



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



Silvio J. Ramos<sup>a</sup>, Guilherme S. Dinali<sup>b</sup>, Teotonio S. de Carvalho<sup>b</sup>, Luzia C. Chaves<sup>c</sup>, José O. Siqueira<sup>a</sup>, Luiz R.G. Guilherme<sup>b,\*</sup>

<sup>a</sup> Vale Institute of Technology – Sustainable Development, Rua Boaventura da Silva, 955, Belém, Pará 66055-090, Brazil

<sup>b</sup> Soil Science Department, Federal University of Lavras, Lavras, Minas Gerais, 37200-000, Brazil

<sup>c</sup> Mineral Development Center of Vale, Rodovia BR 381, km 450, Santa Luzia, Minas Gerais, 33040900, Brazil

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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

\* Corresponding author.

E-mail address: [guilherm@dcs.ufra.br](mailto:guilherm@dcs.ufra.br) (L.R.G. Guilherme).

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  $120 \pm 20$  °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- $2\theta$  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,  $2\theta$  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 <sub>4</sub> – 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

**Table 2**

Typical instrumental settings for REE determination in raw materials and products of the phosphate fertilizer industry used in this study.

Instrument	Perkin Elmer Nexlon 300D
RF Power	~1300 W
Spray Chamber and Nebulizer	Scott (Ryton) with concentric nebulizer
Coolant argon flow rate	15 min <sup>-1</sup>
Auxiliary argon flow rate	1.0 min <sup>-1</sup>
Nebulizer argon flow rate	0.8–1.2 min <sup>-1</sup> (adjusted daily to obtain optimum signal intensity and stability)
Sample uptake rate	Approximately 4.00 mL min <sup>-1</sup>
Sampler cone	Nickel, 1.1 mm aperture i.d.
Skimmer cone	Nickel, 0.9 mm aperture i.d.
Instrument tuning	Performed using a 1 ng g <sup>-1</sup> multi-element solution
Ion transmission	>27,000 cps per 1 ng g <sup>-1</sup> indium
Rinse time between standards or samples	60 s (with 1% v/v HNO <sub>3</sub> )
Take-up and stabilisation time	15 s
Ion sampling depth	Adjusted daily to obtain maximum signal intensity
Ion lens settings	Adjusted daily to obtain maximum signal intensity and optimum resolution

databases ([mineralienatlas.com](http://mineralienatlas.com), 2016; [webmineral.com](http://webmineral.com), 2016) using in-house R scripts (Team, 2015).

### 3. Results

The mean REE concentrations of the standard reference materials obtained by ICP-MS and their respective mean recoveries are presented in Table 3. They show the reliable analytical data accuracy for REE provided by this method.

The REE contents in phosphate concentrate and products varied widely (Fig. 1), with higher levels being found in samples from igneous origin – e.g., from Catalão, Araxá, and Tapira in Brazil – and lower contents in the sample of sedimentary origin, i.e., the Bayóvar phosphorite from Peru. In general, the highest levels of light rare earth elements (LREE – La, Ce, Pr, Nd, and Sm) and  $\Sigma$  REE were found in samples from Catalão, while the highest levels of heavy rare earth elements (HREE – Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y) were observed in samples from Araxá (Fig. 2). The accumulation order of LREE in all samples in descending order was Ce > La > Nd > Pr > Sm > Eu. However, Nd content was higher than that of La in some samples from Araxá and Cajati. For HREE, the accumulation order was Y > Gd > Dy > Er > Tb > Yb > Ho > Tm, whereas Y showed lower concentration than Gd in all raw materials from Catalão.

Table 4 shows the annual production and the estimated exportation of REE for the materials with the highest levels of these elements. We observed that annual REE flow in the Catalão Complex for conventional and ultrafine phosphate concentrates, and SSP are currently 13, 2.5, and 2.1 thousand tons per year, respectively. For the Tapira Phosphate Mine, the current major source of phosphate concentrate in Brazil, the estimated output for LREE, HREE and total REE are about 13, 0.8, and 14 thousand tons, respectively. For the Uberaba Industrial Complex, about 1.6 million tons of phosphogypsum are produced per year, resulting in an estimated annual flow of about 8 thousand tons of REE.

**Table 3**

Certified value, determined concentration and REE recovery on certified materials.

REE	Certified value <sup>1</sup> (mg kg <sup>-1</sup> )	Obtained value (mg kg <sup>-1</sup> )	Mean recovery (%)
Ce	49.1	48.38 ± 0.45	98.5
Dy	2.90	2.87 ± 0.08	97.6
La	24.4	24.06 ± 0.21	98.6
Nd	19.1	20.0 ± 0.23	104
Yb	1.57	1.54 ± 0.09	98

<sup>1</sup> Certified reference material ERM-CC690-calcareous soil.

Ultrafine phosphate concentrates, which are concentrated in the clay-sized fraction, showed higher REE content than conventional phosphate concentrates for all sampling sites. By comparing the total REE levels between phosphate concentrates and their respective products, we observed that about 50–60% of the initial concentration of these elements in the raw material remains in the superphosphates. For the dicalcium phosphate, which is widely used as a dietary supplement in animals, about 20% of the original REE content remains in the product. Finally, for phosphoric acid and its derived product, MAP, the remaining REE level can vary from <5% in the former to about 29% in the latter. Therefore, single superphosphate (SSP) from Catalão and Araxá, and triple superphosphate and phosphogypsum from Uberaba are relevant sources of REE for agricultural soils, with high concentrations of Ce, La, and Nd, generally much more abundant than other REE.

