



# Radiological, chemical and morphological characterizations of phosphate rock and phosphogypsum from phosphoric acid factories in SW Spain

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## ABSTRACT

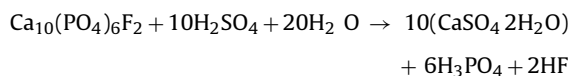
In this work, radiological, chemical, and also morphological characterization was performed in phosphate rock and phosphogypsum samples, in order to understand the behavior of toxic elements. Characterization was carried out using X-ray diffraction (XRD), X-ray fluorescence (XRF), gamma spectrometry and scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX). Our results show that the phosphate rock was mainly composed of fluorapatite, calcite, perovskite, quartz, magnetite, pyrite and kaolinite, whereas phosphogypsum only exhibited dihydrated calcium sulfate. The activity concentration of U-series radioisotopes in phosphate rock was around 1640 Bq/kg. <sup>226</sup>Ra and <sup>210</sup>Pb tend to be distributed into phosphogypsum by up to 80%, whereas the fraction of U-isotopes is 10%. The most abundant trace elements in phosphate rock were Sr, Cr, V, Zn, Y, Ni and Ba. Some elements, such as Ba, Cd, Cu, La, Pb, Se, Sr, Th and Y, were enriched in the phosphogypsum. This enrichment may be attributed to an additional input associated to the sulfuric acid used for the phosphoric acid production. Furthermore, results from SEM-EDX demonstrated that toxic elements are not distributed homogeneously into phosphogypsum. Most of these elements are concentrated in particles <20 μm of high porosity, and could be easily mobilized by leaching and/or erosion.

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## 1. Introduction

Two factories related to phosphoric acid and fertilizer manufacture, owned by Fertiberia and Foret, respectively, are located in the estuary of the Tinto and Odiel rivers (Huelva, SW Spain). This estuary is placed close to the city of Huelva, therefore environmental and safety protection measures have been implemented. It is well established that these industries of phosphoric acid and fertilizers use, as raw material, phosphate rock (of marine sedimentary origin) mainly from Morocco and Senegal [1]. The phosphate rock is, due to its origin, affected by high concentrations of impurities, heavy metals, naturally occurring radionuclides and other so-called trace elements [2,3]. The industrial processes, applied to the phosphate rock in these factories, therefore also lead to high concentrations of toxic elements in both products and wastes. Hence, the presence

of heavy metals, trace elements and natural radionuclide concentrations, at higher than natural levels, would be considered as environmental contamination. In Huelva, these industries use the “dihydrated” process to obtain phosphoric acid, whereby the phosphate rock is treated chemically with sulfuric acid. This process can be described by means of the following reaction [3]:



A by-product of the reaction is calcium sulfate dihydrate (CaSO<sub>4</sub>·2H<sub>2</sub>O), which is called phosphogypsum. Other products are phosphoric acid and hydrogen fluoride. Phosphogypsum is also composed, in lesser concentrations, of toxic elements (impurities, heavy metals and radioactive elements). The concentration of these elements into phosphogypsum may vary mainly depending on the origin of the phosphate rock and, to a lesser extent, on factors such as plant operation and phosphogypsum age [4]. In previous studies, the fluxes and contents of U in the phosphoric acid production process have been determined. The results show that the U content is in greater proportion in phosphoric acid (approximately >80%), while the U content in phosphogypsum is lower [1,5–7]. However, if the whole U content in phosphogypsum is considered, then 23% is bounded to the bioavailable fraction [8]. The same authors reported other stable elements present in the bioavailable fraction: 21% of

*Abbreviations:* PR, phosphate rock; PG, phosphogypsum; TF<sub>R</sub>, transfer factor of radionuclide; TF<sub>S</sub> and EF<sub>S</sub>, transfer factor and enrichment factor, respectively, of chemical specie.

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Ba (19.32 ppm), 6% of Cu (1.92 ppm) and Sr (57.8 ppm), 5% of Cd (0.75 ppm) and Ni (2.15 ppm), and 2% of Zn (5.26 ppm).

In our study, the phosphogypsum is stored in open-air piles near to the factories. It is estimated that annually 2.5 million tons of phosphogypsum are deposited in these piles. Since the 1980s, elemental, chemical and radiochemical analyses have been applied in order to monitor the possible radioactive impact to the estuary [6]. However, further information is required on the elemental and mineralogical characterization, as well as on the distribution of particles in stockpiled phosphogypsum, which can help towards a better understanding of the possible environmental contamination. For this, additional data analysis and identification of data heterogeneity are necessary to fully evaluate the environmental impact and risks [9].

The application of PG in different fields is being studied nowadays. If the PG amounts required by these new uses increase in the following years, a deep decrease of the stored PG would be expected and therefore a reduction in the environmental impact around the PG stacks. At present, the most common uses of phosphogypsum are: in agriculture, as a substitute of gypsum in building, in the production of cement, and as a conditioner of soil for road construction.

In agriculture, this by-product is widely used in highly weathered soils with low levels of extractable nutrients, in soils with high contents of Al and Na, as well as in calcareous soils [10,11]. In the field of construction, it has been used in the manufacture of gypsum boards, bricks and blocks, and in embankment construction Portland cement [12]. Phosphogypsum is also used as a binder for base course mixtures for roads, by replacing clay mixtures [13]. In addition, it can be used in landfills related with urban solid wastes [14].

However, the main restrictions for the applications of phosphogypsum are related to its high content of both toxic elements and radioactivity, and hence it is necessary to obtain a deeper understanding of physical–chemical characteristics of this by-product.

In this work, our experimental techniques, based on the determination of the radioisotope activity concentration in the bulk samples, are extended to determine the phases present in these matrices, since toxic elements may be found in non-mineralized phases. These additional experimental techniques are electron microscopy and X-ray analyses.

The results of this research on the composition and distribution of toxic elements (including radioactive elements) in PG forms the basis of a most extensive study on the mobility of chemical species, thereby enabling us to continue on to the next step of assessing the risks of a possible environmental impact, as well as to provide information on microstructural characteristics of PG for its possible reuse.

Therefore, the objectives of the present study are, firstly, to obtain a comprehensive set of data on chemical composition and radionuclide content, to then identify the crystalline phases and, finally, to check the morphology and particle composition on both Morocco phosphate rock and stockpiled phosphogypsum.

## 2. Materials and methods

Phosphate rock (PR) samples were collected in the Fertiberia factory of Huelva in 2009. In this study 10 representative surface samples of phosphogypsum (PG) were selected from a sample set previously collected. The PG sampling procedure is described by Abril et al. [10]. These PG samples were taken in 2005 from a stack belonging to the phosphoric acid factories, located next to the Tinto river (37° 15.3'N, 6° 54'W). It has been inactive since the beginning of the 1990s. The surface of this PG stack is 0.9 km × 0.6 km, and it has 5–8 m of thickness. This PG stack showed a mean pH of 3. A

rectangular sampling mesh of 50 m × 75 m was established within region stack, which was covered with 16 sampling points. The samples were ground and sieved to 100 μm diameter and, these were then dried at 50 °C for 48 h.

Physical and morphological characterizations were performed on phosphate rock and phosphogypsum by the following techniques: X-ray diffraction (XRD), and scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX). Concentrations of trace elements and radioisotopes were obtained by X-ray fluorescence (XRF) and gamma spectrometry, respectively.

