Mobility of Rare Earth Elements, Yttrium and Scandium from a phosphogypsum stack: environmental and economic implications

*C.R Cánovas**, *F. Macías, R. Pérez López, J.M Nieto*

Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment. Faculty of Experimental Sciences, Avda. Fuerzas Armadas s/n, 21071 Huelva (Spain).

**Corresponding author:*

carlos.ruiz@dgeo.uhu.es

Tel: +34 959219870; Fax: +34 959219440

Abstract

This paper investigates the mobility and fluxes of REE, Y and Sc under weathering conditions from an anomalously metal-rich phosphogypsum stack in SW Spain. The interactions of the phosphogypsum stack with rainfall and organic matter-rich solutions, simulating the weathering processes observed due to its location on salt-marshes, were simulated by leaching tests (e.g. EN 12457-2 and TCLP). Despite the high concentration of REE, Y and Sc contained in the phosphogypsum stack, their mobility during the leaching tests was very low; less than 0.66% and 1.8% of the total content of these elements were released during both tests. Chemical and mineralogical evidences suggest that phosphate minerals may act as sources of REE and Y in the phosphogypsum stack while fluoride minerals may act as sinks, controlling their mobility. REE fractionation processes were identified in the phosphogypsum stack; a depletion of LREE in the saturated zone was identified due probably to the dissolution of secondary LREE phosphates previously formed during apatite dissolution in the industrial process. Thus, the vadose zone of the stack would preserve the original REE signature of phosphate rocks. On the other hand, an enrichment of MREE in relation to HREE of edge outflows is observed due to the higher influence of estuarine waters on the leaching process of the phosphogypsum stack. Despite the low mobility of REE, Y and Sc in the phosphogypsum, around 104 kg/yr of REE and 40 kg/yr of Y and Sc are released from the stack to the estuary, which may imply an environmental concern. The information obtained in this study could be used to optimize extraction methods aimed to recover REE, Y and Sc from phosphogypsum, mitigating the pollution to the environment.

Keywords; leaching test, fractionation processes, REE scavenging, REE fractionation.

1. Introduction

Rare Earth Elements (REE) are a group of chemically similar metallic elements (i.e. lanthanide series). Although traditionally scandium (Sc) and yttrium (Y) were also included in this group, only Y is currently considered as lanthanide (Chakhmouradian and Wall, 2012), forming a group known as REY elements (Ayora et al., 2016). This group of elements, arbitrarily divided into light (LREE: La to Nd), medium (MREE: Sm to Gd) and heavy (HREE: Tb to Lu plus Y) (Hatch, 2012), are becoming increasingly important in the transition to a green, low-carbon economy due to their essential role in permanent magnets, lamp phosphors, rechargeable NiMH batteries, catalysts and other applications (Binnemans et al., 2013). REE are not considered as essential elements for living organisms, although they may have unknown functions in the organisms, especially in innumerable biochemical processes (Migaszewski and Galuszka, 2015). On the contrary, some studies suggested that high concentrations of REE may cause significant environmental impacts on living organisms (e.g. Oral et al., 2010; Pagano et al., 2015). The growing use of these elements by industry has led to an inherent increase of REE emissions into the environment. Thus, it is of paramount importance to address the potential release and transport of REE during all stages of industrial processes. A potential source of REE, Y and Sc to the environment is the fertilizer industry which produces the phosphoric acid needed for fertilizer manufacturing. Phosphoric acid is commonly produced by the chemical reaction of the phosphate rock with sulfuric acid, a process known as wet chemical treatment, responsible for around 90% of the worldwide phosphoric acid production (USGS, 2016). As a result, a by-product known as phosphogypsum is generated. Phosphogypsum is mainly composed of gypsum ($CaSO_4{\cdot}2H_2O$) although may also contain other minor solid phases such as reaction products of the wet process (e.g. alkali fluorosilicates and fluorides), unreacted phosphate rock and gangue mineral particles (e.g. quartz, organic matter and feldspars) (Lottermoser, 2010). The presence of wastewaters from the industrial process, mainly phosphoric, sulfuric, and hydrofluosilicic acids, trapped in the interstices of mineral particles confers to phosphogypsum its acidic nature. In addition, this residual water contains high levels of metals, metalloids and radionuclides (Luther et al., 1993). Due to the high level of impurities, phosphogypsum are often stockpiled in stacks close to the factories and finally covered, and rarely recycled.

During the wet process, elements contained in the phosphate rock are released from their host phases into solution and partitioned into phosphoric acid or phosphogypsum, according to their solubility (Rutherford et al., 1994). Uranium, Th and Pb-210 concentrate in the phosphoric acid whereas most of the Ra-226 and Po-210 are finally contained in phosphogypsum (Lottermoser, 2010). According to different authors (e.g. Rutherford et al., 1994; Al-Masri et al., 2004; Pérez-López et al., 2011), metals (e.g. Cd, Cu and Zn) are preferentially transferred into phosphoric acid. In the case of REE, around 70-85% originally present in phosphate rocks are concentrated in solid phosphogypsum (Binnemans et al., 2015). The weathering of phosphogypsum stacks constitutes an environmental concern due to the release of pollutants into the surrounding environment (e.g. Bolívar et al., 2002; Tayibi et al., 2009; Pérez-López et al., 2015; El Zreli et al., 2016). Unlike metals, metalloids and radionuclides, the mobility of REE in phosphogypsum stacks has not been studied in detail nor have their fluxes into the environment been quantified, despite the potential interest for recovery of these elements from phosphogypsum (e.g. Binnemans et al., 2015; Cánovas et al., 2017). This issue is especially significant taking into account the worldwide growing production of phosphogypsum to support the increasing levels of farming production; around 100-280 Mt of this by-product is generated per year (Parreira et al., 2003) and deposited near the industries due to its limited recycling. An improved understanding of REE behavior during low-temperature water–rock interaction in industrial waste landfills is needed. Thus, this study investigates the factors controlling the mobility of REE under weathering conditions in a phosphogypsum stack in SW Spain and quantifies the REE fluxes to the environment.

2. Methods

2.1. Site description

A fertilizer plant was operating via wet treatment near Huelva city (SW Spain) during almost 40 years (from 1967 to 2010). Sedimentary phosphorite was imported mainly from Morocco to manufacture the phosphoric acid. As a result, around 100 Mt of phosphogypsum were directly dumped on 12 km^2 of salt-marshes of the Tinto River estuary, less than 100 m from the city (Fig. 1). The implementation of a closed-circuit system in 1997 promoted the existence of process water ponds in the central part of the stacks and a system of perimeter channels for collecting all leakages from the piles (Fig. 1). The singularity of this phosphogypsum stack relies on the facts that wastes were deposited over the marshland without any type of isolation and within the tidal prism of the estuary. Under these circumstances, this stack is strongly weathered not only by a downward flow of rainwater during rainy episodes but also by an upward flow of seawater during tidal cycles. In case of weathering by rainwater, these episodes are especially significant as rainfall events in Mediterranean regions are scarce but intense. In addition, the absence of composite liners in the bottom of the stack causes the interaction of these wastes and their weathering agents with the organic matter-rich marshland. As a result, the weathering of the phosphogypsum can occur under oxidizing conditions in the shallowest part and under reducing conditions in the deepest part in contact with the marsh (Pérez-López et al., 2015). Moreover, this phosphogypsum contains anomalously high concentrations of some toxic elements in comparison to others around the world (Macías et al., 2017). In order to avoid the release of pollutants to the estuary during rainy events, the stack has been partially restored. Despite the decrease in the pollutant release observed, these measures seem to be insufficient as permanent edge outflows continue being released from the toe of the stack (Pérez-López et al., 2016). The main chemical difference between edge outflows emerging from the bottom of the stack and process waters stored in surface ponds is the higher element concentration in the latter due to the large residence time in the close-circuit system and to evaporation. Detailed descriptions of physical and environmental setting of Huelva phosphogypsum stack can be found in Pérez-López et al. (2015, 2016) and Macías et al. (2017).

2.2. Sampling and analytical techniques

2.2.1. Water and solid samples

Edge outflows were sampled along the perimeter of the phosphogypsum stack during the dry and rainy seasons (June and November 2014). In addition, some samples of process water contained in central ponds and perimeter channels of the stacks were taken (Fig. 1). In total, 121 water samples were collected during both campaigns. The pH, redox potential (ORP), electrical conductivity (EC) and temperature were measured in the field using a portable Multiparametric Crison MM 40+ equipment. Measured ORP values were referenced to the standard hydrogen electrode (Eh), as proposed by Nordstrom and Wilde (1998). Water samples were filtered with 0.10 μm membrane filters and divided into two aliquots; one unacidified for anion and ammonia determination and the other acidified with HNO_3 to pH < 1 for major and trace element analysis. From an operational point of view, concentrations determined in filtrates were considered to be dissolved.

Concentrations of anions (PO_4, Br, Cl and F) and ammonia in unacidified aliquots were analyzed by high performance liquid chromatography (HPLC) using a Metrohm 883 basic ion chromatograph (IC) equipped with Metrosep columns. The acidified samples were analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; Jobin Yvon Ultima 2) for major elements (Al, Ca, K, Mg, Na and S) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS; Agilent 7700) for REE, Y and Sc. Detection limits were: 0.2 mg/L for S; 0.1 mg/L for Na; 0.05 mg/L for K and Mg; 0.02 mg/L for Al and Ca; and 0.1 µg/L for REE, Y and Sc. All analyses were performed in the laboratories of the University of Huelva. Three laboratory standards, prepared with concentrations within the range of the samples, were analyzed with every 10 samples to check for accuracy. Furthermore, dilutions were performed to ensure that the concentration of the samples was within the concentration range of the standards. Blank solutions with the same acid matrix as the samples were also analyzed. The average measurement error was less than 5%. In addition, the quality of analysis was verified with an OREAS904 certified reference material. The difference between certified and measured values ranged from 0.4% (Ce) to 8.0% (Ho). A triplicate analysis was performed in order to evaluate the precision, being the relative standard deviation (RSD) below than 5 % in all cases.

Solid samples of phosphogypsum were also collected from different depths of the stack (Fig. 1) in boreholes, and obtaining a total of 17 samples. The first 5 samples correspond to the vadose zone (from surface down to 2 m depth) while the remaining samples correspond to saturated zone (from 2 to 8 m in depth). The deepest sample represents the stack basement directly in contact with the estuarine marsh soils. At the laboratory, pore-waters were collected through suction cup lysimeters under N_2(g) atmosphere within a glove box. Eh and pH values were immediately measured in all pore-water samples. After pore-water extraction, solid samples were frozen and then lyophilized to complete dryness using a freeze-dryer. The chemical composition of solid samples was obtained by analyses after aqua-regia pseudo-total digestion. Thus, 10 mL of aqua-regia (12 mol L^{-1} HCl and 15.8 mol L^{-1} HNO_3 in the ratio 3:1) were added to 1 g of phosphogypsum in Teflon reactors and reacted for 20 h in a fume cupboard, and then, simmered on a hot plate for 1 h at 100 ºC. The digestates were diluted with deionized water and stored at 4ºC until analysis. In addition, newly-formed solid precipitates formed from edge outflows were also sampled.

