

**MINERALOGICAL AND CHEMICAL EVOLUTION OF OCHREOUS
PRECIPITATES RELATED TO ACID MINE DRAINAGE PROCESSES
IN THE ROȘIA MONTANĂ GOLD MINE (ROMANIA) AND
IN THE LIBIOLA Fe- AND Cu-SULFIDE MINE (ITALY)**

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INTRODUCTION

The main purpose of the research developed in this Phd thesis was to characterize the mineralogy and the chemistry of ochreous precipitates occurring at the Roșia Montană (Alba County, Romania) and Libiola mines (Sestri Levante, Italy), with particular regard to the ability of autigenic phases to selectively scavenge ecotoxic elements from contaminated solutions during their genesis and successive minerogenetic evolution.

The genesis of ochreous precipitates, in active and abandoned sulphide mines, is mainly due to Acid Mine Drainage processes (AMD; Jambor & Blowes, 1994; Jambor *et al.*, 2000; Nordstrom *et al.*, 2000; Jambor *et al.*, 2003); these processes comprise a concatenated series of mineralogical and chemical reactions triggered by the supergenic interaction between sulphide mineralizations and atmospheric agents. The AMD environments are commonly characterized by the diffuse circulation of Acid Sulphate Waters (ASW; Alpers & Nordstrom, 1991; Jambor & Blowes, 1994; Plumlee *et al.*, 1999; Nordstrom & Alpers, 1999), *i.e.* acid waters ($pH \leq 3$), with high sulphate concentrations (103 a 104 mg/l); together with sulphates several ecotoxic metals (such as Zn, Cr, Cu, Ni, Co, Cd, Pb and As) are mobilized and/or selectively concentrated by ASW. The mixing between mine-waters and unpolluted streams or runoff channels, determines the extensive precipitation of Fe-rich authigenic minerals, composed by complex associations of Fe oxides *s.l.* (Fe-oxides, -oxyhydroxides and -oxyhydroxysulphates; Cornell & Schwertmann, 2003). These minerals are able to uptake many elements from the solutions due to their crystallochemical properties and their adsorption capacity. The genesis and the stability of Fe oxides *s.l.* are controlled by continuous and cyclic variations of the chemical parameters of the solutions (in particular pH , Eh, SO_4 concentration, saturation, activity and speciation of ions).

The Roșia Montană and the Libiola mines were chosen for this study because they are both characterized by active and intense AMD processes causing the widespread circulation of ASW containing high levels of ecotoxic elements, but they occur into two very different geological contexts.

The Roșia Montană gold mine is located in Transilvania (Alba County, Romania) and it extends over an area of about 23.8 km² within the basins of the Roșia and Corna rivers, which, in turn, are tributaries of the Abrud River. The Roșia Montană ore is a world class gold deposit hosted in a “maar-diatreme” complex that intrudes a cretacic sedimentary sequence (Leary *et al.*, 2004). The deposit has been interpreted as an “intermediate-sulphidation epithermal deposit” (Sillitoe & Hedenquist, 2003) and it is hosted into porphyritic dacites, andesites and breccia pipes of Neogene age (14 My; Rosu *et al.*, 2004), characterized by a pervasive adularia alteration with a phyllic overprint (Leary *et al.*, 2004). The main gangue minerals are quartz, adularia, illite, sericite, muscovite, biotite, hornblende, chlorite, calcite, rhodochrosite and rhodonite. The gold mineralizations are associated with polymetallic sulphides (pyrite, marcasite, sphalerite, galena, chalcopyrite, and arsenopyrite; Wallier *et al.*, 2006). After centuries of exploitation, the mine is currently abandoned and comprises about 150 km of underground excavations, two open pits, and four main waste-rock dumps near the open pits (RMGC, 2006). Most of the contaminated waters, circulating in the complex network of underground excavations, flow out from the lowest adit of the mining area, named “Sf. Cruci din Orlea” (714 m asl).

