

**CRYSTALLOCHEMICAL AND MINEROGENETIC STUDY OF OXIDE AND  
OXY-HYDROXIDES RELATED TO AMD (ACID MINE DRAINAGE)  
PROCESSES IN LIBIOLA MINE (SESTRI LEVANTE)**

CRISTINA CARBONE

Dipartimento per lo Studio del Territorio e delle sue Risorse, Università di Genova, C.so Europa 26, I-16132 Genova

Polymetallic mineralizations and their adjoining rocks represent a chemically complex geological system in which supergenic- and hypogenic-fluids trigger mineral reactions that may cause mobilization of major, minor and trace elements; these elements may be dispersed in the environment or stored in authigenic secondary minerals.

The supergenic interactions between sulfide mineralizations and atmospheric agents cause, both in natural outcrops and in abandoned or active mining sites, a series of reactions that progressively involve the sulfides, the gangue and the host rock minerals. These processes are internationally known as ARD (Acid Rock Drainage) and AMD (Acid Mine Drainage) processes (Jambor & Blowes, 1994, and references therein): the sulfides alteration may cause an extreme acidification of the circulating solutions. Mineral alteration as well as circulation of acid water also cause the mobilization, transport and selective concentration of many chemical elements (such as Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Pb) that may reach high level of contamination in the surrounding environment.

As a consequence of these processes, large quantities of authigenic minerals (such as oxides, oxyhydroxides, sulfates, carbonates, clay minerals and amorphous compounds) form through precipitation from circulating solutions. Most of these precipitates are mainly composed of intermixed nanocrystalline and amorphous phases and represent a complex and dynamic system where equilibrium is rarely achieved. In fact, as described by many authors (Jambor & Blowes, 1994; Banfield & Zhang, 2001; Dinelli & Tateo, 2002; Kim & Kim, 2003; Marini *et al.*, 2003; Murad & Rojik, 2003; Carbone *et al.*, 2005a, 2005b), these minerals continuously underwent transformation processes, that comprise dissolution/precipitation and solid state recrystallizations, as a consequence of the cyclic variations of the environmental physico-chemical parameters (Cornell & Schwertmann, 1996).

Most of the knowledge on the nanocrystalline Fe-oxides and -oxyhydroxides and on the other mineral species that form during AMD processes are still based on synthetic phases or natural macrocrystalline analogues (Schwertmann & Taylor, 1989; Cornell & Schwertmann, 1996, and references therein). Recently, due to the expansion of sophisticated analytical techniques that allow the detailed investigations of structures, crystal chemistry, physical- and surfaces-properties of minerals, many progresses have been made (Banfield *et al.*, 2000; Banfield & Navrotsky, 2001; Hochella, 2002). Nevertheless, many problems still remain unresolved and require consideration also for their importance in the Earth Science and for their relevant environmental and technological implications (Cornell & Schwertmann, 1996, and references therein; Sainctavit & Ohresser, 2004). Particularly important are: a) stability fields and transformation processes of the natural nanocrystalline Fe-oxides and -oxyhydroxides assemblages; b) nucleation and growth mechanisms from colloidal aggregates to nanosized crystals (*i.e.*, Schwertmann *et al.*, 1999; Banfield *et al.*, 2000); c) relationships between size and physical properties (such as optical- and magnetic-properties, sorption and ion exchange capacity); d) crystallochemical characterization of low crystallinity mineral species such as 2- and 6-line ferrihydrite, schwertmannite

(i.e., Bigham *et al.*, 1994; Cornell & Schwertmann, 1996; Janney *et al.*, 2001; Loan *et al.*, 2004, 2005). Moreover, the knowledge of these scientific aspects as well as the reconstruction of the entire minerogenetic process is essential for every study on the mechanism of mobilization, diffusion and removal of contaminant elements from polluted waters (Brown *et al.*, 1999), for the geochemical modelization of the contaminated systems and for the realization of mitigation and remediation plans.

