Data assimilation (DA) is the process of improving the dynamical behaviour of models by statistically combining them with observations. There are a variety of DA techniques that rely on different mathematical and statistical approaches (Carrassi et al., 2018). Originally developed for numerical weather prediction, DA has been successfully applied to ocean models, including biogeochemical models (Mattern et al., 2017; Cossarini et al., 2019; Ciavatta et al., 2018; Verdy and Mazloff, 2017; Teruzzi et al., 2018; Fennel et al., 2019), but success critically depends on the information content of the available observations (Yu et al., 2018; Wang et al., 2020). While DA has been shown to yield large improvements in important parameters governing biogeochemical processes (Mattern et al., 2012; Schartau et al., 2017; Wang et al., 2020) and in model estimates of the physical and biogeochemical model state (Hu et al., 2012; Mattern et al., 2017; Ciavatta et al., 2018), it is only starting to be applied to carbonate system properties (Verdy and Mazloff, 2017; Carroll et al., 2020; Turner et al., 2023; Fig. 5).

Application of DA for ocean models is typically applied for one of two purposes: (1) to systematically optimize model parameters, e.g., phytoplankton growth and nutrient uptake or rates of background dispersion, and (2) to estimate the ocean state, e.g., distributions of temperature, phytoplankton biomass, alkalinity (see Fennel et al., 2022, for more details on the practical approaches and examples). The first purpose addresses systematic errors and biases in models and is useful when systematically modifying and testing different model formulations, while the second assumes an unbiased model and addresses unresolved stochasticity, e.g., correcting the locations of mesoscale eddies and current meanders. State estimation offers the potential to constrain variability such that OAE-induced perturbations of carbonate system parameters can be documented even if they are smaller than the natural variability in the study region. Joint estimation of physical and biogeochemical properties is common and can yield significant improvements for both types of properties (Yu et al., 2018). Hybrid approaches combining parameter and state estimation have also been proposed (Kitagawa, 1998; Mattern et al., 2012, 2014) but are less widely used.

Successful application of DA critically requires sufficient observations either of the properties that the model parameters to be estimated depend on or of the state variables that are being estimated. The most commonly used observation type in biogeochemical DA applications is satellite-based ocean colour observations (Mattern et al., 2017; Ciavatta et al., 2018; Teruzzi et al., 2018), which are available at a relatively high temporal resolution and cover large areas of the surface ocean. While these observations are useful for informing model estimates of properties directly linked to processes involving phytoplankton, they provide little information on the carbonate system. Dynamical models are able to quantitatively constrain processes that cannot be measured directly by inferring them from observable properties, but only if the observations contain enough relevant information about the processes of interest. Hence, one of the biggest challenges facing the application of DA to models of the marine carbonate system is the sparsity of observations of the marine carbonate system. Observations of pH, $p\mathrm{CO}_2$, alkalinity, and DIC used to be limited to moorings and research cruises but have more recently been extended by automated observing systems, such as gliders, BGC-Argo floats, and uncrewed surface vehicles (Bushinski et al., 2019). Although these measurements are becoming more common (Chai et al., 2020), they are still sparse compared to what is typically required for DA applications. In this context, an additional challenge is the problem of underdetermination, i.e., if multiple processes or properties of interest can cause a similar change in an observable property, then observing this property alone may not hold enough information to constrain these processes or properties, and more observations are needed (see Fig. 5 and code examples in Fennel et al., 2022). As new platforms are added to the observing system, DA techniques can help guide their optimal deployment and tailor observational programs to the specific needs of OAE applications (see Sect. 4.3 below). Furthermore, statistical and machine-learning approaches are being developed (e.g., Lohrenz et al., 2018; Bittig et al., 2018) that may help overcome the undersampling of carbonate system properties and could feed directly into DA applications.

There is an important subtlety to the application of data-assimilative models when quantifying net CO_2 uptake due to OAE, which is highly relevant for MRV. When the net CO_2 uptake is quantified by calculating the difference between two simulations, one with and one without OAE (one of these is realistic, the other counterfactual), it is not appropriate to assimilate biogeochemical observations of properties affected by the alkalinity enhancement. The assimilation of alkalinity-related observations to constrain one of the simulations in the pair would eliminate the ability to make comparisons between the two. However, assimilation of observations that are unaffected by OAE (e.g., temperature, salinity, oxygen, etc.) can be applied to both simulations of the pair. Further research and method development are required

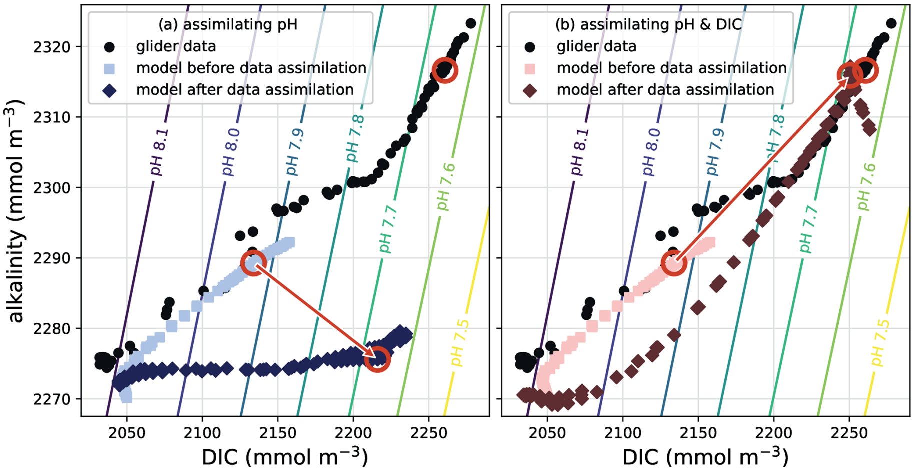

Figure 5. Example of a DA application for state estimation of carbonate system properties within a three-dimensional model of the California Current System. The symbols show glider data and model estimates at the measurement times and locations; one specific data point and its associated model estimates are highlighted by red circles. Each data point consists of measured pH alongside estimated alkalinity and DIC values (see Takeshita et al., 2021, for data source and details). In the model, pH is a diagnostic variable and primarily dependent on the model's alkalinity and DIC estimates. **(a)** When only pH data are assimilated, the model estimates are moved closer to the observed pH values by increments in alkalinity–DIC space that degrade the model's alkalinity estimates. **(b)** The model state estimates improve considerably by assimilating data for DIC (or alkalinity; not shown) together with the pH observations.

to identify the best approaches for leveraging DA in this context.

3.4 Uncertainty analysis

Model results should be paired with sound qualitative and quantitative uncertainty estimates, especially when used for practical decisions. Estimating the uncertainty in model simulations, however, is inherently difficult because typically one is most interested in simulation outputs for which observations are not available (e.g., unobserved or insufficiently observed properties or fluxes in the past, properties and fluxes in the future); hence, standard procedures and metrics for model validation (Sect. 3.2) are not helpful for this aspect. Uncertainty estimates could be based on extensive model parameter and configuration sensitivity studies and comparisons with models that include more realistic representations of uncertain or parameterized processes. Furthermore, since specification of uncertainty is an integral part of DA, DA methodologies provide a useful framework for estimating uncertainty, especially ensemble-based methods.

Any DA application requires uncertainty specification of the observations that are assimilated and can provide uncertainty estimates of the results of the assimilation procedure. Specification of uncertainty in the input data is necessary to inform the DA machinery about how much weight and reach each data point or data type should have in influencing the outcome. The more realistic the uncertainties in the input data, the better the DA outcomes in terms of explanatory or predictive skill. It is important to note that "better" does not mean more precise in this context. Overconfidence in the accuracy of assimilated observations will lead to overfitting and a degradation of predictive skill. In the case of parameter optimization, the output of the assimilation exercise is a set of optimized parameters. The uncertainty in optimal parameters, referred to as a posteriori errors, is determined by a Hessian analysis of the cost function in combination with the uncertainty in the input parameters before optimization, the so-called a priori errors (Thacker, 1989; Fennel et al., 2001). In the case of ensemble-based state estimation, the ensemble spread of the reanalyzed model state provides a spatially and temporally resolved estimate of the uncertainty in the reanalysis (Yu et al., 2018; Hu et al., 2012).

However, an important caveat is that subjectivity enters the uncertainty specification in all of these approaches. For example, in the case of parameter optimization the assumed a priori errors, their probability distributions, and the choice of the cost function are subjective and influence the a posteriori errors (but interestingly the values of the observations themselves do not). In the case of ensemble-based state estimation, the sources of uncertainty inherent in the model simulation have to be specified and simulated by generating variations within a model ensemble. Sources of uncertainty include errors in atmospheric forcing and boundary conditions, model parameters, and structural uncertainty. Uncertainty in forcing and boundary conditions is often represented by perturbing the time of sampling, uncertainty in parameters is represented by sampling from a probability distribution (based on a priori assumptions about the uncertainty in each parameter), and the structural uncertainty is typically represented via brute force inflation factors that amplify ensemble spread. Yu et al. (2018), Li et al. (2016), and Thacker et al. (2012) provide examples where different sources of model uncertainty are accounted for. While the mechanics by which the model ensemble is generated and spreads over time are thus subjective, grossly inappropriate choices will lead to obviously wrong or degraded reanalyses. The success of a DA exercise, which is best judged by an evaluation of whether the predictive power of the model has improved, thus provides a useful reality check on whether the choices for specifying uncertainty were appropriate.

How can the framework for specifying and estimating uncertainty from model ensembles be applied in the context of OAE research? Two different cases should be considered here: (1) model applications where the absolute value of quantities matters for the research question to be addressed and thus the uncertainty in the simulated output and (2) applications where information about the difference between a simulation with and without OAE is of interest and the uncertainty in this difference (e.g., the net CO_2 uptake and its uncertainty in the context of MRV). Examples of the first case include studies of the stability of added alkalinity (i.e., simulation of runaway calcium carbonate precipitation) and studies about the exposure of planktonic and benthic communities to high pH. In this case, the ensemble framework described above can be applied with the caveat that the specification of all the relevant sources of uncertainty is by no means trivial and subjective to some degree.

The second case is highly relevant for MRV of OAE, where one is interested in accurately quantifying the increase in seawater DIC due to OAE with well-characterized uncertainty. In this case, one would use two simulations that are based on an identical model set-up with only one difference, namely a source of alkalinity is applied to one (i.e., one of these two simulations is counterfactual or hypothetical; the other would typically be as realistic as possible). It may be tempting and is conceptually straightforward to apply the ensemble framework for each model of the pair and combine the resulting uncertainties via error propagation. However, in practice this would not provide meaningful estimates because there are sources of uncertainty that are unaffected by OAE (e.g., atmospheric forcing), and accounting for them may significantly overestimate uncertainty in the estimated net CO_2 uptake. A more appropriate approach would be to construct an ensemble of model pairs that explicitly accounts for uncertainty related to the impacts of alkalinity addition. How to specify and simulate the sources of uncertainty directly resulting from OAE in practice remains an open research question.

4 Model experimentation

In this section, we lay out general objectives for model experimentation in the context of OAE research and provide a short historical view of how these model studies have evolved (Sect. 4.1) followed by specific recommendations for observing system simulation experiments (Sect. 4.2) and model intercomparisons (Sect. 4.3).

4.1 General objectives of model experimentation

General objectives of OAE modelling include (1) gaining a better understanding of the biogeochemistry of OAE, including its effectiveness and side effects; (2) supporting experiments, field trials, or commercial deployments, including through the optimization of observing systems; (3) assessing global carbon-cycle and climate feedbacks; (4) understanding the role that OAE can play in climate mitigation efforts; and (5) supporting monitoring, reporting, and verification activities. At a conceptual level, model approaches for OAE can be classified as belonging to one of two groups: idealized or realistic. Idealized modelling approaches are typically driven by research questions of a fundamental nature and aim to develop or test hypotheses or provide improved process understanding while strongly simplifying a range of potentially complicating factors. They are useful for illustrating cause-and-effect relationships and the range of plausible outcomes given strong assumptions. In contrast, realistic modelling approaches aim to include a broad range of contributing factors as accurately as possible and provide detailed hindcasts or predictions that, if the model has skill, can be used for a range of practical applications. In practice, the dividing line between idealized and realistic models is blurry. Of course, no model will ever simulate all aspects of reality; hence even realistic simulations make many assumptions and are prone to errors from multiple sources. It can be effective to apply idealized and realistic approaches in a complementary manner and iteratively.

It is illustrative to briefly review how modelling for OAE research has developed over the course of the last decade. Much of the early work on OAE used idealized models. Model simulations were designed to investigate whether the theoretical concept of OAE could remove large amounts of CO_2 on the global scale. Rather than trying to account for the technical and socio-economic constraints of OAE deployment, the model experiments were designed to investigate what would happen if surface alkalinity were homogeneously increased by massive amounts via a constant addition rate over extremely large regions of the ocean, e.g., in all sea-ice-free waters (Paquay and Zeebe, 2013; Keller et al., 2014; Ilyina et al., 2013; Köhler et al., 2010, 2013). These simulated OAE deployments will never be realized, but the model results suggested that OAE can be viable as a CDR approach. A particular advantage of this idealized approach is that the effect of OAE was easy to detect against internal model variability; i.e., the signal-to-noise ratio is high. The next steps in modelling OAE have remained idealized but have begun to introduce more constraints and better mechanistic or empirically derived components as the experimental OAE date becomes available. Recently, modelling studies tailored to specific regions and modes of application have been conducted to support field trials or commercial deployment (Mongin et al., 2021; Wang et al., 2023). These applications must be as realistic as possible. None of the modelling studies published to date have simulated an actual OAE field trial.

4.2 Recommendations for observing system simulation experiments (OSSEs)

Observing system simulation experiments (OSSEs) use data-assimilative simulations to design new, or modify existing, observing systems such that deployments of observing assets, e.g., floats, gliders, moorings, or surface vehicles, are optimized. General overviews and best practices for OSSEs are provided by Halliwell et al. (2015) and Hoffman and Atlas (2016). Examples of applications to biogeochemical models include Ford (2021), Wang et al. (2020), and Denvil-Sommer et al. (2021). Their goal is to maximize the information gained from a new or modified observing system while keeping the number of required instruments, sensors, or deployments – and thereby cost and effort – low. OSSEs are especially valuable tools in the context of OAE research because the marine carbonate system is still undersampled, observing systems need to be designed and expanded, and new instruments need to be deployed and configured (Boyd et al., 2023).

In practice, this is done with the help of a pair of two different models or model versions, also referred to as twin experiments, as follows. A simulation of one of the models is considered to be the "truth." This simulation is also referred to as the "nature run", and synthetic observations are generated by subsampling this nature run. This subsampling can be repeated with different sampling schemes (e.g., different variable types; different numbers of profiles, transects, and/or fixed-location time series; etc.) to represent different configurations of the observing system. Finally, the synthetic observations are assimilated into the other model for which a non-assimilative simulation, the so-called "free run," is also available. The skill of this data-assimilative simulation, also referred to as the "forecast run," can be assessed against the free run using independent observations that are also sampled from the nature run. In this way the impact of different sets of observations on the data-assimilative model can be measured and assessed.

While conceptually straightforward, care and consideration are required when setting up OSSEs. For example, the choice of the two model versions making up the twin is important. If the models chosen for the truth and forecast runs are versions of the same model implementation that were generated by perturbing initial, forcing, or boundary conditions in one of them, the method is referred to as the "identical-twin" approach. If two different model types are used, they are "non-identical twins". The intermediate approach, where the same model type is used but in different configurations (e.g., different physical parameterizations and/or spatial resolution), is referred to as fraternal twin. The identical-twin approach has been more common in oceanic DA applications, although atmospheric OSSEs have shown that it can provide biased impact assessments (Hoffman and Atlas, 2016) typically because the error growth rate between the truth and forecast runs is insufficient. A direct comparison of the non-identical- and identical-twin approach for an ocean circulation model of the Gulf of Mexico has been conducted by Yu et al. (2018). In their assessment of the impacts of the existing observing system (consisting of satellites and Argo floats), the identical-twin approach provided overly optimistic improvements in model skill after assimilation of data from some observing assets (specifically sea surface height and temperature) but undervalued the contribution from temperature and salinity profiles. They concluded that skill assessments and OSSEs using the non-identical-twin approach are more robust. Similar concerns likely apply to OSSEs for biogeochemical properties, but this remains to be studied systematically.

4.3 Recommendations for intercomparisons

Coordinated, multi-model studies, commonly called model intercomparison projects, or MIPs, are a common approach to assessing model uncertainty. They can be used to explore the simulated range of model behaviours; to isolate the strengths and weaknesses of different models in a controlled setting; and to interpret, through idealized experiments, inter-model differences (IPCC, 2013). Carefully designed experiments can also offer a way to distinguish between errors particular to an individual model and those that might be more universal and should become priority targets for model improvement (IPCC, 2013). These studies rely on common agreed-upon protocols for simulating certain processes and writing of diagnostic output to ensure that best practices are followed, and results are comparable (e.g., Griffies et al., 2016). The best-known model intercomparison project is probably the Coupled Model Intercomparison Project (CMIP; Eyring et al., 2016), which is currently finishing up its sixth phase. Within CMIP6, the carbon dioxide removal intercomparison project (CDRMIP; Keller et al., 2018) is the first project to develop a model intercomparison experiment for ocean alkalinity enhancement. This and other MIP examples, including those conducted at smaller regional scales (Wilcox et al., 2023), provide a blueprint for developing coordinated multi-model experiments.

The following key practices have proven useful in previous coordinated multi-model comparisons. Since broad participation is typically desired, the protocol should be straightforward for modelling groups to implement, otherwise few will have the resources to participate. In practice this means avoiding new implementations of complex code or requiring too many or too long simulations. If applicable, forcing data should be centrally prepared and provided to participants in a standardized way that enables easy modification or reformatting, if needed, for use with different models. Using common simulations that modelling groups are likely to have completed already, e.g., climate change scenarios, as control runs and experimental branching points is helpful for minimizing the number of additional required simulations. It is useful to establish common practices that facilitate the production and analysis of the model output, e.g., what should be archived and shared (Juckes et al., 2020) and data standards governing the structure and required metadata for model output (Pascoe et al., 2020). Shared software to standardize model output, such as the Climate Model Output Rewriter (CMOR; https://cmor.llnl.gov/, last access: 15 November 2023) commonly used in CMIP, can be helpful. To maximize the use of model output, it should be made available for public download with digital object identifiers (DOIs). The Earth System Grid Federation (ESGF) is an example of such a system (Petrie et al., 2021). If applicable, preparing and providing quality-controlled observational data sets for model evaluation is useful for facilitating analytical efforts (Waliser et al., 2020). Coordinating the analysis is helpful to avoid duplicative efforts and ensure consistent application of evaluation metrics. Finally, the design of a coordinated multi-model experiment and all its procedures should be well documented in publications or permanently archived protocols. It is advisable to test the multi-model experiment with a small subset of models before inviting a large number of participants. Furthermore, it is worth remembering that the science questions must be appropriate. MIPs require much effort, and not every science question needs a MIP to be answered.

5 Summary and key recommendations

A range of modelling tools and analysis methods are available for OAE research to address questions from microscales to global scales; however, each of these tools and methods has limitations and caveats that model users and users of model-generated outputs need to be aware of. Furthermore, this new field of research poses questions and challenges that current tools were not designed to address, necessitating further development.

A common objective of all modelling approaches described in this article is to simulate the spatiotemporal evolution of carbon chemistry properties in seawater by accounting for the physical, chemical, and biological processes that determine this evolution. Idealized models, which neglect some aspects of reality in the interest of simplicity and clarity of assumptions, have long been used to test basic questions about OAE. As research questions are becoming more focussed on the practical aspects, feasibility, and ecosystem impacts of OAE, more realistic models are increasingly desirable. A skilful realistic model can provide spatial and temporal context for observations, including estimates of properties and fluxes not directly observed. Such models will include parameterizations of the relevant processes for the research objective to be addressed and will be constrained by observations that contain sufficient meaningful information. However, model formulations of several properties and processes relevant to OAE research remain uncertain or highly simplified. For example, presently used model representations of alkalinity in seawater are likely inadequate and may require explicit representation of at least some of the multiple biotic and abiotic sources and sinks of alkalinity; the mechanisms and triggers for spontaneous calcium carbonate precipitation are only beginning to be described and are not yet represented in models; and the impacts of pH perturbations on plankton diversity and trophic interactions remain an active area of study and unaccounted in biogeochemical models. Furthermore, it is difficult to obtain solid constraints on the seawater carbonate system, especially in sufficient spatial and temporal resolution for robust model validation and DA. Theoretically, knowledge of two of the carbonate system parameters allows calculation of the others, but unfortunately $p\mathrm{CO}_2$ and pH, the pair most accessible to autonomous measurement, result in high uncertainties.

One inherent challenge to OAE research is the multiscale nature of many of the relevant questions. Different modelling tools are available for different spatial scales. While some research questions may fall neatly within the limited spatial range of a particular model, many do not and require a bridging of scales that could be accomplished via new parameterizations yet to be developed or dynamic coupling of different modelling tools. It is important to emphasize that models have to be tailored to the questions they are meant to address. This means considering what level of model complexity is required and seeking parsimonious representations that are well supported by empirical constraints.

It is important to note that even after thorough validation, any model simulation will be prone to errors and uncertainties due to inaccuracies in model inputs, structural uncertainty due to numerical approximation schemes and insufficient process understanding or representation, and inaccurate model parameters and parameterizations. Deviations between models and reality can be reduced by DA, which is typically applied either to systematically optimize model parameters or to produce optimal estimates of the ocean state. Optimization of model parameters addresses systematic model errors and biases; it is useful for systematic testing of different model formulations during model design. State estimation assumes an unbiased model and addresses unresolved stochasticity, thus leading to model states that are in better agreement with the observed ocean state. However, successful application of DA critically requires sufficient observations. Currently, the biggest impediment to implementing data-assimilative models for OAE research is the sparsity of carbonate system observations. OSSEs, data-assimilative simulations that inform how to place observing assets most effectively, will prove useful in this context. It should also be noted that assimilation of carbonate system parameters is not appropriate when models are applied for MRV.

Uncertainty analysis is a necessary component of any quantitative research and will be an essential deliverable for effective approaches to MRV. Ensemble-based DA methodologies provide a useful framework for estimating uncertainty. Consideration of this framework illustrates that the "law of conservation of difficulty" applies here. Quantitative assumptions about the uncertainty distributions of input data and input parameters and of structural uncertainties inherent in the model are required to obtain an uncertainty estimate of the model output; in other words, difficult assumptions about errors have to be made somewhere. A common approach to assessing model uncertainty is by coordinated, multi-model intercomparison. Such studies can be used to explore the range of simulated behaviours and the strengths and weaknesses of different models, and, by elucidating inter-model differences, they can offer guidance on priority targets for model improvement.

Key recommendations arising from this article are as follows:

- Idealized models of particle–fluid interaction are recommended to address questions about dissolution and precipitation kinetics at the scale of particles; realistic local-scale models are recommended for addressing questions about near-field processes in the turbulent environment around injection sites; and larger-scale regional or global ocean models are recommended to support observational design for field experiments, to demonstrate possible verification frameworks, and to address questions about global-scale feedbacks on ocean biogeochemistry.

- When simulating OAE approaches that may generate high oversaturation with respect to carbonate, spontaneous precipitation of carbonates needs to be considered, and appropriate approaches should be developed, e.g., using near-field models to mechanistically represent this process and a meta-model approach to develop parameterizations that are suitable for far-field and larger-scale models.

- Shortcomings in current-generation models in terms of representing physiological responses of the plankton community to OAE (especially when using crushed-rock feedstocks) need to be recognized, better qualified, and addressed. Empirical research exploring physiological sensitivities should be used to develop prioritizations of key model processes comprising early targets for implementation.

- The exchange of solutes between the sediments and overlying water influences the seawater carbonate system with DIC from the remineralization of organic matter being returned to overlying water (and alkalinity if this remineralization occurs anaerobically), dissolution of $CaCO_3$ releasing alkalinity, and burial of $CaCO_3$ acting as an alkalinity sink. Accounting for these exchanges between sediments and overlying water and its variability on tidal, seasonal, interannual, and millennial timescales will likely be necessary in regional and global biogeochemical models that aim to simulate alkalinity cycling.

- River inputs of alkalinity and DIC in regional and global ocean biogeochemical models, including fluxes resulting from land-based CDR applications, should be accurately accounted for. Efforts should be made to improve quantification of riverine fluxes resulting from ongoing field trials and commercial applications and to establish initiatives to effectively track the solute additions from terrestrial alkalinity enhancements.

- When simulating large-scale deployment of OAE in ocean-only models with prescribed atmospheric CO_2, the subtle changes in the atmospheric CO_2 inventory resulting from CDR should be accounted for.

- Models should be tailored to the specific questions they are meant to address while seeking parsimonious representations that are well supported by empirical constraints. For example, for the purpose of MRV it may be appropriate to neglect biological dynamics since the core target is to capture the net air–sea CO_2 exchange associated with the OAE-induced surface ocean $p\mathrm{CO}_2$ anomaly.

- Model validation should be an integral part of model implementation and application. For OAE research, validation is a two-step challenge. First, it is necessary to validate unperturbed model baselines to gain confidence that the natural variability is represented appropriately and to quantify model uncertainties. Second, it should be verified that the model accurately represents the perturbations of an alkalinity addition.

- Since no single model validation metric provides a complete picture of a model's skill, multiple complementary metrics should be used in combination. Furthermore, different points in space and time and a breadth of variable types should be part of any comprehensive validation.

- Data assimilation, the process of improving the dynamical behaviour of models by statistically combining them with observations, should be employed in order to obtain the most accurate model simulations possible, e.g., to optimize model parameters or to estimate the ocean state. The former addresses systematic errors and biases in models, while the latter assumes an unbiased model and addresses unresolved stochasticity.

- When applying data-assimilative models for quantification of the OAE-induced net CO_2 uptake by calculating the difference between a realistic and a counterfactual simulation, it is not appropriate to assimilate biogeochemical observations of properties affected by the alkalinity enhancement as this would eliminate the ability to make valid comparisons between the two simulations. However, assimilation of observations that are unaffected by OAE can be applied to both simulations of the pair.

- Successful application of DA critically requires sufficient observations either of the properties that the model parameters to be estimated depend on or of the state variables that are being estimated. Observing system simulation experiments are recommended to design observing strategies tailored to the needs of specific OAE applications.

- Model results should be paired with sound qualitative and quantitative uncertainty estimates, especially when used for practical decisions. DA methodologies provide a useful framework for estimating uncertainty, especially ensemble-based methods. Coordinated, multimodel studies, commonly called model intercomparison projects, or MIPs, are another common approach to assessing model uncertainty.

Code availability. The base LES code is available at https://github.com/CliMA/Oceananigans.jl (last access: 15 November 2023; Ramadhan et al., 2020). The ROMS code is available at https://perma.cc/3BJY-U4LE (Haidvogel et al., 2008). The University of Victoria Earth System Climate Model is available at https://perma.cc/8VUY-BHSP (Weaver et al., 2001).

Data availability. No data sets were used in this article.

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Legal considerations relevant to research on ocean alkalinity enhancement

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Abstract. This article examines the legal considerations relevant to ocean alkalinity enhancement (OAE) and provides some best-practice guidance for responsible (field) research on OAE. The article examines recent developments in international law in order to inform what may legally be required of researchers when planning and designing OAE research projects. To this end, the article acknowledges unavoidable differences in domestic legal systems but highlights the role of international law, especially as can be found in the London Convention and Protocol, in developing appropriate minimum rules and standards. The article notes that domestic legal systems may wish to account for such minimum international rules and standards when developing permitting conditions and laws for OAE research activities. Additionally, the article examines international agreements and customary international law that find general application to OAE research. This latter examination assists in the identification of areas where additional legal research may also be required. The article concludes by highlighting that it remains crucial for legal researchers to work with the scientific community and those from other disciplines to assist States in understanding the science–policy interface to develop a comprehensive legal framework for ocean-based carbon dioxide removal approaches. This will, in turn, guarantee that field research is carried out in a safe and responsible manner and in a manner that reduces the likelihood of adverse environmental and other consequences.

1 Introduction

This Chapter examines the legal considerations of relevance to ocean alkalinity enhancement (OAE) and, based on recent developments in international law, provides some recommendations that continued research, particularly field research, into OAE should consider. As is the case with other Chapters, nothing in this Chapter should be understood as either advocating for or restricting research into OAE. Rather, the Chapter acknowledges the inevitable application of international law to OAE activities and recommends some best practices that may facilitate responsible and transparent research and accountability.

The ocean is a global resource and any activity that has the potential for negative transboundary impacts must be examined in accordance with the rules and principles of public international law. International law has grown exponentially since the turn of the century and includes numerous legal rules, procedures and institutions aimed at governing the rights and obligations of States with respect to, amongst other things, the effect that their activities may have on the environment of neighboring States and the environment beyond national jurisdiction generally. As an activity that takes place in the ocean, the research and possible (future) deployment of OAE will necessarily be subject to a number of international laws.

Generally speaking, there are two primary sources of international law: (1) international agreements or treaties and (2) customary international law. The former source imposes

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obligations only on those States that have specifically consented to be bound by the relevant treaty. The latter encompasses a set of obligations that are binding on all States, unless a particular State has "persistently objected" to the rule or principle concerned (see Green, 2016). This consideration is important to keep in mind when discussing OAE research and especially when considering the application of the precautionary principle or approach to OAE research.

It should be noted that international law does not generally impose obligations directly on private actors (such as researchers). However, to fulfill their international obligations, States may be required to adopt domestic laws to regulate the conduct of researchers and others operating under their jurisdiction or control. The manner in which States incorporate their international law obligations into domestic legal systems depends on the State in question, and a one-size-fits-all approach to ascertaining how States apply international law within domestic contexts is not possible. However, international law is often relevant in ascertaining the minimum rules and standards that may be required by domestic authorities for researchers and their affiliated institutions to undertake OAE research in the marine environment. How, then, do researchers ascertain which domestic laws apply to their proposed activity? As mentioned, the answer to this question will depend on the State in question but "objective connecting factors" include the geographic location where the activity is undertaken and the nationality, residence or domicile of the actors involved (Mills, 2023). Research projects that make use of vessels at sea, for example, may be subject to the jurisdiction of relevant coastal States and the flag State of the vessel concerned.

Considering the purpose of this guide and the overarching legal considerations applicable to OAE, three general remarks must be stressed. First, the development of international environmental law is a direct response to the increased impact that humankind is having on the environment. Consequently, the environmental laws that may apply to OAE typically aim to prevent or reduce the environmental harm that an activity may have and do not necessarily encourage research – the role of environmental law is centered around reducing and, in some cases, entirely preventing harm to the environment. Second, OAE is one of a suite of ocean-based carbon dioxide removal (CDR) approaches, and in the absence of any law designed for OAE specifically, the laws that find application to ocean-based CDR generally should be assumed as also applying to OAE. Last, scientific research activities should be distinguished from (commercial) deployment of OAE. Both the national and international regulation of research and deployment is likely to be different and, given the objective of this guide, the focus of this Chapter is on research and not (commercial) deployment.

With these brief remarks in mind, this Chapter is divided into seven sections. Following this introduction, Sect. 2 highlights the jurisdiction of States in the various maritime zones established by the 1982 United Nations Convention on the Law of the Sea (UNCLOS, 1982). Section 3 discusses framework international agreements relevant for OAE. This discussion emphasizes that OAE, like all ocean-based CDR approaches, "is a prime example of an activity-based challenge that involves the overlap and interplay of different regimes under international law" (Proelss, 2023, p. 112). Considering the vast literature available, Sect. 3 only focuses on select international instruments of particular relevance, including UNCLOS (Sect. 3.2), the Convention on Biological Diversity (CBD; Sect. 3.4) and the international climate change regime (Sect. 3.5). Additionally, and in considering OAE research activities undertaken in the high seas, the imminent adoption of an agreement under UNCLOS on the conservation and sustainable use of marine biological diversity of areas beyond national jurisdiction is also briefly discussed (Sect. 3.3). Section 4 examines the currently most developed international instrument potentially applicable to OAE research – the 1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (London Protocol or LP). This section details the requirements of the not-yet-in-force amendments to the London Protocol, serving as the basis for some reflection into what future permitting of OAE activities by national, local or municipal authorities might entail. Section 5 highlights some best-practice guidance for OAE (field) research projects, while Sect. 6 notes that a number of areas relevant to the legal aspects of OAE research still require further research. This latter point is especially true with regards to liability regimes, how to respond to unregulated/unauthorized OAE research projects, the potential necessity for insurance and the connection between national and international legal systems and associated needs for relevant national authorities to remain vigilant with regards to international legal developments. Finally, Sect. 7 offers some conclusions.

