Palaeoenvironments revealed from rare earth element systematics in vertebrate bioapatite from the Lower Devonian of Svalbard

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Palaeoenvironments revealed by rare earth element systematics in vertebrate bioapatite from the Lower Devonian of Svalbard

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Abstract

In-situ rare earth element compositions have been measured in early vertebrate microremains from the Lower Devonian basin of Andrée Land (Svalbard), with the aim of obtaining information about their early depositional environment and potential reworking. Vertebrate microremains with different histology were used for the analyses, sourced from two different localities of marginal marine to freshwater sediments from geographically distant parts of the Grey Hoek Formation (Skamdalen and Tavlefjellet members). We selected thelodont and undescribed ?chondrichthyan scales, which allowed us to define potential taxonomic, histological, and taphonomic variables of the REE uptake. Results showed REE concentrations to be relatively uniform within the scales of each taxon, but apparent discrepancies were visible between the studied localities and separate taxa. The compilation of REE abundance patterns as well as REE ratios have revealed that thelodont and ?chondrichthyan originating from the same locality, must have had different burial and early diagenetic histories. The shapes of the REE profiles, together with the presence and absence of the Eu and Ce anomalies, equally suggested different depositional and diagenetic environments for these two sympatric taxa resulting from either stratigraphical or long-distance reworking. The REE concentrations appear to have visible differences between separate dental tissues, particularly between enameloid and dentine of thelodonts, emphasising the importance of in-situ measurements in microfossil biomineral geochemistry.

Key Words: Rare earth elements, paleoenvironment, vertebrate microfossils, Devonian, Svalbard
Introduction

Rare earth element (REE) compositions from fossil vertebrate bioapatite are known to be diagnostic of fossil provenance and reworking (e.g. Trueman 1999; Suarez et al. 2010), and have been used as proxies for palaeoseawater chemistry and redox conditions helping to accomplish palaeoenvironmental and palaeogeographic interpretations (e.g., Wright et al. 1987; Reynard et al. 1999; Trueman & Tuross 2002; Kemp & Trueman 2003; Lécuyer et al. 2004; Patrick et al. 2004; Ounis et al. 2008; Žigaitė et al. 2015). REE concentrations in living fish bones and teeth are very low, since these are not important elements for the metabolic processes of vertebrates (e.g. Elderfield and Pagett 1986; Vennemann et al. 2001). Fossil bioapatites in contrast, display REE concentrations with an enrichment factor of about $10^6$ to $10^7$, (see e.g. Bernat 1975; Wright et al. 1984; Trueman and Tuross 2002). REE patterns are usually strictly similar to the seawater patterns, this is achieved through quantitative intake of REE with little or no fractionation, as is the case for all biogenic phosphates at the seawater-sediment interface (see Reynard et al. 1999). Therefore, fossil bioapatite REE and trace element concentrations are exclusively diagenetic and get incorporated post-mortem usually within a few thousand years during early stages of diagenesis (see e.g. Elderfield and Paget 1986; Patrick et al. 2004; Tütken et al. 2008, Trueman et al. 2011). Because of this, their compositions reflect bottom and pore-water chemistry and can thus be used as proxies for palaeoenvironment (see Wright et al. 1987; Kemp and Trueman 2003; Lécuyer et al. 2004).

The preservation of a palaeoceanographic signal in fossil biominerals depends on the extent of diagenetic alteration and fractionation of REEs during recrystallization or “extensive diagenesis” (Reynard et al. 1999; Lécuyer et al. 2004).

