

North Bohemian Porcellanites and their Mineral Composition: the Case of the Dobrčice Quarry, the Most Basin

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ABSTRACT. Miocene clays overlying the coal seams and transformed by earth fires into porcellanites represent a characteristic lithological member of the Most Basin. Due to their extremely fine grain size, their detailed mineral composition has been determined insufficiently yet. Among countless North Bohemian porcellanite localities, the abandoned quarry near the village of Dobrčice has been chosen and subjected to field as well as to laboratory study (chemical analyses, optical microscopy, X-ray diffraction and electron microprobe analyses). The following mineral phases were found: mullite, tridymite, \pm quartz, Fe,Mg cordierite, K-feldspar, calcic plagioclase, pyroxene, ilmenite, anatase or rutile, hematite, goethite, ulvöspinel, corundum, apatite and scarce monazite.

KEY WORDS: Tertiary–Quaternary, Miocene sediments, coal burning, caustic metamorphism, HT-minerals, X-ray diffraction, electron microanalysis.

Introduction

Porcellanites, also porcelain jaspers or porcellaneous cherts, originate by low-pressure but very high-temperature (caustic) metamorphism of clays or marls. The temperature of transformation may approach sintering or even melting of the affected rock which gains the appearance of industrial porcelain. Porcellanites are mostly of variegated pastel colours, hard but brittle, showing often conchoidal fracture. The source of the transformational heat comes either from burning caustobiotites or from high-temperature volcanic or sub-volcanic rocks. Both types occur in the Czech Republic but only the first mentioned one is present in the region of the Most Basin. Earth fires responsible for the origin of such porcellanites require the denudation of the coal seam and the access of air oxygen. Such denudation process can take place either by natural erosion or by human interference (raw materials exploitation, cuts for transport pathways, foundations of buildings).

Numerous porcellanite occurrences in N Bohemia were used mainly as second-class road aggregates and also as building stone or even jewellery, besides raw material for the manufacture of tools in the Neolithic and Eneolithic (Šrein et al. 2001). The extent of the occurrences ranges from a few m² to several km². The most important localities are shown in the sketch map in Fig. 1, including the studied site near Dobrčice (8 km ESE of Most, 7 km WSW of Bílina).

Geological setting and description of the locality

The Dobrčice porcellanites (Plate 1), derived from sediments of the Overlying Formation above the main Miocene coal seam, are exposed in an erosional block in the eastern part of the basin (Hibsch 1929). They are located on the periphery of the former Mariana open-cast coal mine. The rock, the maximal thickness of which is 15 m, was exploited as aggregate for mine roads and transport trucks. The quarry yielded some 2 million tons of aggregate, was later recultivated, with a wall only 50 m long and 10 m high being exposed today.

This small but instructive remnant lies on the WSW foot of forested Špičák Hill (360 m a.s.l.). The distinct, multi-coloured character of the outcrop attracts the attention already from a distance. The gently inclined complex is composed of variegated porcellanite

beds with alternating red, orange, yellow, blue, violet, pinkish, brown and grey colours. Most types are compact in hand specimens. Sluggish structure is occasionally developed. Individual colours follow precisely the original bedding of the primary clay-dominated succession dipping approximately 20° W. In places, porcellanite beds are folded due to the loss in volume caused by caustic dehydration. Intensive and irregular jointing is a typical feature of the whole succession. The burning coal seam, source of the caustic transformational heat, is hidden just below the present base of the quarry.

Tyráček (1994), on the basis of paleomagnetic data and morphostratigraphic position, determined the age of the Dobrčice porcellanites as the oldest one in N Bohemia: 3.4–3.5 Ma (Late Pliocene, Gauss epoch of normal magnetic polarity). Kvaček and Hurník (2000) found a rich floral assemblage in the porcellanites of this locality. In analogy with another N Bohemian porcellanites, the peak temperature of the caustic metamorphism can be estimated at 980–1050 °C for sintered and up to 1300 °C for vitrified domains (Fediuk 1988).

Rock chemistry

Four samples (location – Plate 1) of different colours, collected by Dr. V. Cajz, were analysed in the Laboratory of the Czech Geological Survey in Prague. The results are given in Tab 1.