2 Jurisdiction over the ocean and defining OAE

The answer to which State has jurisdiction over a particular ocean activity generally depends on the following two considerations: (1) where in the ocean a particular activity takes place and (2) the legal classification of the activity concerned. As far as the "where" goes, an OAE activity that is restricted to the territorial sea, for example, may be subject to a different regulatory framework than if the same activity were undertaken in the exclusive economic zone or in the high seas (see the discussion below). As far as the legal classification of the activity goes, an activity that has some OAE characteristics but which does not meet any agreed legal definition of what in fact constitutes OAE may be regulated differently. In other words, it will be crucial that OAE research projects fulfill any agreed upon definitions found in relevant international instruments and domestic legislation. In this regard, examples can perhaps be drawn from recognized institutions such as the Intergovernmental Panel on Climate Change (IPCC), which defines OAE as a CDR method "that involves [the] deposition of alkaline minerals or their dissociation products at the ocean surface [to increase] surface total alkalinity, and may thus increase ocean carbon dioxide uptake and ameliorate surface ocean acidification" (IPCC, 2022, p. 1809). That said, it should be noted that legal and scientific definitions do not always align, and a definition of OAE should remain flexible (to respond to rapid developments) and account for necessary legal and scientific requirements. This is especially true in the context of ongoing efforts under the London Protocol to potentially regulate OAE projects which qualify as legitimate scientific research (see Sect. 4).

Turning to the "where", the jurisdiction of coastal States (i.e., non-landlocked States) over various parts of the ocean is laid out in the 1982 UNCLOS. In line with this, the ocean is divided into various maritime zones, and the rights and obligations of States are generally determined by where in the ocean (i.e., in which maritime zone) a particular activity is undertaken (see Fig. 1).

Without detailing the legal nuances involved in every maritime zone, it should be understood that the classification of a zone is determined by the distance from a State's baseline, which is normally defined as the low-water line along the coast of a State (Article 5, UNCLOS). OAE activities that take place in the 0 to 12 nautical miles (NM) belt (as measured from the baseline) would generally be subject to the legal regime of the territorial sea; those that take place in the 12 to 200 NM belt would generally be subject to the legal regime of the exclusive economic zone (EEZ); and those that take place beyond 200 NM would generally be subject to the regime of the high seas, including the freedom to undertake scientific research (Article 87, UNCLOS). Over and above these specific zonal regimes, coastal States may also be subject to obligations covering all maritime zones, including the obligation to protect and preserve the marine environment.

Given that the coastline of a State is not drawn in a neat straight line, the general rules applicable in the various maritime zones are necessarily accompanied by a number of exceptions and deviations, including the fact that some States have not designated an EEZ or that the territorial sea of some States does not extend to the full 12 NM, as measured from the baselines (see, for example, the practice of some coastal States bordering the Mediterranean Sea and the designation of Japan's territorial sea bordering the Tsushima, Osumi and Tsugaru straits). Ascertaining where in the ocean a particular OAE activity is to take place is, therefore, a crucial step in evaluating the appropriate legal regime.

The zonal approach enunciated in UNCLOS and the jurisdiction that States enjoy in each zone is briefly summarized in Table 1. Within each identified zone, States must exercise their rights and obligations in accordance with international law and in a manner that does not interfere with the rights and obligations of others. For example, how States exercise sovereignty over their territorial sea is subject to UNCLOS and other rules of international law, including the right of "ships of all States ... [to] innocent passage through the territorial sea" of other States, as recognized in UNCLOS (UNCLOS, Articles 2 and 18).

This brief discussion has shown that in order to identify the laws potentially applicable to an OAE activity, it first needs to be established where in the ocean an OAE activity takes place and the classification of the activity (the scale and intent of the activity often proving relevant for such classification). Following this, the international laws regulating ocean space can be consulted to determine the obligations of States in authorizing OAE research under their jurisdiction.

> *Conclusion 1 – the regulation of OAE research: a top-down approach?*
> International law determines the rights and obligations of States. States then adopt domestic legislation that either meets the minimum standards or rules required by international law or, on the basis of domestic legal systems and individual State considerations, enact domestic legislation that is stricter than the minimum requirements. Thus, depending on where a particular OAE research activity occurs, researchers should (1) be aware of potentially applicable minimum international rules and standards and (2) how the research activity is regulated domestically. Even if an activity is permissible under international law, it may be restricted or prohibited under domestic law. Indeed, situations do exist in which the domestic regulation of an activity may amount to total prohibition of the activity concerned.

In establishing the link between domestic and international law then, an essential question becomes: what are the minimum international rules and standards that may be relevant to research on OAE? There is currently no specific international legal regime that has been established to govern research on OAE. That said, OAE activities do not take place in a legal vacuum. In particular, an evaluation of various international treaties (which individual States have consented to be bound by) and customary international law (comprising universal legal standards that are binding on all States) provides some insight into what such minimum international rules and standards may, at this point in time, entail.

3 Customary international law and relevant framework agreements of general application

A wide body of literature has analyzed the application of existing international legal frameworks to OAE and other ocean CDR techniques (see, for example, Proelss and Steenkamp, 2023; Scott, 2023; Webb et al., 2023; Proelss, 2023; Webb et al., 2021; Brent et al., 2019; GESAMP, 2019; Du, 2023; McGee et al., 2018; Armeni and Redgwell, 2015; Lloyd and Oppenheimer, 2014; Kuokkanen and Yamineva, 2013; Scott, 2013). Applicable international law includes the customary

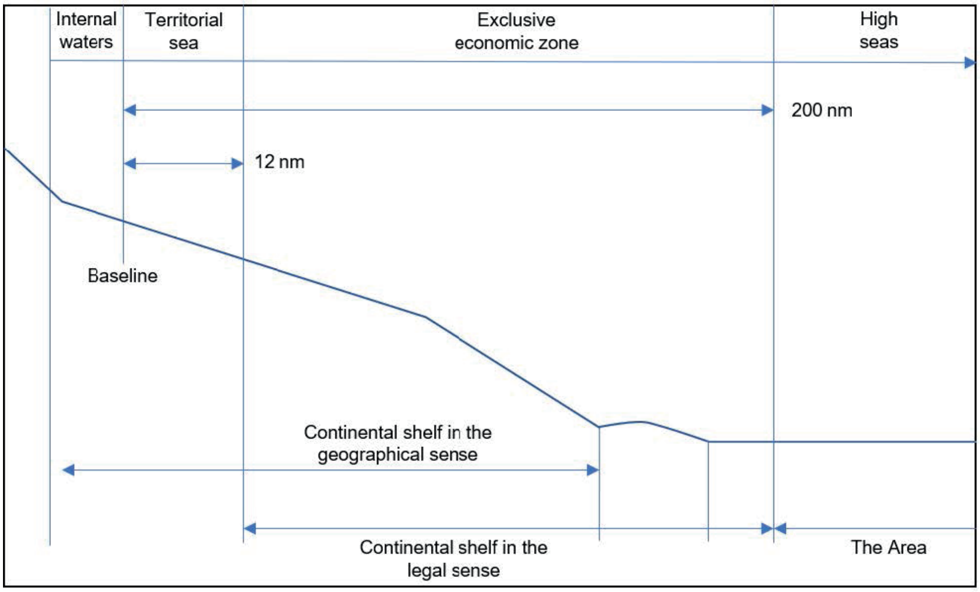

Figure 1. Maritime zones (Tanaka, 2019).

Table 1. Zones and jurisdiction of States in the ocean (largely reproduced from NASEM, 2022, p. 41).

Zone	Location	Status
Territorial sea	Water column from 0 up to 12 nautical miles from the baseline	Part of the sovereign territory of the coastal States. States have sovereignty.
Exclusive economic zone	Water column from 12 up to 200 nautical miles from the baseline	States have sovereign rights to explore, exploit, conserve and manage the natural resources and perform other activities for the economic exploitation of the zone. States have jurisdiction over artificial islands and other structures, over marine scientific research and over the protection and preservation of the marine environment.
Continental shelf	Seabed and subsoil from 12 to 200 nautical miles from the baseline or the outer edge of the continental margin (subject to certain limits)	States have sovereign rights to explore and exploit the natural resources in the continental shelf.
High seas	Water column areas not included in other water column areas designated under UNCLOS	No State has sovereign rights. Freedom of the high seas applies, and the zone is open for use to all States.
The Area	Seabed and ocean floor (including its subsoil) that are beyond the limits of national jurisdiction	The Area and its resources are the common heritage of humankind. Activities in the Area must be conducted “exclusively for peaceful purposes” and “for the benefit of humankind as a whole”.

international law obligations to prevent transboundary harm and the obligation to conduct environmental impact assessments (including associated procedural obligations to consult and notify potentially affected States); UNCLOS and its related instruments; the CBD; the international climate change regime (especially the United Nations Framework Convention on Climate Change (UNFCCC) and the 2015 Paris Agreement); and in the case of alkaline substances or material that may be introduced into the marine environment, the international dumping regime established by the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (London Convention or LC) and the Protocol to that Convention (London Protocol or LP). Additionally, the recent adoption of an agreement under UNCLOS on the conservation and sustainable use of marine biological diversity of areas beyond national jurisdiction (BBNJ Agreement) may also prove relevant for OAE research undertaken in the high seas.

The CBD and the UNFCCC are often referred to as framework agreements. While their framework nature necessitates that they have a wide scope of application, including to OAE research, it also means that the content of many of their most relevant obligations is often vague and ambiguous, requiring interpretation on a case-by-case basis. For its part, UNCLOS provides a comprehensive framework for regulating ocean space, but it is "not a separate or self-contained legal regime" (Boyle, 2005, p. 564). Those provisions of UNCLOS that refer to "rules of general international law" or which incorporate "generally accepted international rules and standards" will need to be carefully examined in ascertaining both their potential application and the scope of any such application to OAE research activities.

Considering the comprehensive literature that is available, the discussion below on customary international law and some select international instruments offers only a brief snapshot. This discussion is, therefore, incomplete and serves rather as a foundation from which best efforts can be made to provide guidelines and recommendations for OAE research. Additionally, this section should be read together with Sect. 4 below, wherein the London Protocol and its not-yet-in-force 2013 amendments – comparably the most developed international law concerning ocean-based CDR – are examined in detail. The focus on the international regime established under the London Protocol should not be understood as negating the relevance of the instruments discussed here or any other international laws. Rather, this should be seen as a consequence of the current regulatory regime and the opportunities that the London Protocol may present in facilitating (or not) OAE field research.

3.1 Customary international law

Relevant customary international law includes the obligation that States must not allow or permit activities within their territories, or in common spaces (such as the high seas), without having regard for the rights of other States or for the protection of the environment, including the marine environment. From this, commentators have extrapolated the following two specific customary international law obligations:

1. "States must take measures to prevent, reduce and control pollution and environmental harm from activities that are under their jurisdiction or control; and

2. States must cooperate to mitigate environmental risks and emergencies through the related duties of notification, consultation, negotiation and, in some cases, by conducting environmental impact assessments (EIAs)" (Boyle and Redgwell, 2021, pp. 152–153).

Importantly, neither of these obligations prohibits transboundary harm in its entirety, and both entail an obligation of conduct and not of result (see, for example, Maljean-Dubois, 2021; Papanicolopulu, 2020; Mayer, 2019, 2018; Wolfrum, 2011).

These rules are also reflected in a number of international instruments and in the jurisprudence of international courts and tribunals. According to the International Court of Justice (ICJ), it is

> every State's obligation not to allow knowingly its territory to be used for acts contrary to the rights of other States [and that a] State is thus obliged to use all the means at its disposal in order to avoid activities which take place in its territory, or in any area under its jurisdiction, causing significant damage to the environment of another State. (2010 *Pulp Mills* case, para. 101)

Therefore, a State undertaking potentially risky activities must act with due diligence, and failure to do so may result in the international responsibility of that State. The obligation of due diligence is variable; i.e., the obligation is susceptible to "change over time as measures considered sufficiently diligent at a certain moment may become not diligent enough in light, for instance, of new scientific or technological knowledge" (ITLOS 2011 Advisory Opinion, 2011, para. 117).

> *Conclusion 2 – OAE and States' international obligation of due diligence.*
> As scientific understanding of OAE advances, the threshold of a State's due diligence obligations may increase or decrease accordingly. Whether or not a State's due diligence obligations have been met must be analyzed on a case-by-case basis. However, to fulfill their obligations, States must, at a minimum, ensure that adequate domestic legislation exists to mitigate the environmental impacts of OAE activities and that such legislation obligates a certain level of vigilance on the part of the State "in their enforcement and the exercise of administrative control applicable to public and private operators" (2010 *Pulp Mills* case, para. 197). Therefore, a strong case can be made that domestic legislation needs to remain flexible in order to adequately respond and adapt to changing circumstances in light of developments surrounding OAE research.

Connected to the second customary international law rule highlighted above is the procedural obligation to undertake an EIA for proposed activities that "may have a significant adverse impact in a transboundary context" (2015 *Certain Activities* case, para. 104). Recent international case law indicates that prior to an EIA, there may also exist a preliminary obligation on States to ascertain risk (2015 *Certain Activities* case, paras. 153–156). The preliminary requirement to first ascertain risk can be connected to the due diligence obligation mentioned above. In other words, establishing the risk of an activity and minimizing or preventing the actual harm or damage of the activity are two distinct obligations owed by States (Viñuales, 2020, p. 112). How States satisfy these two separate obligations is not always evident, but researchers may wish to keep this distinction in mind when clarifying with permitting authorities what their proposed projects may need to fulfill in terms of (1) any necessary EIA and (2) the risk assessment that may be required prior to the EIA itself.

> *Conclusion 3 – what constitutes "harm"?*
> As already mentioned, the fact that there is some measurable harm does not necessarily mean that an activity is illegal. In the context of international law, reference can be made to various thresholds of harm, including harm that is "serious" or "significant". The International Law Commission has noted that the term significant is "not without ambiguity", but that it could be understood as "something more than 'detectable' but [not necessarily] at the level of 'serious' or 'substantial' " (International Law Commission, 2001, p. 152). In the context of OAE research, an evaluation of the degree of harm that an activity may cause could include examining the sensitivity of the proposed research area and the nature, scale and permanence of the effects that any research may have on the area (Brent et al., 2019). Ultimately, however, the evaluation of harm must be done on a case-by-case basis by the State that has jurisdiction over the activity, and researchers should remain aware that harm may be defined differently for similar OAE activities in different jurisdictions. This conclusion is connected to the incorporation of international law into domestic law and how national legal systems may have different thresholds for what harm may be legally tolerated in connection to an authorized research activity.

If the activity in question is deemed to require an EIA, a question remains as to what the EIA should, at a minimum, include. The answer to this question is developed further below, but at this point, it should be stressed that international courts and tribunals have unfortunately not yet provided clear guidance on what the actual content of an EIA should entail. Instead, it has been highlighted that "it is for each [State] to determine in its domestic legislation or in the authorization for the project, the specific content [. . .] required in each case" (2010 *Pulp Mills* case, para. 205).

> *Conclusion 4 – preliminary assessments, EIAs and the London Protocol?*
> The relationship between due diligence, preliminary assessments and subsequent EIAs is not always clearly demarcated. However, an attempt to capture this relationship can nevertheless be found in the 2013 amendments to the London Protocol. In particular, the general assessment framework in the new annex 5 envisages both an initial and subsequently detailed EIA for legitimate "marine geoengineering" research projects. This is not to say that the London Protocol informs the content of any established customary international law. Rather, the regulation envisioned in the London Protocol is reflective of customary international law in requiring, first, an initial EIA and, subsequently, a more detailed assessment. Following this, the London Protocol may provide essential guidance in giving content to what an initial and subsequent EIA in the context of an OAE research project may entail and, ultimately, the future regulation of any OAE research activity (see Sect. 3.6 below).

3.2 The United Nations Convention on the Law of the Sea

With 169 State parties, UNCLOS enjoys near-universal adherence. Even States that are not party to UNCLOS acknowledge the customary international law – and therefore the binding nature – of many of its provisions, including those most pertinent to OAE research, such as the provisions regulating marine scientific research (MSR) and requiring the protection and preservation of the marine environment (Burns, 2023, p. 52).

> *Conclusion 5 – inevitable application of UNCLOS.*
> Any activity that involves a maritime component, no matter whether it can strictly be regarded as an ocean-based CDR approach or not, must be measured against the pertinent requirements of the jurisdictional framework codified in UNCLOS.

Part XIII of UNCLOS, concerning MSR, is particularly relevant for the research stage of OAE (Proelss, 2023, pp. 103–105). Part XIII establishes a number of general principles applicable to MSR, including that research activities (i) be conducted exclusively for peaceful purposes; (ii) be conducted with appropriate scientific methods and means; (iii) not unjustifiably interfere with other legitimate uses of the sea; and (iv) be conducted in compliance with all relevant provisions of the Convention, including those for the protection and preservation of the marine environment (Article 240, UNCLOS). The primary responsibility to ensure that research vessels, including those undertaking OAE research, comply with the relevant provisions of UNCLOS lies with the flag State in question (Burns, 2023, p. 53).

Following the maritime zones established under UNCLOS (see Sect. 2 above), States have the right to conduct MSR within their own territorial seas and EEZs; within the terrestrial sea and EEZs of other States (subject to such other States' prior consent); and in the high seas (Articles 245, 246 and 87, respectively, UNCLOS). As far as MSR in the EEZ of another State is concerned, such other State "shall, in normal circumstances, grant their consent for [MSR] projects by other States or competent international organizations" (Article 246(3), UNCLOS). However, the expectation that such consent normally be granted by, for example, issuing necessary permits will most probably not apply to OAE research projects. This is due to the fact that a coastal State may withhold their consent if the proposed MSR involves "the introduction of harmful substances into the marine environment" (Article 246(5)(b), UNCLOS).

Concerning the protection and preservation of the marine environment, UNCLOS is one of several international treaties that requires States to take active steps to avoid and/or mitigate harm to the marine environment, including harm caused by pollution. Article 1(1)(4) of UNCLOS defines pollution as the direct or indirect introduction by humans of

> substances or energy into the marine environment [...] which results or is likely to result in [...] harm to living resources and marine life, hazards to human health, hindrance to marine activities, including fishing and other legitimate uses of the sea, impairment of quality for use of seawater and reduction in the amenities.

OAE activities, including research activities, might be considered "pollution" under this definition. Specifically, the definition would capture OAE activities that involve the introduction of alkaline material or electric current (as energy) into the marine environment, at least where that introduction will or is likely to result in harm to the environment or humans.

Part XII of UNCLOS sets out an overarching legal regime to protect and preserve the marine environment, requiring States to take all measures necessary to prevent, reduce and control pollution of the marine environment resulting from "any source" (Article 194(1), UNCLOS), including pollution caused by dumping (Article 210, UNCLOS); by vessels (Article 211, UNCLOS); and pollution from or through the atmosphere (Article 212, UNCLOS). Pollution caused by dumping is particularly relevant for OAE (see Sect. 3.6 below). UNCLOS requires States to adopt domestic laws and regulations to prevent, reduce and control pollution caused by dumping and to ensure that dumping is not carried out without the permission of the competent State authorities (Articles 210(1) and (3), UNCLOS). In the territorial sea or EEZ, coastal States have the right to permit, regulate and control dumping but must consider any such dumping together with other potentially affected States (Article 210(5), UNCLOS). Any domestic laws, regulations and measures that States may adopt in this regard shall be no less effective in preventing pollution than global rules and standards (Article 210(6), UNCLOS). It is generally accepted that the London Convention and Protocol contain the relevant "global rules and standards" that national measures must be evaluated against (see Sect. 3.6 below).

Also relevant to OAE is the obligations on State parties to UNCLOS to not transform one type of pollution into another (Article 195, UNCLOS) and to prevent pollution of the marine environment "resulting from the use of technologies under their jurisdiction or control" (Article 196(1), UNCLOS). Concerning the former obligation articulated in Article 195 of UNCLOS, some commentators have noted that this may have implications for OAE and other ocean CDR "projects that remove [carbon dioxide], which may be considered a form of pollution, from ocean waters by adding other materials, which may also constitute pollutants, into the water" (NASEM, 2022, p. 48). UNCLOS provides that where there are reasonable grounds to believe that a planned activity may "cause substantial pollution of or significant and harmful changes to the marine environment, [States shall] assess the potential effects of such activities on the marine environment" (Article 205, UNCLOS). The assessment of these "potential effects" should be understood as incorporating the customary international law obligation to undertake an EIA – and possibly also a preliminary risk assessment – into the framework of UNCLOS (see Sect. 3.1 above).

3.3 The BBNJ Agreement

The BBNJ Agreement was formally adopted in June 2023, opened for signature in September 2023 and will enter into force 120 d after the 60th State ratifies the Agreement. The objective of the Agreement is "to ensure the conservation and sustainable use of marine biological diversity of areas beyond national jurisdiction, for the present and in the long term" (BBNJ Agreement, Article 2). The Agreement will only apply to areas beyond national jurisdiction, but there is, as yet, limited knowledge of what impact the Agreement may have on OAE and ocean-based CDR generally. However, there is considerable reason to believe that aspects of the Agreement will potentially apply to OAE research activities that take place in ocean areas beyond national jurisdiction.

The Agreement makes specific reference to "general principles and approaches" (BBNJ Agreement, Article 7), including the freedom to undertake MSR, the precautionary principle/approach and approaches aimed at building ecosystem resilience to the adverse effects of climate change and ocean acidification. Various provisions of the Agreement may be relevant for OAE research insofar as

1. the establishment of area-based management tools are concerned. This includes the objective of such tools to protect, preserve, restore and maintain biodiversity and ecosystems and to strengthen resilience to stressors such as climate change, ocean acidification and marine pollution.

2. the obligation on States to undertake EIAs. The Agreement contains comparably detailed provisions on EIAs, including screening requirements for activities that may have more than minor or transitory effects or where the effects are unknown or poorly understood (potentially relevant for OAE research), the process for undertaking EIAs, and the monitoring, reporting and review of the impacts of any authorized activities.

3. the establishment of institutional arrangements. The Agreement foresees the establishment of a number of institutions, including a scientific and technical body, a clearing-house mechanism and, most notably, a Conference of the Parties (COP). The COP could potentially regulate a broad range of ocean-based activities undertaken in ocean areas beyond national jurisdiction (including research) but will, at a minimum, keep under review and evaluate the implementation of the BBNJ Agreement.

Most, if not all, of the obligations under the BBNJ Agreement which might find application to OAE research – as an activity that may have unforeseen consequences if undertaken in ocean areas beyond national jurisdiction – are explicitly linked to an obligation on States to authorize or facilitate the actions of actors under their jurisdiction or control. One additional consideration potentially relevant to OAE research, is the fact that the Agreement does not require that an activity be screened or that any subsequent EIA be undertaken if a State determines that the impacts of the activity in question "have been assessed in accordance with the requirements of other relevant legal instruments or frameworks" (BBNJ Agreement, Article 29(4)). Considering the ongoing work of the Contracting Parties to the London Protocol, including the evaluation of whether OAE activities can be considered to be legitimate scientific research under the assessment framework of the London Protocol (see below), the interaction between these two international instruments in relation to OAE research should not be underestimated.

> *Conclusion 6 – the BBNJ Agreement and OAE research.* Despite having been formally adopted, the BBNJ Agreement still needs to attract the required number of State ratifications before it enters into force. However, when it does enter into force, the BBNJ Agreement could have implications for OAE research undertaken in the high seas. Particularly relevant may be the comparably comprehensive EIA requirements in the Agreement for activities planned in the high seas. These relatively detailed requirements – which may be adapted and improved upon by the COP – may prove useful in providing guidance to what may be required of currently ambiguous EIA requirements under other law-of-the-sea instruments such as, for example, UNCLOS. Additionally, the screening and EIA requirements under the Agreement can potentially be displaced or replaced by the ongoing work of the Contracting Parties to the London Protocol related to legitimate OAE research activities, and States and relevant authorities should remain aware of this cross-instrument fertilization as and when the work of the COP to the BBNJ finally commences.

3.4 The Convention on Biological Diversity

With 196 Contracting Parties, the CBD enjoys near-universal participation, and has been found to form "part of the corpus of general international law" (2016 *South China Sea* case, para. 956). As with UNCLOS, the broad mandate and wide scope of application of the CBD means that Contracting Parties have the opportunity to address a range of projects that may have an impact on the environment, including the marine environment. The CBD imposes a number of substantive obligations on Contracting Parties, including to identify activities that "have or are likely to have significant adverse impacts on the conservation and sustainable use of biological diversity, and [to] monitor their effects" (Article 7(c), CBD); to adopt measures for in situ and ex situ conservation of biological diversity (Articles 8 and 9, CBD); to assess the impacts of projects on biological diversity (Article 14, CBD); to regulate access to genetic resources (Article 15, CBD); and with respect to access to and transfer of technology (Article 16, CBD). In addition to these substantive obligations, the CBD also establishes a number of institutional arrangements for the further development, monitoring and implementation of the Convention (Tinker, 1995, pp. 191–194).

As the governing body of the CBD, the Conference of the Parties (COP) has adopted a number of non-binding decisions related to "climate geoengineering". These decisions have been extensively discussed in previous publications (see, e.g., Webb et al., 2023; Brent et al., 2019) and will thus not be analyzed in detail here. However, certain key aspects of the decisions are worth noting. First, the decisions have continuously acknowledged that foundational principles of the CBD, including the precautionary approach, necessarily apply to "geoengineering activities" but concluded that these general obligations offer insufficient international regulation (see COP to the CBD, 2016, para. 2). Second, and given this, the COP has determined that "no climate-related geoengineering activities that may affect biodiversity [should] take place" at the current time but has stated that "small-scale scientific research studies that could be conducted in a controlled setting" may be allowed "if justified by the need to gather specific scientific data and [. . .] subject to a thorough prior assessment" (see COP to the CBD, 2010, para. 8(w)). Here, "climate-related geoengineering activities" mean activities that involve "[d]eliberate intervention in the planetary environment of a nature and scale intended to counteract anthropogenic climate change and its impacts" (COP to the CBD, 2012, para. 5). This definition would encompass large-scale OAE projects that are undertaken with the goal of mitigating climate change (Webb et al., 2021). However, small-scale research projects would likely not be included. As noted above, the COP has indicated that small-scale research projects may be conducted in "a controlled setting" (provided certain other requirements are met) but has not elaborated on what that means. As some scholars have noted, it "could be argued that only research conducted in a laboratory or mesocosm … occurs in a ‘controlled setting”’, but the COP has not commented on this (Webb et al., 2023). As such, and given that the COP decisions are not legally binding, it will be up to individual States to decide whether and how to apply them to OAE research projects.

The COP to the CBD has called for “transparent and effective” regulation of geoengineering activities (CBD COP Doc. CBD/COP/DEC/X/33, 29 October 2010; COP to the CBD, 2010, para. 8(w)). Additionally, and following this, a subsequent decision of the COP in 2014 noted – for the first time – the 2013 amendment to the London Protocol and invited “Parties to the London Protocol to ratify this amendment and other Governments to apply measures in line with this” (COP to the CBD, 2014, para. 1). In 2016, the COP also adopted a decision that emphasized the primacy of the UNFCCC in, amongst other things, the removal of carbon dioxide through “sinks” – the definition of which arguably includes CDR approaches such as OAE (see Sect. 3.5 below; CBD COP Doc. CBD/COP/DEC/XIII/14, 8 December 2016; COP to the CBD, 2016, para. 3).

> *Conclusion 7 – OAE under the CBD framework.*
> Decisions of the COP to the CBD, including those that may find a specific application to OAE research, are not legally binding. As long as the substantive obligations in the CBD are fulfilled (such as those associated with EIAs, for example), nothing in the CBD prevents States from either undertaking or authorizing OAE research projects.

Brief reference should also be made to the recently agreed Kunming–Montreal Global Biodiversity Framework. This non-binding framework includes four overall goals and 23 targets to be achieved by 2030. Among other things, it calls for action on the part of States to

> [m]inimize the impact of climate change and ocean acidification on biodiversity and increase its resilience through mitigation, adaptation, and disaster risk reduction actions, including through nature-based solution and/or ecosystem-based approaches, while minimizing negative and fostering positive impacts of climate action on biodiversity. (COP to the CBD, 2022, target 8)

This broad wording leaves room for future decisions of the COP to possibly (re)address ocean-based CDR approaches. This is especially true for those approaches that may be deemed necessary by the COP of the CBD to combat ocean acidification and/or to increase the resilience of biodiversity by undertaking climate change mitigation action. This could include OAE. The Kunming–Montreal framework may, therefore, provide renewed opportunity for the COP to the CBD to guide ocean-based CDR policy and research, including OAE as an approach that could have co-benefits in combating other ocean stresses such as ocean acidification.

3.5 The international climate change regime

Similar to the CBD and UNCLOS, the climate change regime enjoys near-universal support and is also a framework regime, leaving the content of vaguely worded obligations open to interpretation by States. The foundation of the international climate change regime is the 1992 UNFCCC, which has suitably been referred to as “nested” (Rajamani and Werksman, 2021, p. 497). This apt description is in reference to the intrinsic relationship that exists between States parties and three related instruments, namely the UNFCCC, the 1997 Kyoto Protocol and the 2015 Paris Agreement. In line with this, “the parties to each instrument rely on most of the same institutions, including the governing body of the [Conference of the Parties], to serve all three instruments” (Rajamani and Werksman, 2021, p. 497). In outlining the current state of affairs under the climate regime as it relates to OAE research, this section focuses on the UNFCCC and the Paris Agreement.

The ultimate aim of the UNFCCC is to stabilize “greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the global climate system” (Article 2, UNFCCC). Numerous studies have noted that the UNFCCC regime, including the Paris Agreement, approve the use of CDR approaches to mitigate climate change (see Honegger et al., 2021; Craik and Burns, 2019; Brent et al., 2019; Proelss and Steenkamp, 2023; NASEM, 2022). The reason for this finding is linked to the fact that State parties are required to limit greenhouse gas emissions, including by protecting and enhancing sinks (Article 4(2)(a), UNFCCC). The definition of sinks in the UNFCCC includes “any process, activity or mechanism which removes a greenhouse gas, an aerosol or a precursor of a greenhouse gas from the atmosphere” (Article 1, UNFCCC). This broad definition appears to extend beyond natural processes to also include human interventions such as OAE (NASEM, 2022, p. 44).

For its part, the Paris Agreement aims to hold the increase in global temperatures to well below 2 °C, ideally pursuing efforts to limit such increase to 1.5 °C (Article 2(1)(a), Paris Agreement). The manner in which States achieve this goal is left to their own nationally determined contributions (NDCs); i.e., States determine both the extent to which, and the means by which, they contribute to the achievement of the objectives of the Paris Agreement. The Paris Agreement does, however, call on State parties to “reach global peaking of greenhouse gas emissions as soon as possible” and to “achieve a balance between anthropogenic emissions by sources and removals by sinks of greenhouse gases” (Article 4(1), Paris Agreement). Additionally, the Paris Agreement expressly calls on States to “conserve and enhance, as appropriate, sinks and reservoirs of greenhouse gases” (Article 5(1), UNFCCC). Since the definition of sinks in the UNFCCC applies mutatis mutandis to the Paris Agreement (Article 1, Paris Agreement), OAE and other ocean-based

CDR approaches may, in certain circumstances, constitute mitigation action under the Paris Agreement (Honegger et al., 2021). That said, it should be stressed that neither the Paris Agreement nor the UNFCCC require States to engage in ocean-based CDR, and to date, no specific rules or guidelines have been adopted under the Paris Agreement to regulate ocean CDR. However, important developments in recent years regarding the climate change regime, including how this relates to institutional arrangements, should be highlighted.

In 2019, the COP to the UNFCCC and the COP to the Paris Agreement (the CMA) agreed on the Chile–Madrid Time for Action, which recognized the need to strengthen the understanding of, and action on, ocean and climate change under the UNFCCC (Doc. FCCC/CP/2019/13/Add.1, 16 March 2020). In 2022, the COP and CMA adopted the Sharm el-Sheikh Implementation Plan, encouraging State parties to consider, as appropriate, ocean-based action in their national climate goals, including in their NDCs (CMA, 2023, para. 50).

As one of two permanent subsidiary bodies established by the COP, the Subsidiary Body for Scientific and Technological Advice (SBSTA) regularly considers emerging science and research, including maritime technologies that have potential to contribute to achieving the goals of the UNFCCC and Paris Agreement (UNFCCC Contribution, 2023). Within the forum of the SBSTA research dialogue, experts have emphasized the continued uncertainty surrounding ocean-based CDR approaches and have noted that OAE "may have transboundary risks that are already constrained by international agreements such as the London Protocol and Convention, and by the CBD" (Chair of the SBSTA, 2022, para. 187). The SBSTA has recently encouraged State "[p]arties and relevant organizations to strengthen research and research capacity and to address related research needs", including on the potential opportunities, governance needs, risks and costs of CDR approaches (SBSTA of the UNFCCC, 2022, para. 62).

