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MINERALOGICAL AND GEOCHEMICAL CHARACTERISTICS OF CLAYEY-ALEURITIC LIASSIC ROCKS FROM THE N BORDER OF THE HOLY CROSS MTS., POLAND

Abstract. Liassic mudstones and claystones from the N border of the Holy Cross Mts. were studied. In rocks from the Jakubów and Żarnów II deposits which are characterized by elevated P, Ba and REE contents, minerals of the crandallite group have been found representing the intermediate members of the crandallite-gorceixite solid solution.

Key-words: the Holy Cross Mts., Liassic, crandallite, trace elements, REE.

INTRODUCTION

The occurrences of Lower Jurassic clayey-aleuritic rocks of the N border of the Holy Cross Mts. (Fig. 1) have been known for many years. Some of them were already examined (Stoch 1963; Kozydra 1968; Teofilak-Maliszewska 1968; Stoch and Sikora 1968). Those rocks were (Jakubów, Mroczków, Żarnów, Stara Góra deposits) and currently are (Zapniów, Żarnów II vel Paszkowice deposits) exploited by various users — first of all by the Factory of Ceramic Tiles in Opoczno for the production of wall and floor tiles. Moreover, up to the end of the 1980-ties, their kaolinitic varieties were applied in the production of chamotte refractories in already non-existent factory in Opoczno.

The present paper deals with the results of the study of Liassic rocks from the above mentioned deposits. Its aim was the completion of the hitherto available data on mineralogy and chemistry on these rocks, with special attention to trace elements. Samples were examined by means of granulometric, mineralogical (optical microscopy, X-ray and thermal analyses) and chemical (INAA, ICP-AES, PIGE) methods.

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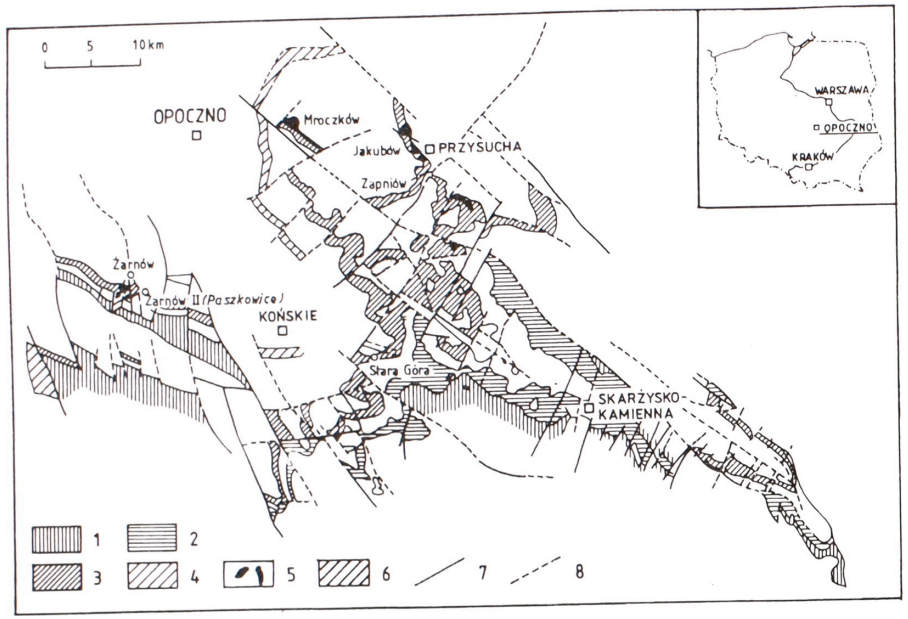

Fig. 1. Deposits of kaolinitic-illitic clays in Rhaetic and Liassic series of N border of the Holy Cross Mts. (after Kozydra 1968)
1 — Rhaetic beds, 2 — Zagaje series, 3 — ore-bearing series (*Zarzecze series*), 4 — Ciechocinek series, 5 — deposits of refractory clays (actually non-exploited), 7, 8 — ascertained and assumed dislocations

RESULTS

The clayey-aleuritic rocks studied are diversified both in colour (light-creamy, reddish, greyish) and degree of compactness. As far as granulometric composition is concerned they correspond, according to classification of Picard (1971), to: clayey (3 samples) and sandy (1 sample) siltstones, silty mudstones (2 samples) and silty claystones (2 samples) (Fig. 2). However, taking into account the mineral composition (Potter et al. 1980), the majority of them represents claystones. They show pelitic, pelite-aleuritic and aleurite-pelite texture and locally contain grains of psamitic fraction (maximum grain size — ca. 0.3 mm). Generally they display oriented structures, expressed by directional position of flaky and platy minerals, and distinct lamination.

