

Rare earth elements (REEs) in vertebrate microremains from the upper Pridoli Ohesaare beds of Saaremaa Island, Estonia: geochemical clues to palaeoenvironment

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Abstract. Rare earth element (REE) compositions of *Nostolepis* sp. scales, spines, plates and tesserae from Ohesaare bone beds were measured by in situ microsampling using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The obtained REE concentrations, normalized to Post-Archean Australian Shale concentrations, were evaluated using basic geochemical calculations and quantifications. The REE compositions were nearly identical across all the morphotypes and histologies of *Nostolepis* microremains, showing flat REE patterns with slight depletion in heavy REEs. There was no visible enrichment in middle REEs, indicating good geochemical preservation of bioapatite and absence of any pronounced fractionated REE incorporation during later stages of diagenesis. The shale-normalized (La/Yb)_{SN} and (La/Sm)_{SN} REE ratio compilations indicated adsorption as the dominating REE uptake mechanism across all datapoints. The absence of well-defined Ce anomaly suggested oxic palaeoseawater conditions, which agrees with the existing interpretations of the Ohesaare sequence as high-energy shoal and regressive open ocean sedimentary environments.

Key words: rare earth elements, palaeoenvironment, *Nostolepis*, Ohesaare, Silurian.

INTRODUCTION

Rare earth element (REE) concentrations in biogenic apatites, including fossil bones, teeth and fish scales, have been used to infer palaeoseawater chemistry and redox conditions (e.g., Wright et al. 1987), to detect reworking of fossils (e.g., Trueman 1999; Suarez et al. 2010), and to accomplish or test palaeoenvironmental and palaeogeographic interpretations (e.g., Reynard et al. 1999; Trueman & Tuross 2002; Kemp & Trueman 2003; Lécuyer et al. 2004; Patrick et al. 2004; Ounis et al. 2008). This can be achieved since the major part of the REEs and other trace elements are incorporated in bioapatite *post-mortem*, directly from the bottom seawater and sediment pore water with little or no fractionation, usually within a few thousand years during early stages of diagenesis (Bernat 1975; Wright et al. 1984; Ederfield & Pagett 1986; Trueman & Tuross 2002; Kemp & Trueman 2003; Patrick et al. 2004; Tütken et al. 2008; Trueman et al. 2011). Bioapatites display REE patterns that are strictly similar to the seawater patterns,

with an enrichment factor of about 10^6 to 10^7 , which is achieved through quantitative intake of REEs (with no associated fractionation) and is active as a rule for all biogenic phosphates at the seawater–sediment interface (Reynard et al. 1999). However, the preservation of this palaeoceanographic signal in marine vertebrate remains depends on the presence and extent of later, fractionated REE uptake during post-depositional recrystallization, or ‘extensive diagenesis’ (Reynard et al. 1999; Lécuyer et al. 2004). This late diagenetic effect is characterized by a strong middle REE (MREE) enrichment relative to light REEs (LREEs) and heavy REEs (HREEs). It leads to ‘bell-shaped’ patterns and is often explained as the effect of extensive re-crystallization (Lécuyer et al. 1998, 2004), which may no longer preserve early diagenetic REE signal reflecting depositional palaeoenvironment. Recently, Herwartz et al. (2011) have demonstrated that in most cases vertebrate bioapatite showed open system behaviour with respect to REE and Hf uptake, which would compromise the REEs as a tool for palaeoenvironmental reconstructions (Herwartz et al. 2013a),

as well as for ^{176}Lu – ^{176}Hf radiometric dating (Herwartz et al. 2013b). However, these studies are based on vertebrate long bones, such as femura, humerus or ribs, which are composed of fine, nanometre-size plate-like crystallites and contain, with a large surface/volume ratio and significant amount, up to 20% organic phase and 5–10% water (Kohn et al. 1999; Enax et al. 2012). A large surface area to volume ratio of bone and dentine crystallites facilitates both the adsorption of REEs, and the substitution of original (primary) biomineral (e.g., Trueman 1999; Herwartz et al. 2013a). In our work, we use fossil bioapatite of dental tissues, such as enamel and enameloid, which is composed of compact and large crystallite (micrometre-sized) biomineral with as little as 1 wt% organic matter (Kohn et al. 1999; Sire et al. 2009; Enax et al. 2012) and in contrast to long bones, demonstrated high potential to preserve an early REE signal (Trueman & Palmer 1997; Kohn et al. 1999; Kemp & Trueman 2003; Trotter & Eggins 2006; Tütken et al. 2008; Trueman et al. 2011). Given the above, REE concentrations can serve as a record of depositional or early diagenetic conditions only as long as it is demonstrated that the later contribution of REEs such as from diagenetic pore fluids, is relatively minor (e.g., Reynard et al. 1999; Trueman 1999; Patrick et al. 2004) and the histology and crystallinity of fossil remains are taken into account (Žigaitė et al. 2013; Fadel et al. 2015).

