Enhanced levels of technology critical metals in mine waters: the case of the Poderosa sulfide mine (SW Spain)

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Environmental context

Natural weathering of rocks may lead to increasing levels of technology critical elements (TCEs) in the environment. Anthropogenic activities can noticeably boost these TCEs release rates. We investigated TCEs release in acid mine drainage outflows from an underground sulfide mine in SW Spain, reporting concentrations some orders of magnitude higher than those observed in natural waters. Findings may contribute to improve the knowledge on TCEs mobility in different geological settings.

Abstract

Extensive extraction of technology critical elements (TCEs) from the lithosphere and their usage results in a growing dispersion and remobilization of these elements within environmental compartments. Other anthropogenic activities such as sulfide mining can lead to increasing levels of TCEs into the environment. We investigated TCEs mobility in acid mine drainage (AMD) outflows from an underground mine in SW Spain for around 2 years. Enhanced levels of TCEs were observed in AMD outflows; average concentrations of 8.2 mg L⁻¹ of REEs, 1.5 mg L⁻¹ of Y, 80 µg L⁻¹ of Ga, 53 µg L⁻¹ of Sc and 42 µg L⁻¹ of Tl were reported. The source of these TCEs in the study site is primarily accessory minerals in host rocks, although the contribution of Ga and Tl by sulfides cannot be discarded. The concentration of TCEs in the AMD outflows seems not to be controlled by precipitation of secondary minerals but by the intensity of chemical weathering inside the galleries. A positive correlation between REEs and Y, and the Si/Na+K ratio seems to indicate that these elements have a greater affinity by resistant minerals to weathering. Further studies are needed at laboratory and field scale to confirm the hypothesis raised in this study

about the source and mobility of technology metals and widen the knowledge in other geological settings.

Introduction

Lifestyle and technological changes, population growth and government policies worldwide have profoundly altered raw materials supply and demand trends since the early twentieth century (Krausmann et al. 2009). This is the case of technology critical elements (TCEs), trace elements whose production and use rates have noticeably increased in the last years for high-tech applications. These elements are now essential components in a wide variety of applications including information and telecommunications technology, semiconductors, electronic displays, optic/photonics or energy-related technologies (Eggert 2011). TCEs may differ from country to country, but usually include Ga, Ge, In, Te, Nb, Ta, Ti, the platinum group elements (PGEs), and rare earth elements (REEs), along with Sc and Y (Cobelo-García et al. 2015). There is a lack of information for most of these elements concerning their sources, transport and fate in different environmental compartments, and in some cases this information may be contradictory. The growing demand of these elements by the industry has led to their extensive extraction from the lithosphere and their worldwide dispersion and remobilization within the biosphere (Cobelo-García et al. 2015). Recent studies highlight the impact of these elements on biogeochemical cycles and on living organism health (Abdou et al. 2019; Romero-Freire et al. 2019). The growing mobility of these elements within the biosphere may pose a serious environmental concern (Pagano et al. 2015; Isildar et al. 2018), and therefore, their release, transport and fate in different environmental compartments need to be further explored.

The concentrations of TCEs in rocks range several orders of magnitude; from hundreds of mg kg⁻¹ down to µg kg⁻¹. The weathering of these rocks leads to increasing levels of TCEs in soils, waters and sediments (e.g. Tremel et al. 1997; Law and Turner 2011; Jin et al. 2017). However, anthropogenic activities can noticeably enhance these release rates. A significant example of such human-induced TCEs dispersion into the biosphere is sulfide mining, where the high acidity generated during acid mine drainage (AMD) processes may notably contribute to the release of dissolved TCEs into the hydrosphere, increasing up to several orders of magnitude the concentrations commonly found in surface waters. For example, Casiot et al. (2011) reported Ti concentrations of up to 534 µg L⁻¹ in a region impacted by AMD in southern France.

The extremely high concentrations of metal/lroids (i.e. Al, Fe, Cu, Zn, Cd, Pb or As) commonly found in AMD have left TCEs in the background and therefore, they have not received much

attention until recently. The release of mining effluents exposes natural waters to excess metals and thereby threatens both human and environmental health (Gopalapillai et al. 2008). However, these effluents can be also a source of raw materials due to the existence of high levels of TCEs and, hence, studies dealing with the levels, transport and fate of these elements in mine sites are needed. In this sense, the Iberian Pyrite Belt (IPB, SW Iberian Peninsula), an area well known for hosting many polymetallic massive sulfide deposits intensely exploited since ancient times, can be considered as a natural laboratory to understand the behavior of TCEs in AMD-affected environments. In fact, Olías et al. (2018) recently reported concentrations of REE ranging from 2.8 to 4.6 mg L⁻¹ in AMD sources of the Odiel River headwaters, which is one of the main fluvial basins draining the IPB. Thus, this study explores the content of some TCEs (i.e. Ga, Ge, Nb, REE, Ta and Tl) in one of the most pollutant sources of the IPB, namely, the Poderosa adit outflow.

Experimental

Site description

The Poderosa mine, located in the northern part of the IPB, is a relatively small size mine (23 ha of affected surface; Grande et al. 2014) with respect to others located in the IPB, despite that, it is considered one of the most pollutant outflows (Cánovas et al. 2018). Two different massive sulfide deposits enclosed in acid epiclastic volcanic rocks are found in the Poderosa mine (Pinedo Vara 1963). Due to its mineral richness, mining activity in Poderosa dates back, at least, to the Roman times, however, the more intense, although discontinuous, mining period comprised from 1880 to 1990. The main sulfides exploited were pyrite (FeS₂) and, to a lesser extent, chalcopyrite (CuFeS₂), chalcocite (Cu₂S) and covellite (CuS). As a result of such intense mining activity, the Poderosa mine preserves a legacy of open pits and flooded underground galleries which cause a permanent pollutant outflows to the Odiel River (Cánovas et al. 2018). The predominance of a Mediterranean type climate, with an average pluviometry of around 750 mm, and characterized by a high inter- and intra-annual variability (around 60% of total rainfall collected between October and January), leads to changes in outflows discharges. A more detailed description of the Poderosa mine can be obtained elsewhere (Cánovas et al. 2018).

Sampling and analytical techniques

A synoptic water sampling was initiated in April 2015 to determine seasonal hydrochemical variations in Poderosa mine outflows with a variable frequency, ranging from fortnightly to monthly. Flow data were obtained by installing a Parshall flume at the mine adit (Fig. 1) together with a level data logger (Schlumberger Cera Diver) with pressure compensation. This device was

programmed to measure every 30 minutes and was discontinuously operating from December 2015 to February 2017 when the device was removed by technical problems. Daily rainfall data were obtained from a rainfall gauge station located at 9 km SE of the sampling point. In order to capture sudden hydrochemical changes associated with heavy rainfalls, a high-resolution sampling was carried out using a Teledyne ISCO autosampler, placed at the adit outlet (Fig. 1), with a sample container holding up to 24 bottles and a polyethylene-made outlet pipe. Samples were pumped by a peristaltic pump, with a scheduled purge stage between samples to avoid cross-contamination. Sample-containing bottles were washed in 10% (v/v) nitric acid and then rinsed with milli-Q water (18.2 M Ω) before sampling. This high-resolution sampling period comprised from October to December 2016, with a frequency of 2-6 h between sampling events. In total, 83 samples were analyzed and used in this study.

