



# Iron and arsenic-rich nanoprecipitates associated with clay minerals in sulfide-rich waste dumps



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## ABSTRACT

The relationships between clay minerals and associated iron and arsenic-rich phases are a main scientific issue in reactive mine waste-dumps. Therefore, this paper documents the composition and morphology of the fine fraction (<2 μm), including the nano-sized Fe and As precipitates, associated with clay minerals in three distinctive sulfide-rich waste-dumps: *Cerdeirinha*, *Lapa Grande*, and *Penedono* (Northern Portugal).

The obtained results indicated that the study sites have similar relative proportions of the detrital materials. However, major differences were observed in the remainder phases, which is in accordance with the mineralogy that was inherited from the respective ore deposits. In general, the clay mineral assemblage is dominated by the presence of illite, halloysite(7 Å), and beidellite. There are also associated minerals, such as jarosite and goethite, as well as amorphous As-rich nanoprecipitates with specific morphologies. Moreover, the results suggested that AMD conditions control the physical–chemical transformations, namely constraining the stability of the secondary phases formed by weathering in the waste dumps. Acidity is responsible for the degradation of the clay minerals, which is reflected in their crystalchemistry, structural order–disorder, and morphology. On the contrary, jarosite is more stable, being a dominant mineral in such environmental conditions. The stability of amorphous ferric arsenates or its evolution to a more crystalline phase is dependent on the Fe:As ratio, which is lower in *Penedono*.

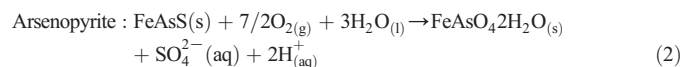
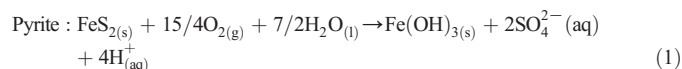
The study of the secondary products, especially the nanoparticles, puts in evidence their ability to control the mobility of trace elements, suggesting potential applications in environmental technology, including remediation of reactive mine waste-dumps.

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## 1. Introduction

The occurrence of soil contamination and metal dispersion in the surrounding ecosystems is a common problem in the presence of sulfide wastes. Therefore, abandoned mine waste-dumps are often an important focus of environmental impact as the sulfide minerals are susceptible to weathering. The weathering reactions produce acid mine drainage (AMD), which is responsible for mobilizing metals, sulfate and acidity (e.g., Hoffert, 1947; Grande et al., 2010). The geochemical evolution of the sulfide wastes is typically accompanied by the development of reaction products, named AMD-precipitates. Eqs. (1) and (2) are used to simply express such mineral–water interactions, involving two common sulfides that mobilize iron and arsenic. They include the development of

new mineralogical structures, here represented by the hydroxide and arsenate phases, the  $\text{Fe}(\text{OH})_{3(s)}$  and the  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}_{(s)}$ , respectively.



The AMD-precipitates may have different compositions and nature, as they represent mild modifications or profound transformations of the primary paragenesis (Alpers et al., 2000; Valente et al., 2014). Iron oxyhydroxides and hydroxysulfates, such as schwertmannite and ferrihydrite, are among the most visible and well characterized materials in sulfide environments (Bigham, 1994; Bigham and Nordstrom, 2000; Murad and Rojik, 2003). Nevertheless, the sulfide-rich wastes

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are generally polymineralic aggregates, whose evolution is marked by other solid phases, such as sulfates, silicates (e.g., clay minerals), metallic oxides, phosphates, and arsenates. These minerals may appear simultaneously with other secondary products of very small size (in the nanometric scale) that did not realize crystalline structure (Valente and Leal Gomes, 2009a,b; Ribeiro et al., 2010). Amorphous and low crystalline precipitates are not so evident in the waste dumps and are more difficult to analyse. Therefore, they are considerably less studied AMD-precipitates. However, they have strong monitoring and environmental relevancies. Although metastable, they give valuable information concerning the composition of the solutions from which they formed as well as the prevailing equilibrium conditions on waste dumps. Furthermore, they have the ability to retain pollutants, such as arsenic, limiting the dispersion of contamination by AMD.

Another group of minerals that lacks information in AMD systems is clay minerals. Although ubiquitous, there are very few references to their interaction with other secondary minerals in AMD (Galan et al., 1999; Uzarowicz et al., 2011; Vazquez et al., 2011). However, clay minerals are key-examples of environmental minerals in accordance with the definition given by Valsami-Jones (2000). Due to their surface properties they are involved in sorption processes, retaining acidity, metals, and metalloids (Hammarstrom et al., 2003). The importance of this group of minerals in AMD is enhanced by their common association with other relevant phases, such as the oxyhydroxides and hydroxysulfates (e.g., goethite and jarosite) (Valente et al., 2012). In addition, composition and morphological modifications, induced in clay minerals by acidity, have not been studied extensively (Uzarowicz et al., 2011).

Several studies were carried out in the North of Portugal, focused particularly on the mineralogy and geochemistry of AMD systems (Valente et al., 2011, 2012). Also, Gomes et al. (2013) present the composition and role of clay minerals, when studying the restoration promoted by natural vegetation in distinct mine waste-dumps. Though, these studies need to be complemented, in order to describe the variety of very fine-grained products that intimately occur in sulfide waste-dumps: clay minerals, goethite, jarosite, and nanoprecipitates (defined as  $< 100$  nm in size) that often occur without crystallinity.

