Sulfate reduction processes in salt marshes affected by phosphogypsum: Geochemical influences on contaminant mobility

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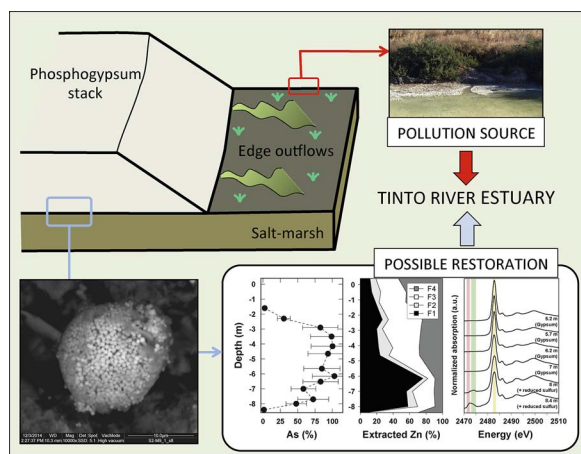[c] Department of Mining Engineering, University of Chile, Av. Tupper 2069, 8370451, Santiago, Chile
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GRAPHICAL ABSTRACT

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ABSTRACT

Sulfate reduction and its associated contaminant immobilization in marsh soils supporting a phosphogypsum stack was examined by pore-water and solid analysis, selective extractions, microscopy and sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy. The negative impact of this stack on estuarine environments is a concerning problem. In the weathering profile, total concentrations of most pollutants increase with depth; instead, dissolved contents in pore-waters increase to middle of the saturated zone but then decrease drastically down to reach the marsh due to sulfide precipitation. Excess of acid-volatile sulfide plus pyritic sulfur over metals bound to the oxidizable fraction indicates that sulfide precipitation is the main mechanism responsible for metal removal in the marsh. Thus, abundant pyrite occurred as framboidal grains, in addition to other minor sulfides of As, Zn and Cu as isolated particles. Moreover, high contents of elemental sulfur were found, which suggest partial sulfide oxidation, but marsh may have capacity to buffer potential release of contaminants. The importance of sulfur species was quantitatively confirmed by XANES, which also supports the accuracy of selective extraction schemes. Accordingly, managing pore-water quality through organic carbon-rich

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amendments over phosphogypsum stacks could lead to a decrease in contaminant loading of leakages resulting from weathering.

1. Introduction

Metal sulfide precipitation can exert a strong control on the species distribution and contaminant mobility under natural conditions in anoxic systems associated with decomposing organic matter. Activity of sulfate-reducing bacteria can be considered as the main mechanism for metal removal from pore-water through insoluble sulfide formation [1–4]. Microbially-mediated sulfate reducing processes can play a crucial role on the natural contamination attenuation in receiving media, as well as on artificial treatment systems [5,6].

Extensive anthropogenic activity and the lack of environmental regulation during the first half of the last century gave rise to many contaminated estuaries in industrialized and urbanized areas worldwide. Estuarine salt-marshes are often the sink of contaminants released from mining and industrial activity developed in the surrounding area. In these organic matter-rich environments, precipitation of sulfide minerals may sequester potentially toxic trace elements [7,8]. However, attenuation associated with these natural processes cannot be considered as a full replacement for restoration technologies, but it can sometimes help decision makers to optimize the best cost-effective and environmental friendly remediation practices [9].

Phosphogypsum is a waste from the production of phosphoric acid by phosphate fertilizer industry following wet chemical digestion of phosphate rock with sulfuric acid. This unwanted waste (mainly gypsum) is often disposed of in large stacks in coastal areas, close to the production plants, as a slurry along with leftover reactants and products from the industrial process [10]. This fact leads to the existence of highly-polluted acidic groundwaters in the waste pile containing high concentrations of metals and radionuclides [11]. Consequently, phosphogypsum stacks commonly constitute a potential source of contamination to the coastal environment [12].

The purpose of this study was to map redox zoning in the weathering profile of a phosphogypsum stack located on an estuarine marsh soil. We traced the formation and spatial distribution of reduced sulfur species in order to elucidate how sulfate-reducing processes in the marsh can control the fate of contaminants in the environment. To achieve this objective, quantitative S speciation data were obtained by combining chemical extractions with S K-edge X-ray absorption near-edge structure (XANES) spectroscopy and electron microscopic observations. Metal contents were analyzed both in pore-waters and in operationally defined selective extractants from solids for mobility discussion. As far as we know, no study has attempted to explore the sulfate-reduction processes associated with phosphogypsum waste and its impact on the environment, especially taking into account the combined use of selective extractions and synchrotron-based spectroscopic techniques. Moreover, this information will allow expanding the overall knowledge about the characteristics that regulate both the residence time and the potential release and transport of metals and metalloids from hazardous wastes to the environmental.