The major mineral components are: kaolinite, quartz and micas. In general, clay substance — which is represented mainly by kaolinite — prevails over quartz (Tab. 1). Cryptocrystalline kaolinite is concentrated predominantly in the groundmass of the rocks studied. Besides, it is subordinately contained within post-mica pseudomorphs. Columnar kaolinite aggregates are also observed, being,

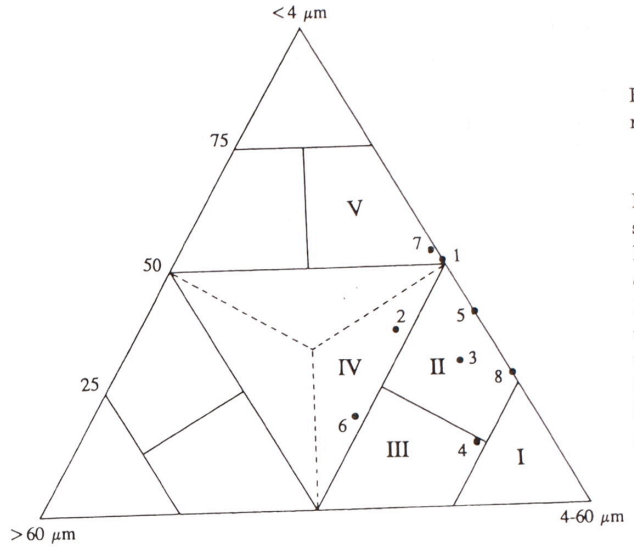

Fig. 2. The position of plots of rocks studied in granulometric classification diagram (Picard 1971)
I — siltstone, II — clayey siltstone, III — sandy siltstone, IV — silty mudstone, V — silty claystone. Samples from deposits: 1 — Jakubów (light-creamy variety), 2 — Jakubów (reddish variety), 3 — Mroczków, 4 — Zapniów, 5 — Żarnów, 6 — Żarnów II, 7 — Żarnów II (light-creamy variety), 8 — Żarnów II (greyish variety)

TABLE 1

Mineral composition of clayey-aleuritic Liassic rocks of Holy Cross Mts. determined by microscopic and XRD analyses

Sample	Rock type	Mineral components:								
		kaolinite	quartz	micas	illite/ /smectite	chlorite	feldspars	crandallite	hematite	heavy minerals
Jakubów (light-creamy variety)	claystone	+	(+)	++ I,HM	(+)	(+)	(+)?	(+)	—	(+)
Jakubów (reddish variety)	claystone	+	+	+ I,HM	—	—	—	—	(+)	(+)
Stara Góra	claystone	+	+	++ I,HM	(+)	(+)	(+)?	—	—	(+)
Zapniów	claystone	+	+	++ M,HM	—	(+)	(+)?	—	—	(+)
Żarnów	claystone	+	+	++ I,(M,HM,B)	(+)	(+)	(+)?	—	(+)?	(+)
Żarnów II	siltstone	+	++	++ I,(M,HM,B)	—	(+)	(+)?	(+)	—	(+)

Explanation of symbols:
++ — main dominant phase,
+ — main phase,
(+) — phase occurring in minor and trace amounts,
— — lack of phase,
Micas: I — illite, M — muscovite, HM — hydromuscovite, B — biotite.

probably, products of crystallization from solutions. On the basis of X-ray analysis it has been stated that kaolinite studied is generally characterized by the high degree of the structural ordering (Fig. 3). This fact results from the values of the X-ray indicator $I_{020}/I_{11\bar{1}}$ (Stoch and Sikora 1967), ranging from 0.58 to 0.82. According to the data of Stoch (1974), also typical for kaolinite-Tc is the symmetric shape of endothermic effect of dehydroxylation of this mineral at about 550—570°C. Micas are represented by fine-flaky illite and hydromuscovite, muscovite and sporadically, biotite flakes. These flakes are up to 0.2 mm in the size. Quartz grains are, usually, very small (below 0.05 mm) but sporadically their size is up to 0.3 mm and they are predominantly sharp-edged.