The Libiola Fe-Cu sulfide ore-deposit (Eastern Liguria, Italy; Fig. 1) provides an excellent natural laboratory for improving understanding on the mineralogy of AMD systems. In fact, this abandoned mining site is characterized by supergenic alteration processes involving the sulfide mineralizations and the adjoining rocks. In particular such processes are still affecting both the pyrite-rich waste rock dumps and tailings impoundments and the remaining outcropping and underground ore bodies. As a consequence, most of the superficial and underground waters circulating in the mining area, are characterized by *pH* generally < 3 and by very high levels of polluting elements in solution (Dinelli & Tateo, 2002; Marini *et al.*, 2003). Mixing between acid waters and stream and/or meteoric waters causes extensive precipitation

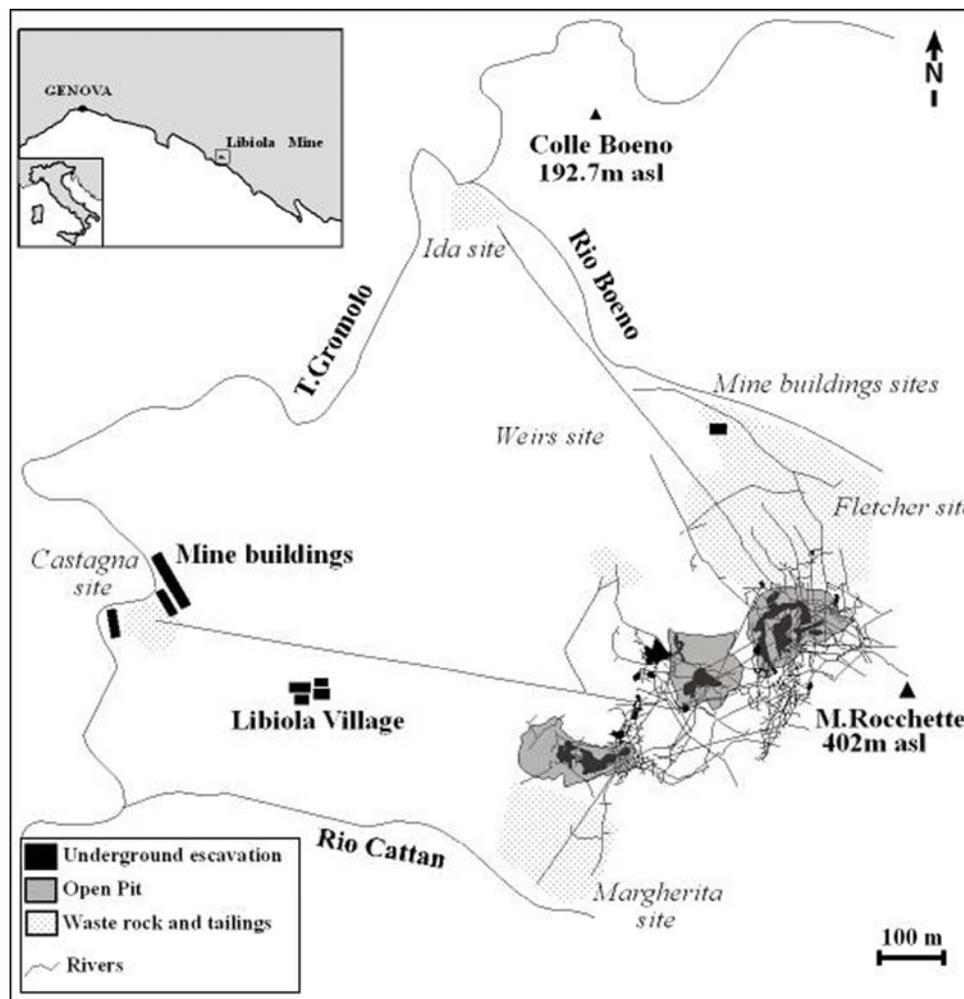


Fig. 1 – Schematic sketch of the Libiola mine area (modified from Marescotti & Carbone, 2003). The sampling sites are marked in italic.

of amorphous and nanocrystalline solid phases that continuously transform and evolve toward more stable mineral assemblages as a consequence of ageing and of seasonal climatic changes. These solid phases are represented by a) unconsolidated precipitates (stream sediments), and b) oxidation crusts (hardpan).

