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The transformation of ferrihydrite into goethite or hematite, revisited

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Abstract

During the oxidation of iron, poorly crystallized phases are firstly formed: 2 line-ferrihydrite and 6-line ferrihydrite, which present for the last phase, a similarity with wustite FeO but also with hematite α-Fe_2O_3. Crystallization increases with time and the solid phase obtained is dependent on temperature and pH. Obviously, high temperature favours the formation of the oxide hematite α-Fe_2O_3. As for the pH factor, it is more complicated. Low and high values of pH (2 to 5 and 10 to14) favour the formation of goethite α-FeOOH, while obtaining hematite is favoured at neutral pH (values around 7). Goethite or hematite are obtained either through a dissolution-crystallisation process or in the solid state, through a topotactic transformation.

Given the structural relationships observed between ferrihydrite and wustite and hematite, it is allowed to think that a structural continuity could exist between wustite $Fe_{(1-x)}O$ and hematite *via* ferrihydrite.

Keywords: **ferrihydrite, goethite, hematite, wustite, structural relationships, topotactic transformation**

Introduction

The hydrolysis of Fe^{2+} and Fe^{3+} ions in solutions, gives rise to iron hydroxides, oxyhydroxides or oxides according to the various reacting conditions used. The control of such reactions is of great importance for the reason that these materials are used as inorganic pigments, raw materials for iron and steel industries and precursor for the production of permanent magnets. Therefore, many studies have been carried out about these compounds. Cornell and Schwertmann [1] have reviewed the whole literature in a book published in 1996. In recent publications have been studied the topotactic transformation in solution, of Green Rust: GRCl (I) into lepidocrocite [2] and the topotactic dehydrations of goethite and lepidocrocite into respectively, hematite and maghemite, under thermal conditions in the solid state [3].

In the case of oxidation of iron, the first phase to precipitate in hydrolysis is usually ferrihydrite, a poorly crystalline oxide, of rough formula 5 Fe_2O_3, $9H_2O$ [4]. Its formula is still being debated. Three proposals have been reported in previous publications, which differ in the O/OH rate: $Fe_5O_7(OH)$, $4H_2O$ or $Fe_5O_3(OH)_9$ or $Fe_4O_5(OH)_2$, $2.6H_2O$ [5, 6]. Ferrihydrite was, for a long time, considered as the trivalent iron hydroxide $Fe(OH)_3$. It appears under two forms according to the number of lines found on the X-ray powder diffraction diagram: 2- line or 6-line ferrihydrite, which clearly depend of the crystallization state. It is metastable and can transform to goethite α-FeO(OH) or hematite α-Fe_2O_3. In fact, the solubility product of ferrihydrite ($K_s = 10^{-39}$) is higher than those of goethite ($K_s = 10^{-41}$) and hematite ($K_s = 10^{-43}$) [7]. The conditions of the transformation of ferrihydrite in solution have been studied by Schwertmann [8, 9]. According to the value of pH, goethite or hematite are obtained either through a dissolution-crystallisation process or in the solid state, through a topotactic transformation. Ferrihydrite is an iron oxyhydroxide of great importance in mineralogy and iron industries. It often occurs as a corrosion product of steel. Nevertheless, the mechanisms of formation of goethite or hematite from the precursor ferrihydrite are not clearly established. The aim of this publication is to bring more explanations about these transformation processes and particularly about the topotactic transformation of ferrihydrite into hematite.

Experimental results and discussion

Schwertmann et *al.* have studied the transformation of ferrihydrite in several publications [5, 8, 9]. They consider that the solid phase obtained is dependent on temperature and pH. Obviously, high temperature favours the formation of the oxide hematite. As for the pH factor, it is more complicated. Low and high values of pH (2 to 5 and 10 to14) favour the formation of goethite while obtaining hematite is favoured at neutral pH (values around 7). In fact, the dissolution of ferrihydrite is decisive. It can be performed either in acidic media or in alkaline ones, according to the following schemes that we propose:

Acidic solutions: $0 \leq n < 3$

$$5\ Fe_2O_3, 9\ H_2O_{(s)} + (30-10\ n)\ H_3O^+_{(aq)} + (6+10\ n)\ H_2O \rightleftarrows 10\ [\ Fe(OH)_n(H_2O)_{(6-n)}\ ]^{(3-n)+}_{(aq)}$$

In these conditions, ionic species found in solutions are dependent of pH. In very low pH (pH< 2), iron is rather dissolved under the complex ion hexaaquairon(III) $Fe(H_2O)_6^{3+}$ ($n = 0$). At higher pH, aquahydroxo complex cations exist, corresponding to $n = 1$, $Fe(OH)(H_2O)_5^{2+}$ and $n = 2$, $Fe(OH)_2(H_2O)_4^+$. Values of acidic constants of the acid/base couples ($Fe(H_2O)_6^{3+}$/ $Fe(OH)(H_2O)_5^{2+}$) and ($Fe(OH)(H_2O)_5^{2+}$/ $Fe(OH)_2(H_2O)_4^+$); pK values near 3 ($pK_1 = 3.05$; $pK_2 = 3.26$ [10]), are in agreement with the existence of these cations at pH values around 3-4. Precisely, in that range of pH, solubility of iron is more important and goethite formation also.