Recent advances have shown the key role that the fine fraction, especially the nanoparticles, plays in aqueous and soil systems (Waychunas et al., 2005; Plathe et al., 2013). Their ability to control the mobility of trace elements may suggest important applications in environmental technology, including remediation of reactive mine waste-dumps.

This paper documents the composition and morphology of the fine fraction ( $< 2$   $\mu\text{m}$ ), including the small-sized Fe and As precipitates, associated with clay minerals. Three sulfide-rich waste-dumps in the North of Portugal were used to represent distinctive AMD environments. The following aims were defined: i) to characterize the mineralogy and geochemistry of clay minerals that prevail at each site; ii) to understand the behaviour of kaolin minerals, smectite, and associated minerals (jarosite and goethite) in distinctive AMD environments; and iii) to describe the morphological and compositional properties of the iron and arsenic-rich nanoprecipitates.

## 2. Materials and methods

### 2.1. Study sites

The three studied sites, *Cerdeirinha*, *Lapa Grande* and *Penedono*, are located in the North of Portugal (Fig. 1), which is a region with a long and large mining tradition. *Cerdeirinha* and *Lapa Grande* (in Northwest of Portugal) resulted from the exploitation of wolframite and scheelite in a skarn ore deposit with abundant pyrrhotite and pyrite (Valente and Leal Gomes, 2007). Although similar, these two waste dumps differ on the proportion of sulfides relatively to other minerals with neutralizing potential (calcite, apatite and Ca-silicates) and on the granularity of

the wastes. At *Cerdeirinha*, silt and clay dimensions prevail and the wastes are more enriched in sulfides.

*Penedono*, a hydrothermal deposit, is located in the Northeast of Portugal (Fig. 1) and the waste dumps resulted from the exploitation of gold in quartz veins with sulfides, associated with second order shear zones (Silva and Neiva, 1990). The waste dumps are composed by small grain size tails, which resulted from milling, hydrogravitic separation and flotation. The inherited mineralogy that characterizes the mine wastes is rather monotone, with high proportion of arsenopyrite and Al-silicates (Valente et al., 2012). Neutralizing phases, such as carbonates, are absent.

### 2.2. Sampling and preparation procedures

Sampling of the three mine soils took place between January and June 2011. Six to eight samples were randomly collected at each waste dump. On the whole, the sampling sites represent the diversity of topographic, microclimatic, and mineralogical conditions. Their location was also affected by the difficulty to access some of the areas, due steep slopes and strong erosion that disturb, especially, *Lapa Grande* and *Penedono*. At each sampling site, a pooled sample was obtained for a 20 cm soil depth from a circular area of 50 cm. Once the samples arrived at the laboratory, they were dried at 40 °C for 72 h and sieved through a 2 mm steel sieve.

### 2.3. Analytical methods

The samples from the  $< 2$   $\mu\text{m}$  fraction were analysed for chemistry and mineralogy. Chemical composition was obtained by inductively-coupled plasma mass spectrometry (ICP-MS) after an *Aqua Regia* extraction for the following elements: Fe, As, Mn, S, P, Na, K, and Al. These analyses were performed at Activation Laboratory, Lda (Actlabs, Canada), including duplicate samples and check precision blanks, whereas accuracy was obtained by using certified standards (GXR series). Also, soil pH was analysed on extracts obtained in accordance with Wilke (2005).

The mineralogy of the samples was analysed by X-ray powder diffraction (XRD) with a Philips X'pert Pro-MPD diffractometer (Philips PW 1710, APD), using  $\text{CuK}\alpha$  radiation. The diffractometer is provided with automatic divergence slit and graphite monochromator. The XRD diffractograms were obtained from powders (bulk sample  $< 2$  mm as well as the  $< 2$   $\mu\text{m}$  fraction) and from oriented aggregates ( $< 2$   $\mu\text{m}$  fraction) in the interval of 3 to 65°2 $\theta$  and 3 to 35°2 $\theta$ , respectively. The equipment was operated with a 2 $\theta$  step size of 0.02° and a counting time of 1.25 s.

Prior to analysis, the bulk samples were air-dried and sieved to  $< 2$  mm grain size and then crushed and ground manually using an agate mortar and pestle. For the separation of the  $< 2$   $\mu\text{m}$  fraction, organic matter was previously removed by treating samples with  $\text{H}_2\text{O}_2$  *p.a.* This treatment was applied to the samples which are more enriched in organic matter, in order to obtain a full dispersion of the clay minerals. The  $< 2$   $\mu\text{m}$  fraction was then obtained by the sedimentation method and the particle-size separation based on Stokes' law. The oriented preparations were submitted to the following treatments: air-dried, ethylene glycol (EG)-solvated, and heated (490 °C). Li saturation (LiCl), heat treatment (300 °C) and ethylene glycol saturation were also applied. Oriented mounts of the  $< 2$   $\mu\text{m}$  fraction on opaque fused silica slide were analysed by XRD according with the Greene-Kelly test (Greene-Kelly, 1952; 1953).

Semi-quantitative analysis on bulk samples was performed by using the peak-height intensities of the diagnostic reflections (Valente et al., 2012). Estimation of the clay minerals was deduced from the diagnostic peaks related to their first-order basal reflections in air-dried conditions or after EG solvation.

Fourier Transform Infrared (FTIR) spectroscopy was applied to the  $< 2$   $\mu\text{m}$  fraction, using a Perkin Elmer Spectrum 65 spectrometer for

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