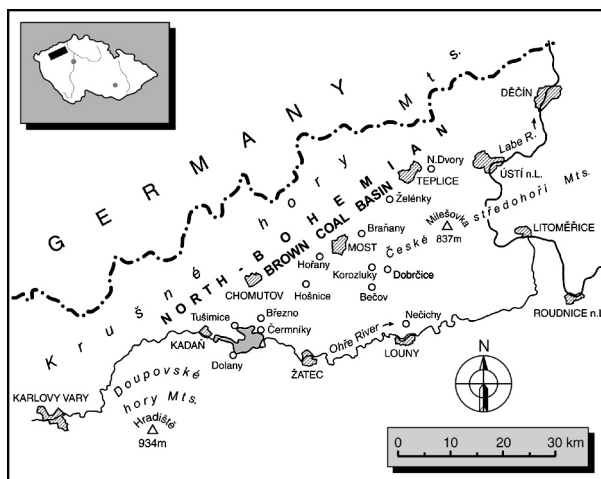


Fig. 1. A sketch-map of important porcellanite sites in the Most Basin (according to Fediuk 1988, supplemented).



Plate 1. Above: General view of the porcellanite locality, Dobřice quarry. Below: A view of the Dobřice quarry with the locations of the analysed samples Do-1 to Do-4.

