Mineralogical and geochemical controls of arsenic speciation and mobility under different redox conditions in soil, sediment and water at the Mokrsko-West gold deposit, Czech Republic

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ABSTRACT

Naturally contaminated soil, sediment and water at the Mokrsko-West gold deposit, Central Bohemia, have been studied in order to determine the processes that lead to release of As into water and to control its speciation under various redox conditions. In soils, As is bonded mainly to secondary arseniosiderite, pharmacosiderite and Fe oxyhydroxides and, rarely, to scorodite; in sediments, As is bonded mainly to Fe oxyhydroxides and rarely to arsenate minerals.

The highest concentrations of dissolved As were found in groundwater (up to 1141 μg L^{-1}), which mostly represented a redox transition zone where neither sulphide minerals nor Fe oxyhydroxide are stable. The main processes releasing dissolved As in this zone are attributed to the reductive dissolution of Fe oxyhydroxides and arsenate minerals, resulting in a substantial decrease in their amounts below the groundwater level. Some shallow subsurface environments with high organic matter contents were characterized by reducing conditions that indicated a relatively high amount of S$^{-2,0}$ in the solid phase and a lower dissolved As concentration (70–80 μg L^{-1}) in the pore water. These findings are attributed to the formation of Fe(II) sulphides with the sorbed As. Under oxidizing conditions, surface waters were undersaturated with respect to arsenate minerals and this promoted the dissolution of secondary arsenates and increased the As concentrations in the water to characteristic values from 300 to 450 μg L^{-1} in the stream and fishpond waters. The levels of dissolved As(III) often predominate over As(V) levels, both in groundwaters and in surface waters. The As(III)/As(V) ratio is closely related to the DOC concentration and this could support the assumption of a key role of microbial processes in transformations of aqueous As species as well as in the mobility of As.

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1. Introduction

In natural systems, As exists essentially in four oxidation states (−III, 0, +III, and +V), as both inorganic and organometallic species. Most of the naturally occurring As is contained in inorganic compounds (Cherry et al., 1979; Cullen and Reimer, 1989), where the relative proportions of As(V) and As(III) species are governed by three main environmental factors: the redox potential, the pH and the biological activity (Cullen and Reimer, 1989). From the standpoint of thermo-dynamics, the predominant forms of dissolved As under oxidizing conditions are As(V) species (H$_2$AsO$_4^-$, HAsO$_4^{2-}$ and AsO$_4^{3-}$), whereas As(III) species (H$_3$AsO$_3^0$ and H$_2$AsO$_3^-$) predominate in reducing

environments (Cherry et al., 1979; Sadiq, 1997). However, several studies have shown that the As(III) concentrations exceed those of As(V) in the permanently oxidizing environment of surface waters and soils, suggesting nonequilibrium thermodynamic conditions due to the slow oxidation kinetics of As(III) (e.g., Cullen and Reimer, 1989 and references therein; Bowell et al., 1994; Sohrin et al., 1997; Macur et al., 2001; Macur et al., 2004). Consequently, the distribution of As species is of considerable environmental concern, since As(III) is the most toxic As species (Cullen and Reimer, 1989).

Under normal soil conditions, the solubility, mobility and bioavail-ability of As are mostly driven by adsorption–desorption processes involving Fe, Al, Mn oxyhydroxides, clay minerals, carbonates (under oxidizing conditions) and sulphide minerals (under reducing condi-tions) (Cullen and Reimer, 1989; Sadiq, 1997). Moreover, secondary arsenate minerals can control the solubility of As when the amount of As exceeds the capacity of the available surface ligand-bonding sites and the concentrations of dissolved arsenate and metal cations exceed