2. Materials and methods

2.1. Study site

The site investigated is a controversial phosphogypsum stack (100 Mt of stockpiled waste and 1200 ha of surface) located directly above salt-marshes of the Tinto River estuary (Huelva, SW Spain), less than 100 m from an urban area with similar extension (Fig. S1 of the Supporting information (SI)). The location of this phosphogypsum stack within the tidal prism makes it a potential source of pollution to the estuarine environment. The excess of highly-polluted acidic water stored in the pore-space of this anthropogenic aquifer emerges forming springs or edge outflows reaching the estuary. Moreover, there is a clear connection between the stack and the estuary, which leads to a potential weathering by seawater intrusion from the deepest part originating these edge outflows. This fact evidences the inefficiency of the preliminary restoration actions based on the addition of an artificial topsoil cover over the bare phosphogypsum [13]. In fact, all disposal modules of the stack, two non-restored zones and other two 'supposedly' restored zones (Fig. S1 of the SI), act as sources of edge outflow waters to the estuary [12].

However, sulfate-reduction and sulfide precipitation processes catalyzed by bacterial activity occur naturally in the salt-marshes supporting the stack and could attenuate some contamination [14]. This deposit area is currently in a legal limbo; the company must ensure environmental restoration of the marsh although only of those areas without previous restoration actions, while social turmoil advocates total restoration or even transportation of the waste to controlled landfills. In this scenario, studying natural processes, such as sulfate reduction in the marsh soils, could allow the optimization of possible effective remediation actions not only in the case of study but also in other estuarine systems affected by industrial waste releases around the world.

2.2. Phosphogypsum coring and sample processing

Phosphogypsum core samples were collected at approx. 0.5 m intervals from stack surface to the underlying marsh soils using a soil-sampling auger (Fig. S1 of the SI). The deepest sample corresponds to the first centimeters of underlying marsh soil (8.4 m at depth). Samples were transferred to polypropylene vacuum bags and rapidly taken to the laboratory within 15 min. At the laboratory, 0.1 μm-filtered pore-waters were collected through suction cup lysimeters under $N_{2(g)}$ atmosphere within a glove box. After pore-water extraction, solid samples were frozen and then lyophilized to complete dryness using a freeze-dryer.

2.3. Chemical and mineralogical analyses

For the pore-water, pH, redox potential (ORP, converted to Eh) and electrical conductivity (EC) were immediately measured after extraction. Determination of Fe(II)/(III) and H_2S concentrations was also immediately performed by spectrophotometric methods. Then, solutions were divided into two aliquots, one not acidified for anion analysis by high performance liquid chromatography (HPLC), and one acidified with HNO_3 to pH < 1 for analysis of major and trace elements by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), respectively. More details of the analytical procedures are described in the Section S1 of the SI.

For the solid samples, the bulk chemical composition was determined by acid digestion with *aqua regia* in Teflon vessels, and then followed by analysis with ICP-OES and ICP-MS. Sulfur speciation analyses were performed; acid-volatile sulfur (AVS, including amorphous Fe monosulfides (FeS), mackinawite, greigite as well as other HCl-soluble sulfides), pyrite-sulfur (Py-S) and elemental sulfur (ES) were differentiated by a three step sequential digestion, and their concentrations were determined using the method described by Duan et al. [15]. In order to study in detail the partitioning of metals, the following sequential extraction procedure from Rauret et al. [16] was also applied

to the solids: (F1) easily soluble fraction (interchangeable metals, associated with carbonates and those soluble in water or under slight acidic conditions), extracted with 0.11 M acetic acid; (F2) reducible fraction (metals bound to Fe and Mn oxyhydroxides), extracted with 0.1 M hydroxylamine hydrochloride at pH 2; (F3) oxidizable fraction (metals bound to organic matter and sulfides), extracted with hydrogen peroxide and 1 M ammonium acetate at pH 2; and (F4) residual fraction (non-mobile metals strongly bound to the crystalline structures), extracted with *aqua regia*. Solutions from sequential extraction were also analyzed by ICP-MS. Finally, the mineralogy was determined by conventional X-ray diffraction (XRD) with CuKα monochromatic radiation and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). Moisture content was determined gravimetrically.

Sulfur K-edge XANES data for the phosphogypsum profile and gypsum, pyrite and elemental sulfur standards were collected at the beamline XAFS of the Synchrotron Elettra Light Source (Trieste, Italy) [17]. XANES data analysis was performed according to standard procedures [18]. The spectra were taken in a range from 2300 to 2700 eV with 0.2 eV step size at the edge region. The spectra were normalized, after background subtraction, by means of Athena software within the IFFEFIT package [19]. The proportion of sulfur species in the samples was calculated by linear combination fitting software included in Athena. Data collection and analysis operations are described in the Section 2 of the SI.