Samples were filtered (through 0.2 μ m) in situ, acidulated to pH < 1 and refrigerated until analysis. The temperature, pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) were measured in situ using CRISON MM40+ equipment. A three-point calibration was performed for both EC and pH (147, 1413 μ S cm⁻¹ and 12.88 mS cm⁻¹, and 4.01, 7.00 and 9.21, respectively), while the ORP was controlled using two points (240 and 470 mV). The ORP values were corrected to obtain the potential referred to the hydrogen standard electrode (Nordstrom and Wilde, 1998).

Samples were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; Thermo Scientific iCAP 6500 Radial) for major elements and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS; Thermo X-Series II) for trace elements at the laboratories of the IDAEA-CSIC. The detection limits were determined by average and standard deviations from 10 blanks, ranging from 0.1 to 0.5 mg L⁻¹ for the major elements (i.e., Al, Ca, Cu, Fe, K, Mg, Mn, Na, S, Si and Zn) and from 1 to 5 μ g L⁻¹ for trace elements (e.g., As, Cd, Co, Ga, Ge, Pb, REE and Tl). A triplicate analysis was performed in order to evaluate the analytical precision error, which was below 5% in all cases. In each analysis sequence blanks were analyzed, and all elements were below the detection limits. The analytical accuracy was confirmed by the analysis of reference materials (NIST-1640).

Data treatment

Chemical speciation was obtained using the CHEAQS program version 2017.3 (Verweij 2017). The CHEAQS model includes inorganic speciation and mineral equilibrium based on the National Institute of Standards and Technology database version 8.0 (NIST 2004). Saturation indices of waters were obtained using the PHREEQC code v2.12.01 (Parkhurst and Appelo 2005). The

Wateq4f database was enlarged with thermodynamic data from schwertmannite (Yu et al. 1999) and other minerals (e.g. melanterite, copiapite, coquimbite) from other databases provided by the code. In this paper, La through Sm are considered light rare earth elements (LREE), Eu through Dy middle rare earths (MREE), and Ho to Lu heavy rare earths (HREE). In order to study fractionation processes along the time, REE concentrations were normalized using the European Shale (EUS) values provided by Bau et al. (2018). Cerium (Ce*) and Europium (Eu*) anomalies were estimated from the expressions $Ce_{EUS}/\sqrt{[La_{EUS} \cdot Pr_{EUS}]}$ and $Eu_{EUS}/\sqrt{[Sm_{EUS} \cdot Gd_{EUS}]}$, respectively (Worrall and Pearson 2001).

Results and Discussion

TCEs concentrations in mine outflows

The intense sulfide oxidation processes inside the mine galleries lead to the formation of highly acidic (average and median pH of 2.0), sulfate and metal/lloid-rich outflows (average concentrations of 6780 mg L⁻¹ of sulfate, 1545 mg L⁻¹ of Fe, 82 mg L⁻¹ of Cu, 76 mg L⁻¹ of Zn, 5.2 mg L⁻¹ of Mn, 2.6 mg L⁻¹ of As, 1.2 mg L⁻¹ of Co, 330 µg L⁻¹ of Cd, 174 µg L⁻¹ of Pb and lesser amounts of other trace metals; Table 1). The high acidity released during sulfide oxidation processes inside the galleries also causes the dissolution of other elements commonly found in the host rocks such as Al (average value of 343 mg L⁻¹), Mg (153 mg L⁻¹), Ca (125 mg L⁻¹), Si (39 mg L⁻¹), Na (17 mg L⁻¹), K (13 mg L⁻¹), Mn (5.3 mg L⁻¹), among others (Table 1).

Among the elements delivered by Poderosa outflows, different TCEs can be found. Thus, REEs exhibited the highest concentrations, with values ranging from 3.8 to 9.7 mg L⁻¹ (average value of 8.2 mg L⁻¹; Table 2). These values are several orders of magnitude higher than those reported in natural waters, commonly not exceeding tens or hundreds of µg L⁻¹ (Migaszewski and Galuszka 2015; Ayora et al. 2016). Such high concentrations are in agreement with others reported in environments affected by AMD, considered the most important process responsible for REE remobilization from host rocks (Nordstrom 2011). For example, Migaszewski et al. (2019) reported average REEs concentrations ranging from 0.2 to 18 mg L⁻¹ in the Wisniówka mining area (Poland), while Cánovas et al. (2016) reported REEs concentrations of 1-2 mg L⁻¹ in the nearby Perrunal mine (IPB). As in other AMD leachates, LREEs are the most abundant in Poderosa outflows (83-85%), followed by MREEs (11-13%) and HREEs (3.5-4.1%) (Table 2). Cerium, Nd and La showed the highest concentrations, with average values of 3.1 mg L⁻¹, 1.8 mg L⁻¹ and 1.1 mg L⁻¹, respectively (Table 2). Figure SM1 (Supplementary Material) shows the REE EUS-normalized pattern in Poderosa outflows, and as can be seen, these waters show the typical enrichment in MREE of waters affected by AMD (Pérez-López et al. 2010).

Such high REEs concentrations may be caused by dissolution of REE-bearing minerals contained in host rocks inside the mine galleries. Figure 2 shows the relationship of REEs with some major elements commonly found in host rock minerals. As can be seen, an apparent linear correlation is observed between REEs and Ca ($R^2 = 0.55$), and to a lesser extent with Mg ($R^2 = 0.48$). However, no correlation was observed between REEs and other crustal elements such as Al or Si. In addition, similar correlation values were observed between these crustal elements and light, medium and heavy REEs. The anomalies of Ce and Eu have been traditionally used to study water-rock interactions in aqueous systems (e.g. Willis and Johanesson 2011; Noack et al. 2014; Olías et al. 2018;). Waters from Poderosa mine showed an absence of Ce anomaly (Ce^*) with a low variation through time (average and median values and interquartile range of 1.1; Table 2). Massive sulfide deposits commonly preserve a strongly positive Ce anomaly inherited from the precursor hydrothermal fluid (Leybourne et al. 2006). Thus, the absence of such strong positive Ce anomaly in waters may indicate a different REEs source than sulfides. In the case of Eu, waters showed a negative anomaly (Eu^*) with barely variations through the study period (average and median values of 0.64; Table 2 and Fig SM1). This Eu anomaly in waters may be inherited from host rocks from which they are in contact with. Reduced Eu exhibits strong partitioning among different minerals during crystallization from magmatic fluids; some minerals are highly enriched such as Ca-plagioclase or highly depleted such as olivine and pyroxene (e.g. Hanson 1980; Nash and Crecraft 1985). This negative Eu anomaly may be not associated with sulfide oxidation but inherited from the dissolution of felsic volcanic rocks, predominant in the study area, as previously reported by Ferreira da Silva et al. (2009).

