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Lithologically-related rare earth element variations the Mio-Pliocene Poznań Formation (Poland)

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Concentrations of rare earth elements (REEs) were determined in 129 clay samples collected from the Mio-Pliocene Poznań Formation in Poland. The REEs occur in a relatively wide range from 58.2 to 1,709 mg/kg. Low North American Shale Composite (NASC)-normalized total REE contents with heavy rare earth element (HREE) depletion were noted in most of the samples analysed. Small variations were detected in the REE contents in the lithologies distinguished. Red clays are characterised by slightly lower REE concentrations relative to green and grey clays. All the Poznań Formation clays exhibit a negative Eu anomaly when normalized to the average of chondrites. Values increase according to the following sequence: grey clays < red clays < green clays. The NASC-normalized REE concentration curves show a positive Eu anomaly. The La_{NASC}/Yb_{NASC} ratio indicates HREE depletion. A small variation in this ratio was observed in the sequence green clays > grey clays > red clays. The variability of the REE contents of the Poznań Formation decreased from west to east.

Key words: Poznań Formation, rare earth elements, clay lithotypes.

INTRODUCTION

The Mio-Pliocene Poznań Formation (Poland), formerly called the Poznań Series, is situated in central and northern Poland and was formed in a large alluvial-lacustrine inland basin (Piwocki and Ziembińska-Tworzydło, 1997). The thickness of these deposits generally ranges from 40 to 60 m (Kozydra and Wyrwicki, 1970). The content of clay minerals is in the range of 35–90% (usually 50–60%). Their composition is mainly dominated by smectites (beidellite-nontronite) and S/I (smectite-illite) mixed-layer minerals with subordinate illite and kaolinite. In the Poznań Formation, these clay minerals show a diverse compositional spectrum. In the northern and north-eastern part, illite and beidellite prevail, with a predominance of beidellite. In the central part, the dominant components are illite and beidellite, and the amount of beidellite is notably reduced. Towards the coastal part of the basin, more sandy sediments occur in which the share of illite and I/S mixed-layer minerals increases. In the southern part of the area, the contribution of kaolinite also increases. In the foreland of the Sudetes this mineral is dominant (Wiewióra and Wyrwicki, 1974, 1976; Wichrowski, 1981; Brański, 1994, 2002; Nieć and Ratajczak, 2004).

Colour is used to discriminate between the three lithostratigraphic levels (units): grey clays, green clays, and red (bright red) clays (Wyrwicki, 1974; Nieć and Ratajczak, 2004). This is related to the presence of various iron minerals (Kozydra and Wyrwicki, 1970). The red-, russet-, and yellow-mottled colouring of red clays containing 6–14% Fe_2O_3 is induced by the presence of hematite and goethite. Finely dispersed iron sulphides give a greyish-blue or greenish colour to the green clays. In the lower part of the grey clays, thin lignite (brown coal) interbeds also occur.

For hundreds of years the clay raw materials of the Poznań Formation have found wide applications. Currently, because of the relatively easy access to the deposits and their substantial thickness, these clays are used in building ceramics (Brański, 1994, 2012; Piwocki, 2002; Wyrwicki, 2002). Another application for the clays of the Poznań Formation is their use for the protection and restoration of the environment (Brański, 1994, 1998, 2002). Low permeability and high malleability, as well as good and very good sorption capacity, and the ion exchange properties of clays belonging to the beidellite and polymineral types make them suitable as an insulator material in landfills (Łuczak-Wilamowska, 2013).

The rare earth elements (REEs), also called lanthanides, are a family of fifteen elements from lanthanum to lutetium (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu)

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(Henderson, 1984). According to recommendations by the International Union of Pure and Applied Chemistry (IUPAC), scandium and yttrium are also included in the REE group (Connelly et al., 2005). The REEs, due to their similar chemical and geochemical properties, are a coherent series. REEs are usually divided into two conventionally termed groups:

– light REE (LREE) from La through to Eu;
– heavy REE (HREE) from Gd through to Lu.