Do-1 Red porcellanite			Do-2 Grey porcellanite			Do-3 „Scoria“			Do-4 Yellow porcellanite			Cordierite C		Mullite M		Tridymite T		Hematite He		Anorthite An		Quartz Q		
dÅ	I	ident.	dÅ	I	ident.	dÅ	I	ident.	dÅ	I	ident.	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	
8.49	60	C	8.47	58	C	8.46	45	C, Ap				8.45	80											
5.39	27	M	5.36	14	M	6.44	1	An	5.38	7	M			5.39	50					6.53	4			
4.93	9	C	4.89	6	C	5.38	7	M	4.97	2	?													
4.66	6	C	4.64	5	C	4.91	9	C	4.86	3	?	4.91	30											
4.36	51	T	4.33	11	T	4.67	8	C, An	4.26	36	T, F, Q	4.67	12			4.37	80			4.68	9	4.26	16	
4.12	68	T	4.09	87	T	4.26	5	T	4.18	5	Goe					4.12	100							
4.08	61	C	4.08	100	C	4.08	53	C	4.09	42	T	4.09	75											
3.85	30	T	3.79	6	T	4.04	65	An	3.91	4	T					3.86	60			4.04	22			
						3.77	10	An	3.79	3	An										3.78	14		
						3.67	30	He													3.62	15		
						3.62	14	An																
3.43	46	M	3.47	11	K				3.46	13	K			3.43	95									
3.39	100	C, M	3.42	20	M				3.43	15	M	3.39	70	3.39	100									
			3.37	60	C, M	3.38	30	C, M	3.39	19	M													
									3.34	100	Q												3.34	100
3.25	9	T	3.25	10	T	3.26	10	T	3.25	4	T, F					3.24	48							
3.14	28	C	3.13	22	C	3.18	23	An	3.19	2	An													
3.05	23	C	3.04	26	C	3.13	28	C, Py				3.13	100											
3.02	19	C				3.04	22	C				3.05	65											
									2.944	7	T, An, Py	2.969	2	T, An							2.952	17		
2.890	11	M	2.881	8	M	2.830	5	T, An, Py, Ap	2.891	5	M			2.886	20					2.829	12			
			2.828	4	T																			
2.696	24	He				2.689	100	He, Goe	2.740	7	Il													
2.686	15	M	2.687	9	M			M	2.699	6	M			2.694	40					2.700	100			
2.652	13	C	2.644	9	C	2.647	9	C, An				2.653	25								2.656	7		
2.548	27	M	2.541	18	M, K	2.551	10	M	2.550	11	M, K, Il			2.542	50									
2.512	14	T, He	2.503	11	T	2.510	72	He, T, An, Py	2.509	7	T					2.523	25	2.519	70	2.524	10			
									2.460	12	Q												2.457	9
2.428	9	M, C	2.381	4	K	2.429	4	M, C, Py	2.430	4	M	2.431	12	2.428	14									
2.325	7	C, T	2.346	7	C, T	2.346	14	C, T, Ap	2.388	2	K													
2.291	7	M, T	2.291	5	M, T	2.278	3	M, T	2.349	1	T	2.337	25	2.292	20	2.325	20							
									2.283	5	M, T, Q			2.298	19								2.281	8
2.210	37	M, He	2.204	17	M	2.201	15	M, He	2.237	4	Q, Il											2.236	4	
2.176	3	C							2.212	12	M			2.206	60									
2.122	12	M, C	2.116	5	C, M	2.140	4	An, M, C	2.129	10	M, Q	2.174	14											
2.098	6	C	2.083	9	C, K, T	2.094	9	C, Py	2.089	2	T, K	2.112	12	2.121	25							2.140	14	
						2.069	2	C	2.030	4	T	2.101	10			2.077	12					2.128	6	
2.029	17	T	2.033	12	T	2.029	7	T	1.982	4	Q	2.061	2											
									1.955	1	T					2.038	11							
1.946	1	C, T	1.957	1	C, T							2.174	14											
						1.935	3	An, Ap	1.989	1	M, K	1.949	6											
1.883	6	C, M	1.880	6	C, M	1.873	4	C, M	1.839	2	M	1.884	10	1.887	8									
1.840	5	M, He				1.833	25	He, M, Ap	1.819	9	Q			1.841	10					1.841	40			
												1.799	10											
1.793	2	C	1.798	2	C	1.795	3	C, An																
						1.771	3	An	1.740	2	K, Il													
						1.743	2	Py	1.714	2	M, T	1.708	8	1.712	6	1.710	8							
1.714	6	M, C, T	1.710	4	M, C, T				1.693	2	M	1.693	40	1.700	14									
1.693	13	M, C, He	1.689	10	M, C	1.690	32	M, C, He	1.672	2	Q					1.694	45							
									1.658	1	Q													
									1.627	2	T					1.635	8						1.672	4
																						1.659	2	
1.602	5	M, He	1.601	13	T, M, T, K	1.607	6	He, M	1.604	4	T, K, M													
						1.592	8	C, Py				1.590	12	1.600	20	1.600	10	1.599	10					
1.577	1	M												1.579	12									
									1.542	7	Q													
1.525	17	M	1.524	8	M	1.528	3	M	1.526	9	M			1.524	35									
1.496	2	He	1.494	2	K	1.484	26	He, Py																
1.460	6	M																						
1.446	7	M, He	1.443	5	M	1.448	20	M, He	1.444	3	M			1.460	8									
			1.423	2	T									1.442	18									
1.402	2	M	1.404	3	M, K	1.405	1	M	1.406	1	M, K			1.405	8									
									1.383	5	Q													
1.364	2	?	1.374	5	K				1.376	6	K, Q													
1.350	3	M	1.353	3	M, T	1.344	3	M, He	1.349	1	M			1.349	6	1.351	5	1.350	3					
1.336	4	M	1.331	1	M				1.337	1	M			1.336	12									
1.315	2	He				1.314	2	He																
						1.307	4	He																

Tab. 2. X-ray powder diffraction data on porcellanite samples from Dobřice near Most compared with data on standard phases. Explanations: An-anorthite, Ap-apatite, C-cordierite, F-K-feldspar, Goe-goethite, He-hematite, Il-ilmenite, K-corundum, M-mullite, Py-pyroxene, Q-quartz, T-tridymite, ident.-identification.