3. Results and discussion

3.1. Sulfate reduction

Values of pH and Eh in the pore-waters along the profile are shown in Fig. 1a. The water table in the phosphogypsum stack was at a depth of approx. 3 m. Pore-waters were characterized by acidic conditions, with pH values that decreased from 3.0 to 2.2 in the unsaturated zone and then were stabilized to 2.1–2.2 in the saturated zone, though with a slight increase in the deepest part (Fig. 1a). This pH increase was more pronounced in the marsh soil surface in contact with phosphogypsum, with a pH of 4.1 (Fig. 1a). Eh values were maintained at around 480 mV in the first 7 m depth, but then decreased progressively toward the marsh to 320 mV (Fig. 1a).

Dissolved sulfate concentrations in pore-water increased gradually with depth from 1.3 to 6.2 g/L (Fig. 1b); while aqueous sulfide concentrations were below detection limit in the entire profile. Dissolved

Fe concentrations also increased with depth from 2.4 mg/L in surface to 500 mg/L at 7.5 m depth, being the sharpest increase at this last depth (Fig. 1c). However, correlated to pH increase and Eh decrease, Fe concentrations decreased rapidly in the last meter of the profile up to 270 mg/L. Most of the total Fe corresponded to Fe(III) in the unsaturated zone, between 20 and 60% to Fe(II) in the first meters of the saturated zone, and finally percentages of 100% of Fe(II) are reached in the deepest samples (Fig. 1c).

The partitioning of the reduced sulfur species in the phosphogypsum solid with depth is shown in Fig. 1d. As expected, reduced sulfur species were inexistent in the shallowest 5.5 m depth. From 5.5 m depth, reduced sulfur species, mainly Py-S, were present in all samples down to the marsh base. Elemental sulfur and Py-S were the dominant species of reduced sulfur, especially in the deepest samples, i.e. basement of phosphogypsum stack and first centimeters of marsh, with values of up to 9.34 g/kg and 6.48 g/kg, respectively. AVS concentrations were much lower with values of up to 176 mg/kg in the deepest samples (Fig. 1d).

The geochemical evolution of the pore-water seems to be consistent with the presence of the reduced sulfur species in the solid. The decrease of Fe(II) in the last meter could be due to microbial sulfate reduction and pyrite sulfide precipitation. These processes might have contributed to the increase in pH of the pore-water, due to the alkalinity produced by bacterial activity, and to the decrease of Eh observed in the zone of interaction with salt marshes. Sulfate reduction conditions are commonly associated with Eh values ranging from −300 to 0 mV and circumneutral pH. However, the lower pH values and more positive redox potentials observed in this study have been also previously described in other sulfate-reducing environments [20]. This process naturally occur in acidic environments as long as there are anaerobic conditions, sufficient organic carbon, and the presence of acid-tolerant sulfate-reducing bacteria, as has been previously observed in the Tinto River sediments [21]. Other possibility is that bacterial activity is active in pore-water microenvironments that are more alkaline and reducing than the general solid chemistry.

AVS corresponds to Fe monosulfides which directly form by microbial sulfate reduction in presence of Fe(II) in solution. These monosulfides are the first phases that often precipitate in most natural aqueous systems and act as intermediate precursors necessary for the formation of most stable pyrite through reactions either with H_2S or with ES [22]. In anoxic sediments, Fe monosulfides together with ES can be also generated by abiotic reduction of Fe(III) oxides coupled to the oxidation of aqueous sulfide. The Fe monosulfides and ES so formed
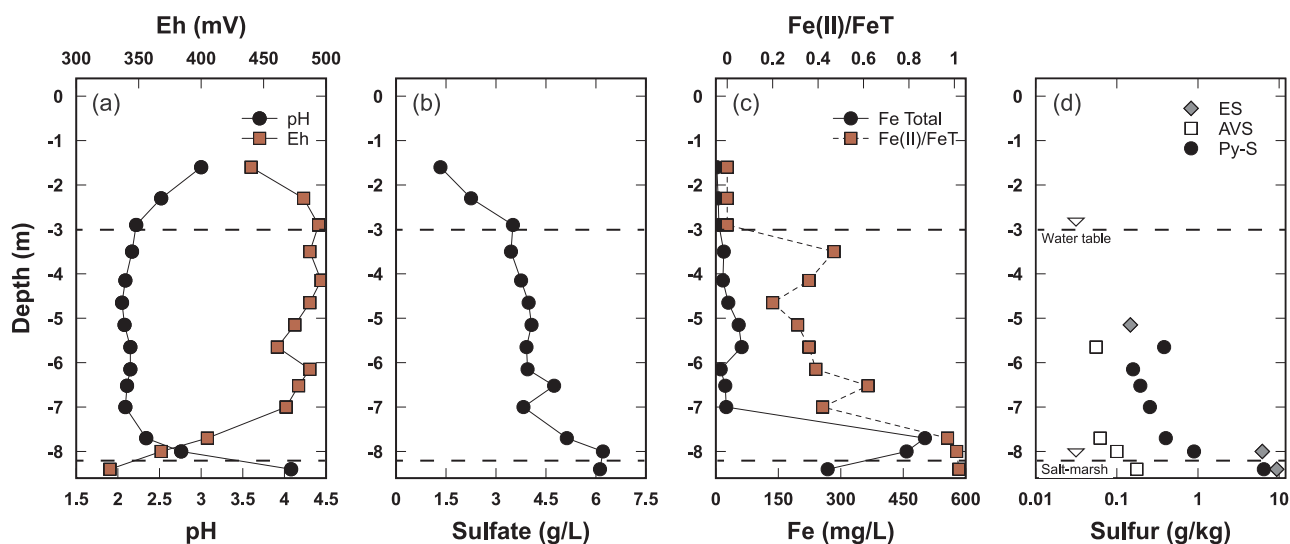