Extensive re-crystallization is often characterized by a strong middle REE (MREE)
enrichment relative to light REE (LREE) and heavy REE (HREE), leading to “bell-shaped” patterns (Lécuyer et al. 1998; 2004). Recently, Herwartz et al. (2011) have demonstrated that the bioapatite of vertebrate long bones, such as femora, humeri and ribs, composed of fine, nanometer-size plate-like crystallites with a large surface/volume ratio, shows open system behavior in respect to REE and Hf uptake, and therefore should not be used for REE analyses aiming at palaeoenvironmental reconstructions, and equally not for $^{176}$Lu-$^{176}$Hf radiometric dating (Trueman 1999; Herwartz et al. 2013a). However, fossil dental tissues such as enamel and enameloid with compact and large crystallites and as little as 1 wt% of organic matter, demonstrate high potential to preserve an early REE signal (Trueman and Palmer 1997; Kohn et al. 1999; Kemp and Trueman 2003; Trotter and Eggins 2006; Tütken et al. 2008; Sire et al. 2009; Trueman et al. 2011; Enax et al. 2012) and can be used as proxies for early depositional environment. For example, the redox conditions of marine palaeobasins can be determined from the presence or absence of a cerium (Ce) anomaly. Its occurrence in REE patterns of sedimentary rocks has been identified as an indicator of anoxia (or absence of anoxia) in the bottom seawater or pore waters of the basin sediment (e.g. Wright et al. 1987; Bau and Dulski, 1996; Reynard et al. 1999). Nevertheless, it must be used with caution in paleoenvironmental interpretations: a negative Ce anomaly is a strong indicator of an oxic depositional environment, but the lack of a Ce anomaly or a positive Ce anomaly indicate reductive, anoxic conditions, which also may reflect solely the pore water anoxia (Kemp and Trueman, 2003; Johannesson et al. 2006; Planavsky et al. 2009). REE patterns can also serve as indicators of water salinity. Modern seawater REE patterns are known to display negative Ce anomalies, and enrichment in HREE (see de Baar et al., 1991), while flat REE profiles suggest fresh groundwater (cold) or riverine environments (Yuan et al 2014), and positive La anomalies have been reported in rivers (Kulaksiz and Bau, 2011). However, it is important to emphasize that a fossil dental tissue REE record can be interpreted as a proxy for the
palaeoenvironment only if it can be demonstrated that the late diagenetic contribution of REE is relatively minor (e.g. Reynard et al. 1999; Trueman 1999; Patrick et al. 2004; Fadel et al., 2015; Žigaitė et al. 2013; 2015).

In this work we analysed dental tissues of early vertebrate microremains from the Lower Devonian basin of Andrée Land (Svalbard), in an attempt to retrieve geochemical information about their early depositional environment and potential reworking. Two different localities of marginal marine to freshwater sediments from geographically distant parts of the same Grey Høek Formation were sampled. To be able to identify potential taxonomic, histological, and taphonomic variables of the REE uptake, we have chosen vertebrate microfossils with two contrasting types of histology: thelodont scales and probable ?chondrichthyan scales (see also Žigaitė 2013a,b). REE analyses have been performed in-situ, using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), in order to obtain intra-tissue compositions, which required micrometer-scale spatial resolution. The measured REE values are explored below using basic geochemical calculations and quantifications, with the aim of identifying the presence of reworking and the nature of early-burial palaeoenvironmental conditions.

Geological setting and material

The thelodont and ?chondrichthyan scales used in this study come from the Andrée Land territory in the northern part of Spitsbergen Island, Svalbard archipelago. Stratigraphically the material originates from the Lower Devonian Old Red Sandstone succession referred to as the Andrée Land Group (Blomeier et al. 2003), and represents deposition in a continental rift basin along the northern margin of the Old Red Sandstone (ORS) landmass. The succession is essentially confined
to a major graben with a unique depositional history, involving a shift from coarse
clastic red-beds, mainly of alluvial fan and fluvial origin, to a series of more greyish
fluvial and possibly deltaic sediments illustrating the transition from the southern arid
zone to the equatorial tropics. The nature of the basin and the palaeoenvironmental
conditions are as yet poorly understood, although it plays an important role as a
regional niche and separate biogeographical province in the Early Devonian.

Vertebrate microfossils are quite common in the Andrée Land deposits, and
include isolated micromeric elements of the dermal exoskeleton (dental scales or
dermal denticles, see Žigaitė et al. 2013b) of acanthodians, chondrichthians, and
thelodonts (Ørvig 1969; Blieck et al. 1987; Blom and Goujet 2002; Žigaitė et al.
2013a). Scales analysed comprise two taxa, the thelodont *Talivalia svalbardia* and
an undescribed probable *?chondrichthyan*, both of which come from the Grey Hœk
Formation in the upper part of the Andrée Land Group succession. The Formation is
Early to Middle Devonian in age, and consists mainly of grey and black sandstones
and siltstones, interbedding with calcareous claystones and siltstones with carbonate
nodules (Blomeier et al. 2003). It is subdivided into three lithographical units: the
Verdalen, Skamdalen and Tavlefjellet members (Blomeier et al. 2003; Volohonsky et
al. 2008). Scales of *T. svalbardia* come from the two latter members: the
Gråkammen locality, Skamdalen member, which represents the Lower Grey Hœk
Formation, and the Tavlefjellet locality, Tavlefjellet member, which represents the
Middle Grey Hœk Formation (Žigaitė et al. 2013a). The *?chondrichthyan* scales
originate from the Gråkammen locality (Žigaitė et al. 2013a). Material used for this
study was obtained from the palaeontological collections of the Paris National
Natural History Museum (Museum national d'histoire naturelle), France.

