RESEARCH ARTICLE

Geochemical and mineralogical characterization of phosphogypsum and leaching tests for the prediction of the mobility of trace elements

Fatima Akfas[1] · Abdellatif Elghali[1] · Jean-Louis Bodinier[1,2] · Fleurice Parat[2] · Manuel Muñoz[2]

Abstract

Phosphoric acid manufacturing generates large amounts of phosphogypsum (PG); a by-product generally disposed in the surface or evacuated in the seawater without any pretreatment. Phosphogypsum may host non-negligible amounts of valuable elements such as rare earth elements (REEs), which are critical elements on the global market. Surface disposal of PG may be a sustainable option to allow further processing in order to recover valuable elements. However, surface disposal exposes PG to atmospheric conditions (e.g., water, oxygen) which may increase their reactivity and accelerate the release rate of chemical species. This study aims to evaluate the trace element release rate from PG at atmospheric conditions. The studied PG samples were collected from a Moroccan phosphate treatment plant. The samples were characterized for their (i) chemical composition using inductively coupled plasma optical emission spectrometry (ICP-OES) for major elements and inductively coupled plasma mass spectrometry (ICP-MS) for trace elements; (ii) mineralogical composition by X-ray diffraction (XRD), scanning electron microscope equipped with energy-dispersive spectrometer (SEM–EDS), laser-induced breakdown spectroscopy (LIBS), and the mineral chemical composition was analyzed by electron probe microanalyzer (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS); and (iii) chemical species release rate using leaching tests over 24 h at 25 and 60 °C. Chemically, the PG samples were mainly composed of Ca (23.03–23.35 wt.%), S (17.65–17.71 wt.%), and Si (0.75–0.82 wt.%), and non-negligible amounts of trace elements: REE (344–349 ppm), Cd (3.5–7.4 ppm), U (9.3–27.4 ppm). Mineralogically, the PGs are mainly formed by gypsum (94.2–95.9 wt.%) and quartz (1.67–1.76 wt.%). In terms of chemical species release, the PGs showed a higher reactivity at 60 °C compared to room temperature with a higher release rate at the beginning of the leaching tests. Quantitatively, the PG samples released 3.57–4.11 µg/L/day of REE, 3.18–17.29 µg/L/day of U, and 1.67–5.49 µg/L/day of Cd. Based on the leaching results, we concluded that the trace elements (e.g., U, Cd, REE) are incorporated in PG crystal lattice, which may explain their low concentrations in the leachates. Consequently, total digestion of PG matrix is required to solubilize REE.

Keywords Phosphogypsum · Rare earth elements · Liquid/solid partitioning · Leaching behavior · Microanalysis · Retention mechanisms

Introduction

Fertilizers are key ingredients for feeding a growing global population. Since the world agricultural demand is increasing for reaching the nutritional needs of the raising population (1.1% per year according to Our World in Data, 2020), the role of fertilizer is crucial (Cordell et al. 2009). The phosphate fertilizer industry, in particular, is critical to sustain agricultural production levels and to maintain the level of farming production worldwide. Natural phosphates are mainly used as a source of phosphorus (P) which is an essential nutrient for plants and animals and can contribute to sustainable agricultural intensification (e.g., Neset and Cordell 2012).

Phosphoric acid is a key element of the phosphate fertilizer value chain. It is usually produced (i) either by pyrometallurgy through thermal reduction of phosphate rock in an electric furnace to produce elemental phosphorus, or (ii) by hydrometallurgy through acid digestion of phosphate

✉ Abdellatif Elghali
abdellatif.elghali@um6p.ma

[1] Geology & Sustainable Mining Institute, Mohammed VI Polytechnic University, Lot-660, 43150 Benguerir, Morocco

[2] Geoscience Montpellier, University of Montpellier, Cedex 5 34095 Montpellier, France

rocks by sulfuric acid. The latter process, also known as "wet digestion" or "wet acid method" (Lottermoser 2010), is the most widely method (account for 90% for the worldwide phosphoric acid production) used because of its low cost (USGS 2016).

Morocco is the second phosphate producer in the world; its production reaches 23 million tons per year (Jasinski 2017). In the recent period, Morocco has established a large chemical industry to manufacture phosphoric acid, which is primarily obtained through the "wet acid method" of phosphate rock (Tayibi et al. 2009). In this process, the previously washed phosphate rock is concentrated by flotation and digested with sulfuric acid to obtain phosphoric acid and phosphogypsum as a by-product through the reaction (1) (Tayibi et al. 2009) :

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5(CaSO_4.2H_2O) + HF \qquad (1)$$
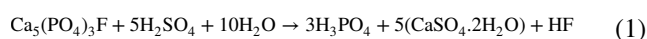
whereby 5 tons of phosphogypsum are generated for every ton of phosphoric acid. As worldwide rock phosphate production increases and P_2O_5 consumption from fertilizers rises, global phosphogypsum output is expected to reach 100–280 Mt per year (Yang et al. 2009).

Phosphogypsum contains significant amounts of trace elements such as REE, Cd, As, and Cr. Phosphogypsum is frequently disposed of in large stockpiles without taking any previous treatment, which can cause serious environmental contamination of soils, water, and atmosphere (Bisone et al. 2017; Haneklaus et al. 2022). Leaching of PG may or not produce problematic leachates (Berish 1990; Langmuir 1997). Negative effects of leachates on the environment are due to their high content of metals, metal(loid)s, and radionuclides (El Zrelli et al. 2015; Pérez-López et al. 2015; Tayibi et al. 2009). However, the toxic effects of trace elements depend on their accumulated amounts, their chemical forms, and their release rate (Chernysh et al. 2021). On this ground, phosphorus must also be considered. Although phosphorus is not intrinsically toxic, but it may cause significant algal blooms within restricted water bodies, potentially leading to rapid eutrophication of lakes and rivers (Gaudry et al. 2007).

On the other hand, certain applications have been recently developed to valorize PG in various sectors: in agriculture for soil amendment or as fertilizer (Chernysh et al. 2021); in the bricks manufacturing, cement industry, and as a potential alternative for natural gypsum largely consumed in construction (Cánovas et al. 2018; Haneklaus et al. 2022; Saadaoui et al. 2017). Moreover, the presence of rare earth elements in PG can convert this waste into a valuable resource (Cánovas et al. 2017; Simandl 2014). REE concentration in PG varies greatly based on several factors including the chemical composition of the used phosphate rock, the type of the used phosphoric acid process, and the plant operational efficiency.

According to various studies, the PG contains about only 0.4% REE, representing 70–85% of the REEs that were initially contained in the phosphate rock (Habashi 1985). However, if selective and efficient REE recovery methods are developed, the huge volume of generated PG generated may compensate their relatively low REE content (Cánovas et al. 2017).

To achieve circular economy and sustainable development in mining context, mining by-products need to be reprocessed, treated, or at least partially valorized to decrease their environmental footprint (Croteau et al. 2005). The assessment of the environmental impact of a mining by-product requires a good knowledge of its geochemical and mineralogical characteristics (Elghali et al. 2021; Jamieson et al. 2015). Consequently, prediction of the environmental behavior of trace elements is crucial (Guerrero et al. 2021). Additionally, understanding the distribution and mobility of chemical species within phosphogypsum may also guide its valorization, especially REE recovery.

Detailed geochemical and mineralogical characterization is a key factor to (i) quantify penalizing and valuable elements within phosphogypsum, and (ii) predict their environmental behavior (Blowes et al. 1998; Parbhakar-Fox et al. 2018). Additionally, several leaching test procedures were developed recently to investigate the reactivity of solid material. The objective of these studies was to predict the release rate of chemical species (penalizing and valorizing elements) in controlled conditions such as temperature, liquid-to-solid ratio, and flushing frequency.

It is known that detailed characterization of industrial by-product is a key factor for a further reprocessing (Amar et al. 2021). Thus, the main objective of this paper is to carry out a full characterization of PG samples. The characterization was performed using: (i) a geochemical characterization for major and trace elements in PGs and (ii) a detailed mineralogical characterization of PGs, and (iii) a prediction of the mobility of trace elements of trace using leaching tests. Two samples of PG were analyzed for their chemical composition in terms of trace, minor, and major elements using ICP-OES and ICP-MS. Besides, mineralogical compositions were characterized using X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive X-ray analysis (SEM–EDX). Subsequently, the stoichiometry of the mineral phases was analyzed by electron probe microanalyzer (EPMA), and their trace element contents by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Furthermore, the laser-induced breakdown spectroscopy (LIBS) was used to map the spatial distribution of major and light elements. Finally, the mobility of trace elements was evaluated using water leaching tests as a function of temperature (room temperature and 60 °C) and time (up to 24 h).