	(a)	(b)	(c)	Mullite	Cordierite	Sekaninaite
	%	%	%	%	%	%
SiO ₂	46.51	74.81	53.19	29.04	49.46	45.10
TiO ₂	3.76	4.25	0.65	0.79	0.01	0.04
Al ₂ O ₃	42.88	16.14	29.81	69.63	33.58	30.63
Fe ₂ O ₃	–	–	–	0.50	0.14	0.91
FeO	3.76*	1.45*	8.11*	–	2.12	17.85
MnO	0.20	0.14	0.24	–	0.08	0.92
MgO	1.11	0.75	6.73	–	12.06	1.69
CaO	0.06	0.10	0.09	–	0.03	0.39
Na ₂ O	0.34	0.60	0.54	0.18	0.14	0.68
K ₂ O	1.38	1.76	0.64	0.06	0.30	0.03
H ₂ O+	–	–	–	–	1.71	1.84
H ₂ O–	–	–	–	–	0.10	0.12
Σ	100.00	100.00	100.00	100.20	99.73	100.20

Tab. 3. Electron microprobe analyses of areas with prevailing mullite (a), tridymite (b), cordierite (c) component in porcellanites from Dobřčice (sample Do-1).

Notes: *Determined Fe was recalculated to FeO. Our results are compared with values in Deer, Howie and Zussman (1962, 1986) for mullite and cordierite, in Staněk and Miškovský (1975) for sekaninaite.

by letters. Diffraction data of the identified mineral phases are compared with standards Deer et al. (1962, 1986) in Tab. 2. The results of EMPA of domains with prevailing mullite (a), tridymite (b) and cordierite (c) in sample Do-1 are compared with standards in Tab. 3.

Our analytical data do not express pure mineral composition but are influenced by the surroundings. Cordierite has not been recognized yet in the N Bohemian porcellanites by the previous authors. It shows substantial amounts of iron, thereby approaching sekaninaite – the Fe member of the series. Similar locations of light spots in the X-ray image of areal distribution of Mg and Fe (Fig. 3) confirm the presence of this transitional phase.

From the crystal structure point of view, cordierite is polymorphous with indialite – the high-temperature form with hexagonal symmetry. Cordierites exhibit some departures from hexagonal symmetry as indicated by their distortion index Δ . Cordierites ideally have high Δ values, intermediate values of Δ represent metastable forms. Through distortion, hexagonal symmetry is lowered to orthorhombic (pseudohexagonal). Diffraction patterns of cordierite and indialite differ in the range of 29–30° 2 θ (for Cu radiation). Two or three peaks appear in this range in cordierite, while these diffractions unite in a single maximum in indialite. The analysed mineral is the cordierite modification.

Miyashiro (1957) studied various stages of departures from hexagonal symmetry and suggested the use of the index of distortion, Δ , from the X-ray powder diffraction pattern according to equation $\Delta = 2\theta_{131} - (2\theta_{511} + 2\theta_{421}) / 2$ (Cu radiation). As