Alkaline solutions: $3 < n \leq 6$

$$5\ Fe_2O_3, 9\ H_2O_{(s)} + (10n-30)\ OH^-_{(aq)} + (66-10\ n)\ H_2O \rightleftarrows 10\ [\ Fe(OH)_n(H_2O)_{(6-n)}\ ]^{(n-3)-}_{(aq)}$$

At higher pH than 7, iron is dissolved under the complex anions, $Fe(OH)_4(H_2O)_2^-$ (n = 4), $Fe(OH)_5(H_2O)^{2-}$ (n = 5) and eventually at very alkaline pH, under $Fe(OH)_6^{3-}$ (n = 6). In these conditions the solubility of iron increases and goethite is obtained again.

In contrast, when pH values are around 7, H_3O^+ and OH^- concentrations are too weak for dissolving enough amount of ferrihydrite for the formation of goethite through the solution. Therefore, the transformation is performed mainly in the solid state, giving rise to hematite in solutions that present the minimum of solubility for ferrihydrite. In fact, at this stage the main dissolved entity would be the neutral complex $Fe(OH)_3(H_2O)_3$ but its concentration being too weak, the transformation in the solid state is dominant and hematite is obtained according to the scheme:

$$5\ Fe_2O_3,\ 9\ H_2O_{(s)} \rightleftarrows 5\ \alpha\text{-}Fe_2O_{3(s)} + 9\ H_2O$$

These hypotheses agree well with experimental results found by Schwertmann et *al.* In fact, these authors have determined the rate, r = (Hematite)/(Hematite + Goethite) in the solid obtained from the transformation of ferrihydrite, in relation with temperature, pH and reacting time. At room temperature the maximum of the rate value ($r = 0.75$) obtained at pH = 7, corresponds to predominant hematite. In acidic solutions the minimum of the rate value ($r = 0.05$) is obtained at pH = 4 and corresponds mainly to the formation of goethite. It is to be noticed that at $pH < 4$, r increases strongly ($r = 0.38$ at pH = 2.6) so that, we can conclude that solubility of iron is not the unique factor for the formation of goethite. We think that goethite is obtained in solution only from aquahydroxo cations, $Fe(OH)(H_2O)_5^{2+}$, $Fe(OH)_2(H_2O)_4^+$ or anions $Fe(OH)_4(H_2O)_2^-$, $Fe(OH)_5(H_2O)^{2-}$, $Fe(OH)_6^{3-}$. That explains why at low values of pH, hematite is favoured, insofar as iron exists in solution mainly under the form of the complex hexaaqua ion, $Fe(H_2O)_6^{3+}$ which seems to inhibit the formation of goethite. Therefore, it is probable that the presence of hydroxo ions is required for obtaining goethite, α-FeO(OH). Moreover, if the concentration of OH^- is important (pH>12), goethite appears alone. Iron oxyhydroxide is certainly formed by condensation of aquahydroxo ions, performed by olation and oxolation processes between OH and H_2O ligands, which give rise to Fe-OH-Fe and Fe-O-Fe bridges, found in goethite [5, 11].

In contrast, hematite is formed through the dehydration and the internal atomic arrangement of the solid ferrihydrite. The two different transformation processes enter into competition and one of them becomes dominant according to the reacting conditions.

As the two phases ferrihydrite and hematite display similar crystal structures we propose a hypothesis of a topotactic transformation, which is able to explain the formation of the oxide at so low temperatures.

Relationship between wustite and ferrihydrite and hypothesis of topotactic transformation of ferrihydrite into hematite

In order to have a better understanding of the transformation, it is necessary to describe the crystal structure of the two solids.

The structure of hematite, α-Fe_2O_3, has been determined by Pauling and Hendricks in 1925 [12] and revisited in 1970 by Blake *et al.*[13]. It is isostructural with corundum, α-Al_2O_3. The space group is $R\bar{3}c$ (N° 167, rhombohedral symmetry) and the lattice parameters given in the hexagonal cell are: a = 5.0346 Å, c = 13.752 Å. The structure has a three-dimensional framework built-up with trigonally distorted octahedra FeO_6, linked to thirteen iron neighbors by one face, three edges and six vertices [3]. The surrounding of oxygen is tetrahedral OFe_4. The structure can be described as a slightly distorted h.c.p.(hexagonally close-packed ABA) stacking of anions O^{2-} (fig.1). Iron ions are located in octahedral sites, two thirds of the sites are occupied [1]. Layers are stacked along the c axis but periodic small shifts of anions and especially more important shifts of cations are responsible of the increase of this axis, three times ABA distance [3].

Synthetic and natural ferrihydrites are poorly ordered and exhibit a continuum from amorphous to partly crystallized phase characterized by their XRD patterns. The least crystalline variety shows two broad peaks (2-line ferrihydrite) and the more crystalline six broad peaks (6-line ferrihydrite). The main difference between 2-line and 6-line ferrihydrite is the size of their coherent scattering domains [14]. Cornell and Schwertmann [1] suggested that 2-line ferrihydrite does not transform to 6-line ferrihydrite with time because these two forms precipitate under different conditions. In contrast, more recent works conclude that probably 6-line ferrihydrite may be an intermediate metastable in the conversion of 2-line ferrihydrite into hematite [15, 16, 17] and this hypothesis was confirmed recently by the calculation of Gibbs free energy of formation for the two forms of ferrihydrite [18].