The objective of this study is to describe the genesis and evolution, the mineralogical properties, and microstructural features of the nano- and microcrystalline Fe-oxyhydroxides and of the Fe-, Al- and Cu-hydroxysulfates present forming in the Libiola mine area. The stream sediments provide ideal targets for the mineralogical and mineralogical characterization of the AMD processes being possible to directly measure and monitor the physico-chemical parameters of the environment. Moreover, the oxidation crusts that extensively cover all waste rocks and tailings deposits may allow the reconstruction of the weathering sequences from the alteration of sulfides to the authigenesis and progressive evolution of secondary minerals.

## STREAM SEDIMENTS

During the period from March 2006 to January 2007 stream sediments samples were collected for every season; moreover, at each sampling site, pH, Eh and temperature were measured *in situ*. The selected sampling sites are representative of stream sediments that occur as soft muds close to the main mine adits and as loose suspensions associated with overland flow of mine drainage. Precipitates were collected by suctioning the loose floc or by removing muds from the streams bed. All precipitates were filtered through a 16  $\mu\text{m}$  membrane filter and then dried at room temperature for X-ray (XRPD) and transmission electron microscopy (TEM) analyses. Samples were preliminary distinguished, on the basis of their colour, in ochreous, milky-white and greenish precipitates.

### *Ochreous precipitates*

The ochreous precipitates vary in color from ochre to yellow, red and brown and form from solution characterized by strong acidity ( $2.4 < \text{pH} < 4.5$ ) and Eh value between 300 and 670 mV. The results show that the pH, Eh, and  $\text{SO}_4$  are the most important factors that control the mineralogical composition of the solid phase:

1) jarosite ( $\text{KFe}(\text{OH})\text{SO}_4$ ) forms only in extremely acid ( $\text{pH} < 2.5$ ), high Eh (600-650 mV) and  $\text{SO}_4$  rich ( $< 5400$  ppm) solution and occurs as well crystallized lamellae.

2) Goethite ( $\alpha\text{-FeOOH}$ ) forms in wide range of pH (2.3-4.4), Eh (370-640 mV) and  $\text{SO}_4$  (1200-5300 ppm) and occurs as a subrounded nanocrystals (5-10 nm) often in association with jarosite, schwertmannite, ferrihydrite and Fe-amorphous phases.

3) Schwertmannite ( $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$ ) is present in all sampling sites and mainly forms at pH between 2.4 and 3.67, Eh between 470 and 630 mV, and  $\text{SO}_4$  concentration between 700 and 5000 ppm. Schwertmannite is metastable respect to goethite and tends to re-dissolve producing goethite nanoparticles as a consequence of ageing and of pH, Eh, T, and  $\text{SO}_4$  concentration variation. Schwertmannite occurs as tiny needles that coalesce to form rounded aggregates that are 200 to 500 nm in diameter; this unique “pin cushion” morphology have been observed in all samples.

4) 2- and 6-line ferrihydrite ( $\text{Fe}_5\text{O}_8\cdot 4\text{H}_2\text{O}$ ) and Fe-amorphous phases are characteristic of the pH range 2.7-3.9 with Eh between 450 and 630 mV and low  $\text{SO}_4$  concentration. TEM results revealed two types of 6-line ferrihydrite characterised by different morphologies: 1) the most frequent 6-line ferrihydrite occurs as spheroidal nanocrystals forming a “massive” texture; 2) the second type occurs with

the “mohair” texture described by Šucha *et al.* (2002) with crystal characterized by unusual fibrous features.