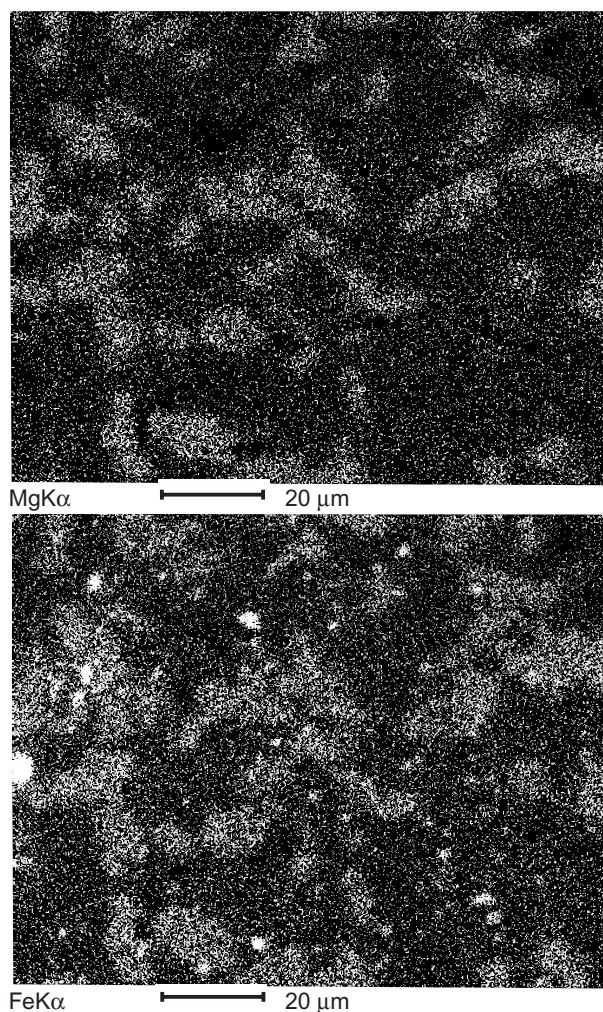


Fig. 3. X-ray image of the areal distribution of Mg and Fe (sample Do-1). After comparing lighter areas in Mg K α image with corresponding lighter areas in Fe K α image, location of cordierite mineral phase can be read.

the hexagonal symmetry is approached, 3 cordierite peaks (511, 421 and 131) converge and Δ tends towards zero in indialite. Δ : 0.31 was described as the highest value for cordierite. The value 0.17 determined in the present samples corresponds to the intermediate-state cordierite (Fig. 4) in the sense of the classification of Langer and Schreyer (1969). Critical region from 2 θ CuK α 28–30° of the X-ray pattern was run by using scanning speed 0.024°/min. (ca. 1/40° per minute). Graphite monochromator was used together with divergence slit 1/4°, receiving slit 0.1, scatter slit 1/4°.

As indicated by X-ray diffractograms, sample Do-2 contains a higher proportion of cordierite relative to mullite and tridymite than sample Do-1. Moreover, corundum was determined in Do-2. K₂O contents determined by wet silicate analyses (Table 1) in samples Do-1 and Do-2 may be connected with the presence of K-feldspar. This cannot be, however, confirmed by X-ray diffraction because of the coincidence with the principal identified components. Point microprobe analysis indicated somewhat higher content of K-feldspar in some places of sample Do-1; similarly, X-ray image of the areal potassium

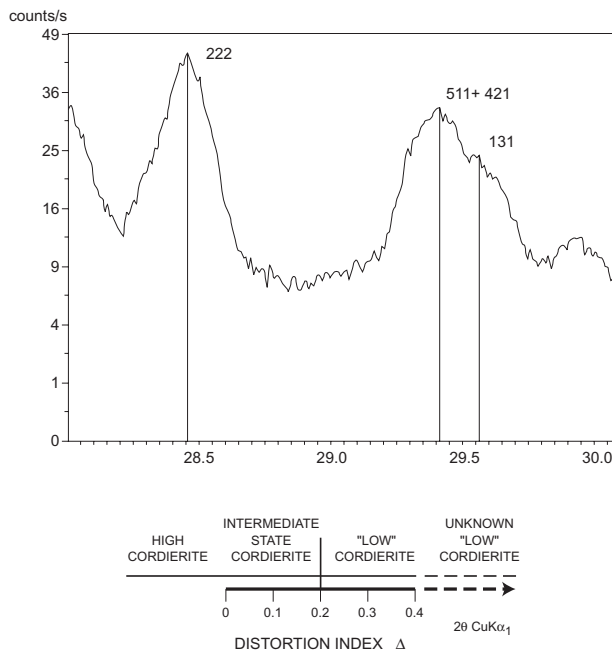


Fig. 4. A part of X-ray diffractogram in the range of 28–30° 2θ for copper radiation from porcellanite sample (Dobrčice quarry) permitting to classify cordierites on the basis of the distortion index, Δ (Langer and Schreyer 1969).

distribution showed a positive presence of K-feldspar in sample Do-2.

Sample Do-3 resembles scoria and differs in its appearance and chemical and mineral composition from other samples. As shown by chemical analysis (Tab. 1), it has a considerable Fe content. X-ray diffraction pattern (Fig. 2c) and diffraction data (Tab. 2) indicate hematite as the prevailing component. For data on one hematite grain see Tab. 4. Tab. 5 gives the result of point analyses compared with selected standard analyses of apatite. This mineral binds rare earths elements, namely Ce, La and Nd. Some determined elements evidently do not belong to this mineral but reflect the composition of the nearest vicinity – in particular the amounts of Si, Al, Fe, Mn, Mg. In X-ray pattern, diffraction peaks of apatite coincide with those of other components present in the sample. Comparing X-ray images of the phosphorus and calcium distribution from a particular place

wt. %		wt. %	
SiO ₂	0.68	MgO	0.63
TiO ₂	0.76	CaO	0.16
Al ₂ O ₃	1.19	Na ₂ O	–
FeO	95.93	K ₂ O	0.16
MnO	0.49	Σ	100.00

Tab. 4. Electron microprobe analysis showing chemical composition inside the hematite grain (sample Do-3).

in sample Do-3 (Fig. 5), light spots at identical positions inform of apatite spread in the X-rayed area.