Materials and methods

Samples

The phosphogypsum (PG) samples were collected from the Jorf Lasfer industrial complex of the OCP group in Morocco resulted from the acidic attack of sedimentary phosphate. A preliminary drying at 100 °C of the samples was performed prior to the characterization steps. The same samples were also rinsed with pure water to eliminate the remaining interstitial phosphoric acid, then dried for 24 h. These two washed samples, as well as the raw samples, were analyzed by ICP-OES and ICP-MS and prepared as thin sections for microanalysis. Figure 1 illustrates the overall approach used for this study.

Chemical characterization

Chemical composition of solid samples in terms of major and minor elements was analyzed using ICP-OES (inductively coupled plasma optical emission spectroscopy) at SARM platform (Nancy, France) after a total digestion using HNO_3. Then, the mixture was fused with $LiBO_2$. For the major components, the relative standard deviation was less than 5%. Trace elements were analyzed using ICP-MS (inductively coupled plasma mass spectrometry) at the AETE platform and Geosciences Montpellier laboratory in France. To prepare the solution to be analyzed, 100 mg of powder from each sample was weighed using a precision balance (± 1 mg). QA/QC of the chemical analysis consisted of analyzing four blank samples as well as four international standard samples (COQ1, BCR, Blc1, and Blc2). Blank samples are used to detect contamination during an acid attack or analysis. Two acid attacks are carried out with 3 mL of ultrapure 4 N HNO_3 + 0.5 mL of 70% suprapure $HClO_4$ in Savillex® followed by evaporation at 120 °C. Each of the acid attacks was separated by evaporation of the liquids at 120 °C. Following the acid attacks, the 3 evaporations were carried out at 150–190 °C with 69% HNO_3 suprapure (0.5 mL then 2×0.25 mL), which will lead to the formation of a solid precipitate. The obtained residues are then diluted with water with 1.5 mL of HNO_3 for a 1:8000 solutions to ovoid oversaturation of the ICP-MS during the measurements. Volatile elements (CO_2, C_{org}, F, and S) were analyzed at SARM platform (Nancy, France). Total sulfur and carbon were analyzed using element analyzer. The concentration of F was determined by wet precipitation ferrothiocyanate spectrophotometry using a Varian Cary 50 spectrophotometer.

Mineralogical characterization

The mineralogical composition of raw PG samples was determined using an MPD Panalytical X'Pert PRO diffractometer equipped with a copper anticathode tube at the RRXG platform at the University of Montpellier, France.
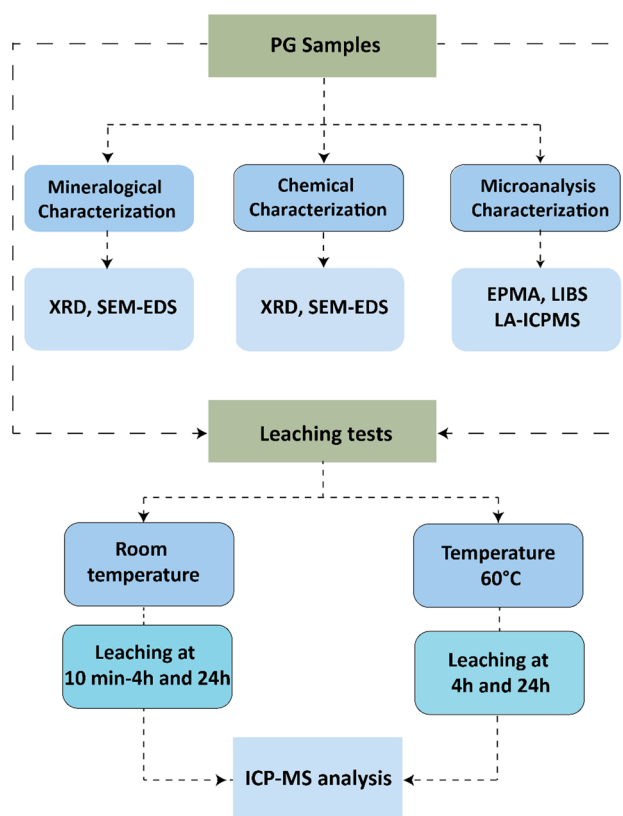
Fig. 1 The methodological approach of this study

The measurement was carried out at room temperature on a range Ө [10–70°] with a scanning speed of 0.2° min^{-1}. In order to identify the abundance of crystallized phases, the solid samples were finely ground and then carefully placed in the diffractometer sample holder. The identification and quantification of the crystallized mineral phases were done using Profex software which implements the Rietveld method (Rietveld 1969), using the crystallography open database (COD 2013).

Major (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) and volatile (F, S, Cl) chemical species of the minerals forming PG samples were analyzed using electron probe microanalyzer (EPMA) at Geoscience Montpellier, France. The measurements were performed on polished thin sections. The analysis was carried out using CAMECA SX100 electronic microprobe at acceleration of voltage of 15 kV and a beam current of 10 nA. The beam size was about 10 μm. The measurements were done after the instrument calibration; the standard materials used for calibration were wollastonite for Si and Ca, TiO_2 for Ti, Al_2O_3 for Al, forsterite for Mg, Fe_2O_3 for Fe, rhodochrosite for Mn, albite for Na, orthoclase for K, fluorapatite for P, lithium fluoride (LiF) for F, chlorapatite for Cl, barite for S, CdS for Cd, UO_2 for U, vanadinite for Pb, Cr_2O_3 for Cr, yttrium-bearing glass for Y, and REE-bearing glass for La. The detection limits are lower

than 200 ppm for Mg, Al, Si, Cl, La, Ce, Y, and K; lower than 400 ppm for Na, P, S, and Fe; lower than 617 ppm for Ca; and lower than 120 ppm for F.

Trace element contents in phosphogypsum were determined in situ on thin section by a laser ablation system (GeoLas Q+platform with an Excimer compEx102 laser) coupled with a plasma source mass spectrometer (LA-ICP-MS) (ThermoFinnigan Element XR) at AETE platform, Montpellier, France. Phosphogypsum analyses were performed with a fluence of 12 J/cm^2, a frequency of 7 Hz, and a beam size adjusted according to the size of the mineral (77 or 102 μm). The analyses are calibrated using an international standard (Nist612) and the concentration of CaO wt.% of the analyzed minerals (determined for each mineral by electron probe microanalyzer). BIR-G1 standard is used as an external standard. To control the analyses and to detect possible contamination during the LA-ICP-MS analysis, data processing was performed using GLITTER® software (Griffin 2008).

Chemical microanalysis and imaging of selected spots of PG samples were obtained with JEOL JSM 5600 SEM and CamScan X500FE CrystalProbe coupled to a dispersive of UltimMax 100 energy (EDS) at Geoscience Montpellier, France. The samples were analyzed at 20 keV for a counting time of 0.5 s. EDS data processing was performed by AZtecHKL software from Oxford Instruments.

Laser-induced breakdown spectroscopy (LIBS) imaging technique was used at CNRS, Villeurbanne, France, to highlight the difference in the distribution of major and light elements in phosphogypsum samples before and after leaching. LIBS measurements were performed at room temperature under ambient air pressure. Details about the LIBS instrument and analytical protocol used for this study are described in Fabre et al. (2018). The light radiation emitted by the plasma is then collected by an optical system and analyzed using a spectrometer. The sample was analyzed using a Nd: YAG laser with a pulse energy of 600 μJ operating at 100 Hz and a lateral resolution of 13 μm. During the analysis, the sample surface is scanned through single laser pulses by a 15×magnification objective (LMM-15X-P01, Thorlabs) in a pixel-by-pixel manner to induce the breakdown of the material.

Elemental deportment

The element-to-mineral conversion method is a traditional and straightforward method for estimating mineral grades by solving a set of mass balance equations formulated between chemical assay and theoretical chemical composition calculated based on mineral abundance and their microanalysis. The method is limited to relatively simple mineralogy in which the number of minerals does not exceed the number of analyzed components and the chemical composition of the minerals (mineral matrix) is known (Ntlhabane et al. 2018). Mathematically this can be written in the following form (Parian et al. 2015):

$$A \times x = b; \begin{bmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & \ddots & \vdots \\ a_{n1} & \cdots & a_{nn} \end{bmatrix} \times \begin{bmatrix} x_1 \\ \vdots \\ X_n \end{bmatrix} = \begin{bmatrix} b_1 \\ \vdots \\ b_n \end{bmatrix}$$

A is the matrix of mineral chemical composition, x is the vector containing the unknown mass fraction of minerals (bulk mineralogy) in the sample, and b is the vector containing the sample's analyzed chemical composition. In this work, "Solver" tool within EXCEL® method was used for the non-linear minimization routine (Elghali et al. 2018). Using mineralogic and geochemical characteristics of phosphogypsum, the deportment of trace elements of studied samples was calculated.

Leaching tests

In this study, the leaching tests were used to quantify the mobility of chemical species of interest (e.g., REEs) and impurities from PG and to estimate the behavior of chemical species during surface storage of phosphogypsum. The leaching experiments were performed using ultrapure water with agitation for 10 min, 4 h, and 24 h. Additionally, to study the fractionation of element in high temperature, leaching tests were carried out at 60 °C. All residual phases of each leaching test were analyzed for their chemical composition by ICP-MS.