There is also a third discriminated subgroup, medium REE (MREE) from Sm through to Ho, which partly overlaps the LREE and HREE (Migaszewski et al., 2016). Rare earth elements are highly dispersed and commonly occur in minerals that are very durable and resistant to weathering (Kabata-Pendias and Pendias, 1999). There are more than 250 minerals containing REE, including ~70 minerals in which REEs have a more specific role, for instance monazite-(Ce), (Ce, La, Nd, Th)[PO4], bastnäsite-(La) (La, Ce)[F, CO_3], cheralite $Ca_{0.5}Th_{0.5}[PO_4]_2$ and xenotime $Y[PO_4]$. The REEs have been produced from ~20 minerals, but only some of them are mined and processed (Paulo, 1999).

The mean REE content in clay sediments varies in a wide range from 79 to 259.7 mg/kg (Kabata-Pendias and Mukherjee, 2007). It varied in clay sediments primarily due to its lithology, genesis and age. In the Cretaceous and Pliocene sediments of central Portugal (kaolinite, illite and smectite deposits), the total content of La, Ce, Sm, Eu, Tb, Yb and Lu varies from 190 to 323 mg/kg (Prudencio et al., 1989). The REE concentrations in the Eocene Oshosun Formation (southwestern Nigeria) – black and grey shale, and also clay – were in the range of 176.76–374.31 mg/kg (Ajayi et al., 2006). In Pliocene red loess clays from the Chinese Loess Plateau, a ΣREE is lower – in range of 131–198 mg/kg (mean of 146 mg/kg) (Ding et al., 2001). A similar range of REE content (139–252 mg/kg) was recorded in Cretaceous Shale taken from the vicinity of Corelato Perticara in the southern Apennines (Cavalante et al., 2014). In the Upper Cretaceous smectite, illite, and kaolin and mixed-layer illite-smectite clay interbeds from western Portugal (Aveiro and Taveiro regions), the total concentration of La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu varied from 66.1 to 272 mg/kg (Marques et al., 2011). Much higher REE contents were noted in the older clay deposits. Studies of the Havensville and Eskridge shales from Kansas and Oklahoma dated from the Lower Permian (marine) – encompassing montmorillonite, kaolinite, and illite – showed the presence of ΣREE in the range of 5.4–1,732 mg/kg (Cullers et al., 1975). In Precambrian clay-rich strata from the Buwambo kaolin deposit (central Uganda), in which kaolinite is the dominant mineral, the REE contents ranged from 70.18 to 2,186 mg/kg (Nyakairu et al., 2001). Unlike in sedimentary clay deposits, it has been observed that (some) residual clays contain higher levels of REEs, up to several thousand milligrams per kilogram, marking these clay rocks as potential REE ore deposits (Foley et al., 2014; Yuan et al., 2014). For instance, in the Xuanwei Formation the total REE concentrations were in a wide range of 89.0 to 9,965 mg/kg (Zhang et al., 2016).

The purpose of the present study conducted in the Mio-Pliocene Poznań Clay Formation was to:

– determine current REE concentrations in the Poznań clays;
– to describe variations of REE contents in different parts of the alluvial-lacustrine basin;
– to establish the relationships between the REE contents and the different lithologies.

SAMPLES AND METHODS

129 samples were collected from 18 clay deposits: Bojanice, Brzostów, Budy Mszczonowskie, Chwalimierz II, Cienia I, Fordon, Gozdnica, Kunice III, Mirostowice Dolne, Nietążkowo I, Rudak I, Sierakowice, Stopka II, Słowiany, Sośnica, Szydłów II, Tadeuszów-Rudzienko, and Witaszyce (Fig. 1 and Table 1). Samples were collected from vertical profiles in all deposits, except for the Witaszyce deposit.

After acid digestion (using a mixture of HNO_3, $HClO_4$, HF), the REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) concentrations were determined using inductively coupled plasma-quadruple mass spectrometry (*ICP-QMS*; model *ELAN DRC II*, *Perkin Elmer*). Due to polyatomic interferences in the multi-element technique (ICP-QMS), mathematical corrections were applied to eliminate spectral interferences. In addition, to minimise matrix effects, samples were diluted tenfold prior to measurement. The analysis was performed in the presence of an internal standard (Rh and Re) solution. Quality control included double digestion of selected samples and double sample measurements. The relative standard deviation (RSD) values were <3% for most of the samples analysed. The estimated limit of quantification of La, Ce, Pr, and Nd was 0.5 mg/kg, and for Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu it was 0.05 mg/kg.