**Sampling and analytical techniques**
Considering the nature of *in-situ* microanalyses, we have chosen to analyse only post-pectoral scales of the thelodonts, and ‘body’ scales of chondrichthyans, which are the most common in the dermal exoskeleton of these taxa, and as a result, the most abundant microremains in the fossil record. Post-pectoral scales are also less fragile than other types of thelodont scales, such as cephalo-pectoral, precaudal and pinnal scales (e.g. Žigaitė and Goujet, 2012; Žigaitė 2013), which facilitate the process of grinding and polishing. Preparation of the samples was conducted in the Imaging and Analysis Center (Natural History Museum of London), apart from the extraction of the microremains by mechanical and acetic acid preparation of calcareous sandstones, and transmitted light microscopy, which were performed at the Paris National Natural History Museum (Museum national d'Histoire naturelle).

Prior to analyses, two-dimentional (2-D) sections of the scales were obtained from vertical anterior – posterior cuts along the longitudinal axis of dental scales (Fig. 2). The scales were embedded in araldite epoxy resin (Buehler epoxy resin with a mix of 50g of resin to 1 g of hardener), and prepared through a series of grinding and polishing steps similar to the protocol described in Pérez-Huerta and Cusack (2009), with a final 5 min treatment of 0.06 µm colloidal silica. Finally, samples were cleaned in an ultrasonic bath and dried at room temperature.

**Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)**

The compositions of trace and rare earth elements (REE) were obtained by LA-ICPMS at the Imaging and Analysis Center of Science Facilities Department, the Natural History Museum, London (UK). Analyses were performed using a New Wave Research NWR193 193nm excimer laser ablation accessory coupled to an Agilent Technologies 7500cs ICP-MS. Data were acquired for 120s at each analysis site, taking individual points in different scale tissue regions (dentine or enameloïd). Background signals were collected for the first ca 60s and the laser fired at the sample to collect sample signals for the remaining acquisition time. Data were collected using the time resolved method and were processed offline using
LAMTRACE software (Simon Jackson, Natural Resources, Ottawa, Canada).

Elemental concentrations were calculated using the National Institute of Standards and Technology (NIST) standard reference material 612 for calibration and calcium was used for internal standardization. The limit of detection was taken as 1σ of the mean background count, and the data filtered at twice this limit (2σ). Calculated precision was better than 3% RSD (at 1σ error) when using 43Ca as internal standard. The REE concentrations were measured in parts per million (ppm), see Table 1, and were normalized to both Orgueil (CI chondrite) concentrations (Palme and Jones 2005), and to Post-Archean Australian Shale (PAAS) concentrations (McLennan 1989). For the calculations in this work we used shale-normalised (PAAS) values, since as a sedimentary rock it represents closer overall REE concentrations, and is commonly applied in fossil bio-mineral studies (see Kemp and Trueman 2003; Pucéat et al. 2004; Trotter and Eggins 2006; Tütken et al. 2008; Kocsis et al. 2010; Herwartz et al. 2013b).

Results

REE compositions were quite distinct between the two localities and different taxa, but showed uniform values within each taxon and within each dental tissue analysed (Fig 3, A-D). Offsets in absolute REE concentrations were visible between thelodont dentine and enameloid, dentine REE values being distinctively higher (Fig.3,A,C). Unlike thelodonts, the chondrichthyan scales did not display any significant inter-tissue variability of the REE abundances, except for a variable degree of Eu depletion correlated with different types of tubular dentine (see Žigaitė et al., 2013b) (Fig.2; Fig.3,B). In addition, the overall REE concentrations of the chondrichthyan scales were greater than those of the T. svalbardia scales from the same locality (Gråkammen, Fig.3,D). Only the Lanthanum (La) concentrations in both T. svalbardia and chondrichthyan scales were similar, ranging from 100 to 180 ppm,
while all the other REE concentrations and normalised abundances were 3 to 10 times greater in the chondrichthyan scales, if compared to the thelodonts (Fig.3,A,B,D).