The Libiola Fe-Cu sulphide mine is located about 8 km NE from the town of Sestri Levante (Eastern Liguria, Italy) and extends over an area of about 4 km² within the basin of Gromolo Creek, between its left tributaries Rio Boeno and Rio Cattana. Libiola represented one of the most important Italian mine for Fe- and Cu-

sulphide exploitation and it has been classified as a “stratabound Volcanic-associated Massive Sulphide deposit” (VMS; Zaccarini & Garuti, 2008). The deposit is the result of a hydrothermal oceanic stage followed by a tectono-metamorphic event that caused the recrystallization and the thickening of the primary mineralizations (Ferrario & Garuti, 1980). The mining area is mainly characterized by pillow basalts with minor serpentinites, gabbros, and ophiolitic breccias outcrops. The sulphide ores (pyrite, chalcopyrite, and minor sphalerite mineralizations) mainly occur toward the top of the pillows basalt sequence. The main gangue minerals are quartz and chlorite (Marescotti & Carbone, 2003). After about a century of exploitation, the mine is currently abandoned and comprises about 32 km of underground excavations, three open pits and five major dumps scattered throughout the entire mining area; minor waste rocks and tailings dumps are also located close to the main mine adits (Marescotti & Carbone, 2003). Waters that interact with the complex network of galleries of the mine flow out mainly from four adits that are characterized by a perennial flow of ASW, even though there can be remarkable differences in the ASW discharge, depending on precipitation rates (Marescotti *et al.*, 2011).

SAMPLING AND ANALYTICAL METHODS

In order to evaluate the spatial evolution of the mineralogy and chemistry, samples of ochreous precipitates and related mine waters were collected from the lowest adits of the two mine sites up to their confluence with the unpolluted streams of the two mining areas. The samples were collected in specific points where a wide precipitation of secondary minerals was present. Several parameters (temperature, pH, Eh and electrical conductivity) were measured *in situ* with portable instruments.

At the Roşia Montană mining area, the sampling started from the “Sf. Cruci din Orlea” mine adit up to the confluence between the Roşia and the Abrud rivers (for a total distance of about 5 km; Fig. 1). After the confluence of Roşia and Abrud rivers the influence of the ASW input was still present for hundreds of meters as evidenced by the high turbidity due to the extensive presence of suspended ochreous precipitates.

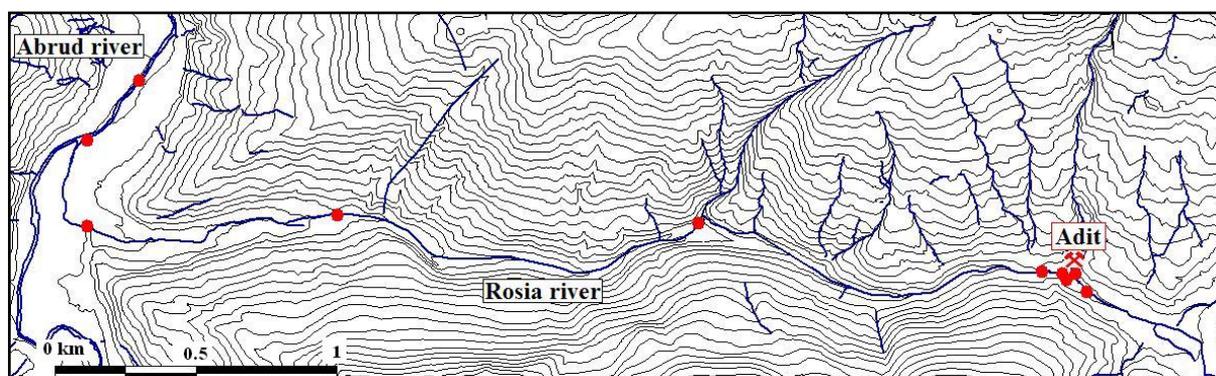


Fig. 1 - Schematic map of Roşia River. The main streams of the mine area are depicted in blue. The black arrows indicate the flow direction of Roşia and Abrud rivers. The red circles indicate the sampling points.