According to the International Union of Pure and Applied Chemistry (IUPAC) recommendations, Y and Sc have been also considered as REEs, however, earth scientists have traditionally set Sc aside due to its small ionic radius, similar to that observed for Mg, Fe^{2+} , Zr, and Sn (Chakhmouradian and Wall 2012). The average concentration of Y in Poderosa outflows was $1535 \mu g L^{-1}$, with values ranging from 720 to $1993 \mu g L^{-1}$ (Table 2). This value was in direct contrast with the low Y concentrations observed in natural stream waters; Leybourne and Johannesson (2008) reported an average Y concentration of $88 ng L^{-1}$ in streams ($n = 546$) of Eastern Canada, that is, several orders of magnitude lower than that reported in Poderosa outflow. The similar origin and geochemical behavior between REE and Y is evidenced by the high correlation observed among these elements ($R^2 = 0.92$; Fig. 2). The different affinity of minerals to host REEs can lead to fractionation processes; while LREEs tend to occupy the larger sites of 8–10 coordination numbers and concentrate preferably in carbonates and phosphates, Y and HREEs occupy 6–8 coordination sites and are abundant in oxides and a part of phosphates

(Dill 2010). However, no differences were observed between Y and both groups of REEs; similar correlations ($R^2 = 0.89-0.91$) were found in waters.

Scandium concentrations in surface waters are also generally very low, in the parts per trillion range (Samson and Chassé 2016). In the case of Poderosa, the average concentration of Sc is $53 \mu\text{g L}^{-1}$, with values ranging from 14 to $158 \mu\text{g L}^{-1}$ (Table 2). Trivalent scandium is sometimes compared with Y^{3+} and the trivalent REEs with respect to their geochemical behavior (Wood and Samson 2006), however a poor correlation was observed between Sc and these elements (Fig. 2) in Poderosa outflows. Although no simple correlation is observed between Sc and Si and above all Al, a general trend seems to exist, although the highest Sc concentrations did not coincide with the highest concentrations of Al and Si (Fig. 2).

Due to their low concentrations in natural waters, below the parts per billion range (e.g., Chen 2006; Shotyk et al. 2017), Ga has received scarce attention in the past. However, their use in the modern semiconductor industry and other applications, has caused increasing environmental concentrations. Chen (2006) reported Ga concentrations of up to $19 \mu\text{g L}^{-1}$ in groundwater of an industrialized area of Taiwan. Sulfide mining may also lead to increasing levels of Ga; concentrations of up to $184 \mu\text{g L}^{-1}$ were observed in Poderosa outflows (average value of $80 \mu\text{g L}^{-1}$; Table 2). Gallium has a crustal geochemistry similar to that of Al, however they might be fractionated during weathering processes (Shiller and Frilot 1996). Figure 3 shows the relationship of Ga and other elements in the Poderosa outflows. As can be seen, an apparent correlation between Al and Ga exists, however the deviation of some samples from this trend may suggest certain fractionation processes during mineral weathering in Poderosa galleries. Gallium, as well as P and Rb, can be incorporated into feldspars (Deer et al. 2001). This fact could explain the similar evolution followed by these elements in Figure 3. However, Ga also exhibited the same trend than other elements commonly found in sulfides, such as S, Cd, Mo, Fe, or Co (Fig. 3; some not shown).

A similar behavior would be expected for Tl whose concentrations range from 28 to $73 \mu\text{g L}^{-1}$ (average value of $42 \mu\text{g L}^{-1}$; Table 2). Thallium can be incorporated not only into the alkali micas and feldspars by substitution of K^+ , Rb^+ , and Sr^+ , due to its similar geochemical affinity (Law and Turner 2011) but also in sulfides such as pyrite, chalcopyrite, sphalerite, galena or marcasite (Lis et al. 2003). The high correlation observed between Tl and Rb, and to a lesser extent K, points out at alkali feldspars and micas as most probable Tl carrier minerals in Poderosa. On the other hand, the lack of correlation with Sr may suggest the existence of geochemical controls for the latter element inside the galleries. In addition, Tl showed high correlation with elements

contained in sulfide (Fig. 3) such as As, Co and Pb (not shown), with lower values observed for Fe.

Seasonal variations of TCEs concentrations

The existence of long-term fluctuations in chemical composition of AMD outflows in sulfide mining-related anthropogenic aquifers has been widely reported, especially in the IPB (e.g. Cánovas et al. 2016; Caraballo et al. 2016); and has been attributed to the coupling of hydrogeological and geochemical processes inside the underground system. Thus, Caraballo et al. (2016) identified three different processes responsible for the recorded long-term variability in these AMD outflows: 1) pyrite and enclosing rocks dissolution, responsible for the background element concentrations; 2) evaporitic salts precipitation/dissolution processes, which act as temporal sinks/sources of metals inside the galleries during the inter-annual dry and wet periods, and 3) rainfall fluctuations, which control the AMD flow rate variability.

The Poderosa outflow was characterized by low discharge values, ranging from 0.58 and 12 L s⁻¹ (average values of 1.1 L s⁻¹; Table 1), mainly controlled by recharge processes in the mine galleries after rainfalls. Figures 4 and 5 show the seasonal hydrochemical variations observed in AMD outflows from Poderosa. As can be seen, the baseline flow from Poderosa is around 1 L s⁻¹, however intense episodes of rainfalls lead to sharp increases of flow; up to 5.3 L s⁻¹ on April 22nd 2016, 11.5 L s⁻¹ on May 11th 2016, 2.8 L s⁻¹ on December 16th 2016 and 11 L s⁻¹ on February 13th 2017. The increase in flow caused a sharp increase in EC values (up to 14 mS cm⁻¹) and a decrease of pH values (down to 2; Fig. 4). These sharp increases in flow also caused a different response among elements (Fig. 5). For example, Fe and especially As and Pb increased drastically their concentrations coinciding with the flow increases, as can be seen mainly during the highest flow observed on May 11th 2016; e.g. from 1787 to 2295 mg L⁻¹ of Fe, from 2865 to 4563 µg L⁻¹ of As, and from 209 to 544 µg L⁻¹ of Pb. This increase in concentration may be attributed to the dissolution of soluble salts previously precipitated inside the galleries. These processes have been already reported in both underground and surface mining environments (e.g. Hammarstrom et al. 2005; Cánovas et al. 2016). Both water level fluctuations and temperature increasing by exothermic oxidation of sulfides inside the galleries contribute to intense evaporation of the generated metal-rich waters. Such evaporative processes lead to the precipitation of sulfate salts, whose composition strongly depends on the chemical composition of waters from they come from (Buckby et al. 2003). Thus, metal retention is observed when water level drops inside the galleries and while a release is caused when water level rises. Among the TCEs studied, only TI seems to be slightly affected by sulfate salts precipitation/dissolution,