**REE abundance patterns**

Addressing the aforementioned inter-tissue discrepancies in absolute concentrations of REE, we have used shale-normalized REE values to produce tissue-selective plots for each studied scale. The resulting REE abundance patterns revealed significant differences between the two localities, Tavlefeljet and Gråkammen, and between the two different taxa from the Gråkammen locality. Chondrichthyan REE patterns were “bell-shaped”, displaying the enrichment in medium rare earths (MREE) (Fig.2,A,B), similar to more moderate “bell-shaped” patterns of *T. svalbardia* from Tavlefeljet. *T. svalbardia* from Gråkammen had flat profiles, and much lower overall REE concentrations (Fig.2,A,C). At the same time, REE patterns of *T. svalbardia* from both Tavlefeljet and Gråkammen displayed significant positive Europium (Eu) anomalies (Fig.2,A,C), compared to the chondrichthyan scales from Gråkammen, the REE patterns of which did not show any positive Eu anomaly, but on the contrary a negative one of a lesser degree (Fig.2,B).

**REE ratios**

We have calculated ratios for the Cerium (Ce) anomaly ([(Ce/Ce*)=Ce/(0.5La+0.5Pr)]$_{SN}$ where SN refers to Shale Normalised) and the Praseodymium (Pr) anomaly ([(Pr/Pr*)=Pr/(0.5Ce+0.5Nd)]$_{SN}$) in an attempt to reveal the redox potential of the bottom waters and sediment pore waters (after Bau and Dulski 1996). The ratios of *T. svalbardia* thelodont scales from the Tavlefeljet locality lacked both Ce and La anomalies (Fig.4, field I), whereas *T. svalbardia* from Gråkammen locality displayed a positive La anomaly (Fig.4, field IIa). The ratios of the chondrichthyan scales from Gråkammen were very uniform, plotting outside the fields of positive Ce or positive La anomalies (Fig. 4).
Discussion

Our results suggest that the REE concentrations and normalized abundance patterns obtained from early vertebrate microremains do reflect the taphonomic conditions and early diagenetic history. The REE compositions do not show any specific taxonomic behavior, but have visible inter-tissue differences reflecting the biomineral structure and compactness of the studied hard tissues. In the Gråkammen locality, two different diagenetic settings for the thelodonts and chondrichthians can be suggested from the presence of a positive Eu anomaly in *T. svalbardia* but not in the ?chondrichthyan scales. The reduced Eu$^{2+}$ of the pore waters is known to partition strongly into calcite producing a positive Eu anomaly, which leaves pore waters depleted in Eu leading to negative Eu anomalies (Trueman et al., 2003). Positive Eu anomalies are quite unusual in sediments, however, its presence in fossil bioapatite would suggest locally reducing conditions, most likely caused by the microbial decomposition of organic matter (Trueman et al., 2003; Fadel et al., 2015). In oxidized environments, the Eu is present as a trivalent cation (Eu$^{3+}$) non soluble in water, while in a reductive environment, the bivalent form (Eu$^{2+}$) is mobile and can be transported by diagenetic pore waters. The pore water enriched in Eu$^{2+}$ can reprecipitate under low oxygen content and create a positive Eu anomaly. This process is rare but has been reported in Pleistocene muds of the Amazon deep-sea fans and in a few other similar depositional environments (MacRae et al. 1992). The rarity of these processes of dissolution and reprecipitation, however, suggests that Eu anomalies cannot alone be used to assess the reductive or oxidizing conditions (Martinez-Ruiz et al. 1999), but can indicate the difference in diagenetic histories, as in our case between the chondrichthyan and thelodont microremains, originating from the same locality (Fig.2,A,B).

