

## Palaeoenvironmental signatures revealed from rare earth element (REE) compositions of vertebrate microremains of the Vesiku Bone Bed (Homerian, Wenlock), Saaremaa Island, Estonia

Alexandre Fadel<sup>a,b</sup>, Živilė Žigaitė<sup>a</sup>, Henning Blom<sup>a</sup>, Alberto Pérez-Huerta<sup>c</sup>, Teresa Jeffries<sup>d</sup>, Tiiu Märss<sup>e</sup> and Per Erik Ahlberg<sup>a</sup>

<sup>a</sup> Subdepartment of Evolution and Development, Department of Organismal Biology, Uppsala University, Norbyvägen 18A, 752 36 Uppsala, Sweden; Zivile.Zigaite@ebc.uu.se

<sup>b</sup> Laboratoire Géosystèmes, Université Lille 1, CNRS UMR8217, Villeneuve d'Ascq 59655, France

<sup>c</sup> Department of Geological Sciences, University of Alabama, 2018 Bevill Building, Tuscaloosa, AL 35487, USA

<sup>d</sup> Earth Science Department, Imaging and Analysis Centre, The Natural History Museum, Cromwell Road, SW7 5BD London, UK

<sup>e</sup> Institute of Geology at Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

Received 16 July 2014, accepted 30 January 2015

**Abstract.** Rare earth elements (REEs) have been analysed from fossil vertebrate microremains (thelodont scales) from the Vesiku Bone Bed, Saaremaa, Estonia, using in situ microsampling by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Well-preserved scales of three species of the genus *Thelodus* (*T. carinatus*, *T. laevis* and *Thelodus* sp.) show very uniform REE patterns with slightly lower overall REE concentrations in enameloid than in dentine, with enrichment in middle REEs, depletion in heavy REEs and pronounced negative europium anomaly, but no cerium anomaly. The results of this study suggest a similar diagenetic history and possibly contemporaneous habitats for all three *Thelodus* species, as well as possible suboxic to anoxic conditions of the bottom and pore waters during the formation of the Vesiku Bone Bed.

**Key words:** Vesiku Bone Bed, rare earth element, REE, palaeoenvironment, thelodonts, Silurian.

### INTRODUCTION

The rare earth element (REE) composition of fossil bioapatite has been recognized as an important source providing geochemical information about the palaeoenvironmental settings, and depositional and diagenetic history of different vertebrate assemblages (e.g. Wright et al. 1987; Reynard et al. 1999; Trueman & Tuross 2002; Lécuyer et al. 2004; Tütken et al. 2008). The concentrations and patterns of REEs and trace elements can be used to reconstitute the early burial conditions and to recognize reworked specimens within fossil assemblages. They indicate the extent of biomineral geochemical alteration of specimens during diagenesis, and, in some cases, are used as a proxy for ancient seawater conditions (e.g. Kohn et al. 1999; Kemp & Trueman 2003; Suarez et al. 2010; Herwartz et al. 2011; Trueman et al. 2011). The REE and trace element concentrations in fossil bioapatite are exclusively diagenetic, since these elements are not important for the metabolic processes of vertebrates and are present in very low concentrations in modern fish bones and teeth (e.g. Ederfield & Pagett 1986; Vennemann et al. 2001).

Nevertheless, REEs can get incorporated directly from the seawater during early diagenesis, with little or no fractionation, and therefore have potential to reflect bottom and pore-water chemistry of a given palaeobasin (see Wright et al. 1987; Kemp & Trueman 2003). In this way their concentrations can be used to infer an early burial palaeoenvironment (e.g. Lécuyer et al. 2004).

