

Dissolution techniques for determination of rare earth elements in phosphate products: Acid digestion or alkaline fusion?



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ABSTRACT

Several studies have been carried out to compare and/or improve instrumental analytical techniques capable of quantifying trace elements, rare earths included. Sample dissolution is a key step in this process and the choice of the most appropriate technique depends on many factors, e.g., digestion power, laboratory workability, available instrumentation, and timing. Alkaline fusion and acid digestion are often the preferred techniques for decomposition of geological samples due to their precision and accuracy. The aim of this study was to evaluate dissolution techniques for determination of REE in phosphate products by ICP-MS. For this, twenty samples of phosphate products were selected from the fertilizer quality control program of the Brazilian Ministry of Agriculture, Livestock, and Food Supply. Samples of these products were digested by either microwave digestion or alkaline fusion. Both methods yielded accurate results, with alkaline fusion being slightly more efficient than microwave digestion in the extraction of light REE. However, this difference between methods was not observed for heavy REE and it did not affect the REE signatures. The information provided in this paper can assist in the choice of dissolution techniques for REE quantification, especially in phosphate fertilizers. In addition, the equations provided in this paper may also be used to interconvert the results from both methods.

1. Introduction

Rare earth elements (REE) comprise 17 chemical elements in the periodic table, specifically the 15 lanthanides plus scandium and yttrium (IUPAC, 2005). Contrary to what the name may suggest, these elements are fairly abundant in nature (Shyam and Aery, 2012), except for promethium, which does not occur naturally in the Earth's crust (Šmuc et al., 2012). These elements are widely used in products from a variety of metal and high-tech industries. For instance, La is used in high refractive index glass, whereas Nd, Sm, Gd, and Dy are utilized in rare-earth magnets (Anan et al., 2012; Liu et al., 2012). For this reason, the industrial demand for REE has increased (Du and Graedel, 2011).

Besides, REE are also used in agriculture, mainly as fertilizers in China (Anan et al., 2012; Brioschi et al., 2012), and in livestock, as additives for pig and poultry feed (He et al., 2010). A major REE input into agricultural soils is through P fertilizers, which may contain high amounts of REE, due to the high affinity of these elements for P compounds (Loell et al., 2011; Ramos et al., 2016a). Phosphate fertilizer

products are thus relevant diffuse sources of REE to the environment (Ramos et al., 2016b). In view of the growing concern about the impact of REE additions in agroecosystems, a correct quantification of these elements is very important. For that, we first have to develop dissolution techniques for REE that allow for their precise and accurate quantification in a variety of sources.

The analytical techniques most frequently used for REE quantification are instrumental neutron activation analysis – INAA (Turra et al., 2011), isotopic dilution mass spectrometry – IDMS (Saha et al., 2014), total reflection X-ray fluorescence – TXRF (Wu et al., 2010), inductively coupled plasma atomic emission spectrometry – ICP/AES, and inductively coupled plasma mass spectrometry – ICP/MS (Tanase et al., 2014). Several authors have mentioned that ICP-MS has a superior detection capability when compared with other methods, and presents high precision and accuracy, currently making it the most suitable technique for REE quantification (Spalla et al., 2009; Saha et al., 2014; Tanase et al., 2014). However in an extensive review, Zawisza et al. (2011) have shown that precision and accuracy of REE-ICP-MS analysis

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Table 1
Phosphate products evaluated in this study.

Identification	Samples	P ₂ O ₅ content (%)
1	Phosphate rock	35
2	Magnesium thermophosphate	17
3	Monocalcium phosphate	18
4	Magnesium multiphosphate	18
5	Triple superphosphate	41
6	Monoammonium phosphate	48
7	12 60 00	60
8	09 48 00	48
9	17 44 00	44
10	05 36 00	36
11	03 27 00	27
12	08 24 16	24
13	06 24 16	24
14	02 20 20	20
15	00 18 18	18
16	04 14 08	14
17	10 10 10	10
18	06 10 18	10
19	12 05 00	05
20	Dicalcium phosphate	19

also depend of many others factors, e.g. matrices.

Although several studies have been carried out in order to compare and/or improve instrumental analytical techniques for quantifying the trace elements in geological materials (Kin et al., 1999; Cotta and Enzweiler, 2012; Fedyunina et al., 2012; Pinto et al., 2012) it is often the sample preparation that poses the most serious limitations on the accuracy and precision of analytical data (Jarvis, 1990). The chemical dissolution techniques constitute a prior step and can contribute up to 30% of the total error in analysis for elementary quantification (de Oliveira, 2003). Therefore, it is necessary to test chemical dissolution techniques regarding their efficacy in order to apply the methodology that ensures greater REE quantification precision.

