

## Rare Earth Elements (REE) recovery as a by-product of fertilizer production from sedimentary Phosphate deposits – Conceptual evaluation

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Worldwide, phosphate deposits are classified into three main categories: a) phosphorites (sedimentary phosphate deposits), b) apatite-rich igneous rocks and related residual deposits, and c) modern and ancient guano accumulations. Marine phosphorites are the most significant in terms of global phosphate production, reserves and resources. Phosphorites average approximately 460 ppm total rare earth elements ( $\Sigma$ REE), are enriched in REE relative to typical shale (207 ppm  $\Sigma$ REE), and can contain more than 1600 ppm of  $\Sigma$ REE. Total concentration and proportions of individual REEs within phosphorites vary substantially.

Currently, China produces the vast majority of the world's REE supply. Rapid increases in internal demand for REE have motivated the Chinese government to introduce limits and taxes on REE exports. The resulting insecurity regarding global REE supply created a rise in REE prices. The world's REE demand for 2010 was estimated at 125 000 tonnes. Assuming average REE content of 460 ppm  $\Sigma$ REE in phosphorite, the world's phosphate production of 170 million tonnes represents over 70 000 tonnes of contained REE.

Considering the phosphorites of the Fernie Formation in British Columbia (Canada), at current REE prices, a tonne of phosphate rock has an 'in the ground value' of more than US\$ 160. This is more than the current market value of high-quality commercial phosphorite concentrate (approximately US\$ 130-150). The above rudimentary considerations indicate that at current REE prices, the economic viability of REE recovery as a by-product of phosphate mining should be re-evaluated.

## *In situ* SXRF determination of trace element abundances in aqueous fluid at 1 - 3 GPa and 300 – 500°C: Applications to subduction zone element cycling

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Interpreting trace-element variability in arc magmas that are hypothesized to have an aqueous fluid signature is predicated on having a quantitative understanding of the aqueous fluid-mediated trace-element transfer at PT conditions attending slab-sediment devolatilization. Experimental efforts to quantify the element-scavenging potential of aqueous fluid (s) were historically performed *ex situ* by recovery-type experiments. Here, we report further development of a synchrotron-based hydrothermal diamond anvil cell technique that allows *in situ* quantitative determination of trace element abundances in aqueous fluid at PT conditions appropriate for slab devolatilization. Notably, *in situ* reversals can be performed. The technique was developed by measuring the dissolution of YPO<sub>4</sub> (xenotime), a proxy for the behavior of heavy rare earth elements (HREE), in aqueous fluid at 1 to 3 GPa and 300 to 500°C. Yttrium concentrations and pressure were measured *in situ* by using synchrotron X-ray fluorescence (SXRF) and X-ray diffraction (XRD) of gold, respectively. Yttrium standards were measured in the same sample chamber as xenotime experiments, and a multi-point standard calibration curve was used to calculate Y abundances in the fluid in the xenotime dissolution experiments. This ensures a constant fluorescence excitation volume for the standards and the unknowns. The new data indicate that Y (HREE) concentrations in aqueous fluid are relatively constant at 300 to 500°C and 1 to 3 GPa, suggesting that increasing temperature, at a given pressure, does not increase the HREE-scavenging ability of aqueous fluid. These data have important implications for HREE recycling in subduction zone environments.