To assess whether the products can be traced back to their respective raw materials based on REE signature, we performed a hierarchical clustering analysis on the matrix of euclidean distances calculated from REE levels normalized by the Ce concentration in each sample. The results are presented in the form of a dendrogram in Fig. 3, which shows seven clearly distinct clusters, two of them (VI and VII) having only one sample and five others (I–V) having 2–4 samples consistently grouped, with a bootstrap support higher than 80%. Cluster I was predominantly composed of materials from the Barreiro Mine in Araxá and the SSP from Araxá. Cluster II includes raw materials and SSP from the Catalão Mineralochemical Complex, having very homogeneous REE signatures and grouping with a bootstrap support of 100%. Group III, with a bootstrap support of 97%, includes both conventional and ultrafine phosphate concentrates from the Tapira Phosphate Mine, as well as TSP and phosphogypsum from Uberaba Industrial Complex. In fact, phosphate concentrates from Tapira are fed to the Uberaba Industrial Complex by a mineral pipeline for the production of TSP, phosphoric acid, and phosphogypsum (a by-product). The Araxá Mineralochemical Complex has two operational mines, F4 Mine and Barreiro Mine, whose phosphate concentrates are normally used for SSP production. The grouping of SSP from Araxá with samples from the Barreiro Mine (Group I), rather than with those from F4 Mine (Group V), indicates that this SSP was produced with raw materials from the Barreiro Mine. This grouping was probably due to their lower proportion of HREE when compared with raw materials from F4 Mine. Finally, Group IV was composed by raw materials from Cajati, whereas the raw material from Patos de Minas and the dicalcium phosphate from Cajati were completely distinct from all other samples with regards to their REE signatures, each forming separate groups.

We found a great diversity in terms of mineral phases in phosphate concentrates and also in the final products, with apatite, carbonate-fluorapatite, and carbonate-hydroxyapatite being the major crystalline components carrying REE in the samples analyzed, with a minor presence of accessory mineral phases, e.g. anatase, britholite, rutile, loparite, and tritomite (Fig. 4). In general, Brazilian phosphate concentrates, especially from Catalão, Araxá, and Tapira, contained a more diverse array of REE-carrying mineral phases than the sedimentary phosphorite from Bayóvar-Peru.

### 4. Discussion

In Brazil, the raw materials used to produce phosphate fertilizers are mostly igneous, metasedimentary, carbonatitic, and lateritic from the Precambrian age. These deposits are made up of different minerals, among which apatite is the most abundant, with enrichment of REE in some locations, especially in those with rocks of carbonatitic origin (Lapido-Loureiro et al., 1989). Hughes et al. (1991) reported that among all igneous rocks, those containing carbonatitic apatite have the highest REE contents, which renders this mineral the most important one in controlling REE content in igneous rocks. Fleischer and Altschuler (1986) who published an analysis of REE in apatite from many origins, observed that igneous apatite shows a diverse REE