The major components are accompanied by subordinate amounts of mixed layer illite/smectite, heavy minerals (predominantly zircon), hematite, organic substance, minerals of crandallite group, chlorites and probably — feldspars. The phosphate minerals of crandallite group were only identified in the rocks from Jakubów and Żarnów II (Fig. 3). Their participation estimated on the basis of the P_2O_5 content (Tab. 2.) amounts to 1.5 and 0.5 wt.%, respectively. Heavy minerals are represented mainly by zircon and subordinately by tourmaline and rutile. Their grains do not exceed 0.05 mm in size.

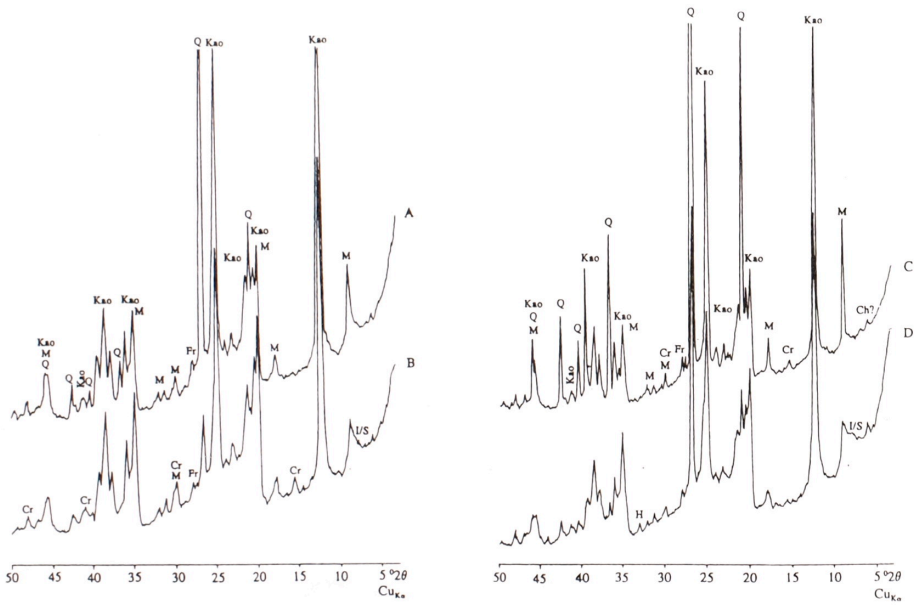

Fig. 3. Selected X-ray patterns of the rocks studied
Samples from deposits: A — Zapniów, B — Jakubów (light-creamy variety), C — Żarnów II, D — Żarnów. Symbols: Ch — chlorite, Cr — mineral of crandallite group, Fr — feldspars, H — hematite, I/S — mixed layer illite/smectite, Kao — kaolinite, M — micas, hydromicas, Q — quartz

TABLE 2

Chemical analyses of clayey-aleuritic rocks of N border of the Holy Cross Mts. carried out by ICP-AES (in wt.%)

Component	Jakubów		Żarnów	Żarnów II (white variety)	Zapniów	Stara Góra
	(light-creamy variety)	(reddish variety)				
SiO_2	47.1	48.9	51.6	68.4	65.2	57.9
TiO_2	1.12	1.19	1.16	0.88	0.91	0.97
Al_2O_3	34.9	33.6	30.6	21.3	23.2	24.5
Fe_2O_3	1.31	2.61	2.61	0.79	0.89	3.74
MnO	<DL	<DL	<DL	<DL	<DL	0.03
MgO	0.52	0.43	1.05	0.35	0.39	1.16
CaO	0.25	0.21	0.39	0.18	0.17	0.27
Na_2O	0.09	0.08	0.10	0.07	0.09	0.11
K_2O	2.40	1.45	2.28	1.27	1.63	2.55
P_2O_5	0.49	0.11	0.10	0.12	0.11	0.08
LOI	11.5	11.6	10.7	6.91	7.59	8.60
Total	99.68	100.18	100.59	100.27	100.18	99.91

DL — detection limit.