For the reason of the very poor crystallization of the 2-line ferrihydrite only the structure of the 6-line ferrihydrite has been determined and was the matter of discussions. The structure was first described in 1967 [19] but more recently a new structural model was proposed, consisting of a mixture of two phases [20]. One of them is composed of close packing anionic layers ABACA (defect-free phase in comparison with hematite Fe_2O_3 : Fe/O = 2/3) and the other is built-up with two structural fragments ABA and ACA randomly distributed within a hexagonal super-cell (defective phase compared to hematite). Very recently, the structure was revisited by Jansen et *al* [21] on the basis of the last model proposed. The crystal structure of ferrihydrite can be described as a superposition of two components:

- a defect-free phase of trigonal space group $P\bar{3}1c$. Cell parameters given in a hexagonal cell are: a = 2.955Å, c = 9.37Å. The structure is built-up with close packing layers of O^{2-}, OH^- , stacking along the c direction according to: ABACA (fig.2a),

- a defective phase which consists of a subunit of the precedent phase, displaying a trigonal P3 space group and cell parameters, a = 2.955 Å, c = 9.37/2 = 4.685 Å. This phase is composed of random sequences of ABA and ACA layers (fig.2b). Splitting of atomic positions of iron in the P3 group, gives rise to a higher degree of disorder due to varying occupancies and additional vacancies but the structure is nevertheless, similar to the defect-free one [21]. Atomic positions of these phases are reported in table 1.

If we suppose now, that in the defect-free structure, occupancies rate for atoms could be equal to 1, the Fe/O rate should be equal to 1, so that the compound formula should be FeO. In fact the structure presents a similarity with the structure of wustite FeO, similarity which appears very well on the figure 3. Wustite belongs to the NaCl structural type (space group Fm3m; a = 4.33Å)[1] and displays a cubic close packing ccp stacking of oxygen layers ABC (fig.3a, 3c). The main difference between the two structures is due to the stacking of anionic layers, ABACA in ferrihydrite and ABC in wustite. This difference leads to a modification of the orientation of iron octahedra in ferrihydrite, giving rise to zigzag planes parallel to (1 0 2) and (-1 0 2) (see fig.3a, 3b). Obviously, in ferrihydrite exist numerous vacancies since Fe/O rate is very inferior to one. In addition, wustite also has not a stoichiometric composition ($Fe_{(1-x)}O$) for the reason that a partial oxidation of divalent iron gives rise to trivalent iron and the creation of cation vacancies. Ferrihydrite is built-up like wustite, with iron octahedra involving O^{2-} but also a part of OH^- in this case. Each octahedron could be linked to nineteen neighbors by one face, nine edges and nine vertices (fig.4b). Remember that this number of neighbors is never reached because of the vacancies of cations observed in ferrihydrite (fig.4c).

If a crystalline relationship exists between ferrihydrite and wustite (see fig. 3 and 4), a relationship can be also formulated with hematite and a topotactic transformation probably occurs between the two phases [8, 9]. On the figure 5 are reported the projection of the crystal structure of ferrihydrite along the direction [-1 1 0] (fig.5a, 5b) and the projection of hematite along the direction [0 1 0] (fig.5c). When iron vacancies in ferrihydrite are ordered like on the figure 5b, a similarity with hematite appears without any doubt. That is also confirmed on the figure 4 where is exposed the evolution of atom surroundings from wustite to hematite. Therefore, during the transformation of ferrihydrite into hematite, vacancies become ordered so that the crystallization state increases. In parallel, light displacements of iron and oxygen atoms are performed and the stacking of layers ABA, which characterizes the crystal structure of hematite, is obtained (fig. 5c). Consequently, the surrounding of oxygen atoms becomes tetrahedral instead of octahedral, due to iron vacancies (fig.4c, 4d). The loss of water, arising from OH condensation and adsorbed water, is relatively weak.

Simple relations can be established between lattice parameters of the two solid phases. They are reported in table 2. The contraction of the structure after the transformation appears to be moderated, around 2%. It is conform to the fact that the defect-free structure has the Fe/O rate of hematite.

Conclusion

The oxidation of divalent iron salt solutions gives rise to different Green Rusts: GR(I), GR(II) built-up with brucitic layers in which coexist divalent and trivalent iron cations. The structural cohesion of these two-dimensional phases is assured by the presence of anions (Cl^-, SO_4^{2-}, CO_3^{2-}, PO_4^{2-}, ...) located in the interlayer space. Many papers have been published about this subject. Bibliographic references can be obtained in a very recent publication [22]. Green Rusts transform easily by oxidation either into lepidocrocite or into goethite according to the conditions used [2]. Oxides, hematite, maghemite or magnetite can be prepared in the solid state, from oxyhydroxides by thermolysis [3].

