

# Unconventional resources of REE: challenges for exploration and processing, with the example of Estonian phosphorite

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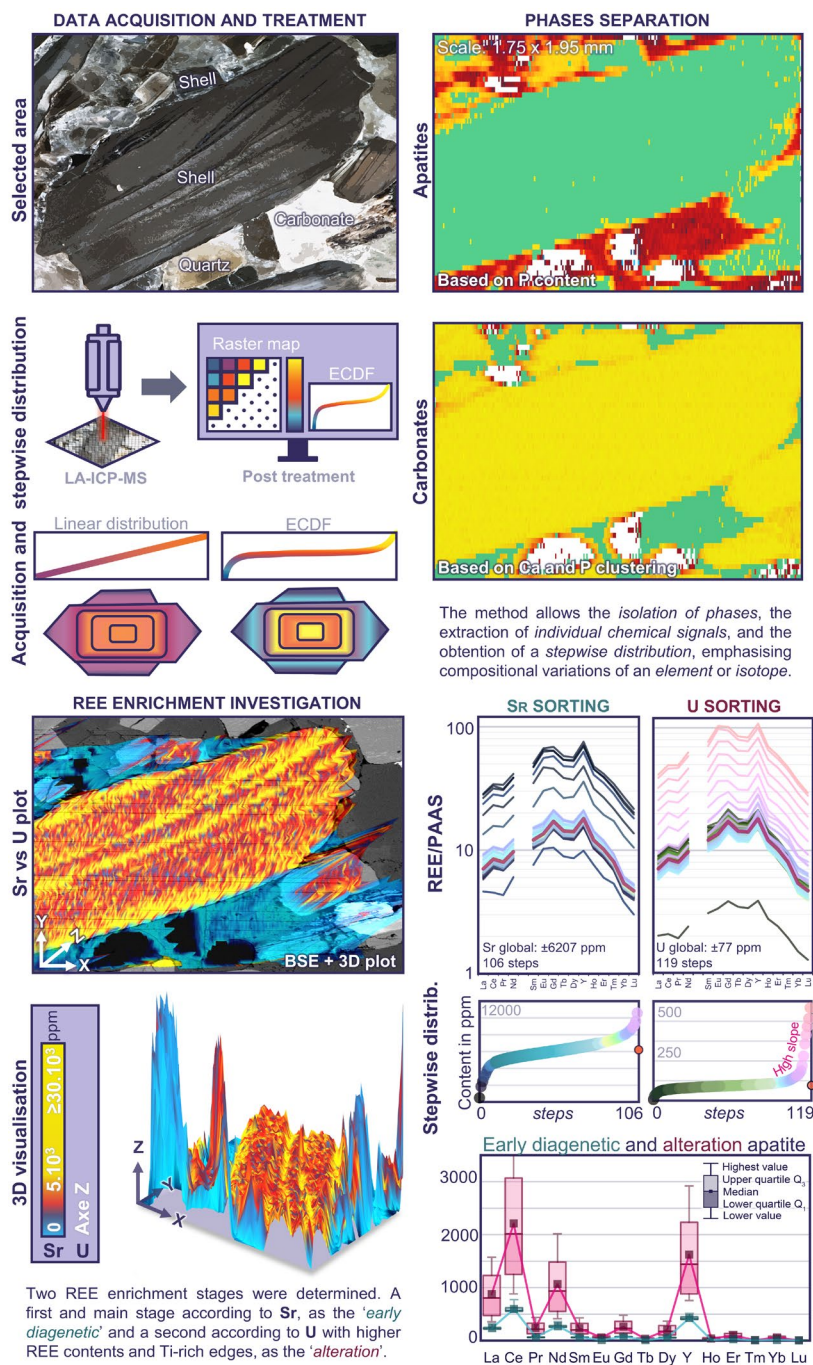
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The fifteen lanthanides, Sc and Y, are commonly grouped under the rare earth elements (REE) appellation. These elements are widely used in high-tech industries and are especially needed for low-carbon energy components such as wind turbines and permanent magnets. Contrary to their name, rare earths commonly occur in the earth's crust but rarely in minable quantities. The three main types of REE deposits are igneous carbonatite containing bastnaesite ((La,Ce,Y)CO<sub>3</sub>F) and monazite ((Ce,La,Nd,Th)PO<sub>4</sub>), monazite placer, and ion-adsorption clays ores from subtropical regions. The growing demand for green technology and the scarcity or availability of conventional resources have spurred interest in exploring unconventional deposits (Balaram 2023).