The aim of this work is to test the potential of REE compositions of vertebrate microremains from Ohesaare beds as a source of geochemical information and proxy to early depositional palaeoenvironment. Ohesaare is a famous fish locality, known already since the pioneering work by C. Pander in 1856, who described shields of the heterostracan *Tolypelepis undulata*, plates of the osteichthyan *Lophosteus superbus* and a number of jaw bones of acanthodians (Pander 1856). In addition to well-preserved macroscopic vertebrate remains, the dermoskeleton microremains of a number of squamate early vertebrate species are extremely abundant in Ohesaare and form bone beds in several levels of the section (Nestor 1990; Märss & Nestor 2014). Scales and spines of different morphological groups and variable histologies of the genus *Nostolepis* have been selected for this purpose in order to compare data from fossil apatite biomineral of different hard tissue structure and crystallinity, while avoiding any potential inter-taxonomic bias.

Ohesaare beds represent the youngest Silurian sedimentary rocks in the entire Baltic area. Saaremaa was part of the Baltic palaeobasin in the Silurian, located in equatorial latitudes (Cocks & Torsvik 2005), and represents a wide range of tropical shelf environments with the accumulation of various calcareous deposits

and occurrence of rich and diverse biotas (e.g., Nestor & Einasto 1997; Hints et al. 2008; Männik 2014). Diverse and rich benthic fauna and intense bioturbations in the Ohesaare section indicate shallow nearshore environments. The presence of such trace fossils as *Cruziana* and *Skolithos* has led to interpretations that this part of the basin presumably had high hydrodynamic energy (Vinn & Wilson 2013; Vinn 2014). In this work we present results of the first REE analyses from fish microremains of this important early vertebrate site and the first quantitative interpretations of the REE data record as a proxy to palaeoredox conditions and palaeoenvironment.

GEOLOGICAL SETTING

The Ohesaare cliff section (Fig. 1) is one of the most famous and fossiliferous Palaeozoic localities in Estonia and is part of the Ohesaare Formation, Ohesaare Regional Stage. The presence of the conodont *Ozarkodina remscheidensis* allows us to correlate the Ohesaare Stage with the upper Pridoli and the following *Oulodus elegans detortus* conodont Biozone identifies it as the youngest Upper Silurian sequence in Estonia (Märss & Männik 2013; Männik 2014). It represents a carbonate platform succession of the high-energy open shoal and open shelf facies belts, characterized by intercalated thin-bedded limestones and marlstones formed during a considerable shallowing event (Hints et al. 2008; Vinn & Wilson 2013). These strata are rich in fossils, including macro- and microremains of agnathans and fishes, conodonts, diverse shelly fauna and associations of invertebrate microfossils, with intense bioturbation and *Skolithos* trace fossils (Nestor 1990; Vinn & Wilson 2013; Märss & Nestor 2014), altogether indicating shallow-water environment.

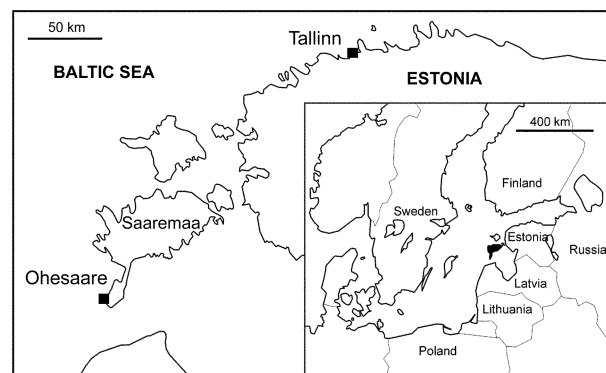


Fig. 1. Location of the Ohesaare cliff, Saaremaa Island, Estonia. Modified from Vinn (2014).

