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The role of AMD secondary minerals in controlling environmental pollution: Indications from bulk leaching tests

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ABSTRACT

Weathering of sulphide minerals produces a large variety of Fe-oxide-bearing ochreous, varicoloured precipitates and efflorescences of variably soluble sulphate salts. These secondary minerals play an important role in acid mine drainage processes and, more generally, for environmental pollution, since they can be either a sink or a source for acidity and toxic metals. At Libiola mine, eastern Liguria (Italy), the secondary minerals directly form through precipitation from acid sulphate waters within waste-rock dumps and outcropping mineralized bodies as well as within streams and runoff channels. Within waste-rock dumps they are present mainly as cement, filling the inter-clast porosity, and/or as coating and ephemeral efflorescences on the outcropping surfaces. Their stability represents a major environmental issue due to the potential importance of these phases in controlling metal distribution in the surface environment. This paper presents a detailed mineralogy and geochemistry characterisation of these materials, investigating the tendency for different types of secondary minerals (hardpans, ochreous consolidated precipitates, ochreous colloids, non ochreous colloids) to release metals after a simple mixing with deionised water for 12 days. Within the different types of deposits, hardpans showed the lowest tendency to release metals, in contrast to ochreous colloids and ochreous concretions that gave the highest concentrations.
Nickel was the element most easily extracted by this treatment, even from non-ochreous colloids, while iron was much less readily leached. Dissolution experiments carried out on efflorescent sulphate salts demonstrated that these materials have a strong acid producing affinity which led to their complete dissolution. These results indicate that secondary phases associated with acid mine drainage can play an important role in controlling trace metal mobility, acting either as scavengers, to remove metals, from solutions or also as secondary sources of metal contamination during the interaction of these materials with surface waters.

1. Introduction

Acid mine drainage (AMD) is triggered by the oxidation of sulphide minerals (predominantly pyrite), during and after mining activities, and can cause severe environmental pollution due to the acidification of circulating waters and to the release of contaminants (including transition-, heavy-, and semi-metals) to the soils and waters (Frau and Marescotti, 2011; Jambor et al., 2003; Nordstrom and Alpers, 1999; Taylor and Konhauser, 2011). Another important consequence of AMD is the widespread precipitation of secondary minerals, which extensively form throughout the mining area when oversaturated acid sulphate waters (ASW) undergo sudden physico-chemical changes (e.g., mixing with uncontaminated waters or through evaporation processes) that can cause the precipitation of a wide range of oxyhydroxide and sulphate mineral phases.

The characteristics of the secondary minerals forming during AMD depend on variations in chemical conditions of the receiving environment (particularly variations in pH, Eh, and T). From a genetic point of view, three main settings for secondary mineral formation can be distinguished: 1) unconsolidated precipitates, flocs, and loose suspensions forming from ASW solutions within streams, rills, and runoff channels receiving mine waters; 2) consolidated crusts and hardpans precipitating from seepage drainage of contaminated solutions within waste-rock dumps and tailings; 3) efflorescent salts forming mainly on the surface of waste-rock deposits, tailings, and mine soils due to evaporation of mine waters in dry periods or as a consequence of the heat produced by the exothermic reactions active during sulphide oxidation (Flohr et al., 1995; Nordstrom, 2011).

The mineralogy of the secondary minerals forming in these three settings is quite variable but the main minerals can be grouped into three broad groups: 1) Fe-oxides, -oxyhydroxides, and -oxyhydroxysulphates (such as ferrihydrites 2 and 6-lines, goethite, hematite, schwertmannite, and jarosite) and other low crystalline Fe phases; 2) hydrous Ca-, Fe-, Al- and other metal-sulphates (such as gypsum, melanterite, copiapite, halotrichite, chalcanthite, epsomite); 3) other metal rich phases, usually with low crystalline, such as basaluminite-like Al minerals, woodwardite-like Cu minerals and hydrozincite.

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All these minerals have specific fields of stability within the wide range of pH and Eh conditions that typically occur in AMD environments (Accornero et al., 2005; Bigham et al., 1996; Cravotta, 1994; Dinelli and Tateo, 2002; Dinelli et al., 1998; Dinelli et al., 2001; España et al., 2005; Jambor et al., 2003; Jones et al., 2011; Kumpulainen et al., 2007; Marescotti et al., 2012; Marini et al., 2003; Nordstrom, 2011; Podda et al., 2000; Sánchez España et al., 2006; Tumiati et al., 2008; Zuddas and Podda, 2005).

The role of these secondary minerals in controlling the fate of ecotoxic metals in AMD environments is one of the most debated topics. There are a number of extensive reviews that investigate the role of secondary AMD minerals in mitigating and/or exacerbating acidity and ecotoxic metal mobility, including those by Jambor et al. (2000), Cornell and Schwertman (2003), Frau and Marescotti (2011), Nordstrom (2011). Efflorescent salts are often very soluble and represent only a temporary host for many metals, as discussed for example by Alpers et al. (1994, 2000), Buckby et al. (2003), Frau (2000), Jerz and Rimstidt (2003), Hammarstrom et al. (2005), Valente and Gomes (2009). Ochreous precipitates reduce metal mobility through adsorption or coprecipitation (Carlson et al., 2002; Hammarstrom et al., 2005; Lottermoser, 2003) and may represent a more stable sink for metals.

The geochemistry, mineralogy, and environmental impacts of ochreous deposits and secondary minerals in the Libiola mining area (Eastern Liguria, Italy) have been previously investigated by a number of authors (Accornero et al, 2005; Carbone et al., 2005a,b, 2011, 2012; Dinelli and Tateo, 2002; Dinelli et al., 1998, 2001; Marescotti and Carbone, 2003; Marescotti et al., 2010, 2012; Marini et al, 2003). With this work, we aim to extend the knowledge to the other secondary mineral types occurring in different settings or forming at different physico-chemical conditions in this important mining area. Moreover, we have integrated the existing data sets with leaching experiments to evaluate the effective potential of the different mineral species in either temporarily or permanently storing the metals under a range of geochemical conditions.