#### *Milky-white precipitates*

Milky-white precipitates form from solutions characterised by pH and Eh between 4.5 and 6.45, and 180.2 and 390.7 mV respectively. XRPD patterns show only two very broad peaks at 3.37 and 2.26 Å due to the exclusive presence of amorphous phases. The amorphous nature of these precipitates is confirmed by SAED analyses that however, in some cases, show a well defined diffraction pattern due to nanocrystalline aluminosilicates phases. TEM and HR-TEM images combined with AEM analyses show that the milky-white precipitates are mainly composed by aggregates of globular Al-amorphous phases.

#### *Greenish precipitates*

Greenish precipitates form from solutions characterised by pH value of 7.02-7.54, Eh value of 60 and 275 mV and low concentration of SO<sub>4</sub> ~ 1500ppm. XRPD patterns are characterised by a well-defined peak at 10.9 Å and a broad and low intense peak at 5.39 thus evidencing the presence of hydrowoodwardite [(Cu<sub>2</sub>Al<sub>2</sub>(SO<sub>4</sub>)(OH)<sub>8</sub>·nH<sub>2</sub>O)], a poorly crystalline Cu-Al-hydroxysulfate. TEM and HR-TEM images and AEM analyses confirmed the presence of hydrowoodwardite as the main constituent. It occurs in globular aggregates often characterised by the presence of scattered nano-sized native copper crystals (2-10 nm).

The bulk chemistry of the three stream sediments groups (major, minor, and trace elements) is quite constant in the different seasons; nevertheless it vary significantly among the different stream sediment types. Ochreous samples, composed almost exclusively by Fe-oxides, Fe-oxyhydroxides and jarosite, have the highest Fe and K contents. The high contents of S, Cu, Pb, Zn, Ni, As, Cd, and Ag testify the capacity of these mineral species to scavenge metals and other toxic elements from the circulating solutions, mainly through absorption and co-precipitation mechanisms. The greenish precipitates are strongly enriched in chalcophile elements derived from sulfides alteration, such as Cu and Zn. The milky-white samples are dominated by Al and show high affinity for several minor and trace elements such as P, As, Ba, and Rb.

### OXIDATION CRUST (HARDPAN)

The studied samples are: a) mineralised fragment which represents the transition from the unaltered sulphides to the authigenic Fe-rich assemblages, and b) stratified Fe-rich crust formed by ageing of stream sediments precipitated from acid mine waters discharged at mine adits. After a preliminary characterisation by transmitted and reflected light microscopy, SEM-EDS and TEM-EDX analyses, selected samples have been studied by a combined use of μ-XRF and μ-XRD employing a focussed beam of synchrotron radiation at the ESRF ID-18F beamline (Grenoble, France). The experiment was performed using polymer compound refractive lenses (CRL) achieving a X-ray spot size of 2 μm (Nazmov *et al.*, 2004).

The μ-XRF analyses were performed using an excitation energy = 28 keV and spectrum were collected using a Si(Li) solid state detector with detection limit = 0.01 ppm for 30 < Z < 35 and < 0.1 ppm for Z > 25 with an exposure time of 15 sec. The μ-XRD patterns were obtained using monochromatic X-rays of λ = 0.44285 Å and spectrum were collected using a high resolution MAR CCD camera with an exposure time of 30 sec; the resulting imaging plates were processed and converted into diffraction pattern employing the computer program FIT2D.

The  $\mu$ -XRF has been used to localize trace elements in the involved minerals and to find a correlation among different elements present in the sample. At the same time, simultaneous  $\mu$ -XRD patterns acquisition supplied information about the nature of the constituting minerals. These combined techniques allowed to correlate the chemical and mineralogical variations across 2 to 4 mm long transects characterized by submicrometric to micrometric mineralogical and textural heterogeneities.