Results

Chemical properties of phosphogypsum

Chemical characteristics of PGs are presented in Table 1. PGs are mainly composed of S and Ca with about 17.65–17.71 wt.% and 23.03–23.35 wt.%, respectively. The main impurities in PG are F (~0.8 wt.%), P (0.19–0.24 wt.%), Si (0.75–0.82 wt.%), and Al (~0.04 wt.%).

Based on ICP-MS analysis, trace element concentrations were found in the following order of abundance Sr > Y > Ba > La > Nd > Ce > Ti > Gd > Dy > Pr > Lu > Sm > U > Er > Yb > Cr > Cd > Th. PG from sedimentary phosphate rock showed variable concentrations of Cu, Pb, and Zn. A significant concentration of REE was analyzed in phosphogypsum samples. The trace element concentrations are high for heavy-REE (179.96–182.47 ppm), light-REE (161.28–163.70 ppm), and to a lesser extent U (9.30–27.37 ppm) and Th (3.05–3.33 ppm) for the analyzed PG samples. The most abundant REE in PG is Y (127.29–133.79 ppm) followed by La (60.75–60.10 ppm), Nd (47.07–46.44 ppm), and Ce (39.07–37.73 ppm). In terms of metal(loid)s, the studied samples contain Cu (1.56–1.51 ppm), Zn (4.24–4.30 ppm), Cd (3.22–7.36 ppm), and As (1.94–1.81 ppm). Additionally, non-negligible

Table 1 Major and trace element composition of phosphogypsum. *d.l*, detection limit

		d.l	Unit	PG-1	PG-2
Major elements ICP-OES	SiO_2	0.05	wt.%	1.76	1.61
	Al_2O_3	0.04	wt.%	0.15	0.15
	TiO_2	0.02	wt.%	< d.l	< d.l
	Fe_2O_3	0.015	wt.%	< d.l	< d.l
	MnO	0.015	wt.%	< d.l	< d.l
	MgO	0.03	wt.%	< d.l	< d.l
	CaO	0.02	wt.%	32.23	32.68
	Na_2O	0.02	wt.%	0.18	0.19
	K_2O	0.01	wt.%	< d.l	< d.l
	P_2O_5	0.1	wt.%	1.09	0.85
	S	–	wt.%	17.71	17.65
	CO_2 total	–	wt.%	0.41	0.36
	Corg	–	wt.%	0.10	0.09
	F	–	wt.%	0.84	0.83
Trace elements ICP-MS	As	0.003	ppm	1.94	1.81
	Cu	0.0143	ppm	1.56	1.51
	Zn	0.0564	ppm	4.25	4.28
	Cd	0.0066	ppm	3.50	7.38
	Sr	0.0014	ppm	630	674
	Sc	0.0026	ppm	0.44	0.39
	Ti	0.1136	ppm	12.9	14.3
	V	0.0016	ppm	1.94	1.89
	Cr	0.0115	ppm	5.85	6.06
	Li	0.0045	ppm	0.39	0.30
	Y	0.0002	ppm	127.3	133.8
	Ba	0.0015	ppm	63.3	58.1
	La	0.003	ppm	60.7	60.1
	Ce	0.002	ppm	39	38
	Pr	0.0001	ppm	11	11
	Nd	0.0019	ppm	47	46
	Sm	0.0005	ppm	9.85	9.63
	Eu	0	ppm	2.48	2.45
	Gd	0.0004	ppm	12.1	12.2
	Tb	0	ppm	1.79	1.77
	Dy	0.0003	ppm	12	12.2
	Ho	0	ppm	2.84	2.89
	Er	0.0001	ppm	8.63	8.91
	Tm	0	ppm	1.16	1.21
	Yb	0.0001	ppm	6.79	7.48
	Lu	0.0001	ppm	1.00	1.14
	U	0.0001	ppm	9.3	27.4
	Pb	0.0005	ppm	1.93	1.88
	Th	0.0001	ppm	3.04	3.34
	ΣREE	–	ppm	344	349

concentrations of Ba were measured (50–70 ppm). Sr was found in significant concentrations ranging from 500 to 600 ppm. In the gypsum structure, Sr and Ba often replace Ca.
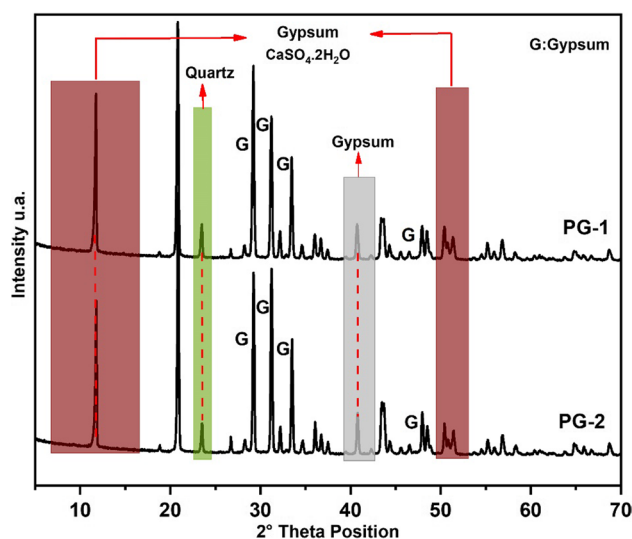
Fig. 2 X-ray diffraction pattern of PG raw samples

Other elements, such as Ti, As, Sc, V, and Mn, were detected in variable concentrations (Table 1). The presence of these elements in the PG samples can be explained by the transfer of these elements from the phosphate rock and sulfuric acid.

Mineralogical characteristics of phosphogypsum

The mineralogical composition of the PG samples is presented in Fig. 2. Diffractogram analysis shows that PG consists mainly of around 90 wt.% of calcium sulfate dihydrate ($CaSO_4.2H_2O$) and trace amounts of quartz.

Because of their low concentration (< 5 wt.%), other minerals such as fluorides, phosphates, and sulfides were not identified by XRD. However, SEM–EDS analysis revealed trace amounts of residual fluorapatite on the surface of gypsum, mainly resulting from unreacted phosphate rock during phosphoric acid manufacture. From the EDS maps, it can be seen that for the two phosphogypsum, the most abundant elements are sulfur and calcium followed by oxygen and phosphorus (Fig. 3). This study confirms the abundance of the two-gypsum building blocks, sulfur, and calcium. The first is derived from sulfuric acid, and the second from calcium phosphate, which is abundant in the raw material.

The optical microscopy observations and BSE images (Fig. 4) showed that the phosphogypsum grains presented three textures: (i) needle-shaped crystals with a uniform distribution, (ii) elongated crystallites, and (iii) fine agglomerated needles with low crystallinity. Various factors can influence the morphology of the phosphogypsum samples such as the nature of the chemical process, the composition of the phosphate rock, and the presence of organic matter. The morphology and the crystal size of PG crystals depend

on the presence of water-soluble and water-insoluble impurities in phosphates (Becker 1989). In addition, dihydrate and hemihydrate processes used for the manufacturing of phosphoric acid influence the adjustment and crystal shapes (Kybartienė et al. 2018).