Phosphogypsum samples and newly-formed precipitates from edge outflows were mineralogically characterized. X-ray diffraction (XRD) patterns of samples were obtained with a Bruker D8 Advance diffractometer with Cu Kα radiation. Diffractometer settings were 40 kV, 30 mA, a scan range of 3-65º 2Θ, 0.02 2Θ step size, and 2.4 s counting time per step. Phosphogypsum samples were also examined by scanning electron microscope coupled with energy dispersive spectrometer (SEM-EDS; FEI-Quanta 200 equipped with a microanalyzer EDAX Genesis 2000).

2.2.2. Leaching tests

Two different leaching tests were performed to selected solid phosphogypsum samples of the depth profile (8 samples) with the aim to assess the mobility of REE under different weathering conditions. Samples were subjected to the EN 12457-2 (EU, 2002) and TCLP (USEPA, 1992) leaching tests, established by current EU and US regulations, respectively, on waste disposal and classification. On the one hand, the EN 12457-2 leaching test has been used not only to evaluate the suitability of wastes for waste disposal acceptance in European landfills but also to study metal release from mineral-processing wastes (e.g. Macías et al., 2012; Vemic et al., 2015). Samples came into contact with deionized water at a liquid to solid ratio of 10:1, followed by stirring for 24 h, centrifugation, filtration of the supernatant and determination of dissolved elements. This leaching test allows estimating the potential leaching of REE, Y and Sc by phosphogypsum during rain events.

On the other hand, the TCLP leaching test was originally designed to simulate co-disposal with municipal wastes, although its applicability has been also extended to the hazardousness classification of mineral-processing wastes (Al-Abed et al., 2006; De Andrade Lima et al., 2008; Macías et al., 2012).Samples were extracted with a solution of acetic acid buffered to pH 4.9 for 18 h by stirring on a shaker with a liquid to solid ratio of 20:1. Following the extraction, samples were centrifuged, and the supernatant filtered, acidified with HNO_3 and stored at 4ºC until analysis. This leaching test would simulate the interaction of the upward flow from the basement and/or the downward water flow from the surface with the organic matter-rich marsh soils. Results obtained from both tests were compared to total composition with the purpose of quantifying the proportion of REE, Y and Sc released by each simulated weathering process.

2.3. Data treatment

In order to study fractionation processes during the weathering of the stack waste material, REE concentrations were normalized using the North-American Shale Composite (NASC) values (Gromet et al., 1984). The shape of the NASC-normalized REE patterns was described using the NASC-normalized ratios, $(MREE/LREE)_{NASC}$ and $(HREE/MREE)_{NASC}$, calculated as the average of all permutations of those inter-element ratios (Stolpe et al., 2013). The LREE (light-REE) included in the ratio calculation were La, Pr, Nd, and Sm; the MREE were Gd, Tb, and Dy (middle-REE); and the HREE (heavy-REE) were Ho, Er, Tm, Yb, and Lu. Both Ce and Eu were excluded from calculation due to their anomalous redox activity. Cerium $(Ce/Ce^*)_{NASC}$ and Europium $(Eu/Eu^*)_{NASC}$ anomalies were calculated from the expression $Ce_{NASC}/\surd[La_{NASC}\cdot Pr_{NASC}]$ and $Eu_{NASC}/\surd[Sm_{NASC}\cdot Gd_{NASC}]$ found in Worrall and Pearson (2001) and Taylor and McLennan (1985), respectively.

Chemical speciation and saturation indices of solutions were calculated by PHREEQC code v2.12.01 (Parkhurst and Appelo, 2005) using the database provided by Lawrence Livermore National Laboratory (llnl.dat). Around 10% of collected samples exhibited high values of ionic strength (above 0.7), thus speciation analysis and saturation indices calculated for these samples have a higher uncertainty. The database was completed with thermodynamic data for REE phosphate reported by Liu and Byrne (1997).

3. Results and discussion

3.1 REE, Y and Sc mobility under different weathering scenarios

The phosphogypsum stack encloses significant concentrations of REE, Y and Sc which can be potentially released under weathering by natural environmental factors. The pseudo-total concentration of REE in the phosphogypsum solid is higher in the vadose zone (from 425 to 828 mg/kg), reaching its maximum at the interface with the saturated zone (Fig. 2A). The REE concentration in the saturated zone ranged from 264 to 452 mg/kg. Regarding Y, a concentration of 204 mg/kg was recorded at the surface, decreasing down to the contact with the saturated zone (Fig. 2A). The concentration of Y remains constant along the saturated zone (around 110 mg/kg), except some higher values observed at 6 and 7 m depth. The pseudo-total concentration of Sc in the solid displays a similar trend (values ranging from 2.1 to 5.1 mg/kg along the profile) with a maximum observed at 7 m depth (6.0 mg/kg; Fig. 2A). These changes in element concentration between saturated and vadose zones, and within saturated zone may be related to the different raw material used during the phosphoric acid manufacturing and/or to the stronger weathering of the saturated zone.

Despite the relatively high concentrations observed along the phosphogypsum stack, the mobility of REE, Y and Sc during weathering by rainwater appears to be extremely low. Figure 2B shows the release of these elements under the EN 12457-2 leaching test. The release of REE scarcely accounts for 0.09% of the total enclosed in the phosphogypsum. Although higher total REE concentrations were observed in the vadose zone, there are no appreciable differences in REE release by rainwater along the depth profile. The potential release of Y is even lower; an average value of 0.03% of the total release is recorded along the stack, although as opposed to REE, a higher potential release of Y is observed in the saturated zone (2 times higher than in the vadose zone). A similar trend is observed for Sc, although the maximum release is observed at 4-6 m depth with values of up to 0.66% of the total content. The simulation of the interaction of phosphogypsum with organic matter-rich solutions, analogue to those from salt-marshes, provided slightly higher values of release (Fig. 2C). Around 1.8%, 1.0% and 0.38% of Sc, Y and REE (of average), respectively, were released in the TCLP leaching test. A higher release was observed for Y and REE in the vadose zone, i.e. up to 4.4% and 1.4% of the total, respectively, in the shallowest sample. In the case of Sc, the higher release rate (5.6%) was found at 6 m (Fig. 2C). Thus, the transfer of REE by interaction of organic-rich marshland soils with the stack must be of minor importance. In this sense, Davranche et al. (2012) indicated that organic matter, pH and reducing conditions are the main factors controlling REE behavior in wetland areas. The establishment of reducing conditions acts indirectly through the increase in pH caused by H^+ consumption, which promotes organic matter desorption as colloids from the soil matrix, giving rise to a release of REE. However, these Eh-pH conditions were not achieved in the marsh soil surface in contact with phosphogypsum (Eh of 320 mV and pH 4.1), which could explain such low REE release during the TCLP.

These strikingly low values contrast with the high potential release reported by Macías et al. (2017) for some metals and metalloids (i.e. Al, As, Cd, Cu, Fe, Pb, Ni, Se and Zn) under the same leaching procedures. The differences of mobility observed among these elements may be related to the different waste material within the phosphogypsum stack. In the case of elements such as Zn, Cd or As, significantly released by interaction with water or organic acids, they may be hosted in pore waters or by easily or moderately soluble mineral phases (e.g. sulfate) along the phosphogypsum stack (Macías et al., 2017). However, in the case of REE, Y and Sc, these elements may be hosted by less soluble minerals (e.g. fluoride or phosphate).

3.2 Source of REE, Y and Sc in phosphogypsum

The first question to be answered is whether REE, Y and Sc are contained in pore waters or, conversely, in the mineral assemblage of phosphogypsum. Figure 3A-D shows profiles of element concentrations in pore-water and their contribution in respect to solid phosphogypsum using sample moisture measurements according to Clemente et al. (2008). The concentrations of REE and Y follow an increasing tendency up to a peak at 5 m depth in the saturated zone (163 and 44 µg/L of REE and Y, respectively; Fig. 3A and B) and then decrease down to the bottom. In the case of Sc, the maximum concentration in pore waters is observed at 2.3 m depth (up to 240 µg/L; Fig. 3C). In total, less than 4.5% of Sc and even lower values of REE and Y (below 0.12%) are contained in pore waters. Thus, these elements are chiefly hosted by mineral phases.

Sedimentary phosphate rock is mainly composed of fluorapatite which contains significant concentrations of REE, Y and Sc (Binnemans et al., 2015); thus, the most feasible source of these elements must be unreacted phosphate existing in the phosphogypsum. Another possibility would be the occurrence of secondary minerals during the acid attack of the phosphate rock. In this sense, Köhler et al. (2005) suggested that although REE are readily released during apatite dissolution in the industrial process, they may be also easily precipitated as secondary phosphate phases during the reaction. High phosphate concentrations are found in pore waters, reaching maximum values in the saturated zone (up to 7600 mg/L) and then decreasing down to the bottom of the stack (Fig. 3D). Around 20-30% of total phosphate in the saturated zone is contributed by the phosphoric acid contained in pore waters, whereas the remaining 70-80% must be phosphate minerals enclosed in the solid, which could be subjected to dissolution by pore waters. In this sense, pore waters show undersaturation in respect to fluoroapatite and MREE and HREE phosphates, whereas equilibrium with respect to LREE-PO_4 is observed in the saturated zone (Fig. 3E and F). Thus, these REE-rich phosphates (i.e. fluoroapatite and REE-phosphate), originally present in the phosphogypsum, could be dissolved under weathering conditions and subsequently release REE and Y into pore waters. This is supported by the similar tendency of phosphate, REE and Y in pore waters (Fig. 3A-B and D). Although no phosphate minerals were detected in XRD patterns and SEM images of solid phosphogypsum, the semiquantitative chemical analyses provided by the EDS revealed the ubiquitous presence of P in amorphous phases attached to gypsum surface (Fig. 4A). On the other hand, the low concentration of REE, Y and Sc observed in comparison with those found in solid phosphogypsum could be also due to a mineralogical control of secondary minerals precipitating from pore waters. For example, fluoride has been previously reported as a good REE scavenger (e.g. Bouhlassa and Salamen, 2013). The precipitation of fluoride minerals such as cryolite and fluorite is predicted in the saturated zone according to the geochemical calculations with PHREEQC (Fig. 3E). This latter mineral has been identified in the solid phosphogypsum, forming small mineral spheres attached to the gypsum surface (Fig. 4B). Therefore, it is hypothesized that phosphate minerals may act as sources of REE and Y in phosphogypsum while fluoride minerals may act as sinks, controlling their mobility.

