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Mineralogy and chemical forms of lead and zinc in abandoned mine wastes and soils: An example from Morocco

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ABSTRACT

Chemical extractions coupled with quantitative X-ray powder diffraction (XRPD) were used to define the chemical and mineralogical forms of Pb and Zn in abandoned wastes and soils from the Upper Moulouya mining district (Morocco). The aim was to provide baseline data required to assess metal mobility and bioavailability. Wastes and soils were sampled inside the mine sites of Zeïda, Mibladen and Aouli, both in exploitation and processing areas. Additional potentially unaffected soil samples were taken outside the Mibladen site. pH of wastes and soils is alkaline as a consequence of carbonate abundance (on average 36%). Total Pb and Zn concentrations have a wide spread of values (Pb: 0.041–17.25 g kg^{-1}; Zn: 0.051–276.5 g kg^{-1}), with tailings from all mines and soils from Mibladen processing area exhibiting the highest concentrations. Very low or no detectable contamination characterizes the soils from exploitation areas and those collected outside Mibladen. Zinc contamination is mainly restricted to Mibladen processing area, where Zn ores from other Moroccan mines were possibly processed. The sequential extraction procedure for metal fractionation indicates that in contaminated samples Pb and Zn are mainly present in the acetic acid extractable fraction, likely as carbonates, (Pb up to 80%; Zn up to 52%), while in less or not contaminated soils both metals are mostly associated with the reducible fraction, presumably as iron oxides (Pb up to 68%; Zn up to 80%). Eight minerals containing Pb and Zn were identified: cerussite, anglesite, galena, hydrozincite, smithsonite, sphalerite, willemite and hemimorphite. Cerussite is the most important Pb-host. Hemimorphite and smithsonite account for most Zn. According to the alkaline conditions and to the low solubility of Pb and Zn mineral phases, it can be suggested that within the studied environment mobilization into solution in aqueous systems and bioavailability of Pb and Zn have a low potential. Nevertheless, given aridity and strong winds, inhalation of airborne particulates may be a concern.

1. Introduction

The use of metals in human history has been cause of great benefits, as well as of unexpected harmful consequences. In fact, mining activities often represent an important source of pollution of heavy metals, which may be introduced into the atmospheric, terrestrial and aquatic ecosystems (Passariello et al., 2002). Many cases of chemical contamination have been described in former mining areas, where significant amounts of various elements were mobilized by weathering and leaching from abandoned mining wastes (for example Abrahams and Thornton, 1987; Hamilton, 2000). In semi-arid areas, the dispersion of soluble and particulate metals is often enhanced because soils are typically scarcely vegetated (Navarro et al., 2008). Furthermore, where soil consists of fine mine detritus, severe erosion problems caused by wind and water runoff may occur (Chopin et al., 2003). The extent and degree of heavy metal contamination around mines vary depending upon the mineralogical and geochemical characteristics of both ore and host rocks, as well as on the degree of mineralization of the tailings (Johnson et al., 2000). The fate and transfer of metals are complex and depend on the transport process involved, on the size and mineralogy of eroded particles and on the soil and sediment properties (Razo et al., 2004).

Evaluation of total concentration of metals and metalloids in soils is generally used as the first reference indicator for comparing pollution level with legislative limits; nevertheless the natural occurrence of toxic elements in soils, especially in disused mining areas, requires further analyses to detect the mobilization due to erosion and leaching to groundwater (Giuliano et al., 2007). The total amount of heavy metals in solid samples is an efficient approach to detect environmental contamination but it is not enough to evaluate the influence of each element in potential pollution of the ecosystem (Ure and

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Davidson, 2002). The biological availability, the potential toxicity, the interaction with organic-mineral constituents and the metal mobility, all depend on the form in which they are present in solid samples (Allen, 1997). An approach to this problem is to apply various chemical extractants, either singularly or sequentially in order to assess the forms, or at least the main pools, in which metal contaminants occur in solid samples (e.g. Adamo and Zampella, 2008; Ure and Davidson, 2002). However, it is now widely recognized that the forms determined by chemical extractions are inevitably operationally defined (Bacon and Davidson, 2008; Hillier et al., 2001). Mineralogical techniques such as electron microscopy and X-ray powder diffraction (XRPD), among many other instrumental methods, are often used to elaborate on the data obtained by chemical extractions (e.g. Hudson-Edwards et al., 1996; Ryan et al., 2002; Schön, 1995). Many different procedures can be used to obtain quantitative information from XRPD data but they have traditionally required a considerable investment of time compared to the relatively straightforward use of XRPD for phase identification (Hillier et al., 2001). In recent years, however, there have been significant developments in the use of the full pattern fitting methods for quantitative mineralogical analysis (Omotoso et al., 2006).

Direct methods are more sophisticated than chemical methods and need a high level of specialization to be routinely included in metal speciation studies. Nevertheless, a complementary use of the chemical and mineralogical approaches may provide a more realistic picture of the actual forms of heavy metals in solid matrices (Adamo et al., 2002; Hillier et al., 2003; Ryan et al., 2008; Venditti et al., 2000a,b).

In this study we have applied heavy metal speciation by sequential chemical extractions and quantitative mineralogical determination by XRPD, to define Pb and Zn chemical and mineralogical forms and phases in mine wastes and soils from the former lead mining district of the High Moulouya valley (Morocco).

The aim was to provide the base line data required to assess metal mobility/bioavailability based on the combined use of chemical and mineralogical methods to assess the forms in which the metals reside.