SAMPLING AND ANALYTICAL TECHNIQUES

Nostolepis sp. body scales, spines, coronate plates and stellate tesseræ were selected from samples collected in situ from the lower part of the Ohesaare cliff sequence. *Nostolepis* spines, coronated plates, stellated tesseræ and body scales were chosen for geochemical analyses, in order to cover the largest variability of bioapatite tissue histologies and morphological variety of microremains. Acetic acid preparation of the samples was carried out at the Department of Earth Sciences of Lund University, Sweden. Extraction of the microremains and mechanical preparation of each scale for geochemical analyses was performed at the Department of Earth Sciences and the Department of Organismal Biology (Uppsala University, Sweden) and at the Imaging and Analysis Center (Natural History Museum of London, UK). The elemental compositions were obtained by Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Imaging and Analysis Center of Science Facilities Department, Natural History Museum, London (UK). The LA-ICP-MS technique is widely used to determine in situ mineral elemental compositions and offers the necessary high spatial resolution enabling the analysis of REE and trace element compositions of micromeric scales in situ at a separate tissue level. Analyses were performed using a New Wave Research NWR193FX excimer laser ablation accessory coupled to an Agilent Technologies 7500s ICP-MS with an enhanced sensitivity S-option interface. Data were acquired for 120 s at each analysis site, taking individual points in different scale tissue regions (dentine or enameloid). Background signals were collected for the first ca 60 s and the laser was fired at the sample to collect sample signals for the remaining acquisition time. Data were collected using the time-resolved method and processed offline using LAMTRACE software (Simon Jackson, Macquarie University, Sydney). 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 were filtered at twice this limit (2σ). The calculated precision was better than 3% RSD (at 1σ error) when using ^{43}Ca as internal standard. The REE concentrations obtained were normalized to Post-Archean Australian Shale (PAAS) concentrations (LA-ICP-MS) of McLennan (1989). The obtained in situ REE compositions are explored below using basic geochemical calculations and quantifications in order to determine early burial palaeoenvironmental conditions. The analytical methods used in this study are similar to those used in Fadel et al. (2015).

RESULTS AND DISCUSSION

The shale-normalized REE patterns are nearly identical across all the morphotypes and histologies of *Nostolepis* scales and spines analysed and have relatively flat (unfractionated) shapes with slight depletion in HREEs (Fig. 2A–D). Low concentrations of HREEs are attributed to coastal or marginal marine environments, as opposed to the characteristic HREE-enriched profiles of the open ocean seawater (see Patrick et al. 2004). There is no visible enrichment in MREE (‘bell-shaped’ patterns), which suggests good preservation of the ‘early’ REE signal, with major REE incorporation mainly via adsorption mechanism and during early stages of diagenesis (Trueman & Tuross 2002; Lécuyer et al. 2004). The shale-normalized compilation diagram of $(\text{La}/\text{Yb})_{\text{SN}}$ and $(\text{La}/\text{Sm})_{\text{SN}}$ REE ratios defined by Reynard et al. (1999) equally suggests the REE incorporation predominantly occurred via adsorption (Fig. 3) as opposed to ‘late’ or ‘extensive’ diagenesis, where REE uptake is prevailed by substitution mechanism and re-crystallization of bioapatite. The $(\text{La}/\text{Yb})_{\text{SN}}$ and $(\text{La}/\text{Sm})_{\text{SN}}$ ratio compilation results are also very similar across all the scales and spines analysed, both between the separate scale species and between different histologies within a single scale, tessera or spine. The average $(\text{La}/\text{Sm})_{\text{SN}}$ ratio of all the *Nostolepis* microremains is 0.73, with 0.81 average ratio for spines, 0.67 for coronate plates, 0.63 for body scales and 0.69 for stellate tesseræ – all largely exceeding 0.3 and corresponding to early (unfractionated) REE uptake as defined by Lécuyer et al. (2004). The observed slightly higher $(\text{La}/\text{Sm})_{\text{SN}}$ ratio in the *Nostolepis* spines also implies their better geochemical preservation, which can be explained by the spine histology of particularly compact dentine biomineral (Valiukevičius & Burrow 2005).