3.3 Transport of REE, Y and Sc within the phosphogypsum stack.

Once dissolved in pore waters from the mineral assemblage, these elements may be released to the environment from the phosphogypsum stack through edge outflows. During the transport of these waters from the stack to the environment, hydrochemical changes may occur due to water-mineral interactions. Table 1 shows the basic statistics of edge outflows collected during the sampling campaigns of June and November. The chemical composition of edge outflows is strongly influenced by the interaction of the pile with estuarine waters (Pérez-López et al., 2016), as evidenced by the high concentrations of Na and Cl (average values ranging from 6.7 to 8.8 g/L for Na and 12.2 to 12.9 g/L for Cl; Table 1). High concentrations of Ca, phosphate, sulfate or fluoride were observed due to mineral dissolution processes along the stack. Median values of 173 µg/L of REE, 77 µg/L of Sc and 35 µg/L of Y were recorded during the sampling performed in June 2014, although maximum concentrations of 673, 243 and 175 µg/L, respectively, were reached for these elements (Table 1). Median values for REE and Y were lower during sampling performed in November 2014 (131 and 33 µg/L, respectively) than those observed in June, which is just the opposite of that observed for Sc whose median value was slightly higher (109 µg/L; Table 1). Despite this fact, the maximum concentrations of these elements were found in November (up to 8621, 5422 and 386 µg/L; Table 1). These concentrations are noticeably similar to those observed for pore waters in the saturated zone.

On the other hand, the solubility of metals is strongly dependent on speciation. In natural waters, trivalent REE and Y are commonly strongly complexed by hard ligands such as fluoride, sulfate, phosphate, carbonate, organic acids and hydroxide (e.g. Wood et al., 1990; Marsac et al. 2011: Davranche et al., 2015). In the case of organic matter complexes, Tang and Johannesson (2003) reported a preferential REE complexation within the pH ranges from 4.8 to 7.9. Due to the acidic conditions found in edge outflows released from the phosphogypsum stacks, ligands such as carbonate, organic matter and hydroxide can be negligible. The REE speciation in acidic waters has been widely studied. Gimeno-Serrano et al. (2000) reported that REE-sulfate complexes and free ionic forms are commonly the dominant species in acidic sulfate solutions while complexes with other active ligands may be important only when their concentrations are unusually high. Such conditions are met in the edge outflows, with average concentrations of PO_4 and Cl of around 11 and 12 g/L, respectively. Lower concentrations were observed for sulfate (average values of 6.3 g/L) and F (0.6 g/L), while the concentration of other ligands such as Br and NO_3 are not significant (average of 67 and 32 mg/L, respectively). Figure 5 shows the speciation across the lanthanide series. As can be seen, REE are mainly complexed by fluoride (∑LnF, 38-81% of total species), followed by phosphate (∑$LnPO_4$, 10-46%), free cations (∑Ln^{3+}, 4-11%) and sulfate (∑$LnSO_4$, 1.0-7.6%).

Complexations by chloride, nitrate and bromide are negligible. These latter complexes do not account for a significant part of dissolved REE even in saline waters and environments polluted by agriculture (Wood, 1990). This author also reported a dominant complexing role of fluoride at high concentrations (above 10^{-4} mol L^{-1}), low total sulfate concentration (below 10^{-4} mol L^{-1}) and acidic pH conditions (2-5). Nevertheless, these conditions differ from those observed in the edge outflows. Sulfate concentrations are two orders of magnitude higher and pH values range from 1 to 3. Johanneson and Lyons (1995) reported significant REE complexation by F in acidic waters with F/SO_4 molar ratios of approximately 0.01 or greater. The acidic waters arising from the phosphogypsum stack have molar ratios noticeably higher, between 0.05 and 4, thus, fluoride may prevail as complexing agent for REE despite being found at lower concentration than other ligands (i.e. PO_4, Cl and SO_4). This fact contradicts the finding of Gimeno Serrano et al. (2000) who reported prevailing REE phosphate complexation with total dissolved phosphate concentrations ranging from 0.1 to 0.01 mol L^{-1}. Total phosphate concentrations observed in edge outflows, average value of 0.15 mol L^{-1}, were even higher than those reported by these authors.

Another striking fact is the change in speciation pattern observed across the lanthanide series (Fig. 5). A progressive increase in fluoride complexation is observed across the series (from 31% for La to 81% for Lu). This fact, previously reported by Gimeno Serrano et al. (2000), is attributed to the steady increase of REE stability constants with increasing atomic numbers (Millero, 1992; Luo and Byrne, 2000). The opposite tendency is observed for phosphate complexes (from 46% for La to 13% for Lu). This trend is also observed for Y, with average values of 78% and 15% for fluoride and phosphate complexes, respectively. As commented before, phosphate and fluoride may control REE speciation in edge outflows emerging from the phosphogypsum stack. However, an additional question arises here; could the occurrence of phosphate and fluoride minerals control REE solubility in these waters, as occurs with the pore waters? Table 2 shows the saturation indices of edge outflows in respect to main fluoride and phosphate minerals as well as other phases (i.e. sulfate and chloride). In the case of phosphate and fluoride, PHREEQC predicts undersaturation in respect to main REE phosphate and fluoride minerals, except those formed by LREE (La to Sm). Although Byrne et al. (1996) affirmed that the precipitation of Y and REE phosphates in natural environments does not result in discrete mineral phases for each element but in major phosphates by coprecipitation, Köhler et al. (2005) reported a relative enrichment in LREE in rhabdophane ((Ce, La, Nd)$PO_4 \cdot H_2O$) during apatite dissolution. In any case, the mineralogical analysis (XRD; Fig. 6) performed in newly-formed precipitates around edge outflows did not reveal the presence of these LREE phosphate minerals. However, the amorphous nature and the low proportion in respect to major phases (e.g. gypsum or halite) of this secondary phosphate may preclude its identification by XRD.

On the other hand, the presence of malladrite (Na_2SiF_6) was identified by XRD in the edge outflows precipitates (Fig. 6). This finding agrees well with the PHREEQC results that predict oversaturation of edge outflows in respect to cryolite, an Al hexafluoride analogue to malladrite. Figure 7 represents the activities of some aqueous species (F^-, SO_4^{2-}, Ca^{2+} and Al^{3+}) in edge outflows and the equilibrium windows of some mineral phases (i.e. fluorite, cryolite, gypsum). As can be noted, waters are strongly oversaturated in respect to fluorite (Fig. 7A). However, in the case of hexafluorides, such as cryolite, samples are slightly oversaturated and aligned over the equilibrium window during both sampling periods (June and November; Fig. 7B), suggesting a theoretical solubility control of F in waters. Then, the precipitation of hexafluorides such as cryolite and malladrite, this latter identified by XRD (Fig. 6), could be responsible for the low mobility of REE in the stack. These results coincide with those obtained from pore waters and reinforce the hypothesis that phosphate minerals may act as sources of REE in the phosphogypsum stack and fluoride minerals as sinks. However, more detailed studies are needed to test this hypothesis. The XRD patterns also revealed the presence of other minerals such as different sulfate (i.e. gypsum and hexahydrite) and halite. Although gypsum seems to be slightly undersaturated, it appears to exist a solubility control in edge outflows; samples are aligned under the equilibrium line of gypsum (Fig. 7C). It is interesting to remark that the weathering of the phosphogypsum stack by estuarine waters is enhanced in relation to rainfalls due to the salt effect. The presence of minerals such as hexahydrite and halite in the edge outflows precipitates (Fig. 6), despite undersaturation of waters predicted by PHREEQC, would be explained by evaporative processes in shallow outflow channels.

3.4 REE fractionation processes during the fertilizer life cycle

Although REE are a group of chemically similar metallic elements, differences in ionic radii, oxidation state or particle-solution interactions may cause fractionation processes in aqueous systems (Bau, 1996). These fractionation processes have been profusely reported in rivers, estuaries or seawater (e.g. Bau et al., 1997; Sholkovitz and Szymczak, 2000; Verplanck et al., 2004; Leybourne and Johannesson, 2008). However, these processes have not been properly addressed in by-products generated during the manufacturing of phosphate fertilizer. Figure 8A displays the NASC-normalized patterns of sedimentary phosphate rocks from Morocco and

Tunisia, phosphogypsum samples and its weathering products (i.e. process waters contained in perimeter channels, pore waters and edge outflows emerging from the stack base). Both phosphate rocks and phosphogypsum stack exhibit similar patterns with a relatively flat pattern and a strong negative Ce anomaly (average Ce/Ce* of 0.36 and 0.38, respectively). This pattern seems to be similar to that observed in edge outflows (average Ce/Ce* of 0.33), although even stronger Ce anomalies are observed in pore waters (average Ce/Ce* of 0.19). However, a different pattern is observed for process waters contained in the perimeter channels, characterized by an upward positive trend of strong enrichment of MREE in relation to LREE, and HREE in relation to MREE, typical of the phosphate fertilizer (Otero et al., 2005).

Figure 8B displays a plot of $(HREE/MREE)_{NASC}$ vs. $(MREE/LREE)_{NASC}$ of phosphate rocks, phosphogypsum samples, process waters and edge outflows. As can be noted, high spatial dispersion in REE fractionation in the phosphogypsum stack seems to occur. Phosphogypsum samples from the saturated zone, process waters, most edge outflows and pore waters (not shown in Fig. 8B) are enriched in MREE in relation to LREE ($(MREE/LREE)_{NASC}$ values of 1.5 to 3.5). However, phosphogypsum from the vadose zone and phosphate rock samples evidence a higher enrichment in LREE ($(MREE/LREE)_{NASC}$ values of 0.72 to 1.47) than the latter group. This fractionation process could be related to the dissolution of secondary LREE phosphates previously formed during apatite dissolution in the industrial process. In this sense, Köhler et al. (2005) reported an enrichment in LREE (Ce to Eu) in secondary rhabdophane ($(Ce, La, Nd)PO_4{\cdot}H_2O$) precipitated from apatite dissolution. Both pore waters and edge outflows are found close to equilibrium in respect to LREE phosphate. Thus, the higher residence time of waters in the saturated zone may enhance dissolution processes of these secondary phosphates giving rise to a depletion of LREE in comparison with the vadose zone, which would preserve the original REE signature of phosphate rocks. This fractionation process between vadose and saturated zone, nevertheless, is not observed in another phosphogypsum stack (Fig. 8B) reported by Bisone et al. (2017). Samples from the saturated zone also evidenced a similar enrichment in HREE in relation to MREE than process waters. This enrichment in HREE could be related to bacterial activity. For instance, Takahashi et al. (2005) reported enhance adsorption processes of REE onto bacterial cell walls which caused an enrichment in HREE. However, no biological samples were collected in this study and therefore this hypothesis cannot be tested.

