Economic Geology, v. XXX, no. XX, pp. X–X

Antimony in Mine Wastes: Geochemistry, Mineralogy, and Microbiology

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Abstract

Antimony (Sb) is a valuable mined commodity, used mostly in fire retardants, and considered a critical element. It is also a potential environment hazard classed as a carcinogen. Antimony is concentrated in tailings and waste rock from Sb mines as well as other locations, such as precious metal deposits, where Sb is present in the ore but not recovered. This review covers the aqueous geochemistry, isotope chemistry, mineralogy, and microbiology of Sb in the context of mine waste. The primary minerals stibnite and sulfosalts may release Sb in surface and groundwaters and result in contamination of soils, plants, and river sediments. In some cases, Sb mobility is limited by its adsorption and incorporation into Fe (oxyhydr)oxides. At higher Sb concentrations, precipitation of Sb secondary hosts such as tripuhyite ($FeSbO_4$, relatively insoluble) and brandholzite ($Mg[Sb(OH)_6]_2 \cdot 6H_2O$, highly soluble) influence Sb concentrations in water associated with mine waste. Although Sb is nonessential to organisms, microorganisms are involved in oxidation, reduction, and methylation processes that can drive biogeochemical transformations. Limited toxicological information about Sb makes it challenging to establish regulations or guidelines limiting the concentration of Sb. Antimony is frequently associated with arsenic in mine waste, and remediation design is often based on the assumption that both metalloids behave in a similar way. However, new research suggests that in some environments, this is not the case, and Sb should be considered based on its unique biogeochemical behavior.

Introduction

Antimony (Sb) is present in mine wastes where it is the commodity mined or an accessory element accompanying the principal commodity, typically gold (Au), silver (Ag), or gold and base metals (e.g., copper (Cu), aluminum (Al), tin (Sn), lead (Pb), nickel (Ni) and/or zinc (Zn); (Schwarz-Schampera, 2014). Understanding the geochemical, mineralogical, and microbiological factors that control the mobility of Sb in the mine waste environment is important because it is both a critical element, and thus a target for extraction, and an environmental hazard.

Critical elements are those of high economic importance and vulnerable to risk of supply (Graedel et al., 2015). Most of the Sb mined is used in fire retardants, with other important uses including lead-acid batteries, plastic catalysts, ceramics, semiconductors, and lead alloys (Schwarz-Schampera, 2014; Seal et al., 2017). In medicine, Sb has been used for the treatment of tropical diseases schistosomiasis and leishmaniasis (Berman, 1988). Based on 2020 figures, the majority of the global production of Sb is from China (U.S. Geological Survey, 2021). Production from China has declined from previous years due, in part, to stricter environmental standards and price decrease. Australia, Bolivia, China, Canada, Mexico, Kyrgyzstan, Russia, South Africa, Turkey, and Tajikistan have substantial reserves (Seal et al., 2017; U.S. Geological Survey, 2021).

Antimony has no known essential biological function in plants or animals and in some forms, notably antimony trioxide (Sb_2O_3), it has been identified as a carcinogen. It is considered a priority pollutant by the European Union and the US Environmental Protection Agency (Obiakor et al., 2017; He et al., 2019). It is regulated in drinking water but rarely regulated in mine waste effluents, likely because of limited toxicity data. Aside from mine tailings and waste rock, other sites of Sb contamination include shooting ranges, where Sb from ammunition accumulates in soil, and areas near metal smelters and refineries. Information from the distribution, concentrations, and solid speciation of Sb from these sites provides useful data for understanding the mobility of Sb in mine waste, as does the data from exploration programs using Sb as a vector for finding ore deposits.

Some aspects of Sb behavior in the environment have been considered controversial, and several questions remain. Does Sb behave in a similar way to arsenic (As), another metalloid often found with Sb, usually at higher concentrations? Why has Sb been reported as both mobile and immobile in contaminated environments? Can we identify the natural background of Sb in near surface soils and sediments given that average concentrations are generally very low?

Within the last decade, several reviews of Sb in the environment have been published, with various perspectives identifying general research gaps (Filella et al., 2009, including a summary of Sb reviews to that date), the establishment of a natural background in geologic and environmental media (Reimann et al., 2010), behavior in soil (Wilson et al., 2010), secondary minerals (Roper et al., 2012), isotopes (Wen et al., 2018), economic and environmental geology (Seal et al., 2017), bioaccumulation and ecotoxicity (Obiakor et al., 2017), biogeochemical cycles (He et al., 2019), and human exposure and uptake (Belzile et al., 2011; Filella et al., 2012, 2013a, b). This review focuses on the behavior of Sb in mine waste and the relevant factors controlling its mobility.