Although not considered as an analytical procedure for assessing total concentration, acid digestion is one of the most used techniques for dissolution of geological samples. This method consists of sample dissolution in acids, in open or closed systems, under varying temperature and pressure (Fedyunina et al., 2012). However, by this technique, not all types of matrices are dissolved, due to the presence of refractory minerals (Trail et al., 2012). In general, these refractory minerals are associated with REE, and thus the REE levels may be underestimated (Fedyunina et al., 2012).

Another dissolution technique widely used is lithium metaborate fusion, also known as alkaline fusion (Cotta and Enzweiler, 2012). This technique involves the use of a fluxing agent and high temperatures, resulting in the formation of a glass easily soluble in nitric acid (Totland et al., 1992; Panteeva et al., 2003). This process is effective for the dissolution of the main forms of silicates, such as refractory minerals (Cotta and Enzweiler, 2012; Pinto et al., 2012). Thanks to that, alkaline fusion is considered a true “total concentration” analytical technique. On the other hand, this technique has disadvantages, such as high reagent consumption, higher sample dilution, longer time for sample preparation, and a possible interference of the fluxing agent added to the matrix (Bayon et al., 2009).

Table 2
Isobaric corrections factors.

Element	Mass	Correction factor
Eu	150.920	-0.00054 * Ba137
Gd	156.934	-0.01806 × Pr141
Tb	158.925	-0.01747 * Nd143-0.00018 * Pr141
Dy	162.930	-0.0044 × Sm147
Yb	173.939	-0.005865 * Hf178-0.02115 * (Gd160-0.093976 * Dy163-0.042596 * Nd146)
Lu	174.941	-0.01424 * (Tb159-0.0215 × Nd146)

Table 3
Optimized operating conditions of ICP-MS.

Instrument	Perkin Elmer NexIon 300D
RF Power	~1300 W
Spray Chamber and Nebulizer	Scott (Ryton) with concentric nebulizer
Coolant argon flow rate	15 L min ⁻¹
Auxiliary argon flow rate	1.0 L min ⁻¹
Nebulizer argon flow rate	0.8–1.2 L min ⁻¹ (adjusted daily to obtain optimum signal intensity and stability)
Sample uptake rate	Approximately 4.00 mL min ⁻¹
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 ⁻¹ multi-element solution
Ion transmission	> 27,000 cps per 1 ng g ⁻¹ indium
Rinse time between standards or samples	60 s (with 1% v/v HNO ₃)
Takeup 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

Because of different limitations, such as the lack of specific equipment, alkaline fusion or acidic digestion may be sometimes unfeasible to be used in some laboratories, what may favor the choice of one technique over the other. To the best of our knowledge, no study has yet addressed the bias introduced by each of these dissolution techniques on REE quantification in phosphate products, and how their results can be interconverted. In this study, we aim to contrast the REE quantification by ICP-MS in twenty phosphate products, including most of the marketed fertilizers and animal supplements in Brazil, using acid digestion and alkaline fusion for sample dissolution.

2. Experimental

2.1. Sample and sampling

For this study, 20 phosphate products (19 fertilizers and one feed supplement) were selected from the quality control program of the Brazilian Ministry of Agriculture, Livestock, and Food Supply (MAPA). These products include most of the commercial single and mixed phosphate fertilizers used in agriculture in Brazil, as well as a dicalcium phosphate, which has a historically significant use for animal supplementation (Table 1).

The phosphate products were prepared and analyzed following a quality assurance/quality control (QA/QC) program to ensure accurate and reliable analytical data. The samples were air-dried and ground to pass through a 150-mesh nylon sieve. Samples from all products were digested in triplicate by either microwave digestion or alkaline fusion.

2.2. Alkaline fusion and microwave digestion

For the alkaline fusion method, 0.1 g of each phosphate product was fused with 1.4 g of lithium tetra-metaborate (34.83% Li₂B₄O₇; 64.67% LiBO₂; 0.5%LiBr) in platinum crucibles at 1000 °C in a fusion machine