The other route for obtaining iron oxyhydroxides and oxides, exposed in this publication, proceeds through poorly crystallized phases which are firstly formed: 2 line-ferrihydrite and 6-line ferrihydrite. In contrast with GR, they display a three-dimensional structure. The last phase presents a similarity with wustite FeO. Crystallization increases with time and goethite or hematite is obtained in relation with values of pH. Hematite is favored at neutral conditions. In this case the transformation of ferrihydrite is not performed by a dissolution-crystallization process but by a topotactic transformation, insofar as crystal structures of the two phases display an evident relationship. Given the structural relationships observed between ferrihydrite and wustite and hematite, it is allowed to think that a structural continuity could exist between wustite $Fe_{(1-x)}O$ and hematite *via* ferrihydrite:

$$\text{wustite} \longrightarrow \text{Ferrihydrite} \longrightarrow \text{Hematite}$$

The general formula for these solid phases could be:

$$Fe(II)_{(1-3x)}\, Fe(III)_{2x}\, O_{((2-y)/2)}\, (OH)_y,\ z\ H_2O$$

If x = y = z = 0, then FeO is obtained; if x = 1/3 and y = z = 0, it is $Fe_{2/3}\,O$ or Fe_2O_3. In the case of the most probable formula given for ferrihydrite, $Fe_5O_7(OH), 4H_2O$ [5], x = 1/3, y = 0.133 and z = 0.533. That leads to the formula: $Fe_{0.666}\ O_{0.933}\ (OH)_{0.133}$, $0.533\ H_2O$. The sum of O^{2-} and OH^-, located in layers of anions (here equal to 1.066) must be equal to one, in order to compare easily with hematite: $Fe_{0.666}O$. Therefore, the formula obtained:

$Fe_{0.625}\ O_{0.875}\ (OH)_{0.125}$, $0.5\ H_2O$, shows that it is an iron defective phase compared to hematite (see the description of the structure of ferrihydrite). The transformation of ferrihydrite into hematite is performed according to the following scheme:

$$Fe_5O_7(OH), 4H_2O \rightleftarrows Fe_5O_{7.5} + 4.5\ H_2O$$

The loss of water is due to the OH decomposition and to H_2O molecules which are probably adsorbed for the reason of the bad crystalline and fine-grained state of ferrihydrite.

Therefore, the dehydration of ferrihydrite $Fe_5O_7(OH)$, $4H_2O$, gives rise to $Fe_5O_{7.5}$ equivalent to Fe_2O_3. The loss of water issued from OH belonging to the anion layers is not important. That explains perfectly why the structure of ferrihydrite is lightly affected during its transformation into hematite (contraction of the structure around 2%). This fact is in favor of the formula chosen for ferrihydrite, $Fe_5O_7(OH)$, $4H_2O$, even if the O/OH rate is not necessarily fixed and can probably var~~ies~~y around a value near seven. Therefore, ferrihydrite is rather a hydrated oxide than an hydroxide.

Nevertheless, this hypothesis based upon crystal relationships, cannot be confirmed easily because of the very bad crystallization state of these precursor phases.

In addition, interactions of other cations such as Zn^{2+}, Fe^{2+}, Ni^{2+}, Mn^{2+} can catalyse [4, 23] or inhibit [13] the transformation of ferrihydrite, while bacteria like *Shewanella putrefaciens* can reduce trivalent iron into divalent iron so that goethite or lepidocrocite turns back to GR [24, 25]. In these conditions, it is evident that the study of iron oxides or oxyhydroxides presents a great difficulty and is always an actual problem.

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Table 1: Atomic positions of ferrihydrite, according to Jansen et *al.*[21]
(without site occupancies)

Defect-free phase, P-31c

Atom	site	x	y	z
O1	2b	0	0	0
O2	2d	2/3	1/3	1/4
Fe(III)	4f	1/3	2/3	0.136

Defective phase, P3

Atom	site	x	y	z
O1	1a	0	0	0
O2	1c	2/3	1/3	1/2
Fe1	1b	1/3	2/3	0.163
Fe2	1b	1/3	2/3	0.337
Fe3	1b	1/3	2/3	0.663
Fe4	1b	1/3	2/3	0.837

Table 2: Relation between crystal axes of ferrihydrite and hematite

Ferrihydrite P-31c	Hematite R-3c	Relations between axes	comments
a_F = 2.955 Å	a_H = 5.0346 Å	$\overrightarrow{a_H} \Leftrightarrow (\overrightarrow{a_F} + 2\,\overrightarrow{b_F})$ (5.12 Å)	weak contraction inside layers,due to the loss of OH. (- 1.6%)
b_F = 2.955 Å	b_H = 5.0346 Å	$\overrightarrow{b_H} \Leftrightarrow (\overrightarrow{a_F} - \overrightarrow{b_F})$ (5.12 Å)	idem
c_F = 9.37 Å	c_H = 13.752 Å	$\overrightarrow{c_H} \Leftrightarrow 3/2\ \overrightarrow{c_F}$ (14.055 Å)	weak contraction between layers, due to the loss of H_2O. (- 2.2%)
γ = 120°	γ = 120°		