The EPMA analysis of minerals reveals that phosphogypsum is dominated by gypsum phase, with the presence of fluorine and quartz phases. Three Ca-sulfate phases can be identified based on Ca and S contents: bassanite, dihydrate gypsum, and anhydrite. The presence of these phases was revealed by Bourgier (2007). According to the EPMA results, the gypsum phase is composed of 37.07 wt.% CaO and 51.48 wt.% of SO_3, which corresponds to the bassanite phase. Calcium sulfate phases also contained several trace elements such Cd (14.4 ppm), U (13.51 ppm), La (32.5 ppm), Ce (59.5 ppm), Y (39 ppm), Cr (10.8 ppm), and Fe (12.5 ppm). The fluorite phase is mainly composed of F (43.67 wt.%) and Ca (38 wt.%). The chemical composition of fluorite revealed
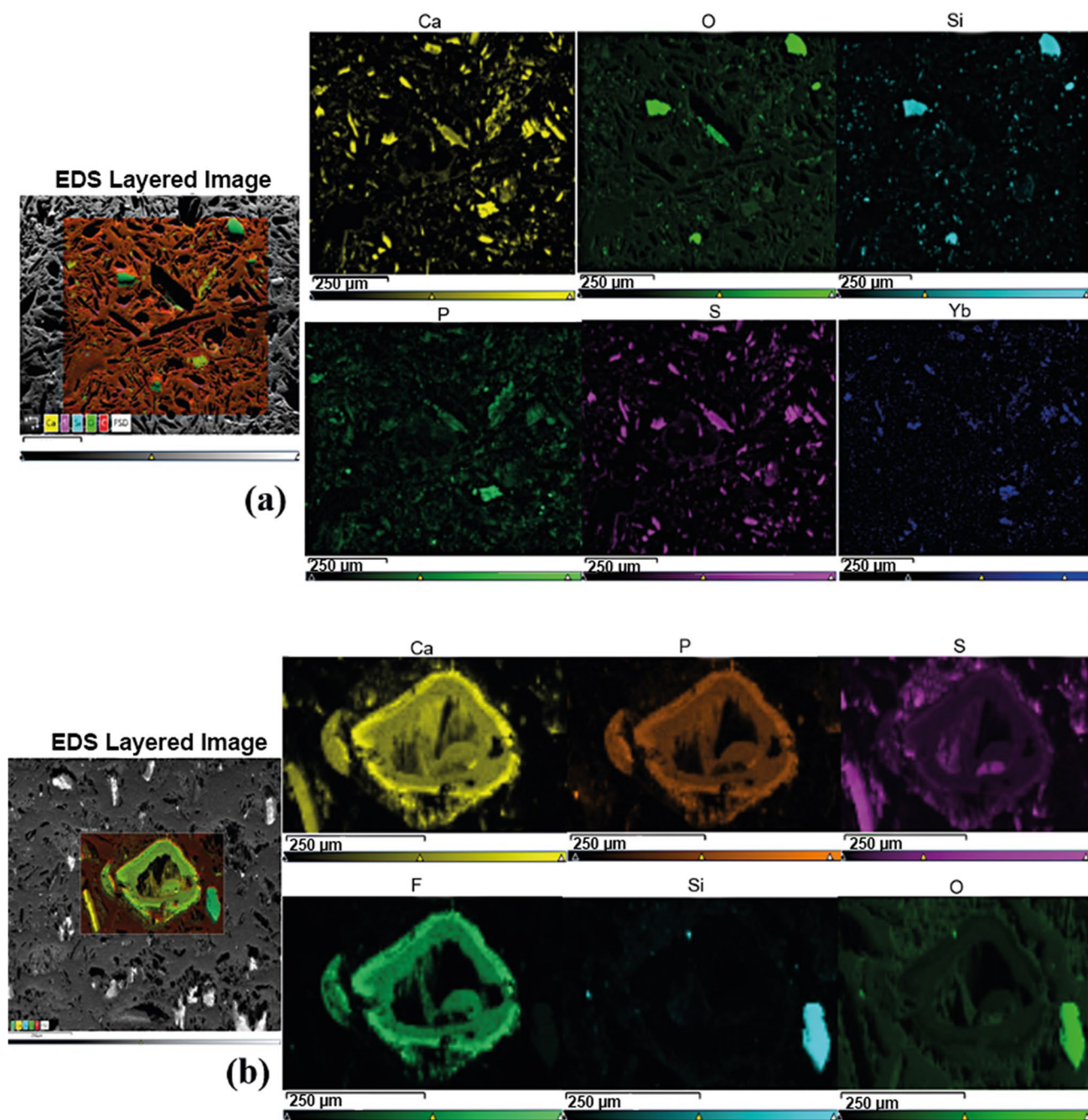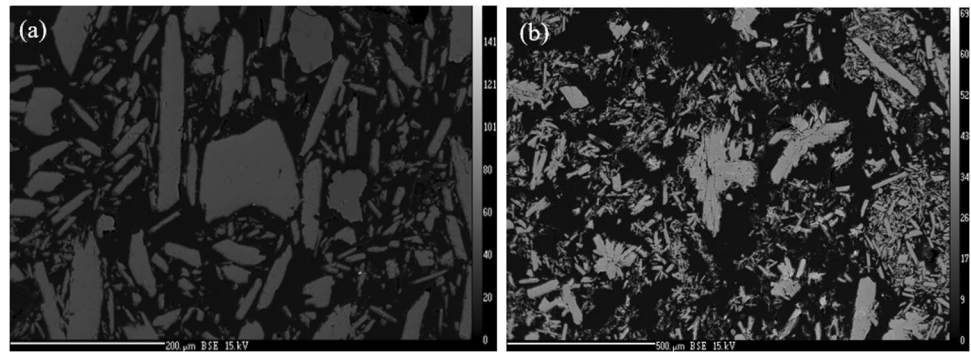

Fig. 3 EDS elemental maps of PG-1 (**a**) and PG-2 (**b**)

Fig. 4 Backscattered electron micrograph image of phosphogypsum

non-negligible REE levels; it contains 56.6 ppm of Y, 14 ppm of La, and 56.9 ppm of Ce. Fluorite also contained 14.8 ppm of U and 15.35 ppm of Cd. Quartz, on the other hand, contained low quantities of REE and heavy metals (Table 2).

In this study, each sample was examined for several chemical species using LA-ICP-MS (Table 3). Characterization results revealed the different chemical enrichment of trace elements in phosphogypsum mineral phases. Quantitatively, REE, Th, and U were detected in significant concentrations in fluorite phase. Quartz characterized by the presence of high concentration of Ba, Zn, and Pb.

In gypsum phase, Rb, Ga, and Sr are the most abundant elements.

To summarize, trace element concentrations in excess of 100 ppm in phosphogypsum samples are as follows (in order of abundance): $Y > Sr > La > Ce$ for the fluorite phase, $Ga > Tb > Sr$ for gypsum, and Sr, Y, and Ti for quartz. The elements found in concentrations ranging from 100 to 10 ppm include (in decreasing order of abundance) $Sm > Yb > Er$ for fluorine, $La > Ba > Ti$ for gypsum, and $Ce > Zn > U$ for quartz. Elements typically present in concentrations below 10 ppm include Pb, Sc, Hf, Co, Sb, Cs, Hf, Ta, and Sn.

Table 2 Average chemical composition of phosphogypsum in wt.% by electron probe microanalyzer (PG-1/L and PG-2/L: leached samples)

Elements	PG-1 Gypsum	PG-1 Quartz	PG-1 Fluorine	PG-1/L Gypsum	PG-1/L Quartz	PG-1/L Fluorine	PG-2 Gypsum	PG-2 Quartz	PG-2 Fluorine	PG-2/L Gypsum	PG-2/L Quartz	PG-2/L Fluorine
SiO_2	0.12	98	0.32	0.18	99.9	0.16	0.27	99.1	8.74	0.45	99.4	0.41
TiO_2	0.05	0.11	0.02	0.02	< d.l	< d.l	0.03	0.05	< d.l	< d.l	0.09	< d.l
Al_2O_3	0.05	0.001	2.87	0.05	< d.l	3.33	0.05	0.004	2.08	0.09	0.002	3.50
FeO	< d.l[a]	0.02	0.04	0.04	< d.l	0.17	0.09	0.06	< d.l	< d.l	< d.l	0.01
MnO	0.04	0.004	< d.l	0.002	< d.l	< d.l	0.04	< d.l	0.013	0.01	< d.l	0.03
MgO	< d.l	0.002	0.13	< d.l	0.001	0.18	< d.l	< d.l	0.06	< d.l	< d.l	0.18
CaO	39.3	0.04	38.2	39.6	0.06	50.7	38.8	0.08	23.8	35.8	0.06	39
Na_2O	0.04	0.05	0.77	< d.l	< d.l	0.46	0.04	< d.l	0.68	< d.l	0.016	0.74
K_2O	0.01	0.02	0.06	< d.l	< d.l	0.05	< d.l	0.015	0.10	0.001	0.004	0.08
P_2O_5	0.88	0.01	3.49	0.34	< d.l	3.65	0.52	0.03	4.05	1.08	< d.l	2.96
F	0.61	< d.l	36.8	0.40	0.08	39.3	0.71	< d.l	44.3	1.31	< d.l	26.9
Cl	< d.l	0.009	0.35	0.007	0.01	0.08	0.01	0.005	0.35	0.04	< d.l	0.13
SO_3	54.6	< d.l	1.38	54.5	< d.l	1.94	55	< d.l	0.90	39.05	< d.l	1.76
CdO	< d.l	< d.l	0.03	0.004	< d.l	0.015	0.016	< d.l	< d.l	0.003	< d.l	< d.l
UO_2	< d.l	< d.l	< d.l	< d.l	< d.l	0.01	0.009	< d.l	< d.l	< d.l	< d.l	0.03
PbO	< d.l	< d.l	< d.l	< d.l	0.04	< d.l	< d.l	0.01	< d.l	< d.l	< d.l	< d.l
Cr_2O_3	< d.l	< d.l	0.012	< d.l	0.01	0.02	0.03	0.009	0.009	0.011	0.008	0.009
V_2O_3	0.01	< d.l	0.007	< d.l	< d.l	< d.l	< d.l	0.02	< d.l	0.025	< d.l	< d.l
Y_2O_3	0.02	< d.l	0.31	< d.l	< d.l	0.37	< d.l	< d.l	0.08	0.003	< d.l	0.52
La_2O_3	0.02	< d.l	0.08	< d.l	< d.l	0.16	0.008	< d.l	< d.l	< d.l	0.017	0.12
Ce_2O_3	0.02	< d.l	0.05	< d.l	< d.l	< d.l	< d.l	< d.l	< d.l	0.03	0.03	0.07
Total	95.44	98.5	85	95.15	100	100	94.6	99.43	85.3	77.90	99.63	76.67

[a] < d.l, below detection limit

The deportments of rare earth elements, cadmium, uranium, and chromium in the phosphogypsum samples are presented in Fig. 5. The mineralogical composition of the studied samples showed that REE are not uniformly distributed in the matrix of the phosphogypsum. Yttrium is mainly present in three minerals: gypsum [$CaSO_4.2(H_2O)$]—60.77%, apatite [$Ca_5(PO_4)_3F_2$]—34%, and fluorite [CaF_2]—4.73%.

