Trace element-mineral associations in modern and ancient iron terraces in acid drainage environments

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ABSTRACT

Iron-rich sediments commonly cover riverbeds that have been affected by acid drainage associated with sulfide-mineral oxidation. Freshly-formed precipitates correspond to poorly-crystalline oxyhydroxysulfates that recrystallize over time. This study examined the distribution and mineral association of trace elements (e.g., As, Cu, Zn) in modern and ancient (~6 Ma) Fe terraces in the Tinto river basin, Spain. The mineral composition of the terraces was determined by Raman μ-spectroscopy. Chemical digestions, electron probe microanalyses, and synchrotron-based μ-X-ray fluorescence mapping were used to examine As, Cu, and Zn distribution and corresponding mineral associations. Fresh precipitates at modern terrace surfaces were dominated by schwertmannite, which contained high As, Cu, Mn, and Zn concentrations. However, schwertmannite transforms into goethite over days to weeks in the deeper part of the current terraces and into hematite over centuries. Affinity for trace elements was generally highest for schwertmannite and lowest for hematite, which suggests that their retention by Fe terraces decreases during mineral transformation. Hence, schwertmannite acts as temporary sink for contaminants, which are again released over long time periods. These findings should be considered for management and treatment of possible water resources affected by acid mine drainage.

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1. Introduction

The natural weathering of outcropping sulfide ore bodies under meteoric conditions often produces acid rock drainage (ARD). Oxidative dissolution of sulfide minerals can lead to widespread acidification and contamination of water resources. Acid mine drainage (AMD) is generated where sulfide-mineral oxidation is accelerated, such as in mining operations that include excavations, earth works, and waste deposits. The consequences of AMD are generally more severe than ARD because mining activities increase exposed surface area of sulfide-bearing rocks (Amos et al., 2015; Lindsay et al., 2015; Olías et al., 2004; Webster et al., 1998). Dissolution of pyrite [FeS_2] and other sulfides in the presence of oxygen and water releases Fe(II) and SO_4, and generates protons causing acidification of waters. Potentially hazardous trace elements (e.g., As, Cu, Zn) associated to sulfides are also liberated during oxidative dissolution. Subsequent oxidation of Fe(II) can promote spontaneous precipitation of Fe(III) oxyhydroxides and oxyhydroxysulfates from acid-sulfate waters. These waters host extremophile bacterial species such as *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* that catalyze Fe(II) oxidation and accelerate subsequent precipitation reactions (Boon and Heijnen, 1998; Leduc et al., 2002).

Schwertmannite [$Fe_{16}O_{16}(OH)_{12}(SO_4)_2$] is thought to initially be the most thermodynamically stable phase in AMD impacted waters (Bigham et al., 1996). This poorly-crystalline oxyhydroxysulfate phase has a high capacity to sequester As and other potentially hazardous trace elements (Fernandez-Martinez et al., 2010; Fukushi et al., 2003, 2004). However, schwertmannite is metastable and transforms at pH 2–3 into more crystalline phases such as goethite [$FeO(OH)$] and jarosite [$KFe_3(SO_4)_2(OH)_6$] within weeks (Bigham et al., 1996; Davidson et al., 2008). The pH regimes often favor goethite over jarosite precipitation because jarosite forms at lower pH and higher Fe(III) concentrations (Acero et al., 2006). Goethite can subsequently transform into hematite [Fe_2O_3] over the centuries through diagenetic processes (Davidson et al., 2008; Langmuir, 1971). Some studies have pointed out that transformation rates could be affected by high concentrations of trace elements. While the overall rate of schwertmannite transformation to more stable phases decreases with increasing arsenate (Fukushi et al., 2003) and, to a lesser extent, chromate (Regenspurg and Peiffer, 2005) loading, the apparent rate of hematite formation increases in the presence of these ions (Ford, 2002).

Formation of Fe terraces within AMD impacted rivers begins with accumulation and consolidation of schwertmannite on riverbeds (Cáceres et al., 2013). Transformation of schwertmannite into goethite, jarosite, and hematite has previously been observed in Fe terraces within AMD-impacted rivers (Asta et al., 2010; Parviainen et al., 2015;

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Pérez-López et al., 2011). Several laboratory studies have also examined the behavior of As and other trace elements during these transformations; however, the potential for trace element removal or release during these transformations remains unclear. Whereas some studies claim that As sorption capacity increases with crystallinity, particularly at low pH (Gimenez et al., 2007; Mamindy-Pajany et al., 2011), others indicate that As is preferentially retained in less crystalline phases (Bowell, 1994). In addition, relatively few studies have examined trace element behavior during mineral transformations in Fe terraces in field settings (Acero et al., 2006; Pérez-López et al., 2011). Moreover, the research reported shows new insights in different trace elements behavior and uses more precise techniques. Such conflicting results or simple lack of information is also the case for other trace elements. Thus, the main objective of this study was to examine the distribution of trace elements in Fe terraces to assess their potential long-term fate during schwertmannite transformation under natural conditions. Samples from two distinct terraces in the Tinto River basin in SW Spain were collected: one from a newly-formed modern terrace in an AMD-impacted river and one from an ancient Fe terrace away from the modern river channel. These ancient terraces were formed under similar conditions as the currently-formed terraces and were isolated due to the river migration over time (Amils et al., 2007; Fernández-Remolar, 2003).