The shapes of the REE patterns are known to reflect certain palaeoenvironmental conditions (e.g. Reynard et al. 1999; Trueman & Turros, 2002; Patrick et al., 2004; Ounis et al., 2008; Bright et al., 2009). The MREE enriched, or
“bell-shaped” REE patterns are most common and typical for Palaeozoic ichthyoliths, such as conodonts and fish remains (e.g. Wright et al., 1987; Trotter & Eggins, 2006; Bright et al., 2009), and are suggested to arise from the equilibrium fractionation between seawater and biogenic apatite, serving as an indicator of marine environment in Palaeozoic (e.g. Wright et al., 1987; Trueman & Tuross, 2002). This assumption is made in spite of the fact that MREE enrichment is not observed in modern oceanic waters (e.g. Byrne & Sholkovitz, 1996), a discrepancy that is attributed to major differences in oceanic water chemistry before and after the Cretaceous (e.g. Picard et al., 2002; Bright et al., 2009). On the other hand, MREE enriched “bell-shaped” patterns of fossil bioapatites have been often explained as a result of extensive, late diagenetic REE uptake, predominately via preferential substitution of Ca\(^{2+}\) with MREEs (e.g. Raynard et al., 1999; Lécuyer et al., 1998; 2004). However, it has been shown in a number of studies, that the authigenic phosphate precipitates become enriched in MREE already during the early diagenesis (Bryne et al., 1996; Rasmussen et al., 1998).

The REE patterns of the *T. svalbardia* from Tavlefjellet, as well as of the ?chondrichthyan from the Gråkammen locality (Fig. 2,C,B) are both MREE and slightly HREE enriched, showing clear “bell-shaped” REE patterns. This is however not the case for the *T. svalbardia* from Gråkammen, which shows predominantly flat REE profiles, suggesting different taphonomic conditions, and – as long as the marine signature of the Palaeozoic “bell-shaped” patterns is accepted - potentially different habitats of these two different taxa from Gråkammen. However, in that case one would expect certain similarities between the patterns of *T. svalbardia* in both localities, which, apart of the common pronounced positive Eu anomaly, are otherwise quite different (Fig. 2A,C). This gives evidence either for a geological age difference between the two taxa, implying stratigraphical reworking, or otherwise for long-distance reworking between distinct environments. The Gråkammen material of *T. svalbardia* shows low absolute REE concentrations with flattened REE profiles suggesting strong freshwater influence (see Kulaksis and Bau, 201; Yuan et al., 2014). This matches the non-marine origin of the sedimentary sequence at the locality (Blomeier et al., 2003). By contrast, the ?chondrichthyan scales from Gråkammen
have higher overall REE levels and an REE profile that suggests deposition in a marine environment. This could be interpreted as reflecting reworking of the ?chondrichthyan scales from an original marine depositional environment followed by redeposition of these scales in the non-marine sequence of Gråkammen. However, the above interpretation can be justified only if we consider early uptake of the REE for both taxa, and therefore their profiles to reflect the early depositional palaeoenvironment.

The (Ce/Ce*)_{SN} ratio calculations revealed no presence of a Ce anomaly in any of the studied scales (Fig.4), which might be indicative of slightly anoxic conditions during the REE uptake, and accords with the above discussed Eu anomaly. The *T. svalbardia* from Gråkammen locality displayed positive La anomaly, which together with flattened REE profiles suggest a freshwater, possibly riverine environment (e.g. Kulaksis and Bau, 2011). This, in addition to the difference in the shapes of the REE patterns, as well as Eu anomaly (Fig. 3,D), would suggest reworking and certainly separate diagenetic histories for the two taxa from Gråkammen.

To conclude, the REE geochemistry in studied Lower Devonian early vertebrate microremains proves to be a useful proxy for determining reworking in vertebrate microfossil assemblage as deep in time as the Early Devonian, and to a certain extent is suggestive of palaeosalinity and palaeoredox conditions of the bottom water. It is important to add that separate hard tissues, particularly thelodont dentine and enameloid, show notable quantitative offsets in overall REE concentrations, and, in the case of the ?chondrichthyans, even minor qualitative inter-tissue differences. This emphasises the importance of selected *in-situ* measurements when analysing fossil biominerals, if we want to obtain sound geochemical proxies.

**Acknowledgments**
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References


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Figure Captions:

Table 1: Shale normalised (PAAS) REE values and Ce/Ce* and Pr/Pr* ratios for the studied scales. PAAS values were taken from McLennan (1989): 38.2 (La), 79.6 (Ce), 8.83 (Pr), 33.9 (Nd), 5.55 (Sm), 1.08 (Eu), 4.66 (Gd), 0.774 (Tb), 4.68 (Dy), 0.991 (Ho), 2.85 (Er), 0.405 (Tm), 2.82 (Yb), 0.433 (Lu). Equations used for the calculation of ratios: Ce/Ce* = [Ce/(0.5La + 0.5Pr)]_{SN}. Pr/Pr* = [Pr/(0.5Ce + 0.5Nd)]_{SN} (after Bau and Dulski, 1996).