Analyses of XRD were used to determine crystalline phases in PR and PG samples. In this work, a Bruker D8 Advance diffractometer with K $\alpha$  Cu radiation (30 mA current and 40 kV) was used. The patterns of diffraction were obtained in a 2 $\theta$  scanning range from 3° to 70°, with 0.03° and 2 s of scan step and time, respectively.

Morphology and particle composition of samples were performed using a JEOL 6460LV scanning electron microscope (SEM) with acquisition of digital images in both secondary (SEI) and backscattered (BEI) electron imaging modes (maximum resolution 3.5 nm). This device was coupled to an EDX microprobe and fitted with an ATW2 beryllium window (resolution 137 eV at 5.9 keV). The semi-quantitative analysis was performed using the Oxford INCA software.

XRF was employed to determine major elements, impurities and trace elements in the same samples. The analysis was carried out in a Panalytical AXIOS with an Rh tube.

Naturally occurring radioisotopes were determined by gamma spectrometry. In this investigation, a Germanium coaxial detector of extended range (XTRA) manufactured by CANBERRA, with a relative efficiency of 37.1% and FWHM = 1.76–1332 keV <sup>60</sup>Co, was used. This detector has a passive shield of 10 cm of lead, and an active shield composed of a VETO system (scintillator BiconBC-418 model) which works in anticoincidence mode with the XTRA to reduce the background interference. The measurement of the activity of the <sup>238</sup>U series was made by means of the 63.3 keV of <sup>234</sup>Th [15], 352 keV of <sup>214</sup>Pb, 609 keV of <sup>214</sup>Bi and 46.5 keV of <sup>210</sup>Pb photo-peaks.

## 3. Results and discussion

### 3.1. XRD characterization

PR and PG samples were analyzed through XRD to determine their crystalline composition.

In the case of PR samples and according to our results, the following species were observed: fluorapatite (Ca<sub>5</sub>F(PO<sub>4</sub>)<sub>3</sub>), calcite (CaCO<sub>3</sub>), perovskite (Ca(TiO<sub>3</sub>)), quartz (SiO<sub>2</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>), pyrite (FeS<sub>2</sub>), and kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>). This composition is consistent with those published by other authors who have studied phosphate rocks of sedimentary origin from different places [3,16].

Additionally, PG is only composed of calcium sulfate dihydrate (Fig. 1). All samples analyzed show the same crystalline composition. From the literature, the majority of PG samples show this composition, although, in PG from Brazil, calcium sulfate hemihydrate, in addition to the expected CaSO<sub>4</sub>·2H<sub>2</sub>O, was also present [17].

The presence of bassanite is usually explained by losses of water in calcium sulfate dihydrate samples through evaporation at 90 °C [18,19]. This fact was observed when samples of PG, which had been previously dried in an oven at 95 °C for 24 h, were analyzed using XRD. Indeed, the crystalline composition showed a significant change, indicating that calcium sulfate hemihydrate and calcium sulfate dihydrate, can coexist. In Fig. 2, the XRD pattern, where the two calcium sulfate phases can be clearly observed, is given.

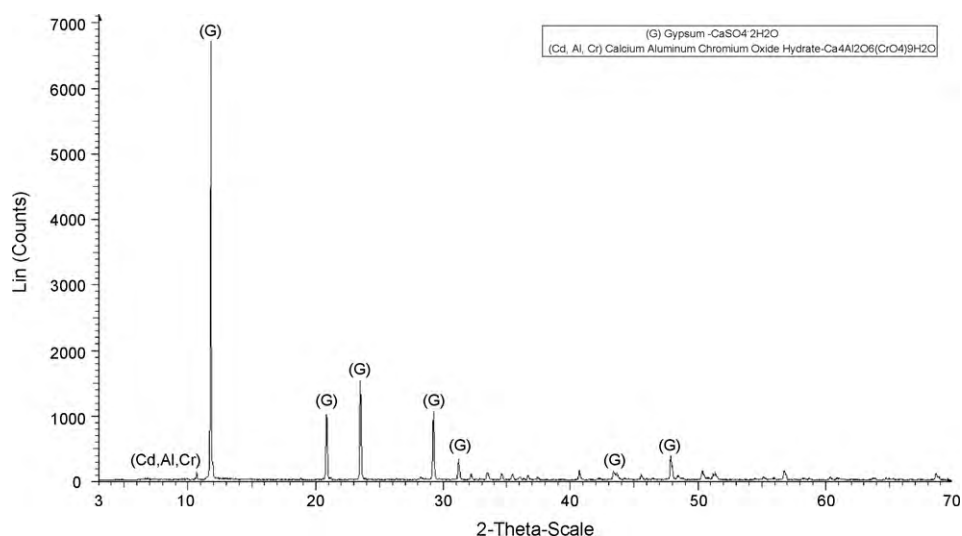


Fig. 1. Diffraction pattern of PG, dihydrated phase of gypsum is the main compound.

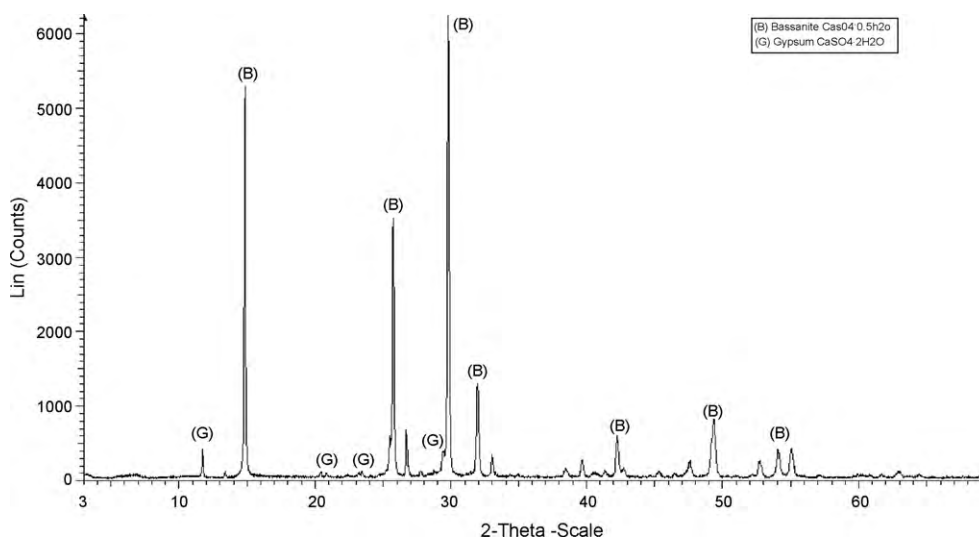


Fig. 2. Diffraction pattern of a sample of PG, which was previously dried at 90 °C.

### 3.2. Radioactive characterization by gamma spectrometry

The activity concentrations in the analyzed samples of  $^{238}\text{U}$ ,  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$ , determined by gamma spectrometry, are shown in Table 1. Due to the short half-life of  $^{234}\text{Th}$ , daughter of  $^{238}\text{U}$ , the activity concentrations of both radionuclides in every sample are considered in equilibrium. Therefore, the activity concentration of  $^{234}\text{Th}$  determined by gamma spectrometry, must be the same activity concentration of its parent. On the other hand,  $^{226}\text{Ra}$  activity concentration was obtained from two lines of  $^{214}\text{Bi}$  (609 and 1120 keV, respectively) and  $^{214}\text{Pb}$  (295 and 351 keV, respectively) in the gamma spectra, for similar reasons.