The clayey-aleuritic rocks of the northern margin of the Holy Cross Mts. are very diversified in chemical composition (Tab. 2, 3, Fig. 4), correlating positively with the variation of grain size and mineral composition.

The majority of trace elements estimated — particularly light REE and sometimes Ba — occurs in these rocks in concentrations higher than the average values computed by Wedepohl (1978) for clay rocks (Tab. 3). Such elements as Sr, Cu, As and Pb occur in lowest amounts.

Taking into account trace element content, one can distinguish light-creamy illite-kaolinite claystone from Jakubów. It is characterized by distinctly higher (when compared with other rocks studied) concentration of light REE and barium (Tab. 3, Fig. 4). Higher amounts of these elements and of phosphorus (about 0.5 wt.% P_2O_5; Tab. 2) are connected with the occurrence of phosphate mineral of crandallite group (identified using X-ray method; Fig. 3), which are known as carriers of light REE. This conclusion is additionally confirmed by their distinctly lower content in the Jakubów red claystone (Fig. 5). No detectable contents (by means of X-ray method) of minerals of the crandallite group were found in these rocks. On the ground of the content of Ba (2500 ppm), Ca (1800 ppm), Pb (40 ppm) and Sr (19 ppm) (Tab. 3), the phosphate mineral in question is probably close in composition to the intermediate member of the crandallite $CaAl_3H[(OH)_6|(PO_4)_2]$ — gorceixite $BaAl_3H[(OH)_6|(PO_4)_2]$ solid solution. Approximate content of gorceixite molecule can be evaluated at about 30%.

As follows from X-ray data, minerals of crandallite group also occur in the claystone sample from Żarnów II deposit. No phosphates of this group occur in

TABLE 3

Some trace elements contents in clayey-aleuritic rocks of N border of the Holy Cross Mts. determined by INAA, ICP-AES* and AAS** methods (in ppm)

Element	Jakubów		Żarnów	Żarnów II			Zapniów	Mroczków	Stara Góra	Data for clayey rocks; after Wedepohl (1978)
	light-creamy	reddish		white	light-creamy	greyish				
Sc	21	24	21	18	18	25	14	23	17	10—25
Cr	170	180	130	125	160	180	120	170	116	33—191
Ni	150	80	80*	20*	<30	<33	20	<30	60*	31—52
Cu	20*	20*	70*	10*	15*	15*	30*	13*	20*	15—110
Zn	<50	<50	62	24	53	150	21	71	43	2—780
Ga	50	n.d.	45	43	n.d.	n.d.	34	n.d.	43	2—55
As	3.4	1.2	1.6	2.1	8.1	1.4	2.1	1.5	2.1	0.3—59
Rb	89	71	125	73	77	14	99	140	131	20—663
Sr	19**	12**	n.d.	n.d.	17**	n.d.	n.d.	n.d.	n.d.	75—838
Zr	435	300*	230	347	240*	290*	412	200*	241	60—470
Sb	1.1	2.0	0.8	0.6	1.0	1.3	0.7	1.0	1.2	0.1—3
Cs	12	10	12	9	8	11	11	11	13	average 5
Ba	2 500	370	1 700*	1 600*	410	510	800*	480	360*	250—800
REE										
La	230	91	73	64	81	86	48	64	48	average 34
Ce	460	170	155	148	180	180	118	130	103	average 67
Nd	200	66	33	72	65	72	54	57	35	average 30.5
Sm	36	11	10	11	10	12	9	10	7	average 6.9
Eu	6.9	2.4	2.0	2.0	1.9	2.5	1.6	2.1	1.2	1.4
Tb	3.9	1.5	1.1	1.2	1.1	1.4	1.3	1.1	0.8	1.0
Yb	4.4	4.8	5.1	3.9	4.1	4.2	3.7	3.7	3.6	average 2.6
Lu	0.59	0.67	0.56	0.57	0.60	0.61	0.58	0.55	0.52	0.7
Hf	8	8	6	9	10	7	8	7	6	2.8—6
Ta	1.5	2.0	2.1	2.1	1.3	1.2	2.2	1.7	1.7	average 2
Pb	40*	20*	n.d.	20*	<DL*	<DL*	<30*	<DL*	10*	5—89
Th	28	28	22	18	18	22	17	24	18	3—30
U	3.8	3.7	2.9	3.8	5.4	2.8	2.9	4.9	3.4	2—8

DL — detection limit, n.d. — not determined.

other analysed samples. However, they may be present there of very similar concentrations of P and light REE (Tab. 2, 3) but in amounts below the detection limit of the X-ray method.

