



Rare earth and trace elements of fossil vertebrate bioapatite as palaeoenvironmental and sedimentological proxies

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Rare earth (REE) and trace element compositions of fossil vertebrate dental microremains have been studied in Silurian and Devonian vertebrate dental scales and spines in-situ, using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Samples were selected from the well-known Silurian bone beds of Vesiku and Ohesaare in Saaremaa island of Estonia, and a number of Lower Devonian localities from Spitsbergen (Svalbard), Andrée Land group. Biomineral preservation was assessed using spot semi-quantitative elemental chemistry (SEM-EDS) and electron back-scatter diffractometry (EBSD) for crystallinity imaging. The obtained PAAS shale-normalised REE concentrations were evaluated using basic geochemical calculations and quantifications.

The REE patterns from the Lower Devonian vertebrate apatite from Andrée Land, Spitsbergen (Wood Bay and Grey Høek formations) did not show any recognisable taxon-specific behavior, but had rather well expressed differences of REE compositions related to biomineral structure and sedimentary settings, suggesting REE instead to reflect burial environments and sedimentological history. The Eu anomaly recorded in two of the studied localities but not in the other indicate different taphonomic conditions and palaeoenvironment, while La/Sm, La/Yb ratios suggest considerable influence of terrestrial freshwater during the early diagenesis. The La/Yb and La/Sm plots also agree with the average REE concentrations, reflecting domination of the adsorption over substitution as principal REE uptake mechanism in the fossils which had significantly lower overall REE concentrations, and vice versa.

Vesiku (Homerian, Wenlock) microremains yielded very uniform REE patterns with slightly lower overall REE concentrations in enameloid than in dentine, with strong enrichment in middle REE and depletion in heavy REE. Negative Europium (Eu) anomaly was pronounced in all the profiles, but Cerium (Ce) anomalies were not detected suggesting possible suboxic to anoxic conditions of the bottom and pore waters during the formation of Vesiku bone bed. In Ohesaare (Pridoli), the REE compositions were nearly identical across all the morphotypes and histologies of acanthodian microremains showing flat REE patterns with slight depletion in HREE. There were no visible enrichment in MREE, indicating relatively good preservation of original bioapatite and likely absence of any pronounced fractionated REE incorporation during later stages of diagenesis. The shale normalised (La/Yb)SN and (La/Sm)SN REE ratio compilations showed adsorption as dominating REE uptake mechanism across all the studied microfossils. The absence of well-defined Ce anomaly suggest oxic palaeoseawater conditions, which agrees with existing interpretations of Ohesaare sequence as high-energy shoal and regressive open ocean sedimentary environment.