Lanthane is distributed between gypsum (73.68%) and fluorite (26.31%). Cerium occurs mostly in gypsum (72.47%) and fluorite (20.75%). The results reveal that 75.56%, 11.84%, and 7.3% of Cd are associated with gypsum, fluorite, and quartz, respectively. Around 97% of U is found in gypsum, 5% in fluorite, and 2% in apatite. More than 94% of the chromium is found in gypsum.

Table 3 Trace element composition of minerals in phosphogypsum in ppm by LA-ICP-MS

	PG-1 Gypsum	PG-1 Fluorine	PG-1 Gypsum	PG-2 Quartz	PG-2 Fluorine	PG-2 Gypsum
Sc	0.51	8.42	0.66	3.49	7.91	0.19
Ti	60.2	72.5	88.0	336.7	50.3	23.1
V	8.65	65.4	10.8	< d.l	11.64	2.4
Cr	43.6	128	121.8	50.6	141.5	22.6
Mn	9.45	44.47	6.89	4.64	2.12	2.53
Co	0.34	0.97	0.11	< d.l	0.57	0.15
Ni	6.12	33.21	5.52	4.36	< 1.52	1.6
Cu	6.84	41	9.1	2.45	2.24	1.21
Zn	23.2	147	26.2	3.14	2.34	4.49
Ga	2.19	25.25	2	0.25	12.05	1.79
As	2.31	13.8	2.63	1.16	4.43	0.61
Rb	0.80	8.60	1.03	1.43	1.313	0.29
Sr	1241	2048	1490	0.37	1712	677
Y	146	2235	147	0.281	1826	116
Zr	1.7	23.60	2.00	0.31	35.38	1.09
Nb	0.19	0.19	0.26	0.03	0.14	0.08
Cd	15.1	141	17.8	2.50	1.11	6.54
Sn	0.18	0.08	0.16	0.63	0.29	0.18
Cs	0.02	0.43	0.04	0.68	0.16	< d.l
Ba	82	51.5	79.5	0.66	123	24.2
La	80	862	83.9	0.04	818	60.8
Ce	51.4	608	42.1	0.07	544	39.6
Pr	13.5	134	11.7	0.04	121	11.02
Nd	58.5	556	51.2	0.22	478	50.5
Sm	12.9	96	10.6	< d.l	84.8	9.84
Eu	3.19	29.7	2.90	< d.l	29.8	2.43
Gd	13.8	110	12.6	< d.l	136	12.5
Tb	2	19.6	1.92	< d.l	20.5	1.68
Dy	14.2	117	12.5	0.14	132	11.6
Ho	3.13	24.7	3.09	< d.l	31.9	2.93
Er	9.06	81.4	9.02	0.04	81.6	7.74
Tm	1.20	12.6	1.15	< d.l	14.16	1.06
Yb	7.29	91.3	7.45	< d.l	112.2	5.66
Lu	1.05	12.5	1.08	< d.l	15.52	0.85
Hf	0.03	0.10	0.04	< d.l	0.12	0.01
Ta	0.01	0.03	0.03	< d.l	0.02	0.006
Pb	4.27	6.80	4.93	5.10	7.14	1.56
Th	3.20	72.2	3.80	0.09	53.8	2.05
U	25.4	329	30	2.79	128.3	25.7
ΣREE	416	5001	398	4.33	1154	331.8

Leaching experiments

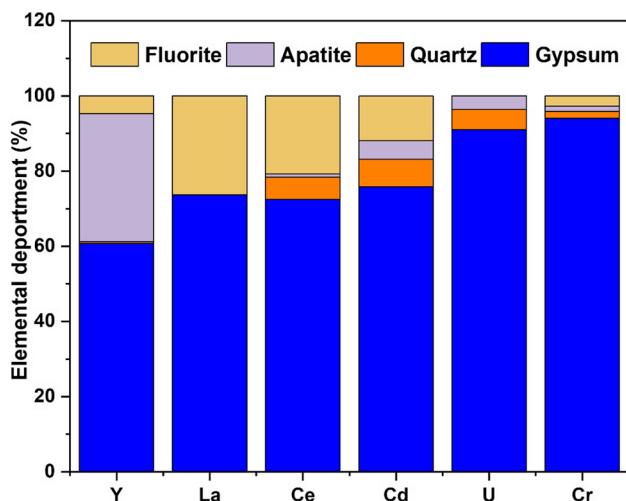The mobility of trace metals and rare earth elements in PGs was estimated using leaching tests. The results of the

leaching tests showed various fractionation behavior with increasing leaching time and temperature (Fig. 6). Also, an estimation of the relative release of each element regarding the total content is including in Table.S1. High release rate of elements was observed at the beginning of the experiments which may correspond to the release of exchangeable and weakly bounded elements. Some elements have a leaching rate that rises as the leaching time increases (e.g., Cd, U, Li, Th, As, Cu). However, other species such as REE, Ba, and Sr show a decreasing release rate as a function of leaching time. The latter may be explained by two mechanisms: (i) reprecipitation of the chemical species after their leaching or (ii) the chemical species became less available for water leaching.

The leaching experiments were carried out at room temperature and 60 °C, in order to investigate the effect of temperature on the leaching of trace elements. At low temperature, a modest leaching is observed, while at high temperature greater leaching is observed. Most of the elements reached high release rate at 60 °C for 24 h. For instance, rare earth element concentrations (Fig. 6a) were 7.96 µg/L for PG-1 and 7.85 µg/L for PG-2. The leaching efficiency of REE is limited by the solubility of phosphogypsum.

Fig. 5 Elemental deportment of REE (Y, La, Ce), Cd, U, and Cr
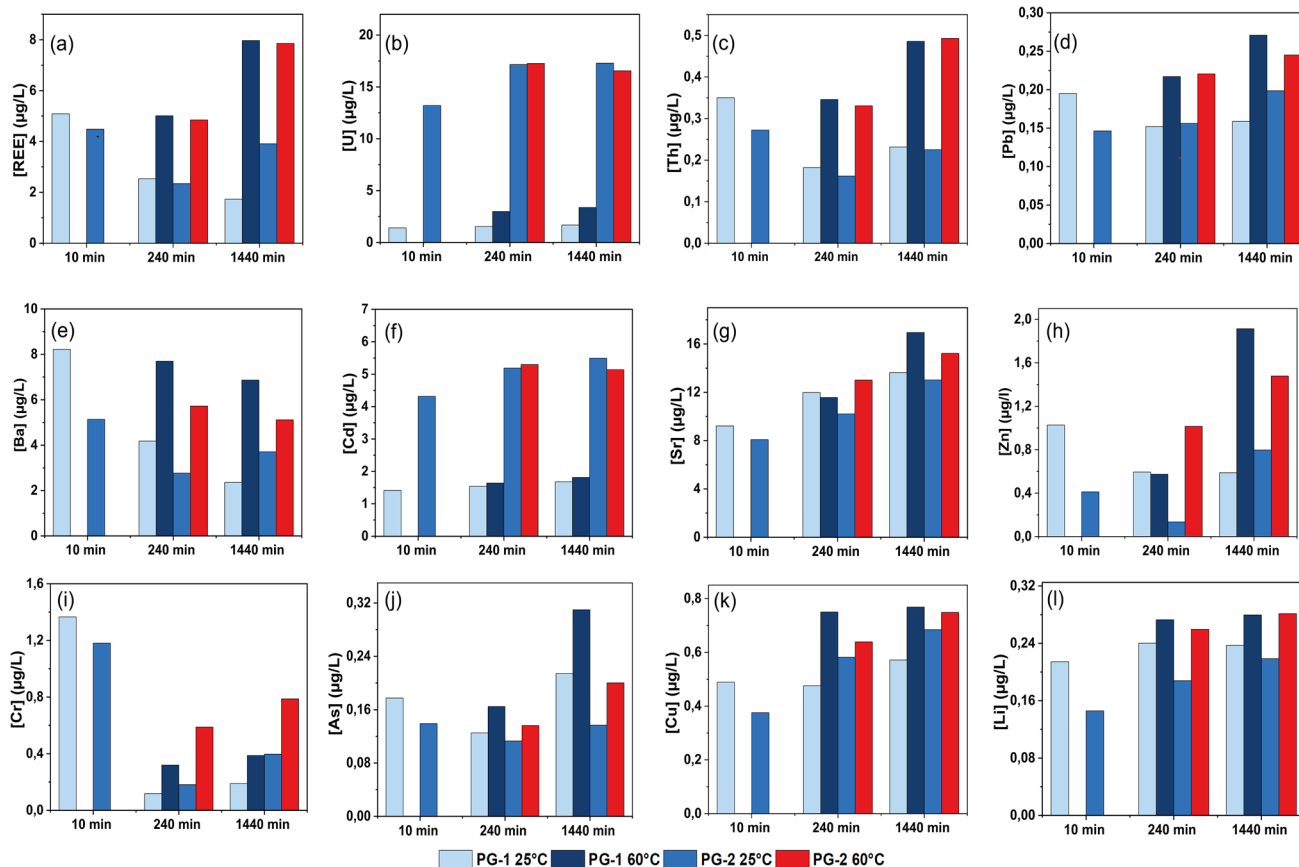
Fig. 6 Evolution of the leaching concentration of trace elements by varying time and temperature