2. Materials and methods

2.1. The study area

Morocco with its large number of metalliferous sites is considered a traditional mining region since antiquity (Chronicle of Mineral Research and Exploration, 1998). One of these sites is the Upper Moulouya lead district which contained one of the largest concentrations of lead in Morocco, with a total output of more than 1 million metric tons (Rajlich, 1983). Currently the area is characterized by a low population density (less than 20 inhabitants per km^2) and poor economic conditions and only few studies have been undertaken to acquire information about the environment contamination by heavy metals from past mining activities (Bouabdli et al., 2005; El Hachimi et al., 2006; El Khalil et al., 2008). Our interest for the area was also due to the fact that it is crossed by the largest Moroccan river, the Moulouya, which, with its 520 km of length and tributaries, drains approximately 53,500 km^2 in the eastern part of the country, spreading contamination far away from the source up into the Mediterranean Sea where it finally flows.

The site of interest, the Upper Moulouya lead district, corresponds to the south-western region of the Oranaise Meseta bounded by High Atlas on Southeast and by Middle Atlas on Northwest (Piqué and Michard, 1989). The region is composed of two separate Paleozoic massifs (Bou-Mia and Aouli). The Paleozoic basement that crops out in these massifs consists of pelitic and quartzitic lithotypes intruded by Hercynian granites and unconformably overlain by a Mesozoic cover consisting of Triassic evaporites/siliciclastics and Jurassic and Cretaceous carbonates/shales (Bouabdli et al., 2005). In the Upper Moulouya district three main lead–barite deposits occur: Zeïda, Mibladen and Aouli (Jébrak et al., 1998) (Fig. 1).

Zeïda (Z) mining area (1490 m a.s.l.; period of active exploitation: 1972–1985) is located 30 km NW of the small town of Midelt, along the Moulouya river's course. At Zeïda the mineralization occurs as stratabound levels in sub-horizontal Permo-Triassic arkosic sandstones, unconformably covering the granite basement (El Jaouani, 2001; Emberger, 1965). In this mine the exploited ore body consisted mainly of cerussite (70% of Pb recovered) and galena (30%) associated with minor chalcopyrite, pyrite and barite. Minor anglesite, wulfenite, vanadinite, pyromorphite and rare sphalerite were also found at Zeïda (Amade, 1965; Direction des Mines, 1990).

Mibladen (M) ore deposit (1400 m a.s.l.; period of active exploitation: 1936–1985) extends over an area of about 60 km^2. The mining area is located 15 km ENE of Midelt in a plateau consisting mainly of Mesozoic carbonates covering the basement (Felenc and Lenoble, 1965). Mainly galena and less frequently barite have been extracted from this deposit, but rare chalcopyrite and pyrite have been encountered as well (Petris, 1963). The most common oxidation products at Mibladen are cerussite, anglesite and vanadinite. Galena, often in association with barite, occurs as impregnations, disseminations or layers of variable thickness in shaly–dolomitic and calcareous–dolomitic sediments (Emberger, 1961; 1965).

The Zeïda deposit may correspond to a Triassic metallogenic event, focused along fault systems or within permeable sandstone. Deep fluids were mobilized during the early extensional movements associated with the opening of the Atlas rift basin. The Mibladen mineralization is related to a distinct metallogenic event superimposed on the first one, and may represent a remobilization of earlier concentrations or a more recent event with metals originating from the same sources, but with a more pronounced contribution of local organic matter (Jébrak et al., 1998). It could be broadly considered as genetically belonging to the Mississippi Valley type class of deposits.

Aouli (A) mine (1130 m a.s.l.; period of active exploitation: 1926–1985) is located 26 km NE of Midelt and at 12 km from the village of Mibladen, in a narrow gorge cut by the Moulouya river. The Aouli ore zone extends over an area of 300 km^2 and consists of a network of veins hosted by metamorphic schists and granites; minor veins occur also in a cover of Permo-Triassic sedimentary rocks (Emberger, 1965). The main ore mineral at Aouli is galena, associated with barite and fluorite in a quartz gangue. Minor amounts of sphalerite, pyrite, chalcopyrite and rare malachite, azurite and cerussite have been also recorded (Nasloubi, 1993; Saunier, 1963).

Mining activity has seriously modified the natural landscape of the High Moulouya valley (Fig. 2). In the three mining areas, different sites are devoted to exploitation and processing activities. Deep excavations filled with ground- and run-off water (used by locals for irrigation and water holes for cattle), mine adits and abandoned pits occur in exploitation sites, where also mine wastes are accumulated in elongated banks up to 20 m high. Processing plants, usually built in close proximity to living areas, are characterized by the presence of several abandoned (and ruined) facilities and waste tailings. Most tailings are accumulated in dumps, preferentially located along fluvial banks without visible safety control. The almost general lack of vegetation cover, coupled with the typical high temperatures and strong winds of this part of Morocco, enhances erosion and transport of waste materials. The nearby Moulouya and Mibladen rivers, along with their tributaries, run through the area and are periodically subjected to flooding, further enhancing the dispersion of contaminants.

Climate of the study area corresponds to that of the Upper Moulouya region, with annual precipitation of 100–400 mm and mean annual temperatures of 12–14 °C, this depending on different locations (Combe and Simonot, 1971; Derrar, 1996). In the region, climate is semi arid and the average annual minimum temperature is reached in January, around 0 °C. In summer the average annual maximum temperature is reached in July (32–33 °C) (Raynal, 1961). The annual rainfall is almost