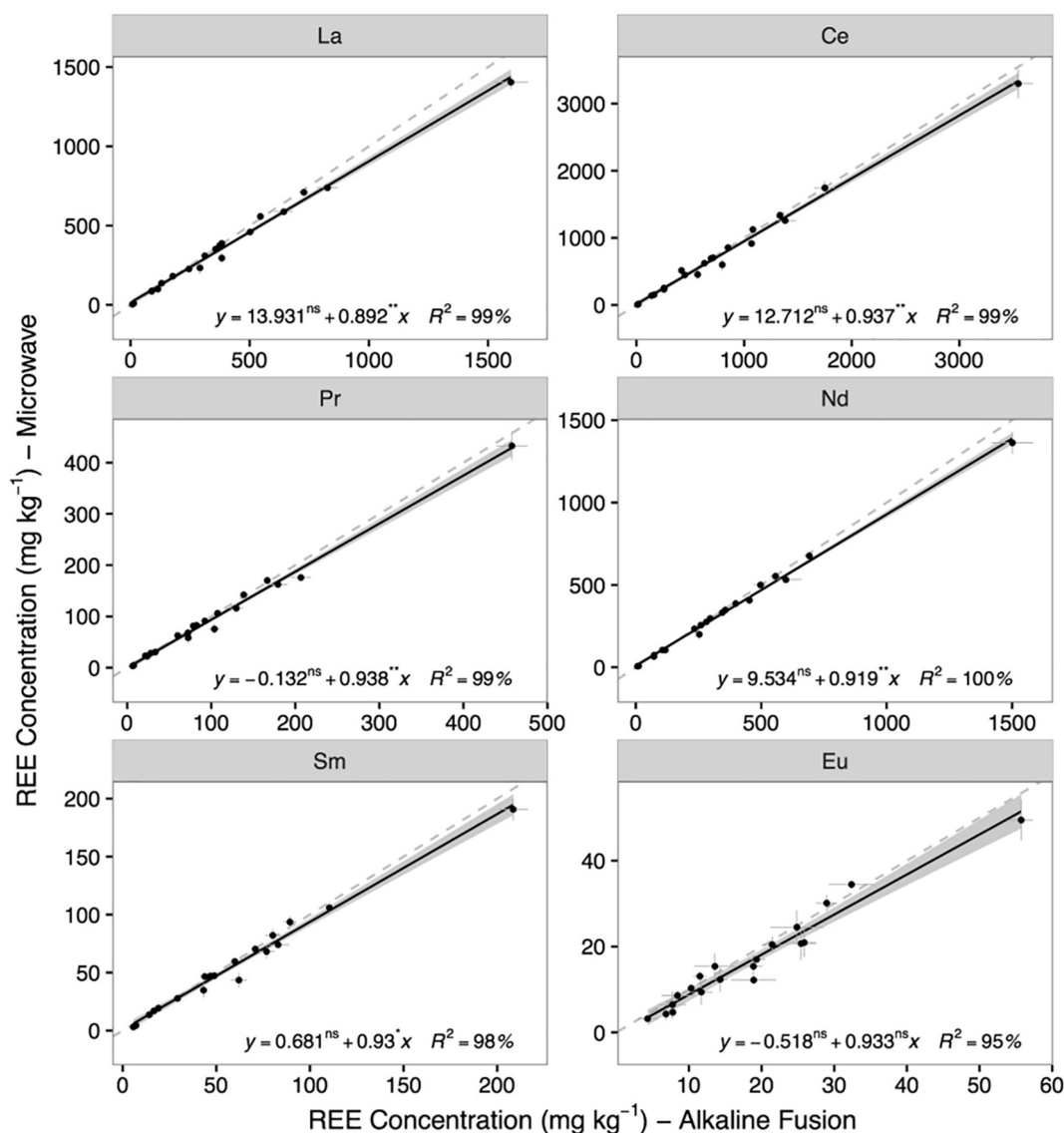


Fig. 1. Linear models relating LREE contents in samples dissolved by microwave digestion (y-axis) and alkaline fusion (x-axis). The points represent the mean ($n = 3$) REE content for each phosphate product, whereas the error bars indicate their standard errors along each axis. The regression line is represented by the black line, and the identity line (1:1 line) is represented by the grey dashed line. For each REE, the fitted coefficients (shown in the equation) are compared to those of the identity line (intercept = 0, slope = 1) and the significance of the test is indicated above each coefficient. * $P < 0.05$; ** $P < 0.01$; ^{ns} non-significant.

(Fluxer BIS, Claisse, Québec, Canada). After cooling, the resulting bead was dissolved in beakers containing 50 mL of a solution of tartaric acid (2.5% v/v) and HNO₃ (10% v/v). 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 solution of tartaric acid (2.5% v/v) and HNO₃ (10% v/v).

In the acid digestion method, the samples were microwave-digested according to U.S. Environmental Protection Agency (USEPA) Method 3051A (USEPA, 2007), using a CEM® Mars-5 microwave system (Mathews, NC, USA). Briefly, a 0.5 g aliquot of each sample was combined with 10 mL HNO₃ in Teflon-1 PTFE vessels and submitted to 0.76 MPa for 10 min in the microwave. All the reagents used were of high purity – Sigma–Aldrich® (St Louis, MO, USA) and the HNO₃ was distilled prior to use in the digestions. After cooling to room temperature, the extracts were filtered (Whatman No. 40 filter) and diluted by adding 10 mL of bi-distilled water.

The certified reference material (CRM) - Calcareous Soil ERM-CC690®, Institute for Reference Materials and Measurements (IRMM),

Geel, Belgium - was included for quality control. Blank and certified reference samples were analyzed in each digestion method.