Another recent development concerns a controversial information note on "removal activities under the Article 6.4 mechanism" that was issued in May 2023. This information note was prepared by the UNFCCC Secretariat at the request of the Supervisory Body that is charged with supervising the market-based mechanism established in Article 6.4 of the Paris Agreement. Unlike the SBSTA mentioned above, this supervisory body is non-permanent, is fully accountable to the CMA and has been specifically established to supervise the Article 6.4 mechanism. In response to a request from the Supervisory Body for "technical information on ... activities involving removals", the Secretariat issued the information note (see Article 6.4, Mechanism information note, para. 2). The information note lists OAE as an "engineering-based removal activity" and provides brief information on the cost, potential, risks and impacts, co-benefits and trade-off and spillover effects of OAE (Article 6.4, Mechanism information note, appendix I). While the information note does not address the feasibility of OAE directly, it does mention that "[e]ngineering-based removal activities [including OAE] are technologically and economically unproven" and that these activities "do not contribute to sustainable development, are not suitable for implementation [and] therefore do not serve any of the objectives of the Article 6.4 mechanism" (UNFCCC Information Note, 2023, para. 39; their Table 3). This conclusion has drawn considerable criticism, with the information note being labeled as "imbalanced" and "ignoring science" (see, for example, Tamme, 2023). It should be stressed that the information note is not an operative document – i.e., it does not regulate OAE or other CDR approaches in a binding manner – but may provide insight into the current work of the UNFCCC to develop a general framework to guide the methodologies needed for removals.

> *Conclusion 8 – interaction between the three relevant framework treaties.*
> The framework nature of UNCLOS, the CBD and the climate change regime means that they will apply to OAE research. The extent to which they apply, however, is decidedly variable. Relevant CBD institutions have not directly addressed ocean-based CDR approaches since 2016. However, their potential to do so remains. UNCLOS and the climate change regime do not specifically regulate ocean-based CDR but are arguably more relevant for OAE activities, especially as this relates to marine scientific research, the protection and preservation of the marine environment and enhancing sinks, including in the ocean. The uniform development of the currently ad hoc and largely ambiguous international obligations found within these framework agreements will be crucial. Researchers, appropriate government departments and permitting authorities should, therefore, remain acutely aware of new developments and strive to enhance international coordination and cooperation when ocean-based CDR approaches, and OAE specifically, are discussed across various international regulatory regimes.

4 The international regulation of "dumping"

As discussed above, UNCLOS imposes a general obligation on States to "prevent, reduce, and control pollution of the environment by dumping" (Article 210, UNCLOS). UNCLOS further directs States to establish more detailed "global and regional rules, standards and recommended practices and procedures" with respect to dumping. Relevant global rules are set out in the London Convention and Protocol. The London Convention was adopted in 1972 with the goal of promoting "the effective control of all sources of pollution of the marine environment," particularly those resulting from the dumping of "waste or other matter" at sea. In November 1996, the Parties to the London Convention adopted a new protocol, which set more ambitious goals for marine protection, aiming to "protect and preserve the marine environment from all sources of pollution" and to "prevent, reduce and where practicable eliminate pollution caused by dumping" of "waste or other matter" (Article 2 LP). As explained further below, the definition of dumping in the London Convention and Protocol is arguably broad enough to encompass the discharge of materials into ocean waters in connection with OAE projects, at least in some circumstances. Nevertheless, questions remain about whether and how OAE will be regulated under the London Convention and Protocol. This section discusses how those instruments have been applied to similar activities – most notably ocean fertilization – to evaluate their (potential) application to OAE.

The Contracting Parties to the London Convention and Protocol have concluded that the two instruments apply to ocean fertilization and, in 2010, adopted an assessment framework to guide the permitting of ocean fertilization research projects. Subsequently, in 2013, the Parties to the London Protocol adopted an amendment that effectively codified the approach set out in the assessment framework. The amendment has not yet entered into force and thus is not yet legally binding on Parties to the London Protocol but could provide an indication of how the parties might approach other ocean CDR activities, including OAE.

> *Conclusion 9 – OAE as pollution caused by "dumping".* Certain OAE research will necessarily involve the introduction of substances into ocean waters. The placement of alkaline minerals or their dissociation products into the marine environment may, at least in some situations, be classified as dumping under international law.

4.1 The London Convention and Protocol

The London Convention was the first global treaty adopted to regulate the dumping of wastes and other matter at sea. In 1996, the London Protocol was adopted with the intention that it would, as between the Contracting Parties, replace the Convention (i.e., if and when ratified by all Contracting Parties). However, this has not yet happened, and more than 30 Contracting Parties to the London Convention are yet to ratify the London Protocol. At the time of writing, the London Convention has 87 parties, and the Protocol has 53.

The purpose of both the London Convention and Protocol is to prevent the pollution of the marine environment by the dumping of wastes and other matter (Articles I LC and 2 LP). Both the London Convention and Protocol require dumping to be permitted by the State under whose jurisdiction it occurs. The two instruments establish quite different constraints on when countries may permit dumping. Under the London Convention, countries may permit the dumping of all substances, except those listed in its annexes. In contrast, the London Protocol reverses the burden of proof, prohibiting countries from issuing permits for the dumping of all substances, except those listed in an annex to the Protocol.

4.2 Is OAE "dumping" under the London Convention and Protocol?

Previous studies have concluded that "non-research [OAE projects] could be permitted under the London Convention but not the London Protocol" (see Webb et al., 2021). The below discussion is not concerned with non-research activities and instead focuses on the extent to which the placement of alkaline material in the ocean in connection with OAE research might constitute dumping under the London Convention and Protocol.

Under the London Convention and Protocol, dumping is defined to include "any deliberate disposal into the sea of wastes or other matter from vessels, aircraft, platforms or other man-made structures at sea" (Articles III(1)(a)(i) LC and 4.1.1 LP).

The phrase "wastes or other matter" is defined to mean "material and substance of any kind, form or description", while the term "sea" is defined as "all marine waters other than the internal waters of States" (Articles III(3) LC and 1(7) LP). Although internal waters are excluded from the definition of sea, Article 7 of the London Protocol requires Contracting Parties to apply the provisions of the Protocol or other effective measures "to control the deliberate disposal of wastes or other matter in marine internal waters where such disposal would be 'dumping'" (Churchill et al., 2022, p. 670).

The London Convention and Protocol identify a number of activities that, while involving discharges into the ocean, do not constitute dumping. Most notably, an activity is not dumping if it involves the "placement of matter for a purpose other than the mere disposal thereof, provided that such placement is not contrary to the aims of" the London Convention or Protocol (Article III(1)(a) LC and Articles 1 (4.2.2) and (4.2.3) LP). This exception is of particular importance for OAE. It may be argued that, even if OAE involves the placement of matter (such as alkaline minerals) into the marine environment, this placement is aimed at increasing the alkalinity of seawater and increasing the uptake of carbon dioxide, rather than the "mere disposal" of the matter. If this view is accepted, OAE will not involve dumping within the terms of the London Convention and Protocol, provided that the placement of alkaline material into ocean waters is found not to be "contrary to the aims of" those instruments.

The objective of both the London Convention and London Protocol is to prevent the pollution of the marine environment caused by dumping. Thus, where an OAE research activity is assessed to potentially result in the pollution of the marine environment, then that activity would be contrary to the objective of the London Convention and Protocol. It would, therefore, not qualify for the placement exception in the definition of dumping in the London Convention and Protocol. That is, an OAE activity that results or is likely to result in pollution would likely be regulated as a form of dumping under the London Convention and Protocol.

4.3 Lessons from the treatment of ocean fertilization under the London Convention and Protocol for OAE research

The way in which the Contracting Parties to the London Convention and Protocol have thus far dealt with ocean fertilization is perhaps indicative of how OAE might be dealt with in the future. The legal developments surrounding ocean fertilization under the London Convention and Protocol have been summarized as follows:

> the meetings of the parties [to the London Convention and Protocol] adopted a resolution in 2008 in which they agreed that, given the then state of knowledge, ocean fertilization activities other than legitimate scientific research should not be allowed. To this end, such other activities should be considered to be contrary to the aims of the Convention and Protocol and not currently to qualify for any exemption from the definition of dumping. "Legitimate scientific research" into ocean fertilization requires a permit. In 2010 the meetings adopted an Assessment Framework to guide States when dealing with applications for such [legitimate scientific research] permits. (Churchill et al., 2022, p. 670)

The abovementioned 2008 resolution, together with the subsequent assessment framework developed to evaluate legitimate scientific research involving ocean fertilization, formed the basis for amendments to the London Protocol in 2013.

In October 2013, the Meeting of Contracting Parties of the London Protocol adopted, by consensus, an amendment designed to regulate marine geoengineering activities (IMO, 2013, Annex 4, Resolution LP.4(8)). However, as commentators have rightly noted, the 2013 amendment is an amendment to "an existing environmental protection treaty, and its capacity to provide a comprehensive governance framework for marine geoengineering activities will therefore be limited by the aims, scope and membership of the London Protocol itself" (Brent et al., 2019, p. 45).

The 2013 amendment will, when it enters into force, add two new Articles and two new annexes to the London Protocol. The first new Article, Article 1.5 bis, defines marine geoengineering as the

> deliberate intervention in the marine environment to manipulate natural processes, including to counteract anthropogenic climate change and/or its impacts, and that has the potential to result in deleterious effects, especially where those effects may be widespread, long lasting or severe.

This definition would seem to include OAE activities. The second new Article, Article 6 bis, consists of three paragraphs. Article 6 bis(1) prohibits the placement of matter for "marine geoengineering activities listed in [the new] annex 4, *unless* the listing provides that the activity or the subcategory of an activity may be authorized under a permit" (emphasis added). Thus, any activity that meets the definition of marine geoengineering that involves the placement of matter into the ocean and that is listed in annex 4 is generally prohibited. There is, however, an exception for activities "authorized under a permit". Article 6 bis(2) requires Contracting Parties to

> adopt administrative or legislative measures to ensure that the issuance of permits and permit conditions comply with provisions of annex 5 and takes into account any Specific Assessment Framework developed for an activity and adopted by the Meeting of the Contracting Parties. A permit shall only be issued after the activity has undergone assessment which has determined that pollution of the marine environment from the proposed activity is, as far as practicable, prevented or reduced to a minimum. A permit shall only be issued if the outcome of the assessment is that the activity is not contrary to the aims of the Protocol.

Ocean fertilization is currently the only marine geoengineering activity listed in annex 4. The annex provides that an ocean fertilization project "may only be considered for a permit if it is assessed as constituting legitimate scientific research taking into account" the general assessment framework set out in annex 5 and "any specific placement assessment framework" (2013 amendments, annex 4 1(3)). Annex 5 largely mirrors the assessment framework adopted by the Contracting Parties to the London Convention and Protocol in 2010. The Parties have agreed that the 2010 framework "should continue to be used" to evaluate proposed ocean fertilization projects (Resolution LP.4(8)). The assessment framework states that only projects meeting the following requirements should be viewed as involving legitimate scientific research:

- "the proposed activity [should be] designed to answer questions that will add to scientific knowledge";
- "the research methodology to be applied should be appropriate and based on best available scientific knowledge and technology";
- the project should be "subject to scientific peer review at appropriate stages";
- "economic interests [should] not influence the design, conduct and/or outcomes" of the project and there "should not be any financial and/or economic gain arising directly from the experiment or its outcomes";
- the project proponent should "make a commitment to publish the results in peer reviewed scientific publications" and have a plan for making "data and outcomes publicly available"; and

- the project proponent should have “the financial resources available before the work commences to fulfill the program of work”.

The assessment framework also outlines requirements for evaluating the impacts of ocean fertilization projects, including a review of the proposed site for the project, the materials to be placed in the marine environment, and the “expected consequences” of that placement, with a particular focus on environmental consequences. According to the assessment framework, a project should only take place if “conditions are in place to ensure that, as far as practicable, environmental disturbance and detriment would be minimized” (2013 amendments, annex 5, para. 26).

After considering the scientific attributes and environmental impacts of an ocean fertilization project, a State may decide to (1) issue a permit for the project, (2) request additional information about the project (if it determines that the information provided is inadequate), or (3) refuse to issue a permit for the project. If a decision is taken to issue a permit, then the permit

> should be reviewed at regular intervals, taking into account the results of monitoring, the objectives of monitoring programmes and relevant research. Review of monitoring results will indicate whether field programmes need to be continued, revised or terminated and will contribute to informed decisions regarding the continuance, modification or revocation of permits. Monitoring provides an important feedback mechanism into future permitting decisions for the protection of human health and the marine environment. (2013 amendments, annex 5, para. 29)

> *Conclusion 10 – regulation under the 2013 amendment is precautionary and not prohibitory.*
> The relatively strict regulation of scientific research in the 2013 amendment exemplifies the precautionary approach encapsulated in the London Protocol itself – relying on elements of risk characterization and risk management – and, thereby, connects the law of the sea as encapsulated in the London Protocol with international environmental law generally. Importantly, and despite these strict requirements, the regime established under the 2013 amendment to potentially regulate ocean-based CDR research is precautionary and not prohibitory.

4.4 Applying the “marine geoengineering” amendment to OAE research

As noted above, and despite not yet being in force, the 2013 amendment currently only applies to ocean fertilization. However, it could be expanded in the future to also apply to other ocean CDR activities that involve the placement of matter in the ocean in connection with marine geoengineering. The definition of marine geoengineering is arguably broad enough to encompass OAE projects, at least where those projects have the potential to negatively affect the marine environment.

> *Conclusion 11 – the 2013 amendments and OAE research permitting.*
> The potential applicability of the 2013 amendment to an OAE activity follows a step-by-step process:
>
> i. OAE must be recognized as marine geoengineering and, subsequently, listed in annex 4;
> ii. once listed in annex 4, and assuming the parties treat OAE similarly to ocean fertilization, the general rule is that the placement of matter in the ocean for OAE will not be permissible unless it is permitted as legitimate scientific research; and
> iii. any permit must meet the requirements of the general assessment framework included in annex 5 and/or any “special assessment framework” adopted for OAE.

There is reason to believe that the Contracting Parties to the London Protocol may be open to regulating OAE as a form of marine geoengineering under the 2013 amendment. In early 2022, the GESAMP Working Group on Ocean Interventions for Climate Change Mitigation (Working Group 41) identified seven marine geoengineering approaches “that the London Protocol Parties might wish to consider for listing in the new annex 4 of the Protocol” (IMO, 2021, para. 3.6). One of the identified approaches was the “alkalinization of the ocean by adding alkaline material directly to the ocean or by electrochemistry” (GESAMP 49/4/8, para. 6.5).

At a meeting of the Scientific Groups of the London Convention and Protocol in April 2022, “a number of delegations generally agreed with the seven marine geoengineering techniques identified by GESAMP” (GESAMP 49/4/8, para. 7). The Scientific Groups re-established the Correspondence Group on Marine Geoengineering and directed it to “provide recommendations on the possible inclusion of marine geoengineering activities in the new annex 4 to the London Protocol” (GESAMP 49/4/8, PARA. 8). In its first progress report issued in August 2022, the Correspondence Group identified four marine geoengineering techniques – including “enhancing ocean alkalinity” – as requiring “priority evaluation” (IMO, 2022a, para. 4). The progress report further recommended that the Contracting Parties

> (1) consider whether the four marine geoengineering techniques identified are within the scope of the London Convention and London Protocol; (2) consider how existing assessment frameworks apply and if they are adequate for assessing these four techniques; (3) if needed, adjust existing frameworks or develop new frameworks to address gaps;

> and (4) consider which of the techniques are suitable for listing in annex 4 to the London Protocol. (IMO Doc. LC 44/5; IMO, 2022a, para. 9)

Subsequently, in October 2022, the Contracting Parties to the London Convention and Protocol adopted a Statement on Marine Geoengineering (IMO, 2022b). This statement agrees with the four techniques identified by the Correspondence Group as requiring priority evaluation and declares that when

> taking into account the precautionary approach outlined in Article 3 of the London Protocol (LP), and while the LP amendment on marine geoengineering awaits entry into force . . . Contracting Parties [are encouraged] to apply annex 5 (the marine geoengineering assessment framework) to evaluate proposed marine geoengineering projects, including the four techniques mentioned above, to apply the utmost caution to their consideration, and to provide information to LP/LC about ongoing and planned marine geoengineering activities. (IMO, 2022b)

Thus, regardless of whether OAE is listed as a marine geoengineering activity in annex 4, it seems likely that Contracting Parties to the London Convention and Protocol will evaluate OAE projects under the assessment framework in annex 5.

5 Best-practice guidance for OAE (field) research

As a matter of best practice, a few general points regarding OAE (field) research should be stressed. First, coherence should be sought at every available opportunity when designing OAE research projects. In this context, coherence refers to best effort attempts at establishing minimum requirements and thresholds for designing and implementing OAE research projects. The need for such coherence is rooted in the different but related mandates of various international regimes and the need for domestic legislation to align with any internationally agreed rules and standards of relevance to OAE research. To this end, best practice surrounding OAE research should account for the general considerations detailed above. These considerations include where in the ocean the project takes place, what exactly may be required by relevant authorities in the context of preliminary risk assessments and any subsequent EIAs and contemporary developments surrounding new international regulation such as those codified in the BBNJ Agreement (see generally Honegger et al., 2022; Smith et al., 2023). Following this, OAE research projects could then apply the assessment framework set out in the 2013 amendment to the London Protocol. Such a step-by-step approach would assist in coherence and ensure that international and domestic legal systems – in their application of international law – adopt similar methods and processes for the authorization and subsequent permitting of OAE research projects. This strive for coherence will facilitate transparency and allow researchers to more accurately pinpoint necessary considerations and legal requirements when designing and undertaking OAE research activities.

Second, OAE research objectives need to be aligned with the overarching policy considerations related to achieving the sustainable development goals of the United Nations, especially as this concerns human rights and biodiversity (see, generally, Enevoldsen et al., 2022; Mace et al., 2021, pp. 70–77). In the words of the IPCC, mitigation action (which arguably includes OAE) must “resolve tradeoffs with [the] sustainable development goals” (IPCC, 2023, p. 31).

Third, it will be necessary to differentiate between large-scale field research and actual deployment. Given the potential need to test certain parameters and experimental designs at scale, this distinction may prove difficult in practice. However, some factors may be indicative of where to draw distinctions between research and deployment. These factors include particular OAE projects meeting agreed upon legal definitions for what constitutes research, transparency requirements akin to research and that ensure that every aspect of a project is publicized and the size or scale of the project. In this regard, size or scale could refer to the geographic scale of the application or effect of the project, as well as the total volume of carbon dioxide removed by a particular OAE activity (see Webb and Silverman-Roati, 2023). Concerning the geological storage of carbon dioxide, the European Union distinguishes between projects “undertaken for research, development or testing of new products and processes” and which projects have a “total intended storage below 100 kilotonnes” (EU Directive, 2009, Article 2(2)).

Fourth, and more specifically, OAE researchers should design projects to meet the requirements set out in the assessment framework. The necessity for this is related to striving for consistency and a possible centralized regime, as well as the fact that this would allow for the identification of shortcomings and subsequent improvements in the application of the assessment framework. In line with the assessment framework, OAE research projects should, therefore, have genuine scientific attributes; they should be designed to answer scientific questions, subject to peer review and transparency requirements and their conduct and outcomes should not be influenced by economic interests. Additionally, projects should also be designed so as to avoid, minimize or mitigate any adverse environmental impacts.

While this is the minimum required to ensure that OAE projects are conducted in accordance with the assessment framework for marine geoengineering, in some instances, best practice may require that project proponents go further. This may be the case where, for example, research is proposed for coastal or other areas with existing human users. In such cases, researchers should consider and take steps to minimize or mitigate any adverse social impacts (e.g., on coastal communities), in addition to addressing environmental impacts as required by the assessment framework. Moreover, whereas the assessment framework focuses on avoiding adverse impacts from research, researchers should also consider potential benefits (both environmental and social). Projects should be designed to maximize any benefits and ensure that such benefits are equitably distributed. This will, necessarily, require effective engagement with potentially affected communities. For further discussion of this, see Satterfield et al. (2023, this Guide), which is dedicated to the social considerations relevant to OAE.

6 OAE and additional legal research needs

The above discussion has highlighted some of the key legal considerations relevant to OAE research, especially for projects undertaken in the field. Importantly, most of the international laws discussed in this Chapter, including the 2013 amendment to the London Protocol, aim to prevent harm to the environment and do not necessarily "consider the growing need to develop geoengineering technologies to ameliorate climate change" (Brent et al., 2019, p. 46).

The above discussion has provided some reflections on how OAE research projects could be designed to fulfill general legal requirements (especially as this relates to environmental law) and the specific requirements under the 2013 amendment to the London Protocol. However, and as noted at the start of this Chapter, this discussion has only provided a snapshot, and additional legal research is needed in a number of areas relevant to the design and subsequent implementation of OAE and CDR research projects generally. A full listing of all research gaps that should be addressed is beyond the scope of this Chapter, but some examples are noted below.

International law's traditional regulation of States, rather than non-state actors, raises important questions for domestic legal systems that should be considered to be a matter of priority. There is also an urgent need for research into the exact substantive and procedural requirements of any mandated preliminary risk assessments and subsequent EIAs (see Sect. 3.1). It may be valuable for legal researchers to undertake similar initiatives to those of the Code Project, which recently examined domestic and international EIA practice in order to identify essential features of what an EIA regime within the context of deep seabed mining may require (Seventh Report of the Code Project, 2023). This may prove useful if done in relation to OAE research, considering the requirements of the 2013 amendment to the London Protocol, instrument-specific obligations requiring EIAs and the jurisprudence of international courts and tribunals.

> *Conclusion 12 – international and domestic legal systems.*
> There is no one-size-fits-all approach to ascertaining how States incorporate international law within domestic contexts. Especially for activities that may have transboundary impacts, however, international law remains relevant in demarcating minimum rules and standards that States are required to incorporate into domestic legislation. The incorporation of international law into domestic systems – particularly in the context of environmental law – is often connected to the discharge of a State's due diligence obligations. As OAE lab research transitions to field research, domestic legislation will need to regulate the activities of public and private researchers and their affiliated institutions. Therefore, States and their relevant authorities will need to remain aware of international developments in order to, at the very least, remain in line with developing international rules and standards specifically relevant to OAE research.

Other additional legal research needs surrounding OAE include issues related to liability and compensation; the responsibility of States for transboundary harm and the associated problems of unregulated or unauthorized research projects by State and non-state actors; the role of soft law instruments and principles of international (environmental) law (Armeni and Redgwell, 2015); and the impact of voluntary codes of conducts and principles for research on ocean-based CDR approaches generally (see, for example, Loomis et al., 2022; The Aspen Institute, 2021; Hubert, 2021). With reference to the issue of liability and compensation, more research is required to assess what this may mean for situations in which OAE research activities result in adverse pollution or other harmful consequences to the marine environment. Notably, both the London Convention and the London Protocol require that "Contracting Parties undertake to develop procedures regarding liability arising from [. . .] dumping" (Article 15 LP; see also the Convention's equivalent in Article X LC). However, despite continued inclusion on the meeting agendas, the establishment of such procedures has thus far eluded the Contracting Parties (Birchenough and Haag, 2020, p. 276).

> *Conclusion 13 – insurance and liability.*
> In line with established and developing principles surrounding international liability for operators and private actors, questions of insurance may be crucial for OAE research and (if deemed necessary) commercial deployment. The assessment framework contained in annex 5 of the 2013 amendments requires that sufficient "financial resources [be] available before the work commences" (annex 5, para. 8). However, there is no mention in the framework if "financial resources" also includes insurance should the research result in harm to the marine environment. Further research is needed to ascertain whether requiring insurance is necessary to account for situations in which a permitted activity results in harm to the marine environment or whether requiring insurance for research activities is an unnecessary

burden for researchers and their institutions. In some cases, this may have far-reaching consequences for national authorities in whose legal systems the freedom of research is constitutionally guaranteed.

Last, it should be noted that although this Chapter has generally focused on framework treaties of general application and one not-yet-in-force instrument that may offer specific application, this does not mean that other international instruments are not applicable. Given that ocean-based CDR approaches are generally aimed at mitigating the effects of climate change, their regulation has traditionally been dealt with as a matter for environmental law. However, the nature and potential transboundary impact of ocean-based CDR approaches results in overlapping scenarios for regulation. In this regard, commentators have noted the connection between CDR approaches and international peace and security (Maas and Scheffran, 2012); intellectual property rights; matters of food security and international trade (Armeni and Redgwell, 2015); human-rights-related instruments (see Webb et al., 2023); and other international instruments specific to the conservation of migratory species and their natural habitats (see, for example, the 1979 Convention on the Conservation of Migratory Species of Wild Animals). These traditionally distinct regimes are, to various degrees, captured in the Sustainable Development Goals (SDGs) of the United Nations. The potential for an activity such as OAE to straddle several SDGs and the impact that this may have on international cooperation and coordination – especially in reaching climate, ocean, poverty eradication and other related SDG targets – also requires further consideration and research.

7 Conclusion

It has recently been determined that OAE “[f]ield trials are urgently needed in both coastal and open-ocean waters” (NASEM, 2022, p. 203). Conclusions such as these, coupled with the urgent need for States to fulfill their climate obligations under various international instruments and the growing number of active projects, necessitates careful regulation of OAE. Any domestic regulatory regimes adopted by States must fulfill their international responsibilities with respect to protecting and preserving the marine environment and safeguarding potentially affected global or local communities. Among other things, States must fulfill their due diligence obligations in ensuring that the activities of researchers, operators and other private actors within their jurisdiction or control are adequately regulated. At the same time, however, any domestic regulations must remain flexible enough to adapt to rapid technological developments and changing international frameworks.

How States regulate OAE research activities will ultimately depend on the State in question, and differences in domestic legal systems are unavoidable. However, developing a robust framework within international law may increase transparency and assist States in adopting uniform requirements associated with preliminary risk assessments, environmental impact assessment, subsequent monitoring and permitting conditions and procedures for OAE research.

There is a need for further legal research on issues related to OAE research. For example, the relationship between OAE research (as an activity with potentially harmful impacts on the marine environment and/or local coastal communities) and the liability of States and private operators requires further consideration. This is especially true with regard to issues of insurance and the impact that this may have on the freedom of research and the role of private investors.

It remains crucial that legal researchers work with the scientific community and those from other disciplines to assist States in understanding the science–policy interface in order to develop a comprehensive legal framework for ocean-based CDR approaches that will, in turn, guarantee that field research is carried out in a safe and responsible manner and in a manner that reduces the likelihood of adverse environmental and other consequences.

Key recommendations: legal considerations relevant to research on OAE

1. The legality of an OAE research activity will depend on the applicable domestic legislation (i.e., in which jurisdiction the research activity is being undertaken). In the adoption of any domestic legislation, national authorities are encouraged to fulfill their international obligations by adopting domestic legislation that incorporates internationally agreed upon rules and standards.

2. The regulation of “pollution caused by dumping” under the 1996 London Protocol is developing rapidly, and its potential application to OAE research is growing. Researchers should stay abreast of recent initiatives (1) to list OAE as a marine geoengineering activity under the 2013 amendments and (2) to provisionally apply the 2013 amendments (IMO, 2023).

3. The 2013 amendments provide a general assessment framework to evaluate whether an activity – which could be an OAE research activity – can be considered to be legitimate scientific research and, therefore, eligible for a permit. This general assessment framework provides minimum requirements that should be satisfied when designing OAE research activities.

4. In line with the assessment framework, OAE research projects must be designed to answer scientific questions; be subject to peer review and transparency requirements; not be influenced by economic interests; and should be designed to avoid, minimize, or mitigate adverse environmental impacts.

5. In addition to addressing environmental impacts, researchers should take active steps to minimize or mitigate adverse social impacts, as this relates to the impact of (field) research on coastal communities.

6. OAE researchers should consider potential benefits form their research work, and research projects should be designed to maximize benefits and mitigate negative consequences.

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Social considerations and best practices to apply to engaging publics on ocean alkalinity enhancement

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Abstract. Ocean alkalinity enhancement (OAE) seeks to increase the alkalinity of seawater for carbon dioxide removal (CDR). Following numerous propositions to trial, test, or upscale OAE for CDR, multiple social considerations have begun to be identified. To ensure that OAE research is responsible (is attentive to societal priorities) and successful (does not prematurely engender widespread social rejection), it will be critical to understand how OAE might be perceived as risky or controversial and under what conditions it might be regarded by relevant social groups as most worthy of exploration. To facilitate the answering of these questions, this chapter does the following: (1) characterizes what is known to date about public perceptions of OAE, (2) provides methodological suggestions on how to conduct social science research and public engagement to accompany OAE field research, and (3) addresses how knowledge gained from social research and public engagement on OAE can be integrated into ongoing scientific, siting, and communications work.

1 Introduction

Following numerous propositions to trial, test, or operationalize ocean alkalinity enhancement (OAE) for carbon dioxide removal (CDR), multiple social considerations have also begun to be identified, if not yet examined more fully (Oschlies et al., 2023, this Guide). A long history of studying the social uptake of new technologies reveals that many never surpass the threshold of social acceptance, including technologies that members of the scientific community had regarded as safe and wise. Some technologies also introduce concrete consequences for communities that are unanticipated or egregious and/or that deepen social inequities. The stigmatization of whole classes of technology can result from early failures with specific approaches, as has been the case for nuclear power. While initially regarded by physical and material scientists as "too cheap an energy source to meter", first-generation reactors were perceived by public groups as born of war, too difficult to manage, and likely to lead to catastrophic harm (Ramana, 2011). Clean-energy advocates have remained trepidatious in their support of second-generation reactors, given the near-complete shutdown of this technology across 4 decades. This rejection has also occurred with genetically modified foods, which a vast majority of scientists believe safe for human consumption and soil health (Directorate-General for Research and Innovation, 2010). New technologies perceived by public groups to be highly risky – even those with potentially significant benefits – may never achieve widespread use, as policy pressure to limit their dissemination are many and democracies, if imperfect, are designed to respect public will.

This chapter aims to set out key research priorities and accompanying methodological approaches to further public engagement and social science research as field-level investigations of OAE proceed. Much of what we cover might also apply to ocean-based CDR more broadly. We recognize that natural science and engineering research on OAE is in its early stages and so accept that a large suite of social consid-

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erations in need of investigation are not yet apparent or will only become so as initial field trial results emerge. We thus mean to equip OAE researchers, developers, policy makers, and funders with suggestions as to how to conduct accompanying social science research and engagement needed for robust and responsible OAE trial and deployment.

Developing approaches to OAE that are socially supported will be critical to the success of this and other mCDR options in the coming decade(s). Many tend to assume that social concerns can be addressed by providing accurate knowledge and improving literacy on the technology in question. However, accurate knowledge by itself is insufficient (although public knowledge and literacy on OAE will likely improve over time). Only in rare cases does such provision of information vanquish any social concerns. At present, some evidence suggests that OAE is perceived negatively or is less acceptable than other mCDR options (Nawaz et al., 2023b). While it is tempting to assume that all that is needed is to "get the numbers right, communicate these, treat people well, and show them that it's a good deal for them and is just like comparable risks" (Fischhoff, 1995) – such an approach will very likely backfire in the case of OAE (Kahan et al., 2015; Pidgeon and Fischhoff, 2013).

Social research and engagement on OAE need to provide unbiased information, but they are about far more than that. Instead, what is needed are open conversations where not only the "facts" are relevant but so too are the social logics, values, and governing conditions relevant to OAE. Importantly, such conversations with publics on OAE need to involve an "opening up" (Stirling, 2008) of research to the many possible formulations that this class of technologies might take so that social priorities can be embedded in the formulations of OAE that follow. This opening-up principle is intrinsic to "responsible research and innovation", or RRI, which emphasizes the incorporation of societal values, needs, and expectations in research on emerging technologies like OAE (Burget et al., 2017). Scholars have highlighted several dimensions to guide RRI approaches including "anticipation", "inclusivity", "reflexivity", and "responsiveness" (Owen et al., 2013). By this, we mean research on OAE must *anticipate* the potential, unforeseen consequences of OAE; it must be *inclusive* in how it assesses potential risks, benefits, and potential alternatives; it must be *reflexively* aware of the limits of understanding and that certain framings of research are not universally held, and it must be *responsive* to the views of social groups and the concerns that they raise, as well as to changing circumstances. In summary, to ensure that OAE research is ethical (is attentive to societal priorities) and successful (does not prematurely engender widespread social rejection), it will be critical to understand in what ways and how OAE might be perceived as risky or controversial and under what conditions it might be regarded by relevant social groups as most worthy of exploration.