The measured concentrations of REE in the Poznań Formation were normalized to average chondrite and to North American Shale Composite (NASC) (Gromet et al., 1984; Piper and Bau, 2013). For all samples the value of the europium anomaly – the enrichment or depletion of the europium content in minerals relative to the content of other REEs – was calculated. In order to investigate the enrichment or depletion in light rare earth elements (LREEs) and heavy rare earth elements (HREEs) of various clay lithologies in the Poznań Formation, La/Yb and La/Sm ratios were calculated. To determine these ratios, their normalized content in the clays tested was used.

Statistical parameters (mean, geometric mean, median, minimum, and maximum values) were determined using *Statistica*. This software was also used to develop histograms and determine REE, Eu/Eu*, La/Yb, and La/Sm ratios.

RESULTS AND THEIR COMPARISON WITH DATA FROM OTHER FORMATIONS

REE contents in the Poznań Formation range from 58.2 to 1,709 mg/kg, with a mean of 176 mg/kg, a geometric mean of 150 mg/kg, and a median of 140 mg/kg (Table 2). The mean contents of individual elements were as follows (in mg/kg): La (32.0), Ce (80.6), Pr (8.40), Nd (32.4), Sm (6.53), Eu (1.38), Gd (4.98), Tb (0.73), Dy (4.1), Ho (0.75), Er (2.02), Tm (0.26), Yb (1.68), and Lu (0.25). The REE concentrations varied substantially in clays of different deposits. The highest mean content was found in clays from the Sośnica deposit (geometric mean of 260 mg/kg), and the lowest in the Chwalimierz II deposit (geometric mean of 78.5 mg/kg; Table 2). The greatest REE concentration variability was noted in the Sośnica deposit, and the smallest in the Stopka II deposit (Table 2).

The Poznań Formation is characterized by a high variability of REE contents. This is particularly evident in relation to Cretaceous and Pliocene deposits from central Portugal and Cretaceous shales from the southern Apennines (Prudencio et al., 1989; Marques et al., 2011; Cavalante et al., 2014). It was

Fig. 1. Study area with Mio-Pliocene clay deposit locations

found that REE concentrations determined in different deposits (except for Brzostów and Witaszyce) of the Poznań Formation examined by Duczmal-Czernikiewicz (2012) is in line with their average contents in clays and shales. An average REE content similar to that of the Poznań clays was reported from coal-bearing deposits in Arkagalinskoe and Dolinskoe, where it is 172.07 mg/kg (Koporulin et al., 2007). In the Poznań Formation, the maximum ΣREE content (~1,700 mg/kg) is nearly the same as that found in the Lower Permian shale layers of Havensville and Eskridge (Kansas and Oklahoma) (Cullers et al., 1975). However, the minimum content of the Poznań clays is nearly 10 times higher.

The REE concentrations normalized to average chondrite exhibit an enrichment of these elements (from several times to >100 times). The NASC-normalized REE concentration patterns indicate that most of the samples analysed are depleted in HREEs (Fig. 2). The curves for all the deposits exhibit a slight enrichment in Ce and depletion in Tb, Ho, and Tm (Fig. 3). The highest depletion of HREEs is seen in the Mirostowice Dolne, Witaszyce and Sośnica deposits and the lowest in the Chwalimierz II and Kunice III deposits.

NASC-normalized REE concentration curves show enrichment in La, Ce, Pr, and Nd, especially in the Mirostowice Dolne, Sośnica and Witaszyce deposits, and depletion of these elements in the Chwalimierz II and Kunice III deposits.

The study shows that the value of europium anomalies in the Poznań clays is higher than in Portuguese Paleogene and Miocene clays, in which the Eu/Euchondrite* ratios range from 0.48 to 0.69, and is also higher than in the loess from the Liyang Plain in southern China (0.63–0.67) (Mao et al., 2011; Lisboa et al., 2015). The value of europium anomalies in Poznań Formation clays is comparable or even lower than in significantly older Permian clays from deposits in Iran where Eu/Euchondrite* ratios range from 0.79 to 1.34 (Mahjoor et al., 2009).

