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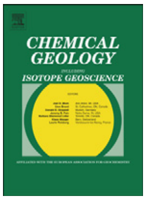

Raman identification of Fe precipitates and evaluation of As fate during phase transformation in Tinto and Odiel River Basins

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ABSTRACT

Newly-formed Fe terrace samples and corresponding water samples of Tinto and Odiel Rivers, as well as, ancient terrace samples representing conditions of ancient Tinto River, were collected and studied by optical microscopy, Raman spectroscopy, X-ray diffraction, scanning electron microscopy, microprobe analysis, pseudo-total digestions, and by chemical analytics. The newly-formed terraces showed that currently schwertmannite is precipitating on the riverbed acting as a sink for arsenic. In a matter of months, this metastable phase transforms into goethite and, eventually, jarosite which are found in the deeper sediments below one centimeter. Due to long-term transformation, well-crystallized goethite and diagenetic hematite were the major phases in the ancient terraces. The microanalyses suggested that goethite retained slightly higher concentrations of As than hematite suggesting that As is mobilized in the transformation process. Additionally, this study shows that Raman spectroscopy is an efficient tool in the mineralogical characterization of Fe(III) oxides, hydroxides, and oxyhydroxysulfates at micro to millimeter scale in these types of samples. However, Raman spectra did not provide insights on the incorporation of As within the crystal lattice of schwertmannite, probably due to its low concentration.

1. Introduction

The outcropping massive sulfides of the Iberian Pyrite Belt (IPB) and the subsequent formation of gossans (thick cap of iron oxides formed as a result of chemical weathering) have influenced the microbiochemistry of the Tinto and Odiel River basins, SW Spain (Nieto et al., 2007, 2013). Sulfide oxidation led to natural Acid Rock Drainage (ARD) over millions of years, and intensive mining since 4500 years ago (Nocete et al., 2014) provoked Acid Mine Drainage (AMD) enhancing the extreme acidic conditions of the river systems. Over prolonged time span a unique microbiochemical environment was created, and iron oxyhydroxides and oxyhydroxysulfates precipitated forming terrace-like iron formations i.e. the precipitates settled as thick, stepped iron accumulations on the riverbed. The ancient Fe terraces are located tens of meters above the current river and they may be as old as several million years (Fernández-Remolar et al., 2005; Essalhi et al., 2011). The Tinto River has been pointed out as a terrestrial analog to iron formations on Early Earth and Meridiani Planum on Mars (Fernández-Remolar et al., 2005).

In AMD-after mining environments, metastable schwertmannite [$Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$] has proven to be good at scavenging arsenic (AsV) from solution (Acero et al., 2006; Asta et al., 2010). However, over time the schwertmannite tends to transform spontaneously into more crystalline phases such as goethite [α-FeOOH] in a matter of months (Acero et al., 2006). Bigham et al. (1996) describe this reaction:

$$Fe_8O8(OH)_{5.5}(SO_4)_{1.25(s)} + 2.5H_2O \rightarrow 8FeOOH_{(s)} + 1.25SO_4^{2-}{}_{(aq)} + 2.5H^+{}_{(aq)}. \quad (1)$$

The eventual precipitation of jarosite [$KFe_3(SO_4)_2(OH)_6$] is also reported (Acero et al., 2006).

On a longer time scale of centuries, goethite is transformed into hematite [Fe_2O_3] through diagenetic processes (Pérez-López et al., 2011) according to the following reaction described by Langmuir (1971):

$$2FeOOH_{(s)} \rightarrow Fe_2O_{3(s)} + H_2O_{(aq)}. \quad (2)$$

Identifying these phases and quantifying the potentially toxic elements that they may carry by adsorption or co-precipitation are

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important in assessing contaminated soils and sediments. Moreover, the search for stability in this type of poorly crystalline iron oxyhydroxysulfate could determine the fate of arsenic with time, and what is now considered a sink could become a long-term source of contamination.

Raman micro-spectroscopy has many applications including biotechnology, mineralogy, environmental monitoring, material science, and pharmaceutical (Das and Agrawal, 2011). In recent studies it has also proven as an efficient method for characterizing Fe(III) oxides, hydroxides, and oxyhydroxysulfates (Mazzetti and Thistlethwaite, 2002; Courtin-Nomade et al., 2003; Frost et al., 2005; Burton et al., 2009; Müller et al., 2010; Das and Hendry, 2011). This study focused on the iron-rich alluvial terraces of different ages in the Tinto and Odiel Rivers. The mineralogical and geochemical composition was studied by optical microscopy, Raman μ-spectroscopy, scanning electron microscope equipped with energy dispersive X-ray spectroscopy (SEM-EDX), electron microprobe analysis (EMPA), bulk powder X-ray diffraction (XRD), and by a pseudo-total digestion. Raman spectroscopy was used to study the mineralogical composition in millimeter scale in undisturbed samples, and the effectiveness of this technique for identifying mineral phases was verified by comparing the Raman spectra and XRD diffractograms of the ground bulk samples.

