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METALS RETENTION AFTER WEATHERING OF A SULPHIDE ORE BODY: UNEXPLOITED GOSSAN VERSUS MINE TAILINGS

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Numerous studies have highlighted the fact that the bioavailability of potentially toxic trace elements (PTTE), such as As, Cd, Cr, Cu, Ni, and Pb, is strongly related to the redox state and chemical form. Since dissolved forms of trace elements are the most bioavailable, the issue of greatest concern is to define the conditions under which these elements may be remobilized in solution up to levels higher than those recommended by National agencies as e.g. the Environmental Protection Agency (EPA). In order to understand and then ideally to prevent trace element mobilization, the characterisation of the contaminant sources, *i.e.* the solid fraction, is crucial.

PTTE concerns for human health are associated with primary sulphide phases and with secondary host phases such as iron or manganese oxyhydroxides, clay minerals, sulphates, carbonates, and phosphates (e.g. Courtin-Nomade *et al.*, 2003; Serrano *et al.*, 2004). Although PTTE bioavailability is generally limited in primary sulphide phases, PTTE can be bioavailable when in secondary host phases as the stability of these host phases highly vary with geochemical parameters such as ionic strength, pH, Eh, and solution composition (e.g. Veeresh *et al.*, 2003; Nachtegaal and Sparks, 2004) and with physical parameters such as particle surface area.

The clear identification of secondary phases is essential to forecast the mobility and potential bioavailability of PTTE incorporated within, but conclusive identification is only possible using chemistry-sensitive investigation techniques with resolution on the micron to sub-micron scale due to the size of the studied particles. In order to determine the speciation of As, Cu and Pb, synchrotron-based diffraction and spectroscopy techniques using focused beams ranging in size from 10 microns to submicron were used on samples from a sulphide ore body that was only partially mined. In this area, both natural and anthropogenically-modified weathering profiles are in close proximity. Furthermore, this sulphide ore body sits in a heavily urbanized area and directly affects water quality in at least one stream by producing acidic conditions and relatively high dissolved PTTE concentrations.

The main sulphide mineral identified is pyrite (FeS_2) which occurs in both disseminated form and as massive lenses more than 30 m long. Piles of fine tailings and mine wastes up to 50 m high remain on the site and stand only a few meters from the closest house. Superficial and ground waters draining the former mine were gathered in 1999 and form now a small creek subject to acid mine drainage (acidic pH $\sim$ 3.1 with ochres precipitation). Coarse-grained waste rock from the mining era is cemented by thin crusts developed all along the slope. These crusts correspond to Fe-rich crusts according to the bulk chemical analyses (Fe up to 32 %), and XRD patterns indicate that they are primarily composed of goethite and jarosite. Those samples represent some of the PTTE-richest samples of the mine materials.

Approximately three hundred meters away from the mine, a gossan has been developed, resulting from the weathering of the unmined portion of the sulphide deposit, which also outcrop here. The ore body is constantly leached by a local creek and/or by interstitial and ground water runoffs which generate acid rock drainage. An important part of unweathered sulphide ore body remains atop the gossan developed on rhyolite and basalt bedrock.

Trace elements, such as As, Cu and Pb, released in waters and trapped in secondary phases, are a major hazard in this area due to their potential toxicity. Furthermore, the total amount of PTTEs discharged to the environment may potentially still be high, due to the high sulphide content of unmined sulfide rocks that are altering naturally.