It was found that the Lachondrite/Ybchondrite ratio in the Poznań Formation indicates LREE enrichment. The value of

Table 1

List of clay deposits of the Poznań Formation studied and their location, number of samples collected, and lithology

No.	Deposit	Location	No. of samples	Lithology
1	Bojanice	Krzemieniewo municipality, Leszno district	6	red, grey, bluish clays
2	Brzostów	Jaraczewo municipality, Jarocin district	7	red, olive, greenish clays
3	Budy Mszczonowskie	Radziejowice municipality, Żyrardów district	7	red, greenish clays
4	Chwalimierz II	Chwalimierz municipality, Środa Śląska district	6	red clays
5	Cienia I	Opatówek municipality, Kalisz district	7	red, bluish clays
6	Fordon	Bydgoszcz	7	red, grey, olive-grey clays
7	Gozdnica	Żagań district	8	grey, green clays
8	Kunice III	Legnica district	7	red, greenish clays
9	Mirostowice Dolne	Żary municipality, Żary district	8	grey, bluish, greenish clays
10	Nietążkowo I	Śmigiel municipality, Kościan district	8	red, grey, yellow-brown clays
11	Rudak I	Toruń	8	red-brown, greenish, greenish-yellow clays
12	Sierakowice	Sośnicowice municipality, Gliwice district	8	red clays
13	Słowiany	Bolesławice district	7	red yellow-grey clays
14	Sośnica	Kąty Wrocławskie municipality, Wrocław district	7	brown-light grey clays
15	Stopka II	Koronowo municipality, Bydgoszcz district	7	greenish, yellow-brown clays
16	Szydłów II	Tułowice municipality, Opole district	7	red clays
17	Tadeuszów-Rudzienko	Dobre municipality, Mińsk district	7	dark grey, greenish clays
18	Witaszyce	Jarocin municipality, Jarocin district	7	greenish clays

Table 2

Descriptive statistics for the total REE contents (mg/kg) of the samples

No.	Deposit	Mean	Geometric mean	Median	Minimum	Maximum	Standard deviation
1	Bojanice	230	195	161	110	455	148
2	Brzostów	149	138	126	85.4	279	67.3
3	Budy Mszczonowskie	148	144	135	107	226	42.9
4	Chwalimierz II	79.0	78.5	78.3	67.3	91.6	9.38
5	Cienia I	161	158	172	94.3	190	32.9
6	Fordon	187	174	163	110	366	85.3
7	Gozdnica	162	155	138	118	256	50.9
8	Kunice III	101	96.6	85.1	73.9	164	33.4
9	Mirostowice Dolne	295	270	227	166	545	139
10	Nietążkowo I	140	132	129	81.4	282	60.8
11	Rudak I	140	135	140	86.0	213	38.5
12	Sierakowice	159	146	143	83.7	277	68.4
13	Słowiany	125	119	137	58.7	165	37.8
14	Sośnica	429	260	200	125	1709	579
15	Stopka II	131	131	128	122	147	8.67
16	Szydłów II	154	153	151	138	176	15.5
17	Tadeuszów-Rudzienko	130	121	122	82.9	240	56.9
18	Witaszyce	244	227	249	107	376	92.8

this ratio is higher than in the Portuguese Paleogene and Miocene clays (5.4–11.9; Lisboa et al., 2015), and in Iran's Permian clays (7.1–10.8; Mahjoor et al., 2009).

The analysis of the calculated La/Sm ratio normalized to average chondrite and NASC shows a LREE enrichment in the Poznań Formation, although in case of the latter this ratio is low. By comparison, the value of this ratio (chondrite-normalised) in the Portuguese Paleogene and Miocene deposits was in the range of 2.0 to 3.4 (Lisboa et al., 2015).