At Libiola, the sampling was performed in one of the four lowest adits of the mining area (*i.e.* the “Ida” adit; 115 m asl) that discharge ASW very close to the confluence between the Boeno and the Gromolo creeks, (Fig. 2). The Ida adit was chosen because it corresponds to the entrance of the longest underground tunnel of the mine area (about 5.5 km) and it is characterized by ASW that continuously flow out through a *waste-rock* dump before the mixing with the unpolluted waters of the Boeno and Gromolo creeks (Fig. 2).

The chemical analyses to determine the anion and cation concentration on mine waters were obtained by means of inductively coupled plasma atomic emission spectroscopy (ICP-OES), atomic absorption spectroscopy (AAS) and chromatography. The chemical characterization of precipitates was performed by means of inductively coupled plasma mass spectroscopy (ICP-MS). The mineralogy of the samples was determined by X-ray powder

diffraction (XRPD) and infrared spectroscopy (IR). Some selected samples, representative of the main mineralogical assemblages, were further analyzed by means of transmission electron microscopy (TEM) and microanalysis (EDX). Finally desorption experiments were carried out on natural mixtures of Fe-oxyhydroxides (goethite) and -oxyhydroxysulphates (jarosite e schwertmannite), sampled at the two mine sites, to investigate the role of these minerals in the control of the mobility of selected ecotoxic elements.

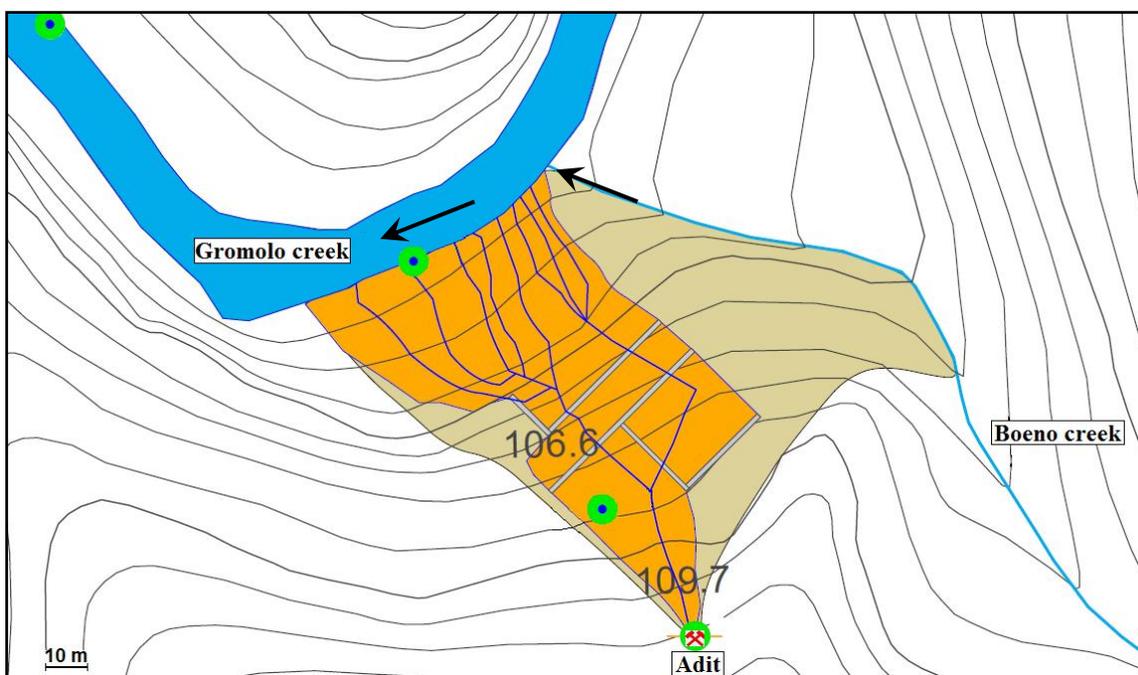


Fig. 2 - schematic map of the water flowing from the “Ida” adit (Libiola mining area) to the confluence with the Gromolo Creek; the waste-rock dump is depicted in light brown whereas the areas interested by the ASW flow in orange. The black arrows indicate the flow direction for Gromolo and Boeno creeks. The green circles indicate the sampling points.