On the other hand, an enrichment of MREE in relation to HREE of edge outflows with respect to process waters is observed ($(HREE/MREE)_{NASC}$ values of 1.7 to 3.4). This fact could be related to the higher influence of the Tinto River estuarine waters on the leaching process of phosphogypsum stacks. As reported by some authors (Elbaz-Poulichet and Dupuy, 1999; Pérez-López et al., 2015) the estuarine waters are characterized by REE patterns with an up-convex curvature in the MREE segment (inherited from the acid mine drainage (AMD) pollution of the Tinto River), which would result in an enrichment of MREE in respect to both LREE and HREE. This could be also the cause of the relative enrichment in LREE with respect to MREE in edge outflows collected in November. Rainfalls collected in November cause the recharge of the saturated zone with freshwaters while in June, characterized by absence of rainfalls, estuarine waters may constitute the main recharge of the saturated zone, causing an enrichment in MREE in relation to LREE. Thus, the prevailing weathering agent could also alter the REE signature in edge outflows.

3.5 Environmental and economic implications

The weathering of the phosphogypsum stack by different factors (i.e. rainfall and estuarine waters) may have serious environmental consequences. Considering the average flow values released from the phosphogypsum stack (around 335000 m^3/yr; Pérez-López et al., 2016) and the average concentration of REE, Sc and Y in edge outflows, around 104 kg/yr of REE and 40 kg/yr of Sc and Y are released from the stack. Although these values are low compared to other pollutants (e.g. As, Cd, Cu, U; Pérez-López et al., 2016), these elements may cause significant environmental impacts on living organisms. This is especially relevant considering the notable contribution of REE, Sc and Y to the estuary by AMD from the Tinto River, which may aggravate the exposure of living organisms to REE within the estuary. Currently, a restoration plan is under evaluation. Planned restoration measures involve removal of ponded process waters and the stack cover with topsoil. However, as reported previously by Pérez-López et al. (2016), these restoration actions would not involve the cessation of the leaching from the stack. For this reason, the growing social and political pressure urges to explore more sustainable solutions to the management of these wastes. Recently, Cánovas et al. (2017) suggested the possibility of considering the phosphogypsum stack as a source of critical raw materials (e.g. REE, Sc, Y, Ga, B, Ge or V). This study points out to phosphate as the main carrier of these elements and to fluoride as REE scavengers in the phosphogypsum stack. The recovery of these elements must rely on the development of optimized schemes to extract them selectively from these minor minerals enclosed in the gypsum. Thus, the information obtained in this study might be useful in the recovery process of these elements from phosphogypsum.

4. Conclusions

This study describes the mobility of REE under weathering conditions in a phosphogypsum stack in SW Spain and quantifies the REE fluxes from the stack to the estuary. The singularity of this phosphogypsum stack relies on the fact that anomalously metal-rich wastes were deposited over the marshland without any type of isolation and within the tidal prism of the estuary, giving rise to strong weathering processes by rainwater during rainy episodes and by seawater during tidal cycles.

Phosphogypsum samples were collected to simulate these weathering processes by leaching tests and the results were subsequently compared to those obtained from edge outflows emerging from the stack. Despite the high concentrations of REE, Y and Sc observed in phosphogypsum, which can be potentially released under weathering by natural factors, their mobility during the leaching tests was very low; less than 0.66% and 1.8% (average) of the total content of these elements were released during the simulation of interaction with rainwater and with organic matter-rich solutions, analogue to those from salt-marshes.

Concentrations of REE, Y and Sc in edge outflows (up to 8621, 5422 and 386 µg/L, respectively) were noticeably similar to that observed in pore waters. Phosphate and fluoride may control REE speciation in edge outflows emerging from the phosphogypsum stack, and the formation of mineral phases may have a critical role in the mobility of these elements. Geochemical and mineralogical evidences suggest that phosphate minerals may act as sources of REE and Y in the phosphogypsum stack while fluoride minerals may act as sinks, controlling their mobility.

Despite the low mobility of REE, Sc and Y in the phosphogypsum stack, around 104 kg/yr of REE, and 40 kg/yr of Sc and Y are released from the stack to the estuary, which may imply an environmental concern. The significant concentration of REE, Y and Sc found in this huge phosphogypsum stack could be recovered based on selective extractive methods to dissolve the minor phases scavenging these elements. Other unresolved issues such as the influence of bacterial activity on REE fractionation processes along the phosphogypsum stack must be nevertheless addressed in the near future.

ACKNOWLEDGEMENTS

This work was supported by the Government of Andalusia through the research project "Phosphogypsum: from the environmental assessment as a waste to its revaluation as a resource (P12-RNM-2260)" and the Spanish Ministry of Economy and Competitiveness through the research project SCYRE (CGL2016-78783-C2-1-R). Authors also want to especially thank the funding support for the Experts Committee on "The environmental diagnosis and the proposal of restoration measures for the phosphogypsum stacks of Huelva", appointed by the City Hall of Huelva. The authors want to thank the funding support of the COST Action TD 1407 to assist to the Workshop on Technology Critical Elements in Rehovot (Israel). The comments and helpful criticisms of two anonymous reviewer and the support of the Editor have considerably improved the original manuscript and are also gratefully acknowledged.

REFERENCES

Al-Abed, S.R., Hageman, P.L., Jegadeesan, G., Madavan, N., J., Allen, D., (2006). Comparative evaluation of short-term leach tests for heavy metal release from mineral processing waste, Sci. Total Environ. 364,14-23. doi:10.1016/j.scitotenv.2005.10.021.

Al-Masri, M.S., Amin,Y., Ibrahim,S., Al-Bich, F. (2004). Distribution of some trace metals in Syrian phosphogypsum. Appl. Geochem. 19, 747–753.http://dx.doi.org/10.1016/j.apgeochem.2003.09.014.

Ayora, C., Macias, F., Torres, E., Lozano, A., Carrero, S., Nieto, J.M., Perez-Lopez, R., Fernandez-Martinez, A., Castillo-Michel, H., (2016). Recovery of rare earth elements and yttrium from passive-remediation systems of acid mine drainage. Environ. Sci. Technol. 50, 8255–8262. doi: 10.1021/acs.est.6b02084.

Bau, M. (1996). Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. Contrib. Mineral. Petrol. 123, 323-333.

Bau, M., Möller, P., Dulski, P. (1997). Yttrium and lanthanides in eastern Mediterranean seawater and their fractionation during redox cycling. Mar. Chem. 56 (1−2), 123−131.

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Yang, Y. Walton, A., Buchert, M. (2013). Recycling of rare earths: a critical review. J Clean Prod 51, 1-22. http://dx.doi.org/10.1016/j.jclepro.2012.12.037.

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Pontikes, Y. (2015). Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review. J Clean Prod 99, 17-38. http://dx.doi.org/10.1016/j.jclepro.2015.02.089.

Bisone, S., Gautier, M., Chatain, V., Blanc, D. (2017). Spatial distribution and leaching behavior of pollutants from phosphogypsum stocked in a gypstack: Geochemical characterization and modeling. J Environ Manage 193, 567-575. http://doi.org/10.1016/j.jenvman.2017.02.055

Bolívar, J.P., Garcia-Tenorio, R., Mas, J.L., Vaca, F., 2002. Radioactive impact in sediments from an estuarine system affected by industrial waste releases. Environ. Int. 27, 639–645. http://dx.doi.org/10.1016/S0160-4120(01)00123-4.

Bouhlassa, S., Salhamen, F. (2013). The effect of fluoride and silicate ions on the coprecipitation of gadolinium with calcium in phosphoric and sulpho-phosphoric media. Radiochim. Acta 101, 175–183. doi: 10.1524/ract.2013.2011.

Byrne, R.H., Liu, X., Schijf, J., (1996). The influence of phosphate co-precipitation on rare earth distributions in natural waters. Geochim. Cosmochim. Acta 60, 3341–3346.

Cánovas, C.R., Pérez-López, R., Macías, F., Chapron, S., Nieto, J.M, Pellet-Rostaing, S. (2017). Exploration of fertilizer industry wastes as potential source of critical raw materials. J Clean Prod 143, 497-505. http://dx.doi.org/10.1016/j.jclepro.2016.12.083.

Chakhmouradian, A.R., Wall, F. (2012). Rare Earth Elements: minerals, mines, magnets (and more). Elements 8, 333−340.doi: 10.2113/gselements.8.5.333.

Clemente, R., Dickinson, N.M., Lepp, N.W. (2008). Mobility of metals and metalloids in a multi-element contaminated soil 20 years after cessation of the pollution source activity. Environ. Pollut. 155, 254–261. http://dx.doi.org/10.1016/j.envpol.2007.11.024

Davranche, M., Gruau, G., Dia, A., Marsac, R., Pédrot, M., Pourret, O. (2015). Biogeochemical Factors Affecting Rare Earth Element Distribution in Shallow Wetland Groundwater. Aquat Geochem 21, 197–215. DOI 10.1007/s10498-014-9247-6.

de Andrade Lima, L.R.P., Bernardez, L.A., Barbosa, L.A.D., (2008). Characterization and treatment of artisanal gold mine stacks. J. Hazard. Mater. 150,747-753. http://dx.doi.org/10.1016/j.jhazmat.2007.05.028.

Elbaz-Poulichet, F., Dupuy, C., (1999). Behaviors of rare earth elements at the freshwater-seawater interface of two acid mine rivers: the Tinto and Odiel (Andalucia, Spain). Appl. Geochem. 14, 1063-1072.

El-Zrelli, R., Courjault-Radé, P., Rabaoui, L., Castet, S., Michel, S., Bejaoui, N., (2016). Heavy metal contamination and ecological risk assessment in the surface sediments of the coastal area surrounding the industrial complex of Gabes city, Gulf of Gabes. SE Tunisia. Mar Pollut Bull http://dx.doi.org/10.1016/j.marpolbul.2015.10.047.

Emsbo, P., McLaughlin, P.I, Breit, G.N, du Bray, E.A, Koenig, A.E (2015). Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis? Gondwana Research 27, 776–785. http://dx.doi.org/10.1016/j.gr.2014.10.008.