2.3. Instrumentation

The REE concentrations in the digested solutions by both methods were determined by ICP-MS (Model NexION 300D, Perkin Elmer, Waltham, MA, USA). Both methods showed satisfactory recovery. Lanthanum and Cerium were analyzed in CRM, and their respectively recovery were $102.1\% \pm 4.91\%$ and $101.4\% \pm 3.25\%$ for alkaline fusion as well as $91.8\% \pm 3.27\%$ and $93.6\% \pm 2.44\%$ for microwave digestion, all in triplicate determinations. Isobaric corrections used for REE quantification as well as operation conditions of the ICP-MS are presented in Tables 2 and 3, respectively. It was not possible to quantify the Lu content in the samples due to the proximity of the calculated LD for this element.

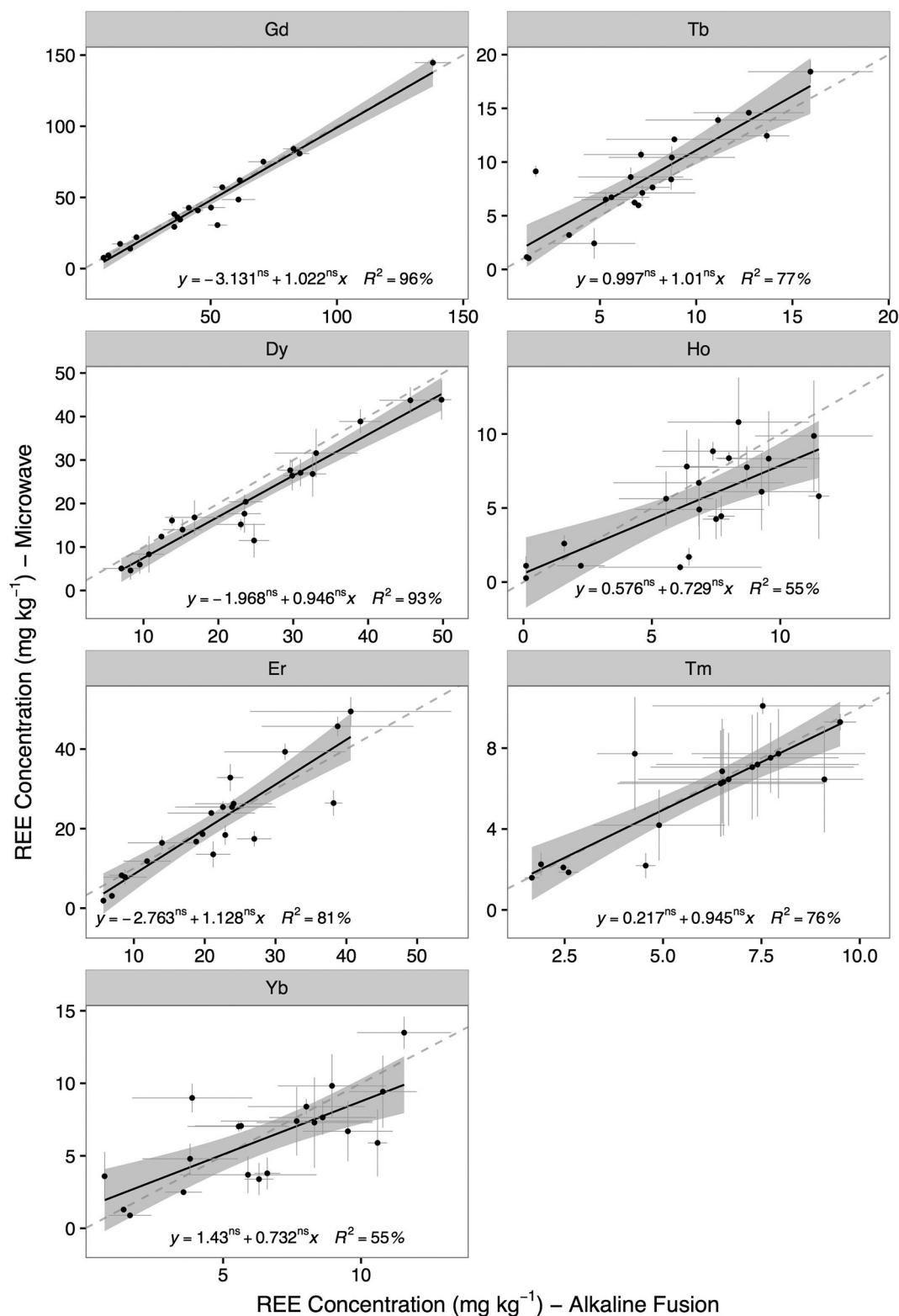


Fig. 2. Linear models relating HREE contents in samples dissolved by microwave digestion (y-axis) and alkaline fusion (x-axis). The points represent the mean ($n = 3$) REE content for each phosphate product, whereas the error bars indicate their standard errors along each axis. The regression line is represented by the black line, and the identity line (1:1 line) is represented by the grey dashed line. For each REE, the fitted coefficients (shown in the equation) are compared to those of the identity line (intercept = 0, slope = 1) and the significance of the test is indicated above each coefficient. * $P < 0.05$; ** $P < 0.01$; ^{ns} non-significant.

