

LA-ICP-MS imaging and semi-quantification: Unlocking the REE potential of low-grade sedimentary ores, application to Estonian phosphorites.

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REEs are employed in a wide range of high technologies. Current sourcing is derived from igneous deposits, a production incompatible with the substantial demand for specific REEs (Nd, Pr, Dy) for low-carbon industries (1). This, along with the scarcity of resources, has spurred interest in waste valorisation and unconventional ores. REE alternative raw sources include numerous low-grade, high-tonnage formations, polymetallic nodules, black-shales, and sedimentary phosphorites. The characterisation and extraction of valuable metals from these are challenges due to deposit complexities and state of knowledge. The latter is particularly important in case of phosphorites, which have been highlighted as potential REE sources. However, REE contents are often below the detection limits of FE-SEM automated mineralogy techniques, thus problematic for recovery planning.

This study focuses on Estonian phosphorites, which constitute Europe's largest phosphate rock reserves and are characterised by apatitised shell fragments (2). Investigations were conducted on Toolse and Aseri deposits. REE distribution determination and apatite enrichment were addressed by the LA-ICP-MS imaging technique developed by Drost (2018), allowing identification and phase discrimination by integrating semi-quantitative data through elements stepwise distribution. Diagenetic stages and apatite compositions were assessed using the following pathfinders as pooling channels: Sr, U, and Ce.

Apatites present homogenous REE patterns, MREE-enriched up to 15-fold compared to PAAS, with Y-Ce anomalies indicative of early-diagenetic overprinting. However, overprint extent varied. In Toolse, shells show less recrystallised textures, with Sr-U depleted stages allowing the tracing of pristine signals. Average REE grade is 1847ppm. In Aseri, U-sorting reveals a second, alteration-driven enrichment in which the fragment's edges present a ΣREE up to 12250ppm. This alteration stage is less pronounced in Toolse, where ΣREE reaches only 4150ppm. Despite enrichment magnitude differences, deposits' distributions are similar: main REEs are Ce(33%), Y(21%), La(12%), Nd(16%) and Dy(3%). On average, U concentrations are 92ppm in Aseri and 31ppm in Toolse, and toxic elements (Cd-Zn-Th) are found in traces. Results indicate the need for fine-loss minimisation during processing for enhanced recovery and provide a first approach to in-situ semi-quantification of low-

grade ores (4).

- 1.Hoshino (2016)
Handbook on the Physics and Chemistry of Rare Earths.
2.Graul (2023) *Journal of Geochemical Exploration*.
3.Drost (2018) *Geochemistry, Geophysics, Geosystems*.
4.Seredin (2010) *Geology of Ore Deposits*

