



Rare earth elements in raw materials and products of the phosphate fertilizer industry in South America: Content, signature, and crystalline phases



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ABSTRACT

Phosphate ores are well-known for containing rare earth elements (REE) in a wide range of contents. The presence of REE in phosphate (P) products may enhance plant and animal development. Yet, our current understanding of the role of different P products as carriers of REE to soils is still incipient, especially regarding the extent to which the original REE content in raw materials remains in their respective products and the changes in crystalline phases associated with the phosphate ore processing. This study evaluated phosphate concentrates used as raw materials in major phosphate industries in South America as well as final products – including P fertilizers, di-calcium phosphate, and phosphogypsum – in order to characterize their REE contents, signatures, and REE-carrying crystalline phases. The results showed that the REE content in raw materials and products from the phosphate industry in South America is highly variable. Phosphorites from Bayóvar Phosphate Mine showed the lowest REE content among the studied raw materials ($\sim 70 \text{ mg kg}^{-1}$). Considering materials of igneous origin, the phosphate concentrate from the Catalão Mineral Complex presented the highest total REE content ($\sum \text{REE}$ up to $16,650 \text{ mg kg}^{-1}$) and the highest concentrations of light REE ($\sum \text{LREE}/\sum \text{REE} \sim 98\%$), whereas those from the Araxá Mineral Complex, especially materials from the F4 Mine, presented the highest contents of heavy REE ($\sum \text{HREE} \sim 1200 \text{ mg kg}^{-1}$). A great variety of mineral phases was found not only in phosphate concentrates but also in final products, with the apatite-group appearing as the main REE-carrying crystalline phase. The REE contents and composition in the final products were generally strongly influenced by their respective raw materials, resulting in a strong match of REE signatures, which reinforces the usefulness of REE signatures as accurate tools for tracing the origin and provenance of final products of the P fertilizer industry.

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1. Introduction

Rare earth elements (REE) are a group of seventeen chemical elements comprising yttrium (Y), scandium (Sc) and the 15 lanthanide elements (lanthanum-La, cerium-Ce, praseodymium-Pr, neodymium-Nd, promethium-Pm, samarium-Sm, europium-Eu, gadolinium-Gd, terbium-Tb, dysprosium-Dy, holmium-Ho, erbium-Er, thulium-Tm, ytterbium-Yb, and lutetium-Lu). These elements have similar properties and, consequently, are usually found together in geologic deposits of phosphate rock.

In Brazil, over 90% of the mined phosphate ores come from igneous complex carbonatite deposits, accounting for 2% of the estimated

worldwide reserves (Zhang et al., 2012). Although there is almost no large-scale exploitation of rare earth minerals in Brazil, the existing resources are significant and occur mainly in association with alkali-carbonatitic complexes (Antoniassi et al., 2015). The main process involved in the genesis of this kind of complex is the residual concentration of unweathered or slightly weathered ore minerals (e.g., apatite) due to the dissolution of carbonates. In these deposits there are several REE-bearing minerals, usually present at extremely fine grain (Cavalcante et al., 2014; Neumann and Medeiros, 2015). As reported by Ani and Sarapaa (2013) carbonatite rocks are known to contain the highest amounts of REE among all igneous rocks, but where these elements reside among the variety of mineral species found in carbonatite is less well understood.

Phosphate ores are well-known for having a wide range of REE contents, and indirect application of REE to agricultural soils is widespread

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due to their presence in many products of the phosphate fertilizer industry (Otero et al., 2005; Turra et al., 2011; Waheed et al., 2011). Several studies have shown positive effects of REE in plants and animals (Cai et al., 2015; He et al., 2010; Hu et al., 2004; Ma et al., 2014). However, our knowledge of the biological role of REE is still in its early stages (Skovran and Martinez-Gomez, 2015). Hypotheses supporting the beneficial effects of REE in plant and animal metabolism include stimulation of the antioxidant system, increased absorption and utilization of nutrients, increased electron transport rate in the photochemical phase of photosynthesis, and reduction of intestinal pathogens growth (de Oliveira et al., 2015; Giraldo et al., 2014; He et al., 2010; Ramos et al., 2016).

The most common process used in the production of phosphate fertilizers is the rock phosphate attack with concentrated sulphuric acid and water. In this process the main products from chemical reactions are phosphoric acid (H_3PO_4), single superphosphate (SSP), triple superphosphate (TSP), and the hydrated calcium sulphate (phosphogypsum), which is one of the by-products of phosphate rock processing. In spite of the widespread use of many products of the P fertilizer industry in agriculture, the current understanding of the role of different P products as carriers of REE to soils is still incipient, especially regarding the extent to which the original REE content in raw materials remains in their respective products and the changes in crystalline phases associated with the phosphate ore processing.

This study evaluated REE contents, REE signatures, and REE-carrying crystalline phases in phosphate concentrates utilized as raw materials in key phosphate industries in South America, as well as in selected final products. Information provided by this investigation will help us better understand the role of products of the P fertilizer industry as carriers of REE to soils and the food chain. In addition, it will allow us to advance the knowledge regarding qualitative and quantitative information about REE in raw materials and final products of the P fertilizer industry in South America, as well as to trace the origin of phosphate fertilizers with the use of REE signatures.