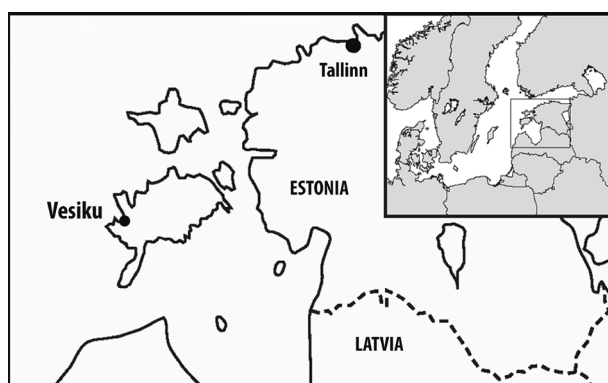
Vesiku is a famous late Wenlock vertebrate locality on the western coast of Saaremaa Island, Estonia, which represents shallow-water lagoonal and shoal facies belts with a large and important taxonomic variety of well-preserved early vertebrates (Nestor 1997; Blom et al. 2002; Märss 2003; Männik 2014). However, many aspects of the depositional environment and taphonomic history of this important vertebrate site remain poorly understood. Mainly, there is a lack of geochemical data from vertebrate fossils, which may reveal the depositional conditions of the bone bed and, by inference, provide insights into vertebrate palaeoecology. The aim of this work is to use REE geochemistry of fossil vertebrate apatite in an attempt to reveal the palaeoenvironmental conditions and depositional history of the Vesiku Bone Bed, and by inference, provide insights into vertebrate palaeoecology.

We analyse thelodont microremains (dermal scales) from the Vesiku Bone Bed by selecting triplicates of body scales of three different species which belong to the genus of *Thelodus* (in case of *Thelodus* sp., it has resemblance to *Oeselia mosaica* (Märss 2005); however, it has not been described yet in Vesiku, and as taxonomy is not among the aims of this article, we leave it in the genus *Thelodus*, as in Märss 1986), in order to be able to assess possible variation in REE signatures between different specimens. This allows us to determine the possibility of different taphonomic histories and reworking, and to avoid any large morphological and/or histological differences that may also potentially bias biomineral susceptibility and rates of REE uptake.

## SAMPLING AND ANALYTICAL TECHNIQUES

The thelodont scales used in this study were collected from the bone bed at the Vesiku outcrop, west coast of Saaremaa Island (Fig. 1). The Vesiku Beds represent the upper part of the Rootsiküla Formation (Rootsiküla Regional Stage), Homerian, Wenlock, lower Silurian. Acetic acid preparation of the samples was carried out at the Department of Earth Sciences of Lund University, Sweden. Mechanical extraction of the microremains and preparation of each scale for geochemical analyses were conducted 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). Scales of three thelodont species, *Thelodus carinatus*, *T. laevis* and *Thelodus* sp., were chosen for geochemical analyses, nine scales in total (triplicates for each species). 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 as it offers the high spatial resolution necessary for analysis of REE and trace element compositions of micrometre-sized scales in situ and at separate tissue levels. The analyses were performed using a New Wave Research UP213AI 213 nm aperture imaged laser ablation accessory coupled to a Thermo Elemental PQ3 ICP-MS with an enhanced sensitivity S-option interface. Data were acquired for 120 s at each analysis site by 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 rest of acquisition time. Data were collected using the time-resolved method and were processed offline with LAMTRACE software (Simon Jackson, Macquarie University, Sydney). Element concentrations were calculated using the National Institute of Standards and Technology (NIST) standard reference material 612 for calibration and calcium for internal standardization. The limit of detection was  $1\sigma$  of the mean background count, and the data were filtered at twice this limit ( $2\sigma$ ). The calculated precision was better than 3% RSD (at  $1\sigma$  error) when using  $^{43}\text{Ca}$  as internal standard. The element compositions were measured in parts per million (ppm), the  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{MnO}$  and  $\text{FeO}$  oxides in weight per cent (wt%). The REE concentrations obtained were normalized to Post-Archean Australian Shale (PAAS) concentrations of McLennan (1989). The obtained in situ REE compositions are explored below using basic geochemical calculations and quantifications in order to determine early burial environmental conditions. The analytical techniques used here are similar to those employed in Žigaitė et al. (2015).