2. Materials and methods

2.1. Site description

The Iberian Pyrite Belt (IPB) is one of the largest massive sulfide provinces in the world, with original massive sulfide reserves estimated at more than 1700 Mt (Sáez et al., 1999). The IPB spans approximately 20,000 km^2 and hosts more than 100 mines, the majority of which are currently inactive. Mining activity on the IPB began approximately 4500 years ago (Nocete et al., 2014). Consequently, vast amounts of tailings and waste rock, and numerous open pits and underground workings, have exposed sulfide minerals to oxidative weathering and produced intense AMD. The legacy of the mining operations has severely degraded water quality in local catchments, which ultimately discharge from the Tinto and Odiel Rivers into the Atlantic Ocean. Consequently, these rivers account for a significant percentage of the total toxic element input to oceans worldwide (Nieto et al., 2013; Olías et al., 2016). Ore deposits are mainly comprised of Fe-rich sulfides such as pyrite [FeS_2], pyrrhotite [$Fe_{(1-x)}S$], chalcopyrite [$CuFeS_2$], and arsenopyrite [$FeAsS$], plus other metalliferous minerals including sphalerite [ZnS] and galena [PbS]. The most intensive mining in the area left several abandoned open pits, including Cerro Colorado, Peña del Hierro, and Corta Atalaya (Fig. 1a).

2.2. Sample collection and preparation

The river basins in the study area feature actively-forming modern terraces in AMD-affected rivers and ancient terraces that formed under similar conditions as the modern terraces but were isolated due to river migration over time (Amils et al., 2007; Fernández-Remolar, 2003). The age of the terraces denotes the maturation degree of the Fe phases. Thus, representative samples of the different stages of maturation were collected at El Alto de la Mesa (ancient terrace) and La Naya (modern terrace). The El Alto de la Mesa sample was collected from an ancient terrace consisting of an accumulation of Fe-oxides approximately 60 m above the modern riverbed (Fig. 1a,b). Stratigraphically, this terrace is defined as a fluvial point-bar sequence that was formed around 6 Ma ago (Messinian age) according to paleomagnetic dating (Essalhi et al., 2011). The modern terrace sample was collected from a freshly-formed terrace in a tributary of the Tinto River in the inactive Zarandas-La Naya mining area (Fig. 1a,c). Physicochemical parameters of the AMD-affected stream were measured in situ in the moment of the sample collection using a

portable Multiparametric Crison MM 40 + equipment (pH = 2.53, redox potential = 423 mV, electrical conductivity = 10.9 mS/cm). The sample thickness was approximately 10 cm, which represented the most recent sedimentation sequence.

In the laboratory, the fresh terrace sample was dried at room temperature in the presence of a desiccant to minimize any mineralogical transformations. Subsamples of interest from both terraces were selected, ground using an agate mortar and pestle, and subjected to conventional geochemical and mineralogical analysis. In addition, undisturbed samples from both terraces were prepared as polished thin sections; these were embedded in polyester epoxy, mounted on quartz glass slides using polyester resin, and polished to a final thickness of approximately 50 μm. All polishing was performed without water to avoid dissolution of water-soluble phases.

2.3. Geochemical and mineralogical analyses

The modern terraces are earthy and porous in nature, which limits the use of point techniques for quantitative chemical microanalysis (Cáceres et al., 2013). Thus, subsamples for detailed geochemical analyses were taken corresponding to color changes with depth. In contrast, bulk chemical analyses of the ancient terrace were conducted because separation was not possible. Subsamples of the modern terrace along with bulk ancient terrace samples (2 replicates per sample) were digested in aqua regia prepared using a 1:3 molar ratio of HNO_3 to HCl and heated at 90 °C to pseudo-dry the solution. These samples were then re-dissolved in 50 mL of a 10% HNO_3 solution and analyzed for major and trace elements by inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo Jarrel-Ash) and inductively coupled plasma-mass spectrometry (ICP-MS, X-series II Thermo), respectively.

An optical microscope (Nikon Eclipse LV100POL) operating in reflected light mode was used to examine mineralogical and textural characteristics of the samples in thin sections. Raman μ-spectroscopy can be used to identify Fe phases of varied crystallinity (e.g. Das and Hendry, 2011). Thus, Raman spectra were collected at the Andalusian Institute of Earth Sciences (Granada, Spain) according to methods described in detail by (Parviainen et al., 2015). Briefly, the Raman microscope (LabRAM HR, Jobin-Yvon Horiba, Japan) was operated in backscattering geometry with a 784 nm excitation beam focused using a confocal microscope (Olympus). Two to four replicate Raman spectra were collected using a Peltier-cooled charge coupled device (CCD) detector and 300 s acquisition time. Mineral transformations and sample degradation were minimized by using D0.3 and D0.6 filters, which were checked with synthetic and natural standards of known composition. A resolution of 3 cm^{-1} and spectral range of 150 to 1350 cm^{-1} were used. Furthermore, bulk powder X-ray diffraction (XRD) was performed by using PANanalytical X'Pert PRO with Cu Kα radiation at the Andalusian Institute of Earth Sciences. Diffractometer settings were: 45 kV, 40 mA, and a scan range of 4–60° 2θ and 4–70° 2θ for newly-formed and ancient samples, respectively, with 0.0084° 2θ step size and 100-s counting time per step. The results of XRD were consistent with the Raman spectroscopy observations and, for this reason, they are provided as Supplementary data (Fig. S1).

Thin sections were also graphite coated and examined using an electron probe microanalyzer (EPMA) at the University of Huelva (Huelva, Spain). Unlike the modern terrace, the ancient sample is a hard mass of consolidated Fe phases that permits the use of point techniques for quantitative chemical microanalysis. Thus, imaging of both terraces and quantitative geochemical analysis of the ancient terrace sample were carried out with a four-spectrometer EPMA (JXA-8200 Superprobe, JEOL Ltd., Japan) using a 5 μm beam and 15 KeV acceleration voltage. Metallic oxides, sulfides, and silicates were used as standards. Numerous analyses ($n = 100$) were performed on areas identified by optical microscopy and Raman μ-spectroscopy.