Unconventional REE resources include a wide range of low-grade, high-tonnage mineral bodies, such as polymetallic nodules, coals, black shales, and phosphorites (Balaram 2023). Most of these deposits are of sedimentary origin and result from multiple complex formation processes, leading to numerous types of mineralisation and high intrinsic chemical variability. Therefore, the exploration and extraction of valuable metals are challenges for the industry in terms of sustainable mining and mineral characterisation (Klyucharev et al. 2013). This issue applies particularly to REE, as they are commonly extracted as by-products (McNulty & Jowitt 2022) from ores in which concentrations can be below the detection limits of the conventional semiquantitative automated mineralogy techniques (Li & Li 2016; Schulz et al. 2020).

The REE in studied Estonian phosphorites are carried by fragments of brachiopod's shells in sandstone, mineralised in carbonate fluorapatite (CFA), an apatite with a highly diverse chemical composition [Ca<sub>10-a-b</sub>Na<sub>a</sub>Mg<sub>b</sub>(PO<sub>4</sub>)<sub>4/6-x</sub>(CO<sub>3</sub>)<sub>3/x-y-z</sub>(CO<sub>3</sub>F)<sub>x-y-z</sub>(SO<sub>4</sub>)<sub>z</sub>F<sub>2</sub>]. Shells themselves are complex objects, the apatite originating from the crystallisation of organic tissues and the precipitation of secondary phosphate during sediment burial. The partitioning and uptake of the individual REEs in them depend on many factors, including inputs from marine sources, oxygenation state of the sedimentary column and REE 'carriers phases' that may have differing affinities for each rare earth (Graul et al. 2023). Estonian phosphorites are similar to placer deposits, often investigated using automated mineralogy techniques such as QEMSCAN<sup>®</sup>, which are very well suited to heavy minerals. However, in the case of shelly phosphorite, this type of analysis is unsuitable since EDS analysis has a lower limit of 0.1 wt.% and the most abundant REEs in shells, such as Y, rarely exceed 0.08 wt.%. The study introduces an innovative LA-ICP-MS mapping method combined with an



**Fig. 1.** Overview of the LA-ICP-MS imaging method and application to shelly phosphorites for REE geochemistry and resources.

empirical distribution function (ECDF) as a powerful, accurate, and cost-effective tool to determine the distribution of REE between apatite varieties (Drost et al. 2018). It allows a good visualisation at different scales, representative measurements, and the identification and discrimination of mineral phases by integrating semiquantitative compositional data through the stepwise distribution of elements. Phosphorites from Toolse and Aseri deposits were selected, and two pathfinder elements were studied to investigate REE distribution and genesis: Sr and U.

Shelly apatites generally have homogenous REE-distribution patterns with positive Y and Ce anomalies, indicative of a progressive uptake, traceable by the Sr distribution (Fig. 1). The average REE content in the studied apatites is 2149 ppm. However, the extent of diagenetic overprint and enrichment varied from one locality to another. In Toolse, the shells show less severely recrystallised textures, with preservation of the Sr- and U-poor early-stage uptake signals. In Aseri, U-sorting reveals a second, diagenetic alteration-driven enrichment stage in which the shell edges present a  $\Sigma$ REE up to 7020 ppm. This alteration stage is less pronounced in Toolse, where the REE content reaches only 4150 ppm.

Based on these observations, the compositions of the apatite species could be modelled to determine phosphorite genesis. A combination of factors such as accumulation of P and nutrients, desorption of Fe-Mn phases and redox fluctuations drove REE enrichment. Developing euxinic conditions and lithogenic input endorsed a later alteration-driven enrichment stage, resulting in highly REE-enriched edges in some localities. Despite differences in enrichment level, the two deposits' REE distribution patterns are similar. Main REEs are Ce (33%), Y (21%), La (12%), Nd (16%) and Dy (3%), and are considered among the most critical elements. On average, U concentrations are 92 ppm in Aseri and 31 ppm in Toolse, and toxic elements (Cd, Zn, Th) are found in trace amounts. To determine ore prospectivity, the mineralisation prospectivity outlook coefficient ( $K_{\text{outl}}$ ) was calculated. It divides the ratio of critical REE (Ce, Ho, Tm, Yb, and Lu) (Seredin 2010). The percentage of critical elements in total REE ( $\text{REE}_{\text{def}}$ ) was plotted by dividing the sum of critical REE by the sum of REE. Based on this approach, both deposits fall in the range of 'promising for economic development' ( $33\% \leq \text{REE}_{\text{def}} \leq 50$ ;  $0.9 \leq K_{\text{outl}} \leq 3.1$ ). Therefore, the ratio of valuable REEs is relatively high in Toolse and Aseri deposits. These ores are potential REE resources as by-products with low toxic element contents and predictable REE and trace elements contents.

The LA-ICP-MS image-based method has provided a better overview of the factors controlling low-grade sedimentary ores' genesis, identified their potential value-adding pathways, and provided an initial approach to semiquantification.

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