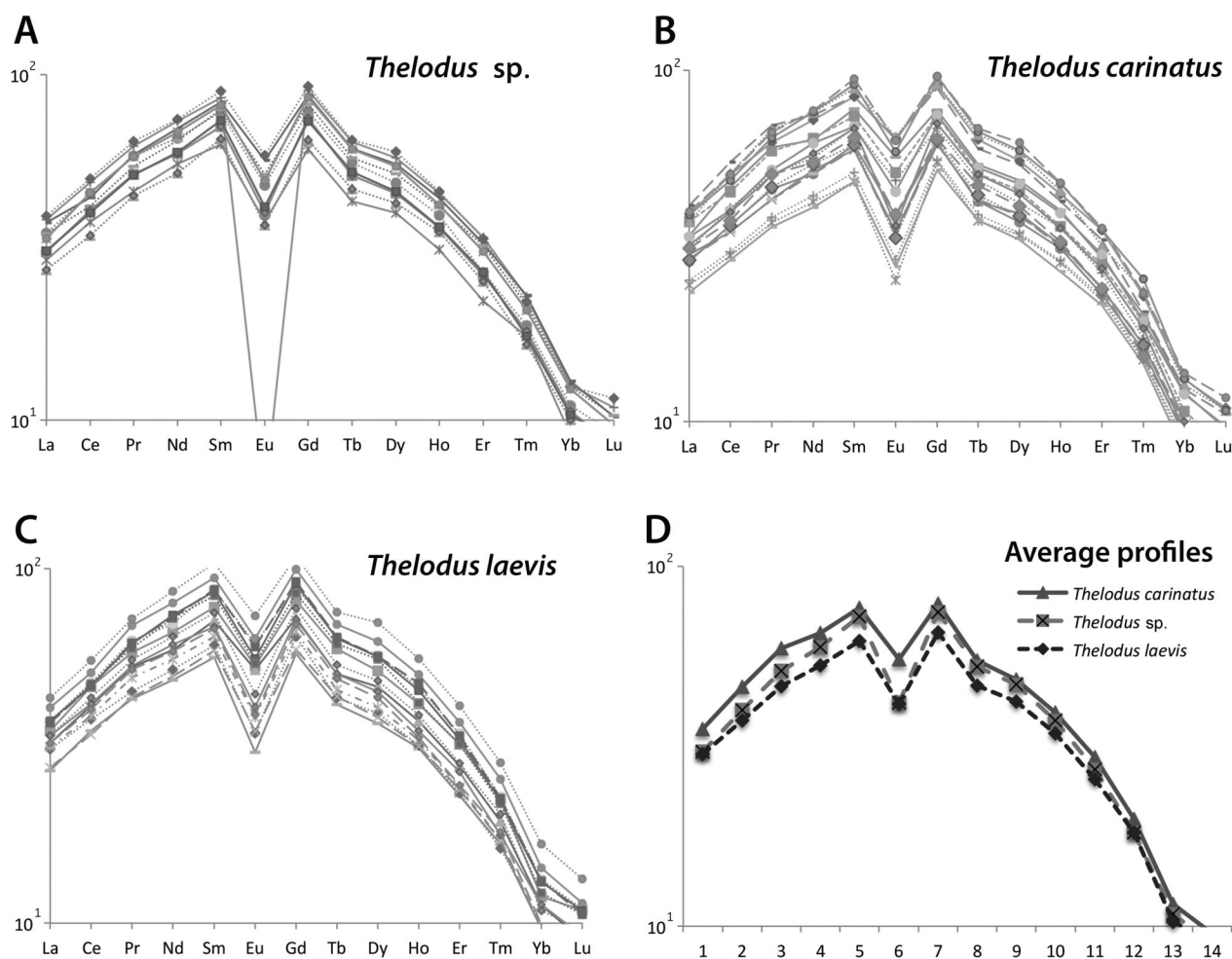


**Fig. 1.** Location of the Vesiku Brook outcrop, Saaremaa Island, Estonia. Modified from Märss & Männik (2013).

## RESULTS AND DISCUSSION

The REE and trace element compositions were very uniform in all scales of the studied thelodont species and revealed no significant variation in the composition among different tissues of each scale (Fig. 2A–C). However, the REE concentrations in dentine and basal tissues were usually slightly higher than those in enameloid. This can be explained by scale histology (higher porosity and higher organic content) and crystallinity (smaller crystallites), both of which make dentine more susceptible to REE uptake.

The trace element compositions were equally uniform among the scales: MnO contents almost never exceeded 0.01 wt% in all scales analysed, FeO was below



**Fig. 2.** Shale-normalized (PAAS) REE patterns, illustrating in situ datapoints for each studied thelodont species, obtained by LA-ICPMS: **A**, *Thelodus* sp.; **B**, *T. laevis*; **C**, *T. carinatus*; **D**, averaged REE profiles of the three species. 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).

0.2 wt% in most of the *Thelodus carinatus* and *T. laevis* scales, but was significantly lower in *Thelodus* sp. scales (<0.05 wt%), with the exception of one most mature *T. laevis* body scale with an open plan pulp cavity (<0.5 wt%), which also had distinctly higher Mn and Fe oxide