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb
Ufine P – Cat	3,800 ±89	7,871 ±74	888 ±76	3,066 ±31	358 ±33	88 ±2	242 ±8	19 ±1	73 ±6	209 ±25	9 ±1	18 ±2	1 ±0.4	7 ±1
Conv P – Cat	3,415 ±135	7,187 ±144	826 ±98	2,886 ±43	354 ±47	87 ±14	235 ±35	18 ±2	76 ±2	213 ±10	9 ±1	19 ±1	1 ±0.3	7 ±2
SSP – Cat	1,926 ±83	3,934 ±65	447 ±66	1,529 ±98	184 ±20	42 ±4	112 ±4	9 ±1	38 ±3	122 ±6	5 ±1	11 ±1	1 ±0.5	5 ±1
Ufine P Bar – Arx	1,513 ±11	3,224 ±20	408 ±7	1,626 ±3	280 ±3	86 ±2	245 ±2	30 ±1	153 ±4	568 ±20	24 ±1	54 ±1	5 ±0.2	29 ±1
Conv P Bar – Arx	1,360 ±18	3,021 ±17	378 ±5	1,480 ±21	247 ±5	72 ±1	203 ±3	24 ±1	116 ±2	511 ±16	18 ±1	41 ±1	4 ±0.3	19 ±1
Ufine P F4 – Arx	1,530 ±18	3,281 ±100	430 ±12	1,710 ±13	315 ±9	100 ±6	290 ±19	39 ±3	208 ±19	826 ±22	34 ±3	80 ±8	9 ±1	47 ±6
Conv P F4 – Arx	1,093 ±89	2,505 ±45	336 ±38	1,370 ±32	256 ±13	82 ±2	246 ±11	38 ±2	183 ±15	694 ±38	31 ±3	71 ±7	8 ±1	41 ±4
SSP – Arx	895 ±68	1,866 ±138	235 ±19	899 ±51	149 ±7	43 ±3	123 ±2	15 ±1	78 ±2	322 ±51	12 ±1	27 ±2	3 ±0.5	14 ±1
Ufine P – Tap	1,680 ±46	2,960 ±51	370 ±8	1,346 ±39	196 ±11	53 ±5	149 ±17	14 ±2	65 ±5	245 ±6	10 ±1	22 ±1	1 ±0.3	12 ±1
Conv P – Tap	1,566 ±92	2,888 ±93	348 ±25	1,301 ±89	190 ±16	52 ±4	148 ±14	17 ±1	83 ±4	238 ±9	12 ±1	27 ±2	1 ±0.3	11 ±1
TSP – Ubb	953 ±72	1,801 ±141	217 ±18	814 ±65	132 ±9	36 ±2	108 ±5	11 ±1	51 ±5	214 ±9	8 ±1	18 ±1	1 ±0.5	11 ±1
MAP – Ubb	399 ±18	809 ±48	96 ±3	373 ±17	68 ±4	20 ±2	63 ±7	5 ±1	33 ±2	168 ±23	5 ±1	13 ±1	1 ±0.3	9 ±1
PhosGyp – Ubb	1,142 ±68	2,204 ±152	267 ±25	984 ±96	138 ±9	35 ±1	95 ±7	10 ±1	38 ±3	108 ±9	5 ±1	11 ±1	0.7 ±0.3	4 ±1
H <sub>3</sub> PO <sub>4</sub> – Ubb	66 ±6	109 ±11	13 ±2	61 ±18	21 ±8	8 ±2	6 ±1	4 ±1	27 ±11	6 ±1	5 ±2	16 ±3	0.3 ±0.1	1.5 ±0.1
Calc P – Caj	296 ±8	722 ±18	95 ±3	405 ±3	67 ±1	18 ±1	55 ±2	4 ±1	23 ±1	75 ±2	4 ±1	6 ±1	0.6 ±0.3	3 ±1
Dol P – Caj	294 ±7	731 ±8	98 ±2	417 ±4	74 ±1	23 ±1	61 ±1	5 ±1	28 ±1	82 ±3	4 ±1	8 ±1	0.6 ±0.3	3 ±1
H <sub>3</sub> PO <sub>4</sub> – Caj	<4	<7	<1	<1	<2	<2	<4	<0.2	<0.5	<3	<0.2	<1	<0.2	<1
CaHPO <sub>4</sub> – Caj	73 ±2	149 ±3	14 ±1	62 ±1	11 ±1	3 ±1	12 ±1	1 ±0.5	5 ±1	24 ±1	<0.2	<1	<0.2	<1
Conv P – PaM	64 ±2	122 ±4	15 ±1	64 ±1	14 ±1	3 ±1	13 ±1	1 ±0.5	11 ±1	96 ±7	1 ±0.5	6 ±1	0.8 ±0.3	4 ±1
P Rock – Bay	15 ±1	<7	<1	<1	<2	<2	<4	1 ±0.5	4 ±1	47 ±1	<0.2	4 ±1	<0.2	<1

Fig. 1. Heatmap showing means and standard errors (n = 3) of REE contents for 20 samples of processed raw materials and products from phosphate fertilizer industry (mg kg<sup>-1</sup>) (see Table 1 for abbreviations). Within each column, darker colors indicate higher REE contents. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

composition, usually containing high LREE content. On the other hand, in sedimentary apatite they found very low levels of LREE, with higher levels of yttrium (Y) in some locations. In agreement with these studies, we observed that phosphorite from Peru showed extremely low REE levels, with Y being the most abundant REE. Piper et al. (1988) also reported low levels of REE in phosphorite from the Peru shelf, with Y predominating over all other REE for some samples. In contrast, the Brazilian phosphate concentrates analyzed in our study, especially those from Catalão, showed considerable amounts of REE, for instance, the total REE content ( $\sum$  REE) for ultrafine concentrate, conventional concentrate, and SSP from Catalão were 16,649; 15,333 and 8365 mg kg<sup>-1</sup>, respectively, about twice as much as those levels

found in materials from Araxá and Cajati. Catalão is one of the biggest phosphate mines in Brazil, and is described as a lateritic rare earths deposit related to hydrothermal and supergene origin in dolomitic carbonatite rocks, presenting important apatite, Ba-pyrochlore, anatase, and REE mineralizations (Tassinari et al., 2001). According to these authors, the REE deposit in Catalão is located in the south border of the open pit of the phosphate mine, having a substantial overlay with it. Our results indicate that Catalão phosphate mine is enriched in REE relative to most of other phosphate ores studied to date (Emsbo et al., 2015).

In the wet process for phosphoric acid manufacturing, when the phosphate concentrate is dissolved with sulfuric acid and recycled as