EU (2002). EN 12457-2, Characterization of Waste, Compliance Test for Leaching of Granular Wastes Materials and Sludges, Part 2: One Stage Batch Test at a Liquid to Solid Ratio of 10 l kg−1 for Materials with Particle Size Below 4 mm (without or with Size Reduction), European Committee of Standardization, CEN/TC 292,12/02/2002 p. 28.

Gimeno Serrano, M.J., Auqué, L.F., Nordstrom, D.K. (2000). REE speciation in low-temperature acidic waters and the competitive effects of aluminum. Chem Geol 165, 167–180.

Gromet, L.P., Dymek, R.F., Haskin, L.A., Korotev, R.L., 1984. The "North American shale composite": its compilation, major and trace element characteristics. Geochim. Cosmochim. Acta 48, 2469-2482.

Hatch, G.P. (2012). Dynamics in the Global Market for Rare Earths. Elements 8, 341. doi:10.2113/gselements.8.5.341

Johannesson, K.H., Lyons, W.B. (1995). Rare earth element geochemistry of Colour Lake, an acidic freshwater lake on Axel Heiberg Island, Northwest Territories, Canada. Chem. Geol. 119, 209-223.

Köhler, S.J., Harouiya, N., Chaïrat, C., Oelkers, E.H. (2005). Experimental studies of REE fractionation during water–mineral interactions: REE release rates during apatite dissolution from pH 2.8 to 9.2. Chem Geol 222, 168-182. doi:10.1016/j.chemgeo.2005.07.011.

Leybourne, M.I., Johannesson, K.H. (2008). Rare earth elements (REE) and yttrium in stream waters, stream sediments, and Fe–Mnoxyhydroxides: fractionation, speciation, and controls over REE+Y patterns in the surface environment. Geochim. Cosmochim. Acta, 72, 5962–5983. doi:10.1016/j.gca.2008.09.022.

Liu, X., Byrne, R.H. (1997). Rare earth and yttrium phosphate solubilities in aqueous solution. Geochim. Cosmochim. Acta 61, 1625–1633.

Lottermoser, B.G., (2010). Mine wastes: Characterization, treatment, environmental impacts. Springer Berlin Heidelberg. Second Edition, 1-301 p.

Luther, S.M., Dudas, M.J., Rutherford, P.M. (1993). Radioactivity and chemical characteristics of Alberta phosphogypsum. Water Air Soil Poll. 69, 277–290.

Luo, Y., Byrne, R.H. (2000). The ionic strength dependence of rare earth and yttrium fluoride complexation at 25°C. J. Sol. Chem. 29, 1089–1099. doi: 10.1023/A:1005186932126.

Macías, F., Caraballo, M.A., Nieto, J.M. (2012). Environmental assessment and management of metal-rich wastes generated in acid mine drainage passive remediation systems, J. Hazard. Mater. 229-230, 107-114. http://dx.doi.org/10.1016/j.jhazmat.2012.05.080.

Macías, F., Cánovas, C.R., Cruz-Hernández, P., Carrero, S., Asta, M.P., Nieto, J.M., Pérez-López, R. (2017). An anomalous metal-rich phosphogypsum: Characterization and classification according to international regulations. J. Hazard. Mater. 331, 99-108. http://dx.doi.org/10.1016/j.jhazmat.2017.02.015.

Marsac, R., Davranche, M., Gruau, G., Bouhnik-Le Coz, M., Dia, A. (2011). An improved description of the interactions between rare earth elements and humic acids by modelling. Geochim Cosmochim Acta 75, 5625–5637. https://doi.org/10.1016/j.gca.2011.07.009.

Migaszewski, Z.M, Galuszka, A. (2015). The Characteristics, Occurrence, and Geochemical Behavior of Rare Earth Elements in the Environment: A Review. Crit. Rev. Env. Sci. Tec. 45, 429–471. doi: 10.1080/10643389.2013.866622.

Millero, F.J. (1992). Stability constants for the formation of rare earth inorganic complexes as a function of ionic strength. Geochim. Cosmochim. Acta 56, 3123–3132.

Nordstrom, D.K., Wilde, F.D., (1998). Reduction–oxidation potential (electrode method). National Field Manual for the Collection of Water Quality Data, Book 9, Chapter 6.5. U.S. Geological Survey Techniques of Water-Resources Investigations, U.S. Geological Survey, Reston, VA (20 pp.).

Oral, R., Bustamante, P., Warnau, M., D'Ambra, A., Guida, M., Pagano, G., (2010). Cytogenetic and developmental toxicity of cerium and lanthanum to sea urchin embryos. Chemosphere 81,194–198. http://dx.doi.org/10.1016/j.chemosphere.2010.06.057

Otero, N., Vitòria, L., Soler, A., Canals, A., (2005). Fertiliser characterisation: major, trace and rare earth elements. Appl. Geochem. 20, 1473–1488. doi:10.1016/j.apgeochem.2005.04.002

Pagano, G., Guida, M., Tommasi, F., Oral, R. (2015). Health effects and toxicity mechanisms of rare earth elements - Knowledge gaps and research prospects. Ecotoxicol. Environ. Saf. 115C, 40-48.http://dx.doi.org/10.1016/j.ecoenv.2015.01.030.

Parkhurst, D.L., Appelo, C.A.J., (2005). PHREEQC-2 Version 2.12: A Hydrochemical Transport Model. http://wwwbrr.cr.usgs.

Parreira, A.B., Kobayashi Jr., A.R.K., Silvestre, O.B., (2003). Influence of Portland cement type on unconfined compressive strength and linear expansion of cement-stabilized phosphogypsum, J. Environ. Eng. 129, 956–960. http://dx.doi.org/10.1061/(ASCE)0733-9372(2003)129:10(956).

Pérez-López, R., Castillo, J., Sarmiento, A.M., Nieto, J.M., (2011). Assessment of phosphogypsum impact on the salt-marshes of the Tinto river (SW Spain): role of natural attenuation processes. Mar. Pollut. Bull. 62, 2787–2796. https://doi.org/10.1016/j.marpolbul.2011.09.008.

Pérez-López, R. Nieto, J.M., de la Rosa, J.D., Bolívar, J.P. (2015). Environmental tracers for elucidating the weathering process in a phosphogypsum disposal site: implications for restoration, J. Hydrol. 529, 1313-1323. http://dx.doi.org/10.1016/j.jhydrol.2015.08.056.

Pérez-López, R., Macías, F., Cánovas, C.R., Sarmiento, A.M., Pérez-Moreno, S.M., (2016). Pollutant flows from a phosphogypsum disposal area to an estuarine environment: An insight from geochemical signatures, Sci. Total Environ. 553, 42-51. http://dx.doi.org/10.1016/j.scitotenv.2016.02.070.

Pérez-López, R., Álvarez-Valero, A., Nieto, J.M., (2007). Changes in mobility of toxic elements during the production of phosphoric acid in the fertilizer industry of Huelva (SW Spain) and environmental impact of phosphogypsum wastes. J. Hazard. Mater. 148, 745–750. http://dx.doi.org/10.1016/j.jhazmat.2007.06.068.

Rutherford, P.M., Dudas, M.J., Samek, R.A. (1994). Environmental impacts of phosphogypsum. Sci. Total Environ. 149, 1–38.

Sholkovitz, E.R., Szymczak, R. (2000). The estuarine chemistry of rare earth elements: comparison of the Amazon, Fly, Sepik and the Gulf of Papua systems. Earth Planet. Sci. Lett. 179, 299–309. http://dx.doi.org/10.1016/S0012-821X(00)00112-6.

Stolpe, B., Guo, L., Shiller, A.M. (2013). Binding and transport of rare earth elements by organic and iron-rich nanocolloids in Alaskan rivers, as revealed by field-flow fractionation and ICP-MS. Geochim. Cosmochim. Acta 106, 446–462. http://dx.doi.org/10.1016/j.gca.2012.12.033.

Takahashi, Y., Châtellier, X., Hattori, K.H., Kato, K., Fortin, D. (2005). Adsorption of rare earth elements onto bacterial cell walls and its implication for REE sorption onto natural microbial mats. Chem Geol 219, 53– 67. doi:10.1016/j.chemgeo.2005.02.009.

Tang J., Johannesson K.H (2003). Speciation of rare earth elements in natural terrestrial waters: assessing the role of dissolved organic matter from the modeling approach. Geochim Cosmochim Acta 67, 2321–2339. doi:10.1016/S0016-7037(02)01413-8.

Tayibi, H., Choura, M., López, F.A., Alguacil, F.J., López-Delgado, A., (2009). Environmental impact and management of phosphogypsum. J. Environ. Manag. 90, 2377–2386. doi:10.1016/j.jenvman.2009.03.007.

Taylor, S.R., McLennan, S.M. (1985). The Continental Crust: Its Composition and Evolution. Blackwell Scientific Publications, Oxford, U.K.

USEPA (1992). TCLP, Method 1311, Rev 0. In SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, US Environmental Protection Agency, Washington, DC, Office of Solid Waste, 1992.

USGS (2016). Mineral Commodity Summaries (2016). U.S. Geological Survey, 2016, Mineral commodity summaries 2016: U.S. Geological Survey, 202 p., http://dx.doi.org/10.3133/70140094.

Vemic, M., Bordas, F., Guibaud, G., Joussein, E., Labanowski, J., Lens, P.N.L., van Hullebusch, E.D. (2015). Mineralogy and metals speciation in Mo rich mineral sludges generated at a metal recycling plant. Waste Manage. 38, 303-311.http://dx.doi.org/10.1016/j.wasman.2014.12.021.

Verplanck, P.L., Nordstrom, D.K., Taylor, H.E., Kimball, B.A. (2004). Rare earth element partitioning between hydrous ferric oxides and acid mine water during iron oxidation. Appl. Geochem. 19, 1339–1354.doi:10.1016/j.apgeochem.2004.01.016.

Wood, S.A. (1990). The aqueous geochemistry of the rare-earth elements and yttrium: 1. Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. Chem. Geol. 82, 159–186.

Worrall, F., Pearson, D.G. (2001). Water-rock interaction in an acidic mine discharge as indicated by rare earth element patterns. Geochim Cosmochim Acta 65, 3027–3040. https://doi.org/10.1016/S0016-7037(01)00662-7.