The study of the Poznań Formation clay lithologies shows that red clays have slightly lower REE concentrations in relation to the other two lithologies (Table 3). Green clays are abundant

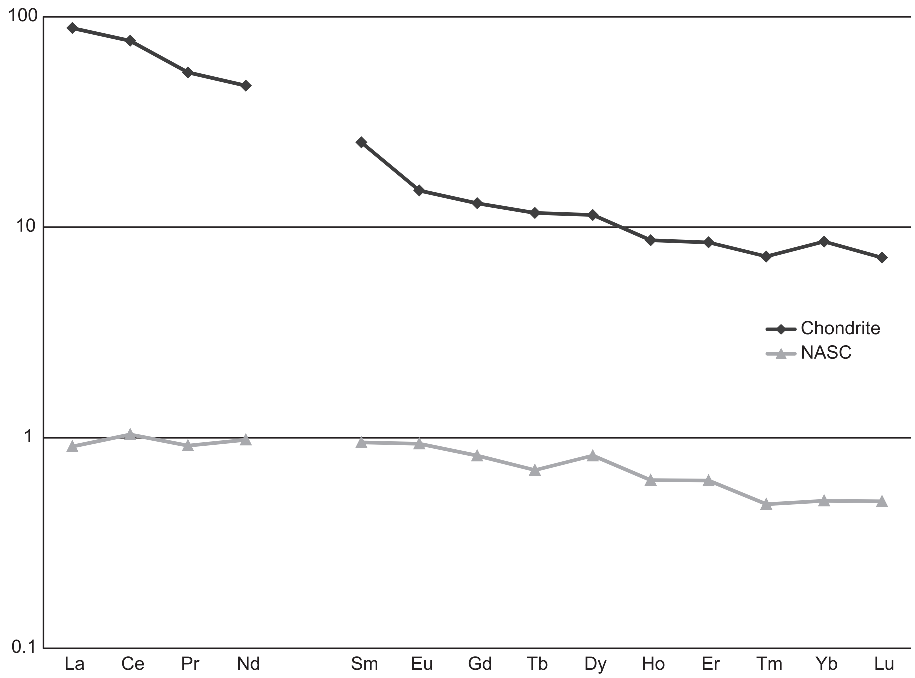

Fig. 2. REE concentration curves for all the clays examined normalized to chondrite and to NASC

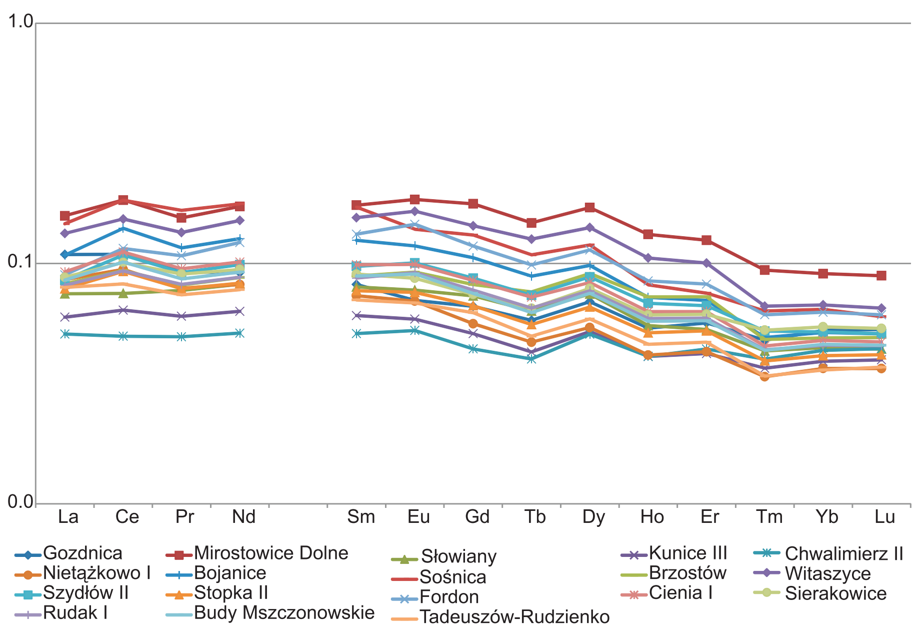

Fig. 3. The NASC-normalized REE concentration curves from all the clay deposits

in REEs from 82.9 to 376 mg/kg. Their average content is 173 mg/kg (geometric mean: 159, median: 155 mg/kg), while the REE contents in grey clays range from 83.9 to 545 mg/kg and the mean is 177 mg/kg (geometric mean: 158, median: 142 mg/kg). In red clays the REE concentrations vary from 58.7 to 1,709 mg/kg and the average value is 178 mg/kg, while the geometric mean (140 mg/kg) and the median (133 mg/kg) are much lower.