According to our results (Table 1), all the radioisotopes, which belong to the U-series, are in secular equilibrium in the PR samples. The activity ratio, close to unity, is obtained when  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Po}$  are compared. This secular equilibrium is expected due to the very old age of the natural deposits of phosphate rock. Moreover, the U contents observed in the analyzed samples show the typical values found in phosphate rock of sedimentary origin, which usually range from 700 to 2600 Bq/kg [16,20].

When the comparison with  $^{238}\text{U}$  activity concentration in igneous PR (376 Bq/kg) [21,22] is performed, it can clearly be observed that  $^{238}\text{U}$  activity concentration is higher in our PR samples than the levels usually observed in igneous rocks, thereby

Table 1

Average activity concentration (Bq/kg) of U-series radioisotopes and activity ratios of the phosphate rock and phosphogypsum samples.

| Sample | Activity concentration (Bq/kg) <sup>a</sup> |                   |                   | Activity ratio                   |                                  |
|--------|---|-------------------|-------------------|----------------------------------|----------------------------------|
|        | $^{238}\text{U}$                            | $^{226}\text{Ra}$ | $^{210}\text{Pb}$ | $^{226}\text{Ra}/^{238}\text{U}$ | $^{210}\text{Pb}/^{238}\text{U}$ |
| PR     | 1640 ± 272                                  | 1566 ± 63         | 1638 ± 110        | 0.95                             | 0.998                            |
| PG     | 100 ± 22                                    | 785 ± 42          | 827 ± 46          | 7.85                             | 8.27                             |

<sup>a</sup> Measurements and 1σ error.

**Table 2**  
Transfer factor ( $TF_R$ ) of some radioisotopes from phosphate rock (PR) to phosphogypsum (PG).

| Isotope           | Activity concentration (Bq/kg) |     | $TF_R$ |
|-------------------|--------------------------------|-----|--------|
|                   | PR                             | PG  |        |
| $^{238}\text{U}$  | 1640                           | 100 | 0.10   |
| $^{226}\text{Ra}$ | 1566                           | 785 | 0.84   |
| $^{210}\text{Pb}$ | 1638                           | 827 | 0.84   |

corroborating the fact that phosphates from sedimentary origins show a higher U content than levels observed in igneous phosphate [3,17].

On the other hand, during the phosphoric acid process, the aforementioned radioactive equilibrium is broken, and every radionuclide is distributed differently depending on its solubility. Thus, the uranium mainly remains in phosphoric acid (under oxidizing conditions, up to 90%), while most of the radium is transferred into phosphogypsum [3,6,23].

Our results are in agreement with this behavior. Thus, the activity concentration of  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  are higher than the activity concentration of  $^{238}\text{U}$  in PG. Moreover, the three radioisotopes show similar concentrations to those previously reported by other authors [4–6,10,24].

The different behavior of the radionuclides under study can be evaluated through a transfer factor evaluated, for every radionuclide, by the following equation:

$$TF_R = \frac{C_{PG} \times f}{C_{PR}}$$

where  $TF_R$  is the transfer factor of the radionuclide of interest,  $C_{PG}$  is the activity concentration of this radionuclide in PG,  $C_{PR}$  is the activity concentration of the same radioisotope in PR, and  $f$  is a production factor defined as the mass (kg) of PG per kg of treated PR. Table 2 shows the transfer factor of every radionuclide.

Taking into account the production data published by the Huelva factories, the value of the production factor  $f$  can be estimated to be 1.66 kg of PG per kg of treated PR [1]. The transfer factor, evaluated according to this data, is shown in Table 2. The  $TF_R$  was close to unity for Ra- and Pb-isotopes, and eight times higher than the  $TF_R$  obtained for U-isotopes. According these data, 80% of  $^{226}\text{Ra}$  and

$^{210}\text{Pb}$  are transferred from the PR to the PG, whereas uranium is transferred at only 10%.

### 3.3. Elemental characterization by XRF

Table 3 shows the concentration (% weight) of the main species and impurities in PR and PG. This table also provides a comparison of those same components in phosphogypsum from different origins.

The PR contents were found to be 42% calcium and 35% phosphorous, accompanied by lower levels of impurities (Si, Al, Fe and Ti). The sedimentary origin of PR is confirmed by observing the concentrations of main elements and impurities, when the typical levels in PR of igneous origin, from Brazil, are compared (Table 3). In Brazilian PR, indeed, the authors reported lower concentrations of Ca and P, and much higher contents of impurities such as Fe, Si, Ti, and Ba [22].

Furthermore, the analyzed PG is mainly  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , which is confirmed through XRF (Table 3). Indeed, the mass of S and Ca is close to 90% of total weight. The major content impurities in PG were  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$ , and, to a lesser extent,  $\text{K}_2\text{O}$ , and  $\text{TiO}_2$ . In PG samples,  $\text{SiO}_2$  may be found as quartz, and together with  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  and/or  $\text{K}_2\text{O}$ , might indicate the presence of clay minerals [3,25]. If the results of main and lesser components are compared to those reported in the literature, then similarity can be observed [2–4,22,26,27].

It is important to note that  $\text{P}_2\text{O}_5$  was also found in PG samples (from 0.6 to 0.85 g of  $\text{P}_2\text{O}_5$  in 100 g of PG). These results are similar, although slightly lower, than typical levels reported by other authors (Table 3) and can be attributed to the non-processed particles of phosphate rock. However, previous publications had reported 2.54 g of  $\text{P}_2\text{O}_5$  in 100 g of PG in fresh PG from the same factories [2]. These higher  $\text{P}_2\text{O}_5$  concentrations in fresh PG could be attributed to the remaining solution of phosphoric acid, which is not present in PG which has been stored for long periods. Therefore, the phosphoric acid, and associated elements, would have been spread into the close environment.

A transfer factor and an enrichment factor, applied to chemical species, are now defined:

$$TF_S = \frac{C_{PG} \times f}{C_{PR}}, \quad EF_S = \frac{C_{PG} \times f}{C_{PR}}$$

**Table 3**  
Mean content (% weight) of major species and impurities in phosphate rock (PR) from Morocco and phosphogypsum (PG) samples, by-product of treatment of this PR. Results are also compared to others published in the current literature. Notes: The sites are the origin of the phosphate rock used as raw material. n.d. means not detected, n.m. means not measured or not reported.

