Rare earth elements distribution in fine-grained deposits from the uppermost Triassic and Lower Jurassic of the Polish Basin: provenance and weathering in the source area

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Nineteen samples of uppermost Triassic and Lower Jurassic claystones and mudstones, which were formed in the epicontinental Polish Basin, were analysed by inductively coupled plasma mass spectrometry (ICP-MS) for rare earth elements (REE) and other selected trace elements (Sc, Y, Th, Zr and U). The results indicate that the source of most of the claystones and mudstones studied were sedimentary rocks of the upper continental crust of old cratonic areas, where the protolith had a mainly felsic character. However, in the latest Triassic a characteristic layer formed, implying significant input from mafic volcanic protolith. It was also found that moderately intense chemical weathering usually favoured increased concentration of the rare earths. Extremely strong hydrolysis, related to episodes of very hot and humid climate (greenhouse events), caused conspicuous impoverishment in REE in residual clays. Weathering and recycling processes modified the composition of REE to some extent, but generally did not obliterate the original characteristics of the protolith. In some samples, enrichment in rare earth elements was observed, caused by admixtures of accessory minerals (being a main carrier of REE) and/or increased sorting during recycling.

Key words: rare earth elements, provenance, palaeo-weathering, uppermost Triassic and Lower Jurassic, Polish Basin.

INTRODUCTION

Rare earth elements and other selected trace elements that occur in siliciclastic rocks, can provide important information on sediment provenance. The chemical composition of sedimentary rocks usually reflects the composition of the sediments and of tectonic conditions during their formation, and the nature of protolith (a primary source), either igneous or metamorphic rocks (Taylor and McLennan, 1985; Bhatia and Crook, 1986; Cullers et al., 1988; McLennan, 1989; McLennan et al., 1993; Cullers, 2000). At the same time, it is necessary to consider that the original composition of sediments studied could be significantly modified, especially in chemical weathering processes, recycling and hydraulic sorting in the environment of deposition, and sometimes also by diagenetic and hydrothermal processes (e.g., Nesbitt, 1979; Cullers, 1988; Condie et al., 1995; Cox et al., 1995; Nesbitt and Markovics, 1997; Bauluz et al., 2000; Singh and Rajamani, 2001).

Preliminary research into the REE geochemistry described here was carried out at the Polish Geological Institute-National Research Institute (Mikulski et al., 2014, 2015). Nineteen samples of claystones and mudstones were taken from the selected archive boreholes, which penetrated siliciclastic rocks of the up-permost Triassic and Lower Jurassic (Mikulski et al., 2014). These rocks were formed in the Polish epicontinental basin, and most of them come from the Mid-Polish Trough (Fig. 1). Over the past few years, various aspects of the mineralogical and geochemical composition of these deposits, along with palaeoenvironmental and palaeoclimatic interpretations, have been studied (e.g., Brański, 2010, 2012, 2014; Pieńkowski et al., 2014; Brański and Pieńkowski, 2014). REE and environmental changes across the Triassic–Jurassic boundary have been studied also in the Tethyan domain (Pálfy and Zajzon, 2012; Lintnerová et al., 2013). However, effects of weathering on the distribution of REE in sediment successions has not been fully explained, and still raises controversies (e.g., Wronkiewicz and Condie, 1987; Middelburg et al., 1988; Banfield and Eggleton, 1989; Price et al., 1991; Nyakairu and Koeberl, 2001; Duzgoren-Aydin and Aydin, 2009).

The purpose of this work is initial characterization of the rare earths in fine-grained sedimentary rocks formed in the latest Triassic and Early Jurassic in the Polish sedimentary basin. The study also attempts to determine their origins and, in particular, the influence of the lithology of the source areas and weathering processes on the REE compositions.

GEOLOGICAL SETTING

During the latest Triassic and Early Jurassic, sedimentation of siliciclastic, continental, marginal-marine and sporadically marine deposits occurred in a large Polish epicontinental sedi-

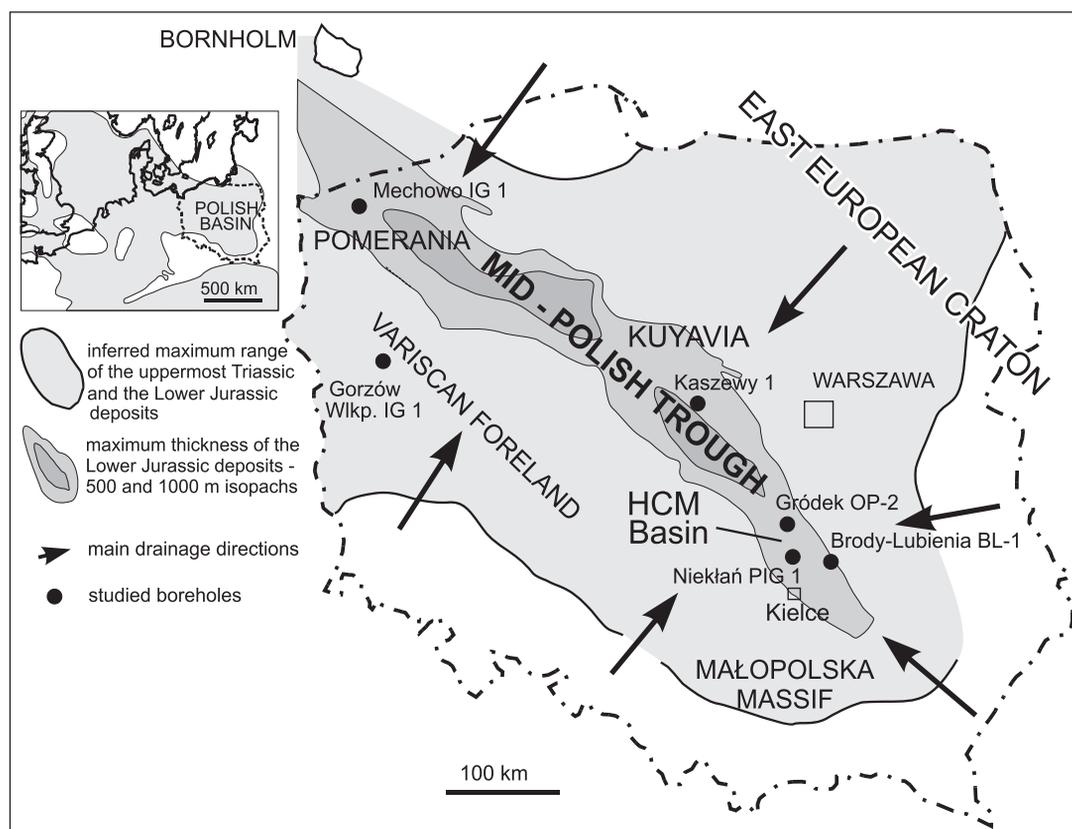* Corresponding author, e-mail: stanislaw.mikulski@pgi.gov.pl