Based on the ‘early’ REE record preservation concluded above, we have calculated and plotted the shale-normalized anomalies of cerium $(\text{Ce}/\text{Ce}^*)_{\text{SN}}$ and praseodymium $(\text{Pr}/\text{Pr}^*)_{\text{SN}}$ in an attempt to reveal the prevailing redox conditions (after Bau & Dulski 1996). The presence of Ce anomaly in fossil bioapatite REE record of ‘weak’ or ‘early’ diagenesis can define the bottom seawater and/or sediment pore water anoxia of marine palaeobasins (see Kemp & Trueman 2003). In the case of rapid sedimentation rates, such as the majority of marginal marine environments, the REE uptake is at large affected by REEs derived from sediment pore waters. In modern shelf seas, sediments are commonly anoxic from within few centimetres of the sediment–water interface, and continued uptake of REEs within this anoxic region would tend to obscure any negative Ce anomaly (oxic conditions) inherited at the sediment–

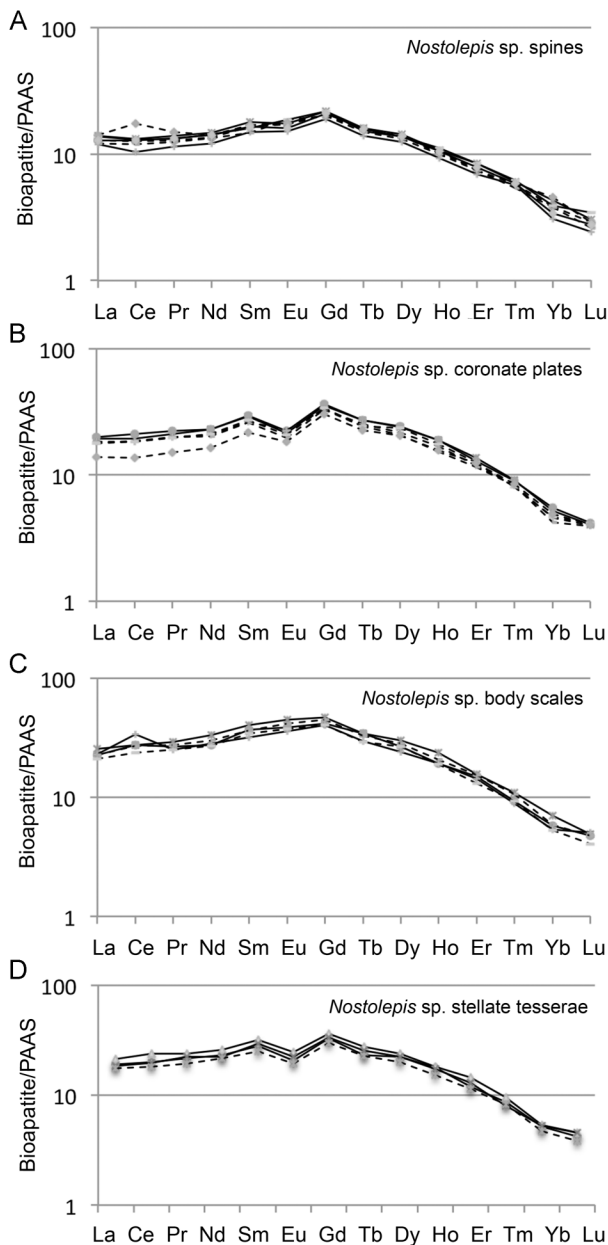


Fig. 2. Shale-normalized (PAAS) REE patterns, illustrating in situ datapoints for each studied thelodont species, obtained by LA-ICPMS: **A**, *Nostolepis* sp. spines; **B**, *Nostolepis* sp. coronate plates; **C**, *Nostolepis* sp. body scales; **D**, *Nostolepis* sp. stellate tesseræ. The PAAS values taken from McLennan (1989) as follows: 38.2 (La), 79.6 (Ce), 8.83 (Pr), 33.9 (Nd), 5.55 (Sm), 1.08 (Eu), 4.66 (Gd), 0.77 (Tb), 4.68 (Dy), 0.99 (Ho), 2.85 (Er), 0.41 (Tm), 2.82 (Yb) and 0.43 (Lu). Dashed lines indicate inner dentine datapoint series.

water interface (Kemp & Trueman 2003). Therefore, negative Ce anomalies in marine fossil bioapatite REE record do suggest oxic conditions in the water column and upper pore waters, but the lack of negative Ce