RESULTS

Water Chemical analyses

Waters from both mine sites evidenced systematic variations of pH , Eh, SO_4 and dissolved metal contents. The mine waters flowing out from the lowest galleries of the two investigated mining areas (“Sf. Cruci din Orlea” adit at the Roşia Montană mine and “Ida” adit at the Libiola mine) were characterized by the lowest pH (2.4-3.2) and the highest Eh (460-650 mV), SO_4 (4000-4800 mg/l), and metal contents (Zn, Cr, Cu, Ni, Co, Cd, Pb and As). Waters collected downstream from the lowest adits, due to the mixing with the unpolluted streams of the two areas, were characterized by different evolution at the Roşia Montană and Libiola mines. At Roşia Montană the mixing between the ASW and the unpolluted water of Roşia river determine only a local variation of chemical parameters and the hydrochemistry of these waters remained almost constant for the entire course of the river (about 5 km). They were comparable with the unmixed ASW ($pH = 2.9-3.8$, Eh = 460-480 mV and metal contents) as a consequence of the constant high flow rate of mine waters (they represent about 8% of the total flow rate of the Roşia basin; RMGC, 2006). A remarkably different hydrochemistry was evident at the confluence between Roşia and Abrud rivers, being characterized by a significant increase in pH (6.3-7), decrease in Eh (≈ 300 mV), and a general reduction of dissolved SO_4 and metal load; these variations were determined either by the dilution due to the mixing and by the extensive precipitation of solid phases.

Waters collected downstream from the “Ida” adit (Libiola mine) to the mixing point with the Gromolo creek were characterized by a remarkable variations of hydrochemistry; the ASW flowing out from the adit were characterized by low pH (2.4-3.2) and high Eh (550-650 mV), SO_4 (4000-4500 mg/l), and metal contents; conversely, after the mixing they show an abrupt increase of pH (6.5-8.2) and a decrease of Eh (160-290 mV), as well as of dissolved SO_4 and metals. These features reflect the relatively very low flow rate and the very short course of ASW seepage that in few tens of meters flow into the Gromolo creek.

Mineralogy of precipitates

Ochreous precipitates from the Roşia Montană and the Libiola mines have been divided on the basis of their genetic environment: 1) unconsolidated precipitates (UP) that formed directly from the solutions; 2) consolidated precipitates (CP) that formed from ASW in areas with slow flow rate and evolve *in situ* forming decimetric layers. It is important to outline that CP precipitates keep the spatial and temporal evolution of the precipitation events and thus they are particularly interesting to understand the mineralogical and chemical transformations occurring as a consequence of their ageing.

The precipitates of the two mine areas evidenced important mineralogical differences. According to XRPD and IR analyses, the dominant minerals within the precipitates from Roşia Montană mine (UP and CP) are represented by K-jarosite [$KFe_3(OH)_6(SO_4)_2$] (stability field: $pH < 3$ and $SO_4^{2-} > 3000$ mg/l; Bigham *et al.*, 1996) and schwertmannite [$Fe_8O_8(OH)_6 SO_4 nH_2O$] (stability field: $2.5 < pH < 4$ and $1000 < SO_4^{2-} < 3000$ mg/l; Bigham *et al.*, 1996; Cornell & Schwertmann, 2003). Jarosite and schwertmannite were stable for the entire course of the Roşia river, due to the constant high acidity and sulphate concentration of these waters ($pH \approx 3$ and $4300 < SO_4 < 4800$ mg/l). TEM analyses performed on selected precipitates samples showed that jarosite mainly occurs as idiomorphic square-shaped lamellae with subrounded corners, whereas schwertmannite is not present with the typical “pin-cushion” morphology (Bigham *et al.*, 1996), but forms subspherical aggregates of subrounded nanoparticles characterized by an electronically dense nuclei. Generally, schwertmannite represents a metastable phase that tends to evolve to more stable minerals, such as goethite (Bigham *et al.*, 1996; Regenspurg *et al.*, 2004; Jönsson *et al.*, 2005). Conversely, in the Roşia Montană precipitates schwertmannite remained stable for the entire course of the Roşia River; this behaviour could be related to the constant chemical parameters of the investigated water course which are compatible with the stability field of schwertmannite. Nevertheless it cannot be excluded a physical removal of the new-forming schwertmannite due to the high hydrodynamic of the Roşia River, that could have inhibited the “ageing” of the sediments and the consequent transformation. The autigenic minerals within the stream sediments of the Roşia River decreased progressively toward the confluence with the Abrud River in favour of minerals of detrital origin (mainly quartz, muscovite, illite, chlorite and biotite).