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the solubility product of the arsenate minerals. A series of secondary arsenate and sulphoarsenate minerals has been identified under oxidizing conditions, including soils, mine tailings and former industrial sites (Magalhães, 2002; Morin and Calas, 2006). Scorodite is the most common arsenate found in the weathering environment of As-bearing sulphide deposits (Dove and Rimstidt, 1985). Subsequent interactions with solutions may cause a shift in the pH to neutral values, with precipitation of Ca, Mg and K–Ba arsenates, such as arseniosiderite, haidingerite, hörnesite, pharmacolite, pharmacosiderite, picropharmacolite, weillite, etc. (Voight et al., 1996; Juillot et al., 1999; Morin et al., 2002; Filippi et al., 2004; Frau and Ardau, 2004; Paktunc et al., 2004). These arsenate minerals are metastable under most natural conditions and their persistence in nature suggests that their solubility may control the concentration of As in waters. This finding is also in accordance with the sparse solubility data available for arsenate minerals (Langmuir et al., 2006).

The goal of the present study is to describe the mineralogical and geochemical processes controlling the release and/or sequestration of As in various redox environments above the Mokrsko-West gold deposit. To achieve this goal, we investigated the As distribution in naturally contaminated soil, stream and fishpond sediments and waters under various redox conditions. We combined detailed mineralogical investigations of solid samples with geochemical observations and with chemical analyses of surface water, pore-water and groundwater.

2. Geological and environmental background

The Mokrsko-West deposit (MWD) is unique among European Variscan gold deposits, both from the economic (gold reserves of about 100 t), and mining (unaffected by mining activities) points of view. The MWD is located in Central Bohemia, approximately 50 km south of Prague. Gold-bearing quartz veins and sheeted veinlets are the main types of mineralization in the deposit, which developed in the marginal part of the Variscan granodiorite belonging to the Central Bohemian pluton (Morávek et al., 1989).

The MWD is characterized by a low sulphide content (generally below 3 vol.%), quartz-dominated gangue with minor calcite and silicate minerals (plagioclase, titanite and sparse amphibole, chlorite, biotite) and by a lack of extensive hydrothermal alteration. Arsenopyrite (FeAsS) is the predominant sulphide (Morávek et al., 1989) and its weathering flux corresponds to approximately 95% of the total input of As into the soil (Drahota et al., 2006). Arsenic also occurs rarely in löllingite (FeAs$_2$), ullmannite (Ni(Sb,As)S) and as a trace element in pyrite (below 1 wt.%) (Malec, 1990). During weathering, the minerals are oxidized and this produces a series of secondary arsenates and As-bearing oxyhydroxides in the soil, namely, arseniosiderite [Ca$_2$Fe$_3$(AsO$_4$)$_3$O$_2$·3H$_2$O], ferrihydrite [5(Fe$_2$O$_3$)·9H$_2$O], goethite [FeO(OH)], minerals of the pharmacosiderite series [K,Ba, Ca)(Fe,Al)$_4$(AsO$_4$)$_3$(OH)$_{4–5}$·5-7H$_2$O], and scorodite [FeAsO$_4$·2H$_2$O] (Filippi et al., 2004; Drahota and Pertold, 2005; Filippi et al., 2007). The large extent of natural As contamination around the MWD is indicated by As levels in the soil of >200 mg kg^{-1} over approximately 1.12 km^2 (Janatka and Morávek, 1990).

The elevated As concentration in the ore and the mobility of As also constitute a potential environmental hazard with groundwater leaching from saprolite and soils. High concentrations of As in the groundwater (255–1690 µg L^{-1}) and surface water (50–340 µg L^{-1}) were encountered in shallow wells and a stream (Fig. 1), respectively (Jílek, 1985; Drahota and Pertold, 2005). The highest As concentrations were detected in the private wells of the village of Mokrsko which were used to supply drinking water until the symptoms of As-related peripheral vascular diseases were detected (Jílek, 1985).

The soils in the area can be defined as cambisols and gley soil and their thickness is between 1 and 10 m, depending on the topography and drainage (Morávek, 1991). The annual precipitation over the past 40 years averaged at 555 mm y^{-1}, and the average temperatures in July rose to 17 °C, decreasing down to −3 °C in January. Additional geological and climatic information can be found in Drahota et al. (2006) and Filippi et al. (2007).