concentrations in the basal part of the scale: 0.05 wt% for MnO and 0.3–0.8 wt% for FeO. Strontium concentrations were quite uniform in different scales, species and tissues, ranging from 1690 to 3200 ppm, with an average of 2200 ppm.

The shale-normalized REE patterns showed relative enrichment in intermediate or middle REEs (MREEs) in all scales analysed, with the exception of europium (Eu), and pronounced depletion in heavy REEs (HREEs) (Fig. 2A–D). The shapes of the REE patterns have been interpreted as indicators of certain palaeoenvironmental

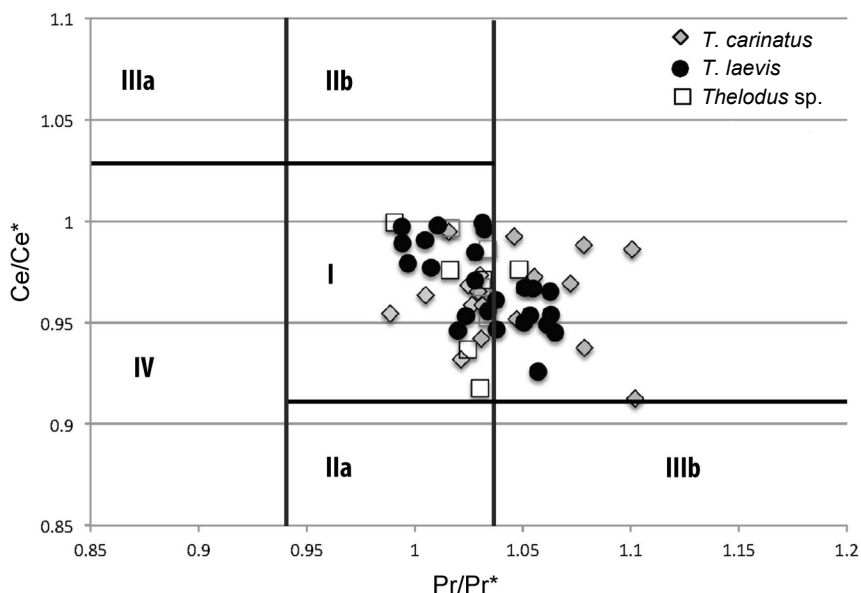
conditions (e.g. Lécuyer et al. 2004; Patrick et al. 2004): the light REE-(LREE)-enriched patterns as typical of coastal environments, the MREE-enriched patterns as indicators of estuarine or closed marine conditions and the HREEs enrichment patterns corresponding to open ocean. However, each of the above shall be taken into account carefully (see Trueman & Tuross 2002): enrichment in MREEs, the so-called ‘bell-shaped’ pattern, is characteristic of most of the post-Cretaceous and Palaeozoic ichthyolith and conodont bioapatite (e.g. Wright et al. 1987; Reynard et al. 1999) and has been reported to reflect equilibrium fractionation between the biogenic apatite and the slightly anoxic or suboxic bottom seawater of that time (see Patrick et al. 2004). At the same time, pronounced ‘bell-shaped’ REE patterns have also been explained as the effect of