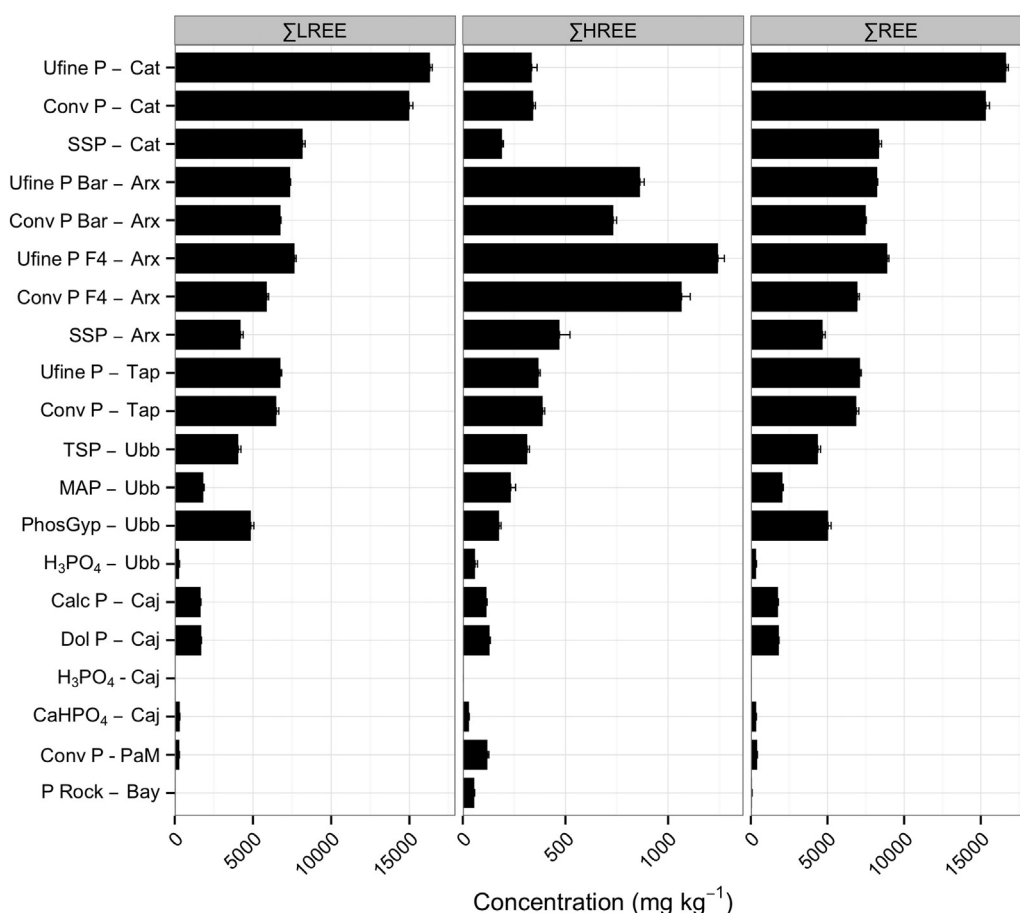


Fig. 2. Sum of light rare earth elements ( $\Sigma$  LREE), heavy rare earth elements ( $\Sigma$  HREE), and total REE ( $\Sigma$  REE) of 20 samples of processed raw materials and products from phosphate fertilizer industry.

diluted phosphoric acid, about 70–80% of the initial REE in the concentrate is retained in the leaching residue of phosphogypsum, with only 20–30% being dissolved in the phosphoric acid leaching solution (Preston et al., 1996; Zhang et al., 2012). In the present study, the phosphogypsum, TSP, MAP, and phosphoric acid from Uberaba are manufactured mainly with phosphate concentrate from Tapira, which is fed into the Uberaba Industrial Complex by a mineral pipeline 125 km long, the first in the world built for this purpose. We found that approximately 70% of  $\Sigma$  REE initially present in the raw materials from Tapira remained in the phosphogypsum produced in the Uberaba Industrial Complex (about 70% for LREE and 50% for HREE). For phosphoric acid, these values were lower, <15% for LREE and about 20% for HREE.

The current advances in flotation technology are allowing complex low-grade phosphorus deposits to be exploited economically. The continuous reduction in grade is forcing industries to produce ultrafine particles in order to liberate P-containing particles from the ore. It is standard practice in the Brazilian phosphate industry to separate the ultrafine concentrates by scrubbing and hydrocycloning. In the present study, we found higher REE contents in ultrafine concentrates than in conventional concentrates, especially for LREE. For instance, La, Ce, Pr, and Nd contents were 30, 31, 28, and 25% higher, respectively, in the ultrafine than in the conventional phosphate concentrate in the F4 Mine of Araxá. It is generally assumed that REE are concentrated in the clay-sized fraction; they also concentrate in fine-grained sediments because their host minerals, including accessory primary and secondary minerals, usually occur in that size range (Cavalcante et al., 2014; Singh, 2009). As described by Cullers et al. (1979) the bulk of the REE elements reside in the fine-grained (clay and silt) fraction, regardless of clay

mineralogy, and also in trace minerals such as zircon, monazite, and apatite. Neumann and Medeiros (2015) reported that Araxá's phosphate ore, as usual for deeply weathered ores, is very fine-grained. Tassinari et al. (2001) who determined the mineralogical compositions and evaluated the potential for mineral concentration through physical processes for saprolitic ore samples from Catalão, also showed that REE are usually present at extremely fine grain sizes. On the other hand, we found that Tb, Dy, Ho, and Er were higher in conventional than in ultrafine phosphate concentrate in Tapira.

Due to their physicochemical properties, REE have been extensively used as tracers of genesis, origin, and geochemical processes in many studies (Laveuf and Cornu, 2009; Laveuf et al., 2012; Smidt et al., 2011). We found similar REE fingerprints among raw materials and their products, indicating their suitability for tracing the materials utilized for phosphate fertilizers manufacturing. REE provides an excellent tracer because they are on fine particles and are probably not influenced by deposition and other fractionating processes (Olmez and Gordon, 1985). But, in some situations, when the industrial process involves purification steps (e.g. MAP production) and introduction of different mineral material (e.g. dicalcium phosphate production) the REE signature of final products can change, making it difficult to identify their raw material based on their REE signature. However, in general, we observed that REE signatures were preserved along the process of phosphate fertilizers production and, therefore, they can be used to identify the raw materials used for each product.