In all clay lithologies, samples with REE contents that vary from 100 to 150 mg/kg are most common (Fig. 4).

The REE concentration curves of the green, grey, and red clays normalized to the chondrite average and to NASC do not

Table 3

Geometric mean REE contents (mg/kg) in the Poznań Formation lithologies

Element	Green clays	Grey clays	Red clays
La	29.8	30.0	26.2
Ce	73.8	72.9	63.9
Pr	7.42	7.40	6.62
Nd	28.4	27.9	25.0
Sm	1.20	1.10	1.05
Eu	5.61	5.45	5.02
Gd	4.31	4.17	3.76
Tb	0.63	0.61	0.56
Dy	3.60	3.50	3.28
Ho	0.67	0.65	0.61
Er	1.86	1.81	1.70
Tm	0.23	0.24	0.23
Yb	1.52	1.58	1.52
Lu	0.23	0.24	0.23
Total REE	159	158	140
LREE	146	145	128
HREE	13.1	12.8	11.9

show any significant differences. It has been documented that all the Poznań Formation lithologies analysed exhibit a negative Eu anomaly when chondrite-normalized and a positive Eu anomaly when normalized to NASC.

The results obtained for the $La_{chondrite}/Yb_{chondrite}$ ratio in the three lithologies (Table 4) indicate that the green clays have slightly higher values. A ratio diversity was noted in each lithology, with green clays > grey clays > red clays, accordingly. The estimate of the $La_{chondrite}/Sm_{chondrite}$ ratio shows the highest value in grey clays.

INTERPRETATION OF RESULTS

The results were also analysed in terms of REE variability in the Poznań Formation within the sedimentary basin. The farther to the east of Poland, the REE concentrations were less diverse. A much greater variation in REE contents was observed in the western part of the basin. The highest REE concentrations were found in the Sośnica and Mirostowice Dolne deposits, and the lowest in Chwalimierz II and Kunice III, which are located in the vicinity of the REE-rich Sośnica deposit. Clays containing the largest amounts of REEs are from deposits in the Lubuski region (Mirostowice Dolne, Gozdnica, and Słowiany). These are genetically linked to the western part of the Precam-