Table 3: Relation between crystal axes of wustite and ferrihydrite

Ferrihydrite P-31c	wustite Fm3m	Relations between axes	comments
a_F = 2.955 Å	a_W = 4.33 Å	$\vec{a}_F \Leftrightarrow \frac{(-\vec{c}_W + \vec{b}_W)}{2}$ (3.06 Å)	weak contraction due to the presence of Fe^{3+} instead of Fe^{2+} but also of OH groups. (- 3.4 %)
b_F = 2.955 Å	b_W = 4.33 Å	$\vec{b}_F \Leftrightarrow \frac{(-\vec{a}_W + \vec{c}_W)}{2}$ (3.06 Å)	idem
c_F = 9.37 Å	c_W = 4.33 Å	$\vec{c}_F \Leftrightarrow 4/3\,(\vec{a}_W + \vec{b}_W + \vec{c}_W)$ (9.99 Å)	weak contraction more important in that direction, also due to Fe^{3+} and OH. (- 6.2%)
γ = 120°	/		

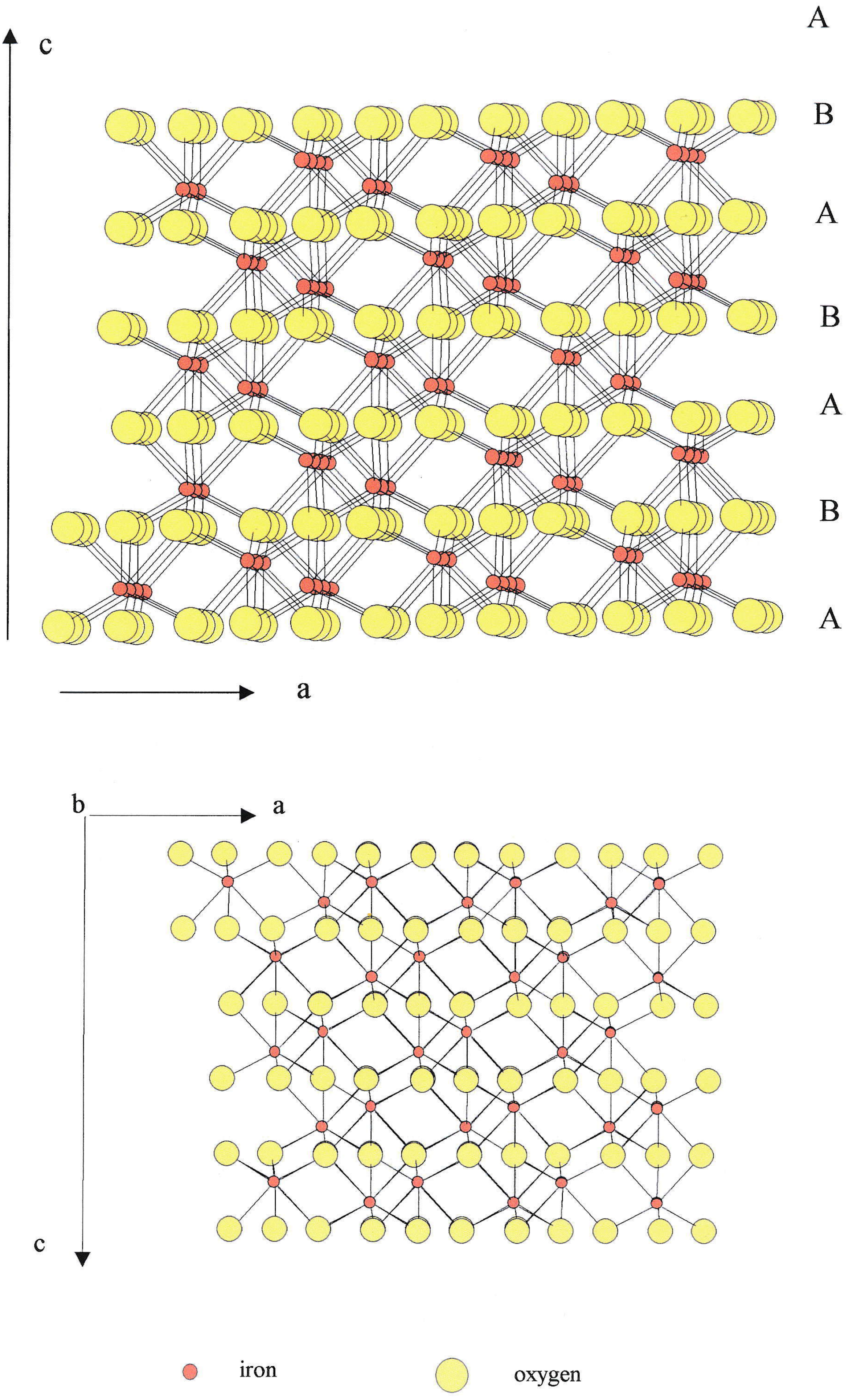
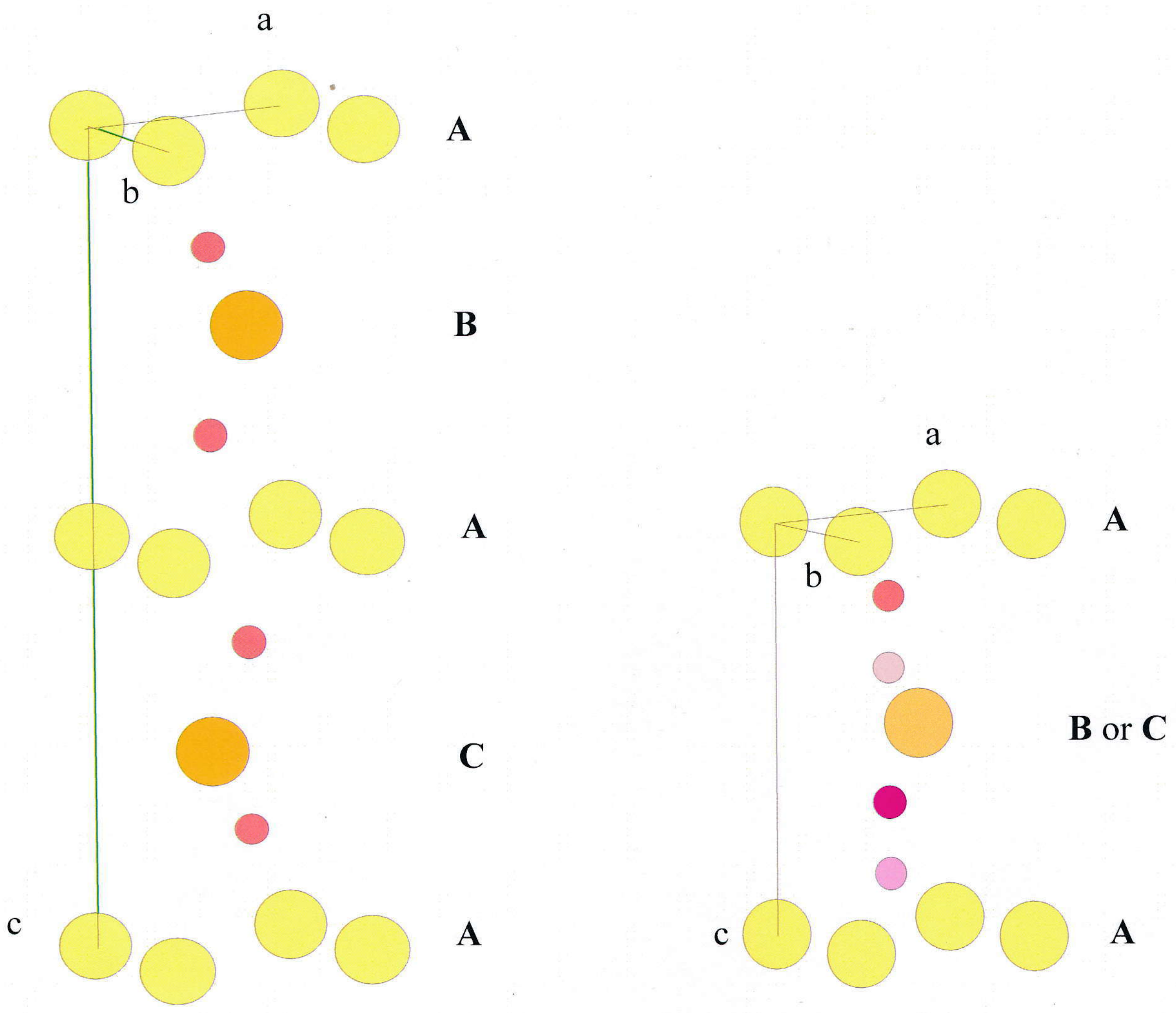