In particular, this paper is focused on 1) the identification and minerochemical characterization of secondary minerals from the different settings observed and sampled in several field campaigns, 2) the evaluation of the role of mineral species within loose precipitates, efflorescences, and crusts in controlling the toxic metal mobility (in particular Fe, Cu, Zn, and Ni).

2. Studied sites, materials, and analytical methods

Prior to its complete closure in 1962, the Libiola mine was one of the most important Italian sulphide ore deposits exploited at various times since the Bronze Age (Campana et al., 1999). The mine site is located about 8 km NE of Sestri Levante (Eastern Liguria, Italy) and extends over an area of about 4 km^2 within the basin of the Gromolo Creek (Fig. 1). The climate is Mediterranean humid and is characterised by an average temperature of 15 °C and rainfall that varies between 1100

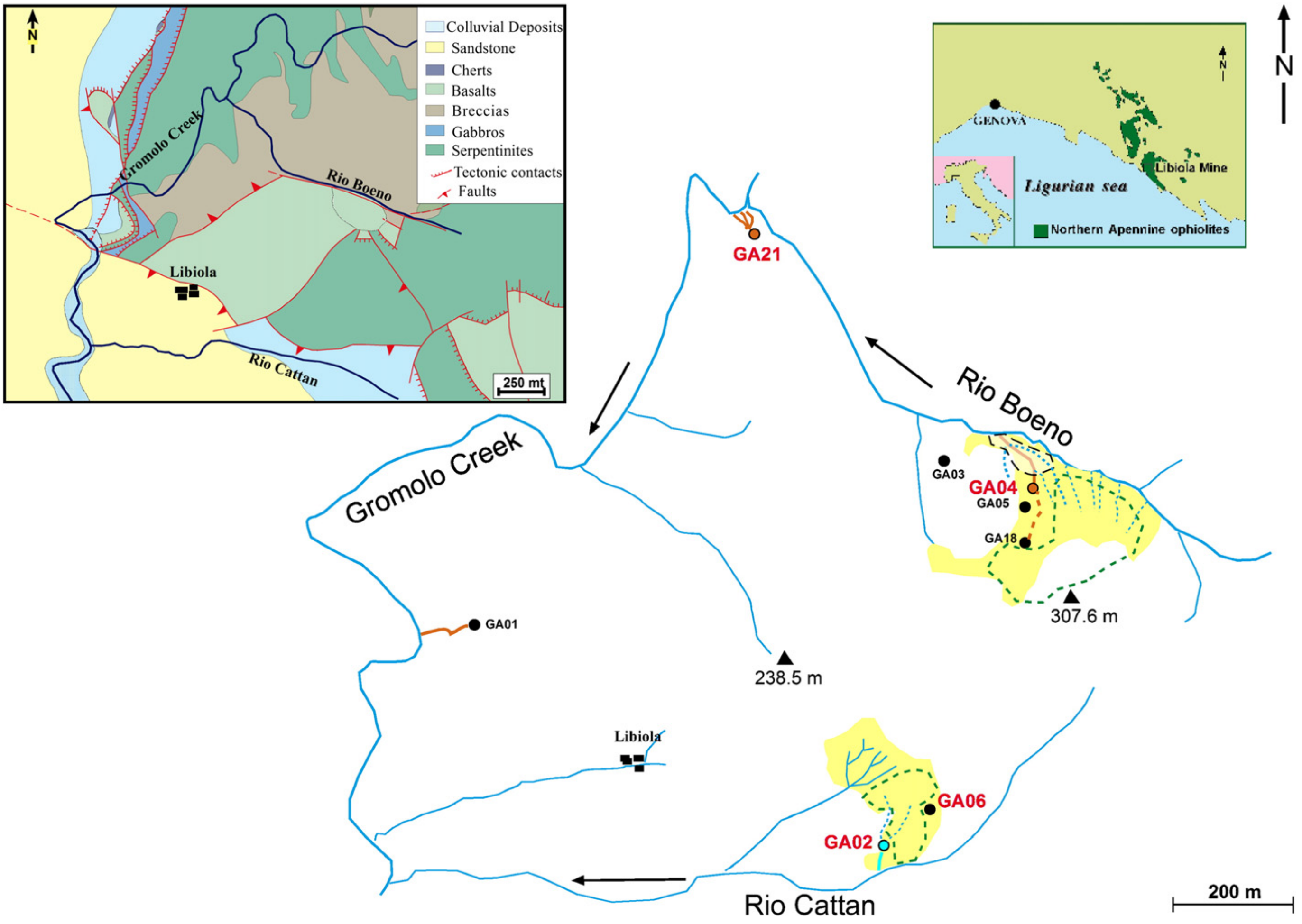

Fig. 1. Schematic map of the Libiola mine area. The main waste rock dumps are shown in yellow; the dots labelled GA02, GA04, GA06 and GA21 (red in colour) represent the adits investigated in this study. The ochreous and light blue coloured area indicate where samples representative of varicoloured precipitates were collected; GA04 area (dashed and filled in white) is the site where milky-white precipitates collected. GA21 is the sampling site for ochre deposit. Efflorescent salt occurrences are indicated inside the green dashed area. The black arrows indicate the flow direction for Gromolo Creek (modified from Marescotti et al., 2012). In the inset the geological map of the Libiola mine area (adapted from Abbate et al. 1980, modified) is shown.