Three primary goals toward these ends include the following:

1. We briefly characterize (Sect. 2) what is known to date about public perceptions of OAE and what is also known or tends to be true about perceptions of new technologies in general. This is meant as both a starting framework for future research on OAE and as a summation useful to scientists and engineers so that a priori assumptions about how people will think about OAE are grounded in this body of research. This existing knowledge will also help scientists understand their social audience and engage with publics when projects are in their early stages. The focus in this section, in particular, is to spell out those factors known to influence public perception – knowledge that is key to communication and to social research that need follow.

2. Our next goal (Sect. 3) aims to spell out several primary research methods that might be employed when conducting public engagement research linked to OAE projects at different stages and scales (e.g., early stage and highly local versus a regional or national mandate to expand OAE as a primary carbon dioxide removing technology). This includes specific approaches most widely used in the social assessment of new technologies, and it includes key principles for conducting ongoing and iterative community engagement, guidance on mapping and working with representative communities, developing baseline understandings of potentially affected communities, and ultimately, involving these groups in decision-making on OAE.

3. Our third and final goal is to address how knowledge gained from social research on OAE might be integrated into scientific, siting, and communications work on OAE – including steps that might ensure continued and quality public engagement.

Our audience across these goals are social scientists and those with whom they work who might use these approaches when conducting engagement research on OAE. By "those with whom they work", we mean those working on or funding OAE science and engineering research. Ultimately one goal is to build literacy about social science approaches to enhance communication across interdisciplinary research teams. This will help ensure that social considerations are robustly considered in projects from the outset and that knowledge of social considerations (e.g., perceptions, impacts) is developed as part of broader OAE research.

What this guide is not. This is not a communication guide for promoting OAE. Social acceptance of OAE will take on a life of its own across different times and places and will be understood and received in ways that cannot be controlled. Rather it is our hope that a solid foundation in the social implications of this new class of technology will better inform its development. For this reason, there is an urgent need to incorporate a wide and diverse body of social research and social groups into the evaluation of OAE so that its potential is explored with all of those it might affect.

A point of clarification. By engagement we mean any social science approach that explores public thinking, responses to, support or rejection of, and/or expectations as to what OAE is, what impacts it might have (positive or negative), or how OAE might better reflect or respond to social concerns. We also take the position that community engagement should be a part of all OAE and all ocean CDR projects (Nawaz et al., 2023a). In this sense, social research and engagement are synonymous terms. By methods for social research, we mean specific approaches to the collection of "data", its analysis, or its interpretation wherein the goal is to understand and address how people think about OAE.

2 Tracking what might influence public perception of OAE

Here we present several factors that already appear or will likely become relevant to public perception of OAE and mCDR based on the limited literature on the topic. We also draw upon insights from broader literature on perceptions of novel technologies and climate mitigation approaches, proximate studies of marine-relevant approaches, and we assume that terrestrial CDR is also instructive to the extent that it shares some features (e.g., crushed mineral material). Thus, specific OAE approaches are ideal, but as these are limited, we also address proximate work on public thinking about any materials added to terrestrial or ocean systems. For example, this may include fertilization approaches (adding material to encourage phytoplankton growth so that such growth might capture atmospheric carbon) or enhanced rock weathering (adding crushed silicates to agricultural lands to capture carbon). Early work on OAE and related technologies draws eight initial propositions regarding perceptions of field-level trials:

1. Overall, OAE and its nearest equivalents are seen as relatively less acceptable, more likely to invoke affectively negative feelings, or to be viewed as relatively more or most risky when compared to other carbon removal strategies (Cox et al., 2020; Jobin and Siegrist, 2020; Bertram and Merk, 2020; Shrum et al., 2020; Spence et al., 2021).
2. Concerns about environmental impacts and perceptions of the vulnerability of ocean and marine systems may be determinative of rejection of OAE and its equivalents (Cox et al., 2020; Nawaz et al., 2023b).
3. Interventions perceived as involving dispersal of materials are less desirable than those involving controlled storage (e.g., burial on land or beneath the seabed) (Cooley et al., 2023).
4. Source materials involving heavy reliance on mining are less likely to be supported (Moosdorf et al., 2014; Spence et al., 2021).
5. Associations of OAE with analogies of waste dispersal or the ocean as "landfill" will likely be aligned with rejection or deep discomfort (Cox et al., 2020; Veland and Merk, 2021).
6. The energy burden of technologies and the status of energy transition activities will likely affect acceptability (Andersen et al., 2022).
7. The justness of the conditions of research and practice will be key and involve at the very least concerns about monitoring (e.g., is there good citizen oversight?) and responsibility of innovators and investors (e.g., is transparency of storage duration clear? Is there a polluter pay model in place) (Ingelson et al., 2010).
8. The political and value considerations held by the publics involved will also likely matter (Satterfield et al., 2023; Shrum et al., 2020).

Below, we discuss these propositions in reference to the three ways in which people's thinking about new technologies tends to unfold. First, judgements about new technologies tend to be linked to or sensitive to the attributes of the technology itself (the features it has and the affective signals associated with those features). Second, judgements tend also to be a function of the attributes of those perceiving the technology (their values, social position or ethical evaluations). Third, views about how the technology is or might be managed or governed are also determinative of judgements (e.g., what policies exist, the quality of research and monitoring, the existence of community involvement and oversight). As we review these in further detail, we discuss how each has or might be used to research OAE's perceived acceptability, riskiness, or social viability.

2.1 Attributes of the technology as predictive of rejection/acceptance

Ultimately, most people evaluate risks as a function of many things, including the attributes or intuitive qualities they assign to or perceive to be characteristic of the technology itself. This is as against or a counter-intuitive claim for many natural and physical scientists or formal risk assessors, who might instead define risk as severity (times) magnitude or mortality and morbidity (Siegrist and Árvai, 2020) Factors that drive perception have been long identified across a diverse range of technologies, including feelings of dread that people may associate with a technology or exposure to it; the degree of control people feel they have over the risk it might pose; the extent to which their exposure is voluntary or not; the perceived severity of its consequences; and one's familiarity with the technology itself (Fischhoff et al., 1978;

Slovic, 2000; Cox et al., 2021). Many such factors have been tested and isolated in prior studies, but perceptions of control will likely be key. This is due to the possibility that people may view the introduction of materials to the ocean as something that cannot be controlled once released or because enhancement might be deemed an irreversible act. Interventions perceived as involving broadcast dispersal of materials are less desirable than those involving controlled storage (e.g., burial on land or beneath the seabed) (Cooley et al., 2023). In the case of fracking, by way of example, perceived benefits of shale gas extraction were offset by the perception that irreversible risks to water systems accompanied this practice and amplified perceived risks overall (Thomas et al., 2017). Genetic engineering has been rejected widely for similar reasons due to the belief that the risks to human or agricultural systems are both catastrophic and irreversible (Sunstein, 2005).

Perceptions that scientists might be unable to contain or control many ocean-based interventions tend to accompany the belief that the consequences of interventions will be negative for marine ecosystems and livelihoods and may also indicate that such approaches will be perceived as highly risky or highly unacceptable. One early UK study found, for example, that support for ocean liming and ocean iron fertilization was lower than support for solar radiation management or solar geoengineering as it has come to be known, because of concerns about the unpredictability and uncontrollability of the ocean environment (Cox et al., 2021). Previous work also suggests that outdoor experimentation carried out at a small scale and under well-controlled conditions is likely to be generally acceptable to affected publics (Cummings et al., 2017). However, the public may also be skeptical of scientists' abilities to carry out controlled and accurate research in atmospheric contexts (e.g., Merk et al., 2015) or in the marine environment, given that it is such an open, interconnected system (Pidgeon et al., 2013; Bertram and Merk, 2020).

Public perceptions are commonly assumed to be shaped as well by the extent to which OAE approaches are viewed as "natural" or not (Bertram and Merk, 2020). Those interventions perceived as "tampering with nature" (Corner et al., 2013; Wolske et al., 2019) or characterized as (un)natural are more likely to be rejected. However, the emerging habit of labelling interventions as "natural" is now so pervasive to have led to an overuse of claims of "nature-based" solutions, which may introduce a backlash effect longer term (Seddon et al., 2020; Bellamy, 2022). Specifically, people may consider promises of OAE as mimicking natural geochemical weathering reactions to be equivalent to a falsehood deserving of distrust. Distrust of natural claims may also occur when the scale of, for example, macro-algae CDR aims to remove a megatonne of carbon dioxide rendering the use of infrastructure, ships, and seabed storage vast enough to be suspect (Osaka et al., 2021).

The "signals" that are perceptually linked to particular aspects of OAE will also be a function of the analogies people draw upon as they make sense of these. That is, people make sense of new and novel technologies by drawing upon old ones (Pidgeon et al., 2012; Visschers et al., 2007). For example, amongst groups in the UK, carbon removal has been found to invoke associations with fracking and shale gas (Cox et al., 2021). It is likely that OAE will invoke its own set of accompanying associations, but one possibility is that materials discharged into the ocean will be perceived as waste products or waste disposal. As Merk et al. (2022) found, in the context of CCS, CO_2 is often perceived as waste even though it is not toxic, radioactive, or explosive.

Lastly, the source of materials used for alkalinity enhancement, rock weathering, or other material-intensive processes may also become a key attribute in the evaluation of this and related CDR technologies. For example, the mining needed to procure materials and the energy costs involved with their sourcing, grinding, and distribution may reduce potential support for this form of CO_2 removal, all the more so if their environmental or social consequences are deemed high (Moosdorf et al., 2014).

Key message. The technology's specific attributes will have a powerful influence on the acceptability of OAE overall, and under no circumstances should any approach be considered "neutral" at the outset. Rather, publics will engage in proposed OAE trials and operation in reference to (a) signals they will *read into* the technology, with (b) some attributes of the technology likely to be perceived as relatively more worrisome including non-site attributes such as the source of materials used in operation and the perceived "broadcast" or "waste-like" assumptions about material distribution in marine systems.

2.2 Attributes of the perceiver – beliefs about ocean systems, values, and worldviews

2.2.1 Beliefs about oceans and marine environment

In need of continued evaluation are also the ethical and value positions that people hold regarding OAE. These include worldviews about what kind of system the ocean is or what kind of political orientations people carry as both are likely influential regarding how OAE will be received or supported. For example, previous research has found that the ocean is often perceived as fragile and pristine (Hawkins et al., 2016; Cox et al., 2021) and finds that interfering with the ocean might be seen as "hubristically" transgressing the human ability to understand and control complex ecosystems (Macnaghten et al., 2019; Wibeck et al., 2017; Gannon and Hulme, 2018). Research in Scotland and Norway has previously shown that publics believe even changes in the open ocean or the deep sea would affect them and that they were not confident in the abilities of experts to protect the marine environment (Ankamah-Yeboah et al., 2020). The concern people express about the ocean is commonly linked to a positive emotional connection with it (McMahan and Estes, 2015). Importantly, previous public perception research on a wider range of marine and terrestrial CDR approaches suggests that emotional connection to the ocean manifests similarly in coastal and inland populations (Cox et al., 2020, 2021). Coastal First Nation populations in British Columbia have also protested strongly against fertilization experiments, which were viewed as insufficiently supported by science and dismissive of legal agreements (Tollefson, 2012; Buck, 2019a).

Such views will likely vary with context of a particular OAE project or be borne of contextually specific local meanings (Mabon and Shackley, 2015; Gannon and Hulme, 2018) and cultural connections to the marine environment – for example, the extent to which the ocean is perceived as an important food or resource provider (Potts et al., 2016). Perceptions may also differ between the Global North and South and Indigenous and non-Indigenous groups (Pidgeon et al., 2013; Carr and Yung, 2018; Whyte, 2018) – there has so far been very little research on the perceptions of publics outside North America and Europe including Indigenous communities within these nations and across the Global South. Views about ocean systems will also articulate with the specific sites of dispersal selected: be that near coastal populations or in the distant ocean or be that seen as despoiling of natural beauty or using a site of a previous industrial activity. Ultimately, views of marine environments are unique and varied, and that variation might include those who view ocean systems as adaptable. Such views tend to be associated with the judgement that alkalinity enhancement and ocean fertilization are comfortable or viable options, whereas notions of the marine system as fragile correspond to discomfort with both these CDR approaches (Nawaz et al., 2023b).

2.2.2 Beliefs about the problem of climate change

Public perceptions of CDR research have tended to assume that climate beliefs can shed light on views about and/or the acceptability of OAE and other CDR. But new research suggests that views on climate urgency might be as or more predictive (Cox et al., 2020; Nawaz et al., 2023b). It is possible that people who find climate change an urgent problem are more inclined to be interested in novel and potentially controversial options in general or because they have lost hope as to energy transitions or in other approaches to capture and store CO_2. It is also possible, however, that people who find climate change to be urgent find new CDR methods to be insufficient, slow, or failing to address structural or root causes of climate change itself (Lamb et al., 2020). Similarly, claims of urgency can be perceived as suspicious justification for poor public consultation or scientific practice.

2.2.3 Ethical positions

Ethically central across several studies is the problem of moral hazard. This refers to people who perceive CDR including OAE as exacerbating ongoing emissions. The logic is that the ongoing failure to decarbonize energy and food systems will only continue if methods to remove greenhouse gases are introduced; that is, CDR is seen as deterring mitigation in the first place (Cox et al., 2018; Markusson et al., 2018; Carton et al., 2023). At the centre of this debate are those who regard net zero as a temporary phase on the path away from fossil fuels,versus those who view net zero as a means to ongoing fossil fuel extraction (Buck, 2020). This tension is likely key to public groups' views on any OAE research and deployment, with those who see OAE as enabling continued emissions as most likely to reject its research and development. Also important here is what sorts of emissions are perceived as being "allowed" to be "counterbalanced" through CDR (Lund et al., 2023; Buck et al., 2023). What emissions are seen as "legitimately" hard to abate/residual? How is (are) the public(s) involved in defining this? Ethical concern for and obligation toward future generations is another morally charged position aligned with discussions of CDR options and with the growth of anti-fossil-fuel norms more broadly (Green, 2018). As with moral hazard concerns, two social trajectories are possible: an unwarranted reliance on CDR in the absence of significant emissions reduction thereby placing future generations in peril (Dooley et al., 2021). Or the assumption that rapid decarbonizing will occur putting generations at risk should modelled projections fail to anticipate that future accurately (Morrow et al., 2020).

2.2.4 Political worldviews

Views on the "truth" of climate change itself, and the policies adopted to address it, have long been politically polarized (Strefler et al., 2018; Campbell and Kay, 2014), and public acceptability of climate policy has been shown to be linked to broader political alliances and cleavages. It is thus reasonable to assume that aspects of this polarization will migrate to carbon dioxide removal. Thus far, it appears that political positions (e.g., those representing left-to-right or egalitarian-to-hierarchical political worldviews) are influential but not absolute. For example, following tutorials on CDR options, some then regarded the threat of climate change as less severe, which also reduced perceived need of mitigation policies. The effect was relatively more pronounced among political conservatives (Campbell-Arvai et al., 2017). Ultimately, conversations across publics need to remain open and heterogenous, not polarized, to enable consideration of options. In addition, those who do attend to and/or recognize a broad set of perceived benefits for some ocean CDR options appear to hold that position and remain more steadfast as concerns acceptability in general and (largely) independent of political position (Satterfield et al., 2023).

Key message. If people view marine systems as fragile, regard mitigating actions as morally compromising to greenhouse gas (GHG) emissions and energy transitions, or adhere to politically polarized positions, they may be less likely to find OAE acceptable. Viewing climate change as an urgent problem could have mixed influences, leading to impatience or suspicion about technologies in early development phases.

2.3 Attributes of risk management and governance

Key to all efforts to address the social viability of OAE, indeed all CDR, is how that technology is or will be managed and the quality of consultative public engagement. This includes attention to environmental justice and the quality of public trust in those managing the technology – its risks and benefits across all phases and locations of the work. Trust itself is sensitive and easy to destroy by early missteps. Similarly, distributional justice will be of primary concern for most people, and so clear articulation of the choice of sites for trial and consultation in advance is of primary concern (McCauley et al., 2019).

2.3.1 Governance

Governance is an all-encompassing term, but across contexts such as this, citizens are most likely concerned with the following operating principles, many of which are out of purview for scientists and engineers and so preparation in advance of any form of public engagement is advised. Governance questions most likely to be central involve (a) how the project will be studied and monitored such as the following: are local actors/citizens involved in monitoring and oversight (e.g., citizen science approaches) and (b) how will their concerns be addressed by the policy and scientific community? What are the conditions under which operation or trial might cease and who controls that decision? What is the distribution of risks and benefits overall and in reference to specific impacted or vulnerable communities? How eventual projects will be financed is also out of purview for most OAE scientists and engineers; however it is wise to anticipate the following questions: what are the likely mechanisms for financing OAE, be that a carbon pricing or similar market mechanism, green bonds and/or impact investing, or "polluter pay" models (Rickels et al., 2021; Bellamy et al., 2021)? More broadly, it is common to be asked how global responsibility will be addressed (Mohan et al., 2021; Bellamy et al., 2021; Morrow et al., 2020). For example, will responsibility for using such technologies be a function of carbon footprints per capita, in reference to lesser histories of emissions or developing country needs, or will cost recovery primarily involve financial incentives for original polluters? Will a public agency or utility operator oversee operations or a trusted but independent entity? Lastly, should an OAE project fail or move into closure, is a social assurance or bond for clean-up or removal of the facility itself in place?

2.3.2 Environmental justice

Environmental justice is itself key to governance, including distributive justice (who suffers the impacts of development versus any gains), procedural justice (how decisions are made and whether they receive robust consideration of those most impacted), and recognition and reparative justice (recognizing and addressing past harms rather than assuming a neutral or benign present) (Batchelor, 2023; Whyte, 2011). In sum, focused consideration must be given to communities, especially vulnerable ones in the Global North and South that might be relatively more affected by OAE trial and operation, including specific delineation of impacts to human health, livelihoods, local biodiversity, and other potential effects. This is often addressed in reference, equally, to potential co-benefits of OAE including whether these differ across contexts or communities. To understand how OAE will impact people, it will be essential to consider specific configurations of projects and specific research or deployment contexts. As such, a more fulsome understanding of the potential consequences (both positive and negative) of OAE will only be understood by engaging with local communities alongside any experimental research on or deployment of OAE. Any possibility that OAE might also produce new inequities should be considered. Central to these questions are First Nation and Tribal communities across settler nations and Inuit and Sami communities in the circumpolar north. In both cases, energy development has already dramatically affected many communities in general and in such a way as to transgress rights and jurisdictional authority. The idea that such technologies can be "sold" as green development has largely resulted in significant loss of trust (Mohan et al., 2021) and has neglected the extent to which communities have a long history of living with the effects of engineered nature (Whyte, 2018). Nesting any CDR option in reference to a community's larger goals is also key – be those economic development, educational opportunities for youth, or pursuit of land claims with nation states. See Salomon et al. (2023), for example, for wider governing principles with regard to Indigenous communities and emerging science.

2.3.3 Trust

Ultimately all research concerning the influence of trust indicates that governance efforts should aim to maintain and enhance civic trust and recognize – equally – that trust is extremely easy to lose across early mis-steps and very difficult to (re-)gain. This is known as the trust asymmetry principle across the risk and behavioural sciences literature (Slovic, 1993; Poortinga and Pidgeon, 2004) and is perhaps the most studied concept when seeking to understand public rejection or acceptance of new technologies (Cummings et al., 2017; Siegrist, 2021) including those aimed at climate mitigation (Boyd et al., 2017). When risk management is badly handled (e.g., unfounded claims of no risk followed by a hazardous event) or responsibility for a failure is side-stepped by public agencies and industry, such actions tend to be received by citizens as a failure of transparency that is difficult to repair and an indicator of future behaviour.

Key message. How OAE or any carbon removal system is governed should be of primary concern. This should address the justness of risks and benefits, particularly when vulnerable communities are involved. Failure to gain or maintain public trust will be central, as is transparency about how the system will be managed and financed, and how impacts are reported and addressed.

3 Beyond known factors: methods moving forward

Having established a minimum set of factors likely embedded in public thinking about the risks or acceptability of OAE, our next goal is to suggest methods for engaging affected and interested groups in OAE. We strongly recommend that a consultation and engagement plan be developed at the outset of any research effort on OAE (whether place-based or not) and throughout its different stages of development. The methods that follow are thus aimed at identifying social concerns or conditions for acceptance across different phases of OAE research and development and across different geographical scales as the scope and range of social constituents for ocean CDR vary. As with the above set of factors (Sect. 2), the methods covered are not exhaustive, but they are those most commonly employed. For clarification we use the language of understanding public views, which is our umbrella term for both (a) the reasons that OAE may be deemed acceptable or not and (b) the impacts that social and/or expert groups co-identify as driving their support or rejection or necessitating attention or additional research. In addition, all methods should involve the following: extensive preparatory work, which we briefly characterize below, and a clear plan on how this research might be iteratively used to inform, modify, or articulate science and engineering practices.

3.1 Doing your homework before sited-based engagement activities or selecting pilot sites

Before any research activities, it is important to establish a baseline understanding of who the potentially affected community might be. This theoretically should begin with first mapping the areas that the project affects – critically, this must go beyond just the physical footprint of the project to also include all the additional land, inputs, and infrastructure that the project uses. In the context of OAE, this affected area is not straightforward as injections of alkalinity into marine spaces travel in fugitive ways, likely proving difficult to "map" or monitor. At the very least, a cursory evaluation of this history of and social considerations in place before committing significant resources to a trial is wise. Because of this ambiguity, it is ideal of course to anticipate the full scope of activities in an area, including future activities and/or sites.

Social characterization analysis of this kind facilitates an understanding of how local political processes and dynamics work, in addition to broader contextual factors. Relevant factors include the following considerations in particular:

- *Social*. What are the demographics in the area? What kind of history exists between community developers and regulators? What is current status of education, health, and living standards? Are there particular historic factors of note (NETL, 2017; WRI, 2010)? Key questions include the following: what vulnerable groups are in the area (e.g., who might be affected by an installation but outside decision authority)? Are areas heavily industrialized and so the burden of development projects is already high? Who is most likely to experience significant impacts associated with otherwise quite small changes?

- *Political*. What kind of local political situation is present? What kind of local and international lobbying/advocacy groups exist?

- *Economic*. What are the major employment sectors? What are economic trends in the region regarding job growth, unemployment, cost of inputs, etc.?

- *Environmental*. What kind of legacy of environmental damage or intervention exists?

Other factors will also be not only relevant but also helpful in selecting pilot sites. It can be assumed that scientists and engineers will have reasons for designating some sites for mesocosm and field trials as "ideal". These might include seeking coastal areas with shallow seabed or turbulent waters to ensure admixture of materials and their locations in the water column are optimal. The same is true when considering the social viability of sites for OAE research and deployment. Ideal sites might include those where *jurisdiction, decision-making authority, and regulatory context are clear*. These include sites where who has jurisdiction as to coastal and ocean space is clear and legal approval to operate has been sought or granted. Sites are less optimal when there is overlapping or competing jurisdiction or if jurisdictional authority is vague or where regulatory/legal context is unclear (e.g., poor designation of activities allowed or of permits needed) (Webb et al., 2021; Hoberg, 2013). Similarly, sites where *trust in local governance and climate action is comparatively sound are optimal* (see Sect. 2.3.3 above). By this we mean sites where the governing body's record to date on energy transitions, civic engagement, or meeting climate targets is clear and supported; where clear rules are in place for suspending trial and operation are agreed upon; and where operators will abide by normal regulatory practices and are not exempt from these when scaling up operations.

3.2 Methodological preparation for all forms of engagement

All methods for engagement require development in reference to information that might be necessary or useful and the tailoring of research to upstream (early-stage development) contexts. For example, as part of specific designs, mini-tutorials might be employed or even staged in additive steps, but the explanations are comparatively minimal and definitional (see Sect. 3.2.5). Conversely, the deliberative and small-group work described below might include extensive advance research on how to provide informational material, when and in what form. Lastly, decision-centric designs that seek to integrate public and expert knowledge might require developing knowledge once known social, environmental, or other impact can be classified or measured. At a minimum, all engagement designs will benefit from the following key considerations.

Tailor methods to the early-stage nature of research on this topic. Given the aforementioned upstream context of research, accept that public concerns and thinking are less formed. This means both (1) ensuring adequate time for participants to learn about OAE within engagement activities and (2) following Stirling (2008) ensuring that engagement efforts remain open-ended regarding the full possible suite of technological configurations and approaches that could arise. This might involve clarifying different possibilities regarding what an "end-stage" technology might look like and how it might vary from the original proof of concept.

Outline potential impacts and uncertainties. Any engagement activity with local groups will inevitably generate many questions around the likely environmental and socio-economic impacts (both positive and negative) of the activities proposed. These impacts should be raised proactively, and areas of uncertainty should be acknowledged. For OAE, these might include, for example, biodiversity-related, fisheries-related, human-health-related, visual/aesthetic, marine traffic, or navigational effects, among other impacts.

Be transparent about the full potential scale of OAE deployment. Ideally, engagement activities should provide participants with what OAE might look like at scale – not just with regard to an individual project's small field trial. While it may be tempting to only engage people on their views regarding very small-scale activities, it will be critical – for both ethical and pragmatic reasons – to explore views on larger-scale implementations. It is well known that understanding large-scale events such as humanitarian disasters is difficult if not beyond comprehension (Slovic, 2007). But this does not preclude the potential usefulness of comparing OAE at the 2 Mt scale as compared to the production and storage (sinking) of macroalgae or the use of offshore direct air capture and storage at similar scales. This would likely throw both social preferences and likely tradeoffs into relief by introducing considerations such as shipping (to gather, bundle, and sink macroalgae) or drilling (to store CO_2 in offshore basalts).

Characterize the full supply chain of OAE activities. Similarly, while it might appear at first glance that engagement only need explore views on direct interventions to marine biogeochemistry, OAE will involve a range of other activities that need to be brought into engagement efforts. This would include both the sourcing and processing of material inputs (e.g., mining of materials), as well as the management and end use of waste outputs.

Recognize and address the challenge of tutorials and communication more broadly. Communication around novel technologies and their potential risks and benefits is likely not an intuitive process for many non-social scientists (and indeed many social scientists). Developing and pre-testing materials – whether tutorials or preparations for Q&As – needs to consider risk communication research (Balog-Way et al., 2020). For example, numbers need to be provided in context so that people can understand them by way of equivalents, such as carbon dioxide removal anchored to the number of cars removed from the roadway. Similarly, different frames can be used to present a topic, and care is needed to avoid frames that might have undue influence on views (e.g., using naturalistic framings as referenced above). Communications need to be pre-tested to ensure that complex concepts involved in OAE are made accessible to a broad base of groups with variable levels of education and existing understanding. Visual aids, relatable analogies, graphic representations, and other approaches will be of use. Where possible, introduction of OAE could include lab visits, site visits, tours (WRI, 2010), or other mechanisms to help people understand the kinds of activities that might be involved. Two-way communication is foundationally important (Abelson et al., 2003; see also Puustinen et al., 2020).

Make sure your narratives of purpose and outcome are clear. Is it clear that the research goal is one of trial only, and/or are operational goals also clear and transparent? It is useful to provide information of proposed research in advance. And, we find, claims of hyper-urgency or naturalness can be read as excuses to avoid regulation or downplay ecosystem or social risks (Osaka et al., 2021). Oppositional actors should be identified and approached so as to research and include their concerns – they will not be speaking for themselves alone (Low et al., 2022).

Clarify the relationship of OAE removals to emissions. With estimates of the potential scale of necessary carbon removal differing widely across approaches, it remains important to clarify and develop greater transparency around what kind of emissions OAE exists to remove and at what scale (e.g., Gt, Mt). Emphasizing the connection to hard-to-abate emissions – rather than the enabling of business-as-usual for fossil extraction – must be clear. Ideally, the temporal horizon for OAE will also be known by those proposing research as compared to other CDR options.

Plan to discuss failure, success, and next steps. Engagement should plan to discuss how the researchers will deem a trial sufficient to proceed to next steps – and under what circumstances it would be deemed not fit for next stages of research.

3.3 Six engagement methods in brief

Accepting that preparatory work noted above is complete, many engagement methods become possible. Below we address six methods commonly used where each is meant to be illustrative only and each is somewhat aligned to the stage and purpose of OAE scientific work. These are listed below and then elaborated more fully in the sections that follow. Table 1, below, also locates all methods in reference to their stage of application and purpose.

Early-stage development (alongside mesocosm experiments or early field trials) includes the following:

1. *World café deliberative approaches* are particularly useful for providing initial insight and scoping of questions people have, fit with local priorities and discourses used by different engaged groups.

2. *Participatory foresight* is particularly useful for understanding current and envisaged governance landscapes, including who is speaking for which communities and what their primary priorities and positions are.

3. *Indigenous methods and protocols* are essential to understanding the research process itself as requiring recognition of histories, engagement protocols, and situating all work in reference to community priorities, knowledge protocols, and relations.

Mid-stage development (scaling up to fuller pilot studies, site selection criteria, or choices across options) includes the following:

4. *Survey research* is appropriate for broad-scale consideration of prevailing positions and the factors that explain these across larger areas or populations and/or in reference to magnitude of specific pro or con positions.

5. *Decision-specific public engagement* is particularly useful for integrating measures that reflect value concerns held by publics or impacts designated by experts. These can then be tracked as "performance measures" that inform tradeoffs or become the basis for developing alternatives to a proposed approach or designing monitoring conditions for a trial.

Late-stage development (seeking large population public views regarding involvement of OAE or similar as a significant part of national policies to meet climate goals) includes the following:

6. *Deliberative polling* seeks to gauge support reflecting regional and population calibrated positions: pro or con. This also includes civic engagement of concerns and consideration in between polls to reflect conversations active in media, popular blogging, or similar civic contexts.

3.4 The deliberative turn

In recent years, social science scholarship on public thinking about new technologies has undergone what is referred to as the "deliberative" turn, which emphasizes the need for social research into public thinking throughout the period of a technology's development. Deliberative work can be most useful in the early to mid-stages of development. Typically, small-group designs involve 10–15 carefully selected participants to reflect as fully as possible the full diversity of a region (e.g., from urban to rural or to specifically address Indigenous or resource-dependent communities). Each workshop generally lasts a minimum of 1 d but often runs over 2 or 3 d or more where needed.

Deliberative methods emphasize communicative competence, mutual and high-quality conversation, and respect for difference across interpretive communities (Parkins and Mitchell, 2005). Motivated by political science theories of deliberative democracy – and greater public participation in policy decision-making (Dryzek, 2002; Fishkin, 1991) – newer research is expressly focused on "upstream" contexts. By this we mean participatory and anticipatory (i.e., early) public engagement where policy development recognizes that scientific knowledge is but one of several ways through which people engage with their environments, in this case ocean-based contexts. Such methods accept that public thinking is value-based, and that environments are understood through interpretive logics that are also perceptual, cultural, ethical, and relational (Eden, 1996; Borth and Nicholson, 2021).

When technologies are new and novel, as is the case for all forms of CDR, designs that "open up" conversation are a priority (Stirling, 2008), where such an opening refers to research practices that expand the diversity of perspectives included and the creativity and ingenuity by which bidirectional exchange and learning occur. Quality of research is regarded as "high" when diversity of stakeholders is evident (especially locally interested parties, and under-served or vulnerable communities, but not developers per se), many media are used for articulating ideas (e.g., written, verbal, visual), and when accessibility and non-coercive qualities in informational materials are ensured. Sessions are typically recorded for use in thematic data analysis once workshops are complete. Results might include summative pro or con positions on a new technology, but more typically they involve a characterization of the following: the research questions or addressing of unknowns that people most seek; the conditions under which proceeding might be deemed most

Table 1. Engagement methods/approaches suited for different-scale project-level engagement research on OAE.