with a slight increase in concentration during the first flow peak (Fig. 5). Other elements, such as Ga and Sc, exhibited a different response upon flow increases; Ga did not show variations while Sc concentration decreased during the first peak while increased in the second peak. In the case of REEs and Y, their concentrations decreased noticeably coinciding with these flow peaks (from 7.1 to 4.3 mg L⁻¹ of REEs and from 1.38 to 0.82 mg L⁻¹ of Y; Fig. 5), which seems to indicate that these elements are not affected by sulfate salts formation, and the decrease may be due to dilution processes.

Apart from dissolution of soluble salts during sharp increases of water level inside the galleries, other geochemical processes can provoke element concentration variations in the AMD outflows. These processes can be inferred from mass ratios in AMD solutions. For example, the Fe/SO₄ mass ratio in AMD sources may provide information on the closeness of waters to the weathering products derived from pyrite oxidation, being 0.29 the theoretical value of pyrite dissolution. Lower values may therefore indicate geochemical processes removing Fe from solution (i.e. secondary Fe minerals precipitation) or the oxidation of non-Fe sulfides. As can be seen in Figure SM2, values were slightly lower (0.20-0.25) than that theoretical for pyrite dissolution (0.29) except at the end of the study period. Table 3 shows the saturation indices of Poderosa outflows with respect to some minerals which could precipitate from these waters (i.e. oxides, sulfates, and phosphates). It can be seen that waters remained chiefly subsaturated with respect to main Fe secondary minerals, such as schwertmannite (average SI of -18), jarosite (SI of -2.0), and Fe(OH)₃ (SI of -4.6). Only in the case of strengite (FePO₄·2H₂O), waters from Poderosa are predicted to be oversaturated (SI of 0.68), however the low concentration of P (average of 0.77 mg L⁻¹) with respect Fe (1545 mg L⁻¹) discards this cause as responsible for the low Fe/SO₄ ratios. Precipitation/dissolution cycles of evaporitic sulfate salts would also explain such values, however, slight differences were observed during flow increases, when dissolution of salts may occur. Therefore, the oxidation of non-Fe sulfides such as chalcocite and covellite, present among sulfides exploited in Poderosa, may be the responsible for such Fe/SO₄ mass ratio values. Thus, the higher Fe/SO₄ mass ratio values would indicate the preferential contact of waters with pyrite-rich mineralization inside the galleries, while lower values would indicate a higher contact with non-Fe sulfides.

Technology metals seem to be preferentially released in different periods than sulfide-related elements (Fig. 5). For example, Sc and Ga reached their maximum concentrations after flow increases, although the peak timing differs among them; Sc peak took place sooner than Ga peak after the second noticeable flow increase (Fig. 5). In the case of REE and Y, these elements decreased notably their concentrations coinciding with the flow increases, reaching, in turn,

their maximum concentrations during the dry periods (Fig. 5). Therefore, it can be seen a different pattern of metal/loid release from Poderosa outflows. This pattern can be clearly seen in Figure SM1, where mass ratios between technology metals and Fe are represented; ratios decreased during the rainy periods and increased during the dry period. However, some differences can be observed among technology metals, as evidenced by the different timing of ratio peaks, while ratios of REEs, Y (not shown), and Tl peaked at the end of the dry period, Sc did immediately after the flow increases. This can be also seen in the REE/Ga mass ratio, which remain almost constant to $0.03\text{--}0.04 \times 10^3$ during the rainy period but increases notably during the dry period (Fig. SM1). As far as we know, there are not reported cases in literature about precipitation of secondary minerals hosting technology metals; only secondary Al sulfate minerals have shown affinity by REEs (Ayora et al. 2016); however, subsaturation is predicted by geochemical codes. The precipitation of phosphate may cause the removal of REEs and Y from Poderosa outflows; waters were predicted to be supersaturated in REEs phosphate (Table 3), however these minerals have not been reported in these environments and, in any case, may have low importance considering the low concentration of P (0.77 mg L^{-1} , Table 1).

The ratio Al/Ga has been traditionally used to study chemical weathering and delivery of metals from rocks to the ocean (Shiller and Frilot 1996). However, there is not a clear pattern through the time (Fig. SM1). The intensity of chemical weathering can be examined using the ratio of dissolved silica to alkali cations due to the higher solubility of these elements (i.e. Na and K) in the weathering process than Si (Shiller and Frilot 1996). Thus, higher Si/Na+K ratios would indicate strong chemical weathering conditions while lower values should indicate weaker conditions. Figure 6 shows the concentration of studied technology metals against the Si/Na+K mass ratio. As can be seen, Ga, Sc and Tl follow an apparent inverse relationship with respect the Si/Na+K mass ratio, while REE and Y (this element not shown) seem to follow a positive trend (Fig. 6). This opposing trend could be indicative of different affinity of technology elements for resistant minerals. Therefore, REE and Y would be preferentially leached from the rocks upon strong chemical weathering conditions (e.g. dry season, high residence time), once the more soluble metals are leached from the rocks upon milder conditions (e.g. wet season, dilution by fresh water). In this case, a good correlation of REE and Y with Si and Al would be expected, however, these elements show a better correlation with Ca and Mg (Fig. 2). This hypothesis should be confirmed in further studies.