Fig. 1. Depth profiles of (a) pH and Eh, (b) sulfate and (c) Fe concentrations in pore-water solutions, and (d) reduced sulfur species in solid phosphogypsum. Fe(II)/Fe$_{total}$ ratio for pore-waters is also shown in (c).

will react and produce pyrite. In the overall reaction, Fe monosulfides are produced in similar amounts as pyrite, which would explain values of AVS/Py-S ratio close to 1 [23,24]. Thus, the low values of AVS/Py-S ratios found in the deepest samples, 0.16, 0.11 and 0.03 at 7.5 m, 8 m and in the marsh contact, respectively, suggest that formation of Fe monosulfides and their transformation to pyrite is not controlled by the availability of Fe(III) minerals. The fact that the content of aqueous sulfide in pore-water is undetectable can be attributed to low iron-monosulfide solubility under Fe-rich conditions [25], which is reflected in a relatively high concentration of pore-water Fe(II) in the deepest samples. An abundance of pore-water Fe(II) in such depths can lead to iron-monosulfide accumulation due to rapid sequestration of bacterially produced H_2S.

Both AVS and Py-S contents in the deeper samples were within normal values compared to other anoxic sediments contaminated by metals [26–28]. However, ES concentrations were extremely high. This sulfur species is a product from oxidation of sulfides, mainly Fe monosulfides or AVS, as the known reductive processes do not yield free ES [29]. The high concentrations of ES found in this study could be indicative of that this oxidation process is not microbially mediated, since biotic oxidation is negligible due to competition from the very rapid abiotic oxidation rate [27]. The abiotic oxidation of AVS could be also associated to the fact that the Eh values are not as low as in other anoxic sulfide-forming environments. This oxidation process does not imply significant changes in the aqueous S concentration or changes in pH [25]. The oxidation in the contact with marsh sediments could be due to the possible hydrological connection between the stack and the estuary by saline intrusion, as already described in previous studies [12,13].

3.2. Influence on metal mobility

The depth profiles of the concentration of trace elements in pore-water and in phosphogypsum solid are shown in Fig. S2 of the SI. From

these data, the percentages of trace elements dissolved in pore-water with respect to the total contents were calculated using sample moisture measurements following Clemente et al. [30] and then plotted in Fig. 2. Full details on these calculations can be found in the Section S3 of the SI. Percentages of dissolved elements in the pore-water space follow the same trend for all contaminants. Values increased with depth in the unsaturated zone until reaching a maximum at the middle of the saturated zone. However, in the last meter of the profile and, mainly, in the contact with the marsh, percentages of all dissolved elements drastically decreased until being depleted from solution (Fig. 2); despite their concentrations in the marsh solid were extremely high in comparison with the rest of the profile (Fig. S2 of the SI).

In the middle of the saturated zone, dissolved percentages reached maximum values of up to 100% for Zn, As and Cu (Fig. 2); i.e., the total amount of these elements was mobile in solution, with concentrations of up to 157, 34.2 and 6.23 mg/L, respectively (Fig. S2 of the SI). The most probable explanation of the high mobility of these contaminants, particularly As, could be related to the quality of the sulfuric acid used in the industrial process, as pointed out by Macías et al. [31]. The sulfuric acid was mainly obtained by roasting pyrite with up to 0.4 wt.% of As. The excess of As-loaded sulfuric acid from the industrial reaction is also deposited along with the phosphogypsum and explains the high mobility observed in the interstices of the stack, which evidences that this phosphogypsum is anomalous compared to others worldwide [31]. On the other hand, lower mobility was observed for the remaining pollutants in the middle of the saturated zone, with values of up to 25–35% for Ni and Sb, 10–20% for Cd, Cr and U, and approx. 5% for Co and Pb. Pore-solutions at these depths were characterized by concentrations of approx. 5 mg/L for U, 1–2 mg/L for Cd, Cr and Ni, and < 1 mg/L for Co, Pb and Sb. Furthermore, Th was absent in the pore-solutions of the entire profile due to its low solubility [32], despite reaching total concentrations of up 10 mg/kg in the solid (Fig. S2 of the SI).