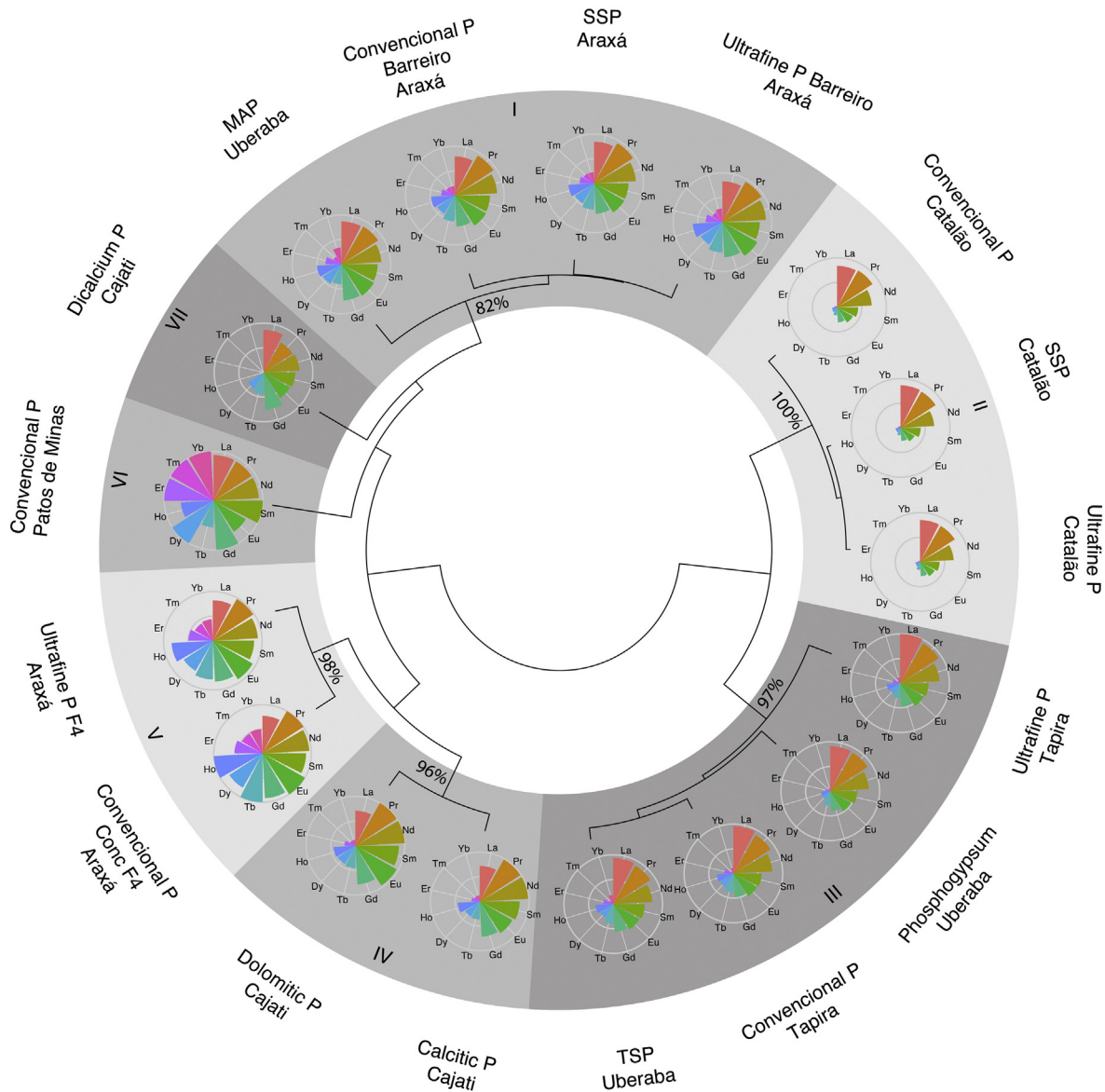
The Brazilian alkaline igneous rocks have a diversified mineralogical composition, which includes phosphates (e.g., carbonate-, hydroxy-, and fluorapatites), oxides (e.g., magnetite, anatase, and perovskite), semi-soluble salts (e.g., pyrite, calcite, and dolomite), and silicates

**Table 4**  
Annual production and the exported amount of REE for the materials studied.

Site	Material	Annual production (t) <sup>a</sup>	Estimated exportation (t) <sup>b</sup>		
			LREE	HREE	Σ REE
Catalão minerochemical complex	Ultrafine P concentrate	150,000	2447 (22)	50 (4)	2497 (22)
	Conventional P concentrate	860,000	12,891 (200)	295 (9)	13,186 (200)
	SSP	260,000	2125 (42)	50 (2)	2175 (42)
Araxá minerochemical complex	Ultrafine P concentrate Barreiro Mine	70,000	517 (2)	60 (1)	577 (2)
	Conventional P concentrate Barreiro Mine	130,000	879 (4)	95 (2)	974 (5)
	Ultrafine P concentrate F4 Mine	170,000	1302 (18)	211 (5)	1513 (19)
	Conventional P concentrate F4 Mine	320,000	1884 (36)	341 (13)	2225 (38)
	SSP	650,000	2736 (106)	306 (33)	3043 (111)
Tapira phosphate mine	Ultrafine P concentrate	160,000	1081 (3)	59 (1)	1140 (13)
	Conventional P concentrate	1,860,000	12,077 (301)	724 (19)	12,801 (301)
Uberaba industrial complex	TSP	810,000	3289 (140)	254 (9)	3544 (140)
	MAP	850,000	1554 (47)	199 (20)	1753 (50)
	Phosphogypsum	1,600,000	7784 (311)	283 (16)	8067 (310)

<sup>a</sup> Total production for each material in 2015, according to the Vale Fertilizantes company.