Speciation of TCEs

The bioavailability, transport and retention of metals in the natural environment strongly depend on their chemical speciation (Tipping et al. 2016). This is particularly important in AMD systems where the precipitation of secondary minerals from sulfide oxidation may constitute important sinks of metals (Nordstrom 2011). The dominant oxidation state of REEs and Y in aqueous solution is +3, and only under strong oxidizing conditions, or extremely reducing conditions, Ce^{4+} , Sm^{2+} , Eu^{2+} and Yb^{2+} are formed (Wood 1990). Trivalent REEs and Y should exhibit strong, predominantly electrostatic complexing with hard ligands such as fluoride, sulfate, phosphate, carbonate and hydroxide, while complexing of these metals with chloride and nitrate is moderately weak (Wood 1990). Although fluoride is considered an important complexing agent of REEs in acidic sulfate waters, its association with Al^{3+} , abundant in AMD systems, makes this anion to have little influence on REEs (Gimeno et al. 2000). In such systems, where concentrations of dissolved sulfate exceed noticeably those of other anions (i.e. phosphate, fluoride, chloride, etc.), REEs complexing with sulfate is favored at acidic pH (e.g. Olías et al. 2018). The chemical speciation modeled for the Poderosa acidic waters showed lanthanide-sulfate complexes ($\text{Ln}(\text{SO}_4)^+$ and $\text{Ln}(\text{SO}_4)_2^-$) accounted for 86-89% of REEs complexes, with minor importance for free metal (10-14%, Fig. SM3). The relatively small radii of Sc^{3+} and Ga^{3+} , somewhat larger than Al^{3+} , and their high charges make these elements to be considered as hard acids, and be preferentially bonded to hard bases such as OH^- and F^- in aqueous solutions (Wood and Samson 2006). In the case of Sc, the geochemical code predicts the predominance of sulfate complexes (average value of 96%), over free Sc^{3+} (4%; Fig. SM4). The opposite trend is observed for Ga, which is mainly found as free Ga^{3+} (96%; Fig. SM4).

Metal speciation can play an important role in metal removal by adsorption/coprecipitation processes. The occurrence of these free metal species could lead to the incorporation of REEs and Ga into Fe and Al minerals by replacement of Fe(III) and Al into the crystal lattice, however, as abovementioned, waters remained subsaturated with respect these minerals. On the other hand, Tl(I) was the dominant species in Poderosa outflows as reported in other aqueous systems, where oxidation of Tl(I) to Tl(III) is only expected in the presence of extremely strong oxidants and high alkalinity (Kaplan and Mattigod 1998; Campanella et al. 2018). Jarosite has been reported as a strong scavenger of Tl (Dutriza et al. 2005), however, waters remained subsaturated with respect to this mineral.

CONCLUSIONS

This work reports enhanced levels of technology metals (i.e. REEs, Y, Sc, Ga and Tl) in AMD outflows from an underground mine in SW Spain. The primary source of these technology metals

seems to be the host rocks surrounding sulfides in this mine site, which suffered a strong chemical weathering due to the high acidity released during sulfide oxidation. REEs and Y showed a good correlation with Ca and Mg, while Sc had it with Al. Gallium and Tl showed good correlations with both crustal (e.g. Rb) and sulfide-related elements (e.g. Co, Cd, etc.). The concentration of these elements in waters seems not to be controlled by precipitation of secondary minerals but by the intensity of chemical weathering inside the galleries. Thus, a general trend in the release of technology metals is observed; those with a greater affinity by less resistant minerals (Sc, Ga and Tl) are initially released upon mild weathering conditions while those with a greater affinity by more resistant minerals are afterwards released upon stronger chemical conditions. These enhanced levels of TCEs in the AMD leachates studied point out to these waters as a promising source that could be exploited as source of raw materials in the near future. However, further studies are needed at laboratory and field scale to confirm the hypothesis raised about the source and mobility of technology metals in this study and widen the knowledge in other geological settings.

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Supplementary material

This paper contains a Supplementary Material section, which will be made available from the journal website when the manuscript be published

Conflicts of Interest

The authors declare no conflicts of interest.

References

- Abdou M, Schäfer J, Hu R, Gil-Díaz T, Garnier C, Brach-Papa C, Chiffoleau JF, Charmasson S, Giner F, Dutruch L, Blanc G (2019). Platinum in sediments and mussels from the northwestern Mediterranean coast: Temporal and spatial aspects. *Chemosphere* **215**, 783–792. <https://doi.org/10.1016/j.chemosphere.2018.10.011>
- Ayora C, Macías F, Torres E, Lozano A, Carrero S, Nieto JM, 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. <https://doi.org/10.1021/acs.est.6b02084>.
- Bau M, Schmidt K, Pack A, Bendel V, Kraemer D. (2018). The European Shale: An improved data set for normalisation of rare earth element and yttrium concentrations in environmental and biological samples from Europe. *Appl. Geochem.* **90**, 142–149. <https://doi.org/10.1016/j.apgeochem.2018.01.008>.
- Buckby T, Black S, Coleman ML, Hodson ME (2003). Fe sulphate rich evaporative mineral precipitates from the río Tinto, Southwest Spain. *Mineral. Mag.* **67** (2), 263–278. <https://doi.org/10.1180/0026461036720104>.
- Campanella B, D’Ulivo A, Ghezzi L, Onor M, Petrini R., Bramanti E (2018). Influence of environmental and anthropogenic parameters on thallium oxidation state in natural waters. *Chemosphere* **196**, 1–8. <https://doi.org/10.1016/j.chemosphere.2017.12.155>.
- Cánovas CR, Macías F, Pérez-López R (2016). Metal and acidity fluxes controlled by precipitation/dissolution cycles of sulfate salts in an anthropogenic mine aquifer. *J. Contam. Hydrol.* **188**, 29–43. <https://doi.org/10.1016/j.jconhyd.2016.02.005>.
- Cánovas CR, Macías F, Olías M (2018). Hydrogeochemical behavior of an anthropogenic mine aquifer: Implications for potential remediation measures. *Sci. Total Environ.* **636**, 85–93. <https://doi.org/10.1016/j.scitotenv.2018.04.270>.
- Caraballo MA, Macías F, Nieto JM, Ayora C (2016). Long term fluctuations of groundwater mine pollution in a sulfide mining district with dry Mediterranean climate: implications for water resources management and remediation. *Sci. Total Environ.* **539**, 427–435. <https://doi.org/10.1016/j.scitotenv.2015.08.156>.