2.4. Statistical analyses

A hierarchical clustering analysis was performed to identify similarities among the samples regarding their REE contents. To eliminate

the abundance variations between odd and even atomic number elements, REE contents were transformed (divided by the respective La content in the sample). After calculating a matrix of Euclidean distances among samples based on their transformed REE contents, samples were

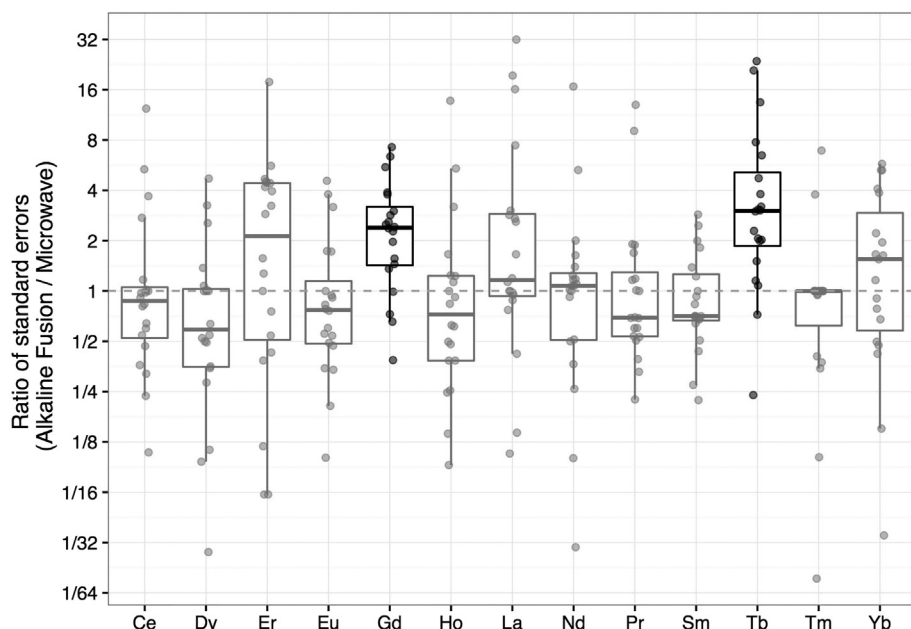


Fig. 3. Ratio of standard errors of REE content. For each REE (x-axis), the points represent the standard error of REE content ($n = 3$) obtained by alkaline fusion divided by the standard error ($n = 3$) obtained by microwave digestion for each sample. The highlighted boxplots are those for which the mean of this ratio was significantly different from 1 (identity) at $P = 0.05$ (Student's t -test).

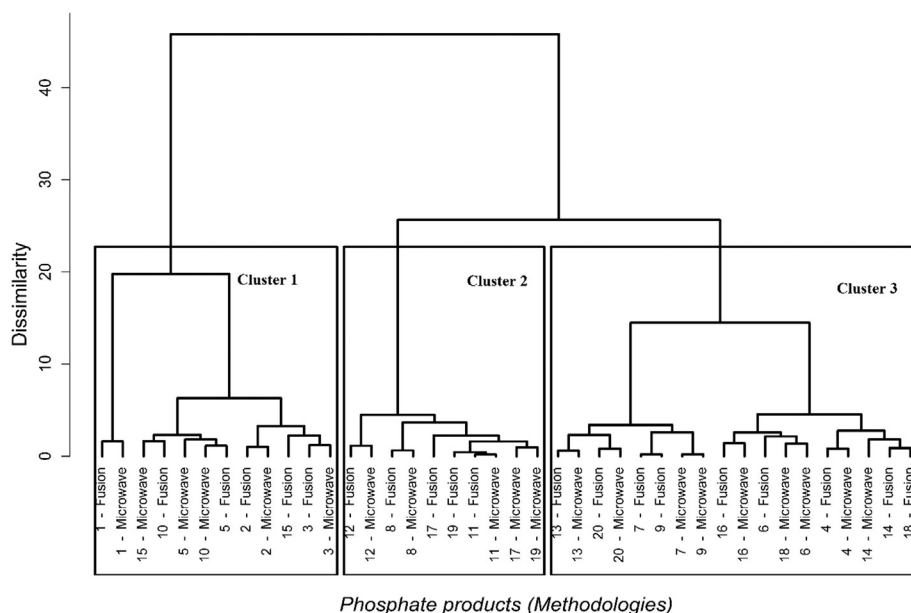


Fig. 4. Dendrogram showing the results of a hierarchical clustering analysis of REE signatures of phosphate products dissolved by alkaline fusion or microwave digestion. The height of the bars connecting the samples indicate their dissimilarity (Euclidean distance). Samples are identified by numbers, according to Table 1, followed by the method of sample dissolution.

clustered by the Ward's algorithm method (Ward, 1963). Groups were formed by cutting the dendrogram according to Mojena (1975), using the 1.25 factor as suggested by (Milligan and Cooper, 1985).