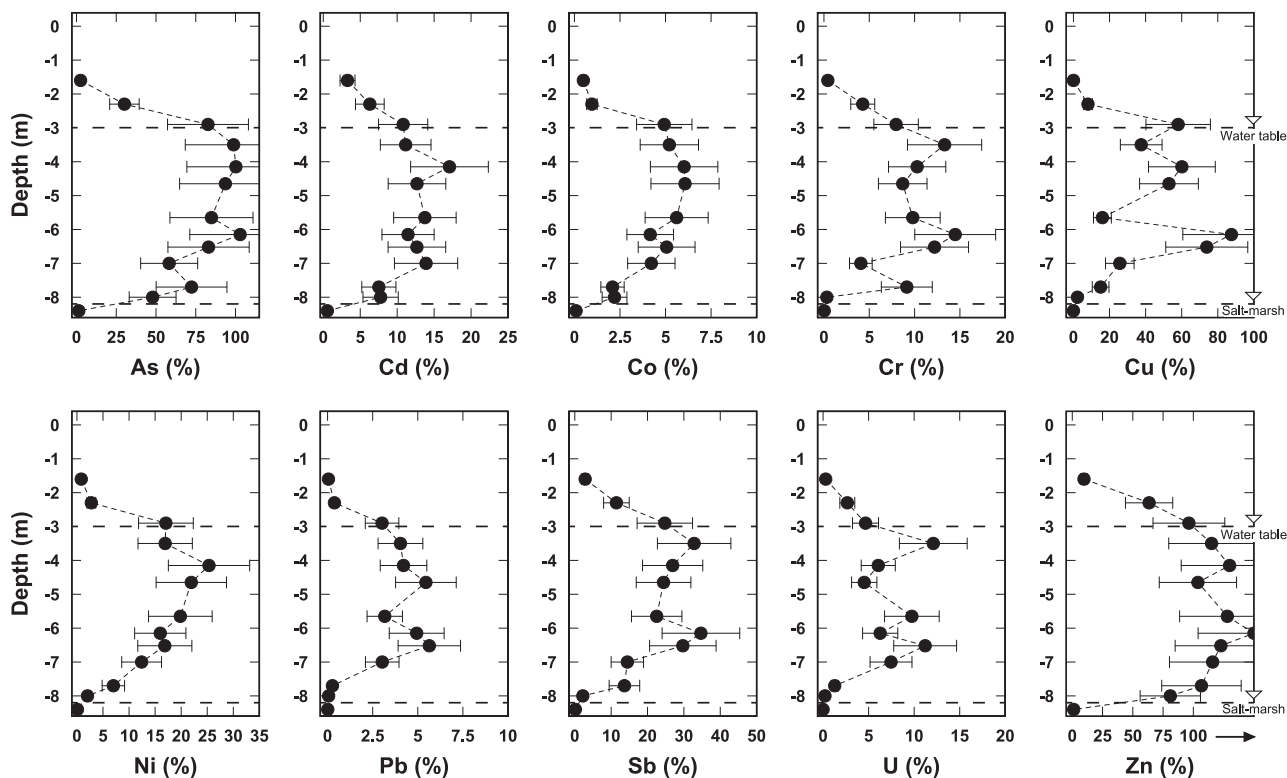The distribution of percentages of trace elements with respect to

Fig. 2. Depth profiles of the percentages of all dissolved elements in the pore-space expressed as a fraction of the total content. Horizontal bars represent possible variations in the calculations associated with the range of densities found in the literature (see more details in the Section S3 of the SI).

total content with depth, obtained by sequential extraction, is shown in Fig. S3 of the SI. The results confirmed the information on contaminant mobility deduced from pore-water chemistry. Percentages leached in the easily-mobile fraction increased to a maximum value at middle of the saturated zone, particularly in the most abundant trace elements such as As (up to 93%), Zn (76%) and Cu (66%). However, these values sharply decreased towards the transition with the marsh basement. Moreover, a significant increase in the fraction bound to sulfides and organic matter, mainly Cu, Zn and to a lesser extent As, was recorded in the underlying marsh surface, with values of up to 74%, 64% and 11%, respectively (Fig. S3 of the SI). It seems therefore reasonable to suggest that the low availability of these potentially toxic trace elements could be controlled by precipitation of metal sulfides, as observed in numerous studies of estuary sediments affected by natural or anthropogenic sources [1,33–35].