In the case of light-creamy claystone from Jakubów, the REE pattern was also estimated for the size fraction separated. We observe in them some REE enrichment in the finest grain-size fractions, i.e. below 2 μm (Fig. 5), what suggests fine-crystallinity of minerals of the crandallite group.

The content of the heaviest REE (Yb, Lu) — contrary to light REE — is similar in all the samples examined (Tab. 3, Fig. 4). It is probably connected with the presence of zircon $Zr[SiO_4]$, considered to be the carrier of heavy REE. Its occurrence in trace amounts was evidenced by microscope studies and confirmed by the Zr content in these rocks, amounting to 300—400 ppm (Tab. 3).

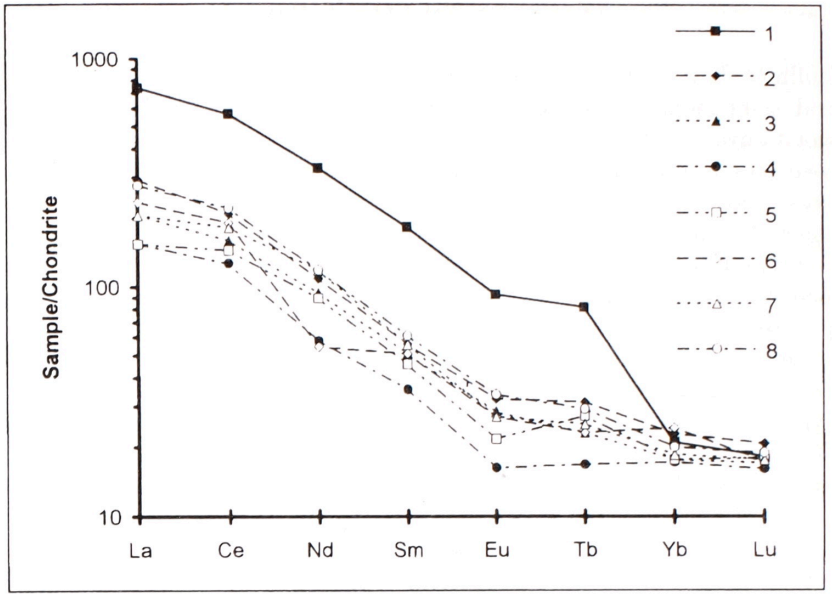

Fig. 4. Chondrite-normalized REE abundances in clayey-aleuritic Liassic rocks of N border of Holy Cross Mts. Samples from deposits: 1 — Jakubów (light-creamy variety), 2 — Jakubów (reddish variety), 3 — Mroczków, 4 — Stara Góra, 5 — Zapniów, 6 — Żarnów, 7 — Żarnów II (white variety), 8 — Żarnów II (greyish variety)

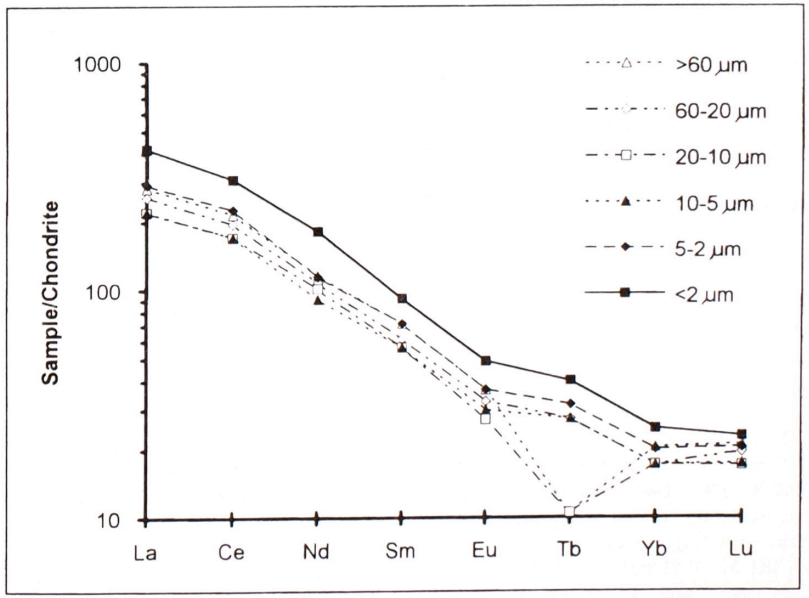

Fig. 5. Chondrite-normalized REE abundances in size fractions separated from the light-creamy claystone of Jakubów deposit

