



# Arsenic mineralogy and mobility in the arsenic-rich historical mine waste dump



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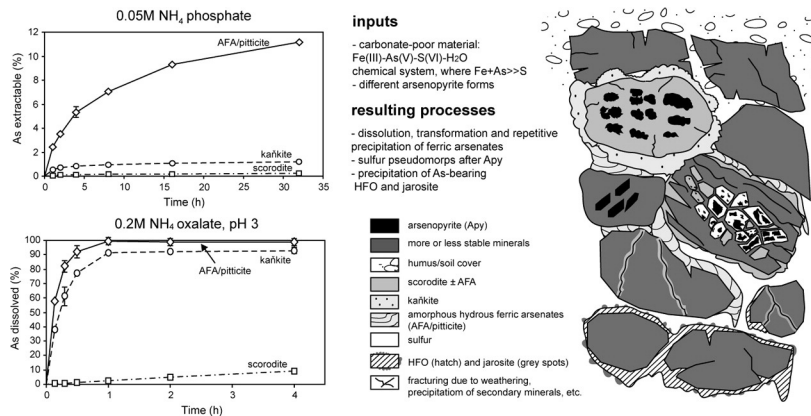
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## HIGHLIGHTS

- More than 250 year-old arsenopyrite-rich mine waste dump was studied.
- Mineral transformation and the environmental stability of different secondary arsenic mineral phases were assessed.
- High efficiency of As sequestration by HFOs suggests a limited impact of the mine waste dump on the surrounding soils.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A more than 250 year-old mine dump was studied to document the products of long-term arsenopyrite oxidation under natural conditions in a coarse-grained mine waste dump and to evaluate the environmental hazards associated with this material. Using complementary mineralogical and chemical approaches (SEM/EDS/WDS, XRD, micro-Raman spectroscopy, pore water analysis, chemical extraction techniques and thermodynamic PHREEQC-2 modeling), we documented the mineralogical/geochemical characteristics of the dumped arsenopyrite-rich material and environmental stability of the newly formed secondary minerals. A distinct mineralogical zonation was found (listed based on the distance from the decomposed arsenopyrite): scorodite (locally associated with native sulfur pseudomorphs) plus amorphous ferric arsenate (AFA/pitticite), kaňkite, As-bearing ferric (hydr)oxides and jarosite. Ferric arsenates and ferric (hydr)oxides were found to dissolve and again precipitate from downward migrating As-rich solutions cementing rock fragments. Acidic pore water (pH 3.8) has elevated concentrations of As with an average value of about 2.9 mg L<sup>-1</sup>. Aqueous As is highly correlated with pH ( $R^2 = 0.97$ ,  $p < 0.001$ ) indicating that incongruent dissolution of ferric arsenates controls dissolved As well as the pH of the percolating waste solution. Arsenic released from the dissolution of ferric arsenates into the pore water is, however, trapped by latter and lower-down precipitating jarosite and especially ferric (hydr)oxides. The efficiency of As sequestration by ferric (hydr)oxides in the waste dump and underlying

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soil has been found to be very effective, suggesting limited environmental impact of the mine waste dump on the surrounding soil ecosystems.

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## 1. Introduction

Abandoned mine wastes containing high arsenic (As) contents are among the most serious sources of environmental pollution. Understanding the geochemical processes which control the precipitation and dissolution of secondary As minerals in abandoned mine wastes is crucial for the formulation of models that predict the environmental impact of these sites. Exposure of waste material containing arsenopyrite to atmospheric conditions usually leads to the formation of acidic mine solutions with high concentration of As, SO<sub>4</sub>, Fe (e.g., Yunmei et al., 2004). The concentration of As is mainly controlled by its precipitation together with aqueous cations, ferric (hydr)oxides and/or hydroxosulfates (Majzlan et al., 2014a, 2014b). The assemblage of secondary As minerals in the wastes is dependent on the original ore mineralogy and conditions that occurred during their formation (mainly redox, pH and ion activities) but can also reflect the stage of progressive oxidation of the mine waste (i.e., the age of the mine wastes). Although solid phase speciation of As is discussed in the literature, most papers focus on relatively low-As wastes that were deposited several decades ago (see references in Majzlan et al., 2014b). Much fewer papers are focused on As-rich mine wastes (e.g., Benvenuti et al., 2000; Jeong and Lee, 2003; Kocourková et al., 2011), and, to our knowledge, there are no detailed studies dealing with several hundred year-old As-rich mine waste dumps.