Differences for the sum of light- or heavy-REE contents between the two methods for each product were tested using Student's t -test at 1% significance level. Regression analyses were used to assess the relationship between REE contents from both alkaline fusion and microwave digestion. All statistical analyses were performed in R (Team, 2015).

3. Results/discussion

Inductively coupled plasma mass spectrometry (ICP-MS) has been extensively used to quantify REE in a variety of materials (Kin et al., 1999; Zhu, 1999; Awaji et al., 2006; Bayon et al., 2009; Pinto et al., 2012), but little is known with respect to how sample dissolution techniques can bias the REE measurement using ICP-MS. Once the decomposition of the samples is a fundamental step for geochemical

analysis, (Chao and Sanzalone, 1992; Yu et al., 2001) in the present study we compare the contents of 14 REE determined by ICP-MS from samples of 20 phosphate products, using two techniques of sample dissolution (alkaline fusion or microwave digestion).

According to their ionic radius and atomic number, REE are usually separated in two different categories, light (LREE – La to Eu) and heavy (HREE – Gd to Lu) (Dołęgowska and Migaszewski, 2013). Among the light REE (LREE), the regression models relating the concentrations obtained by microwave digestion to those obtained by alkaline fusion showed R^2 of at least 95%, indicating a general agreement between the two methods (Fig. 1).

Although considered dissimilar in terms of their sample dissolution capacity, i.e., microwave-assisted acid digestion with HNO_3 is a semi-quantitative dissolution technique, whereas alkaline fusion renders total dissolution, results provided by this study are relevant as quite a few laboratories have the capability of working with both techniques, especially with alkaline fusion, which is a lot more expensive and time-consuming than acid digestion. Even though acid digestions may not