Fig. 1: Map and stratigraphical framework of Andrée Land, Spitsbergen indicating the localization of the different samples.

Fig 2: Laser ablation ICP-MS analysis spots: analysed dermal scale sections of (A) *Talivalia svalbardia* from Gråkammen locality, four (=4) datapoints; (B) *Talivalia svalbardia* from Tavlefjellet locality, seven (=7) datapoints, and (C) the ?chondrichthyan from Gråkammen locality, eight (=8) datapoints. Total of nineteen (=19) datapoints, for histological definition and numbering see Table 1. Scale bars = 0.2 mm.

Fig. 3: Shale normalised (PAAS) REE abundance patterns of (A) *Talivalia svalbardia* scales from Gråkammen locality, (B) ?chondrichthyan scales from Gråkammen locality, (C) *Talivalia svalbardia* scales from Tavlefjellet locality. For A and C, solid lines represent dentine datapoints, dashed lines – enameloid; for B, solid lines represent thick tubule dentine datapoints, dashed lines – thin tubule dentine. (D) Comparison of the three taxa, enameloid and thin tubule dentine datapoint only. For clarity, solid lines in part D correspond to the T.svalbardia profiles (enameloid only), and dashed lines to the profiles of ?chondrichthyan (thin tubule dentine only).
Fig. 4: (Ce/Ce*)\textsubscript{SN} vs. (Pr/Pr*)\textsubscript{SN} diagram, where (Ce/Ce*)\textsubscript{SN} = \[\text{Ce}/(0.5\text{La} + 0.5\text{Pr})\]\textsubscript{SN}, and (Pr/Pr*)\textsubscript{SN} = \[\text{Pr}/(0.5\text{Ce} + 0.5\text{Nd})\]\textsubscript{SN}, ratio anomaly calculations for the two taxa, and two localities, using enameloid REE concentrations only. TAV- Tavlefjellet; GRÅ- Gråkammen. Field I: neither Ce\textsubscript{SN} nor La\textsubscript{SN} anomaly; field Ila: a positive La\textsubscript{SN} anomaly, no Ce\textsubscript{SN} anomaly; field IIb: a negative La\textsubscript{SN}, no Ce\textsubscript{SN} anomaly; IIIa: a positive Ce\textsubscript{SN} anomaly; field IIIb: a negative Ce\textsubscript{SN} anomaly. After Bau and Dulski, 1996.
Fig. 1: Map and stratigraphical framework of Andrée Land, Spitsbergen indicating the localization of the different samples.
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Fig. 3: Shale normalised (PAAS) REE abundance patterns of (A) Talivalia svalbardiia scales from Gråkammen locality, (B) ?chondrichthyan scales from Gråkammen locality, (C) Talivalia svalbardiia scales from Tavlefjellet locality. For A and C, solid lines represent dentine datapoints, dashed lines – enameloid; for B, solid lines represent thick tubule dentine datapoints, dashed lines – thin tubule dentine. (D) Comparison of the three taxa, enameloid and thin tubule dentine datapoint only. For clarity, solid lines in part D correspond to the T.svalbardiia profiles (enameloid only), and dashed lines to the profiles of ?chondrichthyan (thin tubule dentine only).

182x136mm (300 x 300 DPI)
Table 1. Shale normalised (PAAS) REE values and Ce/Ce* and Pr/Pr* ratios for the studied scales. PAAS values were taken from McLennan (1989): 38.2 (La), 79.6 (Ce), 8.83 (Pr), 33.9 (Nd), 5.55 (Sm), 1.08 (Eu), 4.66 (Gd), 0.774 (Tb), 4.68 (Dy), 0.991 (Ho), 2.85 (Er), 0.405 (Tm), 2.82 (Yb), 0.433 (Lu). Equation used for ratios: Ce/Ce* = [Ce/(0.5La + 0.5Pr)]SN. Pr/Pr* = [Pr/(0.5Ce + 0.5Nd)]SN. (after Bau and Dulska, 1996).

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