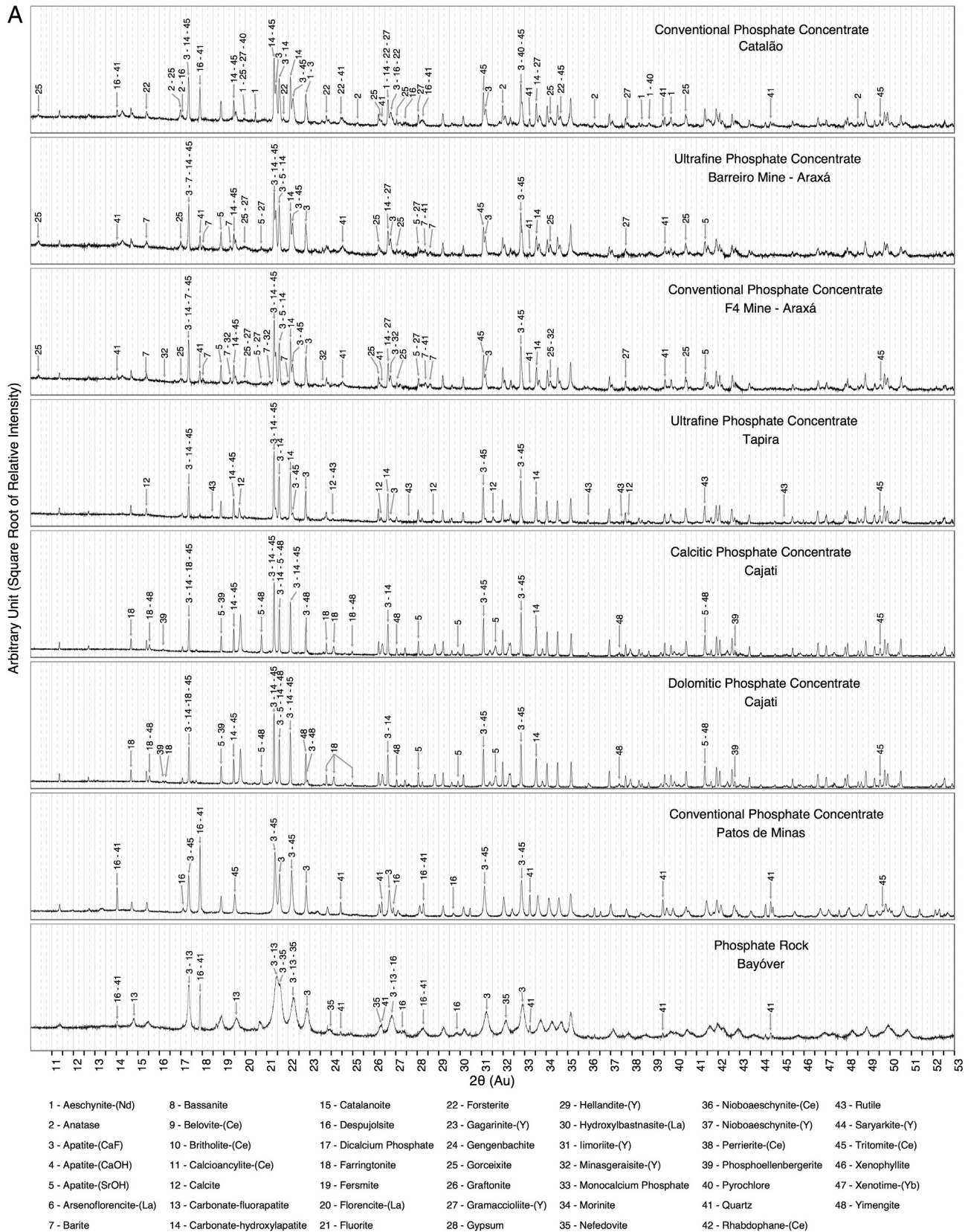
<sup>b</sup> Figures in brackets represent standard deviation.



**Fig. 3.** Clustering of samples of raw materials and products from phosphate fertilizer industry based on their REE contents normalized by their respective Ce content. Groups are indicated with Roman numerals (I–VII) and their bootstrap support (1000 bootstrap replicates) are shown in the respective branches. The radar charts at the tip of terminal branches display the ratio REE/Ce for each sample rescaled to vary between 0 and 1 (maximum across all samples).

(e.g., quartz, pyroxenes, and clay minerals) (Marino et al., 2012). In the present study, all phosphate concentrates were beneficiated from phosphate ore by using a combination of comminution, screening,

scrubbing, and hydrocyclones in order to remove clays, fine-grained iron-aluminum phosphates, and fine-grained iron oxides. We found that apatite, fluorapatite, and hydroxyapatite, taken together, are the



**Fig. 4.** Synchrotron-based X-ray diffraction patterns of A) raw materials and B) products of phosphate fertilizer industry in South America. Peaks are identified by numbers indicating their associated crystalline phases according to the list at the bottom of each subfigure. Chemical compositions for these crystalline phases are given in Appendix A.