As mentioned before, the AVS to Py-S ratio indicates spontaneous pyritization of AVS, which may be also expected to result in pyritization of trace elements associated with Fe monosulfides [36]. Accordingly, the molar ratio of elements, such as As, Cd, Cr, Cu, Fe, Ni, Pb and Zn, released by sequential extraction in the oxidizable fraction to sulfides could be used to differentiate immobilization by sulfate-reduction and sulfide precipitation from other processes that might occur in reducing conditions. In this sense, the sum of the molar concentration of these metals in the first centimeters of marsh (25.3 µmol/g) was much lower than the sum of AVS (5.50 µmol/g) plus Py-S (202 µmol/g). The molar

ratio lower than one would suggest that precipitation of metal sulfides is the main mechanism that contributes to the low availability of metals in the pore-water. The molar deficit of metals could be attributed to that well-crystallized sulfides could become highly insoluble, survive the oxidizable step and be extracted in the non-mobile fraction of the sequential extraction [37]. Therefore, other mechanisms that may control the removal of contaminants in the marsh sediments, such as binding free metal ions in organic compounds [38–40], can be discarded.

On the other hand, uranium (most likely as U^{6+}) may be immobilized in the contact with the marsh by several reduction pathways that often occur in these organic-rich zones: abiotic reduction by iron sulfides that produce uraninite as well as biological mediation via enzymatic activity [41,42]. Due to its low mobility, Th seems to be bound to the insoluble residual phase, as shown by sequential extraction data (Fig. S3 of the SI) and also revealed by previous investigations on phosphogypsum [43].

3.3. Newly-formed solid-phase characterization

Conventional Cu-kα XRD analysis revealed that gypsum is the only crystalline phase in the entire phosphogypsum profile, together with quartz and clay minerals in the first centimeters of marshes (Fig. S4 of the SI). There are no well-defined peaks that allow the identification of the sulfide minerals leading to the contaminant immobilization.
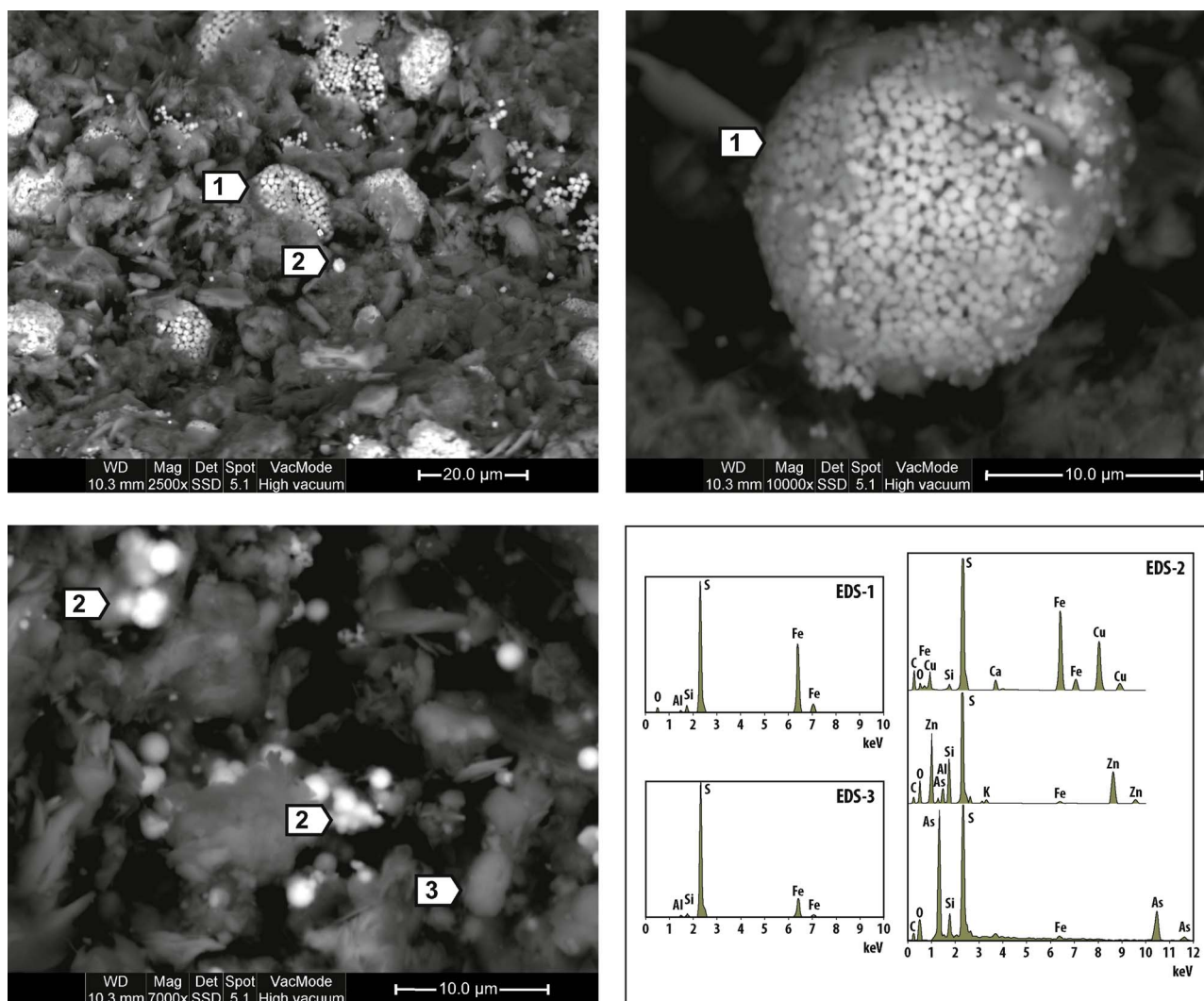