| Component                      | Sedimentary            |                        |                        |                     |                      |                      | Igneous               |                       |
|--------------------------------|------------------------|------------------------|------------------------|---------------------|----------------------|----------------------|-----------------------|-----------------------|
|                                | PR                     | Phosphogypsum (PG)     |                        |                     |                      |                      | PR                    | PG                    |
|                                | (Morocco) <sup>a</sup> | (Morocco) <sup>a</sup> | (Florida) <sup>b</sup> | (Togo) <sup>b</sup> | (Idaho) <sup>b</sup> | (Egypt) <sup>c</sup> | (Brazil) <sup>d</sup> | (Brazil) <sup>d</sup> |
| CaO                            | 42.65 ± 1.87           | 38.14 ± 1.70           | n.m.                   | n.m.                | n.m.                 | n.m.                 | 8.6                   | 37.5                  |
| SO <sub>3</sub>                | 0.95 ± 0.18            | 48.12 ± 9.04           | n.m.                   | n.m.                | n.m.                 | n.m.                 | n.m.                  | n.m.                  |
| P <sub>2</sub> O <sub>5</sub>  | 34.80 ± 0.45           | 0.69 ± 0.01            | 0.84                   | 0.61                | 1.33                 | 2.05                 | 9.1                   | 1.9                   |
| SiO <sub>2</sub>               | 8.25 ± 0.12            | 0.86 ± 0.01            | 5.12                   | 3.57                | 6.68                 | 5.53                 | 11.7                  | 1.4                   |
| Al <sub>2</sub> O <sub>3</sub> | 1.73 ± 0.01            | 0.19 ± 0.001           | 0.18                   | 0.28                | 0.22                 | 0.23                 | 5.15                  | <0.1                  |
| Fe <sub>2</sub> O <sub>3</sub> | 0.27 ± 0.01            | 0.21 ± 0.01            | 0.12                   | 0.08                | n.m.                 | n.m.                 | 39                    | 0.88                  |
| Na <sub>2</sub> O              | 0.48 ± 0.02            | 0.17 ± 0.01            | 0.03                   | 0.05                | 0.03                 | 0.49                 | n.m.                  | n.m.                  |
| K <sub>2</sub> O               | 0.20 ± 0.01            | 0.01 ± 0.001           | 0.03                   | <0.01               | 0.08                 | n.m.                 | n.m.                  | n.m.                  |
| TiO <sub>2</sub>               | 0.04 ± 0.001           | 0.01 ± 0.0004          | 0.093                  | 0.06                | 0.066                | n.m.                 | 15.6                  | 0.6                   |
| MnO                            | 0.005 ± 0.001          | n.d.                   | n.m.                   | n.m.                | n.m.                 | n.m.                 | n.m.                  | n.m.                  |
| MgO                            | 0.57 ± 0.02            | n.d.                   | n.m.                   | n.m.                | n.m.                 | n.m.                 | 2.04                  | 0.3                   |
| BaO                            | n.d.                   | n.d.                   | n.m.                   | n.m.                | n.m.                 | n.m.                 | 1.5                   | 1.1                   |
| SrO                            | n.d.                   | n.d.                   | n.m.                   | n.m.                | n.m.                 | n.m.                 | 0.84                  | 0.47                  |
| LOI <sup>e</sup>               | 8.9                    | 22                     | n.m.                   | n.m.                | n.m.                 | n.m.                 | 6                     | 46                    |

<sup>a</sup> This work. Measurements and 2σ error.

<sup>b</sup> [4].

<sup>c</sup> [21].

<sup>d</sup> [18].

<sup>e</sup> Loss on ignition.

**Table 4**

Transfer factor (TF<sub>S</sub>) of major species and impurities comparing phosphate rock (PR) to phosphogypsum (PG), n.d. means not detected.

| Component                      | Concentration (% weight) |               | TF <sub>S</sub> |
|--------------------------------|--------------------------|---------------|-----------------|
|                                | PR                       | PG            |                 |
| P <sub>2</sub> O <sub>5</sub>  | 34.80 ± 0.45             | 0.69 ± 0.01   | 0.03            |
| SiO <sub>2</sub>               | 8.25 ± 0.12              | 0.86 ± 0.01   | 0.17            |
| Al <sub>2</sub> O <sub>3</sub> | 1.73 ± 0.01              | 0.19 ± 0.001  | 0.18            |
| Na <sub>2</sub> O              | 0.48 ± 0.02              | 0.17 ± 0.01   | 0.59            |
| K <sub>2</sub> O               | 0.20 ± 0.01              | 0.01 ± 0.001  | 0.08            |
| TiO <sub>2</sub>               | 0.04 ± 0.001             | 0.01 ± 0.0004 | 0.42            |
| MnO                            | 0.005 ± 0.001            | n.d.          | –               |
| MgO                            | 0.57 ± 0.02              | n.d.          | –               |

**Table 5**

Enrichment factor (EF<sub>S</sub>) of major species and impurities comparing phosphate rock (PR) to phosphogypsum (PG).

| Component                      | Concentration (% weight) |              | EF <sub>S</sub> |
|--------------------------------|--------------------------|--------------|-----------------|
|                                | PR                       | PG           |                 |
| CaO                            | 42.65 ± 1.87             | 38.14 ± 1.70 | 1.49            |
| SO <sub>3</sub>                | 0.95 ± 0.18              | 48.12 ± 9.04 | 84.59           |
| Fe <sub>2</sub> O <sub>3</sub> | 0.27 ± 0.01              | 0.21 ± 0.01  | 1.30            |

where TF<sub>S</sub> and EF<sub>S</sub> are the transfer factor and the enrichment factor, respectively, of the species of interest, C<sub>PG</sub> is the mass concentration of this species in PG, C<sub>PR</sub> is the mass concentration of the same species in PR, and *f* is a production factor defined as the mass (kg) of PG per kg of treated PR. Table 4 shows the transfer factor of every species. From the results listed in this table, the impurities from PR are transferred to PG in different proportions.

The transfer factor is evaluated in species that are only in PR, whereas the enrichment factor is evaluated in species that are also in the sulfuric acid solution added into the phosphate rock to obtain phosphoric acid. Usually, this enrichment factor was higher than unity (see Table 5). Thus, in addition to the transference of SO<sub>3</sub> from PR, there is an enrichment of this component due to the sulfuric acid used in the phosphoric acid production. The presence of Fe<sub>2</sub>O<sub>3</sub> in some chemical reagents used in the process could explain why it

EF<sub>S</sub> is also higher than the unity. However, the TF<sub>S</sub> values are lower than unity in the rest of the species, because they are not in the sulfuric acid solution.

The concentration of trace elements (ppm) in PR and PG, as well as a comparison of those same components in phosphogypsum from different origins, are shown in Table 6.

According to our results, the concentrations of trace elements were found in the following order of abundance, in PR: Sr > Cr > V > Zn > Y > Ni > Ba; while in PG: Sr > Y > Ba > La > Cu > Cr.

Carbonatites of igneous origin, PR used in Brazil, are enriched in Ba and rare earth element (REE) in comparison with phosphorites of sedimentary origin [22,28]. These authors reported Ba concentrations as impurities, in the order of 1.5% of total weight (see Table 3) while in our PR samples it is present as a trace element (Table 6). Additionally, heavy metal concentration in those igneous PR samples reported by da Conceicao [22] (Cd, 4 ppm; Cr, 70 ppm; Cu, 96 ppm; Ni, 117 ppm; Pb, 44 ppm; Zn, 326 ppm) are higher than those found in this work, whereas Martín et al [2] and Pérez-López et al. [8] also reported heavy metal concentrations in Morocco PR, at levels similar to those found in our study.

In these PG samples, most trace elements are of similar concentrations to those reported by authors in PG obtained from sedimentary PR, however, contents of Ba, La, Sc, Th and U are higher in our PG sample (Table 6).

Yttrium is an element that is commonly considered as an REE due to its similar properties (+3 oxidation states) to those of the Lanthanide series. In these PG samples, Y and La concentrations are as high as those reported by some authors (from 49 to 158 ppm) [2,4,5,25]. However, in Brazilian PG [28], Zr and La are almost 20 times more enriched (Zr, 1280 ppm and La, 1210 ppm), in comparison to levels found in this work.