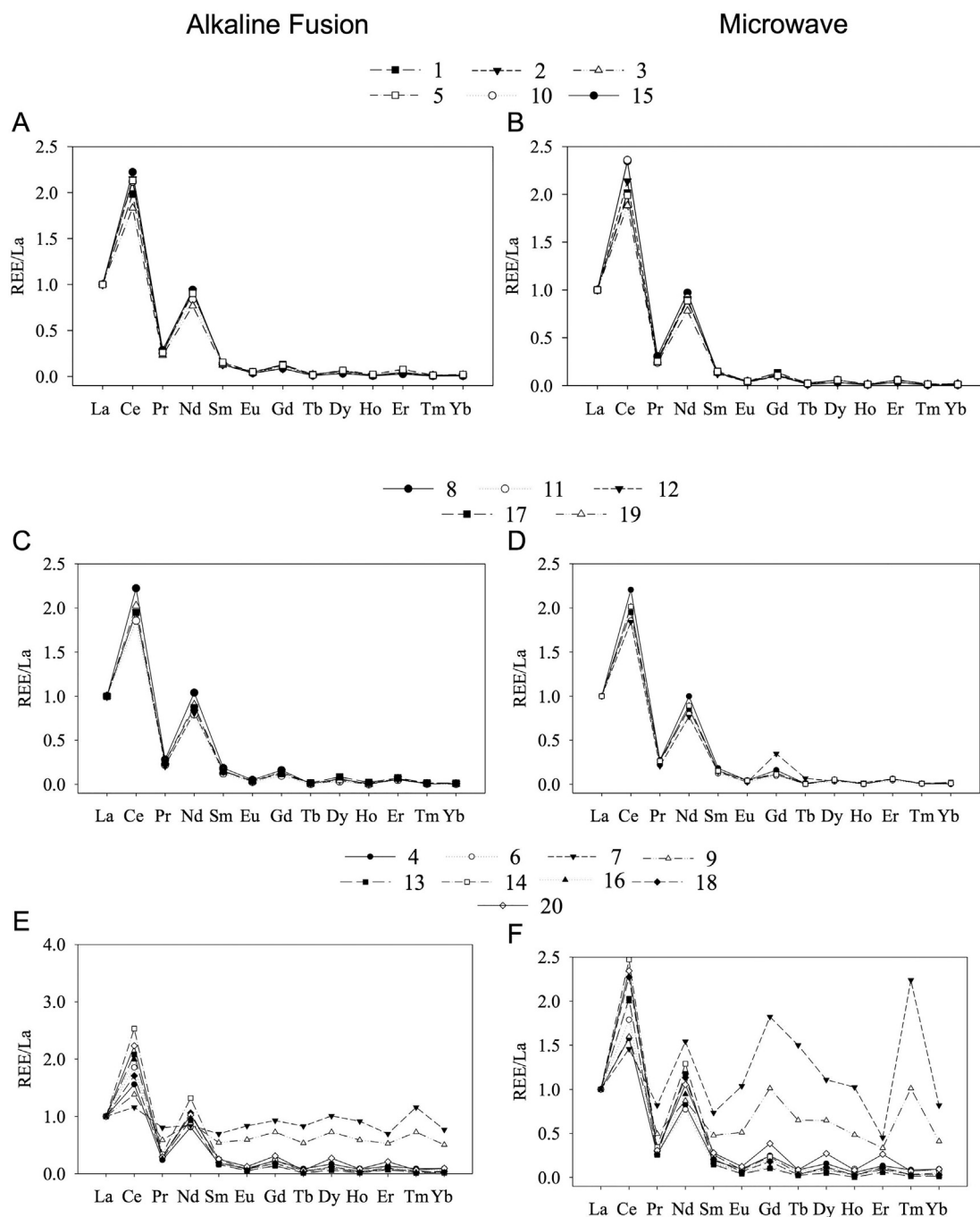


Fig. 5. Normalized levels of REE for all clusters. Samples from cluster 1 are presented in panels A–B; cluster 2, C–D; and cluster 3 E–F. Data is averaged from $n = 3$.

dissolve all types of matrices, they are extremely convenient to digest phosphate fertilizers because: i) they are quite simple procedures that allow the choice of either an open or closed digestion system; and, ii) they treat many samples at once and are easily adapted to robotic operations. Moreover, acid digestion systems do not require the addition of salts to the samples, which can bring impurities and contaminants that may cause matrix and elements interference (Chao and Sanzalone, 1992).

However, for all LREE, except Eu, those regression models differed significantly from the identity line (a line with slope 1), i.e. their slope were significantly less than one, indicating that for those LREE (La – Sm) microwave digestion is less efficient than alkaline fusion to solubilize the phosphate products tested (Fig. 1). Thus, for these elements, it is necessary to use the equations shown in Fig. 1 to convert the results

from alkaline fusion to microwave digestion. Unlike the results found in this work for LREE, Jarvis (1990), Totland et al. (1992) and Navarro et al. (2008) did not observe difference between both methods, except for samples containing refractory minerals. The discrepancy between our results and theirs probably lies on the different matrices being studied, because we studied phosphate fertilizers, which were submitted to industrial processing, whereas they studied naturally occurring geological standards. In addition, unlike this study, Jarvis (1990), Totland et al. (1992) and Navarro et al. (2008) have tested a mix of acids, which may interfere directly in the results. In face of this consideration, the results obtained for microwave digestion in this present work may have been due to the studied matrix. This fact suggests that HNO_3 alone would work well to digest phosphate products, which may represent economy and also less contamination (Pinto et al., 2012)

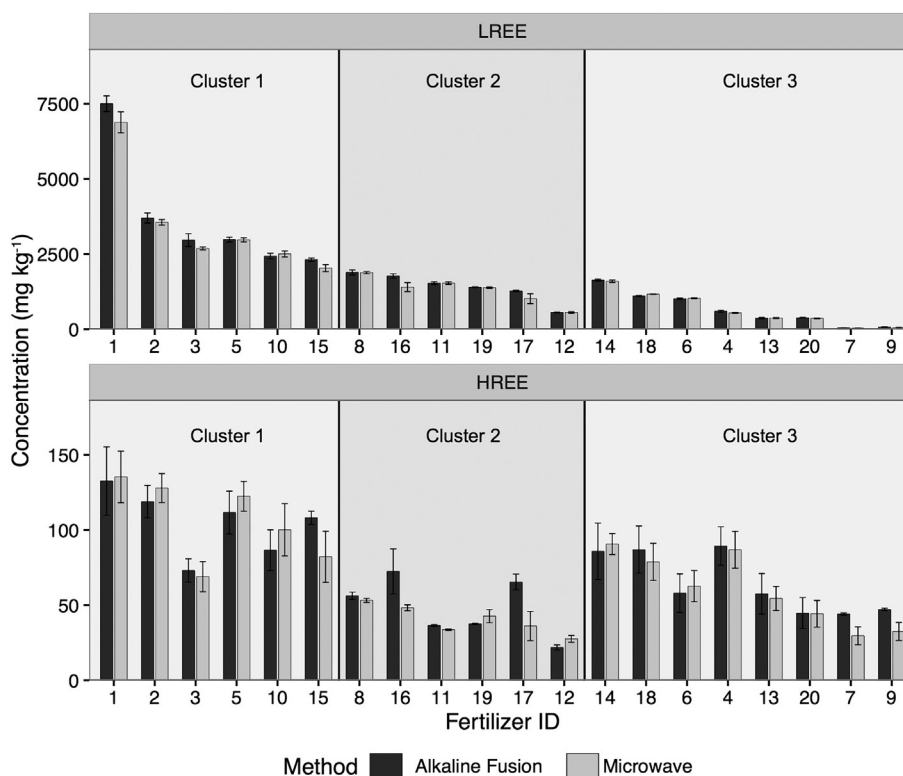


Fig. 6. Sum of light and high REE for both methods. Error bars indicate the standard error of the mean ($n = 3$). The shaded rectangles indicate the groups to which the samples were assigned in the clustering analysis.

