

## Application for beam time at ESRF – Experimental Method

This document should consist of a maximum of two A4 pages with a minimal font size of 12 pt.

### Aims of the experiment and scientific background

Sulfide supergenic alteration processes, also known as Acid Rock Drainage (ARD) processes represent a serious environmental problem in disused mining areas (Jambor J.L. & Blowes D.W., 1994). These processes trigger the acidification of the circulating water and the release and mobilization of potentially toxic elements (Pb, Zn, Ni, Cr, As, Cd, Co, etc.) that in some cases may selectively concentrate up to dramatic levels both in aquatic and terrestrial ecosystems. Accurate mineralogical, chemical and crystallochemical analyses are hence needed in order to understand the mechanisms of alteration of the primary sulfide into the final products that are mainly represented by assemblages of nanometric Fe-oxyhydroxides and sulfates. The precise identification and characterization of the different phases within these natural mineral assemblages is very important also from the environmental point of view because these minerals can substantially contribute to the uptake of toxic elements, even when their mass fraction is relatively low (Kosmulski et al. 2003).

Our aim is to identify the different mineralogical species that originate from alteration of primary sulfides (mainly pyrite, chalcopyrite, and sphalerite) at the Fe-Cu sulfide mine of Libiola (Eastern Liguria, Italy). Moreover we want to relate the distribution and the concentration of trace elements (especially arsenic and heavy metals) within the different mineral species.

The Libiola mine represented from 1864 to 1962 one of the most important Italian exploited sulfide-ores with a production of over 1.000.000 tons of Fe-Cu sulfides. At present the ore deposit is completely abandoned and comprises over 30 km of underground excavations and five major waste dumps scattered over 10 km<sup>2</sup> in the mining area.

We have collected samples evidencing the different stages of alteration from fresh sulfide up to crust completely composed by alteration products, mainly represented by intimate intergrowths of Fe-oxyhydroxides and -oxides, characterised by fine scale heterogeneity (Figure 1).



Figure 1. Intergrowth and association among different mineralogical species at macro- (OM image; left), micrometric scale (SEM image; right).

Previous studies performed on the alteration crusts, evidenced the coexistence of different phases, comprising FeOOH polymorphs and other Fe-oxides and oxyhydroxides such as hematite and schwertmannite. Their relative amounts and crystallinity are strongly dependent on the degree of completion of the ARD processes. On account

of their chemical, structural, and microstructural features their exact identification and distinction resulted extremely difficult and in some cases impossible by means of laboratory X-ray powder diffraction analyses. In particular, the strong line broadening resulting in peak overlapping hinders the detection of secondary phases (that occur in low amounts and scattered along the samples) whose presence has been confirmed by IR and micro-Raman analyses. Inductively Coupled Plasma Mass and Emission Spectrometry analyses evidenced relatively high amount of arsenic and several heavy metals (Co, Pb, Ni, Cd, Sb, Ag, Mo) both in primary sulfides and alteration products (Marescotti & Carbone, 2003).

The knowledge of the distribution of these elements within the mineral phases representative of the different stages of the ARD process can contribute to the understanding of the mechanism of potentially toxic elements uptake, thus providing several target of environmental concern.

### **Experimental method**

We plan to perform scanning  $\mu$ -fluorescence analyses in order to acquire elemental concentration (including trace elements) coupled with  $\mu$ -diffraction as a function of sulfides degree of alteration. We need few  $\mu\text{m}$  spatial resolution (about 3-6 $\mu\text{m}$ ) because this is the scale of the mineral intergrowths in our highly heterogeneous material. The analyses will be performed every 200 $\mu\text{m}$  along a section characterized by different stages of alteration that cover a total area of about 2cm.

These data will be used for:

- identification of the different mineral phases at the different stage of alteration
- characterization of crystallochemical features of the different phases
- evaluation of the trace elements distribution among sulfides and new formed minerals

### **Expected Results**

We expect to identify the several phases occurring at the different stages of the ARD process and their role in the fate of arsenic and heavy metals released during primary sulfide alteration. As a result we are confident to upgrade our knowledge on the different mechanisms involved in the ARD process especially in the light to prevent the pollution caused by potentially toxic elements.

### **References**

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