extensive, late diagenetic re-crystallization (e.g. Lécuyer et al. 2004), where REE uptake has been dominated by substitution, suggesting that the geochemical record does not suit for further palaeoenvironmental reconstructions. Kocsis et al. (2010) and Trueman et al. (2011) concluded open system behaviour and special fractionation of REEs in fossil long bones, however, excluding tooth enamel and other dense biapatites and emphasizing their potential in palaeoenvironmental and even geochronological studies. The quantitative REE incorporation without fractionation has been reported as a major factor in fossil fish dental biapatite during early diagenesis, including Palaeozoic fossils (Reynard et al. 1999). In this way, despite the ambiguities discussed above, the REE patterns of our studied thelodont scales, enameloid in particular, still have a potential to reflect the original early burial conditions, and hence the REE composition of the sediment surface fluids, helping to characterize the depositional palaeoenvironment (see Ounis et al. 2008).

Redox reactions do affect cerium (Ce) and europium (Eu) (see Patrick et al. 2004). The Ce anomaly calculations, proposed by Bau & Dulski (1996), involve ratios of Ce [ $Ce/Ce^* = 2Ce/(La + Pr)_{SN}$  (where SN refers to shale-normalized) and praseodymium (Pr) [ $Pr/Pr^* = 2Pr/(Ce + Nd)_{SN}$ ], which, if combined independently, can reveal the palaeoredox conditions (see

also Patrick et al. 2004; Ounis et al. 2008; Bright et al. 2009). Negative Ce anomalies are strong indicators of an oxic depositional environment (often followed by HREE enrichments and attributed to open ocean environments), while lack of Ce anomaly or positive Ce anomaly (together with LREE- to MREE-enriched profiles) would suggest anoxic conditions. Yet, the latter interpretation must be used with caution while drawing palaeoenvironmental conclusions, particularly as Ce concentrations may reflect solely the pore water anoxia (Kemp & Trueman 2003). In all studied microremains there was no evidence of detectable Ce anomaly (Fig. 3), suggesting possible existence of anoxic or suboxic bottom and pore waters during the formation of the Vesiku Bone Bed.

The reduced  $Eu^{2+}$  of pore waters is known to partition strongly into calcite (producing a positive Eu anomaly), leaving pore waters depleted in Eu, and thus biapatite in these conditions acquires a negative Eu anomaly (Trueman et al. 2003). In this way the presence of Eu anomalies within fossil biapatite implies locally reducing conditions, most likely caused by the microbial decomposition of organic matter (Trueman et al. 2003). The negative Eu anomaly, well expressed in all of our studied scales (Fig. 2D), therefore not only indicates similar diagenetic history and possibly contemporaneous habitats for all the three thelodont species, but also



**Fig. 3.**  $Ce/Ce^*$  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: positive La-anomaly causes apparent negative Ce-anomaly; IIb: negative La-anomaly causes 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).

suggests the uniform formation of the Vesiku Bone Bed under reducing conditions. This confirms the results and conclusions drawn above from the Ce anomaly, supporting the suboxic to anoxic conditions of the palaeobasin.