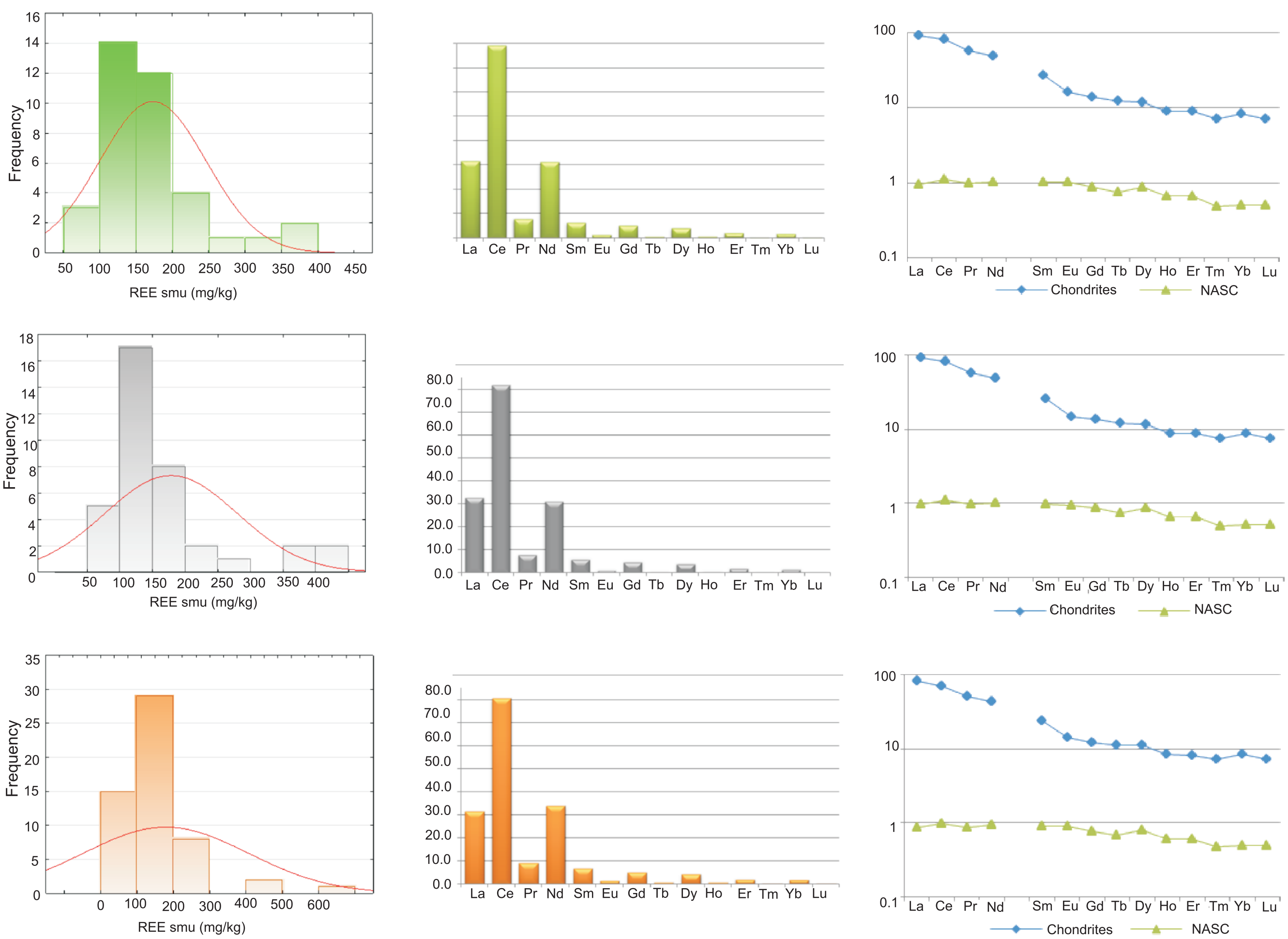

Fig. 4. Histograms, mean REE contents (mg/kg), and REE concentration curves normalized to the chondrite average and to NASC in green, grey, and red clays

Table 4

Statistical parameters for Eu/Eu*, La/Yb, and La/Sm in the Poznań Formation

Lithotype	Ratio	Mean	Geometric mean	Minimum	Maximum
Green clays	$Eu/Eu_{chondrite}^*$	0.84	0.84	0.70	0.90
	Eu/Eu_{NASC}^*	1.26	1.25	1.05	1.34
Grey clays	$Eu/Eu_{chondrite}^*$	0.80	0.80	0.58	0.97
	Eu/Eu_{NASC}^*	1.19	1.19	0.87	1.45
Red clays	$Eu/Eu_{chondrite}^*$	0.83	0.83	0.56	0.93
	Eu/Eunasc*	1.24	1.24	0.83	1.39
Green clays	$La_{chondrite}/Yb_{chondrite}$	11.3	11.0	6.27	22.3
	La_{NASC}/Yb_{NASC}	1.98	1.93	1.10	3.90
Grey clays	$La_{chondrite}/Yb_{chondrite}$	11.0	10.7	5.23	15.6
	La_{NASC}/Yb_{NASC}	1.92	1.87	0.92	2.73
Red clays	$La_{chondrite}/Yb_{chondrite}$	10.2	9.68	4.76	23.9
	La_{NASC}/Yb_{NASC}	1.78	1.69	0.83	4.19
Green clays	$La_{chondrite}/Sm_{chondrite}$	3.57	3.49	1.70	5.25
	La_{NASC}/Sm_{NASC}	1.31	1.28	0.62	1.93
Grey clays	$La_{chondrite}/Sm_{chondrite}$	3.71	3.61	1.75	5.19
	La_{NASC}/Sm_{NASC}	1.36	1.33	0.64	1.91
Red clays	$La_{chondrite}/Sm_{chondrite}$	3.49	3.42	1.99	4.82
	La_{NASC}/Sm_{NASC}	1.28	1.26	0.73	1.77