Fig. 1 : Crystal structure of hematite



a) - defect-free phase, space group P-31c

b) - defective phase, space group P3

Figure 2 : Crystal structure of ferrihydrite

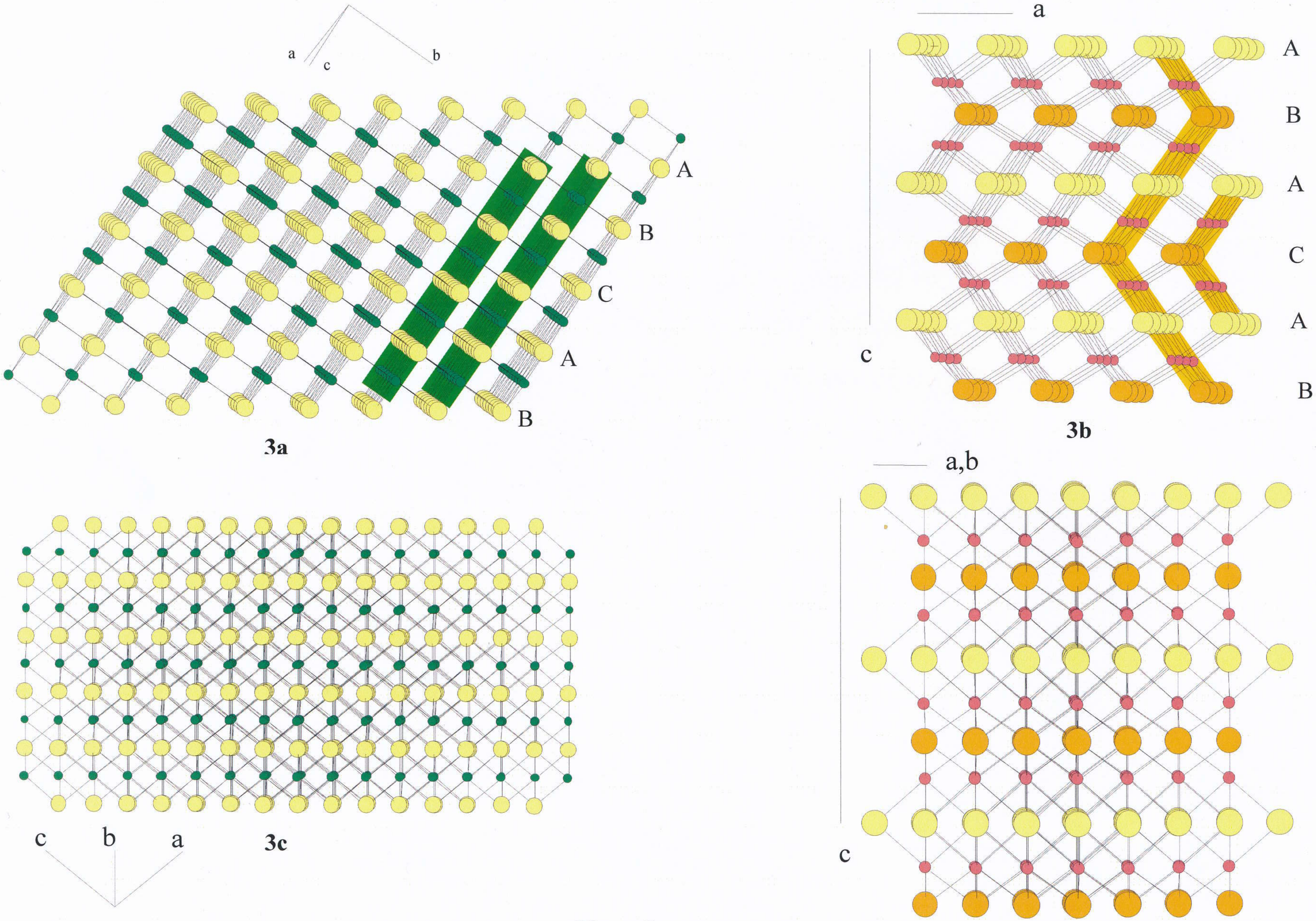


Figure 3
Crystal structure of FeO: 3a, 3c
Crystal structure of ferrihydrite: 3b, 3d
(without vacancies)