Phosphates from sedimentary origin show a major U content in comparison with Th content, whereas igneous phosphates have a minor concentration of U and a considerable amount of Th and REE [3,17,29]. Thus, in the analyzed samples, the U concentration is twice as high as the Th concentration. Furthermore, the Th concentration in PG from Morocco is very low in comparison with Th concentration in PG from igneous rock (from 34 to 70 ppm) [22,28].

**Table 6**

Mean value and range (in parenthesis) of trace element concentrations (ppm) in phosphate rock (PR) and phosphogypsum (PG) samples of this work as well as in phosphogypsum from phosphate rock of different origins, n.m. means not measured or not reported.

| Element        | Sedimentary            |                        |                        |                      | Igneous<br>PG<br>(Brazil) <sup>c</sup> |            |      |
|----------------|------------------------|------------------------|------------------------|----------------------|--|------------|------|
|                | PR                     | Phosphogypsum (PG)     |                        |                      |  |            |      |
|                | (Morocco) <sup>a</sup> | (Morocco) <sup>a</sup> | (Florida) <sup>b</sup> | (Idaho) <sup>b</sup> |  |            |      |
| Ba             | 25 ± 6                 | 98 ± 23                | 43                     | (25–54)              | 47                                     | (23–73)    | n.m  |
| Cd             | <2                     | 6 ± 1                  | <2                     | n.m                  | 10.7                                   | (7–13.2)   | 2    |
| Cr             | 209 ± 19               | 20 ± 2                 | 5                      | (4–6)                | 48                                     | (30–76)    | 3    |
| Cu             | 3.66 ± 0.35            | 21 ± 2                 | 3.4                    | (2.8–4.6)            | 11.4                                   | (8–22.6)   | 4    |
| Ga             | 3.85 ± 0.70            | 1.0 ± 0.2              | 1.2                    | (0.7–1.8)            | n.m                                    |            | n.m  |
| La             | 21 ± 5                 | 86 ± 19                | 39.8                   | (35.5–42.1)          | 73.1                                   | (66–80.3)  | n.m  |
| Nb             | <1                     | 1.0 ± 0.2              | 3                      | (2–4)                | n.m                                    |            | n.m  |
| Ni             | 43.47 ± 0.14           | <1                     | 5                      | (3–7)                | 5                                      | (<1–7)     | 4    |
| Pb             | <1                     | 6.2 ± 1.7              | 10                     | (8–12)               | 13                                     | (10–16)    | 11   |
| Rb             | 4.27 ± 0.17            | 2.0 ± 0.1              | 5                      | (3–6)                | n.m                                    |            | n.m  |
| Sc             | 13 ± 1.8               | 4.7 ± 0.7              | <0.05                  |                      | n.m                                    |            | n.m  |
| Se             | <1                     | <1.75                  | 0.8                    | (0.5–1.1)            | 9.2                                    | (1.8–30)   | n.m  |
| Sr             | 627 ± 102              | 709 ± 115              | 750                    | (651–838)            | 660                                    | (594–738)  | n.m  |
| Th             | <1                     | 4.00 ± 0.64            | 1.5                    | (0.9–1.2)            | <0.5                                   |            | n.m  |
| U <sup>d</sup> | 137 ± 23               | 8.3 ± 1.8              | 4.5                    | (3.6–5.7)            | 7.3                                    | (6.2–10.5) | 25.3 |
| V              | 158 ± 21               | 4.75 ± 0.63            | 6                      | (4–7)                | 20                                     | (15–37)    | n.m  |
| Y              | 49 ± 13                | 144 ± 38               | 71                     | (62–85)              | 125                                    | (110–156)  | n.m  |
| Zn             | 156 ± 18               | 8 ± 1                  | 6.4                    | (4–7)                | 31                                     | (7–45)     | 8    |
| Zr             | 24 ± 3                 | 6.2 ± 0.8              | 54                     | (32–89)              | 48                                     | (34–60)    | n.m  |

<sup>a</sup> This work. Measurements and 2σ error.

<sup>b</sup> [4].

<sup>c</sup> [18].

<sup>d</sup> Value calculated from specific activity concentration obtained by gamma spectrometry.



**Table 7**  
Transfer factor (TF<sub>s</sub>) of trace elements comparing phosphate rock (PR) to phosphogypsum (PG).

| Element | Concentration (ppm) |      | TF <sub>s</sub> |
|---------|---------------------|------|-----------------|
|         | PR                  | PG   |                 |
| Rb      | 4                   | 2    | 0.78            |
| Sc      | 12.98               | 4.75 | 0.61            |
| Zr      | 23.8                | 6.2  | 0.44            |
| Ga      | 4                   | 1    | 0.43            |
| Cr      | 209                 | 20   | 0.16            |
| U       | 137                 | 8.3  | 0.1             |
| Zn      | 156.2               | 8.2  | 0.088           |
| V       | 158.02              | 4.75 | 0.050           |
| Ni      | 43                  | 1    | 0.038           |

**Table 8**  
Enrichment factor (EF<sub>s</sub>) of trace elements comparing phosphate rock (PR) to phosphogypsum (PG).

| Element | Concentration (ppm) |       | EF <sub>s</sub> |
|---------|---------------------|-------|-----------------|
|         | PR                  | PG    |                 |
| Cd      | 1                   | 6     | 10.42           |
| Pb      | 1                   | 6.25  | 10.4            |
| Cu      | 3.66                | 20.75 | 9.44            |
| La      | 21.24               | 86.25 | 6.77            |
| Th      | 1                   | 4     | 6.7             |
| Ba      | 25                  | 98    | 6.53            |
| Y       | 49                  | 144   | 4.91            |
| Se      | 1                   | 1.75  | 2.92            |
| Sr      | 627                 | 709   | 1.88            |

Information about contaminants such as Cd has been reported in PG from Huelva, where it is found in high concentrations. Abril [10] reported a Cd concentration of 2.8 ppm in stockpiled PG, which is low in comparison with the minimal value reported in this paper (5 ppm). Syrian PG from sedimentary phosphate rock shows very high concentrations of Cu and Zn, and a low concentration of Cd; 51.7, 37.7 and 0.8 ppm, respectively [30]. In comparison with these results, the Cu and Zn in this work are lower although the Cd is found to be higher.

On the other hand, Martín et al. [2] reported some concentrations of trace elements in fresh PG from the same factories. The concentrations found were Ni, 13 ppm; Cu, <6 ppm; Zn, 18 ppm; Sr, 718 ppm; Y, 158 ppm; and Pb, <18 ppm. Our findings present similar concentrations of Cu, Pb, Sr and Y, although the Zn concentration is lower in old PG and no Ni concentration is detected.

Stockpiled PG from the same factories has also been characterized [8]. In that study, a Ba concentration of 92 ppm was determined, which is confirmed by that found in this work; furthermore, they also reported high concentrations of Ni (43 ppm) and Zn (263 ppm). The differences between fresh PG and PG stockpiled over a long period may be explained by the fact that trace elements tend to be emplaced into the PG matrix, although they are not distributed in a homogeneous manner in samples.

Table 7 shows the transfer factor (TF<sub>s</sub>) of some trace elements determined in this work. According to these values, the transference of some elements is clearly observed. Thus, trace elements such as Rb, Sc, Zr and Ga, show a transference of 78, 61, 44, and 43%, respectively. Other elements, such as Cr, Ni, Sc, V and Zn are also transferred from PR. In the same way, Table 8 shows the enrichment factor (EF<sub>s</sub>), higher than unity, of trace elements determined in this work. Some trace elements (Ba, Cd, Cu, La, Pb, Se, Sr, Th, and Y) are deeply enriched.