The secondary minerals occurring in the ochreous precipitates (UP and CP) of the Libiola mine are characterized by goethite [$FeOOH$] (stability field: $2 < pH < 4$ and $1200 < SO_4 < 5300$ mg/l; Marescotti *et al.*, 2011) and K-jarosite; schwertmannite is present in trace amounts both in UP and CP precipitates, despite the genetic environment should be favorable to its direct precipitation, as evidenced from previous work from the same area (Marescotti *et al.*, 2011). This behaviour can be explained considering an almost complete transformation of schwertmannite into goethite in the studied samples. TEM analyses performed on selected precipitates samples show that goethite is always present as irregular-shaped and electronically dense aggregates of randomly oriented nanoparticles. On the basis the results, it is not clear if goethite represent the transformation product of precursor schwertmannite or it was directly formed by precipitation from ASW. XRPD analyses evidenced that the precipitates forming at the confluence with the Gromolo creek were exclusively composed of amorphous Fe-oxyhydroxides; this feature could be the consequence of the very rapid mixing that cause an abrupt increase of pH and the extensive precipitation of solid phases.

Chemistry of precipitates

The ochreous precipitates of both mine sites evidenced high concentrations of As, Pb and other metals of environmental concern (Cu, Zn, Ni, Co, and Cr) thus suggesting the effective control on their mobility by the autigenic phases (jarosite and schwertmannite at Roşia Montană; jarosite and goethite at Libiola). Either at Roşia Montană and Libiola mines, Zn and Cu represent very mobile elements under acid pH conditions (2.6-3.8) and remain in solutions until neutral-alkaline pH values (> 6.5 ; Smith, 1999; Lee *et al.*, 2002; Sanchez Espana *et al.*, 2005; Balistrieri *et al.*, 2007). The mobility of Cr, Ni and Co was strongly influenced by the pH variations in both mine sites. At the Roşia Montană mine, Cr, Ni and Co were preferentially partitioned in the precipitates forming in the final portion of Roşia River, which was dominated by detrital minerals. At the Libiola mine, Cr, Ni and Co were partitioned in the precipitates forming from ASW that were almost exclusively composed by goethite and jarosite. The secondary minerals precipitation influenced Pb and As concentration in the solution; these elements are less mobile at $pH < 4$ and are easily scavenged by the neof ormation solid phases (Williams, 2001; Sanchez Espana *et al.*, 2005; Balistrieri *et al.*, 2007; Nordstrom, 2011). At the Roşia Montană mine As and Pb were preferentially partitioned in the precipitates forming at very low pH (2.7-3.8). Arsenic is known as one of the most toxic elements and is therefore of great interest in environmental studies. The bulk chemistry analyses on the Roşia Montană precipitates forming from ASW (UP and CP) evidenced significant arsenic concentrations (2400-2900 ppm). Mineralogical analyses performed on these precipitates did not show direct evidences of As presence in the structure of jarosite and schwertmannite. Nevertheless, as demonstrated by Carlson *et al.* (2002), an important indirect evidence of arsenic incorporation in the schwertmannite structure could be its morphology which, in the studied samples, was characterized by the absence of the typical whiskers.