**Fig. 1. General palaeogeography and location of the borehole sections studied
(modified from Pieńkowski, 2004; Brański, 2012, 2014)**

HCM – Holy Cross Mountains

mentary basin (Pieńkowski, 2004; Pieńkowski and Schudack, 2008). The maximum subsidence, resulting in maximum thickness of these deposits, occurred in the axial zone of this basin, called the Mid-Polish Trough (MPT). At the end of the Triassic, sedimentation took place in terrestrial conditions. The Rhaetian was mostly a tectonically quiet time, but at the Triassic-Jurassic boundary rejuvenation of the MPT took place. In Early Hettangian times, thermal subsidence, which had been gradually declining since the Early Triassic (Dadlez et al., 1995), conspicuously accelerated. Moreover, pronounced transtension-related local subsidence was superimposed on the thermal subsidence in the MPT, particularly in the Holy Cross Mountains segment of the MPT (Hakenberg and Świdrowska, 1997; Brański, 2006, 2011). The younger stages of the Lower Jurassic were formed mainly under conditions of gradually decelerating subsidence, and sedimentation was mostly controlled by sea level changes (Pieńkowski, 2004; Pieńkowski and Schudack, 2008). The stratigraphy of the Triassic/Jurassic transition and of the Lower Jurassic is shown in Table 1. Because these formations have relatively poor biostratigraphic documentation, the stratigraphic subdivision is based on the sequence stratigraphic correlation and chemostratigraphy (Pieńkowski, 2004; Hesselbo and Pieńkowski, 2011; Pieńkowski et al., 2012).

Fine-grained sedimentation, which dominated in the lowermost and upper Zagaje Formation (Upper Rhaetian and Lower Hettangian), took place also during deposition of the Lower-Middle Rhaetian Wielichowo Beds (Wagner, 2008; Pieńkowski et al., 2012, 2014), of the Przysucha Ore-bearing Formation (Upper Hettangian, occurring only in the Holy Cross Mountains region), of the Gielniów Formation (Lower Pliensbachian), and

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Stratigraphy of the uppermost Triassic and Lower Jurassic in the epicontinental Polish Basin (after Pieńkowski, 2004; Wagner, 2008; Pieńkowski et al., 2012)

System	Stage	Formation
Jurassic	Toarcian	Borucice Formation
		Ciechocinek Formation
	Pliensbachian	Drzewica (Komorowo, Blanowice) Formation
		Gielniów (Łobez) Formation
	Sinemurian	Ostrowiec Formation
	Hettangian	Przysucha Ore-bearing Formation (Skłoby Formation)
		Skłoby Formation
		Zagaje Formation
Triassic	Rhaetian	Wielichowo Beds
	Norian	Zbąszynek Beds

of the Ciechocinek Formation (Lower Toarcian). The fine-grained rocks (interbedded with heterolithic deposits and subordinate fine-grained sandstones) are calcium-free. The remaining Lower Jurassic formations in the Polish Basin are dominated by sandstones and sandy heterolithic deposits. The Rhaetian–lowermost Hettangian sediments were deposited in continental, alluvial-lacustrine environments. The remaining

Lower Jurassic strata represent brackish-marine/marginal-marine deposits with deltaic/fluvial intervals (Pieńkowski, 2004; Brański, 2011). The uppermost Triassic and Lower Jurassic deposits were buried to depths of approximately 1000–3000 m (Brański, 2011, 2012, 2014). This took place until the Late Cretaceous, when the MPT area was uplifted and subjected to recurrent weathering and intensive erosion, which occurred mainly in the Paleogene.

It should be noted that the uppermost Triassic–Lower Jurassic deposits were formed in a very dynamic period of Earth's history. In recent years, abundant evidence of large-scale, rapid global environmental change has been collected. The most severe changes, related to large magmatic provinces and marked carbon cycle perturbations, took place at the Triassic–Jurassic (Central Atlantic Magmatic Province – CAMP) and Pliensbachian–Toarcian (Karoo-Ferrar magmatic province) transition intervals (e.g., McElwain et al., 1999; Hesselbo et al., 2000, 2002; Pálfy et al., 2001; Cohen and Coe, 2007; Cohen et al., 2007). Rising atmospheric carbon dioxide concentrations caused a greenhouse climate and resulting abundant rainfall, rising temperatures and intensification of weathering and erosion in the source areas. Occurrence of climatic shifts in the Polish Basin has also been supported by patterns of mineralogical and geochemical data (cf. Brański, 2009a, b, 2010, 2011, 2012, 2014; Hesselbo and Pieńkowski, 2011, Pieńkowski et al., 2012, 2014; Brański and Pieńkowski, 2014).

MATERIALS AND METHODS
OF REE RESEARCH

Rare earth elements were examined in nineteen samples of mudstone and claystone, collected from the cores of various archive boreholes drilled in the Polish Basin and representing different stratigraphic units of the uppermost Triassic and the Lower Jurassic. The studies covered sections of the Niekłań PIG 1, Kaszewy 1, Mechowo IG 1 and Brody-Lubienia BL-1 boreholes. Individual samples from the Gródek OP-2 and Gorzów Wielkopolski IG 1 boreholes were also examined (Fig. 1 and Table 2).