Engagement methods/ approaches	Stage of application	Requirements	Purpose	Questions the method can begin answering	RRI principle(s) addressed by the method
(1) World café*	Early-stage	Background regarding local context (governance, political, cultural, demographic, etc.)	Initial insight, scoping of people's questions and concerns, fit with local priorities, discourses in play, understanding governance and operating conditions	What are primary concerns and ethical considerations? How does OAE align or not with local priorities? "No-go" zones – what actions and/or locations are off the table? What questions should researchers be asking in further iterations? Does the project need to change or alter project design?	Inclusivity & reflexivity
(2) Participatory foresight	Early-stage	Background regarding local (governance) context	Scoping plausible future (perceived) threats and opportunities which could be presented by OAE in a given setting, identifying governance instruments that may be robust across plausible OAE futures	What are local stakeholders' understandings of feasible and desirable OAE developments? How can different types of knowledge (i.e., academic, practitioner, local and indigenous) be integrated into OAE project planning and governance processes?	Anticipation & inclusivity
(3) Indigenous methods	Early-stage	Deep reflection on colonial research practices and their reshaping through Indigenous methods	Co-construction of research priorities, how the marine system involved is classified and what it is constituted of	What impacts are deemed most important, which species or sites are most culturally important? What histories of place define the marine-scape? Whether or not OAE articulates with Indigenous priorities and future development?	Inclusivity & reflexivity
(4) Decision-making designs	Mid- and late-stage	Clear "decision context" is known, i.e., what are different potential options on the table for consideration	Inform specific decisions; highlight trade-offs; consider and/or develop alternative solutions; integrate knowledge and values of experts and publics	How do different groups weigh trade-offs involved in OAE options? What specific features of options (ecological impacts, ownership questions, funding, etc.) are particularly important to informing views?	Inclusivity & reflexivity
(5) Surveys	Early- and late-stage (early: for understanding broad, coarse-scale understanding of views and factors that drive them, later stage specifics on large-scale field trials)	Clear "sample frame", or understanding of who should be delineated as relevant groups for weighing in on an OAE project	Broad-scale consideration of prevailing positions across large areas or populations and/or verification of positions in general versus those proposed by specific vocal groups	Suited to questions of distribution of acceptability or rejection of different CDR options. Widely used for revealing latent variables that influence acceptability, broadly stated	Inclusivity
(6) Deliberative polling	Late-stage: in association with large-scale field trials	Clear policy question to ask participants, e.g., "should we implement XYZ project"; clear sample frame, or understanding of who should be delineated as a relevant group.	Understand approval or disapproval from statistically representative sample; understand logics and thinking behind these approval/disapproval findings	Would participants approve of a specific version of OAE?	Inclusivity

* Similar methods include deliberative mapping, citizen panels, and mini-public.

viable (e.g., use of citizen oversight, or concurrent gains across renewable deployment); and elaborated details as to the social logics used to comprehend OAE research (as necessary, urgent, unwise, etc.). The spectrum of methods is itself spread across a continuum of those more highly analytic and decision-centric through to those more deliberative, though attention to both is crucial (Renn, 1999, 2004, 2015).

Inclusive participant sampling considerations are key to the success of all deliberative methods. Key selection criteria are diversity in terms of age, gender, ethnicity and racialized groups, educational and occupational background, as well as in terms of stance on OAE research (pro, con, ambivalent). The inclusion of dissenting or opposing voices is expressly necessary to enable inclusive deliberative engagement. It is also necessary to make engagement events and processes accessible to groups that otherwise might be excluded. Some ways of doing this include selecting venues that are easily accessed by public transport; publicizing planned activities in advance and across multiple outlets; offering engagement events at multiple, asynchronous, convenient times; and offering events in languages other than the lingua franca, where relevant; offering to provide free childcare for event participants; considering compensating participants for their time; and including virtual engagement options (Ross et al., 2022; NTEL, 2017).

3.4.1 Engagement approach 1: world café and mini-public approaches (early stage and possibly throughout)

The world café method is a participatory process that aims to facilitate meaningful and inclusive discussions among large groups of people (Brown, 2005; Pidgeon et al., 2009; see Pidgeon, 2021, for a CDR example). It is commonly used to explore complex issues, generate new ideas, and foster collective wisdom. The purposes of a world café are to promote collaborative dialogue, tap into collective intelligence, foster innovation and creativity, and encourage action planning (Löhr et al., 2020). More generally, the method provides a platform for open and inclusive conversations where diverse perspectives on an issue can be shared and explored. The key strengths of the world café are its inclusivity, creativity, scalability, and flexibility. It is designed to include diverse perspectives, leading to a sense of issue ownership from participants, and provides interactive space for scoping a broad range of perspectives about an issue. Its success also lies in its usefulness across academic and practitioner need for rapid but also systematic insight (Schiele et al., 2022).

The structure of a world café typically involves participants being seated at small tables with designated hosts to facilitate the conversation. The process begins with a brief introduction and a "big" question or theme, which attendees are asked to discuss. Each table can focus on a specific sub-question or topic related to the theme. Participants engage in several rounds of conversation, with each round lasting 20–30 min, while hosts stay at their tables to ensure continuity. Materials such as paper tablecloths, large poster templates, sticky notes, and markers are provided to help the participants at each table creatively document conversations. After each round, participants move to different tables, cross-pollinating ideas and building on previous discussions, with key insights and ideas captured and documented. The conversation is often followed by a plenary session where participants collectively reflect on patterns, themes, and insights that emerged and identify potential actions and strategies based on the collective wisdom generated during the conversation. Brief surveys assessing views of one or more technologies can be included when multiple cafes (and mini-publics) across a region are expected.

Sampling considerations in all designs emphasize diversity of participants. In early stages breadth of participants is key; in later-stage research the focus is likely locally affected communities and so more localized representation. It is assumed that different knowledge systems and reasonings will be in place and that the boundaries between these can be difficult to overcome, however collaborative.

3.4.2 Engagement approach 2: participatory foresight workshops (early stage)

Participatory foresight workshops (with stakeholders from industry, civil society, local communities, local and regional administration, etc.) can be used to scope a wide range of plausible future threats and opportunities which could be presented by OAE in a given setting (Elsawah et al., 2020). They can also be used to identify governance frameworks/instruments that would be robust across plausible OAE futures (e.g., they have been used to explore the potentials of global SRM governance and mCDR policy frameworks).

The structure of a participatory foresight workshop generally involves (1) scanning, in which participants are asked to identify a broad range of political, economic, social, technological, environmental, and other factors that could shape OAE development within a given setting and a given time frame; (2) a deliberate group process to reduce this collection of factors down to several that the group considers key to the future of OAE; (3) joint imagining of different ways these factors may develop in the future; (4) a deliberative process to map how these factors may interact in the future; (5) the creation of narrative descriptions (in the form of short texts) by smaller groups of participants which detail their joint vision of a specific future, and which include several of the factor projections from the list previously developed; and (6) a group back-casting exercise to create a timeline of the key technological, economic, political, and social changes that would have to happen between today and each imagined future.

Participatory foresight processes are designed to draw upon the various knowledge types, perspectives, assumptions, expectations, and worldviews of those involved

(Pereira et al., 2023; Rutting et al., 2023). The outputs can thus only be as diverse as the range of voices in the room. Having a well-considered participant selection strategy is key. Including the widest possible range of affected stakeholder voices will result in more inclusive future thinking and learning. When a broad range of voices are included, the foresight method is effective for facilitating trans- and interdisciplinary communication and learning about future (OAE) challenges and solutions. It can be useful as an early stage "anticipatory assessment" tool for scoping the societal and political feasibility and desirability of OAE in a given context, with a specific set of stakeholders. It can help to widen understanding of feasible and desirable OAE developments based on the interactions between a broad range of political, economic, technological, and social risks and benefits. Such participatory foresight approaches can also be used to identify ways that OAE (and other CDR approaches) may be integrated into existing governance landscapes. These insights will always be context dependent, but generalizable lessons may be learned from drawing on comparative case studies.

As public license is ultimately key to the development of OAE, using designs of this kind can help develop OAE-specific policies and build trust across differing publics. In such cases, the goal is to co-produce, quite literally collectively draft, regulatory frameworks involving publics and administrative representatives. Success has been mostly widely demonstrated in urban design or the creation of "smart cities" (Marsal-Llacuna and Segal, 2017), as well as contexts such as wind farm operation and siting. Both qualitative and quantitative methods are used to evaluate and refine decision-making, policies, and regulatory commitments (Simao et al., 2009; Jami and Walsh, 2017).

3.4.3 Engagement approach 3: indigenous methods and protocols (early stage and throughout)

Over the last decade, the emergence of Indigenous scholarship and fundamental methodological insights have transformed the practices of social scientists, inspiring critiques of the research enterprise as colonial and extractive. The former refers to the many ways that knowledge derived from "Western" canons has developed to justify dispossession of lands (Dell and Olken, 2020), assert claims of racial and social inferiority, and maintain apartheid-equivalent governing practices (Wolfe, 2006). The latter refers to research deemed as solely benefiting the researcher in reference to both the knowledge acquired, the benefits that follow (to the researcher and not the community), and the purpose for which it is used. Decolonizing these practices includes all methods to a large extent, but it is particularly crucial for approaches involving Indigenous community engagement. Indeed, all engagements with Indigenous groups that consider siting projects on or near their territorial lands and water require methodological reflection. There is a diversity of capacity and political positions within and across all communities, but three priorities for research design are fundamental.

Firstly, it must be recognized that the history of colonization is de facto a history of profound re-engineering of Indigenous territories through mineral, oil, and gas extraction; large-scale logging operations; agricultural transformations; and overfishing. More often than not these activities have been justified by states as necessary for *progress* or as solutions for environmental, economic, and social prosperity (Whyte, 2018). The misrecognition of this history is, for example, central to a failed ocean fertilization trial, ethically (and problematically) justified as beneficial to phytoplankton growth and so to migrating salmon in waters offshore where the experiment took place (Buck, 2019a, b). Justifications of pejorative, anthropogenic change also fall short in Indigenous contexts where there exists a long history of positive shaping of ecosystems, terrestrial and estuarine foods, fire regimes, etc. (Whyte, 2018; Buck, 2015).

A second priority is to design research in a fundamentally collaborative manner by which we mean (a) to develop research questions such that they are co-created, offering robust inclusion of community priorities, starting with *their* definitions of the impacts that matter and *their* framing of research such that it meets existing priorities (be they rents for use of territorial space, implications for resources and local economies, or recognition and governance of all operations) (https://www.un.org/esa/socdev/unpfii/documents/DRIPS_en.pdf, last access: 16 November 2023). And (b) it is important to meaningfully involve Indigenous partners in analysis, interpretation, and communication of results. Key here, too, is recognizing Indigenous people as rights holders, not stakeholders, including the right to free prior and informed consent, and the right to sue should operators not abide by law and policy. Lastly, (c) many communities have their own protocols and established research agreements, which spell out all conditions of work and expectations for accountability. These often also define ethical and intellectual property expectations and compensation for time and require negotiation and agreement (e.g., https://www.sealaskaheritage.org/sites/default/files/ResearchPolicy.pdf, last access: 16 November 2023). In addition, communities may identify places and topics around which they refuse to engage (Simpson, 2007, 2014). Such protocols, including those seeking to address reparations for past harms, are or can be legally binding and seek to re-establish First Nation or Tribal community rights to jurisdictional authority and decision-making (e.g., MOU "Namgis and Crown").

A third priority is to design research practices and categories such that they reflect and honour ontologies and epistemologies of Indigenous knowledge systems (e.g., Swinomish Health Indicators; https://swinomish-nsn.gov/ihi2/index.html, last access: 16 November 2023). This includes land-based, relational histories with non-human relatives; particular worldviews evident in their languages; and responsibilities to territory (Marsden, 2002). Also central are storied or narrative forms of interpretation and evidence, knowledge encoded in place names and oral histories (Marsden, 2002), and knowledge about the particular colonial histories that have also disrupted these. Positioning the voices of community members as knowledge-holding experts and recognizing their cultural authority is foundational as compared to the sole authorial voice of the OAE researcher.

Comprehensive direction and reflection on these approaches can be found in the work of Tuhiwai-Smith (2021), Kovach (2021), Wilson (2020), and Tuck and Yang (2021), among others.

3.4.4 Engagement approach 4: structured decision-making – integrating public and expert insights (mid-stages)

Designs more analytically focused seek all of the above but employ greater structuring of engagement methods to ensure that the conversation is descriptive (e.g., as to what research or information matters to the decision) and evaluative (e.g., which OAE designs across alternatives are most desired, safe and why) and that modifications or alternatives are key. These methods provide a central opportunity of integrating public and expert knowledge in the evaluation of its feasibility, as well as environmental and social impacts of OAE.

All such methods are both knowledge- and value-centric and aim to convert values or social priorities to performance measures that can be used to evaluate policies, actions, or specific decisions (Renn, 1999; Estévez et al., 2015; Mahmoudi et al., 2013; Burgman et al., 2023). For example, if the case were deciding upon different locations for a pilot installation of an OAE facility, high public support might be a function of designs that prioritize social benefits (e.g., which can include expert knowledge on tax revenues or social priorities for learning or employment opportunities), require relatively less energy (e.g., again, based on expert assessment), work with locally trusted institutions and actors (who might define ethical parameters and assign consent), and offer outcomes or conditions co-designed (e.g., such as ensuring that work will cease should problematic impacts follow).

An illustrative approach covered here known as *structured decision-making* (Gregory et al., 2012) is motivated by theory derived from the decision sciences and is part of a larger set of *prescriptive* methods derived from multi-attribute decision-making (Keeney, 1996; Renn, 1999). These aim to respect and address routine and often semi-conscious habits that are pervasive across judgements about new technologies such as those *described* in Sect. 2 above. Thinking or information processing of this kind is often referred to as rapid, fast, or "system 1" thinking as it engages affective cognition or processing (Kahneman, 2011). Prescriptive theory instead accepts these behavioural phenomena as a given and thus deploys a series of steps that "slow down" thinking and articulate decisions in reference to "structured steps" to activate deliberative or "system 2" thinking.

Three key strengths of structured decision-making are that it (a) uses small-group collaborative design to develop the criteria and indicators or "metrics" that will be used to evaluate an OAE project, for example; (b) combines both local concerns and knowledge with expert and/or scientific information where available; and (c) integrates factual and value-based information into the analytic portions of the work.

Detailed method advice is available (e.g., Gregory et al., 2012) with many cases drawn from resource management, but the central steps are as follows with iteration across these assumed:

1. *The decision context* for the workshop including the timing, purpose, and bounds of the work must be established, including how the insights gained will be used. For example, this method might be used to compare the viability of different sites for OAE trials or it might involve the conditions under which trials can or cannot proceed.

2. *Develop objectives* by establishing these for the analysis of project options and the different metrics by which these might be evaluated. Here it is critical to involve and respect all forms of knowledge (expert, local, and Indigenous where applicable) and to include as wide as necessary a set of objectives. For instance, one of many objectives might include "maintaining high water quality", which might itself include several sub-objectives including water safety (perhaps measured as possible contaminant levels for humans, fish, or marine mammals), water aesthetics (measured by local people in reference to colour, smell, pattern, or turbidity), and flow (do materials stagnate or move and disperse). A full set of objectives might include groups such as environmental impacts (of which water is one and species of concern might be another), social consequences, governance considerations, and financial considerations. As above, each matter to the decision underway and each may include several sub-objectives and their measures. Measures can be qualitative or quantitative.

3. *Develop alternatives* by considering the different alternatives by evaluating each across the above objectives, accepting that some objectives might be deemed relatively more consequential or important than others. This includes discarding options that are poor across objectives and modify plans such that better alternatives and their conditions might be developed.

4. *Consider consequences* once a smaller set of alternatives have been isolated; discuss these in reference to the possible consequences of each, accepting that some alternatives may be eliminated due to the possibility of significant harms.

5. *Evaluate tradeoffs* as it is usually the case that no one option is perfect and that tradeoffs are instead involved. Deliberate which tradeoffs are acceptable or relatively more desirable and which are not or non-negotiable. Revise the plan accordingly.

6. *Implement and monitor.* Should a project go ahead, develop a plan to follow its operation and monitor its progress.

3.4.5 Engagement approach 5: survey design (early and especially mid-stages)

Historically, studies of the perceived impacts, risks, and acceptability of new technologies have relied heavily on survey questionnaires, and this remains the case. More recently, mixed method designs, using a blend of survey and deliberative workshops, have been prioritized (Cox et al., 2020). These approaches address some of the limitations of surveys by providing participants with more opportunity for learning and by allowing for a deeper exploration of these reflections. Such insights can be used to better interpret and illuminate positions found in large, representative surveys. The goal of survey research is not to obtain consent or to treat results as a poll but rather to illuminate the factors that may help explain judgements as they exist and change (Fowler, 2013; Gray and Guppy, 1999).

Whether combined with smaller-group work or not, survey research benefits from several key design principles. The first is that designs are well hypothesized, which means isolating a "dependent" or outcome variable of interest (e.g., acceptability or perceived risk), alongside a larger set of demographic, knowledge, and value-based variables (e.g., regarding participants' perceptions regarding nature, politics, vulnerability, ocean systems), often known as explanatory variables, which might predict that dependent variable. Many such factors are covered in Sect. 2 above. Common dependent variables of focus include acceptability/support, both risk *versus* benefit and risk *and* benefit measures, negative versus positive feelings toward a technology, reported support for enabling policies, or willingness-to-pay to offset GHG emissions. Survey approaches should also specify whether the goal is to elicit initial heuristic responses or more reasoned views (described above as "system 1" vs. "system 2" thinking). Approaches that elicit system 1 thinking tend to be more useful in early-stage research, where judgements might be more fully impressionistic, rapid or intuitive; the second option might better serve surveys employed once a technology is better known and views on it have become relatively stable.

A second principle is ensuring robust tutorials for novel concepts and technologies. A challenging question is how to present OAE in a survey when the very idea of it is so new. A well-established approach is to provide information via a short, pithy paragraph at the beginning of the survey – this text should provide key information in as neutral a format as possible. When a topic is new, such as OAE or mCDR, assumptions that information to be provided can truly be "neutral" should, however, be treated with skepticism. All descriptions frame responses, intentionally and not; thus it is better to be explicit about the design logic of any tutorial – for example, being inclusive of risk *and* benefit language. Where approaching "neutrality" in a tutorial is particularly difficult, split samples and multiple tutorials may prove useful to investigating the effect of different framings.

Proper sequencing of a survey questionnaire is another important principle. Best practices involve beginning with dependent variables before moving to explanatory variables, to avoid any order effects (Greenberg and Weiner, 2014). Because, again, this topic is so new, another strategy is to provide information in stages, which changes the structure of the survey itself. Sequential designs necessitate more cumulative or pathway structures, which intentionally route participants through a series of questions that build a portrait of thinking as it emerges. The assumption here is that new topics are complicated, and thus it is cognitively easier for people to have questions decomposed into steps that help clarify thinking (Gregory et al., 2016). Typically, these begin with a global "first question" that looks at a discrete value position and then seeks to unpack that, given additional questions or considerations. An alternative approach is to begin with a tradeoff between two positions (e.g., positive or negative toward an action, policy or technology) and then seek to delve into the value, factual, or policy basis for that position (Hagerman et al., 2021). Such designs can also reveal whether positions are relatively fixed or open to consideration of information or alternatives as provided.

Any survey's sampling strategy is key to the representativeness of results, their quality, and their reliability and validity given the survey's goals. Sampling can range from convenience approaches to careful representative sampling, which is closely and systematically reflective of the total population frame designated (e.g., all people in a country or region), including target sampling (e.g., climate activists). Sampling errors are common and the considerations are many, but good reviews of survey design principles and sampling problems are widely available (e.g., https://scholar.harvard.edu/files/stantcheva/files/How_to_run_surveys_Stantcheva.pdf, last access: 16 November 2023).

3.4.6 Engagement approach 6: deliberative polling (later stages)

Deliberative polling is a method that bridges deliberation with conventional polling via random sampling and offers a few advantages as an engagement method for OAE research. Adding "deliberation" to polling offers participants the opportunity to reflect and consider options, rather than just offer "top of head" opinions (Fishkin and Luskin, 2005). As it is extended (multi-day) in nature, this method also offers more opportunity for participants to process new information, as compared with other options like interviews or surveys (Fishkin et al., 2000). These opportunities for discussion, reflection, and clarification are likely critical in the context of a complex technology and context, such as with OAE. Adding random sampling to deliberation ensures representativeness of participation, a feature that distinguishes this from other deliberative approaches like focus groups or citizen juries, which cannot necessarily offer insight into views amongst a wider population. Deliberative polling thus can produce a useful understanding of what a larger public might think about OAE – if they were given the opportunity to take the time to consider, reflect, and discuss the full suite of relevant perspectives and options (Mansbridge, 2010).

Deliberative polling follows this structure: participants are provided with balanced briefing materials that offer a launchpad for broader discussion. These materials lay out different arguments and provide rigorous, factual, impartial (as much as possible) information relevant to a policy proposal. These materials are vetted in advance by an advisory board, for balance and accuracy. Participants gather for deliberations, either in person or online through a platform, usually for multiple days (e.g., a weekend) (Fishkin and Luskin, 2005). Participants spend the weekend in small-group discussions led by moderators and in sessions where they can ask questions to policy experts. Participants are asked to talk, listen, comprehensively consider different views, and weigh different arguments. At the beginning and end of the deliberations, participants are asked to answer a questionnaire about their views.

The outcome of deliberative polling activities might be a deeper understanding of how a representative sample in a given area views a potential deployment of OAE. Importantly, what deliberative polling does *not* offer is production of a consensus (Fishkin et al., 2000). Instead, the emphasis is on understanding overall views and the aspects of such a deployment that might produce greater or lesser confidence or support.

3.5 A note on "consent"

What consent to an activity like OAE might mean is complex and not easily resolved, in part because of different understandings of consent (Wong, 2016). Regardless, in the context of infrastructure development projects, climate mitigation activities, and international law, it is considered best practice to obtain the free, prior, and informed consent of affected communities (Rayner et al., 2013; WRI, 2007). Consent may appear most critical at the time when implementation of a large-scale activity is being considered (e.g., building a plant), but it may also be key to early research stages. Processes of participation and consent-seeking should be ongoing from early stages throughout later stages of research and deployment and should be iterative as activities, proposals, and plans evolve. While this chapter focuses primarily on early-stage research, consent will likely be an issue that increases in importance as later stages of research and operation unfold, as the magnitude of activities and affected groups continues to grow. Ultimately, if a group rejects a proposal or even conversation, following best practices means that "no" must be respected.

4 Post-engagement activities: making engagement transparent, accountable, and responsive

The gold standard for societal engagement is to ensure that communication and learning is bi-directional and responsive and includes mutual learning across scientists and stakeholders. OAE projects will benefit from remaining open to change in research practice as a function of public engagement – indeed, researchers should ultimately be prepared to cease operations or move elsewhere if it becomes evident that the proposed project is not societally feasible in a given context. It will be essential to understand the many perceptual, value, and governance drivers of views that people hold, publics and experts alike, as these continue to prevail in thinking across many new technologies. A few principles to ensure that engagement is of high quality and *responsive* are outlined below.

Make engagement two-way. For public engagement to be meaningful, it has to be incorporated back into the project to inform and shape the project moving forward. Achieving this will likely depend on the specifics (e.g., team size) of individual projects. A few things will be helpful in ensuring that this occurs: (1) regular collaboration and dialogue across social science and/or engagement teams with the broader team, such as regular feedback sessions and check-ins following the initial engagement activities; (2) involvement of social scientists or engagement specialists in decision-making processes to ensure that community views and priorities are meaningfully addressed; and (3) incorporation of specific community collaborators into a closer relationship with the research team (e.g., Indigenous leaders in local area) (for motivating engagement, see Maund et al., 2020). Projects may want to co-draft an explicit "two-way engagement statement" to encourage and improve transparency around commitments and plans (see https://www.energy.gov/sites/default/files/2022-08/Creating%20a%20Community%20and%20Stakeholder%20Engagement%20Plan_8.2.22.pdf, last access: 16 November 2023). One fundamental element of such two-way engagement is making data openly available and involving local communities in monitoring efforts. Researchers and funders should therefore explore opportunities for supporting platforms for community members to follow monitoring and maintain access to monitoring data (https://www.energy.gov/sites/default/files/2022-08/Creating%20a%20Community%20and%20Stakeholder%

20Engagement%20Plan_8.2.22.pdf, last access: 16 November 2023). Engagements that emphasize responsive, two-way engagements with local stakeholders have been shown to result in sustained mutual learning between experts and citizens and to improve community ownership and overall project outcomes (Ross et al., 2022).

Begin conversations about community benefit agreements (CBAs) early. CBAs are contracts between project developers and communities that provide support for a project conditional on the developer providing a set of socio-economic benefits (https://www.energy.gov/justice/community-benefit-agreement-cba-toolkit, last access: 16 November 2023). At an early stage of small-scale field trials, it may seem premature to begin a conversation on how benefits of an OAE project might be distributed if deployed at scale. However, such arrangements can be a point of discussion in the early stage and may prove critical to more lasting views on a potential project.

Inform modelling efforts. Modelling is one area of potential importance in terms of incorporating engagement findings. Models, especially integrated assessment models, are designed to seek techno-economically optimized outcomes: modifying models to solve for diverse "societally desirable/acceptable" outcomes (i.e., taking distributive justice into account, relative distribution of costs and benefits, etc.) may help provide answers to the questions affected publics are most interested in. Bringing modellers, social scientists, and stakeholders into the conversation early and often to engage them in reflexive or situated modelling practices may be one way to do this (Schulte et al., 2022; Low and Schäfer, 2020; O'Neill et al., 2020; Salter et al., 2010). This should be done at all stages of the modelling process: upstream input might involve using public engagement outcomes to inform future modelling efforts, for example by identifying societally relevant questions about OAE that might be modelled in the future. Downstream input might involve bringing stakeholders and modellers together to discuss whether the model outputs have answered societally and scientifically relevant questions (i.e., to aid decision-making on OAE) or whether modification of the technology itself improves social outcomes. For example, upstream, modellers might ensure inclusion of environmental impacts precisely because they could produce social consequences. Concentrated but highly localized additions of alkalinity might be omitted as inconsequential from an overall biophysical point of view. Yet, inclusion in modelling might be warranted because such additions could result in localized reductions of dissolved CO_2, negatively affecting phytoplankton and thus fisheries. Downstream, unanticipated negative findings linked to trace materials might be further modelled for their capacity to introduce health effects or to stigmatize waters important to a coastal community's tourism (Nawaz et al., 2023a). More broadly, all modelling could potentially benefit from citizen science engagement. A recent study aimed at methods to track marine plastics, for example, used data collection of this kind via easily useable sensors to enhance the accuracy of modelling the volume and point source of plastic waste and debris (Merlino et al., 2023).

Research outcomes should be available and accessible. Beyond informing publics about the project itself, research outcomes should be shared widely and well beyond the immediate project context. This might mean, for instance, not just publishing in an academic outlet but also producing materials, such as fact sheets and community briefing summaries, that can be understood by local groups in both immediate and other areas and sharing these via different venues (i.e., at local meetings, online, in schools and libraries).

5 Summary of recommendations

No chapter of this kind can address all potential factors and linked methods, let alone the detail that makes each tractable. However, what does matter for each audience is largely discrete and so we summarize this chapter by designating how it might serve (a) social science public engagement leads working on OAE projects, (b) natural science/engineering leads on OAE research, and (c) funders looking to support OAE research.

Social science leads can use this guide to reference some of the factors that have explained why people support or reject some new technologies in reference to both features of the technology itself, the values of those evaluating the technology and its context, and the features of OAE's management and governance. We have also provided recommendations as to why historical context matters and how that might affect perceptions or influences the articulation of future threats and opportunities. We have offered tailored suggestions as to which methods might align with different research and development stages for OAE, with references to fuller guidelines herein. And we have provided recommendations on what it means to conduct work that is inclusive; reflects Indigenous knowledge protocols and designs; and opens up deliberative and civic conversations whereby the knowledge and values people have can be used in meaningful and concrete ways across decision-centric methods. This can include decisions that are well structured and deliberated and that combine public and expert knowledge. How all research might then be incorporated back into science and engineering research design and so inform the research moving forward is also of potential use to social scientists in this field.

Natural science and engineering leads. We understand that the work described in this chapter is not work that most natural and engineering scientists will do, but they can use this to help curate their direction to social science researchers who might do that work or to understand methods in reference to their context or stage of work, particularly early stages. Most importantly, it will help them understand when and where problems of public perception are not simply due to a lack of knowledge and to instead seek engagement practices where knowledge is co-produced and where deep understanding and integration of public concerns into their own methods (e.g., modelling) and design (e.g., materials used or siting chosen) is a priority. Several suggestions are also offered as to how to expand their own thinking and communication beyond details of the technology itself and instead how OAE might articulate with how people think about risk, how the full lifecycle and governance of an OAE system might influence views, and how the power of conversational approaches (such as world café designs) can enhance trust and openness as technologies evolve. Brief guidance on how a plausible future's threats and opportunities can be scoped with stakeholders is provided, as are decision-centric methods. The latter are optimal for stages where key operational features (siting, materials, monitoring) and environmental or social conditions might be modified to address public concerns. This chapter might also be useful for understanding that all research is context dependent and sensitive and that communities with histories of colonialism and marginalization might not view options to "engage" as desirable, might not share the classifications of nature that scientists can assume, but may be more open to conversation and collaboration when using Indigenous methods referenced here. More broadly, this chapter emphasizes that all those involved in OAE research projects should actively and transparently reflect on the knowledge, assumptions, and values driving their work.

Funders and proponents of OAE. Much of what we have already referenced above applies to this group as well. But, in particular, using deliberative and decision-centric designs to hold conversations about community benefit agreements might be key, with the assumption that work on such agreements should begin early, recognize jurisdictional authority, and accept that some contexts will simply not be viable sites for OAE projects. Budget calculations for project work will become easier via review of this chapter so that engagement efforts are understood and properly funded. Similarly, the goal of engagement will be clearer and so too how to best produce high-quality knowledge of what is viable socially and why.

Key recommendations

Social considerations and best practices to apply to engaging publics on ocean alkalinity enhancement include the following:

1. Views on OAE will reflect if and how different groups perceive the distribution of alkaline materials in marine systems (Sect. 2.1).
2. If people either (1) view marine systems as fragile, (2) regard mitigating actions as morally compromising to GHG emissions and energy transitions, or (3) adhere to politically polarized positions, they may be less likely to find OAE acceptable. Viewing climate change as an urgent problem could suggest opposite effects including impatience or suspicion about technologies in early development phases (Sect. 2.2).
3. How OAE is governed (how the system will be managed, financed, monitored) and who is represented in those processes (particularly those with jurisdictional authority, including Indigenous groups) will be key to determining views. Maintaining public trust is centrally important, as is early discussion during all engagements of potential large-scale operations (Sects. 2.3–2.4, 3.2, and 3.4.3).
4. Integration of social science work should begin at the earliest stages and include natural and engineering investigations that reflect key public concerns; integrate collaboration across research teams; and involve a specified plan for feedback and modification of research as new findings, questions, and insights arise (Sect. 4).
5. Six engagement methods are provided, each tailored to research that is either early stage (mesocosm experiments or early field trials), mid-stage (scaling up to fuller pilot studies, site selection criteria, or determining choices across options), or late stage (seeking large population public views regarding involvement of OAE as a significant part of national policies to meet climate goals) (Sect. 3.3–3.5).

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Monitoring, reporting, and verification for ocean alkalinity enhancement

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Abstract. Monitoring, reporting, and verification (MRV) refers to the multistep process of monitoring the amount of greenhouse gas removed by a carbon dioxide removal (CDR) activity and reporting the results of the monitoring to a third party. The third party then verifies the reporting of the results. While MRV is usually conducted in pursuit of certification in a voluntary or regulated CDR market, this chapter focuses on key recommendations for MRV relevant to ocean alkalinity enhancement (OAE) research. Early stage MRV for OAE research may become the foundation on which markets are built. Therefore, such research carries a special obligation toward comprehensiveness, reproducibility, and transparency. Observational approaches during field trials should aim to quantify the delivery of alkalinity to seawater and monitor for secondary precipitation, biotic calcification, and other ecosystem changes that can feed back on sources or sinks of greenhouse gases where alkalinity is measurably elevated. Observations of resultant shifts in the partial pressure of CO_2 (pCO_2) and ocean pH can help determine the efficacy of OAE and are amenable to autonomous monitoring. However, because the ocean is turbulent and energetic and CO_2 equilibration between the ocean and atmosphere can take several months or longer, added alkalinity will be diluted to perturbation levels undetectable above background variability on timescales relevant for MRV. Therefore, comprehensive quantification of carbon removal via OAE will be impossible through observational methods alone, and numerical simulations will be required. The development of fit-for-purpose models, carefully validated against observational data, will be a critical part of MRV for OAE.

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1 What is MRV?

In this contribution, we consider monitoring, reporting, and verification (MRV) for marine carbon dioxide removal (mCDR), confining our focus to determining the amount of additional CO_2 removed from the atmosphere and the durability of that removal. Investment in CDR is motivated by an interest in mitigating climate change, so the value of a CDR purchase stems from its correspondence to genuine removal (Smith et al., 2023). MRV must, therefore, provide estimates of net carbon removal and the uncertainty of those estimates (e.g., Palter et al., 2023). Delivering uncertainty estimates will enable markets to value carbon removal projects appropriately by applying discount factors scaled in accordance with uncertainty (e.g., Carbon Direct and Microsoft, 2023).