FIGURES

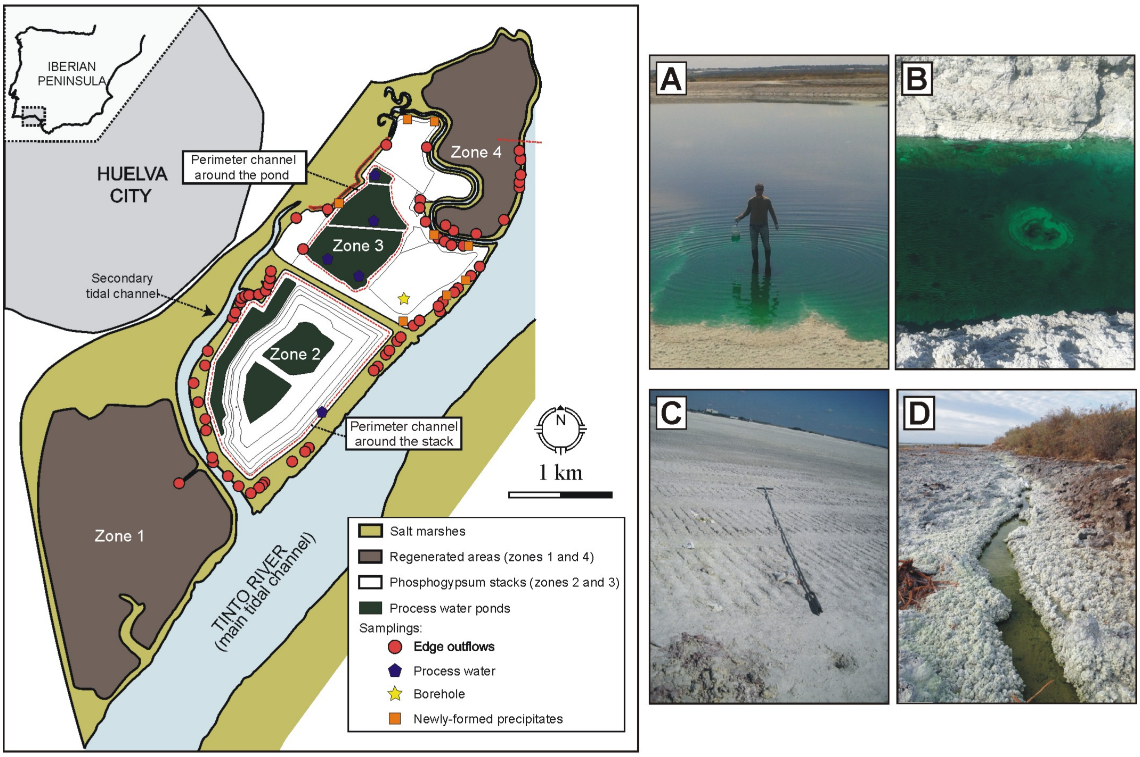

Figure 1. Location map of the Huelva phosphogypsum stack (SW Spain), showing the sampling points and images of process waters contained in ponds (A), perimeter channels (B), solid phosphogypsum (C) and edge outflows (D).

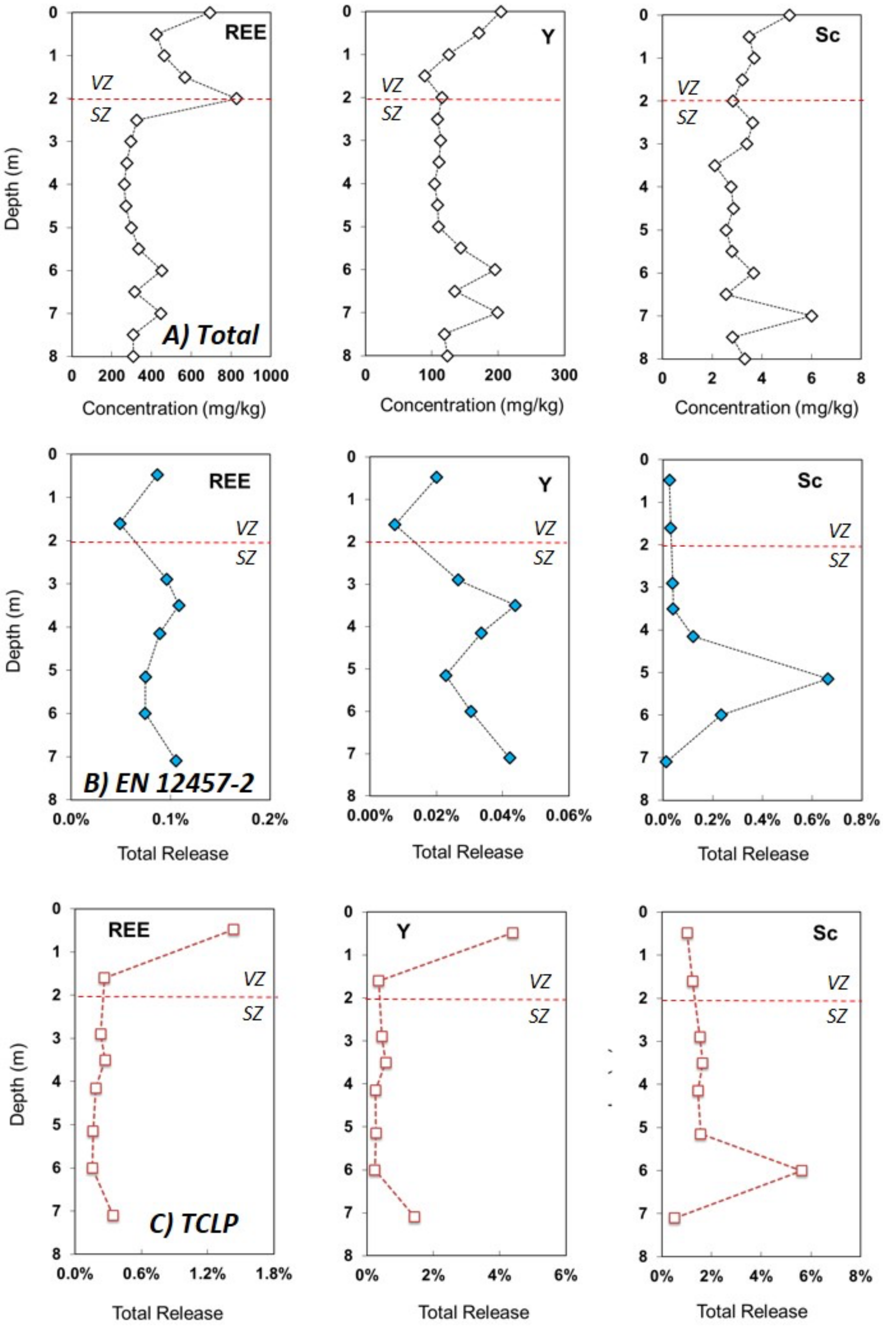

Figure 2. Rare earth elements (REE), Y and Sc concentrations (expressed as mg/kg) in the stack and total release (%) during TCLP and EN-12457 leaching tests.

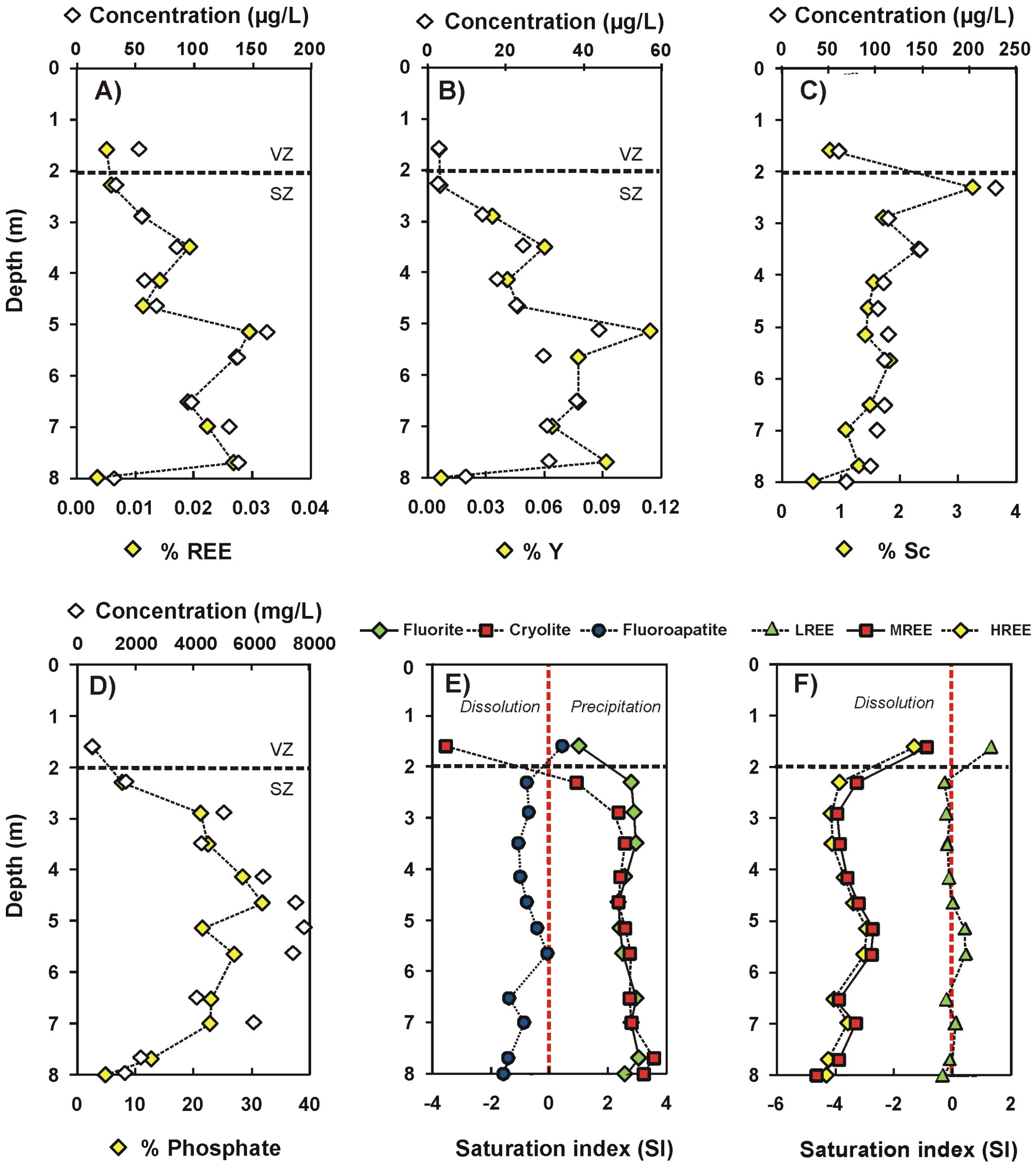

Figure 3. A-D) Plots of concentration of REE, Y, Sc and phosphate in pore waters and contribution to total content. E-F) Saturation indices of main fluoride and phosphate minerals. For the sake of simplicity LREE, MREE and HREE phosphate minerals in F) were calculated from La, Tb and Lu.