The REE, Sc, Y, and Th analyses were performed in the Chemical Laboratory of the Polish Geological Institute – National Research Institute, using mass spectrometry with ICP-MS technic. After acid digestion, the samples were diluted 20 times with a solution of 1% HNO_3. Total solution of elements contained in the samples was achieved by use of hydrofluoric acid and chloric acid (VII – oxidation of fluorine and chlorine in acid). Dried and powdered samples were initially treated with nitric acid (V) in order to distribute organic matter and dissolved in a mixture of perchloric and hydrofluoric acid (VII). In order to improve the procedure for dissolution, digestion was repeated three times. In the last stage, after evaporation to dryness (on a hot plate, to a temperature of 150 ± 10°C) the residue was dissolved in dilute nitric acid (V). The solution obtained was submitted to analysis by ICP-MS. Detection limits were 0.5 ppm for LREE and 0.05 ppm for HREE. The results are collected in Appendix 1*. Some other

Table 2

List of claystone and mudstone samples from the Upper Triassic and Lower Jurassic studied by ICP-MS

No.	Sample	Borehole	Beds or Formation	Stratigraphy
1.	Nk/187.5	Niekłań PIG 1	Zbąszynek Beds	Triassic, Norian
2.	Nk/178.4		Wielichowo Beds	Triassic, Rhaetian
3.	Nk/167.8		Wielichowo Beds	Triassic, Rhaetian
4.	Nk/162.3		Zagaje Formation	Triassic, Rhaetian
5.	Nk/157.7		Zagaje Formation	Jurassic, Hettangian
6.	Nk/32.0		Zagaje Formation	Jurassic, Hettangian
7.	Gr/204.1	Gródek OP-2	Przysucha Ore-bearing Formation	Jurassic, Hettangian
8.	K/1973.8	Kaszewy 1	Zbąszynek Beds	Triassic, Norian
9.	K/1480.3		Ostrowiec Formation	Jurassic, Sinemurian
10.	K/1465.2		Ostrowiec Formation	Jurassic, Sinemurian
11.	K/1464.3		Gielniów Formation	Jurassic, Pliensbachian
12.	K/1463.7		Gielniów Formation	Jurassic, Pliensbachian
13.	K/1462.3		Gielniów Formation	Jurassic, Pliensbachian
14.	M/1130.0	Mechowo IG 1	Zagaje Formation	Triassic, Rhaetian
15.	M/700.5		Gielniów Formation	Jurassic, Pliensbachian
16.	BL/185.5	Brody-Lubienia BL-1	Drzewica Formation	Jurassic, Pliensbachian
17.	BL/162.0		Ciechocinek Formation	Jurassic, Toarcian
18.	BL/159.0		Ciechocinek Formation	Jurassic, Toarcian
19.	GW/815.0	Gorzów Wlkp. IG 1	Ciechocinek Formation	Jurassic, Toarcian

Nk, Gr, BL – Holy Cross Mts. segment of MPT, K – Kuyavian segment of MPT, M – Pomeranian segment of MPT, GW – Fore-Sudetic Monocline (northern part)

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elements analysed by portable spectrometer (i.e. Zr and U) were included in the data interpretation.

The overall interpretation was reinforced by results of prior published analyses: whole-rock mineral composition, clay mineral composition (in <0.002 mm fraction) and the major element contents (Brański, 2010, 2012, 2014; Pieńkowski et al., 2014). Various mineralogical and geochemical weathering indices have also been calculated (Brański, 2014; Pieńkowski et al., 2014). Selected results of these previous studies are collected in Appendix 2.

RARE EARTH ELEMENT RESULTS

The most important results of the research are shown in tabular form (Table 3, Appendixes 1 and 3) and in the charts (Figs. 2–6). Characteristics of the rare earths are shown (Fig. 3) in graphs standardized in relation to chondrite (Taylor and McLennan, 1985). In addition, the contents of elements in the samples analysed are shown also in relation to standard mudrocks (Fig. 4), in this case to post-Archaic Australian shale – PAAS (Taylor and McLennan, 1985), considered to be a typical deposit of cratonic provenance, derived from passive continental margins (McLennan, 1989).

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Minimum, maximum and average contents of the rare earth elements (REEs) and selected trace elements in the samples studied

	Triassic	Jurassic	PAAS[1]
Sc	10.2–24.1 (16.7)	7.9–23.7 (15.0)	16
Y	10.8–81.1 (35.2)	14.5–39.5 (22.0)	27
La	4.8–441.6 (114.0)	28.8–114.7 (49.4)	38.2
Ce	8.8–1131.9 (270.0)	58.5–234.4 (105.9)	79.6
Pr	0.9–128.8 (30.4)	6.7–25.3 (11.3)	8.8
Nd	3.5–499.6 (118.4)	25.3–86.9 (41.1)	33.9
Sm	1.11–97.45 (23.23)	4.64–13.83 (7.29)	5.55
Eu	0.35–19.09 (4.57)	0.76–2.32 (1.35)	1.08
Gd	2.16–70.77 (17.65)	4.02–8.76 (5.36)	4.66
Tb	0.35–8.28 (2.21)	0.53–1.32 (0.78)	0.77
Dy	2.12–33.44 (10.25)	2.97–7.80 (4.50)	4.68
Ho	0.44–4.29 (1.61)	0.56–1.59 (0.90)	0.99
Er	1.33–8.75 (4.06)	1.62–5.17 (2.74)	2.85
Tm	0.21–0.92 (0.53)	0.24–0.83 (0.41)	0.41
Yb	1.59–4.68 (3.37)	1.61–5.78 (2.75)	2.82
Lu	0.24–0.68 (0.47)	0.25–0.91 (0.43)	0.43
Th	12.13–23.40 (17.26)	10.99–51.89 (20.21)	14.60
ΣLREE	19.5–2318.4 (560.6)	124.7–477.4 (223.4)	167.2
ΣHREE	8.4–131.7 (40.1)	11.3–32.2 (17.9)	17.6
ΣTREE	34.1–2450.1 (600.7)	136.0–509.6 (241.3)	184.8
L/H*	1.3–17.6 (9.8)	8.9–15.9 (12.3)	9.5
La_N/Yb_N	0.88–63.77 (18.54)	8.76–17.25 (12.09)	9.16
La_N/Gd_N	1.85–6.41 (5.06)	5.21–11.73 (7.58)	6.84
Gd_N/Yb_N	0.48–12.26 (1.08)	1.12–2.00 (1.64)	1.34
Eu/Eu*	0.48–0.70 (0.64)	0.53–0.68 (0.63)	0.65
Th/Sc	0.77–2.29 (1.13)	0.73–2.82 (1.37)	0.91
La/Sc	0.20–37.42 (8.99)	2.27–5.08 (3.35)	2.39
La/Th	0.21–35.70 (8.85)	1.80–3.39 (1.75)	2.62

[1] – after Taylor and McLennan (1985); * – LREE/HREE

REEs IN MUDSTONES AND CLAYSTONES OF THE LOWER JURASSIC

In samples of fine-grained rocks representing the Lower Jurassic, the contents of the elements analysed are not very varied and are generally similar to their contents in standard shale. The total content of lanthanide elements ranges usually from 136 to 334 ppm, the average of their contents in the mudstone samples studied (241.3 ppm) is slightly higher than in the case of PAAS (184.8 ppm). Only in one sample, K/1463.7 (from the lowest Pliensbachian in the Kaszewy borehole section) the content of lanthanide elements is significantly higher – 509.6 ppm (Appendix 1 and Table 3). The ratio of light to heavy REEs in these samples is also somewhat higher than in the reference shale and varies within the limits of 8.9–15.9 (average 12.3). The europium anomaly is similar to that in standard shale. The ratio of Eu/Eu* varies in a fairly narrow range 0.53–0.68 (0.63 on average), which is slightly higher or slightly lower than in PAAS (Table 3 and Appendix 3). The scandium content varies from 8 to 24 ppm, yttrium from 14 up to 40 ppm, and thorium from 11 to 52 ppm. The highest content of these elements was also found in sample K/1463.7 sample, which is also significantly enriched in lanthanide elements.