For the heavy REE (HREE), the determination of REE concentration was highly variable for each sample, regardless of the sample dissolution technique, and consequently none of the regression models differed significantly from the identity line, i.e. differences between the two dissolution techniques regarding HREE contents were not significant (Fig. 2), specially for Gd and Tm. It is well known that restitic minerals, those mineral resistant to dissolution by acid attack, are enriched in REE, especially in HREE (Kanazawa and Kamitani, 2006; Hanchar and Van Westrenen, 2007; Laveuf and Cornu, 2009; Trail et al., 2012). The high variability observed for HREE may be due to variation in the content of restitic minerals, such as zircon, in the samples.

Furthermore, for Gd and Tb in Fig. 2, the variability of alkaline fusion results (horizontal error bars) were apparently higher than that from microwave digestion (vertical error bars). To test if the two methods differ significantly in the variability of their results, for each REE we calculated the log of the ratio between the standard errors (calculated from three replicates for each sample) of the two methods and tested if it differs significantly from zero (equivalent to a 1:1 ratio). This analysis indicated that the results from alkaline fusion were significantly more variable than those from microwave digestion for Gd and Tb (Fig. 3).

To further test the effect of each dissolution technique on the similarity among samples with regard to their REE signatures, we performed a hierarchical clustering analysis, presented as a dendrogram in Fig. 4. This dendrogram shows three clearly distinct clusters. In general, even though slight differences (vertical distances in the dendrogram) in REE signatures could be observed for the same sample between the dissolution techniques, the samples were consistently placed in the same cluster, regardless of the dissolution technique, which is desirable for the purpose of tracing parent materials. Cluster 1 includes 30% of the observations (Samples 1, 2, 3, 5, 10 and 15 for both dissolution techniques), and it includes the single and mixed phosphate fertilizers for which we found higher contents of light rare earth elements (LREE). Cluster 2 includes 25% of the samples. This cluster consists of mixed

fertilizers (Samples 8, 11, 12, 17 and 19). Cluster 3 includes 45% of the observations, and it includes single and mixed phosphate fertilizers and the feed supplement. This grouping was helpful to assist us explaining the results obtained for the sum of LREE and HREE levels (Fig. 6), as well as for comparing REE signatures (Fig. 5).

It is well established that REE contents can be used for tracing the origin of phosphate products (Otero et al., 2005; Ramos et al., 2016a). Fig. 5 shows the normalized REE signatures for samples of the three clusters. The normalized data of clusters 1 and 2 (Cluster 1 - Fig. 5-A and B and cluster 2 - Fig. 5-C and D) confirm that these groups have similar signatures, independently of the dissolution method, indicating that they possibly share the same parent material. On the other hand, the same was not clear for cluster 3, which showed a small difference in their signature, especially for HREE (Cluster 3 - Fig. 5-E and F). As mentioned before the signatures also indicated a general agreement between the two methods once they showed great similarity, except for cluster 3. For this cluster, it seems that HREE were responsible for the dissimilarity between the signatures. As discussed for Fig. 2, HREE quantification was considerably variable in this study possibly because of the presence of restitic minerals in the samples.

Finally, we calculated the total content of LREE and HREE for each sample to investigate if these quantities are influenced by the dissolution techniques. We found no significant effect ($P < 0.05$, Student's t -test, false discovery rate correction) of the dissolution technique on either LREE or HREE content, as shown in Fig. 6. In contrast to this result, Panteeva et al. (2003) reported that alkaline fusion was better than microwave digestion to analyze HREE. However, these authors have analyzed felsic rocks only. In general, samples from Cluster 1 were richer in both LREE and HREE as compared to the other clusters.

4. Conclusions

- 1- The evaluated methods of sample dissolution showed the same ability to extract REE when applied to LREE and HREE categories.

- 2- In this study, alkaline fusion was slightly more efficient than microwave digestion for the extraction of La, Ce, Pr, Nd, and Sm.
- 3- The contents of individual HREE were highly variable for both methods of sample dissolution. Gd and Tb contents were more variable when alkaline fusion was used.
- 4- The clustering of the samples based on REE signatures was consistent among dissolution techniques.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gexplo.2018.11.016>.

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