When the gypsum reaches its solubility limit, no additional REE can be leached since the remaining REEs are trapped inside undissolved PG particles. A significant amount of U (Fig. 6b) and Cd (Fig. 6f) is released, reaching 17.29 µg/L and 5.49 µg/L, respectively. However, only 0.24 µg/L of Pb and 0.49 µg/L of Th (Fig. 6c) are leached. Heavy metals exhibit almost the same behavior with concentrations reaching 1.47 µg/L for Zn (Fig. 6h), 0.29 µg/L for Li (Fig. 6l), and 0.2 µg/L for As (Fig. 6j). Chemical species such as Ba (Fig. 6e) exhibited concentrations lower than 10 µg/L. The temperature has a catalytic effect that can promote the leaching of chemical species (Fig. 6). At 60 °C, we observed a significant release of elements, which can be explained by the increase of the solubility of PG under 60 °C compared to room temperature. A significant difference of partitioning of Cd and U is remarkable between the two samples due to high concentration of these elements observed for PG-2 compared to PG-1, which can indicate that the release rate of these elements from the phosphogypsum depends on their initial concentrations in the raw samples.

Furthermore, studies of minerals' composition of leached samples were performed using LA-ICPMS to evaluate the changes in the chemical composition of the identified minerals in the phosphogypsum due to the leaching procedure (Table 4). The results of the calculation of the estimated release of each element comparing to the total content are presented in Table.S2. The following LA-ICP-MS results presented the trends of trace elements after 10 min of leaching in room temperature. We observed that several trace elements such as Cr, Mn, V, and Ti might be eliminated by simple water washing. Other elements such as REE, Th, and Sr are more retained in the phosphogypsum matrix, so their release requires full dissolution of the PG matrix using strong chemical. The concentration of these elements is similar in both in the leached and the raw samples.

Concentration of major and light elements changes between raw and leached samples as it can be derived from LIBS maps (Figure.S1). A careful analysis of the LIBS total spectra reveals differences in the intensity of some elements between the raw and the leached samples. Using the National Institute of Standards and Technology (NIST) atomic spectroscopy database, the wavelengths of various spectral lines present in the LIBS spectra of all elements were identified (Fig. 7).

The decrease of major element concentrations was quantified by calculating the average difference between the raw and leached sample. Considering that the area investigated in both samples is much larger than the typical grain size and therefore is large enough to be comparable. Ca (Fig. 7a, b) and S (Fig. 7c) showed a decrease of 22% and 13%, respectively. The concentration of P decreased by 43% compared to the raw sample (Fig. 7a). A slight decrease of Si, Ba,

and Al has been recorded (Fig. 7a). On the other hand, the concentration of fluorine and aluminum showed a decrease of 6% for both of them (Fig. 7c).

Discussion

Chemical behavior of elements in phosphogypsum

In general, the behavior of trace elements is governed by rules related to retention mechanisms (Manceau et al. 2002; Scheidegger and Sparks 1996). Several physico-chemical phenomena occur during the retention of trace elements from the solid phase to the liquid phase or vice versa. Among the mechanisms often cited is adsorption (physisorption, chemisorption), which occurs when molecules attach to the surface of solids. Other possible mechanism is precipitation, which results in the formation of a new solid phase through the passage of a supersaturated species from the liquid phase. Other mechanisms can also occur such as ion exchange, isomorphic substitution, surface complexation, and inclusion (Deschamps et al. 2006). These different retention mechanisms can occur simultaneously with a greater or lesser relative importance. Depending on the nature of the cation and the chemical conditions of the medium, one mechanism may be predominant.

The water leaching experiment was carried out for various time durations and temperatures in order to measure the mobility of trace elements occurring in the phosphogypsum. Figure 8 presents the liquid/solid fractionation of chemical species following PG leaching. The mobility of trace metals in phosphogypsum can be divided into three categories: (i) the elements with the highest mobility including U, Cd, and Cu; (ii) those with intermediate mobility such as Pb, Th, and Sr; and (iii) those with low mobility as REE and Ba. As a result, it is possible that the trace elements are not retained in the phosphogypsum matrix through the same mechanism and are not equally distributed. Therefore, they are not leached and transported in the leachates in the same way or at the same rate.

The results of leaching tests revealed that the diverse retention mechanisms of trace and minor elements, as well as their distribution in the phosphogypsum, control their mobility and geochemical behavior.

The geochemical behavior of rare earth elements demonstrates that they are trapped in the residue, resulting in a low fractionation ratio (Fig. 8a), which may be explained by their presence in insoluble phases in the phosphogypsum. According to the EPMA and LA-ICP-MS results, REEs are mostly found in the fluorine phase. The elemental deportment calculation, which considers the quantification of mineral phases and the concentration of elements in each mineral, revealed that REEs are associated with gypsum, the abundant phase

Table 4 Trace element composition of minerals in leached phosphogypsum samples in ppm by LA-ICP-MS

	PG-1/L Gypsum	PG-1/L Gypsum	PG-1/L Gypsum	PG-2/L Fluorine	PG-2/L Gypsum	PG-2/L Gypsum
Sc	0.76	0.36	0.32	0.56	0.57	< d.l
Ti	76.4	66.8	33.8	171.9	186	70.6
V	3.33	2.6	1.93	10.2	3.1	2.6
Cr	47.5	66.6	73.3	303.1	62.8	109.8
Mn	1.88	5.64	4.12	17.7	1.54	4.7
Co	0.78	< d.l	0.43	0.98	0.23	0.62
Ni	6.01	5.69	< d.l	4.63	3.25	2.12
Cu	5.05	2.45	1.73	5.41	3.04	3.07
Zn	2.49	1.29	1.48	12.37	1.68	2.47
Ga	2.23	1.62	1.62	3.07	2.21	1.88
As	1.1	0.95	0.69	1.87	1.08	1.18
Rb	0.43	0.09	0.13	1.26	0.22	0.16
Sr	624	663	642	1476	921.3	672
Y	229	179	149	488	241	206
Zr	3	2.66	1.81	7.62	6.02	4.04
Nb	0.26	0.26	0.17	0.67	0.57	0.36
Cd	0.59	0.88	< d.l	8.80	1.48	1.3
Sn	0.25	0.42	< d.l	< d.l	0.12	< d.l
Cs	0.015	< d.l	< d.l	0.063	< d.l	< d.l
Ba	88.58	65.4	52.1	112	96.4	66.4
La	82.95	74	64	214	104	88
Ce	58	45	42	84	65	48
Pr	14.2	12.4	10.3	36.8	16.5	14.1
Nd	77.1	46.1	44.8	130	71.1	52.8
Sm	12.5	9.79	10.4	32.6	16.2	11.8
Eu	3.61	2.77	2.59	7.27	3.67	3.2
Gd	20.9	14.1	12.5	25.3	20.3	16.5
Tb	2.19	2.09	1.79	4.94	2.84	2.05
Dy	16.1	15.7	12.7	36	21	15
Ho	3.47	3.42	2.85	10.5	4.99	3.49
Er	10.9	9.25	9.03	30.9	15.7	10.8
Tm	1.56	1.45	1.2	5.33	2.3	1.63
Yb	11.4	8.55	6.95	44.1	16.2	11.5
Lu	1.67	1.23	0.98	3.15	2.07	1.37
Hf	0.06	0.05	0.03	0.10	0.06	0.03
Ta	0.01	0.02	0.02	0.03	0.03	0.008
Pb	2.23	2.26	1.89	3.72	3.26	2.51
Th	6.69	3.34	2.65	16.1	7.94	5.6
U	11.3	7.51	6.49	194	18.3	14.4
ΣREE	554	426	372	1156	697	485