Graphic characteristics of the rare earths in these Lower Jurassic claystone and mudstone samples are similar to those of PAAS (Fig. 3). There is an enrichment of light rare earth elements (LREEs), and distinct fractionation within them, almost flat curves as regards heavy rare earth elements (HREEs), and a moderate-sized europium anomaly. Total REE fractionation (La_N/Yb_N – 12.09 on average), fractionation within LREEs (La_N/Gd_N – medium 7.58) and also within HREEs (Gd_N/Yb_N – 1.64 on average) are slightly larger than in PAAS (Table 3). The general similarity of all the samples taken from the Lower Jurassic to the standard shale is clearly visible on the chart showing the REE content in relation to PAAS, where their characteristic patterns are almost flat (Fig. 4).

Only sample Nk/1463.7 shows significant (more than doubled) enrichment in rare earth elements. Nevertheless, the shape of the REE content plot in relation to the chondrite (Fig. 3) in this sample is very similar to the graphic characteristics of the average contribution of all the elements in PAAS. This means that enrichments of the individual elements are in general distributed evenly in this sample, although their fractionation (especially within the LREE) is greater (La_N/Yb_N = 13.41; La_N/Gd_N – 11.73) (Appendix 3).

REE IN MUDSTONES AND CLAYSTONES OF THE UPPERMOST TRIASSIC

In four specimens examined representing the Upper Triassic, the contents of the elements analysed are more variable than in the Jurassic samples (Appendix 1 and Table 3). Only in two samples (Nk/187.5 and M/1130.0) are the contents of REEs close to their content in standard shale (PAAS). The total share of lanthanide elements is very broad, ranging from just 34 up to 2450 ppm (Table 3). The highest REE content was observed in sample Nk/178.4 of the Lower–Middle Rhaetian and the lowest one in sample Nk/162.3, representing the Upper Rhaetian (Appendix 1). Both samples come from the Niekłań PIG 1 borehole core and they are separated in the profile just by 16 metres. In the first case, the total content of rare earths is more than an order of magnitude higher, and in the second several times lower than in the reference shale. Also,
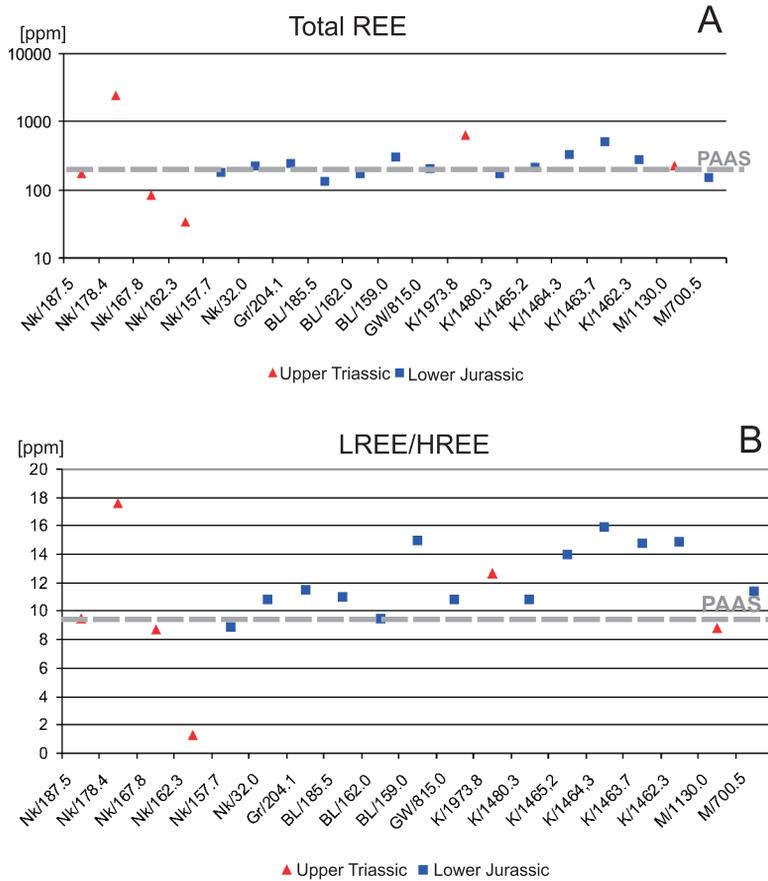
Fig. 2. Rare earth elements in samples of the fine-grained rocks studied

A – total REE, **B** – ratio of the light to heavy elements

ments. The samples studied show both slightly smaller and slightly larger europium anomalies than in standard shale (Appendix 1 and Table 3). Scandium and thorium contents are relatively stable and range between 10–24 ppm and 12–23 ppm, respectively. The highest share of scandium was found in sample Nk/162.3, which is at the same time very poor in REEs. The yttrium concentration is more varied (from 11 to 81 ppm), and its highest content was observed in sample Nk/178.4 sample, which was particularly rich in REEs.

Graphic characteristics of the rare earths in the uppermost Triassic mudstone samples are quite different in relation to that of reference shale (Figs. 3 and 4). Only in the case of two samples with REE contents close to PAAS (Nk/187.5 and M/1130.0), their graphic characteristics are similar to the average characteristics of the standard shale (significant enrichment and quite distinct fractionation within LREE and almost flat HREE curves). In their case, the content of REEs standardized to PAAS, shows as almost a horizontal line with a value of 1 (Fig. 4). Of note is the relatively significant negative europium anomaly of sample M/1130.0 (Eu/Eu* = 0.48), as well as its considerable enrichment in thorium and impoverishment in scandium in relation to the reference shale (Appendixes 1 and 3).