While we recognize the importance of determining ecosystem impacts of ocean alkalinity enhancement (OAE) deployments, assessment of OAE effects on ecosystems are covered in Eisaman et al. (2023, this Guide), Iglesias-Rodríguez et al. (2023, this Guide), Riebesell et al. (2023, this Guide), and Fennel et al. (2023, this Guide) and will not be considered MRV in this guide unless they impact the efficiency of OAE (e.g., biogenic calcification). In addition to monitoring carbonate chemistry parameters for MRV (discussed below), assessing ecosystem impacts would require monitoring other biogeochemical, environmental, or ecological changes that may arise from OAE application, such as changes in nutrient fluxes, particulate loading, and phytoplankton community structure. In the same vein, side benefits (e.g., an increase in pH due to OAE) are also not considered MRV for this contribution. Finally, for this guide, we do not consider life cycle assessment (LCA), which might entail accounting for, e.g., CO_2 emissions from manufacturing, transportation, and deployment. While LCA is extremely important for quantifying the net carbon removed by a CDR strategy, this contribution focuses on MRV following OAE deployment in the ocean.

To determine the amount and duration of CO_2 removal, MRV must deliver an assessment of two interrelated metrics:

1. *Additionality.* This refers to the net quantity of CO_2 removal above a counterfactual baseline after OAE has been conducted in the ocean. Additionality should include assessments of phenomena such as precipitation-induced loss of alkalinity or a response in biogenic calcification that could reduce the ability of alkalinity addition to induce CDR.

2. *Durability.* This refers to the average time over which CO_2 is sequestered from the atmosphere by a given deployment. We have minimal concerns about OAE in the context of durability as OAE increases the ocean's buffer capacity and hence its ability to store CO_2 as dissolved inorganic carbon (DIC) on timescales associated with alkalinity cycling in the ocean – with residence time far exceeding 10^3 years (Middelburg et al., 2020). Therefore, storage durability does not require an explicit methodology for quantification, but we can instead assume that CO_2 removed via OAE will be stored mainly as bicarbonate (HCO_3^-) for $> 10^3$ years. For CDR, the depth of where atmospheric CO_2 is stored in the oceans matters when it is stored as dissolved CO_2 (as is the case for macroalgae cultivation or iron fertilization). However, in the case of OAE, CO_2 is stored mainly as HCO_3^-, which cannot be exchanged with the atmosphere, so surface ocean storage is chemically safe. Keeping alkalinity (and thus HCO_3^-) in the surface ocean has benefits for ocean acidification, although these are very minor and heavily depend on whether alkalinity-enhanced seawater has been equilibrated with atmospheric CO_2 (see Fig. 3 in Bach et al., 2019). Furthermore, retaining alkalinity (HCO_3^-) in the surface ocean can enhance durability by limiting interactions with sediments and thus avoiding substantial loss terms to OAE, such as the risk of inducing secondary $CaCO_3$ precipitation in sediments and the reduction in natural alkalinity release (Fuhr et al., 2022; Moras et al., 2022; Bach, 2023; Hartmann et al., 2023). We acknowledge that there are potential ways to lose alkalinity (HCO_3^-) in the surface ocean, such as via the induction of biotic calcification. However, there is currently no reason to assume the deep ocean is a much safer place to store atmospheric CO_2 as HCO_3^-.

Further, as highlighted above, effective MRV systems must deliver estimates of the uncertainty in these metrics. To quantify these metrics, MRV for OAE must assess the following questions.

1. *How much alkalinity was effectively added to seawater?* The difficulty of answering this question depends on the technology used for OAE. For example, understanding the dissolution kinetics of mineral particulates is a requirement to quantify alkalinity additions for crushed-rock feedstocks but much less of a concern for electrochemical techniques and alkalinity added in dissolved form.

2. *Has there been precipitation or biogenic feedback changing the efficacy of the alkalinity addition?* Seawater is mostly above saturation in the surface ocean with respect to calcium carbonate; thus, the addition of alkalinity has the potential to induce precipitation of carbonate minerals (Moras et al., 2022), which would reduce the OAE efficiency (i.e., mole of DIC sequestered per mole of TA added). Abiotic $CaCO_3$ (or $MgCO_3$) precipitation is very slow but increases when the saturation state increases. Such high saturation states can occur near alkalinity release sites. Furthermore, calcifying organisms in the ocean, such as coccolithophores, can respond to OAE by modifying their growth rate or the

relative amount of carbonate mineral production (Bach et al., 2019). Finally, enhanced saturation states could also reduce natural carbonate dissolution; this may have the effect of more effectively transferring alkalinity (in particulate form) from the surface ocean to depth or changing natural alkalinity sources from sediments or coastlines (Bach, 2023). Understanding these feedbacks of OAE via the calcium (and/or magnesium) carbonate cycle is important for OAE MRV.

3. *What is the ensuing perturbation to the air–sea exchange of CO_2 resulting from the OAE deployment?* Alkalinity shifts carbonate equilibrium reactions away from aqueous CO_2, thereby reducing seawater pCO_2; CDR occurs when the atmosphere equilibrates with the altered surface ocean via air–sea CO_2 exchange. A primary goal for MRV is to quantify this perturbation flux; notably, however, in many envisioned circumstances, the alkalinity addition will be entrained in the ocean flow, causing the OAE signal to be transported away from the injection site and potentially away from the sea surface; coupled with the fact that CO_2 gas equilibration occurs slowly (Jones et al., 2014), the ensuing air–sea flux perturbation will occur over large regions in space and time.

In our assessment, observations alone are unlikely to provide a sufficient basis for quantifying the net carbon removal accomplished by OAE deployments. MRV for OAE requires the development of quantitative estimates of air–sea CO_2 exchange. Since the ocean is constantly moving and CO_2 takes a long time to equilibrate across the air–sea interface, robust MRV would require intensive observations over large areas and over long time periods. High-quality carbon markets will require uncertainty bounds for net carbon removal estimates that would be prohibitively expensive to obtain via investment in direct observing over such scales, except perhaps in targeted intensive observational arrays. A further complication with observations is that assessments of net carbon removals associated with OAE deployments require quantifying air–sea CO_2 flux relative to a counterfactual scenario: the air–sea CO_2 exchange that would have occurred without OAE intervention. Observing a counterfactual scenario is impossible in a strict sense, but it could be possible to use observations to assess counterfactual scenarios by leveraging analogs, such as nearby unperturbed regions, or statistical constructions, such as predicted seawater pCO_2 from empirical models built from historical observations of the carbon system and predictor variables like temperature, mixed-layer depth, and chlorophyll (e.g., Landschützer et al., 2020; Rödenbeck et al., 2022; Sharp et al., 2022).

In practice, comparison with such analogs is a challenging task due to the heterogeneous nature of the ocean air–sea CO_2 flux field, as well as the potential for OAE effects to spread over very large spatial and temporal scales. Notably, the background air–sea CO_2 flux field is highly dynamic on local to global scales. The ocean both absorbs and releases a massive amount of CO_2 each year; the net flux amounts to an uptake of about $10\,\mathrm{Pg\,CO_2\,yr^{-1}}$ – but this net flux is a small residual of large gross fluxes (about $\pm 330\,\mathrm{Pg\,CO_2\,yr^{-1}}$) (Friedlingstein et al., 2022). OAE can increase CO_2 flux into the ocean when the alkalinity enhancement reduces seawater pCO_2 below atmospheric CO_2. However, OAE can also decrease CO_2 flux into the atmosphere when alkalinity enhancement reduces seawater pCO_2 closer to atmospheric pCO_2. Both cases will constitute CDR as it leads to a net increase in DIC in the ocean reservoir (Bach et al., 2023). Geographic patterns of CO_2 ingassing and outgassing are controlled by the ocean's large-scale and subtropical overturning circulations (e.g., Iudicone et al., 2016), mesoscale and submesoscale motions (e.g., Nakano et al., 2011; Ford et al., 2023), variations in winds (e.g., Andersson et al., 2013; Nickford et al., 2022), storms (e.g., Nicholson et al., 2022), upwelling dynamics, local inputs from rivers (e.g., Mu et al., 2023), exchanges with sediments, and biology (e.g., Huang et al., 2023). Outside the tropics, there is pronounced seasonal variability in air–sea CO_2 fluxes mostly driven by phytoplankton blooms that draw down CO_2 in the surface ocean during spring and summer (e.g., Fassbender et al., 2022), and winter mixing that brings carbon-rich waters to the surface. All these dynamics are subject to variations in the climate and ocean circulation caused by internally fluctuating modes of variability or external forcing associated with CO_2 emissions and other human activities.

Given the complex nature of the ocean biogeochemical system, robust MRV for high-quality carbon removal markets will presumably depend on model-based approaches when quantifying net CO_2 removals. Ocean biogeochemical models (OBMs) will be a critical tool in this context (see Fennel et al., 2023, this Guide). These models represent the physical, chemical, and biological processes affecting the distribution of carbon, alkalinity, and nutrients in the ocean. OBMs represent inorganic and organic carbon pools, alkalinity, and nutrients as tracers with units of mass per volume (or mass) of seawater. OBMs are based on ocean general circulation models (OGCMs) that represent the movement of tracers mediated by ocean circulation and mixing. Biogeochemical tracers, including DIC and TA, have sources and sinks from processes such as biologically mediated production and remineralization of organic matter. Boundary fluxes for OBM tracers include riverine inputs, aeolian deposition, sediment–water exchange, and air–sea gas exchange. Fennel et al. (2023, this Guide) provide an overview of the most relevant modeling tools for OAE research, with high-level background information, illustrative examples, and references to more in-depth methodological descriptions and further examples.

2 Specificities of MRV for marine CDR

The natural ocean carbon cycle is extremely dynamic on a wide range of temporal and spatial scales, typically spanning more than 10 orders of magnitude (Sarmiento and Gruber, 2006). These scales range from that of the ocean skin, a thin layer of less than a millimeter in contact with the atmosphere where air–sea CO_2 exchange is controlled by molecular diffusion, to that of the global ocean circulation that typically transports dissolved carbon over more than a 1000 years and 10 000 km. As such, the ocean represents a challenging environment for MRV, especially compared to MRV of land-based CDR techniques. Three specific timescales are to be considered when discussing challenges for MRV of mCDR and in particular OAE.

The first timescale relates to natural variability in carbonate chemistry, especially $p\mathrm{CO}_2$ and alkalinity, due to biological, chemical, and physical processes in the ocean. Such variability can be substantial on daily and seasonal timescales. For example, using in situ observations from 37 stations spanning diverse ocean environments, Torres et al. (2021) showed that in the open-ocean stations, the average seasonal cycle of $p\mathrm{CO}_2$ was $49 \pm 23\,\mu\mathrm{atm}$ (inter-station mean and standard deviation) and that diurnal variability could also be as high as $47 \pm 18\,\mu\mathrm{atm}$. Temporal variability at coastal stations where OAE is likely to be deployed – due to proximity to existing infrastructure, energy supply, and human resources – is significantly higher, with seasonal variability in $p\mathrm{CO}_2$ being $210 \pm 76\,\mu\mathrm{atm}$ and diurnal variability reaching $178 \pm 82\,\mu\mathrm{atm}$ (Torres et al., 2021). OAE-induced changes in $p\mathrm{CO}_2$ are likely to be lower than the range in natural variability, complicating MRV. For example, an increase in alkalinity of $10\,\mu\mathrm{mol\,kg^{-1}}$ would result in a decrease in $p\mathrm{CO}_2$ of around $20\,\mu\mathrm{atm}$ (given temp = 20 °C; salinity = 35; initial $\mathrm{TA} = 2200\,\mu\mathrm{mol\,kg^{-1}}$; $\mathrm{DIC} = 1965\,\mu\mathrm{mol\,kg^{-1}}$, and no secondary precipitation or biotic calcification). Historical carbonate system variability, like the examples given here, can be used in sensitivity studies to assess the detectability of a given OAE perturbation for different observing systems (Mu et al., 2023).

The second of these timescales relates to air–sea CO_2 equilibrium. This timescale is particularly relevant for OAE as it determines the time required from an alkalinity-driven shift in surface seawater carbonate equilibria to a new air–sea CO_2 equilibrium and the resulting atmospheric carbon uptake. It is well established that the characteristic timescale for air–sea exchange of CO_2 is on the order of 6 months (Sarmiento and Gruber, 2006), but Jones et al. (2014) have shown that the time to reach air–sea CO_2 equilibrium is highly variable at the regional scale, ranging from less than a month to several years, with especially long values in the northern North Atlantic, the Atlantic subtropical gyres, and the Southern Ocean. This regional variability is explained by the dependency of the air–sea CO_2 equilibrium timescale on the gas transfer velocity, the depth of the mixed layer, and the baseline carbonate chemistry of seawater. More precisely, this timescale shortens with higher gas transfer velocities and Revelle factors, but lengthens with deeper mixed layers and larger ionization fractions (i.e., the ratio between DIC and dissolved CO_2).

The third of these timescales relates to ocean physical processes and alkalinity and carbon transport away from the injection location. First, horizontal currents, ranging from a few centimeters to a few meters per second, can potentially transport the OAE signal away from the initial injection site, thus complicating MRV. A simple calculation shows that a mean flow of $0.5\,\mathrm{m\,s^{-1}}$ could transport the alkalinity signal more than 100 km from the initial site in 6 months. Second, vertical entrainment, mixing, and/or other subduction processes might also transport the OAE signal to depths below the seasonal mixed layer, potentially hindering atmospheric CO_2 uptake and associated MRV.

Lessons learned from mesoscale in situ ocean iron fertilization (OIF) studies can be applied to MRV for OAE, especially during pilot studies of unenclosed OAE-perturbed patches of surface waters that are upscaled beyond a few square kilometers. Ocean circulation and mixing will cause a range of effects that are scale dependent and will influence MRV strategies as it is used to target pilot studies and, eventually, larger deployments ($100\,\mathrm{km}^2$ scale). This presupposes that elements of MRV will be needed at all spatial scales during the development and testing of an mCDR method.

The success of OIF in tracking and repeated sampling of a coherent patch of perturbed waters over a timescale of weeks was due to the use of SF_6 as an ocean tracer (e.g., Coale et al., 1996), and, in one instance, using a quasi-controlled volume within a mesoscale eddy (Smetacek et al., 2012). For example, the use of SF_6 allowed dynamic upper-ocean behavior to be observed during an OIF perturbation, in which the perturbed water was subducted under less dense water in a few days, leading to the termination of the study (Coale et al., 1998). Subduction is a risk for the MRV of OAE trials being conducted in nearshore waters, and the use of tracers such as SF_6 would be crucial for observing this behavior.

At larger spatial scales (i.e., for perturbations done in waters not bounded by eddies $> 100\,\mathrm{km}^2$), ocean physics imposes a strain and concurrent rotation of a perturbed patch of ocean; as such, OIF studies revealed the perturbed patch of waters can "grow" in areal extent from 100 to $> 1000\,\mathrm{km}^2$ via the entrainment of the surrounding "control" seawater (Law et al., 2006). Such entrainment sets up concentration gradients that lead to fluxes into (in the case of OIF, nutrients are resupplied to the nutrient-depleted patch) and out of (in the case of OIF, chlorophyll which has accumulated due to OIF and iron that has been added) the perturbed waters. Such artifacts may dilute the more alkaline waters in the patch of unenclosed OAE perturbed waters, which may hinder aspects of MRV such as detection of the OAE signal above a background level or biological side effects resulting from OAE.

3 Observation-based techniques for MRV and limitations

OAE depends on multi-step processes to achieve mCDR. First, the intervention raises ocean alkalinity in order to lower seawater $p\mathrm{CO}_2$, and then atmospheric CO_2 must equilibrate with the altered waters. These processes point to many of the variables that would ideally be observed in an OAE MRV scheme. Measurements of total alkalinity (TA) and DIC are important to quantify the background state of the carbon system, which determines the $p\mathrm{CO}_2$ response per unit change in alkalinity. Further, measurements of TA might help verify that alkalinity has been added effectively, although signal-to-noise ratios may be insufficiently strong to enable robust detection and attribution of TA anomalies (Mu et al., 2023). In addition, pH is an important measurement to ensure that the OAE deployment conforms with water quality limits (usually $\mathrm{pH} < 9$) and that the deployment does not create conditions that induce precipitation. Finally, $p\mathrm{CO}_2$ at the ocean's surface is a key control on air–sea CO_2 exchange and is thus an important measurement target.

With extensive measurements of these variables along the Lagrangian pathway of a perturbed water mass, a carbon budget could theoretically be closed by constraining the time rate of change and making inferences about important driving processes such as air–sea gas exchange; such a budget could, in theory, be used to support quantification of CDR for a given OAE deployment. Though appealing in its comprehensiveness, the reality of observing all of the parameters needed to quantitatively close a perturbed carbon budget and compare it against an unperturbed counterfactual is likely impossible in the near to medium term, even in the context of highly monitored field trials. The difficulty is inherent in the fact that the patch of water perturbed by the addition of TA is likely to be turbulently dispersed in the ocean, and its signal diluted below the limit of detectability by mixing over the timescale required for CO_2 equilibration (He and Tyka, 2023; Mu et al., 2023; Wang et al., 2023).

This leads to the conclusion that MRV via direct observational approaches should not be expected to completely follow every molecule of additional CO_2 resulting from an OAE deployment – as doing so would set an insurmountable barrier to MRV. Instead, we outline what can feasibly be observed, what questions these observations can answer, and which questions are left to be addressed in statistical and/or prognostic models with their attendant uncertainties.

Various autonomous sensors hold promise to inform the results of an OAE deployment, both in field trials and for sampling that might offer constraints on open-water applications and data for model validation and/or assimilation.

The most direct measurement relevant to OAE experiments is TA, which would reveal if the initially planned perturbation was successful. Though autonomous sensors for TA have been in development for several years (Briggs et al., 2017), they are not commercially available at the time of writing, and the laboratory analysis of bottle samples cannot currently be replaced or even supplemented by sensor-based measurements (see Cyronak et al., 2023, this Guide). Nevertheless, laboratory analysis of TA in bottle samples can be compared to "baseline" measurements taken before the alkalinity is added or outside the expected patch area. It is worth noting that measuring a TA increase near the OAE deployment point may be possible, but once the OAE-perturbed water has dispersed in the ocean flow, the signal-to-noise ratio will likely be too low to make any accurate quantification. This is also the case for attempting to quantify CDR using DIC, as discussed below. The TA in the OAE-influenced patch may also be compared to a predicted counterfactual TA constructed from regression methods built with historical salinity (and other available) data, like the Locally Interpolated Alkalinity Regression (LIAR) method (Carter et al., 2018).

In contrast to TA, to determine the ocean uptake of CO_2, there are effective equilibrator-based autonomous $p\mathrm{CO}_2$ systems (e.g., ASVCO2™, MAPCO2) capable of measuring $p\mathrm{CO}_2$ with a nominal accuracy of 2 µatm (Rik Wanninkhof, personal communication, 2023), although they are restricted to the top few meters of the surface ocean due to the fact that equilibrators cannot be submerged. There are also in situ $p\mathrm{CO}_2$ sensors that rely on equilibrating seawater $p\mathrm{CO}_2$ with air through a membrane (e.g., Pro-Oceanus CO2-Pro™ CV, CONTROS HydroC® CO_2) or a pH-sensitive dye (e.g., SAMI-pH), followed by infrared detection or colorimetric spectroscopy. Due to fluctuations in the pressure of equilibration and calibration issues, the real-world accuracy of these instruments is ∼ 5 µatm (Rik Wanninkhof, personal communication, 2023). The existence of autonomous $p\mathrm{CO}_2$ sensors is potentially important because while it is difficult to detect changes in the carbon inventory of the ocean with measurements of DIC, it can be done with measurements of $p\mathrm{CO}_2$ (Wanninkhof et al., 2013). These $p\mathrm{CO}_2$ sensors can be deployed on moorings (MAPCO2, ProCV) and autonomous surface vehicles like Wave Glider (ASVCO2) (Chavez et al., 2018) and Saildrone (Sabine et al., 2020; Sutton et al., 2021; Nickford et al., 2022). These sensors have the advantage of being able to collect measurements continuously in harsh weather and with much reduced involvement from skilled analysts relative to field surveys with bottle collection. Most analysis focuses on collecting and analyzing calibration samples and performing quality control on data.

Sensors that measure pH on autonomous profiling floats, gliders, or moored platforms could provide additional data useful for MRV. Unfortunately, as demonstrated by Wimart-Rousseau et al. (2023), pH sensors on profiling floats have relatively large uncertainties that may compromise their usefulness for MRV of field deployments. Moreover, these uncertainties are largest near the ocean's surface, where they would be most useful in the MRV context, as knowledge of the surface ocean disequilibrium is needed for CDR. Uncertainties in pH of 0.01 roughly translate to a $p\mathrm{CO}_2$ uncertainty of 10 µatm (Wimart-Rousseau et al., 2023), but even achieving such accurate pH measurements will require significant advances in sensor accuracy and/or post-processing data analysis tools to correct surface pH data. Nevertheless, a fleet of pH-measuring profiling floats can provide observational data critical for model evaluation and for quantifying baseline carbonate chemistry in the ocean.

Another MRV-relevant aspect of OAE that is well suited for sensor measurements is the reduction in OAE efficiency via OAE-induced precipitation of carbonates (see Schulz et al., 2023, for further context). For example, marine calcifiers, such as coccolithophores, may benefit from high-alkalinity and pH conditions, thus reducing OAE efficiency (Bach et al., 2019), but this effect is still uncertain (Gately et al., 2023). Autonomous optical sensors for particulate inorganic carbon (PIC) based on the birefringence of calcite and aragonite have been in development for several decades (Bishop, 2009; Bishop et al., 2022). Since the deployment of the first prototype on a profiling float in 2003, this optical PIC sensor has been re-engineered several times, and the most recent versions require further re-engineering to correct for thermal and pressure effects, as well as misalignment effects of the linear polarizers (Bishop et al., 2022). A new autonomous PIC measurement concept was recently proposed by Neukermans and Fournier (2022), which may overcome the aforementioned issues. Such PIC sensors are currently under development and are expected to cover a PIC concentration range of 0.5 to $500\,\mu g\,C\,L^{-1}$ (Neukermans et al., 2023). These PIC sensors are intended for use on autonomous platforms such as floats profiling up to 2000 m deep, autonomous moorings, tethered buoys, or Saildrones. Such PIC sensors would thus enable careful autonomous monitoring of PIC concentration in the epipelagic and mesopelagic ocean, as well as in shallow-shelf seas. In addition, ocean color satellites can be used to obtain global maps of coccolithophore PIC concentration in the surface ocean at daily frequency using a variety of remote sensing algorithms (see Balch and Mitchell, 2023, for a review of remote sensing PIC algorithms and limitations). Both remote sensing and in situ observations of PIC concentration can contribute to assessing secondary precipitation and OAE efficiency.

Other more remote tail risks of OAE include alterations to carbon production and flux, for example, via shifts in phytoplankton community structure (Ferderer et al., 2022) or alterations in the availability of high-density biominerals such as opal or calcite, which may ballast particulate organic carbon (POC) flux to the deep ocean (Armstrong et al., 2001; Klaas and Archer, 2002). Ballasting of POC flux by coccolithophore calcite and the resulting increase in the sinking velocity of POC aggregates has been confirmed in many experimental studies and may be an important mechanism in some ocean regions. This potential secondary effect of OAE on POC flux could be monitored from autonomous profiling floats equipped with a PIC sensor (Neukermans et al., 2023).

Wind speed should be measured since it is the most common correlate for air–sea gas exchange, and there are wind speed and gas exchange parameterizations that predict gas transfer velocities well in the open ocean (e.g., Ho et al., 2006). Therefore, in these settings, measurements of wind speeds are sufficient to characterize air–sea gas exchange. However, since gas transfer velocities as a function of wind speed differ between the open and coastal oceans (e.g., Dobashi and Ho, 2023), depending on the OAE deployment location, $^{3}He\,/\,SF_6$ tracer release experiments might have to be performed to determine this relationship (see Wanninkhof et al., 1993). While it is likely unfeasible to couple every individual OAE operation with a $^{3}He\,/\,SF_6$ dual-tracer release during the deployment phase, during the testing phase such experiments will be useful for calibrating and evaluating models that will most likely be used to determine the efficiency and efficacy of CO_2 equilibration.

4 Model-based techniques for MRV and limitations

OBMs can be used to explicitly represent the effects of OAE by conducting numerical experiments in which the model is provided with forcing data that represents alkalinity additions. Developing and validating models in the region and scale of OAE deployment should be a priority to enable functional frameworks for MRV (see Fennel et al., 2023, this Guide).

A model integrated forward in time with the alkalinity additions will simulate the transport of the associated mass of alkalinity and its ensuing effect on biogeochemical processes, including air–sea gas exchange. These simulations can be used to evaluate net carbon removal by comparing integrations that include the OAE signal to others in which that forcing is not present – i.e., the baseline counterfactual condition or "control." If an ensemble of integrations is performed, the variation in net carbon removal across the ensemble can be used to assess uncertainty. Notably, there are different potential sources of uncertainty. If intrinsic variability in ocean dynamics is considered the dominant source of uncertainty, an initial condition ensemble could provide an appropriate representation of uncertainty. If model structure, in contrast, is the dominant source of uncertainty, alternative approaches to ensemble construction could be employed, including perturbing parameters or using multiple models (see Fennel et al., 2023, this Guide, for further discussion). Explicit simulation of OAE deployments can be compared to observations, including measurements from background observing systems, as well as bespoke data collection efforts associated with the OAE project. In some cases, explicit data assimilation (DA) procedures may be applied (see Fennel et al., 2023, this Guide), potentially reducing model–data misfits and improving confidence in the model simulations. One challenge of applying DA to MRV is estimating additionality, which requires information about both the actual temporal evolution of the system and the counterfactual condition, i.e., the state of the system that would have occurred in the absence of the CDR intervention. The counterfactual condition is impossible to observe directly, and to the extent that observations contain an imprint of the CDR, DA cannot be used to generate explicit estimates of the baseline state. This raises conceptual issues because simulations conducted with and without DA are not directly comparable; thus, a difference between DA-constrained and free-running models cannot provide a valid estimate of additionality. Further research is needed to understand and address these problems. Potential solutions may rely on the assumption that CDR signals are very small relative to the background variability and thus essentially negligible in the context of the constraints on model solutions imposed by DA. Further, if the CDR interventions can be assumed to have negligible impact on physical variables (e.g., temperature, salinity, currents), it may be possible to use DA selectively on just these variables.

4.1 Modeling alkalinity addition

For the effects of OAE to be properly simulated, models must be supplied with the correct amount of alkalinity applied as forcing. Alkalinity additions, if performed over hours to days, are likely to occur on scales much smaller than the ensuing anomaly generated in air–sea CO_2 exchange, typically occurring over months to years (see Sect. 2). For this reason, MRV frameworks must invoke a separation of concerns, wherein near-field (i.e., within a few kilometers of the source) processes are treated differently than the broader regional effects. Explicit modeling of near-field dynamics is likely to require different modeling frameworks (e.g., McGillicuddy, 2016) than those simulating the full expression of the OAE effects in the ocean – however, it is not necessarily a requirement to simulate near-field dynamics in the context of MRV. Near-field processes must be constrained by direct observations, and/or their dynamics must be accurately captured in verified parameterizations applied to models too coarse to simulate the local effects explicitly (e.g., Fox-Kemper et al., 2019). Notably, different OAE technologies and feedstocks present different challenges in this regard (see Eisaman et al., 2023, this Guide). Electrochemical techniques, which might produce, for instance, an alkalinity-enhanced stream from an outfall pipe, are different from crushed-rock particulates where dissolution kinetics come into play. Moreover, as discussed in Fennel et al. (2023, this Guide), ancillary constituents (e.g., iron or nickel) associated with rock-derived feedstocks may induce biological responses with impacts on the total efficacy of the OAE process.

4.2 Representing OAE effects

To provide a suitable basis for MRV applied to OAE deployments, models must meet several requirements and provide a sufficiently accurate representation of alkalinity additions. First, models must provide a reasonable representation of ocean circulation and mixing; these processes are critical to determining the residence time of added alkalinity in the surface mixed layer, where gas exchange with the atmosphere is possible. Given that the equilibration timescale for CO_2 via gas exchange is long, the residence time of alkalinity-enhanced water parcels at the ocean surface is likely a primary control on the efficiency of uptake (He and Tyka, 2023). Second, the models must accurately capture the surface ocean $p\mathrm{CO_2}$ anomaly induced by alkalinity additions. This implies having a correct representation of the carbon system thermodynamics (see Fennel et al., 2023, this Guide). Further, since the change in $p\mathrm{CO_2}$ depends on the background DIC : TA ratio (Hinrichs et al., 2023), it is important that the model has a good representation of the mean state prior to perturbation (Planchat et al., 2023). Third, presuming an accurate representation of the change in $p\mathrm{CO_2}$ and the transport of alkalinity following injection, the model must be able to simulate air–sea CO_2 exchange with sufficient accuracy. Notably, the gas transfer velocity is highly uncertain, particularly in coastal environments where many OAE deployments are likely to occur (e.g., Dobashi and Ho, 2023). If surface water residence times are much longer than the gas equilibration timescale, uncertainty in the gas transfer velocity may not contribute substantially to the overall uncertainty – but in intermediate regimes where the two timescales are comparable, uncertainty in the gas transfer velocity may be an important consideration. Finally, a comprehensive assessment of OAE efficacy will depend on accurate characterization of feedbacks in the biological system. If there are changes in the natural distribution of calcification or organic carbon export, this term should be quantified, or its potential magnitude and impact on overall carbon transfer should be assessed as a component of the uncertainty budget. At present, further empirical research is required to enable modeling systems to treat this aspect of OAE effects robustly (Fennel et al., 2023, this Guide).

5 The way forward for MRV of OAE

There is much work to be done to establish how to optimize monitoring OAE with respect to which observations are needed and at what spatial and temporal resolution and duration. Nevertheless, early field trials should all monitor the initial increase in alkalinity (i.e., both measured and modeled). Baseline alkalinity measurements should be made so that the range of concentration within its natural variability is known before the deployment of alkalinity. Furthermore, if the enhancement is done via the dissolution of pulverized rocks or minerals (e.g., olivine, brucite), the dissolution rate needs to be known under in situ conditions. Knowledge of this rate includes the dependency on various factors such as temperature and salinity but also to what extent minerals become buried in sediments and how this change in exposure affects dissolution. If the enhancement is done via electrochemistry, the dosing rate of the solution (e.g., containing NaOH) should be quantified and reported with complete information about the measurement methods and a thorough accounting of their uncertainties.

Furthermore, any potential secondary precipitation caused by the alkalinity enhancement (e.g., if alkalinity is added too quickly, brucite precipitation could occur) should be monitored. Monitoring of secondary precipitation is particularly critical in the non-equilibrated state (i.e., before atmospheric CO_2 influx has occurred) and when the alkalinity-perturbed patch is in close contact with sediments since the risk for secondary precipitation is particularly high under these circumstances (see Eisaman et al., 2023, this Guide; Schulz et al., 2023, this Guide).

Finally, the drawdown of CO_2 in the ocean due to alkalinity addition should be measured. Given the potential natural variability in pCO_2, especially in coastal regions, monitoring of pCO_2 should also be done before the OAE deployment. Considering the spatial scales and timescales discussed above, these measurements will need to be complemented by modeling approaches.

MRV of CO_2 influx after the application of OAE will likely depend on fit-for-purpose modeling (see Fennel et al., 2023, this Guide). Exceptions to this may apply if the deployment is made in an enclosed area where the water is confined, or the deployment is made in a heavily instrumented and surveyed area of the ocean. Models used to constrain atmospheric CO_2 influx must be calibrated and evaluated with observations. Observations of the following physical and chemical processes are needed to improve frameworks for modeling CO_2 influx, but this is not an exhaustive list of observations that would benefit models:

- observations of ocean currents from acoustic Doppler current profilers (ADCPs), Lagrangian floats, tracers like SF_6, and remote sensing;
- observations of air–sea gas exchange from ^3He / SF_6 tracer release experiments;
- temperature and salinity profile measurements;
- measurements of carbonate chemistry parameters (i.e., TA, pH, pCO_2, and DIC).