#### *Transition from unaltered sulphides to authigenic Fe-rich assemblages*

Results of  $\mu$ -diffraction analyses performed on mineralised fragment allowed to characterize the transition from unaltered to completely oxidised sulphide-bearing crusts. The transition is marked by the disappearance of the sulphide mineralisation assemblages (pyrite +chalcopyrite + quartz) that are progressively replaced by goethite. The altered layer is composed exclusively by goethite with minor amounts of bernalite ( $\text{Fe}(\text{OH})_3$ ) that also occasionally occurs, associated with pyrite. No other Fe-oxides and -oxyhydroxides were detected.

$\mu$ -fluorescence patterns evidenced that most of the metals (Ni, Zn, Cu and Mo) released during sulphides alteration are efficiently uptaken by the new formed goethite and bernalite.

#### *Stratified Fe-rich crust*

Results from  $\mu$ -diffraction analyses show that stratified crusts are characterized by mineralogical heterogeneity even at the micrometric scale; the different coloured layers mark the transition from goethite-rich zones (containing significant amounts of 6-line ferrihydrite) to almost pure hematite-rich zones (without 6-line ferrihydrite). Minor amounts of other mineral species, such as lepidocrocite and phyllosilicates, are occasionally present. The absence of 6-line ferrihydrite in the hematite rich-bands indicates that the transformation process of ferrihydrite vs. hematite is complete, confirming the results of a previous TEM study (Carbone *et al.*, 2005).

Chemical analyses obtained with  $\mu$ -XRF, combined with  $\mu$ -XRD patterns, evidenced a significant mineralogical control on the mobility of chemical elements of environmental concern (such as Ni, Cu, Zn, As, Se, Rb, Sr, Nb, Mo, and Ag); in particular, goethite-rich layers are enriched in Ni and Zn, whereas hematite-rich precipitates selectively concentrate As, Se, Mo, Cu.

## REFERENCES

- Banfield, J.F., Welch, S.A., Zhang, H., Ebert, T.T., Penn, R.L. (2000): Aggregation-based crystal growth and microstructure development in natural iron oxyhydroxide biomineralization products. *Science*, **289**, 751-754.
- Banfield, J.F. & Navrotsky, A. (2001): Nanoparticles and the environment. *Rev. Mineral. Geochem.*, **44**, 349 p.
- Banfield, J.F. & Zhang, H. (2001): Nanoparticles in the environment. In: "Nanoparticles and the environment", J.F. Banfield & A. Navrotsky, eds. *Rev. Mineral. Geochem.*, **44**, 1-58.
- Bigham, J.M., Carlson, L., Murad, E. (1994): Schwertmannite, a new iron oxyhydroxy-sulphate from Pyhasalmi, Finland, and other localities. *Mineral. Mag.*, **58**, 641-648.
- Birch, W.D., Pring, A., Reller, A., Schmalte, H.W. (1993): Bernalite,  $\text{Fe}(\text{OH})_3$ , a new mineral from Broken Hill, New South Wales: description and structure. *Am. Mineral.*, **78**, 827-834.
- Brown, G.E., Foster, A.L., Ostergren, J.D. (1999): Mineral surfaces and bioavailability of heavy metals: a molecular scale perspective. *Proc. Nat. Acad. Sci. USA*, **96**, 3388-3395.
- Carbone, C., Di Benedetto, F., Marescotti, P., Martinelli, A., Sangregorio, C., Cipriani, C., Lucchetti, G., Romanelli, M. (2005a): Genetic evolution of nanocrystalline Fe-oxides and -oxyhydroxides assemblages from the Libiola Mine (Eastern Liguria, Italy): structural and microstructural investigations. *Eur. J. Mineral.*, **17**, 785-795.