In the case of the sample richest in the lanthanides (Nk/178.4; representing the Lower–Middle Rhaetian in the Niekłań borehole section), the graph of their standard contents normalized to chondrite clearly deviates from the characteristics of the average values for PAAS (Fig. 3). Of note here are not only very high contents of REEs, but also their very strong fractionation (La$_N$ – Yb$_N$ – up to 63.77) (Appendix 3). There is also extremely strong HREE fractionation (Gd$_N$/Yb$_N$ – up to 12.26), which is recorded as a very steep curve, while the curve of light elements is similar to the average characteristics of the reference shale (La$_N$/Gd$_N$ – 5.20). Detailed analysis of each REE content in this sample (Appendix 1) and their pattern in relation to PAAS
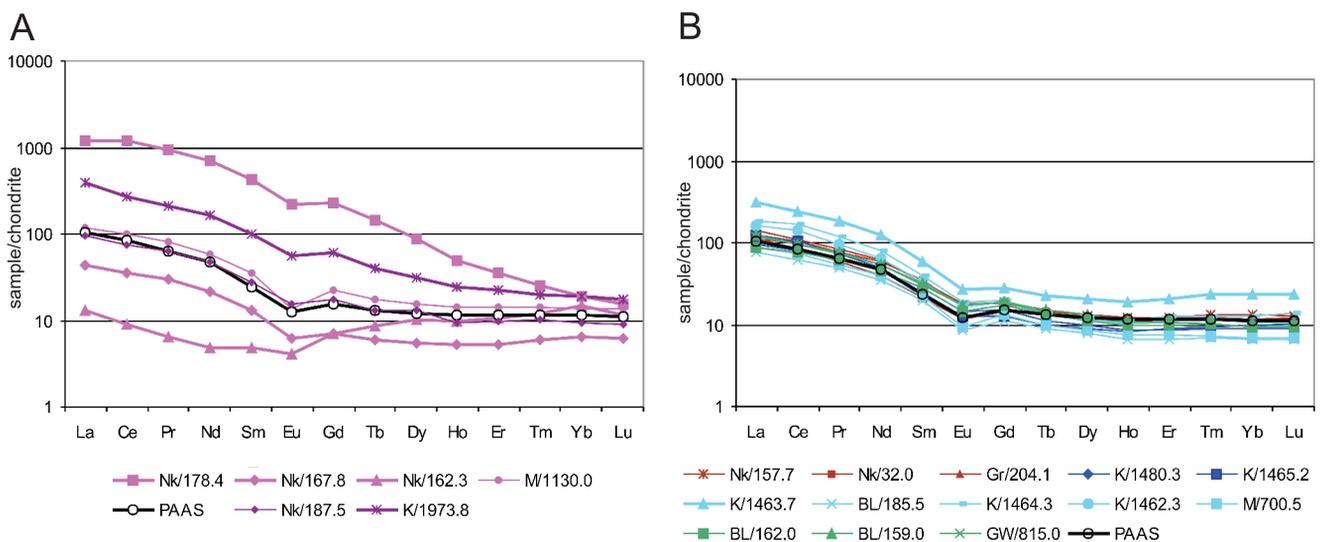
the ratio of light to heavy REEs is very diverse and varies within a very wide limit of 1.3–17.6 (Table 3). This means that two samples taken from the uppermost Triassic are strongly enriched in light rare earth elements, while two others are very poor in these elements and relatively enriched in the heavy ele-

Fig. 3. Characteristics of the rare earths in the samples studied normalized to chondrite (Taylor and McLennan, 1985)
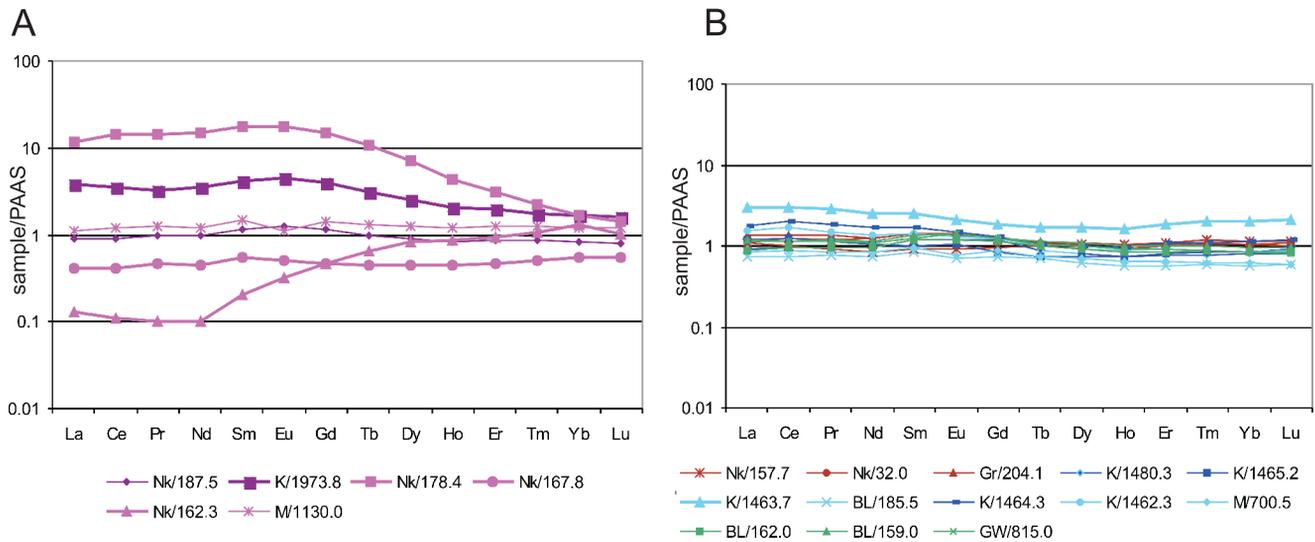
A – Upper Triassic, **B** – Lower Jurassic

Fig. 4. Characteristics of the rare earths in the samples studied normalized
to post-Archean Australian shale – PAAS (Taylor and McLennan, 1985)