Desorption experiments

The aim of the experiments performed on natural samples of ochreous precipitates was to investigate the adsorption/desorption processes involving ecotoxic elements (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, and Pb) and to verify the type and the amount of elements that can be temporarily or permanently removed by the solid phase from the contaminated solutions. As known, the use of natural samples in these experiments is a source of notable difficulties both for the experiment set-up and data interpretation. However, these drawbacks can be partly overcome or at least minimized when well characterized samples are used. Three samples from the Roşia Montană and the Libiola mines were chosen on the basis of their mineralogical and chemical characteristics: two samples were composed by mixtures of schwertmannite and jarosite in different proportion (Roşia Montană mine) and one sample was composed exclusively by goethite (Libiola mine). These samples were chosen, because of the well known capacity of these three minerals to uptake a wide range of trace elements from the solutions.

Batch desorption experiments consist in shaking solution containing the solid phase, until the desorption equilibrium is reached. A reaction time of 48 hours was used and, at appropriate time intervals, a 5 ml aliquot of solution was sampled from the reaction beaker and then filtered and acidified for the ICP-MS analysis. A solid/solution ratio of 1:200 (g:ml) was used and the duration of each experiment was limited to 48 h in order to minimize the dissolution of solid phases. The pH of the solutions was left to drift freely to the value generated by the interaction with the solids. A stable acid pH value (2-3) was quickly reached in few minutes after the beginning of the experiments.

Precipitates consisting of K-jarosite and schwertmannite mixtures showed a different behaviour with respect to the release of Al, Mn and Ni, due to the different relative proportions between the two phases in the mixtures. Al could be incorporated in the structure of jarosite by substituting Fe^{3+} (in octahedral coordination sites; Welch *et al.*, 2008) and therefore it could be permanently stored in the solid phase. Conversely Ni and Mn appear to be preferentially adsorbed by schwertmannite and therefore they could be easily released to the solution. The samples composed by mixtures of schwertmannite and jarosite did not release As in solution during the whole experiment, thus suggesting that As is preferentially incorporated in the structure of

schwermannite and jarosite by substituting sulphate (as arsenate). Another possible explanation for the very low As desorption, could be the acid pH rapidly reached during the experiment. In fact, arsenic tends to be released easily by these solid phases only at near-neutral pH condition (Frau *et al.*, 2008).

Precipitates consisting of goethite mixtures released less elements if compared with jarosite and schwermannite mixtures. These behaviours can be explained considering that Al^{3+} , Cr^{3+} , Cu^{2+} , Co^{3+} , Ni^{2+} , Mn^{3+} can be incorporated in the goethite structure by substituting Fe^{3+} .

CONCLUSIONS

The ochreous precipitates forming from the ASW at Roşia Montană and Libiola mines represent a highly dynamic mineralogical and chemical system. The mineralogy of the precipitates varies significantly as a consequence of variations of the chemical parameters of the evolving solutions (mainly pH, Eh, and SO_4 concentration) which, in turn, are mainly controlled by the mixing between ASW flowing from the lowest adits of the two mines and the unpolluted water of the main streams of the respective basins.

The results indicate that most of the environmental problems, related to the acid mine drainage processes, have deleterious effects not only in the mining areas because they determine acid pH and toxic metals mobilization for several kilometers from the pollution sources. Even if most of the authigenic phases forming from ASW can efficiently scavenge numerous trace elements from the associated waters, most of the uptaken trace elements are generally rapidly released during the mineralogical evolution triggered by the physico-chemical variations in the environment or simply by ageing.

The results from the Roşia Montană and Libiola case studies indicated that the role of secondary minerals as “mitigating agents” is highly ephemeral. Minor pH-Eh oscillations cause rapid mineralogical transformations, via dissolution-precipitation or solid-state transformation, which, in turn, control the trace elements that will be mobilized or permanently stored within the solid phases.

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