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Synergies in elemental mobility during weathering of tetrahedrite [$(Cu,Fe,Zn)_{12}(Sb,As)_4S_{13}$]: Field observations, electron microscopy, isotopes of Cu, C, O, radiometric dating, and water geochemistry

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ABSTRACT

Tetrahedrite [$(Cu,Fe,Zn)_{12}(Sb,As)_4S_{13}$] is commonly present in many ore deposits and may be transferred to mining waste. Here, we describe the behavior of all elements in tetrahedrite during oxidative dissolution in a natural oxidation zone at Piesky (Slovakia), this being a long-term analogue of weathering of tetrahedrite-rich mining wastes. Electron microprobe work identified initial, early, advanced, and mature stages of weathering. The initial stages include formation of secondary covellite and chalcocite, the following stages only oxidic products, divided into greenish masses and brown veinlets. Both of them are nanocrystalline mixtures of minerals. The masses are Cu-Sb-As-rich and consist of a nanocrystalline pyrochlore phase. The veinlets are Fe-Sb-As rich and contain tripuhyite, goethite, and pyrochlores. Quantitative elemental budgets show that some elements (Zn, S, Ni, Co) are rapidly lost whereas others (especially Cu and As) are retained and form copper arsenates in the mature stages of weathering. About 10% As and almost 50% of Sb are lost during weathering, likely released into water; some Sb is stored in secondary minerals such as camérolaite, cualstibite, or tripuhyite. Light carbon isotopic composition ($\delta^{13}C$ down to $-11.1‰$) document significant biological contribution for C in the secondary minerals. Copper isotopes become progressively heavier during weathering (from initial $\delta^{65}Cu$ of $-2.45‰$ in tetrahedrite up to 4.3‰ in some azurite samples but $-6.3‰$ in covellite and chalcocite), documenting cyclic removal of light copper isotopes into covellite and chalcocite. The observation of elemental synergies during weathering of tetrahedrite shows that the solubility and mobility of As is controlled by copper arsenates, not by iron oxides, in an environment rich in tetrahedrite but poor in pyrite. Antimony, another element of environmental concern, is mostly released into water and creates low-concentration anomalies in stream sediments and soils.

1. Introduction

Sulfide minerals form in reducing environments from a variety of hydrothermal fluids in the crust. When exposed to the oxidizing and wet atmosphere, they react and alter to a wide variety of supergene minerals as a function of many parameters, including the chemical composition of the primary ores. The processes and products are of interest to mineralogists, geochemists, metallurgists, and environmental scientists. Although there is a number of studies on the weathering of simpler and common sulfides, such as pyrite (see below), complex matrices, such as tetrahedrite, were not investigated in detail (with the exception of Borčinová Radková et al., 2017). Better understanding of the weathering processes of primary minerals can provide valuable information about geochemical coupling, that is, geochemical

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synergies, interferences, and barriers of elements that commonly pollute the environment around active and abandoned mining sites.

Mineralogy of the weathering products of pyrite and pyrrhotite was established early and much of the work was summarized by Jambor (1994, 2003). The initial conversion of the primary sulfides to secondary sulfide phases was observed, for example the transformation of pyrrhotite to marcasite (Hammarstrom et al., 2001; Koski et al., 2008). The final products in mature systems are goethite, lepidocrocite or hydrous ferric oxide (e.g., Gunsinger et al., 2006; Lindsay et al., 2015), with occasional abundant ferric sulfates (Jamieson et al., 2005). Weathering of arsenopyrite in natural conditions yields mostly hydrous ferric oxide, hydrous ferric arsenate, or scorodite (Basu and Schreiber, 2013; Mihaljevič et al., 2010; Mandaliev et al., 2014; Lara et al., 2016), with rarer jarosite or pharmacosiderite (e.g., Murciego et al., 2011). Most of the studies document the spatially close and chemically strong association of Fe and As (e.g., Walker et al., 2005; Lalinská-Voleková et al., 2012). This synergy may be further enhanced by formation of ternary complexes by the addition of Ca, either in X-ray amorphous products (Voegelin et al., 2010) or in yukonite and arseniosiderite (Paktunc et al., 2003).

Little work has been done specifically on weathering of chalcopyrite, as this mineral is usually a subordinate component of pyrite- or pyrrhotite-dominated ores. Koski et al. (2008) report that chalcopyrite is replaced by iron oxides, in agreement with a similar work of Kučerová et al. (2014) who identified also additional rare malachite, cuprite, and delafossite.

Weathering of antimony sulfides was investigated mostly on stibnite, to a lesser extent on other Sb minerals. Common weathering products include the minerals from the pyrochlore group (stibiconite, roméite, and bindheimite) and tripuhyite, accompanied often by goethite and hydrous ferric oxide with adsorbed or incorporated Sb (Diemar et al., 2009; Okkenhaug et al., 2011; Mitsunobu et al., 2011; Courtin-Nomade et al., 2012; Leverett et al., 2012; Lalinská-Voleková et al., 2012).