in PG. As a result, we proposed that gypsum could be considered as the main REE-bearing phase, and the insoluble phase (fluorine) controlling the REE mobility. Indeed, there is some discussion about the minerals that host REE in PG. Some authors (e.g., Borges et al. 2016; Santos et al. 2006) highlight different minerals, such as sulfates, carbonates, fluorides, and phosphates, as the main REE-bearing minerals. In this context, the presence of F has been also considered

in several works on REE extraction, but it is not abundant in PG. It is known that fluorine phase could present a powerful REE host in geological matrices (Ayora et al. 2016; Cánovas et al. 2017) and act as replacement phases for calcium in the crystal lattice structure. Sedimentary phosphate rock is composed primarily of fluorapatite that contains significant concentrations of REE, Y, and Sc (Binnemans et al 2015). Thus, the most feasible source of these elements must be
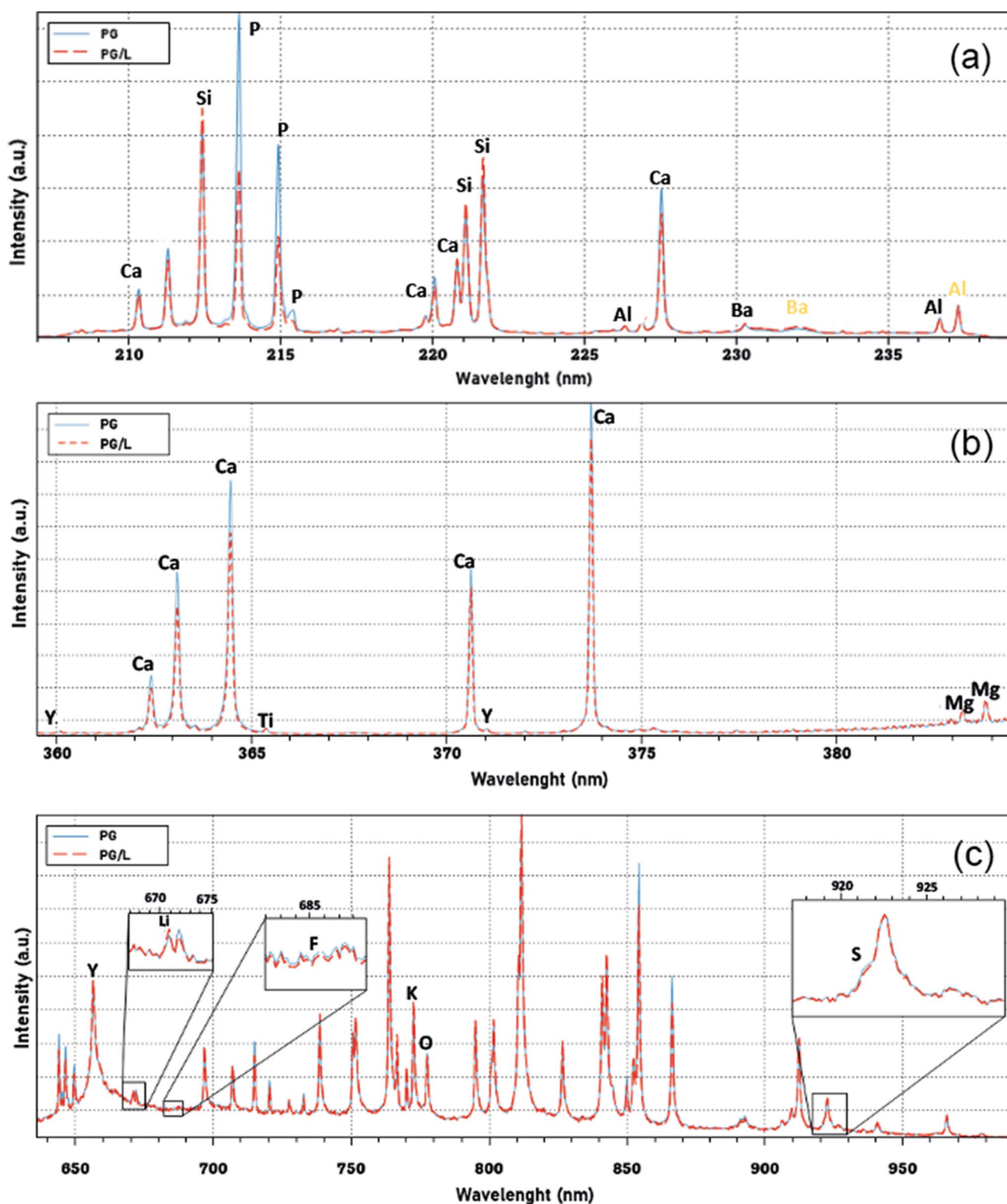
Fig. 7 Total emission spectral collected in the regions; **a** 207–239 nm, **b** 360–385 nm, **c** 590–599 nm for raw (PG) and leached sample (PG/L) samples

the non-reacting phosphate in phosphogypsum. Another possibility would be the formation of secondary minerals (fluorine) during acid attack of phosphate rock. In this perspective, Köhler et al. (2005) suggested that REEs are easily

Fig. 8 Liquid/solid fractionation of elements after PG leaching

Leachate | PG after leaching | PG before leaching
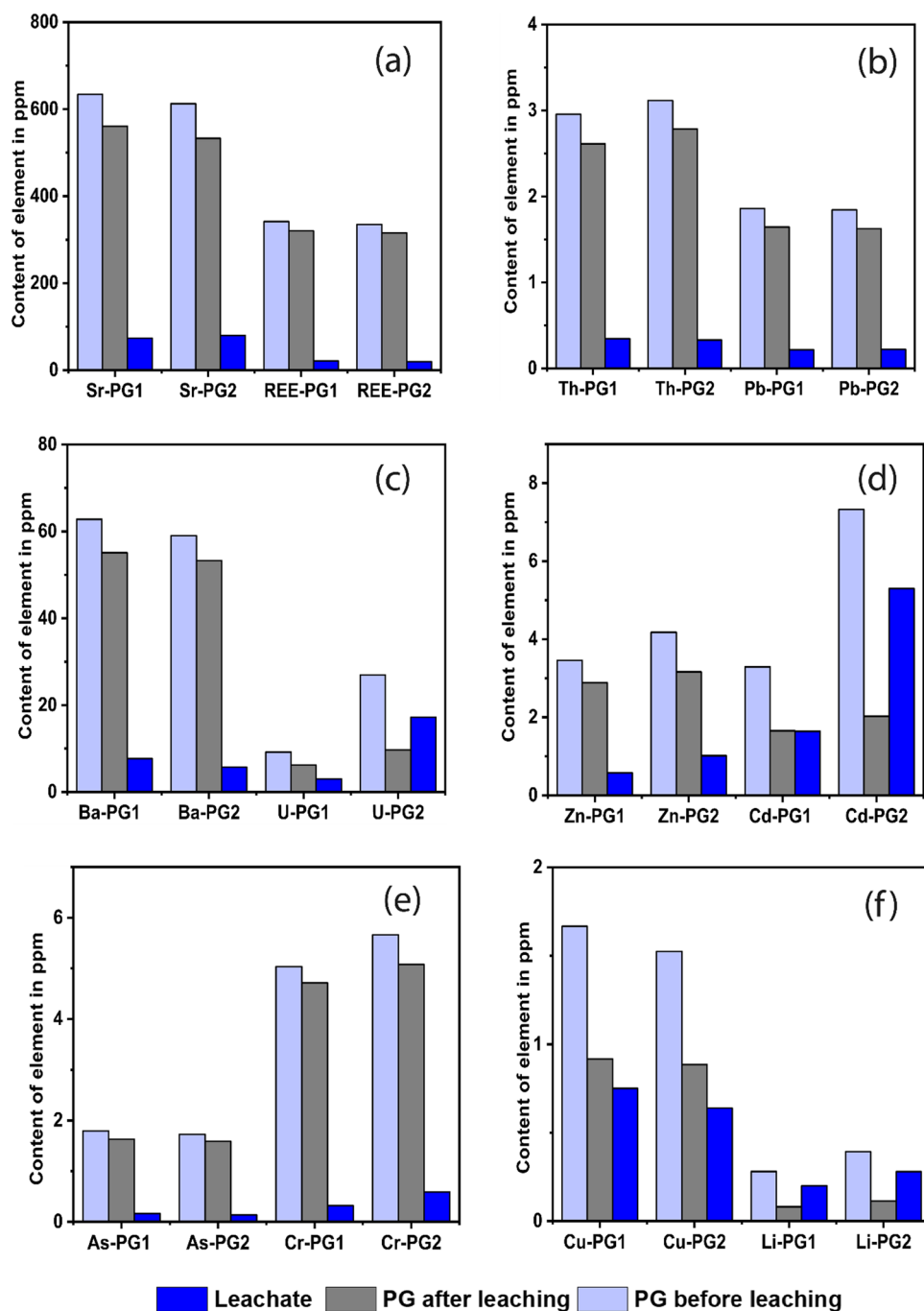
released when apatite is completely dissolved during industrial process, and they can also be easily precipitated as secondary phosphate phases during the reaction. Therefore, it can be suggested that phosphate minerals can act as sources of REE in phosphogypsum while fluorinated minerals can act as secondary phases controlling their mobility. According to Shivaramaiah et al. (2016), the majority of REEs (Eu as a model) are found on the surface of the gypsum crystal as a separate secondary phase, namely, a metastable amorphous/nanocrystalline phase in which Eu is associated with

phosphate and sulfate as counterbalancing ions. On the other hand, gypsum could be considered as the main REE vector as reported by Habashi (1985). Consequently, REE recovery is possible only if the PG matrix is destroyed. This explains their low mobility even at high temperatures and after 24 h of leaching. Accordingly, the results obtained in this work agree with these findings.