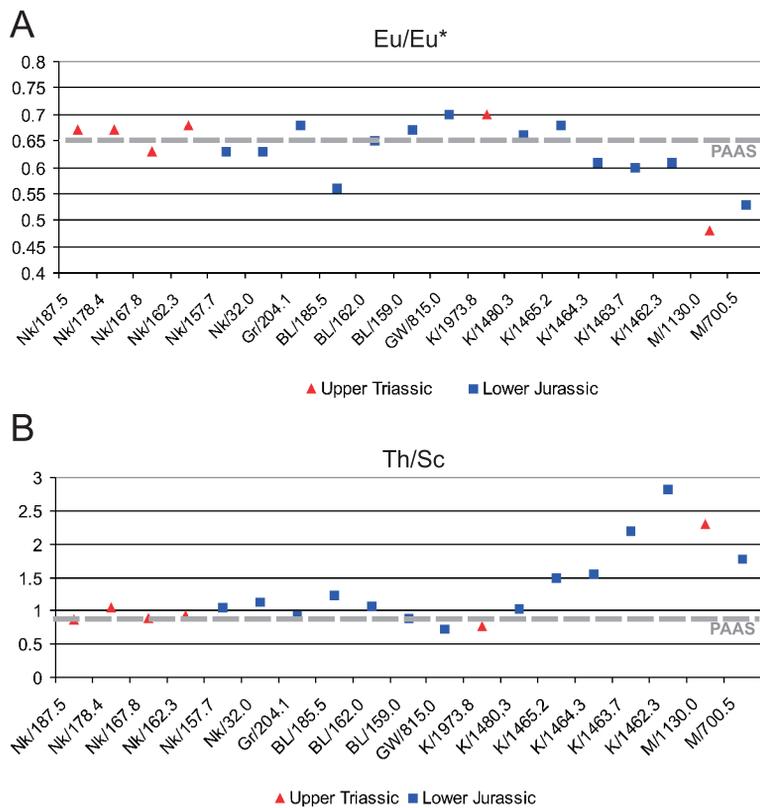**A** – Upper Triassic, **B** – Lower Jurassic

Fig. 5. Europium anomaly (A) and the ratio of Th/Sc (B) in the samples
of fine-grained rocks studied

(Fig. 4) reveals that the enrichment in REEs applies in particular to light and medium elements, while the heavy elements are elevated to a much lesser degree. Compared to the reference shale, the sample is enriched three times in yttrium, while slightly depleted in scandium and thorium (Appendix 1).

The REE characteristics (normalized to chondrite) of sample K/1973.8 (Upper Norian in the Kaszewy 1 profile; Fig. 3), also differs from the REE characteristics of PAAS. This sample also contains much higher lanthanides than does the reference shale

and is characterized by much stronger fractionation (La_N/Yb_N – 20.93). It is worth of notice that the fractionation of light REEs (La_N/Gd_N – 6.41) here is almost the same as in PAAS, while the HREE curve shows a clear slope (Gd_N/Yb_N – 3.26) (Appendix 3 and Fig. 3). A slight positive anomaly of the MREEs (medium rare earth elements; samarium, europium, and gadolinium) is also observed – it is visible especially in the chart showing relation of REE to PAAS content (Fig. 4). This sample is clearly enriched in yttrium and slightly depleted in thorium, and the content of scandium is almost the same as in PAAS (Appendix 1).

A totally different, completely unusual REE characteristic has been observed in sample Nk/162.3 that contains the least amount of rare earths. The graphic characteristics of the normalized values to chondrite (Fig. 3) shows relative depletion of light elements in relation to heavy (La_N/Yb_N just 0.88), as well as increase of successive values within the HREEs (Gd_N/Yb_N – 0.48) (Appendix 3), causing a reverse slope of the curve, i.e. enrichment in heavy elements in relation to the medium ones. The content of the lightest lanthanides (lanthanum-neodymium) is 8–10 times less than the standard content, while heavy elements concentration is similar to their share in PAAS, and, in the case of ytterbium, even higher (Appendix 1 and Fig. 4). The layer from which this sample was taken, is significantly enriched in scandium and thorium, while slightly depleted in yttrium (Appendix 1).

In the case of the next sample representing the Rhaetian (Nk/167.8), the value curve standardized to chondrite (Fig. 3) is similar to the average REE patterns in PAAS, although fractionation of elements is smaller (La_N/Yb_N – 6.85) (Appendix 3). In general, although the sample contains significantly less rare earths than the reference shale, depletion in individual rare earth elements (more or less twice) is noted here fairly evenly, which clearly illustrates the almost horizontal line when normalized to PAAS (Fig. 4). The sample is significantly enriched in scandium and thorium, while clearly impoverished in yttrium (Appendix 1).
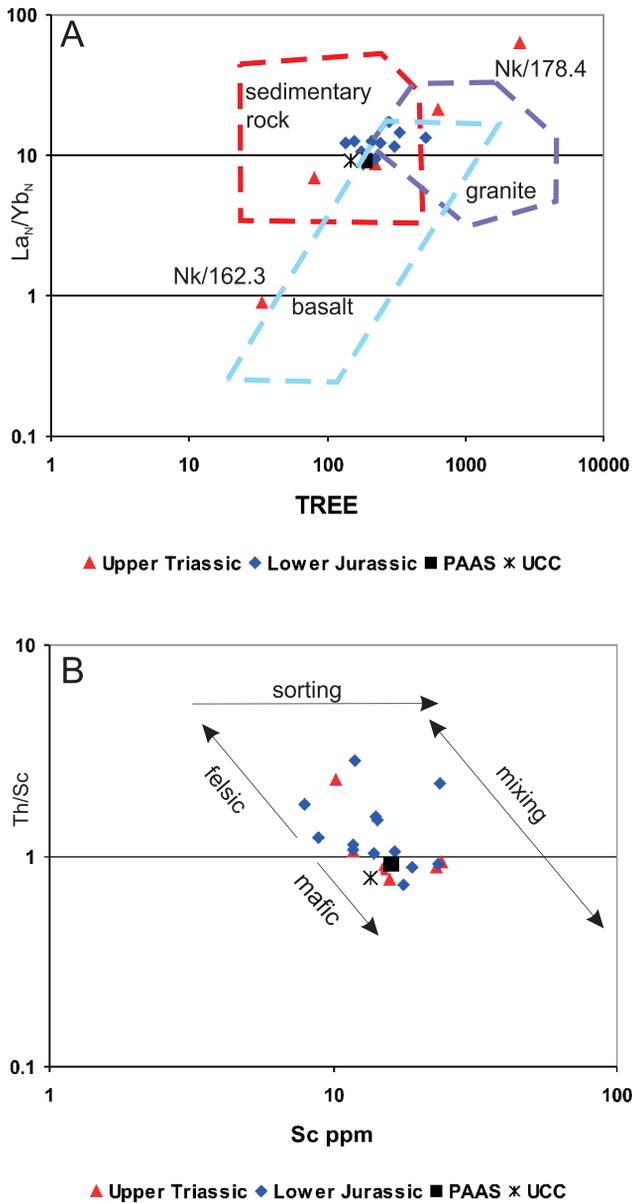
▲ **Upper Triassic** ◆ **Lower Jurassic** ■ **PAAS** ✕ **UCC**