brian Bohemian Massif (Sudetes) which mainly encompass metamorphic and magmatic rocks. Generally, the clays containing the smallest amounts of REEs are from the group of Wrocław deposits (Kunice III, Chwalimierz II). These were also supplied by the Bohemian Massif (Sudetes), but from its central part, which is made up of rocks of various rocks of varied petrology e.g. Precambrian shale and gneiss, and Upper Cretaceous sandstones. Clays from Sierakowice and Szydłów II (in the vicinity of Opole and Gliwice), characterized by average REE contents, were fed mainly from the western areas of the Carpathians fold belt. Clays from the Kujawski (Stopka II, Fordon, Rudak I) and Mazowsze (Budy Mszczonowskie, Tadeuszów-Rudzienko) regions were supplied from different areas of the East European Craton, with relatively low REE concentrations. Deposits located in the central part of the basin (Nietążkowo I, Bojanice, Brzostów, Witaszyce, Cienia I) probably had mixed sources, but also favourable conditions to increase REE accumulation.

In the Poznań Formation clays, as in all sedimentary rocks, the contents of rare earth elements depends on clastic material composition and its origin, i.e. the REE contents in the source rocks. This study has shown that in the Poznań Formation clays, no matter what clay lithology, the highest REE contents occur in the western part of the basin, in which a much greater variation in REE contents was also observed. This part of the basin was supplied from the Bohemian Massif (Sudetes), where the crystalline rocks, post-magmatic mineralisation, as well as sedimentary rocks occur. Lower and less variable REE contents were observed in the central and eastern parts of the basin, which were fed by the Carpathians and the East European Craton that consist of sedimentary rocks.

The characteristic colours of the clay lithologies of the Poznań Formation is related to the presence of various iron minerals. The red clays comprise Fe in the form of oxides and hydroxides – hematite and goethite. Deposition of clays under oxidising conditions (red clays) facilitated REE mobility from minerals and their scavenging by authigenic iron oxyhydroxides was relatively small. In these clays the iron concentration was the highest, while the median REE content was the lowest (133 mg/kg) and they characterize the highest share of samples containing REEs in the range of 50–100 mg/kg. The green clays show significantly lower Fe contents (in the form of sulphide – pyrite). In contrast, the median REE content was the highest (155 mg/kg) and the highest number of samples with REE contents in the range of 150–200 mg/kg. Sedimentation of clays under reducing conditions (green clays) constrained the release of REEs from allochthonous minerals (plagioclase, pyroxene, hornblende, and zircon, in which REEs were probably dispersed).

The elevated $La_{chondrite}/Yb_{chondrite}$ ratio, which indicates LREE enrichment, suggests that the presence of REEs in clays is associated with plagioclase debris (in which LREE enrichment compared to pyroxenes and amphiboles is characteristic), also other feldspars, and especially clay minerals (Taylor et al., 1983; McLennan, 1989; McLennan et al., 1993). Small differences for each lithology was found in the series of green > grey > red clays.

CONCLUSIONS

The REE contents in the Poznań Formation ranged from 58.2 to 1,709 mg/kg, with a mean of 176 mg/kg, a geometric mean of 150 mg/kg, and a median of 140 mg/kg. Clays from the Poznań Formation are characterized by REE contents similar to those from other clay deposits.

Little diversification of REE contents was found in the different Poznań Formation clay lithologies. Red clays had slightly lower REE concentrations compared to green and grey clays. Total REE values for green and grey clays can be considered similar.

Different REE concentrations were found in different deposits. The highest mean content was in Mirostowice Dolne (geometric mean – 270 mg/kg), and the lowest in Chwalimierz II (geometric mean – 78.5 mg/kg).

Poznań Formation deposits are characterized by the enrichment of REE as compared to the chondrite pattern, visible in the graphs of their normalized average content. At the same time these clays are characterized by impoverishment in REE compared to the NASC pattern. All lithotypes of the Poznań Formation show negative chondrite-normalized Eu anomalies. NASC normalization exhibited a positive Eu anomaly.

The $La_{chondrite}/Yb_{chondrite}$ ratio indicates LREE enrichment. Small differences among the lithologies was found in the pattern: green > grey > red clays.

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