Based on ICP-MS results, Ba and Sr are presented in PG with significant concentration in PG, despite this fact they are poorly soluble (Fig. 8a–d). It was found that the presence

of Sr has been linked to gypsum by substitutions of Ca in the crystal lattice, and Ba is mainly precipitated as insoluble phase ($BaSO_4$) (Rutherford et al. 1994).

From the leaching experiment, we observed that uranium preferentially leached (Fig. 8c), which can be explained by the fact that it is adsorbed on the surface of gypsum crystals as U(VI) in the form of uranyl ion (UO_2^{2+}) (Fávaro 2005). According to Rutherford et al. (1994), thorium appears in the oxidation state (+IV) and could form insoluble complexes with fluorides, hydroxides (formation of $Th(OH)_4$ for pH > 5), and phosphates, which may explain why thorium mobility remains low even when the time and temperature of leaching tests are increased (Fig. 8b). Concerning Pb, it was found that it is present in the phosphogypsum in the form of insoluble lead precipitates with sulfate or carbonates (Al-Masri and Al-Bich 2002) resulting in a low release rate (Fig. 8b).

According to leaching results, Cd, Cu, Cr, and Li have a high liquid/solid fractionation (Fig. 8d–f), which can be explained by the fact that they are fixed via adsorption or they are weakly bounded to the surfaces of gypsum, which is a reversible phenomenon (Arocena et al. 1995). These elements are released significantly by interaction with water. Thus, they can be hosted in the interstitial waters or in easily to moderately soluble mineral phases along the phosphogypsum matrix (Macías et al 2017a, b).

Criteria for assessing the quality of phosphogypsum

Except for Cd, the heavy metal levels of the phosphogypsum samples do not exceed the frequent effect concentration requirements (CFE) (Papaslioti et al. 2018) (Table 5). As, Cr, Ni, Cu, Pb, and Zn contents in phosphogypsum were lower than the rare effect concentration (REC). The Cd content in the first sample was above the concentration producing a probable effect (CPE) threshold but was lower than the concentration causing an occasional effect (COE) in the second sample. The phosphogypsum can be considered as a rare effect heavy metal-contaminated material because the concentration of metal(loid)s does not present any harmful effect on the environment.

Potential application of phosphogypsum for an integrated management approach

Phosphogypsum is a byproduct extensively produced by phosphate-based fertilizers industries. As a result, its management presents a significant challenge. In general, there are three options for dealing with PG: (i) disposal in the sea or rivers, (ii) surface storage, or (iii) recycling and valorization (Macías et al. 2017a, b). With the implementation of environmental protection conventions, a new strategy for reusing this material should be envisaged in order to avoid its challenging management. Waste reuse and valorization are the best available practices of waste management currently accessible (Bisone et al. 2017). Thus, valorizing phosphogypsum reduces costs related to its management and even generates a financial benefit and reduces its environmental footprint. Further integrated management plan includes the potential application in construction materials such as plaster (Moalla et al. 2017), concrete, and construction materials (Chen et al. 2018).

A developed approach of extensively recycling PG for industrial application can be used as a source of rare earth elements. Recycling REEs from these alternative waste sources by hydrometallurgical processes is becoming a sustainable and practical solution due to low energy consumption, low waste generation, few emissions, environmental friendliness, and economic feasibility. Due to the low concentration of REEs in PG (normally < 0.1 wt.%) and their tiny and complicated existence as mineral phases, the recovery of REE from PG would be extremely difficult in terms of both technology and economics. Various physicochemical pre-treatment techniques have been applied to increase the concentration of REEs in PG prior to extraction. Carbonation, roasting, microwave heating, grinding, and recrystallization have all been employed extensively for this purpose (Wu et al. 2018; Yang et al. 2019). Several research papers

Table 5 Quality criteria for phosphogypsum (*REC*, rare effect concentration; *TCE*, threshold concentration producing an effect; *COE*, concentration of occasional effects; *CPE*, concentration producing a probable effect; *CFE*, concentration of frequent effects)

Criteria for assessing the quality of freshwater sediments								
Concentrations (mg/kg)								
Groups	Substances	REC	TSE	COE	CPE	CFE	PG-1	PG-2
Metals and metalloids	Arsenic	4.1	5.9	7.6	17	23	0.14	0.17
	Cadmium	0.33	0.6	1.7	3.5	12	4.31	1.41
	Chromium	25	37	57	90	120	0.18	1.36
	Copper	22	36	53	200	700	0.37	0.48
	Nickel	ND	ND	47	ND	ND	ND	ND
	Lead	25	35	52	91	150	0.14	0.94
	Zinc	80	120	170	310	770	0.41	1.02

have been published in this area to improve the recovery of REEs from phosphogypsum using various approaches (Innocenzi et al. 2014; McLellan et al. 2013; Mukaba et al. 2021). Several conventional techniques were used to recover rare earths from phosphogypsum, including the use of strong inorganic acids such as H_2SO_4, HNO_3, and HCl (Walawalkar et al. 2016). The direct leaching of PG requires the control of several parameters including contact time, solid to liquid ratio, temperature, chemical agent concentration, particle size, and agitation speed (Lütke et al. 2022).

Walawalkar et al. (2016) developed a technique for recovering REE using HNO_3. They obtained a REE recovery of 85% and showed that the REE recovery increases with the increasing acid concentration. In the other hand, Hammas-Nasri et al. (2016) conducted a study using a double H_2SO_4 leaching step. The results showed that PG have a low solubility under normal conditions resulting from the common ion effect, but the low cost of H_2SO_4 makes it a good candidate. Like H_2SO_4, the leaching of REEs from PG with HCl was found to be moderately low which was attributed to the relatively poor solubility of calcium sulfate in the HCl solution due to the salt out effect. According to Ismail et al. (2015), low to moderate REE leaching efficiencies have been reported through direct leaching of PG using HCl. To increase the leaching efficiency of REEs, a two-step extraction process was investigated using HCl (1.5 M) and the average extraction level increases from 51 to 81% (Ismail et al. 2015).

Despite a large body of literature on the recovery of REEs from PG, there has not been a detailed characterization of REE in phosphogypsum to identify the distribution, oxidation states, and understanding of the local mineralogy enrichment of these elements. Additionally, an intensive development of a mineralogical approach will be required to design an optimal process for REE recovery. Based on the findings of this investigation, microanalysis revealed that the fluorine is the mineral phase had a significant concentration of REE. This result should be used in future research to optimize the extraction of REE from PG and increase their yield in the finished product.

Conclusions

Based on a combination of geochemical, mineralogical, and microanalytical data, this study is performed to provide a full characterization of PG samples. The experimental and theoretical results obtained lead to the following conclusions:

– The mineralogical analysis revealed that PG is mostly composed of gypsum with the presence of minor phases such as quartz and fluorine as identified by EPMA and SEM–EDS.

– Chemically, PG was composed of Ca and S as major elements with variable concentrations of trace elements REE (344.32–349.14 ppm), Cd (3.50–7.40 ppm), and U (9.3–27.4 ppm) distributed uniformly throughout the PG matrix.

– Elemental deportment calculation showed that the majority of REE, Cd, and U are associated with the gypsum phase.

– Based on leaching results, the mobility of trace elements was variable as a function of the temperature and leaching time. The temperature has a catalytic effect promoting an increase in the chemical species release rate as the solubility of PG increases. The PG samples, at room temperature, generated 3.73–4.73 µg/L/day of REE, 2.76–13.20 µg/L/day of U, and 1.67–5.49 µg/L/day of Cd. However, at 60 °C it generated 7.85–7.96 µg/L/day of REE, 3–17.26 µg/L/day of U, and 1.81–5.14 µg/L/day of Cd.

– This study shows that PG contained non-negligible amounts of critical elements (e.g., REE). Consequently, PG can be considered as a high tonnage/low grade REE ore. Knowing the high criticality level of REE, PG must be considered as a resource and not a waste.

Declarations

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