The enrichment in PG samples may be explained by the transference of trace elements from both PR and an additional input, which in this case would be attributed to H<sub>2</sub>SO<sub>4</sub> used in the acid treatment. Due to the high enrichment of some trace elements in PG, it can be assumed that their primary source is sulfuric acid, due

to its characteristics attained at the point of manufacture. In Huelva, sulfuric acid is manufactured by local industries. These industries use pyrite (FeS<sub>2</sub>) from the Iberian Pyrite Belt as a raw material, which is enriched in Cd, Cu, Pb, and Zn as well as some light REE, such as La and Ce [31].

Elements, such as strontium and barium are enriched by about 188 and 650%, respectively. The increase of these elements in phosphogypsum is expected, since their chemical behavior is similar to that of calcium.

Other elements enriched in PG are Pb, Cd, Cu, Cr, and Se. The presence of these trace elements into PG may be explained by the presence of clays or iron oxides–hydroxides, where trace elements tend to be concentrated by adsorption and fixation, or by accumulation onto its surfaces [25].

The heavy metals (Pb, Cd, Cu, Cr, and Se) are considered hazardous elements and of environmental concern due to their high toxicity, since they are of great risk to human health [32].

Hence, high amounts of these toxic elements are being produced together with PG. By calculating the annual production of these trace elements, it can be concluded that these amounts would be: Sr, 2126 tons; Ba, 294; Y, 431; Cu, 62; Cr, 60; and Cd, Zr and Zn at around 20 tons each. All these amounts of toxic elements are being stockpiled within the estuary of the Tinto and Odiel rivers, thereby representing latent risk of contamination.

Additionally, it is known that PG is used in some agricultural activities. The continued use of this by-product also provides and increases the toxic element concentration in soils, and modifies those contents in plants, and as a consequence, in the whole food chain. Some work warns against the accumulative character of certain heavy metals such as Cd and Ra in soils and their transfer to plants [33,34]. Other authors have also studied Zn, Ni and radionuclides, which are taken up by plants as micronutrients [35,36].

### 3.4. SEM-EDX characterization

By using SEM in SEI and BEI mode, the morphology of PR particles was determined, see Fig. 3. Most of the particles exhibit angular shapes with estimated sizes between 3 and 80 μm. The semi-quantitative composition of phosphate rock particles was determined by SEM-EDX, which showed high contents of Ca and P and impurities such as Fe, Al, Mg, Na, and S.

In the samples analyzed in BEI mode, slightly bright white particles were observed. Based on SEM-EDX, those particles were found to have a different composition, mainly of iron, and some trace elements, such as lead, barium and REE. As is shown in Fig. 4, these particles tend to form thin layers or to be embedded in the phosphate rock grains. In addition, it is important to note that certain trace elements appear in association with the composition of these particles.

The morphology of the PG particles was determined using SEM in SEI mode (see Fig. 5). The PG crystals exhibited shapes in the form of tables, in acicular form, in tubular form, as small crystal clusters and rhombic forms. The size of particles was varied. Large crystals were of a size between 110 and 160 μm in length, from 50 to 60 μm in width, and of a thickness from 5 to 10 μm; acicular crystals showed dimensions from 40 to 60 μm in length and fine crystals showed a diameter <15 μm.

Using SEM-EDX, the composition of the PG crystals was obtained, which showed contents of mainly Ca and S (Fig. 6).

As in PR, slightly bright white particles were also observed in PG. In this case, particles appear as agglomerates and display a high degree of porosity, and a large surface area.

The elemental composition, determined using SEM-EDX, showed that each particle is composed of different elements to those in PR. Thus, most particles found were of Pb, Fe, Ba and Ag as well as lanthanides such as Ce, La, and Nd (see Fig. 7).

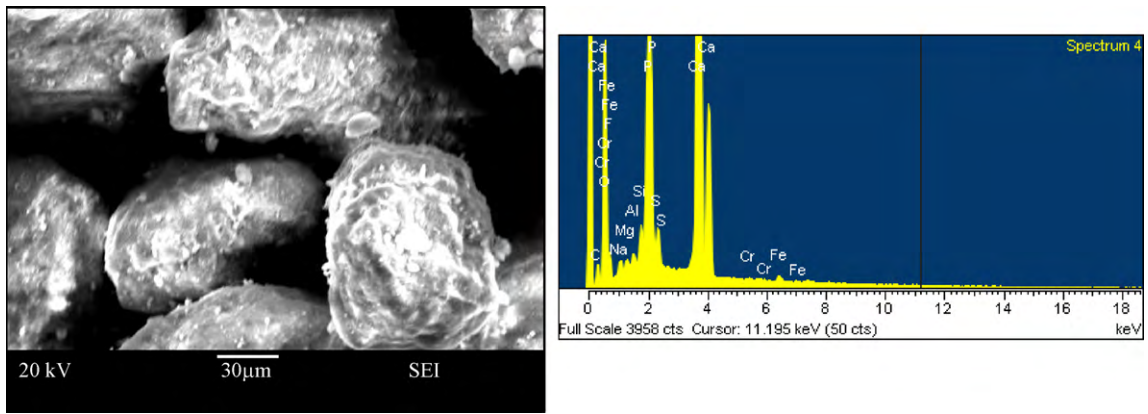


Fig. 3. Morphology of PR grains as well as their composition (obtained by a spot on the PR grain), bar 30 μm.