2. Materials and methods

2.1. Site description

Tinto and Odiel River Basins cross through the IPB, which is one of the largest massive sulfide deposits worldwide with estimated total reserves of over 1700 Mt (Leistel et al., 1998; Sáez et al., 1999). The IPB extends from south of Lisbon in Portugal to north of Seville in Spain. The ore deposits, consisting mainly of metal sulfides (e.g. pyrite [FeS_2], pyrrhotite [$Fe_{(1-x)}S$], chalcopyrite [$CuFeS_2$], sphalerite [ZnS], galena [PbS], arsenopyrite [FeAsS], tetrahedrite–tennantite [$(Cu,Fe)_{12}Sb_4S_{14}$–$Cu_{12}As_4S_{13}$]) and hosted by shales and volcanic rocks, were formed from the Late Devonian to the Early Carboniferous (Tornos, 2006). Parts of the ore deposits have been exposed to atmospheric conditions over a prolonged period since Oligocene, i.e. over 24 Ma (Essalhi et al., 2011) causing the oxidation of sulfides, natural ARD, and deposition of iron-rich sediments in the riverbeds. These authors suggest that the formation of the iron terraces probably was a continuous process. The older terraces represent natural conditions before mining era, whereas due to extensive mining in the area since 2500 B.C. (Nocete et al., 2014) the water quality further decreased and iron terraces associated with AMD processes occurred since then. Over a hundred mines have operated in the area during the past centuries (Tornos, 2006), which discharge their highly-polluted acidic leachates into the river systems. Nearly all of the mining districts are currently abandoned representing an almost inexhaustible source of AMD, characterized by low pH (0.88–3.2) and high elemental concentrations (Egal et al., 2008; Hubbard et al., 2009; Asta et al., 2010; Nieto et al., 2013). As a consequence, iron terraces precipitate reflecting the mining impact.

2.2. Sampling, sample preparation, and analysis

On the one hand, water and undisturbed samples of newly-formed iron terraces were collected in some AMD-affected streams of three abandoned mine districts. The terrace samples were collected at La Naya (LN) district within the Tinto river basin in October 2012 and February 2013, whereas water samples were only collected during the latter sampling campaign. The sample LN-1 was collected at an underground gallery pithead (tunnel 16), and samples LN-2 and LN-3 were taken from a nearby ditch receiving water from pyrite-rich tailings. The sample LN-3 represents a recent terrace located only few meters from the current flow path of the ditch that was formed probably a few years ago. Moreover, solid and water samples were collected at Tinto Santa Rosa (TSR) and Perrunal (PER) districts within the Odiel River basin in February 2013 (Fig. 1). On the other hand, solid samples were taken in October 2012 from ancient terraces of the Tinto River at formations outcropping at La Naya (LY), Nerva (NV), and Alto de la Mesa (AM). The ancient terraces of LY and NV are located 10 to 15 m above the current riverbed, whereas AM has the highest location at 60 m being the oldest formation. The Alto de la Mesa terraces are defined as an alluvial deposit with alternating sequences of coarse and fine sediment layers as a consequence of different flow regimens. The sample AM-1 corresponds to distal and AM-2D to proximal location in the ancient Tinto River, and the other samples represent intermediate locations.

The water samples were filtered with 0.45 μm nylon filters and acidified with HNO_3 to pH 1 in the field. In the laboratory they were kept at 4 °C until analysis. The pH, redox potential (Eh), and electric conductivity (EC) were measured in the field using a portable Multiparametric Cison Mm 40+ equipment, and both dissolved oxygen (DO) and temperature were measured in the field using Hanna Instruments HI 9142. Water samples were analyzed for trace and major elements by inductively coupled plasma mass spectrometry (ICP-MS, X-series II Thermo instrument) and inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Jarrel-Ash instrument), respectively, at Institute of Environmental Assessment and Water Research (CSIC Barcelona). The detection limits were on the order of 1 ppb for traces and between 1 and 0.2 ppm for major elements.

The newly-formed sediments were dried at room temperature at the laboratory. Polished thin sections of approx. 50 μm were prepared of all solid samples using epoxy resin and polyester resin. They were examined by reflected-light optical microscope, SEM-EDX and EMPA qualitative chemical characterization, and Raman μ-spectroscopy for mineralogical identification of the iron phases. Additionally, the newly-formed terraces and samples LY-2B and AM-2D were divided into subsamples according to the observed layering where number one corresponds to the top layer and the lowest sample corresponds to the average depth of 3 to 5 cm depending on the sample thickness. Aliquots of all of the solid samples were ground using an agate mortar. The ground samples were investigated using bulk XRD, Raman spectroscopy, and chemical digestion.

The acceleration voltage of the Leo 1430VP SEM equipped with EDX (Oxford instruments, INCA 350) was set to 20 keV and the beam current to 80 nA at the Centro de Servicios Científicos (CIC) at the University of Granada. The JEOL JXA 8200 EMPA was set to 15 keV and beam current of 10 nA was used at the University of Huelva. The exposure time of the microprobe was prolonged to 100 s in order to better gauge the trace elements that appear in concentrations close to their detection limits. Additionally, to better quantify the trace concentrations in the terrace samples, aliquots of 0.2 g of ground samples were digested with aqua regia which is considered as a pseudo-total digestion. The chemistry of these samples was analyzed by ICP-MS and ICP-OES at Institute of Environmental Assessment and Water Research (CSIC Barcelona). Raman spectra were collected with a LabRAMHR spectrometer (Jobin–Yvon, Horiba, Japan) with backscattering geometry at Instituto Andaluz de Ciencias de la Tierra (IACT). The excitation beam (a diode laser emitting at 784 nm) was focused with a confocal Olympus microscope. Raman signals were collected in a Peltier-cooled CCD detector (1064 × 256 pixels). The spectral range was from 150 to 1350 cm^{-1} at a resolution of 3 cm^{-1}. Raman shift calibration was performed using the 521 cm^{-1} line of silicon standard. To avoid sample degradation and transformation of mineral phases, a filter (D0.3 or D0.6) was used for the thin sections. The acquisition time was set to 300 s with 2 to 4 accumulations, and ×50 objective was used. The thin sections were analyzed making a cross section from the surface to bottom of each sample in order to observe the mineral transformation in detail. On the other hand, the Raman spectra of the ground samples were obtained as signal average of two spectra, during 150 s each. Due to the high probability of degradation of the ground