- 423 Casiot C, Egal M, Bruneel O, Neelam V, Parmentier M, Elbaz-Poulichet F (2011). Predominance
424 of aqueous Tl(I) species in the river system downstream from the abandoned Carnoules mine
425 (Southern France). *Environ. Sci. Technol.* **45**, 2056-2064. DOI: 10.1021/es102064r
- 426 Chakhmouradian AR, Wall F (2012). Rare Earth Elements: minerals, mines, magnets (and more).
427 *Elements* **8**, 333-340. DOI: 10.2113/gselements.8.5.333
- 428 Chen HW (2006). Gallium, indium, and arsenic pollution of groundwater from a semiconductor
429 manufacturing area of Taiwan. *Bull. Environ. Contam. Toxicol.* **77**, 289-296.
430 <https://doi.org/10.1007/s00128-006-1062-3>.
- 431 Cobelo-García A, Filella M, Croot P, Frazzoli C, Du Laing G, Ospina-Alvarez N, Rauch S, Salaun P,
432 Schäfer J, Zimmermann S (2015). COST action TD1407: network on technology-critical elements
433 (NOTICE)—from environmental processes to human health threats. *Environ. Sci. Pollut. Res.* **22**,
434 15188-15194. <https://doi.org/10.1007/s11356-015-5221-0>.
- 435 Deer WA, Howie RA, Zussman J (2001). Rock-forming Minerals. Volume 4A. Framework silicates:
436 Feldspars. Second Edition. The Geological Society, London, 972 pp.
- 437 Dill HG (2010). The “chessboard” classification scheme of mineral deposits: mineralogy and
438 geology from aluminum to zirconium. *Earth Sci. Rev.* **100**, 1–420.
439 <http://dx.doi.org/10.1016/j.earscirev.2009.10.011>.
- 440 Dutrizac JE, Chen TT, Beauchemin S (2005). The behaviour of thallium (III) during jarosite
441 precipitation. *Hydrometallurgy* **79**, 138–153. <https://doi.org/10.1016/j.hydromet.2005.06.003>
- 442 Eggert RG (2011). Minerals go critical. *Nat Chem* **3**, 688–691.
443 <https://doi.org/10.1038/nchem.1116>.
- 444 Ferreira da Silva E, Bobos I, Xavier Matos J, Patinha C, Reis AP, Cardoso Fonseca E (2009).
445 Mineralogy and geochemistry of trace metals and REE in volcanic massive sulfide host rocks,
446 stream sediments, stream waters and acid mine drainage from the Lousal mine area (Iberian
447 Pyrite Belt, Portugal). *Appl. Geochem.* **24**, 383–401.
448 <https://doi.org/10.1016/j.apgeochem.2008.12.001>.
- 449 Gimeno MJ, Auqué L, Nordstrom DK (2000). REE speciation in low- temperature acidic waters
450 and the competitive effects of aluminum. *Chem. Geol.* **165**, 167–180.
451 [https://doi.org/10.1016/S0009-2541\(99\)00166-7](https://doi.org/10.1016/S0009-2541(99)00166-7).

- 452 Gopalapillai Y, Chakrabarti CL, Lean DRS (2008). Assessing toxicity of mining effluents:
453 equilibrium- and kinetics-based metal speciation and algal bioassay. *Environ Chem* **5**(4), 307-315
454 <https://doi.org/10.1071/EN08027>.
- 455 Grande JA, Valente T, De la Torre ML, Santisteban M, Cerón JC, Pérez-Ostale E (2014).
456 Characterization of acid mine drainage sources in the Iberian Pyrite Belt: base methodology for
457 quantifying affected areas and for environmental management. *Environ. Earth Sci.* **71**, 2729.
458 <https://doi.org/10.1007/s12665-013-2652-0>.
- 459 Hammarstrom JM, Seal II RR, Meier AL, Kornfeld JM (2005). Secondary sulfate minerals
460 associated with acid drainage in the eastern US: recycling of metals and acidity in surficial
461 environments. *Chem. Geol.* **215**, 407–431. <https://doi.org/10.1016/j.chemgeo.2004.06.053>.
- 462 Hanson GN (1980). Rare-earth elements in petrogenetic studies of igneous systems. *Annu. Rev.*
463 *Earth Planet. Sci.* **8**, 371–406.
- 464 Isildar A, Rene ER, van Hullenbusch ED, Lens PNL (2018). Electronic waste as a secondary source
465 of critical metals: Management and recovery technologies. *Resour. Conserv. Recycl.* **135**, 296-
466 312. <https://doi.org/10.1016/j.resconrec.2017.07.031>.
- 467 Jin L, Ma L, Dere A, White T, Mathur R, Brantley SL (2017). REE mobility and fractionation during
468 shale weathering along a climate gradient. *Chem. Geol.* **466**, 352–379.
469 <http://dx.doi.org/10.1016/j.chemgeo.2017.06.024>.
- 470 Kaplan D, Mattigod S. (1998). Aqueous geochemistry of thallium. In: Nriagu, J. (Ed.). Thallium in
471 the Environment. John Wiley & Sons Inc., New York, pp. 15-29.
- 472 Krausmann F, Gingrich S, Eisenmenger N, Erb KH, Haberl H, Fischer-Kowalski M (2009). Growth
473 in global materials use, GDP and population during the 20th century. *Ecol. Econ.* **68**, 2696–2705.
474 <http://dx.doi.org/10.1016/j.ecolecon.2009.05.007>.
- 475 Law S, Turner A (2011). Thallium in the hydrosphere of south west England. *Environ. Poll.* **159**,
476 3484–3489. doi:10.1016/j.envpol.2011.08.029.
- 477 Leybourne MI, Cousens BL (2005). Rare earth elements (REE) and Nd and Sr isotopes in
478 groundwater and suspended sediments from the Bathurst Mining Camp, New Brunswick:
479 water–rock reactions and elemental fractionation. In Rare Earth Elements in Groundwater Flow
480 Systems (ed. K. H. Johannesson). Springer, Dordrecht, pp. 254–293.
- 481 Leybourne MI, Clark ID, Goodfellow WD (2006). Stable isotope geochemistry of ground and
482 surface waters associated with undisturbed massive sulfide deposits; constraints on origin of

- 483 waters and water–rock reactions. *Chem. Geol.* **231**, 300–325.
484 <https://doi.org/10.1016/j.chemgeo.2006.02.004>.
- 485 Leybourne MI, Johannesson KH (2008). Rare earth elements (REE) and yttrium in stream waters,
486 stream sediments, and Fe–Mn oxyhydroxides: fractionation, speciation, and controls over REE+
487 Y patterns in the surface environment. *Geochim. Cosmochim. Acta* **72**, 5962–5983.
488 doi:10.1016/j.gca.2008.09.022.
- 489 Lis J, Pasieczna A, Karbowska B, Zembruski W, Lukaszewski Z (2003). Thallium in soils and stream
490 sediments of a Zn–Pb mining and smelting area. *Environ. Sci. Technol.* **37**, 4569–4572. DOI:
491 10.1021/es0346936.
- 492 Migaszewski ZM, Gałuszka A. (2015). The characteristics, occurrence, and geochemical behavior
493 of rare earth elements in the environment: a review. *Crit. Rev. Environ. Sci. Technol.* **45**, 429–
494 471. DOI: 10.1080/10643389.2013.866622.
- 495 Migaszewski ZM, Gałuszka A, Dołęgowska S (2019). Extreme enrichment of arsenic and rare
496 earth elements in acid mine drainage: case study of Wiśniówka mining area (south-central
497 Poland). *Environ. Pollut.* **244**, 898–906. <https://doi.org/10.1016/j.envpol.2018.10.106>.
- 498 Nash W, Crecraft H (1985). Partition coefficients for trace elements in silicic magmas. *Geochim.*
499 *Cosmochim. Acta* **49** (11), 2309–2322.
- 500 NIST (2004). In: Martell, A.E., Smith, R.M. (Eds.), NIST Standard Reference Database 46 Version
501 8.0, Gaithersburg, USA.
- 502 Noack CW, Dzombak DA, Karamalidis AK (2014). Rare earth element distributions and trends in
503 natural waters with a focus on groundwater. *Environ. Sci. Technol.* **48**(8), 4317–4326
504 <https://doi.org/10.1021/es4053895>.
- 505 Nordstrom DK (2011). Hydrogeochemical processes governing the origin, transport and fate of
506 major and trace elements from mine wastes and mineralized rock to surface waters. *Appl.*
507 *Geochem.* **26**, 1777–1791. DOI: 10.1016/j.apgeochem.2011.06.002.
- 508 Olías M, Cánovas CR, Basallote MD, Lozano A (2018). Geochemical behaviour of rare earth
509 elements (REE) along a river reach receiving inputs of acid mine drainage. *Chem. Geol.* **493**, 468–
510 477. <https://doi.org/10.1016/j.chemgeo.2018.06.029>.
- 511 Pagano G, Guida M, Tommasi F, Orce R (2015). Health effects and toxicity mechanisms of rare
512 earth elements. Knowledge gaps and research prospects. *Ecotoxicol. Environ. Saf.* **115**, 40–48.
513 <https://doi.org/10.1016/j.ecoenv.2015.01.030>.