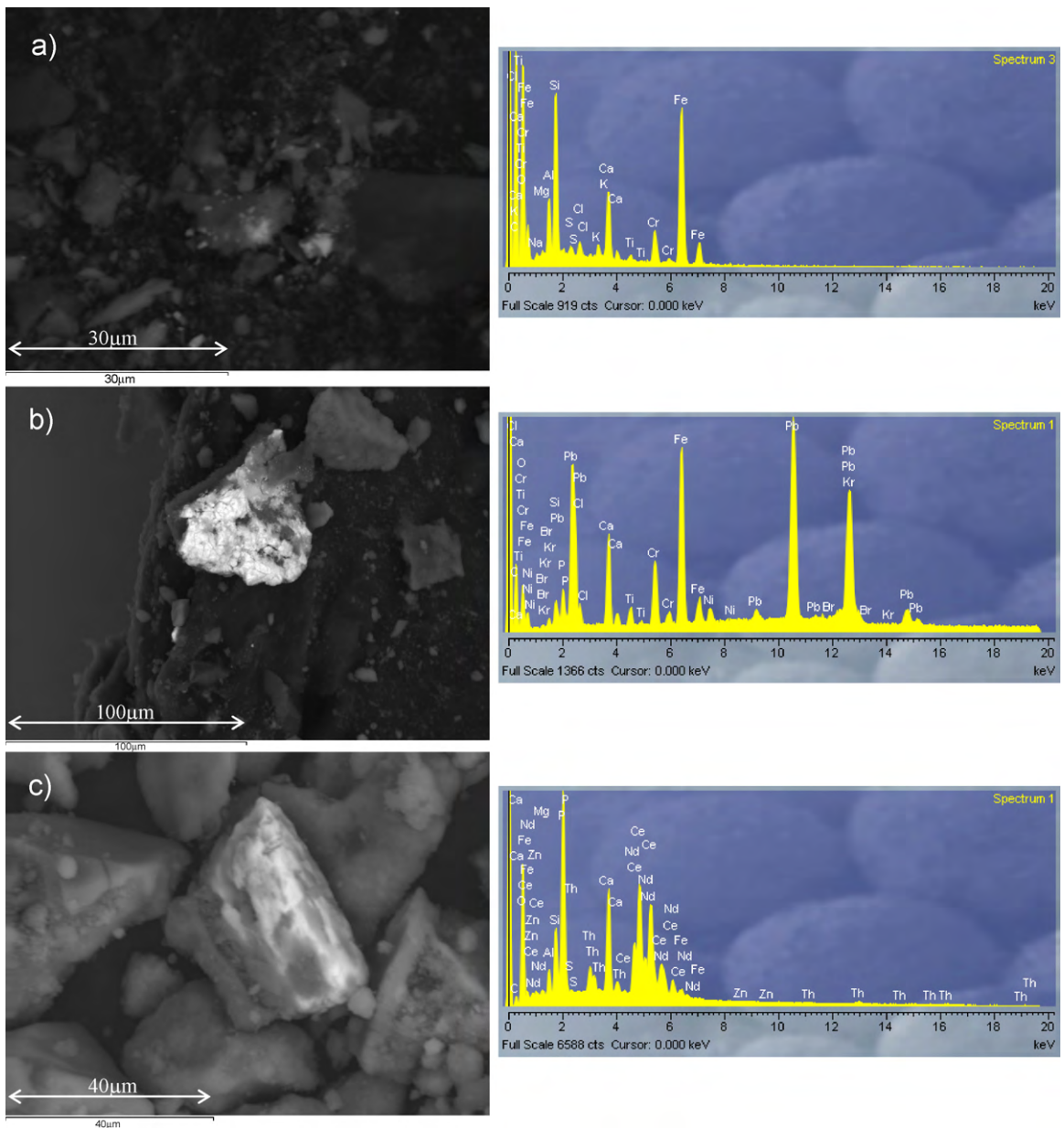
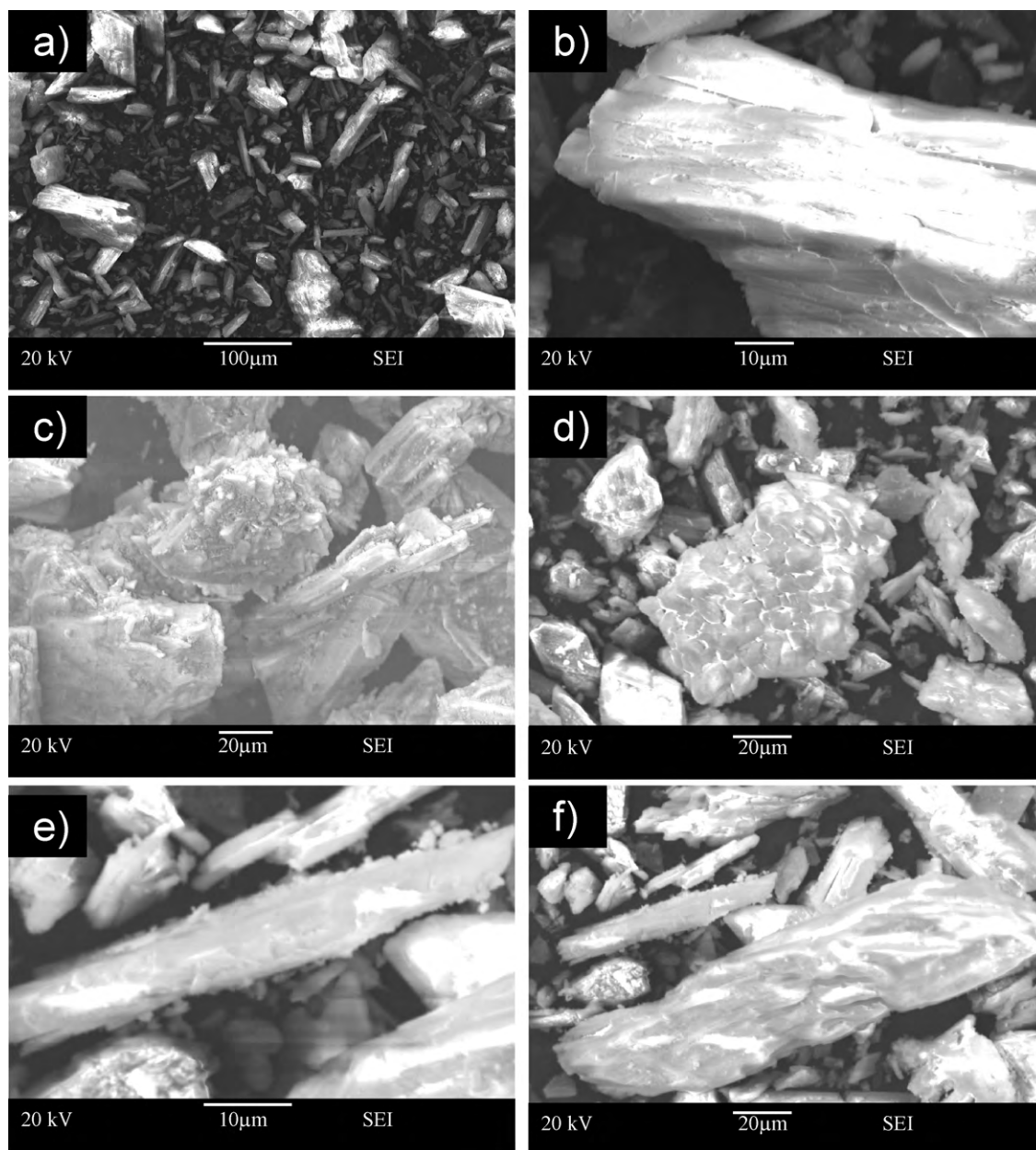
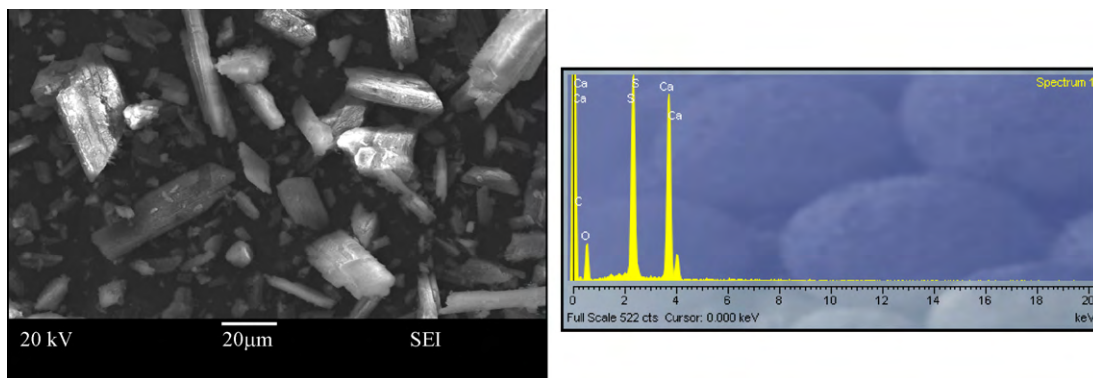


Fig. 4. Using SEM-EDX with a spot on the particles, it was found particles composed by different elements: (a) iron (bar 30 μm), (b) lead (bar 100 μm) and (c) cerium–lanthanum–neodymium (bar 40 μm).

