

REE+Y distribution in Tremadocian shelly phosphorites (Toolse, Estonia): a geochemical and mineralogical investigation for European Critical Raw Material

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Sedimentary phosphorites are the primary sources of nitrogen-phosphorus-potassium fertilisers, and they have recently been highlighted as a potential economic source of rare earth elements (REE). The growing need for clean technologies strongly influences the demand for REE, and in Europe, most deposits have not been investigated in detail since the 1970–1980s. Assessing the economic potential of phosphate deposits and understanding the geological history of REE accumulations is thus essential to exploring deposits and would help to secure sustainable access to a wide range of the elements listed as critical raw materials.

Lower-Ordovician shelly phosphorites in Estonia are among Europe's most extensive phosphate rock reserves, with a tonnage of approximately three billion tonnes. The ore consists of sandstone rich in phosphatic brachiopod fragments deposited in a shallow marine peritidal environment of the Baltic Paleobasin. A detailed geochemical and mineralogical investigation was conducted on the northern part of the Toolse deposit.

The PAAS normalised REE+Y patterns were relatively homogeneous throughout the deposit, with little variability, except for cerium (Ce) and yttrium (Y). The REE+Y contents of the phosphorites indicate a distinctive middle-REE (MREE) enriched 'bell-shaped' pattern along with heavy-REE (HREE) enrichment for Y. In the lower part of the deposit, the Σ REE+Y concentration is enriched up to 12-fold, compared to the average shale, reaching up to 1234 ppm. LREE enrichment is observed in these horizons, with a 9-fold peak at neodymium.

The profiles indicated multistage uptake during transport, deposition, and early diagenesis associated with a steep redox gradient developed during the beginning of marine transgression. Positive Y anomalies show an initial REE+Y uptake by hydroxyapatite through Ca-substitution in an oxic environment near the sediment–water interface. The sediment burial induced the formation of carbonate-fluorapatite (CAF) and a shift to the REE adsorption-uptake mechanism, reinforced by the shell's intercrystalline porosity. The transition to a suboxic environment resulted in the reductive dissolution of Mn-(oxyhydr)oxides and LREE release in porewater, leading to an overprint of the original REE signal, resulting in positive Ce anomalies. MREE enrichment occurred during early diagenesis due to desorption