To our best knowledge, there were no studies specifically designed to study the weathering processes and products of tetrahedrite, apart from the recent work in our group (Borčinová Radková et al., 2017). This lack of mineralogical investigation is compensated to a certain extent by the interest of materials scientists and metallurgists. The extractability of tetrahedrite and related minerals was studied as As, Sb, Bi, and other elements are considered to be "penalty" elements, undesired in the copper concentrates (Baláž et al., 1998; Havlik and Kammel, 2000; Awe et al., 2012; Lane et al., 2016). Another driving force is the wish to produce antimony concentrates from minerals other than stibnite (Dupont et al., 2016) because the market with stibnite and antimony is almost exclusively controlled by China. Mineralogical studies on the decomposition of tetrahedrite, either in oxidation zones or in tailings, should be a component of this effort. On the way to the circular economy, these studies may help the metallurgical work and guide the research on the re-use of mining waste, including old dumps and tailings.

The synergies among multiple elements are easier to screen and understand if these elements are present in higher concentrations and released by weathering of a single source mineral. These synergies exist also in the cases where one or a few elements are much more abundant than other ones but in this case, they may be difficult to track and to understand. For this reason, we have decided to study the processes of weathering of tetrahedrite, a fairly common primary sulfide and one of the so-called "trash-bag" among minerals, that is, a mineral able to accept a wide variety of elements into its crystal structure.

The crystal structure of tetrahedrite and related phases was solved and re-solved many times (see Makovicky, 2006 for a summary). The structure is commonly viewed as a complicated derivative of the sphalerite structure, and less commonly as a maximally collapsed sodalite-type framework (Makovicky, 2006). The crystal chemical formula of this mineral group is $\mathrm{Cu}_6^{[3]}(\mathrm{Cu}, \ldots)_6^{[4]}(\mathrm{Sb,As})_4^{[3]}\mathrm{S}_{12}^{[4]}\mathrm{S}^{[6]}$, with many substitutions possible. Compositions with Cu^{2+} are less stable than the composition without this species. Cu^{2+} is thus avoided by substitution of Zn, Fe, Hg, Cd, Mn, Co, Ni, or Pb into the tetrahedral sites; note that not all these metals are found in appreciable quantities in natural members of the tetrahedrite-tennantite series (Klünder-Hansen et al., 2003; Karup-Møller and Makovicky, 2004). The substitution of Bi for As/Sb is limited (Klünder-Hansen et al., 2003). At low Fe content per unit cell, the metal is mostly trivalent. At full Fe substitution at the tetrahedral sites (2 Fe per formula unit), iron converts to the divalent state (Makovicky et al., 1990). Intermediate, mixed valence state is observed in between these end states. In terms of terminology, the compositions with prevailing Sb are tetrahedrite (i.e., not only the Sb end-member) and the As-dominated compositions are tennantite. Compositions that are very rich in Ag or Hg have specific names but they do not apply to the work reported here.

In this work, we have investigated weathering of the complex tetrahedrite-tennantite solid solution and the associated elemental mobility at Piesky, a small abandoned deposit near the village of Špania Dolina in Slovakia. The results presented here augment those of Borčinová Radková et al. (2017) who focused on the fate of antimony and arsenic but paid little attention to the other elements. Using a suite of techniques, from field work at a meter scale, through electron microprobe and previous micro-X-ray diffraction and micro-X-ray absorption spectroscopy (Borčinová Radková et al., 2017) at a micrometer scale down to transmission electron microscopy at a nanometer scale, we were able to characterize the processes that govern weathering and elemental mobility of all elements in the tetrahedrite. Furthermore, the relative mobility and fate of the elements is well documented by the identification and investigation of supergene minerals which are not directly spatially associated with the primary sulfides. Stable isotopes of carbon, oxygen, and copper were investigated to evaluate the biological contribution to weathering and to determine the transient steps between the primary ores and the supergene minerals, respectively. Uranium and lead isotopes were used to determine the age of the oxidation zone. Water samples were taken in the abandoned underground spaces, analyzed for major and trace components, and examined in terms of saturation with respect to the supergene minerals found.

1.1. Geological setting

The Špania Dolina - Piesky deposit is situated 1.2 km north of the village of Špania Dolina in the Starohorské Mountains (Fig. 1), central Slovakia. The hydrothermal mineralization is hosted by Permian arcoses, sandstones and greywackes (Vozárová et al., 2014). At Piesky, these rocks are overlain by Triassic sandstones, limestones, and dolomites. Other rock types are present in the wider areas of the village of Špania Dolina but not at Piesky (Fig. 1). Sulfide minerals are mostly disseminated directly in the Permian siliciclastic rocks, with some accompanying quartz, carbonates, and baryte. Tetrahedrite is the dominant sulfide mineral (Sejkora et al., 2013) with minor amounts of chalcopyrite and accessory arsenopyrite, bornite, galena, cobaltite, pyrite and sphalerite (Michňová, 2009). The primary mineralization could be perhaps correlated with young (Alpine) tetrahedrite-baryte-dolomite mineralizations at larger Sb-Au deposits in this area (e.g., Slavkay and Chovan, 1996) but such a link has not been firmly established. The deposit has a well-developed oxidation zone with a variety of supergene copper carbonates, sulfates, arsenates, and phosphates (e.g., Figuschová, 1977; Pauliš, 1977; Řídkošil, 1978; Řídkošil and Povondra, 1982; Števko and Sejkora, 2014), making this area popular among mineral collectors. Production of copper and silver flourished in the Medieval times but persisted, to a limited extent, until the 1990s. In the very last stages of mining, the old dumps were re-processed. Throughout the history, mining targeted the oxidation zone. In the early days of intensive underground mining, the ore was manually sorted and no flotation was used. Except for a few cosmetic attempts to remediate the impressive dumps, no environmental measures were