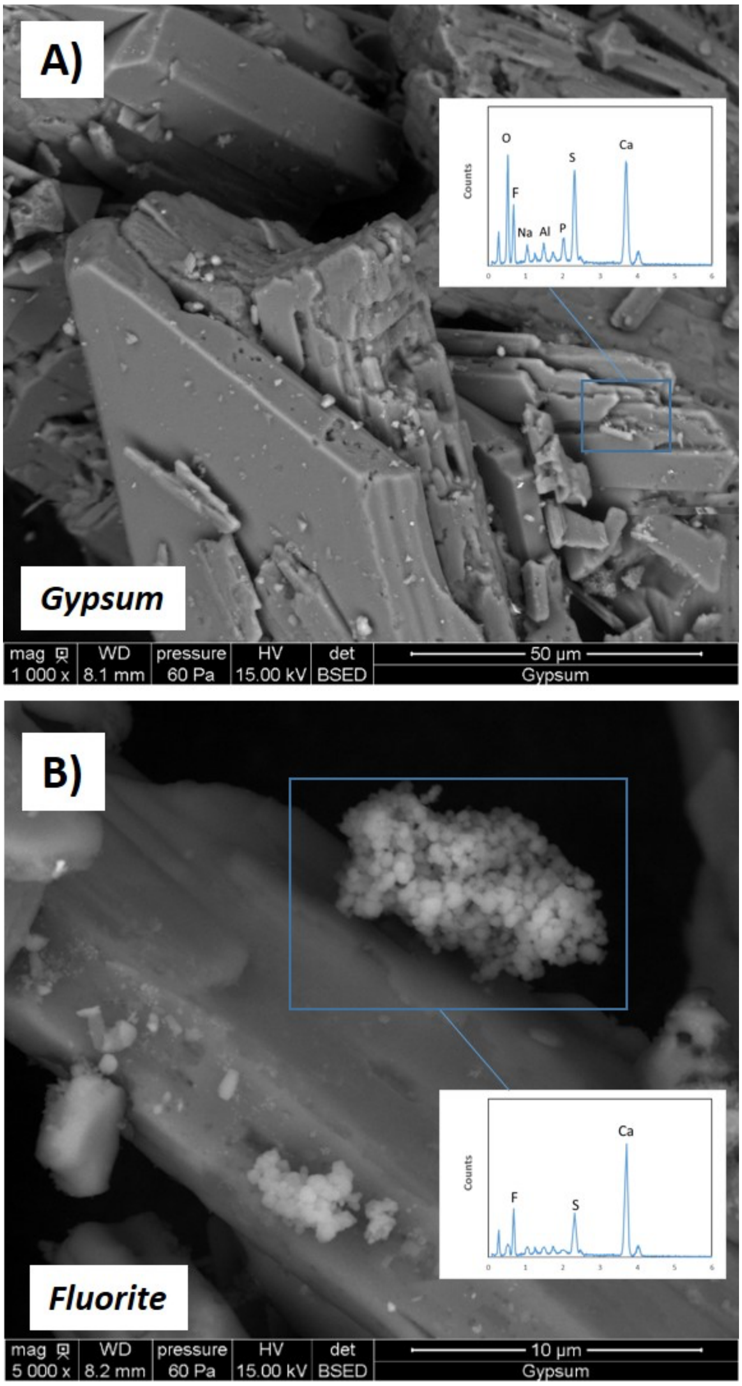

Figure 4. SEM images of gypsum (A) and fluorite (B) attached to the mineral surface

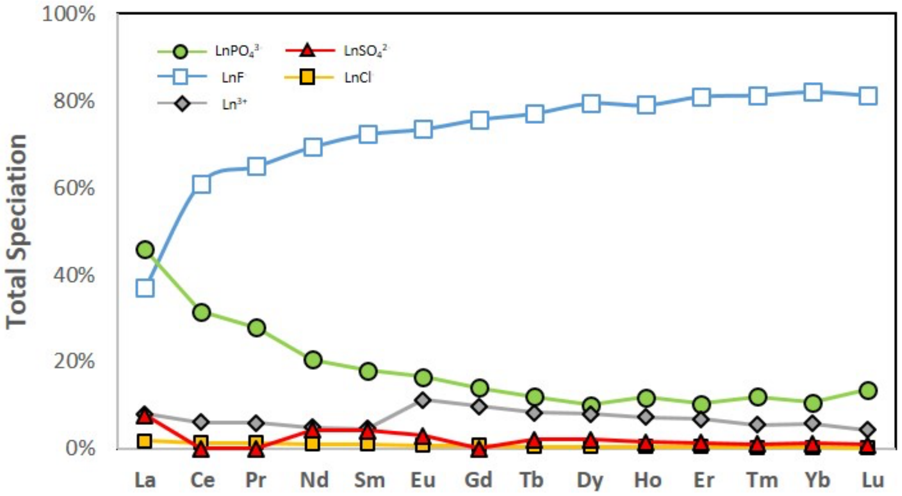

Figure 5. REE speciation across the lanthanide series in edge outflows collected in the Huelva Phosphogyspum stack. Ln; lanthanides.

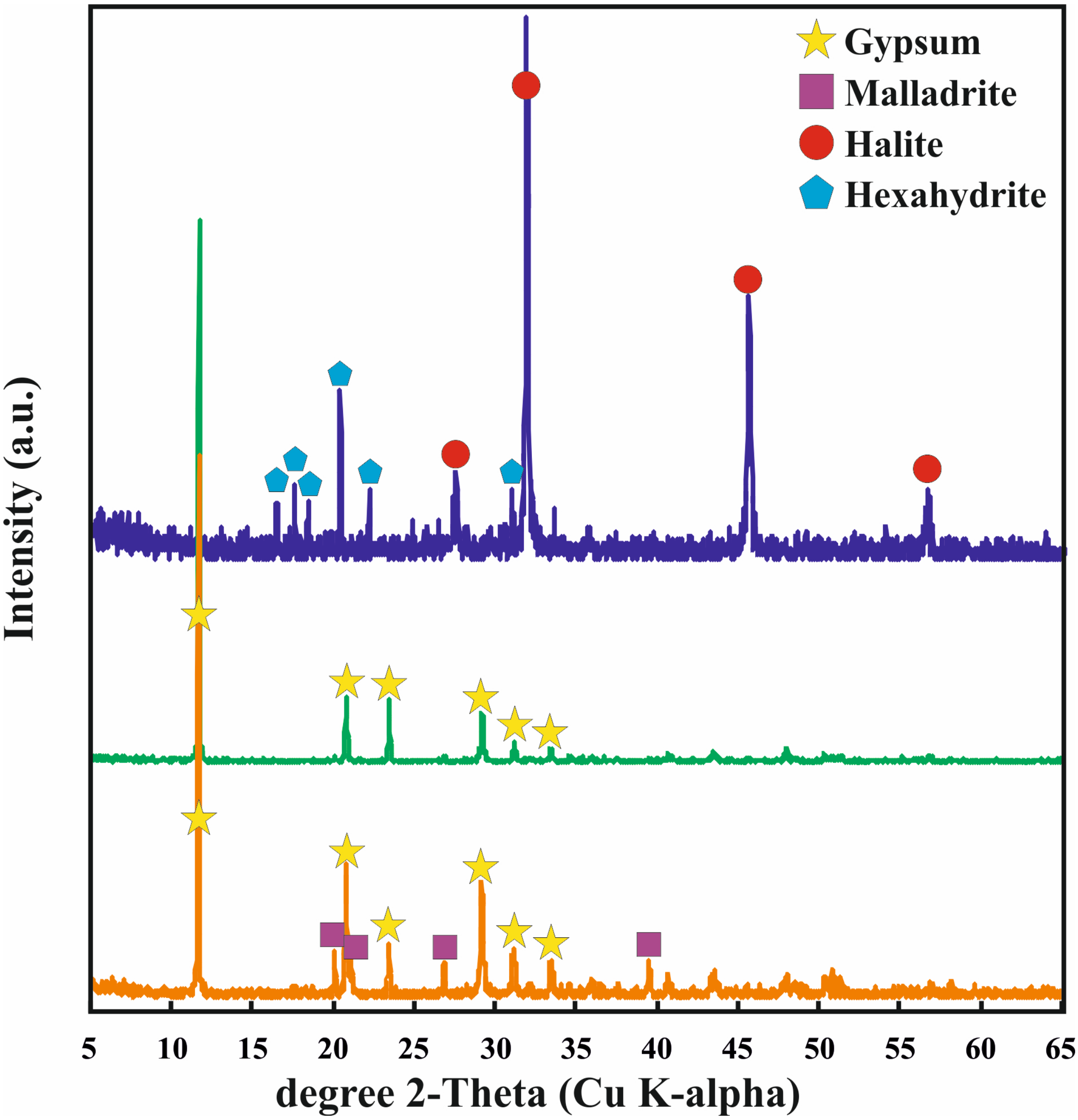

Figure 6. Selected XRD patterns of newly-formed precipitates collected in edge outflows,