Fig. 3. SEM images and EDS spectra of newly-formed metal sulfides in the phosphogypsum samples located at 8 m depth and in the contact with the salt-marsh.

However, powder samples of the deepest zones examined with SEM contained abundance of authigenic sulfide mineral grains, as revealed by the typical morphology in framboids (Fig. 3). These newly-formed precipitates were not found with SEM in other depths other than near the contact with the marsh sediment. Framboids ranged from 5 to 30 μm in diameter with an average value of ~10 μm and corresponded to pyrite, as shown by EDS analysis (EDS-1; Fig. 3). Octahedral crystallites comprising individual framboids were of uniform size with less than 1 μm in diameter. Some individual spherical crystals of ~1 μm were also present and corresponded to other newly-formed sulfides containing Cu, Zn or As (EDS-2; Fig. 3). Moreover, some pellets or globule-like grains mainly composed by S were attributed to elemental sulfur (EDS-3; Fig. 3).

The lack of diffraction effects of sulfides using conventional X-rays must probably be due to that these newly-formed minerals of crypto-crystalline size precipitate within a set of more abundant and crystalline minerals such as gypsum. However, this limitation can be overtaken using techniques based on synchrotron radiation. Fig. 4 shows the sulfur K-edge XANES spectra of samples from 5 m depth to the first centimeters of marsh soil. The dominant presence of sulfate in all samples was clearly seen by the characteristic peak at ~2482 eV, as can be checked by comparing with the gypsum standard. In the deepest sample of phosphogypsum and in the marsh surface, spectra showed also peaks between 2472 and 2473 eV that could be characteristics of some inorganic sulfides such as pyrite and elemental sulfur, as can be deduced from the standard compounds (Fig. 4). Linear combination fitting of XANES data with contributions from reference standards suggested that gypsum comprised 100% of total S in the phosphogypsum samples to 7 m depth. However, XANES data of the deepest samples exhibited 30% of elemental sulfur in the phosphogypsum at 8 m depth and 29% of elemental sulfur and 6% of pyrite in the marsh contact (Fig. 4).

The relative abundance of the inorganic sulfides identified with XANES was comparable to data from reduced sulfur extraction. No iron monosulfides such as greigite and mackinawite, whose peaks in XANES spectra would be lower than 2472 eV [42], were detected. Therefore, Fe monosulfide concentrations found in the deepest zones, as well as some reduced sulfur species found between 5 and 8 m (Fig. 1d), should be below detection limit even by using synchrotron techniques. On the other hand, the absence of sulfur in organic forms in the deepest samples, whose peaks would be higher than 2473 eV [44], again suggests that the sulfide precipitation is the main mechanism that decreases mobility and, consequently, reduces bioavailability of contaminants, as above deduced by the ratio between sequential extraction oxidizable metals and sulfides. As mentioned previously, abundance of elemental sulfur suggests sulfide oxidation processes likely linked to a deep seawater recharge. Albeit, attenuating capacity of the sulfate-reduction processes seems to limit the potential re-release of metals during such oxidation.

4. Environmental implications

Given the uncertain future of the phosphogypsum stack, managing pore-water quality should be a priority action since excess of groundwater is currently the main vector of contamination through edge outflows to the Tinto River estuary. Chemical composition of edge outflows is very similar to that found in pore-water in the middle of the saturated zone, where maximum levels of contamination were observed, which would be indicative of stagnant and non-renewable waters near marshland basement associated to possible subsidence due to overpressure [13]. In these deepest zones, awareness of sulfate-reduction processes in the contact with marsh sediment could be critical before setting up any remediation attempt. In fact, this route of action could be occurring now in those previously restored zones.