3. Methods and materials

3.1. Soil and sediment sampling and preparation

The three sampling profiles lie at an increasing distance from the primary ore mineralization in the east (characterized by soil profile M1) to the gaining stream in the west (characterized by soil profile M3); soil profile M2 characterizes the relatively flat area in the surroundings of the village of Mokrsko (Fig. 1). Down hole (non-rotation) hammer-drilling equipment (Kobra, USA) was used to reach the relatively consolidated saprolite in a depth from 133 to 351 cm. The 22 soil samples studied were classified as slightly acidic brown soil (Cambisol) (FAO, 1998). Clayey-silt horizons were only found in the M3 profile; they correspond to gley soil. The sediment samples (S1, S2, S4) of the stream and one sample of the fishpond bottom (S7) were collected manually at a depth of 5 cm using a stainless steel trowel. The solid samples were rapidly (within 2 min) placed in N$_2$-filled sterile air- and water-proof polyethylene bags, deaerated in the field for 5 min with a stream of N$_2$ and then cooled during transportation until they could be processed in the laboratory. The samples were divided into several subsamples within 5 h of collection in the field. Some of them were immediately used for determination of water-soluble As-species, pH and Eh measurements, some of them were dried, homogenised and sieved through a 2 mm sieve to determine the total concentrations of the elements, and the remaining subsamples were frozen for mineralogical investigation. Immediately prior to the mineralogical investigation, the subsamples were removed from the bags, placed on a plastic sheet and allowed to dry and oxidize at room temperature (20–25 °C). The soil and sediment samples were then gently ground with a wooden roller and sieved through 0.25 and 0.125 mm sieves. The XRD of several untreated soil samples revealed the predominant soil mineralogy as quartz, plagioclase, orthoclase, biotite, and amphibole. The clay fraction predominantly contained kaolinite, vermiculite, chlorite, and mixed layered illite–smectite.

3.1.1. Geochemical and mineralogical analysis

The temperature, pH$_{H2O}$ and the redox potential (Eh) of the stream and fishpond sediments were measured directly in situ, using Schott–Geräte Handylab 2 pH meter. The soil pH$_{H2O}$ and Eh were measured within 8 h of sample collection using a 1:2.5 (w/v) ratio of untreated, homogenised solid–water suspension after 1-hour agitation (Pansu and Gautheyrou, 2006). The redox potential values measured in the field and laboratory were referred to the standard hydrogen electrode (SHE). The concentrations of SiO$_2$, Al$_2$O$_3$, CaO, MgO, Na$_2$O, K$_2$O, P$_2$O$_5$, SO$_3$, S$^{-2,0}$, Mn, Fe, Ba and As in the <2 mm fraction of homogenised soils and sediments were measured using an X-ray fluorescence spectrometer (XRF, ARL 9400 XP$^+$) with the Uniquant™ 4 analysis program (UNIQUANT 4, 1999). XRF Uniquant is a semi-quantitative method and the associated errors were estimated to be ±0.2 wt.% for SiO$_2$, ±0.1 wt.% for other major constituent oxides and ±0.01 wt.% for minor elements.

In order to characterize As-bearing minerals in the soils and sediments, heavy-minerals were separated using bromoform diluted with 1,4-dioxane ($d = 2.81$ g cm^{-3}) in the 0.25–0.125 mm fraction of 15 samples representing both stream (S1, S2, S4) and fishpond (S7) sediments and the samples from the soil profiles. The soil samples ($n = 11$) were selected according to the pedological and geochemical variations (e.g., the total As concentration in the soil, redox potential) along the soil profiles to take into account possible variations in the mineralogy of the As-bearing phases. A rough quantitative estimate of As-bearing phases (including Fe oxyhydroxides) in the bulk sample was carried out by point counting of the grains from the heavy-