Besides, sample Do-3 contains larger amounts of Ca-plagioclase (anorthite) and cordierite, lower amounts of mullite, tridymite, possibly Mg-pyroxene (enstatite) and goethite – later transformed from hematite (see Fig. 2c and Tab. 2).

Unlike other samples, sample Do-4 contains quartz. Based on X-ray diffraction data it is possible to assume that quartz is the predominating mineral phase (see Fig. 2d and Tab. 2). SiO₂ is present in the tridymite form, too. Mullite is evidenced as well as corundum. Some vacant diffractions are interpretable as belonging to feldspars, namely to plagioclase and K-feldspar. Their amounts in the sample, however, are not significant. Vacant X-ray diffraction ~2.74 Å may belong to ilmenite.

In the backscattered electron image, a grain was found which showed high amounts of REE in the EMPA: 15.75 % Ce, 7.06 % La and 2.61 % Nd. Supposing that the relatively high amounts of these elements are connected with the content of phosphorus in the analysed object, this mineral can be interpreted as monazite (Ce,La,Nd) PO₄.

Tab. 1 shows higher amount of Ti in sample Do-4. As suggested by microanalyses, Ti is partly bound to ilmenite and partly to titanium oxide – probably in the form of anatase for which the X-ray diffraction acknowledgement is missing (Fig. 6). Microanalyses showed the presence of elements which do not belong to titanium phases (especially Si, Al, Mg). Because of their small crystal size, the electron beam is collecting also the information from their vicinity.

	Do-3 %	Apatite %
SiO ₂	3.21	–
Al ₂ O ₃	1.67	–
FeO	2.44	–
MnO	0.21	0.07
MgO	1.82	0.10
CaO	40.44	55.84
Na ₂ O	0.11	–
K ₂ O	0.29	–
P ₂ O ₅	38.01	42.05
F	–	0.16
La ₂ O ₃	2.40	–
Ce ₂ O ₃	7.01	–
Nd ₂ O ₃	2.39	–
H ₂ O+	–	1.86
H ₂ O–	–	–
Σ	100.00	100.08

Tab. 5. Point microprobe analysis in the domain containing apatite (sample Do-3) compared with the standard analysis (Deer et al. 1962).