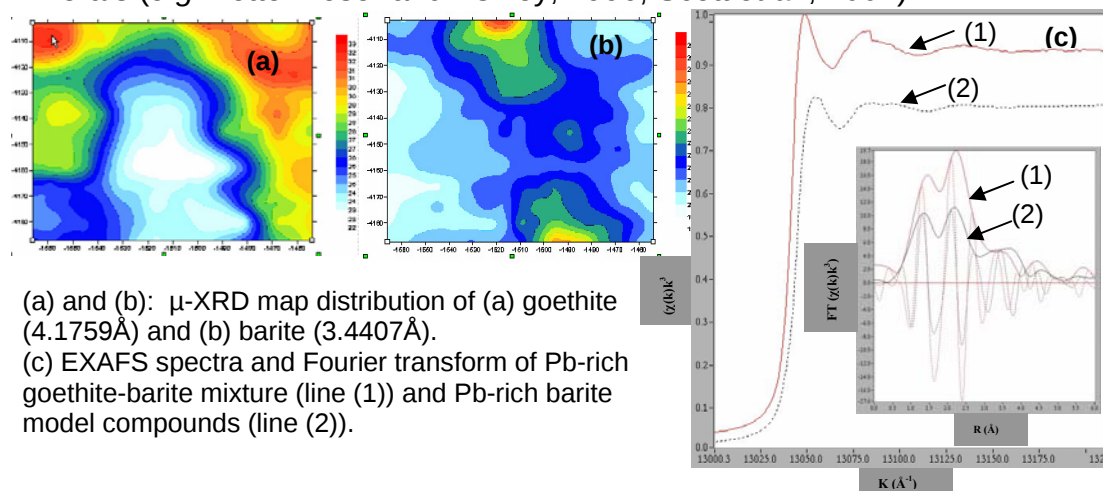
Waste from the former mine and the gossan (natural weathering profile) both contain predominantly Si and Fe. Bulk chemical analyses carried out on mine wastes show PTTE concentrations generally low for As (ca. 100 mg/kg with sporadic concentrations reaching 850 mg/kg in some samples), up to 740 mg/kg for Ba, ranging from 40 to 1500 mg/kg for Cu, up to 370 mg/kg for Pb and reaching 450 mg/kg for Zn. Samples from the unmined portion of the sulphide ore body may present higher bulk concentrations in Ba (up to 2300 mg/kg), Cu (up to 1300 mg/kg) and Zn (1100 mg/kg) but not in As (up to 400 mg/kg) and Pb (up to 260 mg/kg).

Chemical analyses at a micron scale (SEM and EPMA) have revealed several primary and neo-formed PTTE-bearing phases, very small in size (generally between 10 to less than 1 μm). To complete SEM and XRD characterization, techniques like μ -PIXE, μ -Raman, μ -SXRF, μ -XAS and μ -XRD were preferred when lower concentration detection limits were required or when the studied particles size was as small as 1 μm .

Whatever the site, sulphides, mainly pyrite (FeS_2), are the dominant primary hosts for Cu and Pb. These pyrites could also contain As (up to 0.9 at.%) and chalcopyrite (FeCuS_2) and sphalerite (ZnS) as inclusions (size of observed inclusions: 10 x 5 μm).

Micro-XANES pointed out another primary form under which Cu is observed, corresponding to elemental form. These small Cu metal grains (ca. 5 μm in size) are generally noticed at the porosity edge within the hardpan and the gossan samples. They may very locally contain Zn and Pb as highlighted by μ -PIXE elemental mapping.

In the mining site, other Pb-bearing primary minerals have been observed such as barite (BaSO_4) and goethite ($\alpha\text{-FeOOH}$), which are intimately mixed as evidenced by $\mu\text{-PIXE}$ and $\mu\text{-Raman}$. Pb concentrations in the intergrown primary barite-goethite range from 1.2 to 3.4 at.%. Despite the good spatial resolution (1 to 2 μm) of these tools, we were not able to identify which of barite or goethite Pb is preferentially associated with. This knowledge is required to forecast the stability of the Pb retention as these two minerals can behave differently with geochemical parameter variations (e.g. pH, Eh). The preferential association of Pb within barite was highlighted by synchrotron based $\mu\text{-XRD}$ and $\mu\text{-EXAFS}$ (Fig. a, b & c), association in agreement with previous studies in other sites, showing possible substitution between Ba and Pb in some various minerals (e.g. Lottermoser and Ashley, 1996; Scott *et al.*, 2001).