## CONCLUSIONS

The REE signatures in all studied scales of three thelodont species from the Vesiku Bone Bed show very uniform patterns with slightly higher REE concentrations in dentine than in enameloid. The shale-normalized REE patterns show relative enrichment in intermediate or middle REEs (MREEs) and pronounced depletion in heavy REEs (HREEs). There is no detectable Ce anomaly present in any of the scales and measured datapoints, which implies a suboxic or anoxic bottom and pore waters during the early stages of fossilization. The strong negative Eu anomaly characteristic of all scales confirms the presence of reducing conditions and indicates the uniform formation of the Vesiku Bone Bed and similar diagenetic history and common sedimentary environment for the remains of all three thelodont species, which could have existed contemporaneously.

**Acknowledgements.** We would like to thank Git Klintvik (Lund University, Sweden) for acid preparations of the samples and Donglei Chen (Uppsala University, Sweden) for help with the selection and identification of vertebrate microremains. We are particularly grateful to Kévin Lepot (Université Lille 1, France) and Laszlo Kocsis (University of Lausanne, Switzerland) for valuable discussions and advice, and Peep Männik and an anonymous reviewer whose remarks greatly increased the quality of our article. This research has been funded by the Knut and Alice Wallenberg Foundation grant awarded to Per Erik Ahlberg (Uppsala University, Sweden) and is a contribution to the UNESCO and IUGS International Geosciences Programme project IGCP 591 ‘Early to Middle Palaeozoic Revolution’.

## REFERENCES

- Bau, M. & Dulski, P. 1996. Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. *Pre-cambrian Research*, **79**, 37–55.
- Blom, H., Märss, T. & Miller, G. 2002. Silurian and lowermost Devonian birkenoid anaspids from the northern hemisphere. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **92**, 263–323.
- Bright, C. A., Cruse, A. M., Lyons, T. W., MacLeod, K. G., Glascock, M. D. & Ethington, R. L. 2009. Seawater rare-earth element patterns preserved in apatite of Pennsylvanian conodonts? *Geochimica et Cosmochimica Acta*, **73**, 1609–1624.
- Herwartz, D., Tütken, T., Münker, C., Jochum, K. P., Stoll, B. & Sander, P. M. 2011. Timescales and mechanisms of REE and Hf uptake in fossil bones. *Geochimica et Cosmochimica Acta*, **75**, 82–105.
- Ederfield, H. & Pagett, R. 1986. Rare earth elements in ichthyoliths: variations with redox conditions and depositional environment. *Science of the Total Environment*, **49**, 175–197.
- Kemp, R. A. & Trueman, C. N. 2003. Rare earth elements in Solnhofen biogenic apatite: geochemical clues to the palaeoenvironment. *Sedimentary Geology*, **155**, 109–127.
- Kocsis, L., Trueman, C. N. & Palmer, M. R. 2010. Protracted diagenetic alteration of REE contents in fossil bioapatite: direct evidence from Lu–Hf isotope systematics. *Geochimica et Cosmochimica Acta*, **74**, 6077–6092.
- Kohn, M. J., Schoeninger, M. J. & Barker, W. W. 1999. Altered states: effects of diagenesis on fossil tooth chemistry. *Geochimica et Cosmochimica Acta*, **63**, 2737–2747.
- Lécuyer, C., Reynard, B. & Grandjean, P. 2004. Rare earth element evolution of Phanerozoic seawater recorded in biogenic apatites. *Chemical Geology*, **204**, 64–102.
- Männik, P. 2014. The Silurian System of Estonia. In *4th Annual Meeting of IGCP 591, Estonia, 10–19 June 2014, Abstracts and Field Guide* (Bauert, H., Hints, O., Meidla, T. & Männik, P., eds), pp. 123–128. University of Tartu, Tartu.
- Märss, T. 1986. Silurian vertebrates of Estonia and West Latvia. *Fossilia Baltica*, **1**, 1–104.
- Märss, T. 2003. *Paralogania* from the Rootsiküla (Wenlock) and Paadla (Ludlow) stages of Estonia. *Proceedings of the Estonian Academy of Sciences, Geology*, **52**, 98–112.
- Märss, T. 2005. Thelodont *Oeselia mosaica* gen. et sp. nov. from the Wenlock and Ludlow of the East Baltic. *Proceedings of the Estonian Academy of Sciences, Geology*, **54**, 181–190.
- Märss, T. & Männik, P. 2013. Revision of Silurian vertebrate biozones and their correlation with the conodont succession. *Estonian Journal of Earth Sciences*, **62**, 181–204.
- McLennan, S. M. 1989. Rare earth elements in sedimentary rocks; influence of provenance and sedimentary processes. *Reviews in Mineralogy and Geochemistry*, **21**, 169–200.
- Nestor, V. 1997. Silurian. In *Geology and Mineral Resources of Estonia* (Raukas, A. & Teedumäe, A., eds), pp. 99–104. Estonian Academy Publishers, Tallinn.
- Ounis, A., Kocsis, L., Chaabani, F. & Pfeifer, H.-R. 2008. Rare earth elements and stable isotope geochemistry ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) of phosphorite deposits in the Gafsa Basin, Tunisia. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **268**, 1–18.
- Patrick, D., Martin, J. E., Parris, D. C. & Grandstaff, D. E. 2004. Palaeoenvironmental interpretations of rare earth element signatures in mosasaurs (reptilian) from the upper Cretaceous Pierre Shale, central South Dakota, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **212**, 277–294.