Two of the four disposal modules forming the stack have similar characteristics; i.e., the same amount of phosphogypsum was approximately dumped, in the same period of time and using the same technical procedure. It would, therefore, be reasonable to assume that chemical characteristics of the edge outflow waters in both zones are also similar. The only difference is that one zone was already restored by a complex cover of artificial topsoil (zone 4; Fig. S1 of the SI) while the other zone remains unrestored (zone 3; Fig. S1 of the SI). Initially, the cover in the restored zone was installed to prevent weathering by rainwater infiltration and, thus, eliminate edge outflows. In contrast, despite such remediation actions, deep seawater intrusion continues with the leaching process and, hence, with the release of toxic elements to the estuary. However, edge outflows from the 'supposedly' restored zone are equally numerous although with 50% less contaminant loading, mainly As, Cr, Cu and U, than those of the unrestored zone [12].

One of the layers of the complex artificial-soil cover of the restored zone is an organic matter-rich vegetal level that, according to previous laboratory experiments [45], seems to be currently acting as a carbon source that enhances the activity of naturally-occurring sulfate-reducing bacteria in the phosphogypsum. This remediation mechanism was not initially expected, but it could contribute, together with that occurring in the marsh contact, to greater immobilization of pollutants by
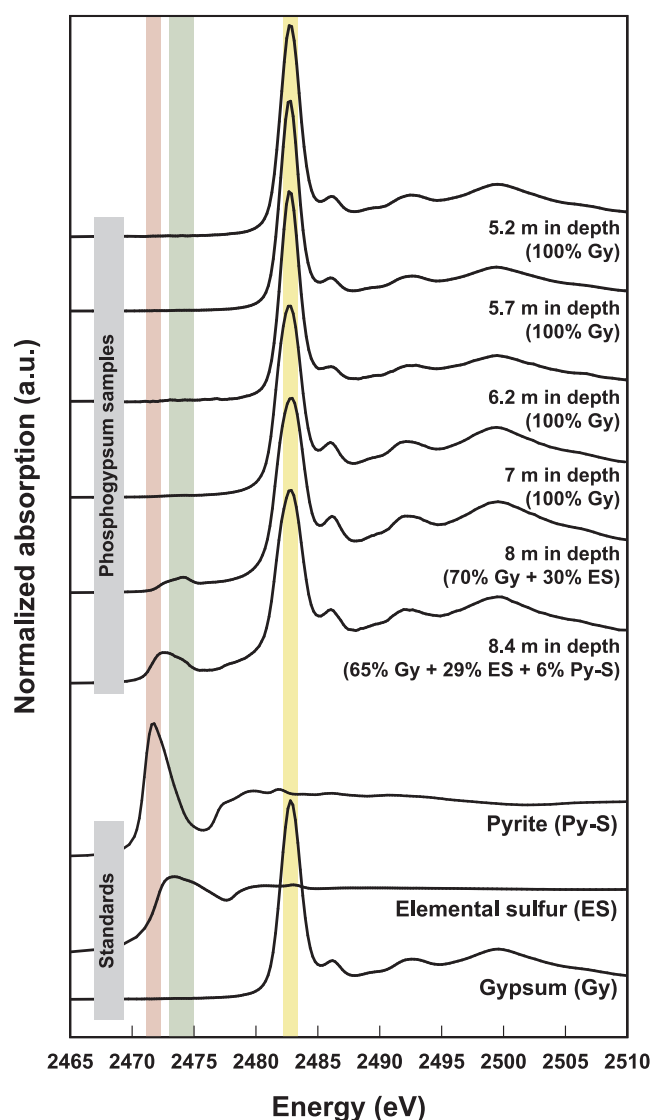

Fig. 4. Sulfur XANES spectra of phosphogypsum samples from 5 m depth to the first centimeters of salt-marsh, together with the reference compounds used for linear combination fitting and the obtained results.

sulfate-reduction processes than in the unrestored zone. In fact, it has been proven that in situ passive amendments of acidic pore-water bearing tailings with a small and dispersed mass of organic carbon have potential to support sulfate-reduction and minimize the associated contaminant loading to receiving waters [46,47]. Thus, these findings could help to optimize the guidelines for restoration actions that are currently being planned.

5. Conclusions

This research is focused on investigating the mobility of trace elements in phosphogypsum piles that have been dumped on estuarine salt-marshes at the bank of the Tinto River estuary (SW Spain) for years. The study describes some sulfate-reduction processes occurring at the contact between stack and marsh and naturally attenuating pollution reaching the estuary through edge outflows. According to the results here presented, expanding such sulfate-reduction processes to the entire phosphogypsum profile with the optimized use of organic carbon-rich amendments could reduce significantly the mobility of contaminants that are subsequently discharged to the Tinto River estuary, which should be taken into account in the already-started restoration. These findings also preclude the social demand of transportation to controlled landfills, because dredgeding and re-dumping polluted anoxic sediments can cause oxidation and release of trace elements bound to sulfides to the environment.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2018.02.001.

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