(a) and (b): $\mu\text{-XRD}$ map distribution of (a) goethite (4.1759 Å) and (b) barite (3.4407 Å).
(c) EXAFS spectra and Fourier transform of Pb-rich goethite-barite mixture (line (1)) and Pb-rich barite model compounds (line (2)).

Authigenic phases such as (i) sulphates, (ii) Fe “oxides” and (iii) Mn products were observed either by bulk X-ray diffraction and/or SEM observations. Sulphates and Fe “oxides” are the two main products at the both sites whereas Mn products were only observed in the gossan samples. Depending on the samples, PTTE show different affinities for Fe or Mn compounds as highlighted by SEM and $\mu\text{-SXRF}$. For example, gossan samples generally contain Cu equally hosted by Mn products and Fe oxides, Pb being preferentially associated with Mn compounds when As is only observed with Fe oxides or sulphates.

(i) Sporadic sulphates correspond to fibrous epsomite or epsomite / watevillite (only observed at the mining site) and are considered higher soluble sulphate salts comparing to the most abundant jarosite (hydronian to potassic or sodic) or schwertmannite identified here at the both sites. These easily soluble sulphates formed during the dry period which last more than 6 months. Even though epsomite is highly soluble, its PTTE content is much lower (e.g. bulk concentrations show 50.2 mg/kg of Ba, 11.7 mg/kg of Cu, 9.7 mg/kg of Ni, 1.3 mg/kg of Pb and 80 mg/kg of Zn) than the amounts measured in the jarosite (concentrations up to 0.31 at.% As, 0.45 at.% Cu, 6.59 at.% Pb or 0.17 at.% Zn – EPMA data). Down the waste rock pile of the former mine, schwertmannite forms a thick layer of ochreous precipitates in the small bed creek. Only schwertmannite at that site contains PTTE (As = 0.16 at.%, Cu = 0.23 at.%, Pb = 0.21 at.%, Zn = 0.14 at.% as measured by EPMA).

At the “natural” site, this mineral formed a thin layer at the very surface of the sulphide ore body with no PTTE associated with. This may be explained because of the constant leaching of this “natural” schwertmannite by the interstitial and ground water runoffs.

(ii) The Fe “oxides” can be present as well-individualized minerals but also fill the porosity around weathered primary minerals. In that last case, they frequently present a typical rhythmical botryoidal “colloform” texture, characteristic of authigenic precipitation from colloidal solution. Whatever their shape, they correspond to more or less well-crystalline goethite as evidenced by μ -Raman or can match to a mixture of goethite/hematite in the gossan as highlighted by Mössbauer spectroscopy. Presence of ferrihydrite and goethite mixture, with predominance of goethite, was also detected by μ -EXAFS studies. An example of PTTE retention is As which is preferentially associated to these ferrihydrite/goethite products as evidenced by μ -SXRF, showing average concentrations ranging from 0.1 to 0.3 at.% (EPMA data).

(iii) The secondary Mn products are only present in the natural site, filling the porosity or around silicates and Fe-oxides grains. The main PTTE detected here are Cu (0.47 ± 0.16 at.%), Pb (1.07 ± 0.77 at.%) and Zn (0.15 ± 0.09 at.%) (EPMA results). The comparison of synthesised amorphous Mn oxide (doped in Cu and Pb) μ -EXAFS spectrum with the spectra obtained on the natural compounds indicates that they do not correspond to Mn oxides as previously supposed. Their identification is still under investigation.

This work highlights the identification of the PTTE-bearing authigenic phases and the distribution of As, Cu, Pb and Zn at the micro-scale. This knowledge will allow forecasting the stability of the PTTE retention according to the specific environmental conditions at the two sites as well as to estimate a potential increase in the contamination of the local creeks, already more or less impacted.

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