While it appears that OBMs will ultimately provide a critical foundation for robust ocean MRV frameworks, they are not currently ready to serve in this capacity (Fennel et al., 2023, this Guide). These models represent complicated systems; Ocean General Circulation Models (OGCMs) are based on fundamental governing equations, but solving these equations numerically requires approximations (e.g., Fox-Kemper et al., 2019). Ocean ecosystems comprise diverse groups of organisms with differing physiological capacities and complex interactions. There are no generally accepted governing equations for these systems; rather, models are built on the basis of empirically determined relationships and theory or hypothesis (e.g., Planchat et al., 2023). For OBMs to provide a credible basis to support ocean MRV, they must be based on broadly accepted theory or well-constrained parameterizations, and they must be explicitly validated relative to the quantification of gas exchange anomalies arising as a result of perturbations in alkalinity. Models have not yet been robustly validated in the context of these explicit requirements.

We note that at this point we have yet to develop the best modeling tools for OAE MRV (and likely MRV for mCDR in general). A rigorous research and development program to establish OBMs as fit-for-purpose, credible tools for MRV is needed. However, there is currently a major problem with basing MRV on models. OBMs are run on high-performance computing architectures, and because they are big calculations, they are very computationally expensive (and therefore financially expensive). It is unlikely that technological innovation will dramatically reduce this computational cost in the next 5–10 years, during which time we will be required to deliver a functional framework for MRV. Therefore, we suggest combining direct model simulations with advanced statistical approaches to overcome the computational challenges. First, we must establish that models can provide credible representations of key CDR processes by ensuring that model output agrees with available observations. Then, we can leverage these models to generate datasets from which to derive robust statistical approximations, including through the application of techniques derived from artificial intelligence and machine learning. For instance, well-calibrated models could be used to produce training data for machine learning algorithms to predict the CDR efficiency of OAE deployments in different locations at different times, i.e., as a function of initial environmental conditions such as water temperature, carbonate chemistry, and mixed-layer depth as suggested in Bach et al. (2023).

Conducting explicit OAE modeling experiments coupled with field trials are important research milestones necessary to identify the long-term approach to robust MRV. It is likely that the models that can effectively support field trials will use regional OGCMs that are capable of high-fidelity simulations of ocean flows at scales commensurate with those driving the initial dispersion of OAE signal on timescales of weeks to months. Unless alkalinity is continuously applied at a level measurable by long-duration observing platforms, the OAE signals are likely to be diluted and less easily tracked with observations. Critically, it is important to demonstrate that the models provide simulations consistent with the carbonate chemistry and deliberate tracer (e.g., SF_6) observations.

Models that compare well to observations can be deemed credible for assessing OAE effects. However, fully explicit mechanistic calculations are computationally intensive and thus unlikely to provide a scalable framework for conducting

MRV under the scenario of widespread OAE deployments. On this basis, it is important that research on OAE field trials aims toward building trust in models to develop approaches to MRV that can be accomplished at a reduced computational cost.

6 Key recommendations for MRV of OAE

Early stage MRV research for OAE may become the foundation on which regulated markets are built. Therefore, such research carries a special obligation toward comprehensiveness, reproducibility, and transparency. To fulfill these obligations, we suggest the following overarching best practice guidelines.

- Field trials should be co-designed with modelers and observationalists to enable the iterative process of model validation and improvement and dynamically informed data interpretation. In some scenarios, co-design may entail the development of formal observing system simulation experiments and data-assimilating state estimates (Fennel et al., 2023, this Guide).
- MRV techniques and results should be well documented and archived publicly and promptly, without restriction (e.g., Planetary Technologies, 2023). Ideally, a central registry of OAE experiments would adhere to FAIR (findable, accessible, interoperable, and reproducible) data standards (Wilkinson et al., 2016). Researchers should eschew any practice that withholds MRV innovation from the community to “build a moat” in support of a commercial mCDR approach.
- Early field trials are recommended to be as comprehensive as possible, monitoring for obvious, first-order risks like secondary precipitation and more remote tail risks like alterations to export production via shifts in phytoplankton community structure and mineral ballasting.
- Model evaluation against observations should be tailored to the key processes in question. Fennel et al. (2023, this Guide) argue that models may be used for a long list of purposes, including, for example, simulating ecosystem effects and sediment–water exchanges. Early MRV efforts can expose model skill and deficiencies in simulating these processes if the relevant observations are prioritized.
- An uncertainty budget should be quantified that includes both known uncertainties (e.g., measurement and mapping errors) and expert estimates of presently unmeasurable risks. A comprehensive assessment of the poorly constrained uncertainties will point to key research areas in the future.

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Data reporting and sharing for ocean alkalinity enhancement research

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Abstract. Effective management of data is essential for successful ocean alkalinity enhancement (OAE) research, as it guarantees the long-term preservation, interoperability, discoverability, and accessibility of data. OAE research generates various types of data, such as discrete bottle measurements, autonomous measurements from surface underway and uncrewed platforms (e.g., moorings, Saildrones, gliders, Argo floats), physiological response studies (e.g., laboratory, mesocosm, and field experiments, and natural analogues), and model outputs. This paper addresses data and metadata standards for all these types of OAE data. As part of this study, existing data standards have been updated to accommodate OAE research needs, and a completely new physiological response data standard has been introduced. Additionally, an existing ocean acidification metadata template has been upgraded to be applicable to OAE research. This paper also presents controlled vocabularies for OAE research, including types of OAE studies, source materials for alkalinization, platforms, and instruments. These guidelines will aid OAE researchers in preparing their metadata and data for submission to permanent archives. Finally, the paper provides information about available data assembly centers that OAE researchers can utilize for their data needs. The guidelines outlined in this paper are applicable to ocean acidification research as well.

1 Introduction

Data management plays a crucial role in bridging the gap between field observations and subsequent research based on these data (Brett et al., 2020). It is an essential component of ocean alkalinity enhancement (OAE) research to help evaluate its potential environmental risks and co-benefits, understand its effectiveness and scalability, and support its measurement reporting and verification (MRV) efforts for carbon credit accounting. Specifically, effective data management enables long-term preservation of data, ensures compliance with uniform metadata and data standards, facilitates interoperability and compatibility, and enables data discovery and access (de La Beaujardière et al., 2010).

Long-term preservation can be achieved by publishing data in archives and preserving them in non-proprietary, archivable formats to ensure accessibility and retrievability

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for extended periods of time, spanning decades to even centuries. This helps prevent data loss or degradation caused by technological obsolescence, human errors, natural disasters, or other factors. Datasets, unlike journal publications, are frequently revised or updated after they are released. This may occur as a result of additional quality control (QC) or the acquisition of additional data or metadata. While ensuring access to the latest version of a dataset is crucial, preserving previous versions is equally important. All historical versions should be retained on a permanent basis. Otherwise, research based on previous iterations of a dataset may become unverifiable.

Data standards are a set of rules and specifications that define how data should be stored, structured, and formatted (Berman and Fox, 2013). Their purpose is to promote consistency and interoperability, reducing ambiguity in data exchange and interpretation. In oceanographic studies, data standards cover elements, such as the technical format for storing data, e.g., Microsoft Excel, Comma Separated Values (CSV), or NetCDF; standardized column header abbreviations and units; standardized methods for calculating certain variables; and missing value indicators. It is worth noting that the new XLSX format is based on OpenOffice XML, unlike the prior binary-based proprietary format of XLS. As a result, it is no longer a proprietary format. By adhering to these standards, researchers can ensure that their data are organized, structured, and formatted in a way that allows for easy sharing, interpretation, and reuse.

Metadata refer to structured information that provides context and details about a dataset, such as its title, authors or creators, observed properties, instruments used, measurement and calibration details, uncertainty, and relevant keywords (Guenther and Radebaugh, 2004). It is often defined as data about data. Metadata serve two main purposes: first, they provide users with detailed descriptions about a dataset, helping them understand it; second, they offer search keywords that make the dataset findable and retrievable. Overall, metadata are a crucial aspect of data management and are essential for subsequent data use.

Controlled vocabularies are defined as lists of pre-defined and standardized terms (Zeng and Qin, 2008). The use of controlled vocabularies plays a very important role in effective data management, as it helps ensure that the data are documented, findable, and accessible in a consistent way. By using a limited and standardized set of terms, controlled vocabularies help improve metadata interpretation and data findability by eliminating spelling variations, synonyms, and other forms of variability. Additionally, controlled vocabularies help facilitate metadata interoperability between different systems, making it easier to exchange and integrate data between different organizations and platforms.

Data citation involves referencing a dataset for the purpose of attributing credit and facilitating access (TGDCSP, 2013). It not only enables data users to acknowledge and give credit to the producers of a dataset used in a research study or project, but also allows readers to access and use the dataset for additional research. Data citation plays an important role in promoting scientific reproducibility and accountability and facilitating data sharing and reuse. As data sharing becomes more prevalent, data citation is increasingly important for tracking the impact of datasets and ensuring that research is built on a strong foundation of credible and transparent data.

In essence, data management is a service aimed at fulfilling the data needs of the research community. Therefore, efforts to establish best practices, such as the creation of new data and metadata standards and controlled vocabularies, should be driven by the needs and preferences of the research community. It is equally important for researchers to adhere to these guidelines when preparing high-quality metadata and data packages for submission to appropriate repositories. While this paper also sheds light on recommendations and requirements for data assembly centers to build customized data management systems that meet the data needs of the OAE research community, the presented data and metadata standards primarily serve submission purposes. During the development of these data and metadata standards, we ensured that they have a wide range of applications in other research fields, including ocean acidification (OA).

2 Data standards

Ocean alkalinity enhancement research encompasses a wide range of topics, resulting in various types of data. These different types of OAE data can be classified into four categories: (a) discrete bottle-based measurements; (b) autonomous measurements from surface underway (e.g., surveys conducted on ships of opportunity, or SOOP), time series (e.g., moorings), and uncrewed platforms (e.g., Saildrones, gliders, Argo floats); (c) physiological response studies, including laboratory, mesocosms, field experiments, natural analogues, and more broadly biological and geochemical experimental studies; and (d) model outputs (Table 1). To ensure consistency and interoperability, it is recommended to use uniform data standards for each type of OAE data (Tanhua et al., 2019; Brett et al., 2020). For category (b), two data standards are available: one for surface underway measurements and the other for autonomous sensor data from uncrewed platforms, including moorings, Saildrones, gliders, Argo floats, etc. This is because the measurement of one of the key variables, the carbon dioxide fugacity ($f\mathrm{CO}_2$), involves the use of two different systems, depending on whether it is monitored during underway operations or time-series mooring. Note that other communities may use FCO_2 to refer to the flux of CO_2 across an interface (e.g., sea–air interface, biosphere–atmosphere interface). It is recommended to use an italicized f for fugacity and a capital F for fluxes. Category (c) may also include abiotic responses, such as (but not limited to) saturation state thresholds for calcium carbonate precipitation, mineral dissolution rate studies, and CO_2 uptake efficiency determinations. In these cases, inorganic variables associated with these data standards should be sufficient to capture all of the relevant study details.

Table 1 presents a list of recommended data standards for each type of the OAE data as mentioned above. This table serves as a reference for researchers and data managers to ensure that their data meet the required standards for long-term preservation, interoperability, and reuse. For all data standards, users may remove irrelevant columns and add necessary ones. The data standard for discrete bottle based observations is described in detail by Jiang et al. (2022). The data standards for surface underway and autonomous sensor measurements are an update to what the community has been using over the last several decades.

The data standard for physiological response OAE studies is developed as part of this study, covering laboratory experiments, mesocosms, field experiments, and natural analogues, and more broadly biological and geochemical experimental studies. It emphasizes the experimental setup while allowing users to document their own response variables. For biological variables, it is important to state the taxonomy (a taxon or a community) upon which the variable is studied. For example, if the growth rate of a certain species of salmon is studied. The “variable/parameter” is growth rate, and “biological subject” is that species of salmon. One could group/capture organismal data in three forms: taxonomic, functional, and phylogenetic. It is recommended to use the species reference databases from the Catalogue of Life (https://www.catalogueoflife.org/, last access: 5 November 2023), Integrated Taxonomic Information System (or ITIS, https://www.itis.gov/index.html, last access: 5 November 2023), World Register of Marine Species (or WoRMS, http://marinespecies.org/, last access: 5 November 2023), or Paleobiology Database (PBDB, https://paleobiodb.org/classic/, last access: 5 November 2023). For life stages, consider using an existing controlled vocabulary like https://vocab.nerc.ac.uk/collection/S11/current/ (last access: 5 November 2023).

Model outputs often involve extensive data volumes, reaching gigabytes or even terabytes, making it necessary to address standards for the operational provision of model data (i.e., making data available for weeks to years), separately from long-term or permanent archiving. The operational provision of model output data typically relies on three integrated standards: network Common Data Form (netCDF) files, the Climate and Forecast (CF) metadata conventions, and the Open source Project for a Network Data Access Protocol (OPeNDAP) libraries for remote data access. NetCDF is an open-source software that has been developed and supported by the University Corporation for Atmospheric Research’s Unidata program (http://www.unidata.ucar.edu/, last access: 5 November 2023) since 1989. NetCDF enables the creation and dissemination of self-contained data files with metadata, using formats that are independent of any specific machine or system. It has long been a standard for generation of model outputs and climatological data products in the ocean and climate modeling communities. The CF metadata conventions provide guidelines for encoding datasets in netCDF, specifying the reporting of space and time coordinates, units, variable names, and other relevant information (Hassell et al., 2017). CF-compliant netCDF files are advantageous due to their self-describing nature, eliminating the need for additional information to interpret their contents. CF is a living and open standard that encourages community participation in proposing enhancements and reporting issues (https://www.cfconventions.org/, last access: 5 November 2023). OPeNDAP, which is based on the Data Access Protocol (DAP), allows remote access to CF-compliant netCDF files stored on web servers through a set of libraries, making compliant datasets highly interoperable and findable. Furthermore, it enables users to request subsets of data without the need to transfer potentially very large files when only a subset is of interest. Together, the netCDF–CF–OPeNDAP standard provides a high level of readability and interoperability for model outputs, gridded data products (e.g., satellite observations), and ocean observations (e.g., Argo). The evolution of these standards and their community-wide acceptance are discussed in Hankin et al. (2010).

The netCDF–CF–OPeNDAP standard enables provision of model outputs in accordance with the FAIR principles (Wilkinson et al., 2016), provided a few conditions are met. NetCDF–CF–OPeNDAP datasets can be **f**indable because machine-readable metadata enable automatic discovery, **a**ccessible because of the standardized communications protocol that is open and universally implementable, **i**nteroperable because of the standardized, machine-readable metadata and data and the ability to subset and aggregate datasets, and **r**eusable because rich metadata using standardized naming conventions can be provided. The necessary conditions for a netCDF–CF–OPeNDAP dataset to qualify as FAIR are that (a) it is openly available and has a globally unique and persistent identifier (e.g., a digital object identifier, or DOI), (b) data and metadata are registered and indexed in a searchable resource, and (c) data are described with rich metadata that include accurate and relevant attributes and remain accessible even if the data are no longer available. Box 1 lists attributes that should be included in netCDF files generated out of a biogeochemical ocean model, including several that are specific to OAE research, for the output to be considered a richly documented dataset. Output from an Earth system model would have slightly different requirements regarding the atmosphere (e.g., atmospheric forcing would not apply).

The discussion thus far has focused on the operational provision of model outputs, i.e., comprehensive datasets that may be available for periods of weeks to years. However, because of their large data volume, they are not amenable to long-term or permanent archiving. Nevertheless, long-term archiving of model-related information in some form that

Table 1. Proposed data standards for the purpose of submitting common types of OAE data. A CTD rosette consists of a metal frame that houses a collection of sensors and water sampling bottles. The abbreviation CTD stands for conductivity, temperature, and depth, which are the three primary variables measured by a CTD sensor. Furthermore, the rosette frame can accommodate additional sensors to measure various oceanographic variables such as oxygen, chlorophyll a, etc.

Types	Definition	Data standards
Profile	The collection of discrete water samples from the ocean at specific locations and depths, using sampling bottles (e.g., Niskin). The samples are then analyzed in a laboratory to determine various oceanographic parameters, such as dissolved inorganic carbon, total alkalinity, dissolved oxygen, and nutrient levels. It can also refer to continuous measurements using autonomous sensors mounted on a CTD rosette.	Column headers for profile data[1] Data file example[2] Jiang et al. (2022)
Surface underway	Continuous measurements of oceanographic variables at the ocean surface using sensors, often in flow-through systems on board research vessels or ships of opportunity (SOOP), to obtain real-time information about the ocean's physical and chemical conditions, such as temperature, salinity, and $f\mathrm{CO_2}$.	Column headers for underway data[3] Data file example[4]
Uncrewed platforms	Continuous measurements of oceanographic variables using autonomous or remotely operated platforms. Examples including time-series mooring, uncrewed surface vehicles (USVs, e.g., Saildrones), profiling floats (e.g., Argo), autonomous underwater vehicles (AUVs, e.g., gliders), instead of traditional crewed research vessels.	Column headers for autonomous sensor data[5] Data file example[6]
Laboratory experiments (Iglesias-Rodríguez et al., 2023, this Guide)	A scientific investigation in which researchers manipulate parameters of the carbonate system in an aquarium of a laboratory to simulate future OAE conditions and observe the responses of one or multiple selected marine organisms.	Column headers for physiological response data[7]
Mesocosms (Riebesell et al., 2023, this Guide)	Mesocosm studies are conducted in large, controlled outdoor tanks or enclosures that simulate natural conditions in the ocean. Mesocosms allow for the examination of multiple interacting factors that can affect the response of a community of marine organisms to OAE, including physical processes, such as hydrodynamics, and complex biological interactions, such as predator–prey relationships.	Data file example[8]
Field experiments (Cyronak et al., 2023, this Guide)	Field experimental studies typically involve the manipulation of total alkalinity and carbon dioxide levels in seawater at natural coastal or offshore sites and then monitoring the response of the surrounding marine ecosystem.	
Natural analogues (Subhas et al., 2023, this Guide)	Natural gradients in carbonate chemistry and other relevant parameters can be used to study the sensitivity of the ocean system to future OAE conditions. The response of marine species and the broader ecosystem can be assessed in terms of their long-term acclimation and adaptation to enhanced total alkalinity.	
Model outputs (Fennel et al., 2023, this Guide)	The outputs of mathematical models that simulate Earth system processes can be used to simulate real-world scenarios, and assess the impacts of different policies, among other purposes.	Balaji et al. (2018)

[1] https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/support/profile.html (last access: 5 November 2023).
[2] https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/support/profile.xlsx (last access: 5 November 2023).
[3] https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/support/underway.html (last access: 5 November 2023).
[4] https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/support/underway.xlsx (last access: 5 November 2023).
[5] https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/support/autonomous.html (last access: 5 November 2023).
[6] https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/support/autonomous.xlsx (last access: 5 November 2023).
[7] https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/support/physiological.html (last access: 5 November 2023).
[8] https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/support/physiological.xlsx (last access: 5 November 2023).

makes datasets reproducible is required but not yet done routinely. We suggest the following as a best practice:

1. Metadata should be permanently archived even for operational datasets (as mentioned above, this is required for a dataset to qualify as FAIR).
2. Essential subsets of operational datasets should be permanently archived, although it may not be immediately clear what these subsets should encompass. At a minimum, data subsets that would are required to support conclusions in publications should be archived.

- ☐ Identifier of permanently archived model code (e.g., in a Git repository) with version number that was used to create the dataset;
- ☐ Permanent reference to an accessible form of documentation describing model equations with concise description of key assumptions, e.g., *How is alkalinity represented? Are active feedback between biological process and carbonate system properties represented in the model? Is dissolution and precipitation of calcium carbonate considered and, if yes, how? Are exchanges between sediment and overlying water represented and, if yes, how?*
- ☐ Input data (e.g., model parameters, initial and boundary conditions) either directly or, where the data volume would be prohibitive, as a comprehensive description of how input data was generated and from which sources to enable reproduction including:
  - Domain bathymetry
  - Initial conditions of all state variables
  - Atmospheric forcing including $p\mathrm{CO}_2$, any depositional fluxes, etc.
  - Lateral boundary forcing if applicable
  - River and groundwater inputs if applicable
  - Comprehensive list of all model parameters including physical and biogeochemical parameters, timestep, start time, output frequency
  - *Alkalinity and related inputs (dose, duration, timing, location)*
  - *Assumptions about solubility of particulate alkalinity feedstocks if applicable*

Box 1. Metadata elements that should be included in netCDF files generated out of a biogeochemical ocean model. Information specific to OAE studies is indicated in italic font. Refer to Fennel et al. (2023, this Guide) for more context.

3. Model code should be permanently archived (e.g., Git versions with DOI), and sufficient metadata should be provided so that investigators can reproduce all model inputs (including initial and boundary conditions, model parameters). This information should allow, in principle, the reproduction of large model output datasets that cannot be permanently archived.

3 Metadata template

Section 2 highlights the importance of including some specific metadata information in netCDF files generated out of ocean model outputs. Apart from fulfilling documentation purposes, such information plays a vital role in facilitating data discovery when utilizing the netCDF–CF–OPeNDAP standard for operational provision of model output data. However, for long-term archiving purposes, data assembly centers commonly implement an independent and comprehensive metadata template. Ideally, these templates should be universally applicable to all data holdings, ensuring comprehensive documentation and accurate discoverability.

Jiang et al. (2015) described a metadata template that can be universally applied to all major types of ocean acidification (OA) data. Its development was driven by the need to document laboratory experiments to study the physiological responses of OA, which was a relatively new type of research at the time. The template benefited from the rich metadata management experiences of the Ocean Metadata Editor (OME) as used by the Carbon Dioxide Information Analysis Center (CDIAC, Oak Ridge, Tennessee, USA). This is especially true for some of the metadata elements associated with ocean carbon parameters, e.g., carbon dioxide fugacity ($f\mathrm{CO}_2$). It features a "variable metadata section", which allows the documentation of all ancillary metadata information of an observed oceanographic variable (e.g., its variable abbreviation, full name, unit, instruments, uncertainty) to be organized around the variable, thus enabling the documentation of rich metadata information for all observed properties. In addition, new metadata elements (e.g., observation type, in situ observation/manipulation condition/response variable, measured or calculated, biological subject, species identification code, life stage) were introduced. As the template was being developed, a bottom-up approach was adopted, and the authors worked with numerous OA scientists from around the world to ensure the produced template conforms to the needs and preferences of the research community. Figure 1 shows a diagram of the relationships between tables to help facilitate the navigation of the many groups of information.

In this paper, an updated metadata template (Version 2.0) is presented to accommodate the documentation of data coming out of OAE research (Table 2). We note that OAE research, while historically linked to acidification research, is

Table 2. Selected components of the new metadata template. ICES is short for the International Council for the Exploration of the Sea (https://vocab.ices.dk/?ref=315). For the latest version of the metadata template, refer to https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/oa-metadata-template/. "NA" is short for "not available".

No.	Component	Description	Controlled vocabularies
1	Submitter	Information about the submitter, including full name, institution, address, email, phone number, a persistent digital identifier (e.g., ORCID), etc.	ORCID: https://orcid.org/
2	Investigators	Information about the investigators, including their full names, institutions, addresses, emails, phone numbers, a persistent digital identifier (e.g., ORCID), etc. This component can be repeated as many times as needed.	ORCID: https://orcid.org/.
3	Author list for citation	Author list in the format of Lastname1, Firstname1 Middlename1; Lastname2, Firstname2 Middlename2; … The information will be used to compose data citation. It is not unusual for this list to be different from the investigators list.	NA
4	Dataset identifiers	This section covers information such as EXPOCODE, Cruise_ID, and digital object identifier (DOI)	NA
5	Dataset title	A brief descriptive sentence that summarizes the content of a dataset.	NA
6	Dataset description	The abstract of a dataset is a brief summary that provides an overview of the dataset's content, purpose, and scope. It is used to provide context and background information to users who are interested in using the dataset.	NA
7	Types of study	There are several types of study designs that can be used to collect and measure oceanographic variables, or examine the physiological responses of marine organisms to OAE. Examples: surface underway, profile, time series, laboratory experiment, mesocosms, field experiments, natural analogues, etc. See Table 4 for a list of controlled vocabularies for this element.	Table 4
8	Treatment type	This element is only applicable if the above element is one of the physiological response studies. This element is designed to indicate whether a physiological response dataset is out of an ocean acidification (OA) or ocean alkalinity enhancement (OAE) study.	OA or OAE
9	Model name	[For model output dataset only] Name of the regional or global model, e.g., GFDL-ESM4.1.	NA
10	Temporal coverage	The start date and end date of the measurement in the format of YYYY-MM-DD.	NA
11	Bounding box information	Information such as the westernmost longitude, easternmost longitude, northernmost latitude and southernmost latitude of the study area (decimal degrees, negative for Western Hemisphere longitude). For laboratory experiment based studies, this field should be used for the location of the organism collection, and for mesocosms, field experiments, and natural analogues studies, this field should be used to indicate the location of the experiment.	NA
12	Sea names	Names of the seas where the data collection takes place, e.g., Gulf of Mexico, Puget Sound, Baltic Sea, etc.	SeaDataNet C16 list (sea areas): https://vocab.seadatanet.org/v_bodc_vocab_v2/search.asp?lib=C16.
13	Location where biological subject was collected	Location where the organisms were collected, e.g., Puget Sound.	SeaDataNet C16 list (sea areas): https://vocab.seadatanet.org/v_bodc_vocab_v2/search.asp?lib=C16.

Table 2. Continued.

No.	Component	Description	Controlled vocabularies
14	Location where the experiment was carried out	Descriptive words about where the experiment was carried out, e.g., Laboratory in Northwest Fisheries Science Center.	SeaDataNet C16 list (sea areas): https://vocab.seadatanet.org/v_bodc_vocab_v2/search.asp?lib=C16.
15	Platform type	Controlled vocabularies for the types of the platform (e.g., research vessel, ships of opportunity, fish vessel, oil tanker, mooring, Saildrone, glider, Argo float). See Table 7 for a list of controlled vocabularies for this element.	Table 7
16	Platform info	Detailed information about the specific platform, including name, ICES* platform code (if applicable), institution that owns this platform, and the country of the platform.	SeaDataNet Ship and Platform Codes: https://vocab.ices.dk/?ref=315
17	Research project	Project, which the data collection is part of. For example, West Coast Ocean Acidification (WCOA) Project.	NA
18	Funding info	Information about the funders that supported the collection of this dataset, including the funding agency name, Project title, and Project identification, Project start date and project end date.	Research Organization Registry (ROR): https://ror.org/.
19	Supplementary information	Any additional information that cannot be accommodated in other metadata fields pertaining to this dataset.	NA
20	Publications describing the dataset	References of peer-reviewed publications that describe this dataset. It is recommended to use https://www.citationmachine.net/ (last access: 5 November 2023) to generate such references.	NA
21	Other datasets collected from this expedition	Sometimes, multiple datasets (e.g., one for chemical measurements, and another one for biological measurements) were produced out of the same research expedition. It is important to link them to each other. Please indicate the unique identification numbers of other published datasets that are related to this one in this field	NA
22	Variable metadata sections	See more details in Table 3.	NA

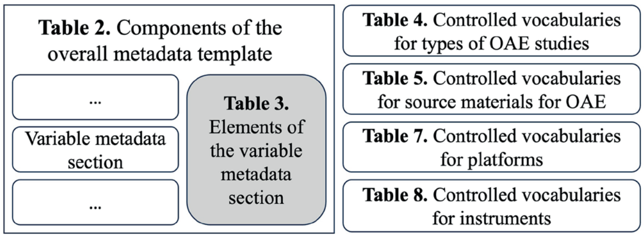

Figure 1. A diagram showing the relationship between Tables 2, 3, 4, 5, 7, and 8.

distinct in its application and may require additional parameters more akin to those found in iron fertilization or other perturbation studies. The revised template specifically allows users to indicate the type of the OAE study and indicate whether its treatment type is for future ocean acidification conditions or for ocean alkalinity enhancement experiments. It also has a new element for the name of the model. For the "people" sections, the address field is split up into road address, city, state/province, zip code, and country for better machine readability. The original title and abstract are replaced with "dataset title" and "dataset description", respectively, to make them distinguishable from the title and abstract of a peer-reviewed publication. The names of some other metadata elements were also changed to make them more self-explanatory. A new metadata element called platform type, which is backed with controlled vocabularies, is added to allow data users to filter the datasets based on the type of the specific observing platform. For example, in the future, a user would be able to search for only Saildrone uncrewed surface vehicle (USV)-based measurements. For the funding information section, two new elements about the start date and end date of the project are added. Most importantly, an element is added to enable multiple datasets generated out of a research expedition or experiment to be linked to each other. Terms that were either obsolete or rarely used (e.g., spatial reference system, purpose, section) were discarded.

Dataset title is a very important element of the metadata. It is often one of the few pieces of information a user can see in the search results. Thus, it is critical for data producers to create titles that are descriptive. It is recommended to follow the template of [observed properties] collected from [observation categories] using [instruments] from [research vessels or other platforms] in [sea names] during [research projects] from [start date] to [end date]. Here is one example: Dissolved inorganic carbon, total alkalinity, pH, temperature, salinity and other variables collected from profile and discrete sample observations using CTD, Niskin bottle, and other instruments from R/V *Wecoma* in the U.S. West Coast California Current System during the 2011 West Coast Ocean Acidification Cruise (WCOA2011) from 2011-08-12 to 2011-08-30.

Dataset description is similar to the abstract of a publication, encompassing essential information on data collection and generation methods, the variables and attributes present in the dataset, as well as any limitations or restrictions on data usage. Moreover, it may provide instructions on accessing and utilizing the data. Here is an example of a well-crafted dataset description: This dataset contains discrete bottle (CTD profile) data of the first West Coast Ocean Acidification cruise (WCOA2011). The cruise took place aboard R/V *Wecoma* from August 12 to 30 in 2011. Ninety-five stations were occupied from northern Washington to southern California along 13 transect lines on the west coast of the United States. At all stations, CTD casts were conducted, and discrete water samples were collected with Niskin bottles. Inorganic ocean carbon variables, including dissolved inorganic carbon (DIC), total alkalinity (TA), pH, as well as dissolved oxygen, and nutrients (silicate, phosphate, and nitrate) were measured. The cruise was designed to obtain a synoptic snapshot of key carbon, physical, and biogeochemical parameters as they relate to ocean acidification (OA) in the coastal realm. During the cruise, some of the same transect lines were occupied as during the 2007 West Coast Carbon cruise, as well as many CalCOFI stations. This effort was conducted in support of the coastal monitoring and research objectives of the NOAA Ocean Acidification Program (OAP).

One of the most important elements of the above metadata template is the "variable metadata section" (Jiang et al., 2015). It enables all ancillary information of a variable to be organized around the observed property (Table 3). Note that here "variables" refer to observed oceanographic properties (e.g., temperature, salinity, dissolved oxygen, pH, nitrate). They should not be confused with other supporting variables such as EXPOCODE, Cruise_ID, year, month, day, yearday, longitude, latitude, depth, flags, etc. The latter elements are important for understanding the dataset, but the "variable metadata section" as described here is not applicable to them. Note that Table 3 shows the available metadata elements for a generic oceanographic variable. Customized variable metadata sections for ocean carbon variables (DIC, TA, $f\text{CO}_2$, and pH) allow additional information to be documented. Refer to the metadata template file for more details about these metadata elements (https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/oa-metadata-template/, last access: 5 November 2023).

Within the "variable metadata section", the metadata element of "in situ observation/manipulation condition/response variable" in Jiang et al. (2015) was replaced with "in situ or manipulated". This change simplified this term, without compromising the purpose of differentiating whether a term is an in situ observed variable or a manipulated variable. New elements such as "discrete or continuous", "manipulation method", "calculation method and parameters", "sampling method", and "analyzing method", "calibration info", "QC steps taken", and "weather or climate quality" were also added. Refer to Table 3 for their detailed descriptions. Metadata elements that were rarely used, such as "purpose", "sections (cruise legs)", "duration (for experiment/settlement/-colonization methods)", and "spatial reference system", were eliminated.

4 Controlled vocabularies

For OAE data management, metadata elements that should be supported with controlled vocabularies include observed properties (e.g., DIC, TA, dissolved oxygen), observation or study types (e.g., surface underway, time series), platforms (e.g., research vessels), sea names, instruments, people, institutions, countries, etc. For platforms, refer to the International Council for the Exploration of the Sea (ICES): https://vocab.ices.dk/?ref=315 (last access: 5 November 2023). For sea names, it is recommended to use the SeaDataNet C16 list (sea areas): https://vocab.seadatanet.org/v_bodc_vocab_v2/search.asp?lib=C16 (last access: 5 November 2023). For countries, use the SeaDataNet C32 list (International Standards Organisation Countries): https://vocab.seadatanet.org/v_bodc_vocab_v2/search.asp?lib=C32 (last access: 5 November 2023). For investigator names, it is recommended to use the list as managed by ORCID: https://orcid.org/ (last access: 5 November 2023). For institutions, refer to the Research Organization Registry (ROR): https://ror.org/ (last access: 5 November 2023). Another two groups of controlled vocabularies related to OAE studies are presented here: (a) types of OAE studies (Table 4) and (b) types of source materials for OAE (Table 5).