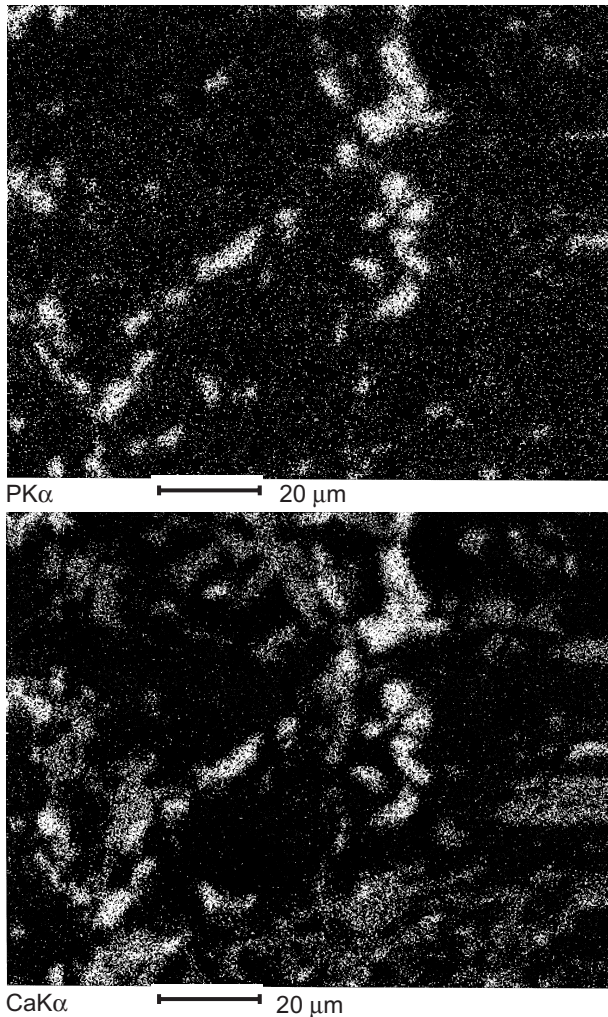


Fig. 5. X-ray images of the distribution of P and Ca from a particular place in sample Do-3. Light areas at identical positions on both images inform of apatite spreading.

Conclusions

Porcellanites of the Dobřiče quarry originated from Miocene clay-dominated sediments by burning of the underlying brown coal seam at the end of the Tertiary (in Pliocene). The typical protolith (samples Do-1, Do-2 and Do-4), was represented by illite-kaolinite clay in which sand proportion was decreasing from the bottom (Do-4) to the top (Do-1). MgO contents increase in the same direction while the amount of CaO decreases. The colour of porcellanites is influenced mainly by the content of Fe and Ti. Sample Do-3, forming a thin bed only (10 cm thick), is markedly different, especially in its very high content of Fe_2O_3 , compensated by lower amount of SiO_2 and Al_2O_3 . It probably originated from a siderite-rich bed (often occurring in N Bohemian Miocene sediments).

X-ray diffraction and electron microprobe analyses revealed the following mineral compositions in individual samples:
 Do-1 (red porcellanite): mullite + tridymite + cordierite, subordinate hematite + Ti-magnetite (ulvöspinel) + K-feldspar;
 Do-2 (grey porcellanite): mainly cordierite + mullite and tridymite + admixture of corundum, subordinate K-feldspar;

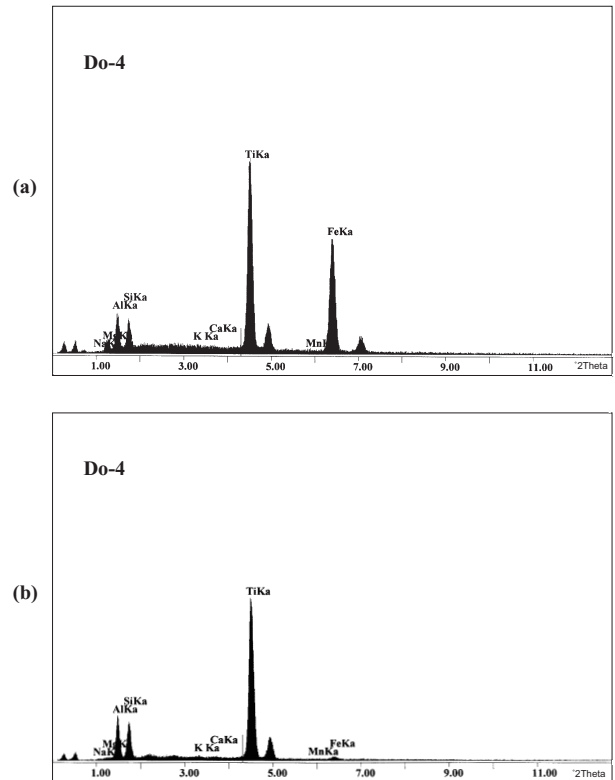


Fig. 6. The energy-dispersive patterns of selected crystals in sample Do-4 demonstrating the composition of (a) ilmenite and (b) titanium oxide – anatase.

Do-3 (brown scoria): large amount of hematite, substantial amount of calcic plagioclase + cordierite, a lesser amount of mullite + tridymite + REE-rich apatite + orthopyroxene, probably spinel and goethite;

Do-4 (yellow porcellanite): mostly quartz, tridymite + mullite, subordinate corundum + K-feldspar + calcic plagioclase + ilmenite + anatase or rutile, scarcely REE-rich monazite.

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