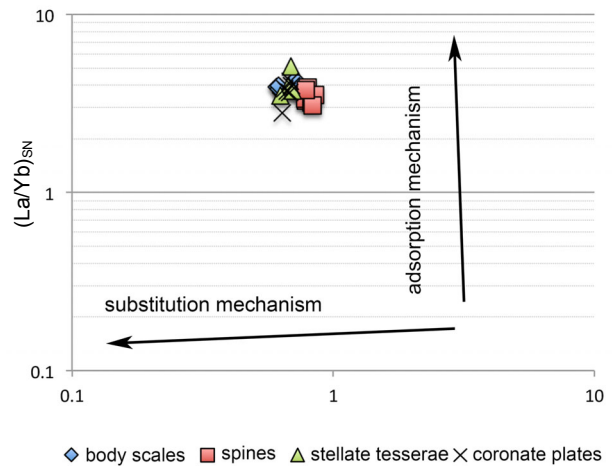


Fig. 3. Compilation of observed $(La/Yb)_{SN}$ vs $(La/Sm)_{SN}$ in microremains of *Nostolepis* sp. from the Ohesaare cliff: spines, scales and plates of different types. The arrows indicate potential shifts induced by fractionation associated with the adsorption (subvertical) and substitution (subhorizontal) mechanisms. After Reynard et al. (1999).

anomaly, or a positive Ce anomaly do not necessarily indicate seawater and/or bottom water anoxia.

In case of our data, there was no indication of Ce anomaly (Fig. 4). A few data points showed apparent positive Ce anomaly caused by a negative La anomaly (as defined by Bau & Dulski 1996), and one data point from the *Nostolepis* body scale showed a real positive Ce anomaly, likely reflecting pore water anoxia

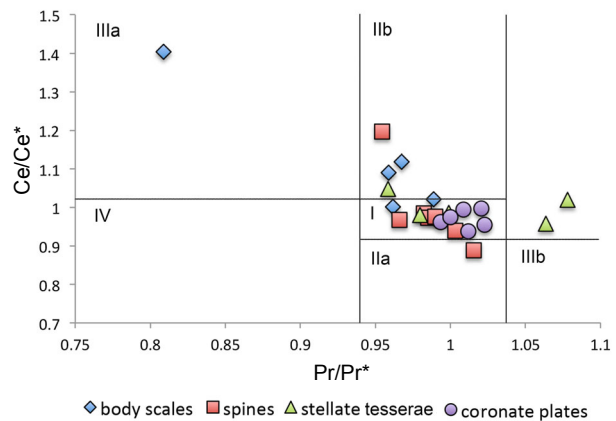


Fig. 4. Ce/Ce^* vs Pr/Pr^* diagram, where $Ce/Ce^* = 2Ce_{SN}/(La_{SN} + Nd_{SN})$ and $Pr/Pr^* = 2Pr_{SN}/(Ce_{SN} + Sm_{SN})$; Field I: no anomaly; IIa: a positive La-anomaly causes an apparent negative Ce-anomaly; IIb: a negative La-anomaly causes an apparent positive Ce-anomaly; IIIa: real positive Ce-anomaly; IIIb: real negative Ce-anomaly; IV: positive La-anomaly disguises positive Ce-anomaly. After Bau & Dulski (1996).

present in most of the depositional settings. These results indicate the absence of any pronounced palaeoseawater anoxia, suggesting oxic conditions, which in turn agrees with the existing sedimentological interpretations of Ohesaare bone beds representing high-energy shoal environment (Nestor 1990; Vinn & Wilson 2013; Vinn 2014).

CONCLUSIONS

Rare earth element compositions were nearly identical across all morphotypes and histologies of *Nostolepis* scales and spines analysed and showed flat (unfractionated) shale-normalized REE patterns with slight depletion in HREEs. No visible enrichment in MREEs indicated good geochemical preservation of bioapatite, with major REE uptake during the ‘early’ or ‘weak’ diagenesis likely via adsorption, with no pronounced fractionated REE incorporation during later stages of diagenesis. The shale-normalized $(La/Yb)_{SN}$ and $(La/Sm)_{SN}$ REE ratio compilation equally suggests that the REE uptake predominantly occurred via adsorption mechanism. There was no clearly defined Ce anomaly present in the analysed microremains, suggesting oxic seawater conditions, which does agree with sedimentological interpretations of Ohesaare beds referring to high-energy shoal palaeo-environment.

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