- Reynard, B., Lécuyer, C. & Grandjean, P. 1999. Crystal-chemical controls on rare-earth element concentrations in fossil biogenic apatites and implications for paleoenvironmental reconstructions. *Chemical Geology*, **155**, 233–241.
- Suarez, C. A., Macpherson, G. L., Gonzalez, L. A. & Grandstaff, D. E. 2010. Heterogeneous rare earth element (REE) patterns and concentrations in a fossil bone: implications for the use of REE in vertebrate taphonomy and fossilization history. *Geochimica et Cosmochimica Acta*, **74**, 2970–2988.
- Trueman, C. N. & Tuross, N. 2002. Trace elements in recent and fossil bone apatite. Phosphates: geochemical, geobiological, and materials importance. *Reviews in Mineralogy and Geochemistry*, **48**, 1–742.
- Trueman, C. N., Benton, M. J. & Palmer, M. R. 2003. Geochemical taphonomy of shallow marine vertebrate assemblages. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **197**, 151–169.
- Trueman, C. N., Kocsis, L., Palmer, M. R. & Dewdney, C. 2011. Fractionation of rare earth elements within bone mineral: a natural cation exchange system. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **310**, 124–132.
- Tütken, T., Vennemann, T. W. & Pfretzschner, H.-U. 2008. Early diagenesis of bone and tooth apatite in fluvial and marine settings: constraints from combined oxygen isotope, nitrogen and REE analysis. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **266**, 254–268.
- Vennemann, T. W., Hegner, E., Cliff, G. & Benz, G. W. 2001. Isotopic composition of recent shark teeth as a proxy for environmental conditions. *Geochimica et Cosmochimica Acta*, **65**, 1583–1599.
- Wright, J., Schrader, H. & Holster, W. T. 1987. Paleoredox variations in ancient oceans recorded by rare earth elements in fossil apatite. *Geochimica et Cosmochimica Acta*, **51**, 631–644.
- Žigaitė, Ž., Fadel, A., Blom, H., Pérez-Huerta, A., Jeffries, T., Märss, T. & Ahlberg, P. E. Rare earth elements (REEs) in vertebrate microremains from the upper Pridoli Ohesaare beds of Saaremaa, Estonia: geochemical clues to palaeoenvironment. *Estonian Journal of Earth Sciences*, 2015, **64**, 115–120.