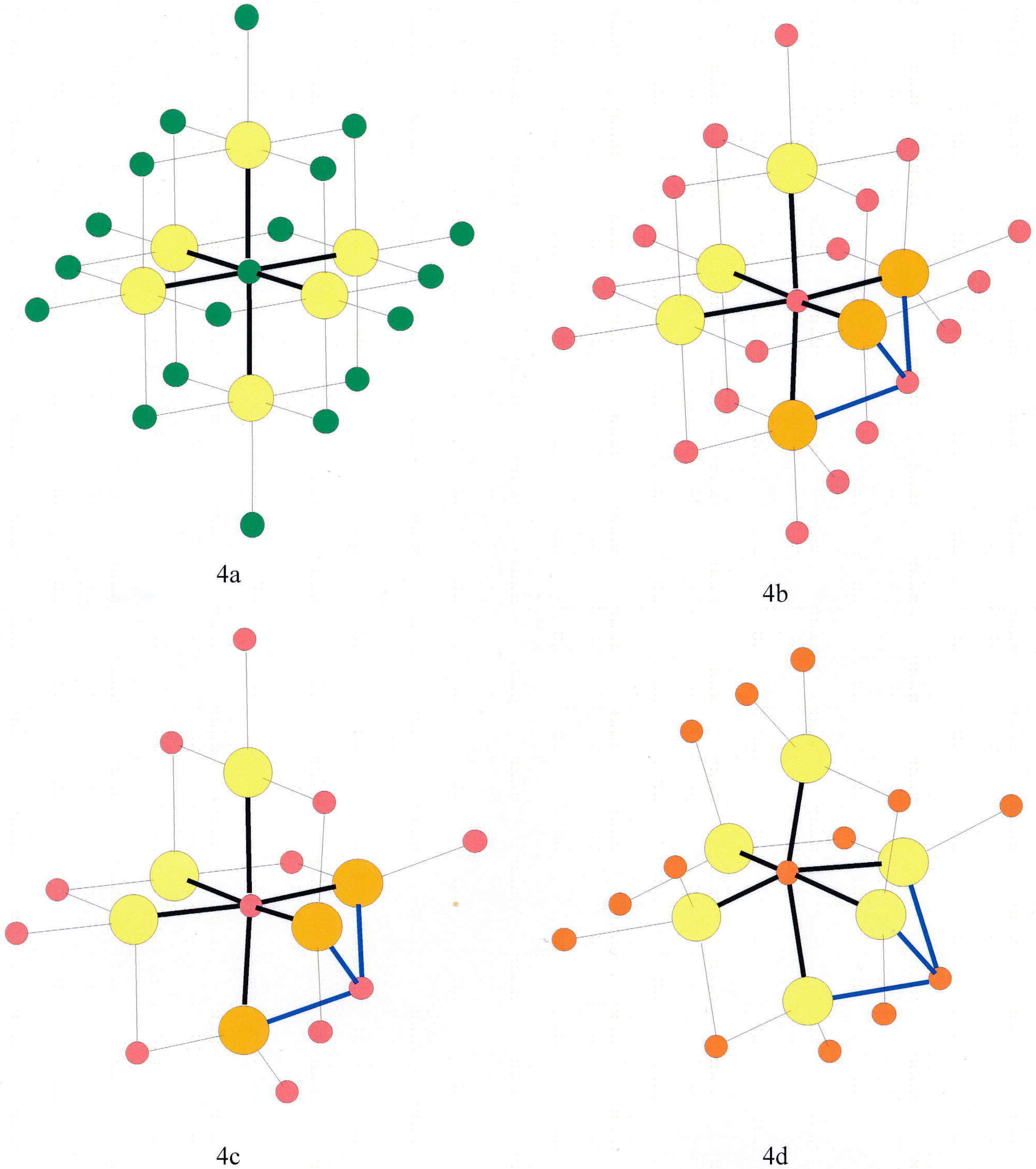


Figure 4 : surroundings of iron and oxygen
4a: Wustite
4b: Ferrihydrite (without vacancies)
4c: Ferrihydrite (with ordered vacancies)
4d: Hematite

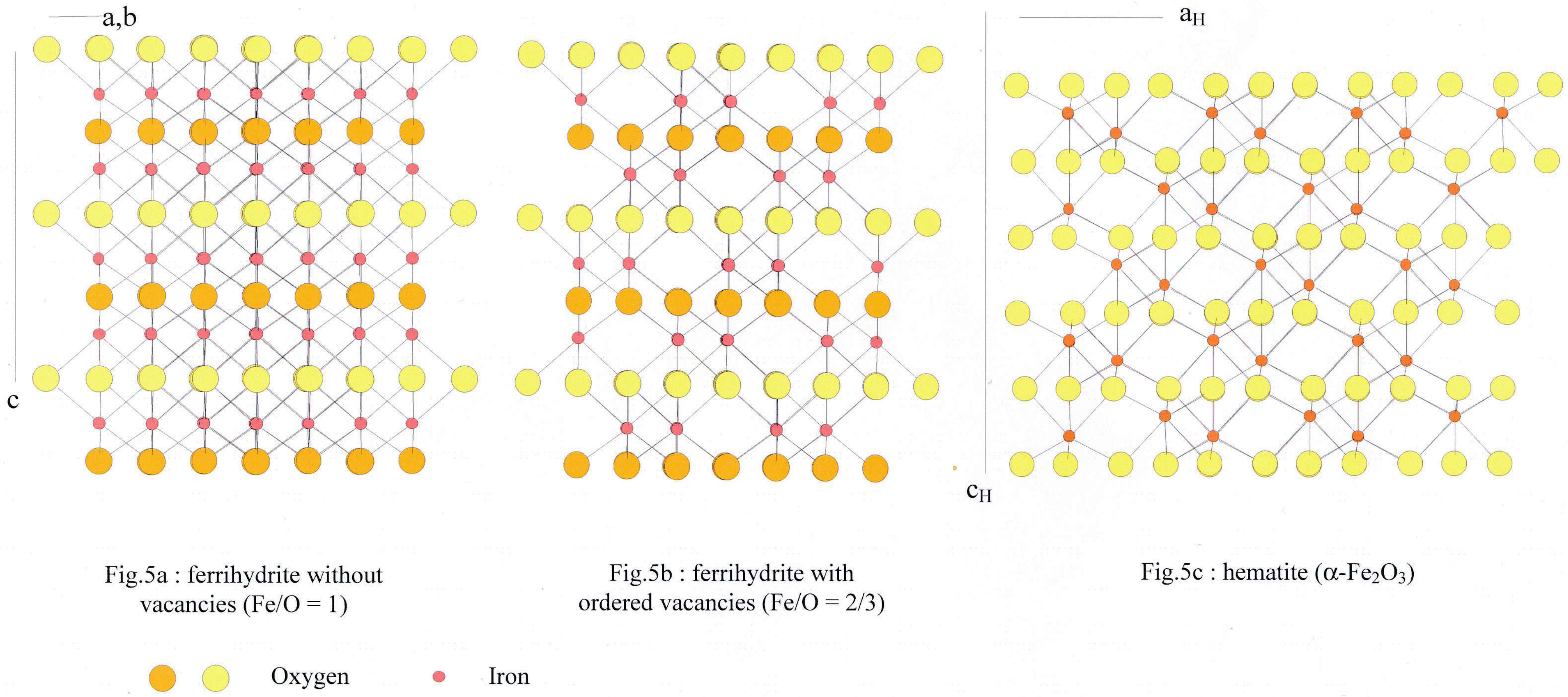


Fig.5a : ferrihydrite without vacancies (Fe/O = 1)

Fig.5b : ferrihydrite with ordered vacancies (Fe/O = 2/3)

Fig.5c : hematite (α-Fe_2O_3)

Figure 5 : Crystalline relationship between ferrihydrite and hematite