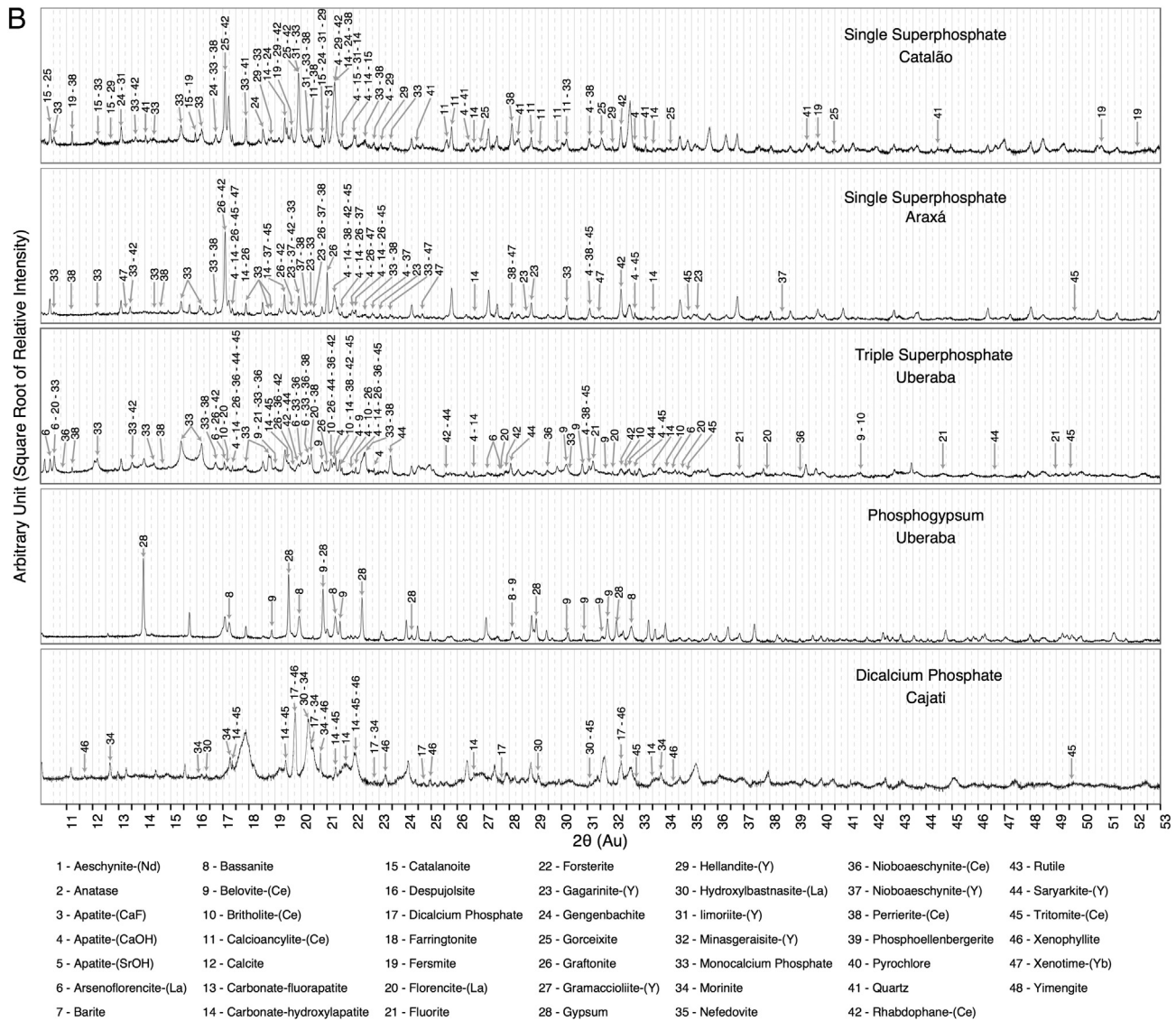


Fig. 4 (continued).

most abundant crystalline phases in raw materials and products, with quartz being the most abundant gangue mineral, especially for raw materials. Neumann and Medeiros (2015) who studied the mineralogical and technological characteristics of the Araxá complex REE (Nb-P) ore, also found that quartz is the main gangue mineral. We also observed a higher diversity of REE-carrying crystalline phases in the superphosphates than in their respective raw materials. This may be due to dissolution-precipitation of REE minerals after the sulfuric acid attack on the raw material, and to the residual concentration of insoluble minerals not detected in the raw materials. The diffraction patterns obtained by conventional XRD usually reveal dominant mineral components, while minor phases are generally at the level of background noise or are unresolved from overlapping dominant reflection. In our study, synchrotron X-ray diffraction was used to give high intensity and high-resolution diffraction data, which provided higher accuracy in identifying mineral phases in all samples analyzed.

Phosphate fertilizers are extensively applied worldwide, and encompass broad REE levels diversity (Abdel-Haleem et al., 2001; Otero et al., 2005; Turra et al., 2011). REE levels in fertilizers are relevant because of the potential loads of REE on the environment associated with fertilizer application. Therefore, the knowledge of REE concentration in fertilizers is essential for assuring food and environmental safety,

especially for areas of intensive agriculture. On the other hand, these elements can also have beneficial effects on plant growth, as indicated by several studies worldwide showing increases in seed germination, root growth, chlorophyll content, plant resistance, and agricultural productivity after REE application (d'Aquino et al., 2009; de Oliveira et al., 2015; Hu et al., 2004; Maksimovic et al., 2014; Ramos et al., 2016). In China, fertilizers are enriched with such elements due to their expected positive effects on plants. Such information is still very scarce for Brazilian agriculture.