- Carbone, C., Di Benedetto, F., Marescotti, P., Sangregorio, C., Sorace, L., Lima, N., Romanelli, M., Lucchetti, G., Cipriani, C. (2005b): Natural Fe-oxides and -oxyhydroxides nanoparticles: an EPR and SQUID investigation. *Mineral. Petrol.*, **85**, 19-32.
- Cornell, R.M. & Schwertmann, U. (1996): The iron oxides: structure properities, reactions, occurrence and uses. VCH, Weinheim, 573 p.
- Dinelli, E., Morandi, N., Tateo, F. (1998): Fine-grained weathering products in waste disposal from two sulphide mines in the northern Apennines, Italy. *Clay Min.* **33**, 423-433.
- Dinelli, E. & Tateo, F. (2002): Different types of fine-grained sediments associated with acid mine drainage in the Libiola Fe-Cu mine area (Ligurian Apennines, Italy). *Appl. Geochem.*, **17**, 1081-1092.
- Hochella, M.F.Jr. (2002): Nanoscience and technology: the next revolution in the Earth sciences. *Earth Planet. Sci. Letters*, **203**, 593-605.
- Jambor, J.L. & Blowes, D.W. (1994): Short course handbook on environmental geochemistry of sulfide mine-wastes. Mineralogical Association of Canada, Short Course Handbook, **22**.
- Janney, D.E., Cowley, J.M., Buseck, P.R. (2001): Structure of 6-line ferrihydrite by electron nanodiffraction. *Am. Mineral.*, **86**, 327-335.
- Kim, J.J. & Kim, S.J. (2003): Environmental mineralogy and genetic characterization of ochreous precipitates from Acid Mine Drainage in Taebaeg, Korea. *Envir. Sci. Technol.*, **37**, 2120-2126.
- Loan, M., Cowley, J.M., Hart, R., Parkinson, G.M. (2004): Evidence on the structure of synthetic schwertmannite. *Am. Mineral.*, **89**, 1735-1742.
- Loan, M., Richmond, W.R., Parkinson, G.M. (2005): On the crystal growth of nanoscale schwertmannite. *J. Cryst. Growth*, **275**, 1875-1881.
- Marescotti, P. & Carbone, C. (2003): La miniera dismessa di Libiola (Sestri Levante, Liguria Orientale): Studio mineralogico sui processi di alterazione di solfuri di Fe e Cu e valutazione del loro impatto ambientale. *Georis. Amb.*, **109**, 45-53.
- Marini, L., Saldi, G., Cipolli, F., Ottonello, G., Vetuschi Zuccolini, M. (2003): Geochemistry of water discharges from the Libiola mine, Italy. *Geochem. J.*, **37**, 199-216.
- Murad, E. & Rojik, P. (2003): Iron-rich precipitates in a mine drainage environment: influence of pH on mineralogy. *Am. Mineral.*, **88**, 1915-1918.
- Nazmov, V., Reznikova, E., Somogyi, A., Mohr, J., Sailea, V. (2004): Planar sets of cross X-ray refractive lenses from SU-8 polymer. *Soc. Photo-Opt. Instr. Eng. Proc.*, **5539**, 235-243.
- Saintavit, P. & Ohresser, P. (2004): [www.synchrotron-soleil.fr/francais/lignes/BL4.pdf](http://www.synchrotron-soleil.fr/francais/lignes/BL4.pdf)
- Schwertmann, U. & Taylor, R.M. (1989): Iron oxides. In: "Minerals in soil environments", J.B. Dixon and S.B. Weed, eds. Soil Sci. Soc. Am., Madison, 379-438.
- Schwertmann, U., Friedl, J., Stanjek, H. (1999): From Fe(III) ions to ferrihydrite and then to hematite. *J. Colloid Interf. Sci.*, **209**, 215-223.
- Šucha, V., Dubiková, M., Cambier, P., Elsass, F., Pernes, M. (2002): Effect of acid mine drainage on the mineralogy of a dystic cambisol. *Geoderma*, **110**, 151-167.