RESULTS AND CONCLUSIONS

Kaolinite showing well ordered structure is characteristic and usually dominant mineral component of the rocks studied. It is accompanied by quartz, micas (muscovite-hydromuscovite, biotite and/or illite, occurring in variable amounts. Moreover, there occur in subordinate amounts: mixed-layer illite/smectite minerals, chlorites, heavy minerals (mainly zircon), hematite and probably feldspars. Besides, in some rocks, particularly in the claystone from Jakubów, the presence of minerals of the crandallite group was evidenced. They represent an intermediate member between crandallite and gorceixite. The phosphate minerals of the crandallite group were not previously found in clayey-aleuritic Liassic rocks of the Holy Cross Mts. Consequently, this is the next occurrence of this minerals in kaolinite-rich clayey rocks in Poland, reported so far by Szpila and Dzierżanowski (1980), Muszyński and Wyszomirski (1982), Stępisiewicz (1987), Szpila (1991) and Gabzdyl and Ryszka (1995).

The results of these studies concerning mineral composition of clayey-aleuritic rocks from N margin of the Holy Cross Mts. are, in general, concordant with the data reported by Stoch and Sikora (1968), both in qualitative and quantitative respect. Additionally, among the minerals analysed by the present authors, those of the crandallite group have been identified. On the other hand, no siderite, reported by the above authors, was found.

The rocks containing minerals of crandallite group distinguish chemically by the increased content of phosphorus, barium and REE, particularly the lightest REE: La, Ce and Nd. Consequently, these minerals can be considered as carriers of light REE as already suggested by Szpila and Dzierżanowski (1980) and Störr et al. (1991). Moreover, generally higher contents of the most of trace elements estimated in the rocks studied are notable when compared with their average concentrations in clay rocks after Wedepohl (1978).

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CHARAKTERYSTYKA MINERALOGICZNO-GEOCHEMICZNA SKAŁ ILASTO-MUŁOWCOWYCH LIASU Z PÓŁNOCNEGO OBRZEŻENIA GÓR ŚWIĘTOKRZYSKICH

Streszczenie

Przedmiotem badań były liasowe skały mułowcowo-iłowcowe ze złóż: Jakubów, Mroczków, Stara Góra, Zapniów, Żarnów i Żarnów II (Fig. 1). W badaniach stosowano metody analizy granulometrycznej, fazowej (mikroskopia optyczna, rentgenografia) i chemicznej (INAA, ICP-AES, PIGE). Charakterystycznym i na ogół dominującym składnikiem badanych skał jest kaolinit o dobrze uporządkowanej strukturze. Towarzyszą mu w zmiennych ilościach: kwarc, miki i/lub illit (Fig. 3, Tab. 1). Spośród minerałów podrzędnych na uwagę zasługuje obecność, niestwierdzonych dotychczas w utworach liasu świętokrzyskiego, minerałów grupy crandallitu (pośrednie człony szeregu crandallit-gorceixyt). Ich obecność zidentyfikowano w skałach z Jakubowa i Żarnowa II (Fig. 3). Skały te wyróżniają się podwyższoną zawartością fosforu, baru oraz pierwiastków ziem rzadkich (Tab. 3), a zwłaszcza najlżejszych z nich (La, Ce, Nd). Minerały grupy crandallitu w analizowanych skałach są nośnikami lekkich REE, co stanowi

potwierdzenie wcześniejszych obserwacji Szpili i Dzierżanowskiego (1980) oraz Störra et al. (1991). Ponadto zwraca uwagę fakt, że także w pozostałych badanych skałach większość analizowanych pierwiastków śladowych występuje w ilościach przekraczających wartości średnie lub ich górne granice, określone przez Wedepohla (1978) dla skał ilastych (Tab. 3).