▲ **Upper Triassic** ◆ **Lower Jurassic** ■ **PAAS** ✕ **UCC**

Fig. 6. Binary comparison charts showing the provenance of the sediments studied: A – La$_N$/Yb$_N$ against total REE (the areas corresponding to the source rocks are based on Yan et al., 2012); B – Th/Sc ratio against Sc content (modified from Fedo et al., 1997)

REE PROVENANCE AND THE INFLUENCE OF PALAEOWEATHERING

In almost all claystone and mudstone samples of the Lower Jurassic, but only in two of the samples representing fine-grained rocks of the uppermost Triassic, rare earth concentrations are not very varied and are close to the REE content in standard shale (Appendix 1, Figs. 2–4 and 6). Their common characteristics, namely: moderately high total REEs (similar to the average in PAAS), moderate enrichment of LREEs in relation to HREEs, a flat HREE distribution and a clear negative europium anomaly indicate that original source of these sediments was mainly recycled and weathered felsic rocks (cf. Tay-

lor and McLennan, 1985; McLennan et al., 1993; Cullers, 2000). In the case of the PAAS average, the total content of rare earths and their characteristics generally suggest a granodiorite protolith (Taylor and McLennan, 1985; Nesbitt and Markovics, 1997). Also chondrite-normalized relations of La/Yb and Gd/Yb (Table 3 and Appendix 3) have values similar to the typical post-archean mudrocks of cratonic provenance. This means that the dominant source of sedimentary material deposited during Early Jurassic times in the continental, and then in the brackish-marine Polish Basin, was old upper continental crust. This conclusion is also supported by the most important geochemical factors (Th/Sc = 0.73–2.82; La/Sc = 2.27–5.08).

The REE concentrations found in the mudrocks studied are generally elevated in comparison to PAAS, which suggests more intense weathering and/or recycling than in the case of source areas for the reference shale. Uranium and thorium relationships (U/Th = 0.23–0.39) and zirconium and scandium (Zr/Sc = 20.2–59.9) also suggests quite strong chemical weathering of source areas and sedimentation in an oxidising environment, with local impact of sediment recycling and hydraulic sorting (Fig. 6). The widespread control of generally strong hydrolysis in areas surrounding the Polish sedimentary basin had already been recognized on the basis of clay mineral composition and major element contents (e.g., Brański, 2012, 2014; Pieńkowski et al., 2014; Brański and Pieńkowski, 2014). A slight variety in the REE concentration in the fine-grained rocks studied may also have been caused by changes in the intensity of weathering, differences in erosion of palaeosol levels (or in zones of weathering covers) and locally by the influence of hydraulic sorting during transport and deposition (cf. Condie et al., 1995; Nesbitt and Markovics, 1997; Bauluz et al., 2000).

Among the samples representing the fine-grained rocks of the Lower Jurassic, only sample K/1463.7 of claystone, taken from a level located just above the boundary between the Sinemurian and Pliensbachian in the Kaszewy 1 borehole, shows significantly elevated (by almost three times) share of rare earth elements. Significant and generally uniform enrichment in LREEs, a flat pattern within the HREEs, a europium anomaly and the relationships between thorium, lanthanum and scandium (Appendixes 1 and 3), indicate the felsic nature of the claystone protolith also in this case. Nevertheless, distinctly higher REE concentrations and some differences in their characteristics (e.g., strong fractionation within LREE) were most likely caused by very intensive recycling of deposits, as demonstrated by the extremely high proportion of Zr, several times higher than in the standard shale (Zr/Sc is as high as 200), as well as by significantly increased Th/Sc ratio (e.g., McLennan et al., 1993; Hassan et al., 1999; Lintnerova et al., 2013). These processes have taken place in conditions of moderate chemical weathering (CIA about 79; the ratio of kaolinite/illite – 0.35; U/Th = 0.35), before a presumed greenhouse event at the beginning of Pliensbachian (Brański and Pieńkowski, 2014). This layer most likely point to the episodic enhancement of erosion and redeposition.

Unlike the fine-grained rocks of the Lower Jurassic, only one-third of the samples representing the claystones and mudstones of the uppermost Triassic show concentrations of rare earths and REE characteristics close to the average of PAAS. Some layers (K/1973.8 sample and, in particular, the sample Nk/178.4) contain a much higher lanthanide content than the reference shale. Sample Nk/178.4 (representing the bottom mudstone layer in the Wielichowo Beds of the Lower–Middle Rhaetian in the Niekłań PIG 1 borehole) is extremely enriched in lanthanides and their graphic characteristics strongly differ from

characteristics of the average values of PAAS (Appendix 1, Figs. 3 and 4). Also in this case, most parameters indicate a felsic character of the protolith (for example, Eu/Eu* = 0.70; Th/Sc = 1.05). In addition, this layer is a kaolinite mudstone (Appendix 2) and it most likely records the first Rhaetian greenhouse episode and intense chemical weathering in the source areas (Brański, 2014; Pieńkowski et al., 2014). However, such a strong enrichment and fractionation of the REEs is hard to explain only by a felsic nature of the protolith and by chemical weathering processes (Fig. 6A). The main reason for such a high concentration of rare earths and their unusual characteristics is most likely a significant admixture of accessory minerals. Very high REE contents (especially of light REEs), a remarkably steep content distribution of the HREEs (Gd_N/Yb_N – 12.26), a slight but distinct relative enrichment in the MREEs (Figs. 3 and 4) and the increased share of P_2O_5 suggest that source of this concentration may be an admixture of monazite (McLennan et al., 1993). However, such a conclusion seems to be challenged by the relatively low thorium contents and high concentration of yttrium (Appendix 1), which may suggest the presence of other REE minerals. In the case of this layer we are probably dealing with the impact of increased admixtures of accessory minerals (apatite, monazite, xenotime?), as the main carriers of REE. Even trace amounts of these minerals in the sample can cause a drastic increase in REE contents (Gromet and Silver, 1983; Cullers et al., 1987; McLennan et al., 1993; Condie et al., 1995; Bauluz et al., 2000). Presumably, the concentration of accessory minerals was largely inherited from the weathered sedimentary cover in the source area. The Zr contents are only a little higher than in the case of PAAS (Zr/Sc = 22.0) and this suggests an insignificant role of recycling or hydraulic sorting. A relatively high ratio of uranium to thorium (U/Th = 0.90), in documented conditions of intense chemical weathering (Brański, 2014; Pieńkowski et al., 2014; Appendix 2), may be just the result of accessory mineral admixtures (which were also a carrier of uranium) or reflect less oxic conditions during sedimentation (Jones and Manning, 1994). Similar (though less extreme) REE characteristics occur also in sample K/1973.8, from the highest Norian in the Kaszewy 1 borehole section. Also in this case, we observe a very significant (more than triple) enrichment in rare earth elements and their increased fractionation, an increase in the slope of the HREE curve, a small MREE positive anomaly and meaningful enrichment in yttrium. Such data also indicate the importance of the felsic protolith and enrichment in accessory minerals, although in smaller quantities than in the case of sample Nk/178.4.