- 514 Parkhurst DL, Appelo CAJ (2005). PHREEQC-2 Version 2.12: A Hydrochemical Transport Model.
515 <http://wwwbrr.cr.usgs.com>.
- 516 Pérez-López R, Delgado J, Nieto JM, Márquez-García B (2010). Rare earth element geochemistry
517 of sulphide weathering in the São Domingos mine area (Iberian Pyrite Belt): a proxy for fluid-
518 rock interaction and ancient mining pollution. *Chem. Geol.* **276**, 29–40.
519 <https://doi.org/10.1016/j.chemgeo.2010.05.018>.
- 520 Pinedo Vara I. (1963). Piritas de Huelva. Su historia, minería y aprovechamiento. Summa.
521 Madrid, Spain (1003 pp.).
- 522 Romero-Freire A, Joonas E, Muna M, Cossu-Leguille C, Vignati DAL, Giamberini L (2019).
523 Assessment of the toxic effects of mixtures of three lanthanides (Ce, Gd, Lu) to aquatic biota.
524 *Sci. Total Environ.* **661**, 276–284. DOI: 10.1016/j.scitotenv.2019.01.155.
- 525 Samson IM, Chassé M (2016). Scandium. In: White W. (eds) Encyclopedia of Geochemistry.
526 Encyclopedia of Earth Sciences Series. Springer, Cham.
- 527 Shiller AM, Frilot DM (1996). The geochemistry of gallium relative to aluminum in Californian
528 streams. *Geochem. Cosmochim. Acta* **60**, 1323–1328.
- 529 Shotyk W, Bicalho B, Cuss CW, Donner MW, Grant-Weaver I, Haas-Neill S, Javed MB, Krachler M,
530 Noernberg T, Pelletier R, Zaccone C (2017). Trace metals in the dissolved fraction (<0.45 µm) of
531 the lower Athabasca River: analytical challenges and environmental implications. *Sci. Total*
532 *Environ.* **580**, 660–669. <https://doi.org/10.1016/j.scitotenv.2016.12.012>.
- 533 Tipping E, Loftis S, Stockdale A (2016). Metal speciation from stream to open ocean: modelling
534 v. measurement. *Environ. Chem.* **13**, 464–477. <http://dx.doi.org/10.1071/EN15111>.
- 535 Tremel A, Masson P, Sterckeman T, Baize D, Mench M (1997). Thallium in French agrosystems—
536 I. Thallium contents in arable soils. *Environ. Pollut.* **95**, 293–302. [https://doi.org/10.1016/S0269-](https://doi.org/10.1016/S0269-7491(96)00145-5)
537 [7491\(96\)00145-5](https://doi.org/10.1016/S0269-7491(96)00145-5).
- 538 Verweij W (2017). Manual for CHEAQS Next, a Program for Calculating Chemical Equilibria in
539 Aquatic Systems.
- 540 Willis SS, Johannesson KH (2011). Controls on the geochemistry of rare earth elements in
541 sediments and groundwaters of the Aquia aquifer, Maryland, USA. *Chem. Geol.* **285** (1–4),
542 32–49. <https://doi.org/10.1016/j.chemgeo.2011.02.020>.

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

Wood SA, Samson IM (2006). The aqueous geochemistry of gallium, germanium, indium and scandium. *Ore Geol. Rev.* **28**, 57–102. <https://doi.org/10.1016/j.oregeorev.2003.06.002>.

Worrall F, Pearson DG (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](https://doi.org/10.1016/S0016-7037(01)00662-7).

Yu JY, Heo B, Choi IK, Cho JP, Chang HW (1999). Apparent solubilities of schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage. *Geochim. Cosmochim. Acta* **63** (19–20), 3407–3416.

Figure captions

Figure 1. Figure 1. Detailed pictures of the Poderosa mine adit and the Parshall flume installed to monitor flow variations.

Figure 2. Relationships among REEs, Y, Sc and some metals commonly found in host rocks (i.e. Ca, Mg, Si, and Al).

Figure 3. Relationships among Ga, Tl and elements commonly found in host rocks (i.e. Al, Rb, P, K, Sr, Rb and Mo) and sulfides (i.e. Fe, S, Cd, Co, As and Mo).

Figure 4. Seasonal evolution of some physico-chemical parameters (i.e. pH, EC and ORP) in AMD outflows from Poderosa mine with respect to flow variations and rainfalls.

Figure 5. Seasonal evolution of some metals and metalloids concentrations in AMD outflows from Poderosa mine with respect to flow variations and rainfalls.

Figure 6. Relationships between some technology metals studied with the ratio Si/Na+K (see text for explanation).

Table captions

Table 1. Basic statistics of main physico-chemical variables (i.e. EC, pH, ORP, flow (Q)) and chemical composition of AMD outflows from Poderosa mine

572 **Table 2.** Basic statistics of selected technology metals (i.e. Ga, Sc, Tl, Y and REEs) concentrations
573 in AMD outflows from Poderosa mine. *Ce and *Eu: Ce and Eu anomaly (see text for
574 explanation).

575 **Table 3.** Basic statistics of saturation indices of selected minerals from AMD outflows of
576 Poderosa mine.