2. Material and methods

Different materials from major producing areas of phosphate industry in Brazil and Peru were sampled, including 12 processed raw materials and 8 products. All materials were sampled twice, in 2013 and 2014, in triplicate. The sampled materials and their respective sites are listed in Table 1. The manufacturing process flowsheet is similar to all phosphate concentrate, and comprises crushing, grinding, desliming,

flotation, leaching, filtration, drying, and packaging. The rock phosphate from Bayovar is an exception to that, because it is only grinded.

For analyses of REE, the solid samples were air-dried and ground to pass through a 150-mesh nylon sieve. All solid samples were digested by means of an alkaline fusion method. In brief, an aliquot of 0.1 g from each sample was fused with 1.4 g of lithium metaborate in platinum crucibles at 1000 °C in a fusion machine (Fluxer BIS, Claisse, Québec, Canada). After cooling, the resulting bead was dissolved in beakers containing 50 mL of a 2.5% solution of tartaric acid and 10% HNO_3 . Each beaker was then transferred to a hot plate at 120 ± 20 °C with magnetic stirring for complete solubilization. After that, the samples were transferred to 100-mL polypropylene volumetric flasks and the volume was completed with a 2.5% solution of tartaric acid and 10% HNO_3 . For phosphoric acid (samples in liquid form), a 1000-fold diluted solution was directly analyzed for REE content.

A certified reference material (Calcareous Soil ERM-CC690®, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium) was included for quality control. Blank and certified reference samples were added to the analytical series. The REE contents in the digested solutions were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Model NexION 300D, Perkin Elmer, Waltham, MA, USA). The instrumental settings used during this study are summarized in Table 2.

For clustering the samples based on their REE signatures, the REE contents for each sample were first transformed by dividing them by the respective Ce content in the sample in order to remove the influence of total REE content on the REE signature. Based on the transformed REE contents, a matrix of Euclidean distances among samples was calculated and used for hierarchical clustering using the Ward's algorithm (Ward, 1963). The bootstrap support for each branch in the resulting dendrogram was calculated using the pvclust package (Suzuki and Shimodaira, 2006).

The crystalline structures of solid samples were evaluated by X-ray diffraction using a synchrotron light source (LNLS, Campinas, Brazil). In short, the samples were air-dried and ground to pass through a 50-mesh nylon sieve. Then, the samples were inserted in capillary quartz samplers with 0.3-mm inner diameter and 0.001-mm thickness. The degree- 2θ goniometry of Debye–Scherrer was chosen for data acquisition and analysis. The incident beam was monochromatic, obtained by a DCM-double crystal monochromator, with Si (111). The measurements were made with a wavelength $\lambda = 1.04021$ nm, 2θ in the 5–120° range, and 2.0 s/step. The resulting diffractograms were interpreted with the aid of the mineralienatlas and webminerals

Table 1
Raw materials and products collected for this study.

Abbreviations	Samples	Characteristic	Sampling site
Ufine P – Cat	Ultrafine phosphate concentrate	Raw material	Catalão minerochemical complex, State of Goiás – Brazil
Conv P – Cat	Conventional phosphate concentrate	Raw material	
SSP – Cat	Single superphosphate	Fertilizer	
Ufine P Bar – Arx	Ultrafine phosphate concentrate from Barreiro mine	Raw material	Araxá minerochemical complex, State of Minas Gerais - Brazil
Conv P Bar – Arx	Conventional phosphate concentrate from Barreiro mine	Raw material	
Ufine P F4 – Arx	Ultrafine phosphate concentrate from F4 mine	Raw material	
Conv P F4 – Arx	Conventional phosphate concentrate from F4 mine	Raw material	
SSP – Arx	Single superphosphate	Fertilizer	
Ufine P – Tap	Ultrafine phosphate concentrate	Raw material	Tapira phosphate mine, State of Minas Gerais - Brazil
Conv P – Tap	Conventional phosphate concentrate	Raw material	
TSP – Ubb	Triple superphosphate	Fertilizer	Uberaba industrial complex, State of Minas Gerais - Brazil
MAP – Ubb	Monoammonium phosphate	Fertilizer	
PhosGyp – Ubb	Phosphogypsum	Fertilizer	
H_3PO_4 – Ubb	Phosphoric acid	Raw material	
Calc P – Caj	Calcitic phosphate concentrate	Raw material	Cajati minerochemical complex, State of São Paulo – Brazil
Dol P – Caj	Dolomitic phosphate concentrate	Raw material	
H_3PO_4 – Caj	Phosphoric acid	Raw material	
CaHPO ₄ – Caj	Dicalcium phosphate	Animal consumption	
Conv P – PaM	Conventional phosphate concentrate	Raw material	Patos de Minas phosphate mine, State of Minas Gerais - Brazil
P Rock – Bay	Phosphate rock	Raw material/fertilizer	Bayóvar phosphate mine, Piura Region – Peru

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