In turn, the REE characteristics of some other layers representing the Rhaetian (Nk/167.8; and especially Nk/162.3) reveal the influence of very intense chemical weathering, which led to a very significant decline in REE contents. Moderate Zr contents (Zr/Sc = 11.8–23.7) suggests an unimportant role of recycling and sorting. Moreover, the results of the REE study in these Rhaetian layers indicate a different nature of the protolith in the source areas, which had already been suggested by previous geochemical and mineralogical research (Brański, 2014). In the case of sample Nk/167.8, the REE concentration is much smaller, but their graphic characteristics (Figs. 3 and 4) are similar to the average characteristics of standard shale, and the most important parameters (Eu/Eu* = 763; Th/Sc = 0.88) still suggest a felsic protolith. On the other hand, other factors (La/Sc = 0.69; La/Th = 0.79) suggest a rather mixed character of primary rocks with some participation of mafic components. Nevertheless, the REE characteristics of the overlaying layer of almost pure kaolinitic claystone (sample Nk/162.3; Appendix 2) already indicates a mafic component in the source area (Fig. 6A). Kaolinite may dominate in conditions of extreme chemical weathering regardless of the primary rock composition (e.g.,

Chamley, 1989). Graphical characteristics (Figs. 3 and 4) and coefficients, show their fractionation (Appendix 3) and point to the following features:

1 – very small concentration of REE in general (more than five times lower than in PAAS);
2 – depletion of light elements relative to heavy elements;
3 – depletion of medium elements in relation to heavy ones (the reverse slope of the HREE curve).

This means that especially strong REE depletion occurs within the light elements, a slighter one within the MREEs, while there is little or no depletion in heavy elements. These characteristics, as well as an increased content of scandium and some other parameters (La/Sc = 0.20; La/Th = 0.21), suggest a more mafic protolith for this claystone, for example, the presence of volcanic detritus (Cullers et al., 1987, 1988; Cullers, 1988, 1994, 2000; McLennan et al., 1993). Unlike most of the sections studied sections, delivery of sedimentary material to the vicinity of the Niekłań PIG 1 borehole was most probably from the south (Pieńkowski, 2004), and source areas were most likely located on the Fore-Carpathian area. Noteworthy, in the earlier studies, extreme chemical weathering during formation of this kaolinite claystone and its association with the greenhouse event at the end of the Triassic period had been postulated (Brański, 2014; Pieńkowski et al., 2014 and references therein). This view is supported by the very low uranium to thorium ratio (U/Th = 0.11). Most probably, the characteristics of different REE provenance were underscored by extremely strong weathering associated with episodes of humid tropical climate. According to some authors (e.g., Roddaz et al., 2006), depletion of deposits in light rare earth elements (that is, the relative enrichment in HREEs in relation to LREEs) may be just due to the fact that their source areas comprised very intensively weathered, older sedimentary rocks. The negative europium anomaly (Eu/Eu* = 0.68) points to very intense hydrolysis that led to a complete transformation of plagioclase. To summarize, recent REE characteristics in residual clay represented by sample Nk/162.3 is most likely associated with both volcanic protolith and very intense chemical weathering at the end of the Triassic.

Despite the fact that the influence of weathering on the distribution of REE in sediment can be controversial, most authors consider that moderately intense chemical weathering leads to the enrichment of sediments in the rare earth elements (in LREEs in particular), while extremely strong weathering can cause pronounced REE depletion as a result of their leaching (e.g., Nesbitt, 1979; Nesbitt et al., 1990; Morey and Setterholm, 1997; Nesbitt and Markovics, 1997; Braun et al., 1998; Roddaz et al., 2006). The results presented herein seem to support this suggestion.

CONCLUSIONS

Results of analyses of rare earths and some other trace elements (especially in Lower Jurassic strata), are mostly close to the average data from the reference mudrocks – post-Archaic Australian shale. They indicate that the dominant source of the claystones and mudstones studied comprised sedimentary rocks of the upper continental crust of old cratonic areas, where the protolith had a mainly felsic character of granodiorite type. Somewhat higher than PAAS concentrations of lanthanides (especially LREE) reflect a higher degree of maturity of the rocks studied. On the other hand, the Upper Triassic strata include also layers with elevated contents of scandium, and significantly depleted in lanthanides (especially LREEs), with graphic characteristics suggest a significant share of mafic vol-

canic protolith (especially the residual Rhaetian layer represented by sample Nk/162.3).

In general, it can be concluded that although the processes of weathering and recycling modified the REE composition to some extent, it did not remove the influence of tectonic domain as well of the main protolith type. In most cases, the lanthanides and some trace elements may be used to specify the provenance even of mature sedimentary rocks, despite the effect of weathering and recycling. On the other hand, REE characteristics are not a good diagnostic tool to determine changes in the weathering regime and in palaeoclimatic conditions – for such interpretations, clay mineral compositions and relations between selected major elements provide a better tool.

Significant REE enrichment was found only in very few layers, most likely enriched in accessory minerals, which were carriers of a variety of REEs. Enhanced sorting in recycling could also have contributed to REE enrichment. Moderately intense chemical weathering usually favours (along with recycling) an increase in concentration of rare earths. However, during extremely strong hydrolysis (linked to tropical climate episodes) even the resistant components may be leached. Such conditions took place, for example, at the end of the Triassic, as a result of catastrophic greenhouse events. Consequently, a clear decrease in REE in some layers of residual clays was observed.

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