In our study, we observed that REE contents in phosphate fertilizers reflect the REE levels in phosphate concentrates, both in regard to their content (Fig. 1) and to their signatures (Fig. 3). Cerium was always the dominant REE, followed by La, Nd, Pr, and Sm. Among the products analyzed, the maximum REE concentration was found for single superphosphate (SSP) from Catalão ( $\sum \text{REE} = 8365 \text{ mg kg}^{-1}$ ), followed by phosphogypsum from Uberaba ( $\sum \text{REE} = 5041 \text{ mg kg}^{-1}$ ), SSP from Araxá ( $\sum \text{REE} = 4681 \text{ mg kg}^{-1}$ ), TSP ( $\sum \text{REE} = 4375 \text{ mg kg}^{-1}$ ), and MAP ( $\sum \text{REE} = 2062 \text{ mg kg}^{-1}$ ) from Uberaba. These results indicate that considerable amounts of REE are being added to Brazilian soils, yet their potential effects are still unknown. Di-calcium phosphate is usually produced by reacting calcium carbonate with phosphoric acid. Consequently, the REE found in di-calcium phosphate in our study



( $\sum \text{REE} = 354 \text{ mg kg}^{-1}$ ) are probably coming from the calcium carbonate used in its production because REE could not be detected in the phosphoric acid from Cajati. Di-calcium phosphate is used as a core raw material in food supplements for cattle, poultry, pets, and shrimps. Previous studies have shown that dietary supplementation with REE could enhance animal nutrient utilization, minimize the growth of intestinal pathogens, and may act as cofactors that replace calcium or other metallic ions during various biological processes, including egg formation in laying hens (Cai et al., 2015; He and Rambeck, 2000; He et al., 2010). The favorable scenario for the REE adds value to the present study because the REE-fertilizers may have agronomic effect and di-calcium phosphate with REE could increase the animal performance.

Regarding the demand side, REE are classified as specialty materials rather than commodities, which implies that the need for them is predominantly driven by technological progress. These elements were identified as having high risk of supply shortage and high impact on the economy (Hislop and Hill, 2011). Considering the importance for strategic sectors of the economy with risks of supply shortage, Moss et al. (2013) described the following REE as “critical”: dysprosium (Dy), europium (Eu), terbium (Tb), yttrium (Y), praseodymium (Pr), and neodymium (Nd). We observed that Nd, Pr, and Y are present in larger amounts than Dy, Eu, and Tb in the samples studied. The highest levels of Nd and Pr were found in raw materials from the Catalão Mineralochemical Complex, while materials from the Araxá Mineralochemical Complex had the largest contents of Y, Dy, Eu, and Tb.

The significant outflow of REE, as reported in Table 4, could be economically exploited, especially the Catalão mine (Tassinari et al., 2001) which has the larger amount of LREE, and the Araxá mine, which showed higher levels of HREE. Phosphogypsum containing REE represents a potentially valuable resource (Zhang et al., 2012) and REE present in this material from the Uberaba Industrial Complex could be promising to be exploited. Considering the estimated size of the phosphogypsum stack in Uberaba (~55 million tons) and its mean  $\sum \text{REE}$  content (PhosGyp – Ubb, ~5000  $\text{mg kg}^{-1}$ , Fig. 2), the potentially exploitable amount of REE would be around 275 million tons.

It is important to evaluate phosphate fertilizers as a source of REE for agricultural ecosystems. If we consider that the main Brazilian phosphate fertilizers are SSP, TSP, and MAP, we estimate that the use of these fertilizers adds approximately 10.5 thousand tons of REE to Brazilian soils. Such amount is close to the annual consumption of important micronutrients (e.g., boron, copper, manganese, and zinc) in Brazilian agriculture (Ramos et al., 2016).

Finally, as discussed earlier, REE occurring in phosphate products may enhance plant and animal performance, but those effects probably depend on the bioavailability of REE, which for phosphate fertilizers are not yet known. Thus, further studies on REE contents in products from the P fertilizer industry need to focus on the total as well as the bioavailable fraction of REE. The total REE content in phosphate products varied by about three orders of magnitude in this study and this variation may be used in the future as an additional criterion to value phosphate fertilizers.

## 5. Conclusions

This study showed that the REE content in raw materials and products from phosphate industry in South America are highly variable. The phosphorite from Bayóvar Phosphate Mine has the lowest REE content among the studied raw materials ( $\sum \text{REE} \sim 70 \text{ mg kg}^{-1}$ ). Among those raw materials of igneous origin, the phosphate concentrates from the Catalão Mineralochemical 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 Mineralochemical Complex, especially the materials from F4 Mine, presented the highest contents of heavy REE ( $\sum \text{HREE} \sim 1.200 \text{ mg kg}^{-1}$ ).

A variety of mineral phases in phosphate concentrates and also in products was found, and the apatite-group seems to be the main crystalline phase that carries REE.

The REE contents in the products were generally strongly influenced by their respective raw materials. Consequently, the REE signatures in the final products of the P fertilizer industry in South America allow, in most cases, the accurate identification of their respective raw materials.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.gexplo.2016.06.009>.

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