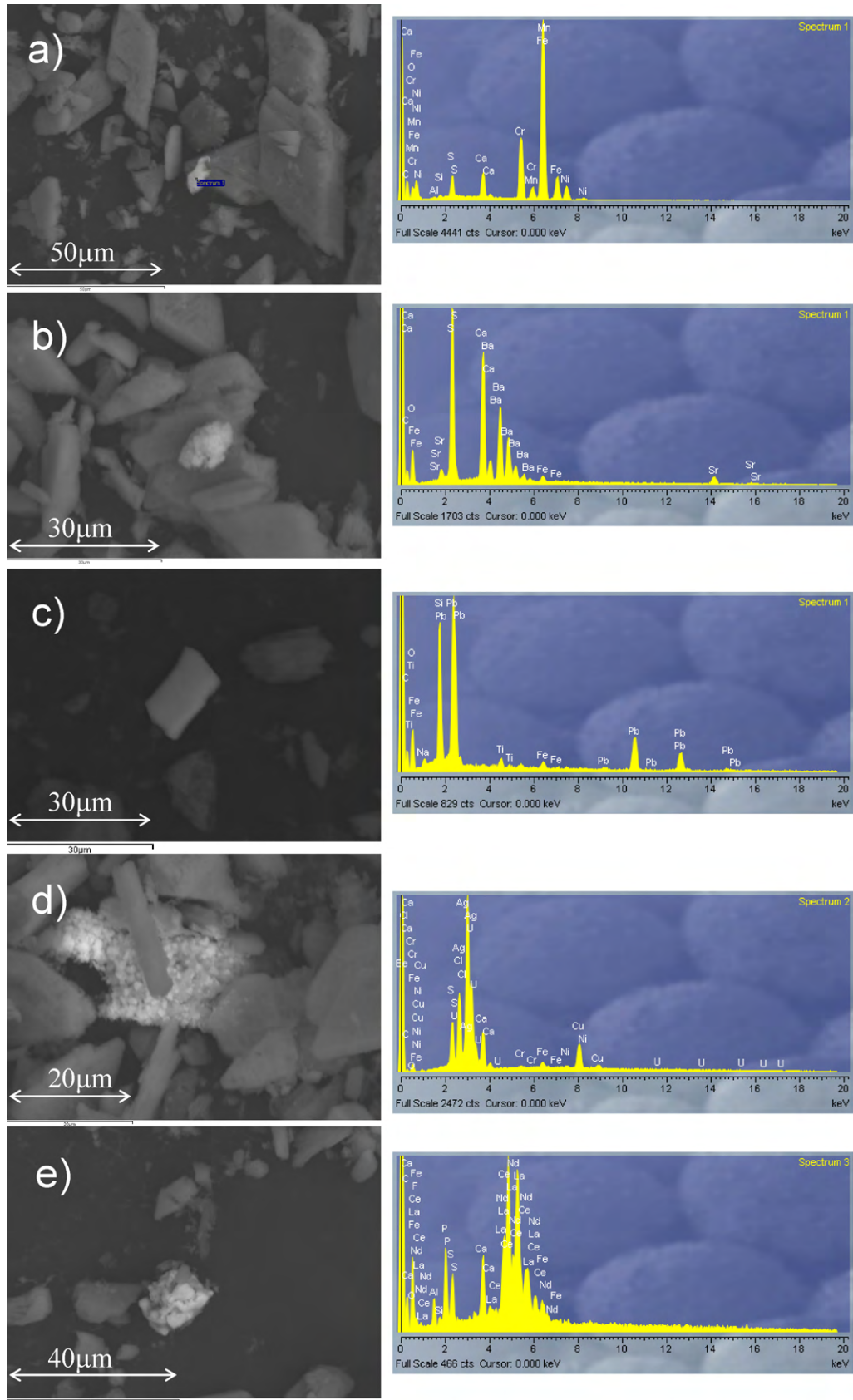


**Fig. 5.** Morphology of particles found in phosphogypsum: (a) bulk phosphogypsum crystals (bar 100  $\mu\text{m}$ ), (b) shape like tables (bar 10  $\mu\text{m}$ ), (c) small crystals clusters (bar 20  $\mu\text{m}$ ), (d) agglomerates (bar 20  $\mu\text{m}$ ), (e) acicular shape (bar 10  $\mu\text{m}$ ), and (f) cylindrical shape (bar 20  $\mu\text{m}$ ).



**Fig. 6.** SEM-EDX analyses of PG crystals, with SEM in secondary electron imaging (SEI) mode shows the crystals morphology and using EDX (by an analysis spot), it was obtained the composition of the main elements, bar 20  $\mu\text{m}$ .





**Fig. 7.** Results of SEM-EDX, where the particles, analyzed by a spot, are composed by different elements: (a) iron (bar 50 μm), (b) barium (bar 30 μm), (c) lead (bar 30 μm), (d) silver (bar 20 μm) and (e) cerium-lanthanum-neodymium (bar 40 μm).

All particles exhibited low concentrations of some trace elements. For instance, in iron particles, elements Mn, Cu, Cr and Ni were found. Elements associated to silver particles were Si and Ca, whereas lead and barium particles showed contents of Ti and Sr, respectively. Particles of some REE elements, Ce, Nd and La, were also found, with a presence of P, Ca and S.

It should be borne in mind that these particles are small in size, with the majority <20  $\mu\text{m}$ . Moreover, these particles presented contents of Si, Al and K, which are the main elements of clays, thereby corroborating both the presence of impurities determined through XRF and the fact that trace elements are adsorbed onto mainly iron oxide surfaces.

#### 4. Conclusions and implications

In this work, the crystalline phases and components in both phosphate rock of sedimentary origin and phosphogypsum were identified using X-ray diffraction (XRD). From our results, fluorapatite, calcite, perovskite, quartz, magnetite, pyrite and kaolinite were the components of phosphate rock; while calcium sulfate dihydrate, was only observed in phosphogypsum. Unfortunately, mineralized phases of trace element compounds in phosphogypsum were not identified by XRD.

The definition of a transfer factor, based on the activity concentration of radionuclides, showed that the most abundant radioisotopes in phosphogypsum were  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$ , which are transferred from the phosphate rock by up to 80%. However,  $^{238}\text{U}$  was only transferred at a level of 10% from the phosphate rock.

Major and minor chemical species concentrations in phosphate rock and phosphogypsum were studied. Another transfer factor, this time based on the mass concentration of chemical species, was thereby defined. Our results can be considered within the recognized data range corresponding to other sedimentary phosphate rocks. Additionally, an enrichment factor, also evaluated as a mass ratio, was defined for some trace elements such as Cd, Pb, Cu, La, Th, Ba, Y, Se, and Sr; where the mass ratio was higher than unity. This enrichment was explained by the presence of these trace elements in the sulfuric acid, which must be considered as an additional input in the phosphoric acid process.

Using SEM-EDX, the PR and PG particles are found to be composed of mainly apatite and gypsum, respectively, and of low quantities of some impurities. In both matrices, most of the trace elements tend to appear concentrated in particles <20  $\mu\text{m}$ , and are always associated to some impurity element or other trace element (as base element).

From an environmental point of view, a clear risk of environmental impact is present due to the enhancement and weak bond of toxic elements in phosphogypsum. Indeed, these elements would be concentrated within small particles with a high surface area, which implies easy mobilization by leaching and/or erosion.

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