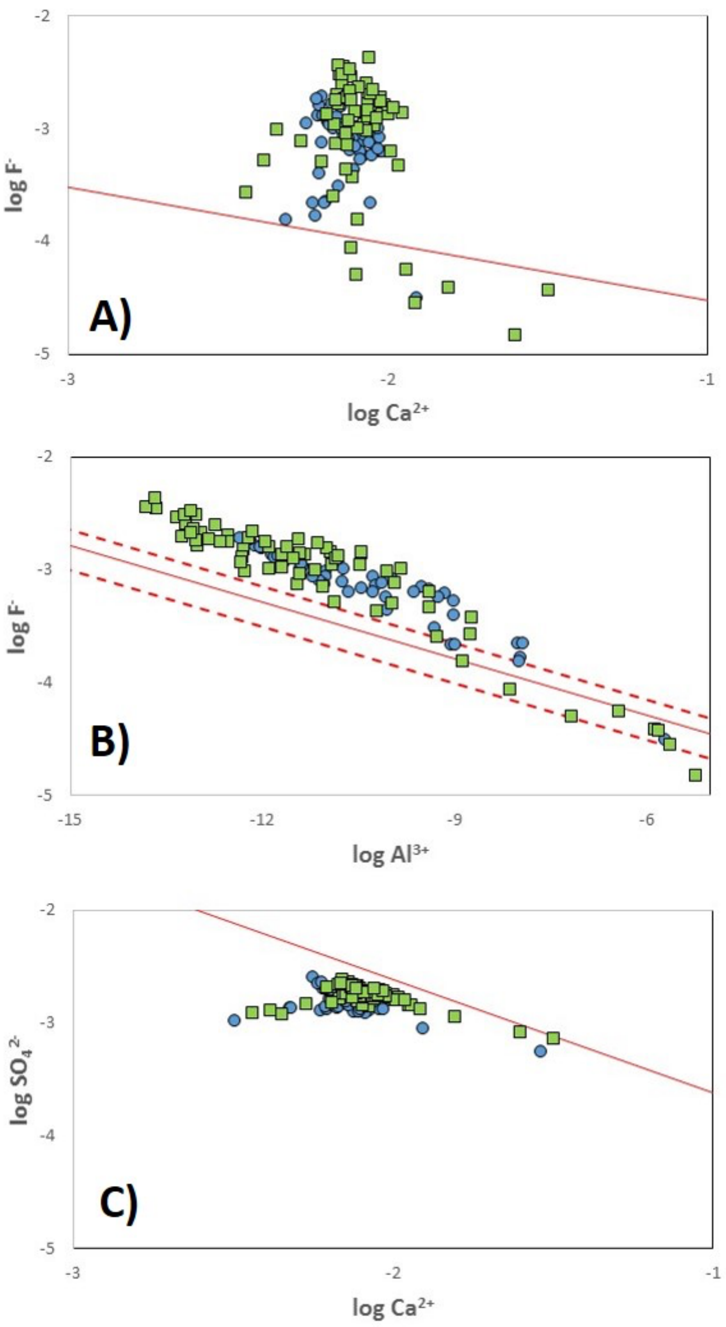

Figure 7. Activities (log scaled) of some aqueous species (F-, SO_4^{2-}, Ca^{2+} and Al^{3+}) in edge outflows and the equilibrium windows of some mineral phases (A and B, malladrite; C. fluorite and D. gypsum). Note: blue circles: June samples; green squares: November samples.

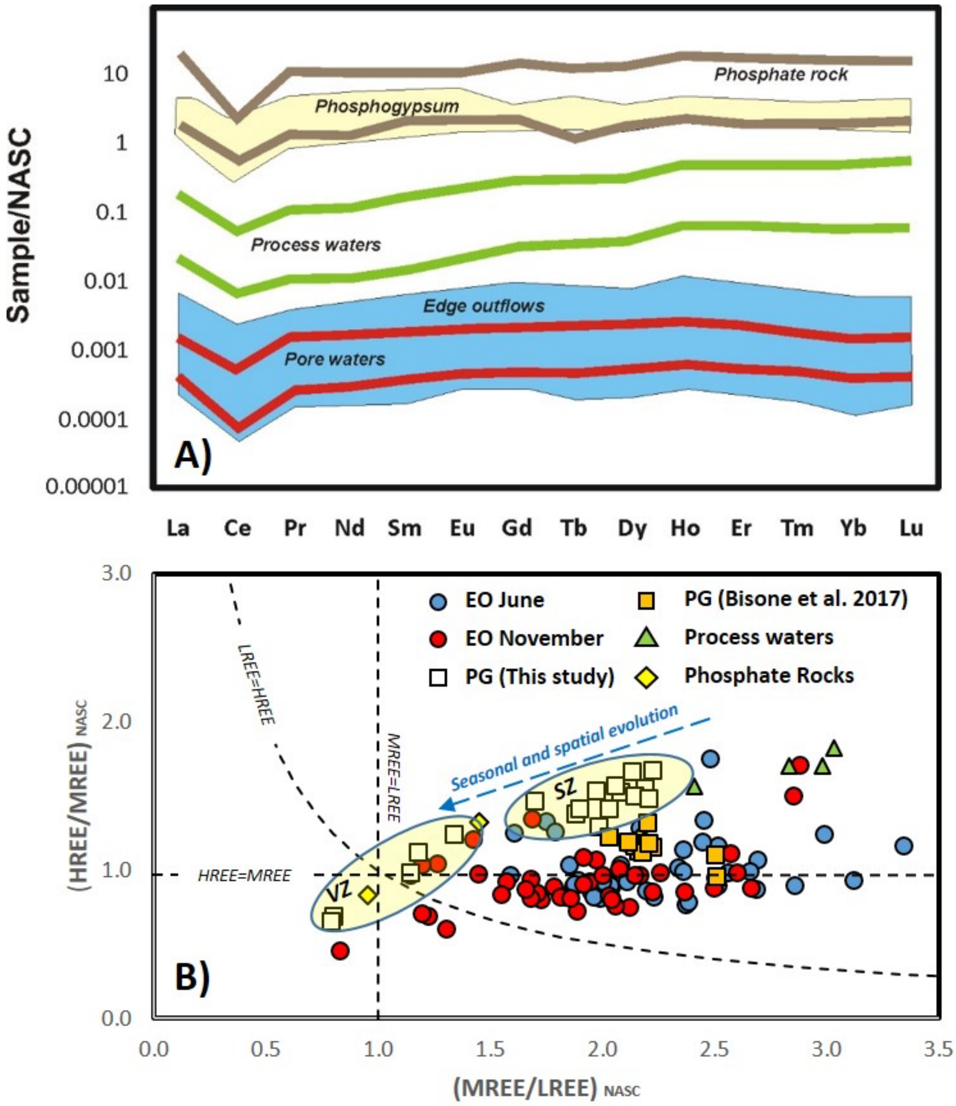

Figure 8. A) NASC-normalized patterns for edge outflows, pore waters and process waters contained in perimeter channels, phosphogypsum stacks and phosphate rocks (from Emsbo et al., 2015); B) Plots of $(HREE/MREE)_{NASC}$ vs. $(MREE/LREE)_{NASC}$ ratios of edge outflows, process waters and phosphogypsum samples reported in this study and in Bisone et al.(2017). EO: edge outflows; PG: phosphogypsum.

TABLES

Parameter	pH	pE	NH_4	F^-	Cl^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Al	Ca	K	Mg	Na	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	REE	Y	Sc
			Main anions (mg/L)							*Main elements (mg/L)*					*Rare Earth Elements plus Y and Sc (μg/L)*																
June 2014 (n= 53)																															
Minimum	1.6	7.5	20	77	4530	24	7.6	724	3677	6.4	527	173	601	3440	6.3	3.6	1.2	5.9	1.0	0.30	1.4	0.18	1.2	0.27	0.70	0.10	0.36	0.10	23	3.7	15
Maximum	3.2	10.2	555	1446	38351	135	200	32654	12113	321	1512	646	2036	14369	200	157	30	140	32	18	50	18	44	19	30	18	24	18	673	175	243
Mean	1.9	8.2	212	631	12869	67	33	11530	5884	59	1174	330	971	6749	58	37	10	43	10	3.7	14	3	13	4	9	2	6	2	217	42	88
Median	1.9	8.1	119	537	11076	61	21	5621	5424	15	1142	321	866	6403	40	25	8.3	31	8.1	2.4	11	2.1	11	2.7	6.9	1.4	4.6	1.2	173	35	77
Percentil 25	1.7	7.9	58	397	7430	51	12	3043	5034	8.1	1034	256	765	4681	23	11	4.3	18	3.7	1.2	5.1	1.0	4.3	1.4	2.9	0.65	1.8	0.58	84	15	41.1
Percentil 75	2.1	8.4	419	830	15102	79	48	20960	6428	80	1347	360	1086	7807	94	54	17	71	17	4.9	23	4.1	21	5.8	15	2.3	9.3	2.2	369	59	118
November 2014 (n=68)																															
Minimum	1.8	6.5	5.2	33	4308	3.4	7.5	1240	4431	0.93	595	190	622	4558	3.8	1.5	0.30	2.0	0.25	0.10	0.10	0.10	0.34	0.10	0.39	0.10	0.10	0.10	15	3.6	36
Maximum	3.1	9.7	928	1651	25441	139	129	49571	10814	456	4541	902	3042	17607	2200	1569	343	1513	389	114	164	105	723	188	617	85	522	89	8621	5422	386
Mean	2.2	8.0	217	602	12195	59	31	10694	6777	54	1401	391	1271	8774	117	76	17	76	18	5.0	9.4	4.3	29	7.2	23	3.1	18	3.2	406	186	140
Median	2.2	7.9	114	551	11590	50	22	4949	6609	12	1369	377	1135	8309	45	23	6.3	28	5.0	1.2	3.0	1.0	6.4	1.4	4.7	1.0	2.5	1.0	131	33	109
Percentil 25	2.0	7.7	57	297	8864	40	12	2912	6095	3.2	1207	328	958	6735	25	11	3.7	18	3.1	0.73	1.4	0.50	3.6	0.65	2.3	0.35	1.0	0.28	75	17	87
Percentil 75	2.3	8.2	399	788	15791	70	44	17590	7361	68	1490	442	1482	10688	91	51	14	63	14	3.8	10	2.8	17	3.9	11	1.2	7.1	1.0	284	67	167

Table 1. Basic statistics of hydrochemical composition of edge outflows collected from the Huelva phosphogypsum stack in June and November 2014.

	Fluoride					**Phosphate**				**Other minerals**		
	Fluorite	Cryolite	REE-fluoride			Fluoroapatite	REE-phosphate			Gypsum	Hexahydrite	Halite
	CaF_2	Na_3AlF_6	$LREE\text{-}F_3{:}5H_2O$	$MREE\text{-}F_3{:}5H_2O$	$HREE\text{-}F_3{:}5H_2O$	$Ca_5(PO_4)_3F$	$LREE\text{-}PO_4$	$MREE\text{-}PO_4$	$HREE\text{-}PO_4$	$CaSO_4{:}2H_2O$	$MgSO_4{:}6H_2O$	$NaCl$
Minimum	-0.85	-1.76	-1.59	-5.13	-5.95	-6.97	-1.15	-4.30	-4.19	-0.96	-3.32	-3.61
Maximum	2.42	4.27	1.37	-1.15	-3.29	2.02	2.03	-0.23	0.07	-0.30	-2.66	-2.05
Mean	1.61	2.85	0.42	-3.56	-4.60	-3.83	0.31	-2.70	-2.66	-0.44	-3.11	-2.96
Median	1.80	3.21	0.62	-3.43	-4.54	-3.79	0.25	-2.58	-2.90	-0.43	-3.13	-2.98
Percentil 25	1.55	2.73	0.31	-4.35	-5.07	-4.52	-0.21	-3.51	-3.40	-0.48	-3.19	-3.28
Percentil 75	2.00	3.63	0.85	-3.04	-4.14	-3.41	0.77	-2.20	-2.46	-0.37	-3.07	-2.74

Table 2. Basic statistics of saturation state of edge outflows in respect to phosphate, fluoride, sulfate and chloride. For the sake of simplicity LREE, MREE and HREE phosphate minerals were calculated from La, Tb and Lu.