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REE sequestration during carbonatite weathering: Insights from X-ray absorption spectroscopy of crandallite.

BRYAN J MACIAG[1], MARTIN SMITH[1], SAM BROOM-FENDLEY[2], MARTIN LI[3] AND PANKAJ KUMAR[1]

[1]University of Brighton
[2]University of Exeter
[3]Imperial College London

The rare earth elements (REE) are essential for manufacturing cutting-edge technology and commonly occur in carbonatite or alkaline magmatic systems. Weathering of intrusive carbonatites can result in supergene REE enrichment; however, the processes involved in mobilizing and concentrating REE are not fully understood. Sokli, northern Finland, is an example of a weathered carbonatite where REE are locally enriched by up to 25 times the bedrock concentration. The REE are partly hosted by crandallite-group (hydrated aluminophosphate) minerals which form at the top of the weathering profile from late phosphate re-precipitation and pseudomorph replacement of pyrochlore. In this study, we explore the structural position of REE in crandallite, using Y K-edge extended X-ray absorption fine structures (EXAFS) and Ce L3-edge X-ray absorption edge structures (XANES), to better understand how crandallite sequesters REE.

A preliminary first-shell analysis of the Y K-edge EXAFS spectra shows a broad and uneven peak when compared to other REE-bearing minerals such as monazite. This broad peak matches well with 2 oxygen shells of 6 O at 2.30 Å and 2.84 Å. These bond distances are more asymmetric than crandallite sensu-stricto (2.65 Å and 2.74 Å), suggesting disorder in the late REE-bearing crandallite at Sokli. Linear combination fitting of the Ce L3-edge XANES spectra shows 93±7% of Ce is incorporated as Ce(III), which is roughly consistent with detrital apatite from the same locality (86±4% Ce(III)). The absence of any Ce anomalies or Ce(IV) phases may indicate that some reduction occurred before crandallite formation. Further analysis of this spectroscopic data is underway to understand the effects of REE incorporation in crandallite-group minerals, which will help inform genetic models of supergene enrichment as well as extraction methodologies.