Controlled vocabularies play a crucial role in data management, enabling researchers to describe their data in a standardized and precise way. Among the various types of controlled vocabularies, observed properties are particularly important, as they describe the measurable characteristics of a survey or experiment. However, observed properties also pose some challenges, as the terms used to describe them can be highly specialized and context-dependent. For exam-

Table 3. Metadata elements available for each observed property in the generic variable metadata section. For the latest version of the metadata template, refer to https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/oa-metadata-template/. "NA" is short for "not available".

No.	Element	Description	Controlled vocabularies
1	Variable abbreviation in the data file	The corresponding column header abbreviation of the variable in the data files, e.g., T, S, DIC, DO	Jiang et al. (2022): https://doi.org/10.3389/fmars.2021.705638
2	Full variable name	Long name of the variable, e.g., water temperature, salinity, total dissolved inorganic carbon content, dissolved oxygen content	Table 1 in Jiang et al. (2015): https://doi.org/10.5194/essd-7-117-2015.
3	Variable unit	Units of the variable, e.g., degrees Celsius, μmol kg^{-1}	NA
4	Observation type	How the variable was observed, e.g., surface underway, profile, time series, model output. For experimental data, this could be laboratory experiments, pelagic mesocosms, benthic mesocosms, natural analogues, etc. See Table 4 for a list of controlled vocabularies for this element.	Table 4
5	Discrete or continuous	Whether the reported results are based on discrete-bottled measurements or continuous sensor measurements.	Discrete vs. continuous
6	In situ or manipulated	Whether the variable reported is from an in situ observation, or from a manipulated experiment.	In situ vs. manipulated
7	Manipulation method	How the seawater chemistry is manipulated (e.g., bubbling CO_2 to make it more acidic, or adding solid substances to increase its alkalinity)	NA
8	Measured or calculated	Whether the variable is measured in situ, or calculated from other variables. For example, salinity calculated from chlorinity is not a calculated variable, but pH calculated from DIC and TA is.	Measured vs. calculated
9	Calculation method and parameters	Information about how the variable was calculated, e.g., using a MATLAB version of the CO2SYS with the dissociation constants of Lueker et al. (2000) for carbonic acid.	NA
10	Sampling instrument	Instrument that is used to collect water samples, or deploy sensors, etc. For example, a Niskin bottle, pump, or CTD is a sampling instrument. See Table 8 for a list of controlled vocabularies for this element.	Table 8
11	Sampling method	Additional information describing how the sample was collected, including more details of the instrument (e.g., the make, model, resolution, precisions).	NA
12	Analyzing instrument	Instrument that is used to analyze the water samples collected with the "sampling instrument", or the sensors that are mounted on the "sampling instrument" to measure the water body continuously. For example, a coulometer, winkler titrator, spectrophotometer, pH meter, thermosalinograph, oxygen sensor, YSI Multiparameter Meter is an analyzing instrument. See Table 8 for a list of controlled vocabularies for this element.	Table 8
13	Analyzing method	Additional information describing how the sample was analyzed, including more details of the instrument (e.g., the make, model, resolution, precisions).	NA
14	Calibration info	Information about how and when the sensor was calibrated (ISO 8601 format: yyyy-mm-dd).	NA
15	Field replication info	Repetition of sample collection and measurement, e.g., triplicate samples.	NA
16	QC steps taken	What QC steps have been taken to improve the quality of the data.	NA
17	Uncertainty	Uncertainty of the results (e.g., 1 %, 2 μmol kg^{-1}), or a description of the uncertainties involved in this method.	NA

Table 3. Continued.

No.	Element	Description	Controlled vocabularies
18	Weather quality or climate quality	The climate quality objective requires that a change in the dissolved carbonate ion concentration to be estimated at a particular site with a relative standard uncertainty of 1 %. The carbonate ion concentration is calculated from two of the four carbonate system parameters and implies an uncertainty of approximately 0.003 in pH; of 2 μmol kg^{-1} in measurements of TA and DIC; and a relative uncertainty of about 0.5 % in the pCO$_2$. The weather objective requires the carbonate ion concentration (used to calculate saturation state) to have a relative standard uncertainty of 10 %. This implies an uncertainty of approximately 0.02 in pH; of 10 μmol kg^{-1} in measurements of TA and DIC; and a relative uncertainty of about 2.5 % in pCO$_2$. Newton et al. (2015).	Weather vs. Climate
19	QC flag scheme	Describe what the quality control flags stand for, e.g., 1 = not evaluated/quality unknown, 2 = good value, 3 = questionable value, 4 = bad value.	NA
20	Biological subject	For biological variables, please state the taxonomy (a taxon or a community), upon which the variable is studied. For example, if you study the growth rate of a certain species of salmon. The "variable/parameter" is growth rate, and "Biological subject" is that species of salmon. You could group/capture organismal data in three forms: taxonomic, functional, and phylogenetic.	Catalogue of Life (COL): https://www.catalogueoflife.org/, Integrated Taxonomic Information System (or IT IS): https://www.itis.gov/index.html, World Register of Marine Species (or WoRMS): http://marinespecies.org/, or Paleobiology Database (PBDB): https://paleobiodb.org/classic/
21	Species ID	A persistent, unique code as an identifier for a taxonomic entry. For example AphiaID in WoRMS, or the Taxonomic Serial Number (TSN) in ITIS.	See above
22	Life stage	Organisms often go through several distinct stages during their development. This can be any stages like egg, embryo, larva, juvenile, and adult.	SeaDataNet development stage: https://vocab.nerc.ac.uk/collection/S11/current/
23	Other detailed information	Other detailed information about how the variable was collected and measured.	NA
24	Method reference	Citation for the method. It is recommended to use https://www.citationmachine.net to generate the citation.	NA
25	Researcher who measured this variable	The name and affiliation of the investigator responsible for measuring this variable.	ORCID: https://orcid.org/.

ple, different prefixes and postfixes may be added to the same basic term, resulting in a proliferation of narrow and highly specific terms (see examples in Table 6). This can make it difficult to find the right term for a given purpose and can also lead to inconsistencies and confusion. Furthermore, different communities may use slightly different terms to describe the same property or may have different conventions for expressing units and dimensions.

The current setup makes it necessary to create multiple variations of the same property, defeating the purpose of controlled vocabularies. Moving forward, it is important to develop clear guidelines and standards to foster collaboration and communication among different communities. Specifically, it is recommended to manage controlled vocabularies for different types of information separately. Imagine the CF convention only has one clean term called "dissolved inorganic carbon", with a preferred unit of "µmol/kg". The list will be significantly shorter, and each of the terms will be much broadly used. It would also be much more cost-effective to manage a shorter list. Ideally, such vocabulary development efforts should be driven by the scientific community to ensure their accuracy, and the developed list will conform to the needs and preferences of their research. Before those clean lists are developed, it is recommended to use the list as documented in Table 1 of Jiang et al. (2015) for the purpose of standardizing observed properties.

Additionally, two new types of controlled vocabularies were introduced. In the metadata template described by Jiang

Table 4. Controlled vocabularies for major types of OAE studies. NVS is short for NERC Vocabulary Server (NVS) (link: https://vocab.nerc.ac.uk/, last access: 5 November 2023). SDN is short for SeaDataNet. “NA” is short for “not available”. Refer to Table 1 for more information about some of these study types. For the latest version of this list, refer to https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/vocabularies/observation-types.html (last access: 5 November 2023).

No.	OAE study types	NVS term [ID] and link
1	Profile	Water bottle stations [SDN:C77::H09] (http://vocab.nerc.ac.uk/collection/C77/current/H09/, last access: 5 November 2023); CTD stations [SDN:C77::H10] (http://vocab.nerc.ac.uk/collection/C77/current/H10, last access: 5 November 2023)
2	Surface underway	Surface measurements underway (T, S) [SDN:C77::H71] (http://vocab.nerc.ac.uk/collection/C77/current/H71/, last access: 5 November 2023)
3	Time series	NA
4	Laboratory experiments	NA
5	Pelagic mesocosms	NA
6	Benthic mesocosms	NA
7	Field experiments	NA
8	Natural analogues	NA
9	Model output	NA

Table 5. Controlled vocabularies for source materials for OAE (based on Renforth and Henderson, 2017; Caserini et al., 2022). See also Eisaman et al. (2023, this Guide). For the latest version of this list, refer to https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/vocabularies/alkalinization-types.html (last access: 5 November 2023).

No.	Source materials	Chemical formula	OAE mechanism
1	Lime	CaO	$CaO + H_2O \rightarrow Ca(OH)_2$; $Ca(OH)_2 + 2CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$
2	Portlandite	$Ca(OH)_2$	$Ca(OH)_2 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$
3	Calcium Carbonate (e.g., calcite/aragonite)	$CaCO_3$	$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$
4	Anorthite	$CaAl_2Si_2O_8$	$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + 2HCO_3^- + Al_2Si_2O_5(OH)_4$
5	Dolomite	$CaMg(CO_3)_2$	$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$
6	Periclase	MgO	$MgO + 2CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^-$
7	Brucite	$Mg(OH)_2$	$Mg(OH)_2 + 2CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^-$
8	Magnesite	$MgCO_3$	$MgCO_3 + CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^-$
9	Forsterite	Mg_2SiO_4	$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4$
10	Mg-rich Olivine (Fe-Forsterite)	$(Mg, Fe)_2SiO_4$	$(Mg,Fe)_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2(Mg,Fe)^{2+} + 4HCO_3^- + H_4SiO_4$
11	Sodium hydroxide	$NaOH$	$NaOH + CO_2 \rightarrow Na^+ + HCO_3^-$ (electrochemical weathering)
12	Natrite	Na_2CO_3	$Na_2CO_3 + CO_2 \rightarrow 2Na^+ + 2HCO_3^-$
13	Nahcolite	$NaHCO_3$	$NaHCO_3 \rightarrow Na^+ + HCO_3^-$

Table 6. Variables related to total dissolved inorganic carbon (DIC) content within the Climate and Forecast (CF) conventions (https://cfconventions.org/, last access: 5 November 2023).

Standard name	Canonical units
mole_concentration_of_dissolved_inorganic_carbon_abiotic_analogue_in_sea_water	$\mathrm{mol\,m^{-3}}$
mole_concentration_of_dissolved_inorganic_carbon_in_sea_water	$\mathrm{mol\,m^{-3}}$
mole_concentration_of_dissolved_inorganic_carbon_natural_analogue_in_sea_water	$\mathrm{mol\,m^{-3}}$
moles_of_dissolved_inorganic_carbon_per_unit_mass_in_sea_water	$\mathrm{mol\,kg^{-1}}$
ocean_mass_content_of_dissolved_inorganic_carbon	$\mathrm{kg\,m^{-2}}$
tendency_of_mole_concentration_of_dissolved_inorganic_carbon_in_sea_water_due_to_biological_processes	$\mathrm{mol\,m^{-3}\,s^{-1}}$
tendency_of_ocean_mole_content_of_dissolved_inorganic_carbon	$\mathrm{mol\,m^{-2}\,s^{-1}}$
tendency_of_ocean_mole_content_of_dissolved_inorganic_carbon_due_to_biological_processes	$\mathrm{mol\,m^{-2}\,s^{-1}}$

et al. (2015), a metadata section called platform is used to document the platform information. This section contains information such as platform name, ID, type, owner, and country. Of these elements, the platform type could play an important role when it comes to data search purposes. SeaDataNet manages a similar list called “seavox platform categories” (L06) for this purpose. However, it does not cover all the terms the OAE research needs. In this paper, we introduce a new list for this purpose (Table 7). Similarly, SeaDataNet has a list called “device categories” (L05) for the types of instruments, although it does not have all the needed terms for OAE research. Table 8 lists instruments that are most likely used in this field.

5 Data citation

For oceanographic research, data citation commonly includes information such as a list of ordered authors, publication year, title, version, repository, and persistent identifier (e.g., DOI or URL) for the dataset. Here is an example of a good data citation: Feely, Richard A.; Alin, Simone R.; Hales, Burke; Johnson, Gregory C.; Juranek, Laurie W.; Byrne, Robert H.; Peterson, William T.; Goni, Miguel; Liu, Xuewu; Greeley, Dana (2015). Dissolved inorganic carbon, total alkalinity, pH, temperature, salinity and other variables collected from profile and discrete sample observations using CTD, Niskin bottle, and other instruments from R/V Wecoma in the U.S. West Coast California Current System during the 2011 West Coast Ocean Acidification Cruise (WCOA2011) from 2011-08-12 to 2011-08-30 (NCEI Accession 0123467). Version 3.3. NOAA National Centers for Environmental Information. Dataset. https://doi.org/10.7289/v5jq0xz1. Accessed on 2023-03-15.

There are three important considerations when it comes to minting DOIs for datasets. Firstly, it is advisable to avoid using different DOIs for different versions of the same dataset. Instead, it is recommended to mint one DOI that covers all versions of the dataset. This approach ensures that users with a DOI can always access the latest version of the dataset, as well as any historical versions. To differentiate between versions, the citation for the dataset should include its version information. Secondly, it is crucial to wait until the dataset is published in a long-term archive with a stable link before minting a DOI. A DOI is only as reliable as the link it resolves to, so it is essential to ensure that the link is stable and will not change in the future. If the link changes later on, the DOI will become broken. Thirdly, it is important to ensure that only one DOI is assigned to a dataset in the data flow. It is not uncommon for a dataset to be submitted to a data assembly center and be forwarded to another data assembly center for different purposes later on. To avoid the risk of confusing users with multiple versions of the same dataset in different places, it is essential to make sure that only one DOI is minted for the authoritative version of the dataset. According to the NOAA plan to increase Public Access to Research Results (PARR), only NOAA National Data Centers are authorized to mint DOIs for NOAA-funded datasets (NOAA, 2015).

6 Data repositories

Ideally, scientists should only need to submit their data once, and all distributed data assembly centers act as regional nodes, thereby contributing to the availability of ocean carbon and acidification data through a centralized data portal. Achieving this goal requires the provision of standardized metadata to the search engine of the agreed-upon one-stop portal. The most recent data management initiative by the UN Ocean Acidification Research for Sustainability (OARS) recommends the use of the GOA-ON Portal as the envisioned one-stop OA data portal. Once implemented, users can use the GOA-ON Portal to search for and access all ocean carbon and acidification data of a specific type. Upon discovering a dataset through the portal, the user can then return to the respective regional data assembly center to access the data files and locate pertinent metadata information. In order for the abovementioned federated system to work, each data assembly center would need to meet the following standards:

Table 7. Controlled vocabularies for platform types. NVS is short for NERC Vocabulary Server (NVS) (link: https://vocab.nerc.ac.uk/). SDN is short for SeaDataNet. For the latest version of this list, refer to https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/vocabularies/platform-types.html (last access: 5 November 2023).

No.	Platform type	NVS term [ID] and link (last access: 5 November 2023)	Description
1	Research vessel	Research vessel [SDN:L06::31] http://vocab.nerc.ac.uk/collection/L06/current/31/	A research vessel is a specialized type of ship or boat that is designed and equipped for oceanographic research. It often has autonomous sensors onboard and laboratories with scientific equipment for analyzing samples, and various other facilities to support research operations at sea.
2	Ship of opportunity (SOOP)	Vessel of opportunity [SDN:L06::32] http://vocab.nerc.ac.uk/collection/L06/current/32/	Ships of opportunity (SOOP) are not specifically designed for oceanographic research but are used to collect scientific data from autonomous sensors opportunistically. They can be cargo vessels, container ships, or other types of vessels that travel predetermined routes across the ocean.
3	Mooring	Mooring [SDN:L06::48] http://vocab.nerc.ac.uk/collection/L06/current/48/	A mooring is a collection of instruments used to measure oceanographic variables over an extended period of time at a fixed station. These mooring systems typically comprise a surface or subsurface buoy, to which the instruments are affixed, and a weighted anchor connected by a line.
4	Drifting buoy	drifting surface float [SDN:L06::42] http://vocab.nerc.ac.uk/collection/L06/current/42/	Drifting buoys are devices that float on the ocean surface, allowing them to follow the current. Typically, these buoys are equipped with a “drogue” – a device like a parachute or sheet – which enables them to be dragged along by the current.
5	Argo float	Drifting subsurface profiling float [SDN:L06::46] http://vocab.nerc.ac.uk/collection/L06/current/46/	Argo floats are a type of profiling float, consists of a cylindrical body that contains sensors for measuring ocean properties and inflatable bladders that allow the float to change its buoyancy and move up and down through the water column. Argo floats drift with ocean currents and surface periodically to transmit data via satellite.
6	Surface glider	Surface gliders [SDN:L06::3C] https://vocab.nerc.ac.uk/collection/L06/current/3C/	A surface glider is an autonomous, uncrewed surface vehicle (USV). Example: wave gliders.
7	Sub-surface glider	Sub-surface gliders [SDN:L06::27] https://vocab.nerc.ac.uk/collection/L06/current/27/	Sub-surface gliders are a type of autonomous underwater vehicle (AUV) that moves through the water using changes in buoyancy and wings to control its movement.
8	Saildrone	Autonomous surface water vehicle [SDN:L06::3B] http://vocab.nerc.ac.uk/collection/L06/current/3B/	Saildrones are a type of autonomous surface vessels (ASVs) that can travel long distances over extended periods of time. These environmentally friendly ocean drones are powered exclusively by the wind (for propulsion) and solar (for the onboard instruments).

1. A long-term archive ensures uninterrupted data access into the future.
2. Strict version control capabilities preserve all historical versions of a dataset on a permanent basis.
3. An online submission interface enables users to prepare metadata in a machine-readable format and to upload data files. Ideally, it should incorporate a user profile management interface, enabling users to keep track of all historical submissions and resume a submission at a later time.
4. A community-driven common metadata template supports the management of comprehensive metadata information needed for ocean alkalinity enhancement research.
5. Metadata are stored in the following:
    a. a user-friendly interface for metadata readability (e.g., HTML);
    b. a machine-readable format to facilitate machine-to-machine interoperability (e.g., XML, SQL);

Table 8. Controlled vocabularies for instrument types. NVS is short for NERC Vocabulary Server (NVS) (link: https://vocab.nerc.ac.uk/). SDN is short for SeaDataNet. "NA" is short for "not available". For the latest version of this list, refer to https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/vocabularies/instrument-types.html (last access: 5 November 2023).

No.	Instrument type	NVS term [ID] and link (last access: 5 November 2023)	Description
1	CTD rosette	NA	A CTD rosette consists of a metal frame that houses a collection of sensors and water sampling bottles (e.g., Niskin).
2	CTD sensor	CTD [SDN:L05::130] http://vocab.nerc.ac.uk/collection/L05/current/130/	The acronym CTD stands for conductivity, temperature, and depth, which are the three primary variables measured by a CTD sensor.
3	Niskin bottle	Discrete water samplers [SDN:L05::30] http://vocab.nerc.ac.uk/collection/L05/current/30/	A Niskin bottle is a type of sampling device used in oceanography to collect water samples at different depths. It is named after the inventor, Shale Niskin, who developed the device in the 1960s.
4	Flow-through system	Continuous water samplers [SDN:L05::31] http://vocab.nerc.ac.uk/collection/L05/current/31/	A flow-through system on a research vessel or ship of opportunity is a system designed to continuously pump seawater from the ocean into the laboratory for scientific research.
5	Thermosalinograph	Thermosalinographs [SDN:L05::133] http://vocab.nerc.ac.uk/collection/L05/current/133/	A Thermosalinograph (TSG) is an instrument used to measure seawater temperature and salinity.
6	Salinometer for discrete salinity measurement	Salinometers [SDN:L05::LAB30] http://vocab.nerc.ac.uk/collection/L05/current/LAB30/	Salinometers work based on the principle of conductivity. They measure the electrical conductivity of the water, which is directly related to its salinity.
7	DIC analyzers based on Coulometers	NA	DIC coulometers are widely used in oceanographic research to measure the concentration of dissolved inorganic carbon in seawater samples. They are often coupled with computer-controlled automated dynamic headspace analyzers that extracts total carbon dioxide from seawater using Single-Operator Multiparameter Metabolic Analyzers (SOMMAs)
8	DIC analyzers based on CO_2 gas detectors	NA	DIC analyzers based on a CO_2 gas detector including Non-dispersive infrared absorption (NDIR) (e.g., Licor LI-850), Cavity Enhanced Absorption Spectroscopy (e.g., Licor's LI-7815), and Cavity Ring-Down Spectroscopy (CRDS) (e.g., Picarro G2131i) detectors.
9	Autonomous DIC sensor	Inorganic carbon analyzers [SDN:L05::86] http://vocab.nerc.ac.uk/collection/L05/current/86/	Autonomous dissolved inorganic carbon (DIC) sensors are devices that can measure the concentration of DIC in seawater or other natural waters in situ, without the need for manual sampling and laboratory analysis.
10	Alkalinity titrator	Titrators [SDN:L05::LAB12] http://vocab.nerc.ac.uk/collection/L05/current/LAB12/	An alkalinity titrator is a device used to measure the total alkalinity of a seawater by titration.
11	Autonomous TA sensor	NA	Autonomous total alkalinity (TA) sensors are devices that can measure the concentration of TA in seawater or other natural waters in situ, without the need for manual sampling and laboratory analysis.
12	Showerhead equilibrator	Equilibrators [SDN:L05::EQUIL] http://vocab.nerc.ac.uk/collection/L05/current/EQUIL/	This type of equilibrator works by spraying seawater into a gas chamber, allowing the CO_2 in the water to equilibrate with a gas mixture in the chamber.
13	Floating air–water equilibrator	Equilibrators [SDN:L05::EQUIL] http://vocab.nerc.ac.uk/collection/L05/current/EQUIL/	An "h"-shaped bubble equilibrator assembly commonly used in MAPCO2 systems on moorings. For more information, refer to Friederich et al. (1995).

Table 8. Continued.

No.	Instrument type	NVS term [ID] and link (last access: 5 November 2023)	Description
14	Membrane equilibrator	Equilibrators [SDN:L05::EQUIL] http://vocab.nerc.ac.uk/collection/L05/current/EQUIL/	While seawater is passed through a membrane, CO_2 in the water diffuses across the membrane and equilibrates with the gas mixture, which is then analyzed to determine the CO_2 concentration.
15	Flask for discrete carbon dioxide measurement	NA	Such flasks are typically made of glass and have a capacity of around one liter. Seawater samples are collected from a specific depth using a Niskin bottle or other sampling device and transferred to the flask without exposing them to the air. The flask is then sealed with a stopper and transported to the laboratory for analysis.
16	Spectrophotometer	Spectrophotometers [SDN:L05::LAB20] http://vocab.nerc.ac.uk/collection/L05/current/LAB20/	A spectrophotometer is a scientific instrument used to measure the amount of light absorbed or transmitted by a sample. It is commonly used for high-quality pH measurements.
17	Handheld pH spectrophotometer	NA	One example of a handheld pH spectrophotometer is the “pHyter”. Refer to Pardis et al. (2022) for more details.
18	pH electrode	pH sensors [SDN:L05::355] http://vocab.nerc.ac.uk/collection/L05/current/355/	A pH electrode, sometimes referred to as a pH probe or pH sensor, is a device used to measure the pH of a solution.
19	Sea-Bird SeaFET	Satlantic SeaFET V1 pH sensor [SDN:L22::TOOL1292] http://vocab.nerc.ac.uk/collection/L22/current/TOOL1292/ Satlantic SeaFET V2 {Sea-Bird Scientific} (shallow) pH sensor [SDN:L22::TOOL1293] http://vocab.nerc.ac.uk/collection/L22/current/TOOL1293/	Sea-Bird SeaFET is a type of oceanographic instrument that is used to measure the pH of seawater in real time.
20	Oxygen titrator	Titrators [SDN:L05::LAB12] http://vocab.nerc.ac.uk/collection/L05/current/LAB12/	An oxygen titrator is a device used to measure the concentration of dissolved oxygen in a water sample, as required for the Winkler method.
21	Oxygen sensor	Dissolved gas sensors [SDN:L05::351] http://vocab.nerc.ac.uk/collection/L05/current/351/	An oxygen sensor or probe or sonde is an electronic device that measures the concentration of dissolved oxygen in the ocean.
22	Sea-Bird SeapHOx	Sea-Bird SBE SeapHOx V2 conductivity, temperature, pH, and dissolved oxygen system [SDN:L22::TOOL1895] http://vocab.nerc.ac.uk/collection/L22/current/TOOL1895/	Sea-Bird SeapHOx is a type of oceanographic instrument that measures both the pH and dissolved oxygen concentration of seawater in real time.
23	YSI	YSI Incorporated [SDN:B75::ORG00475/] http://vocab.nerc.ac.uk/collection/B75/current/ORG00475/	YSI (Yellow Springs Instruments) is a company that produces a variety of water quality monitoring instruments. The YSI sensors are designed to measure a wide range of parameters, including temperature, salinity, and dissolved oxygen.
24	Nutrient analyzer	Nutrient analyzers [SDN:L05::181] http://vocab.nerc.ac.uk/collection/L05/current/181/	A nutrient analyzer is a device used to measure the concentration of nutrients, such as nitrate, nitrite, ammonium, phosphate, and silicate, in water samples.

Table 8. Continued.

No.	Instrument type	NVS term [ID] and link (last access: 5 November 2023)	Description
25	Fluorometers	Fluorometers [SDN:L05::113] http://vocab.nerc.ac.uk/collection/L05/current/113/	Fluorometers can detect photosynthetic pigments such as chlorophyll by transmitting an excitation beam of light and detecting the light fluoresced by the pigments in a sample.
26	High-performance liquid chromatography (HPLC)	High-performance liquid chromatographs [SDN:L05::LAB11] http://vocab.nerc.ac.uk/collection/L05/current/LAB11/	High-performance liquid chromatography (HPLC) is a powerful analytical technique used to separate, identify, and quantify individual components in a liquid mixture.
27	Acoustic Doppler current profiler (ADCP)	Current profilers [SDN:L05::115] http://vocab.nerc.ac.uk/collection/L05/current/115/	Acoustic Doppler current profiler (ADCP), is a type of instrument used to measure water currents in oceans, rivers, and other bodies of water.
28	Mass spectrometers	Mass spectrometers [SDN:L05::LAB16] http://vocab.nerc.ac.uk/collection/L05/current/LAB16/	A mass spectrometer is an analytical instrument used to measure and identify the mass and abundance of atoms and molecules in a sample.
29	Isotope ratio mass spectrometers (IRMS)	Isotope ratio mass spectrometers [SDN:L05::LAB48] http://vocab.nerc.ac.uk/collection/L05/current/LAB48/	An isotope ratio mass spectrometer (IRMS) is a scientific instrument used to measure the isotopic composition of a sample.
30	Barometric pressure sensor	Meteorological packages [SDN:L05::102] http://vocab.nerc.ac.uk/collection/L05/current/102/	A barometric pressure sensor is a device that measures atmospheric pressure, which is the pressure exerted by the weight of the Earth's atmosphere.
31	Microscopes	Optical microscopes [SDN:L05::LAB05] http://vocab.nerc.ac.uk/collection/L05/current/LAB05/	A microscope is an instrument used to observe and magnify objects that are too small to be seen by the naked eye.
32	Scanning Electron Microscopes	Electron microscopes [SDN:L05::LAB07] http://vocab.nerc.ac.uk/collection/L05/current/LAB07/	A scanning electron microscope (SEM) is a type of microscope that uses a focused beam of electrons to create high-resolution images of the surface of a specimen.
33	Biological trawl	Pelagic trawl nets [SDN:L05::23] http://vocab.nerc.ac.uk/collection/L05/current/23/	A biological trawl is a type of fishing net that is towed behind a boat to collect marine organisms from the water column.
34	Phytoplankton net	Plankton nets [SDN:L05::22] http://vocab.nerc.ac.uk/collection/L05/current/22/	Phytoplankton net is used to collect phytoplankton, which are microscopic unicellular autotrophic organisms that form the base of the marine food web.
35	Zooplankton net	Plankton nets [SDN:L05::22] http://vocab.nerc.ac.uk/collection/L05/current/22/	Zooplankton net is used to collect zooplankton, which are microscopic animals that feed on phytoplankton and are important prey for many marine organisms.
36	Flow cytometers	Flow cytometers [SDN:L05::LAB37] http://vocab.nerc.ac.uk/collection/L05/current/LAB37/	A flow cytometer is a scientific instrument used to sort and count cells or particles in a liquid suspension based on their fluorescence and other physical properties.
37	eDNA sampler	NA	Environmental DNA (eDNA) samplers: used to collect and analyze genetic material shed by marine organisms, which can provide information about their distribution, abundance, and diversity.

6. controlled vocabularies utilized to various aspects of the metadata to ensure easy machine-to-machine metadata exchange and successful data findability;
7. data citation with permanent digital object identifiers (DOIs);
8. an existing mechanism to share standardized metadata with the search engine of the agreed upon data portal.

Before such a system is established, it is recommended to share a copy of the data with the Ocean Carbon and Acidification Data System (OCADS) at NOAA's National Centers for Environmental Information (NCEI) or other qualified data assembly centers to ensure timely inclusion into data products, e.g., the Surface Ocean CO_2 Atlas (SOCAT) and Global Ocean Data Analysis Product Version 2 (GLODAPv2). OCADS manages a wide range of ocean carbon and acidification data, including chemical, physical, and biological observations collected from research vessels, ships of opportunity, and uncrewed platforms, as well as laboratory experiment results, and model outputs (Jiang et al., 2023). It has an established setup to channel incoming datasets to existing data products, such as SOCAT (Bakker et al., 2016) and GLODAPv2 (Lauvset et al., 2022). OCADS welcomes submissions from scientists and institutions around the world. Follow this link to access the home page of OCADS: https://www.ncei.noaa.gov/products/ocean-carbon-acidification-data-system (last access: 5 November 2023). Genetics or eDNA raw data are an exception and should be sent to the National Center for Biotechnology Information (NCBI).

In Europe, in situ OA data are typically submitted to National Oceanographic Data Centres (NODCs) along with other types of measurements. Some research groups may also submit their OA data to specialized data assembly centers like SOCAT or publish their experimental data through data publishers like Pangaea. Government monitoring agencies in northern Europe typically send their OA data to the International Council for the Exploration of the Sea (ICES). Data centers may then integrate these data with other measurements in their databases using controlled vocabularies and standardized metadata elements. Since the late 1990s, data centers and associated organizations involved in marine data collection, management, and curation in European countries have collaborated as part of SeaDataNet, SeaDataNet 2, and SeaDataCloud. These projects have developed and adopted common standards for vocabularies, metadata schemas, data formats, and quality control procedures, enabling harmonization and interoperability of diverse marine data across Europe. The SeaDataNet infrastructure and common standards are critical to the operation and strengthening of key data workflows that feed into the European Marine Observation and Data Network (EMODnet), created to support the EU's integrated maritime policies. EMODnet Chemistry generates data products and provides centralized access to data relevant to the implementation of European Union maritime policies, with OA data being one of the four main focuses alongside eutrophication, contaminants, and marine litter. However, the workflow for OA data in Europe is not yet well-established, and there is an opportunity to build a harmonized workflow from data creators to data centers to data aggregators and product creators. Collaboration between data curators, IT and semantic specialists, and scientists can help enrich the semantic annotation of OA datasets with essential metadata information, which is needed to support OA research and monitoring efforts.

7 Conclusions

This paper offers comprehensive guidelines for OAE researchers to prepare their metadata and data for submission to long-term archives. These guidelines encompass a wide range of OAE data types, including discrete bottled measurements and autonomous measurements from surface underway and uncrewed platforms such as moorings, Saildrones, gliders, and Argo floats. Furthermore, they address physiological response studies conducted in various settings, such as laboratory experiments, mesocosms, field experiments, and natural analogues. The paper also provides a universal metadata template and data standards tailored to each type of OAE data. Additionally, it presents controlled vocabularies for observation types, alkalinization methods, platform types, and instruments. These guidelines are also applicable to ocean acidification data.

Key recommendations for data reporting

- Gather metadata elements using the most recent version of the OAE-compatible metadata template (Tables 2 and 3): https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/oa-metadata-template (last access: 5 November 2023).
- Wherever feasible, utilize the suggested OAE-compatible controlled vocabularies for metadata fields (Tables 4, 5, 7, and 8).
- Prepare data files in accordance with the specific data standard designated for the relevant OAE research type (Table 1).

Data availability. No data sets were used in this article.

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cal and physical dimensions of the guidelines, while DB focused on reviewing the biological aspect.

Competing interests. Competing interests are declared in a summary for the entire volume at: https://sp.copernicus.org/articles/sp-oae2023-ci-summary.zip.

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