The abandoned Giftkies mine waste dump represents an example of a substantial local source of historical As pollution. Two factors make this mine waste favorable for study of the As behavior and allows the dump to be considered as a natural laboratory: i) the simple ore mineralogy of the initial waste deposited and ii) the complete preservation of the dump for centuries until the present day (250 years). The results presented in this paper are part of a project whose goal is to evaluate the environmental impact of a historical mine waste rock dump (Filippi et al., 2009; Drahota et al., 2012). The major aim of this part of the project is to characterize the mineralogical evolution of arsenopyrite-rich ore under long-term exposure to atmospheric conditions and to identify the processes controlling the mobility of As in mine waste rich in ferric arsenate mineral phases. Favorable circumstances at the site enabled a short visit to the underground mine, providing an opportunity to study the secondary minerals and compare the As mineralogy in both the environments (mine waste dump versus underground space). This information should aid in capturing the released As in the high As/Fe-systems and production of ferric arsenates and (hydr)oxides and especially in guiding the long-term storage of this dangerous material.

## 2. Site description

The Giftkies deposit is located in the mountainous area (approx. 920 m a.s.l.) in valley of Veseřice Creek (Elbecken valley in archive materials) in the NE part of the world-renowned Jáchymov ore district, Krušné Hory Mountains, NW Czech Republic. The Jáchymov ore district provides classic examples of Ag–As–Bi–Co–Ni–U hydrothermal vein type deposits (Ondruš et al., 2003). However, the subject of historical mining at the Giftkies deposit was a vertically oriented mica schist zone intensively mineralized by arsenopyrite [FeAsS] and less by chalcopyrite [CuFeS<sub>2</sub>] or other scarce sulfides. The hydrothermal As mineralization was mined by 3 adits, one above another, between 1618 and 1771 and this resulted in simultaneous deposition of three mine waste dumps in the vicinity of the adits (Kořan and Mrňa, 1967). The ore was processed in the nearby Ölbecken smelter for manufacturing As

trioxide and partly copper as a by-product (Bufka and Velebil, 2005). The mine was later explored for uranium ores (1950s); however, the mine waste dump under study remained undisturbed. For a general situation at the locality, see Fig. 1a in Drahota et al. (2012).

The studied mine waste dump extends along a steep slope covering approximately 500 m<sup>2</sup> and is covered by thin soil together with sparse spruce woods (Fig. 1). The mechanical erosion of the dump in the steep slope is relatively low. As resulted from the work of Filippi et al. (2009) the present mineralogical situation in the mine dump is interesting especially for the quantity of secondary ferric arsenate phases occurring as various forms of crusts/aggregates and as cement in the rock fragments. The area has an annual rainfall of approximately 750 mm per year and mean annual temperature of 5 °C.

## 3. Materials and methods

### 3.1. Solid sampling and treatment

Seven samples (depth of 30 cm) of mine waste from different parts of the dump were analyzed to characterize the distribution of As in the dump (Fig. 1). Solid samples, used for detailed mineralogical and geochemical work presented here, were then collected in two deeper profiles (PD1 and PD2) (Fig. 1). Profile PD1 was situated in the upper edge of the dump close to the highest content of As discovered by the testing probes. Profile PD2 (identical to profile PD2 in Drahota et al., 2012) was situated at the bottom of the dump where it penetrates the waste material and reaches the underlying buried subsoil. The samples were collected from particular layers that were distinguished based on the variation in color and mineralogical composition (Fig. 2a). Samples for chemical analyses were air-dried at room temperature, homogenized, and sieved to yield the <2 mm fraction.

To concentrate the primary and secondary As minerals dispersed in the loose material, we used the diluted bromoform (CHBr<sub>3</sub>) with a specific gravity of 2.81 g cm<sup>-3</sup> (for details see Filippi et al., 2007). Separated mineral particles, polished and thin sections (prepared from both the concentrated and natural samples) were used for the mineralogical investigation.

### 3.2. Physico-chemical parameters

The mine waste pH was measured in a water suspension after 1 h of agitation (Pansu and Gautheyrou, 2006), using a combined pH electrode (SenTix 21) and WTW multimeter (330/SET-2 pH-meter). The gravimetric water content was determined by weighing the samples before and after drying at 105 °C for >8 h. Total organic carbon (TOC) and total inorganic carbon (TIC) were determined using combustion and/or H<sub>3</sub>PO<sub>4</sub> decomposition with infrared detection on an Eltra CS 500 analyzer. The elemental composition of the samples was analyzed by X-ray fluorescence (XRF) employing an ARL 9400 XP<sup>+</sup> spectrometer under the following conditions: voltage 20–60 kV, probe current 40–80 mA; effective area 490.6 mm<sup>2</sup>. The samples (0.8 g) were finely milled and compacted into tablets with KBr matrix.

### 3.3. Mineralogical analyses

The X-ray diffraction analyses (XRD) of bulk samples and separated mineral phases were carried out using a PANalytical X'Pert Pro diffractometer equipped with a diffracted-beam monochromator and X'Celerator multichannel detector. The analyses were performed under the following conditions: CuK $\alpha$  radiation, 40 kV,

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