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	EC (mS cm ⁻¹)	pH	ORP (mV)	Q (L s ⁻¹)
n	83	82	82	82
Minimum	6.1	1.7	354	0.58
Maximum	14	2.4	609	12
Average	9.9	2.0	409	1.1
Median	9.7	2.0	404	0.89
Standard Deviation	1.6	0.2	42	1.3
Percentil 25	8.9	1.9	380	0.68
Percentil 75	11	2.1	428	1.1

Table 1. Basic statistics of main physico-chemical variables (i.e. EC, pH, ORP, flow

<i>Main Elements (mg L⁻¹)</i>										
Al	Ca	Fe	K	Mg	Na	P	SO ₄	Si	Li	V
83	83	83	83	83	82	83	83	83	83	81
248	71	1052	8.8	94	11	0.32	5022	31	98	28
433	144	3241	29	177	22	2.7	12078	46	302	150
344	125	1545	14	153	18	0.77	6781	39	178	41
344	127	1435	13	157	18	0.65	6492	40	178	39
29	12	333	3.9	13	1.8	0.33	1003	2.8	29	14
331	120	1354	11	150	17	0.60	6265	38	168	36
356	133	1593	14	160	19	0.82	7073	41	186	42

(Q)) and chemical composition of AMD outflows from Poderosa mine

Trace elements (µg L ⁻¹)										
Mn	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Cd	Sb
83	83	83	83	83	83	83	81	83	83	81
2325	802	77	59490	58020	1625	26	42	81	234	22
6628	1838	240	148300	95246	4961	362	116	228	462	167
5284	1158	124	82200	75981	2562	55	65	164	330	34
5366	1126	119	80550	76060	2324	42	61	166	328	29
700	182	26	12950	5919	702	52	14	17	37	17
5103	1059	108	74765	73955	2185	37	56	159	307	28
5657	1202	135	86100	79060	2674	51	70	172	348	34

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Th	U	Pb
82	83	83
46	36	83
213	425	562
83	55	174
67	50	133
31	42	100
63	47	109
97	53	210

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	Ga	Sc	Tl	Y	La	Ce	Pr
n	83	82	82	83	83	83	83
Minimum	54	14	28	720	489	1471	198
Maximum	184	158	73	1993	1569	3656	510
Average	80	53	42	1535	1136	3065	401
Median	75	49	38	1567	1181	3174	412
Standard Deviation	21	26	9.4	173	155	377	48
Percentil 25	69	42	36	1479	1075	2900	381
Percentil 75	82	54	48	1621	1207	3270	431

Table 2. Basic statistics of selected technology metals (i.e. Ga, Sc, Tl, Y and REEs) conce

Technology metals ($\mu\text{g L}^{-1}$)										
Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
83	83	83	83	83	83	83	83	83	83	83
802	225	25	227	34	180	29	69	8	44	5
2076	551	79	599	91	463	78	181	20	121	14
1776	462	67	503	72	373	61	147	17	90	10
1803	471	69	521	73	376	61	149	17	90	10
201	55	9.0	67	8.6	44	7.5	18	2.0	10	1.2
1724	436	64	466	69	353	58	140	16	87	10
1867	493	73	554	77	399	66	160	18	96	11

Concentrations in AMD outflows from Poderosa mine. *Ce and *Eu: Ce and Eu anomaly (see text for explanation)

REE	% LREE	% MREE	%HREE	*Ce	*Eu
83	83	83	83	83	83
3793	83%	11%	3.5%	0.83	0.48
9730	85%	13%	4.2%	1.2	0.81
8155	84%	12%	3.7%	1.1	0.64
8381	84%	12%	3.6%	1.1	0.64
965	0.36%	0.33%	0.12%	0.04	0.04
7809	84%	12%	3.6%	1.1	0.64
8685	84%	13%	3.7%	1.1	0.65

lanation)

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	Fe(OH) ₃	Schwertmannite	Alunite	Jarosite
n	83	83	83	83
Minimum	-6.39	-28.23	-8.25	-5.58
Maximum	0.00	-4.27	-0.39	3.98
Mean	-4.63	-18.08	-5.61	-2.04
Median	-5.02	-18.42	-5.76	-2.10
Standard Deviation	1.42	4.56	1.63	1.62
Percentil 25th	-5.39	-21.18	-6.65	-3.17
Percentil 75th	-4.54	-15.23	-5.31	-1.26

	Strengite	La	Ce	Pr
n	83	83	83	83
Minimum	-0.40	-0.89	0.33	-0.78
Maximum	1.74	0.40	1.64	0.45
Mean	0.68	-0.14	1.03	-0.11
Median	0.64	-0.17	1.05	-0.11
Standard Deviation	0.40	0.32	0.31	0.31
Percentil 25th	0.37	-0.41	0.78	-0.36
Percentil 75th	0.92	0.15	1.29	0.17

Table 3. Basic statistics of saturation indices of selected minerals from AMD outflows

<i>Oxides, hydroxides and sulfates</i>						
Hexahydrite	Anglesite	Melanterite	Copiapite	Coquimbite	Alunogen	Celestite
83	83	83	83	83	83	83
-3.32	-0.96	-5.05	-12.99	-44.66	-7.45	-1.97
-0.03	-0.03	-1.98	-7.50	-41.67	-6.88	-1.60
-2.87	-0.67	-2.48	-10.00	-43.33	-7.15	-1.74
-3.14	-0.72	-2.43	-9.91	-43.28	-7.15	-1.74
0.86	0.20	0.44	1.39	0.75	0.09	0.05
-3.17	-0.83	-2.54	-11.13	-44.00	-7.20	-1.76
-3.12	-0.54	-2.28	-8.75	-42.70	-7.09	-1.71
<i>Phosphates (LnPO₄:10H₂O)</i>						
Nd	Sm	Eu	Gd	Tb	Dy	Er
83	83	83	83	83	83	83
-0.73	-1.47	-2.55	-1.22	-2.49	-1.78	-2.24
0.54	-0.11	-0.13	0.02	-0.13	-0.10	-0.10
-0.05	-0.75	-1.64	-0.51	-1.63	-0.95	-1.47
-0.07	-0.79	-1.81	-0.52	-1.75	-0.99	-1.56
0.33	0.33	0.60	0.32	0.56	0.42	0.46
-0.34	-1.03	-2.08	-0.77	-2.02	-1.30	-1.82
0.25	-0.45	-1.46	-0.21	-1.43	-0.71	-1.22

of Poderosa mine

Gypsum

83
-0.79
-0.47
-0.60
-0.60
0.05
-0.62
-0.57

Yb

83
-2.59
-0.15
-1.77
-1.91
0.57
-2.18
-1.58

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SUPPORTING INFORMATION**Enhanced levels of technology critical metals in mine waters: the case of the Poderosa sulfide mine (SW Spain)**

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Figure SM1. European Shale (EUS) normalized REE pattern of Poderosa mine outflows.

Figure SM2. Evolution of different mass ratios in Poderosa outflows (Sc/Fe, REE/Ga, Ti/Fe and Al/Ga should be multiplied by 1000).

Figure SM3. Average values of REE speciation in Poderosa outflows

Figure SM4. Average values of Ga and Sc speciation in Poderosa outflows