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ISSN 0361-0128; doi:10.5382/econgeo.4937; 17 p.

Geochemistry of Sb in Near-Surface Environment

Antimony belongs to group 15 of the periodic table with atomic number 51 and a relative atomic mass of 121.75 ± 3 g/mol. The position on the boundary between metals and nonmetals defines Sb as a metalloid as it has both metallic (appearance) and nonmetallic (poor conductivity of electricity and heat) characteristics. The proximity of As to Sb in the periodic table explains many of the geochemical and biological similarities between the two metalloids. Antimony can exist in four oxidation states (-III, 0, +III, +V) in minerals and tends to exist in the +III and +V states in aqueous solution. The coordination of Sb(V) with oxygen is octahedral, rather than tetrahedral like As(V) and P(V) (Pauling, 1933).

Aqueous speciation

In natural waters, antimonate (Sb(V)) typically exists in the form of $Sb(OH)^-_{6(aq)}$ at circumneutral and basic pH values or $Sb(OH)^0_{5(aq)}$ at low pH values. Antimonite (Sb(III)) exists mostly in form of $Sb(OH)^0_{3(aq)}$ over a broad range of pH values relevant to natural waters (1.5-11) but can also exist as $Sb(OH)_2{}^+{}_{(aq)}$ under strongly acidic solutions and $Sb(OH)_4{}^-{}_{(aq)}$ under strongly alkaline solutions (Filella et al., 2002a; Fig. 1). Based on thermodynamic predictions, Sb(V) compounds would be expected in oxic environments and Sb(III) in anoxic environments. These two oxidation states have been reported to co-occur in mine waste-influenced waters, exhibiting redox disequilibrium. For example, Sb(V) has been observed in anoxic conditions (Fawcett and Jamieson, 2011), and Sb(III) has been reported in oxic mine water (Borčinová Radková et al., 2020). If reduced sulfur is present, then $SbS^-_{2(aq)}$ can occur in alkaline solutions (Fig. 1B).

Organoantimony compounds can be formed from by complexation with natural organic matter (NOM) or by methylation driven by microbial and fungal species (additional information presented in "Microbiology of Sb in Mine-Impacted Water and Mine Waste"). Organic matter can bind both antimonate and antimonite species, generally increasing the mobility of antimony into water, although the binding strength depends upon NOM hydrophobicity, functional group composition, and pH (Buschmann and Sigg, 2004; Inam et al., 2019). Substantial amounts (up to 30%) of Sb(III) have been reported to be bound to humic acids under environmentally relevant conditions (dissolved organic carbon (DOC) = 5 mg/L; pH 7; Sb(III) = 8.21 nM (1 µg/L), ionic strength = 0.05M), equivalent to 0.74 µmol of Sb(III)/g of DOC (90 µg of Sb(III)/g of DOC). Moreover, humic material may act as a catalyst for the oxidation of Sb(III) to Sb(V) (Buschmann and Sigg, 2004).

Sb isotopes

The two stable isotopes of Sb are ^{121}Sb (57.213% of natural Sb) and ^{123}Sb (42.787% of natural Sb) (Greenwood and Earnshaw, 1984; Chang et al., 1993). Recent studies have demonstrated that Sb isotopes can be used to distinguish anthropogenically derived Sb from natural Sb and to trace biogeochemical processes in mining-affected environments (e.g., Wen et al., 2018). Mine drainage water from the Ichinokawa Sb mine in Japan was slightly enriched in the heavier ^{123}Sb isotope relative to the Sb isotope composition of two stibnite samples (Tanimizu et al., 2011; Fig. 2). This was attributed to preferential adsorption of aqueous $Sb(OH)^-_6$ on Fe hydroxides in sediments in contact with the mine water. Resongles et al. (2015) found significant Sb isotope variations in the mining-affected Orb River ($\delta^{123}Sb = -0.06$ to +0.11‰) and Gardon River in France ($\delta^{123}Sb$ = +0.23 to +0.83‰; Fig. 2). These variations were ascribed to fractionation during the

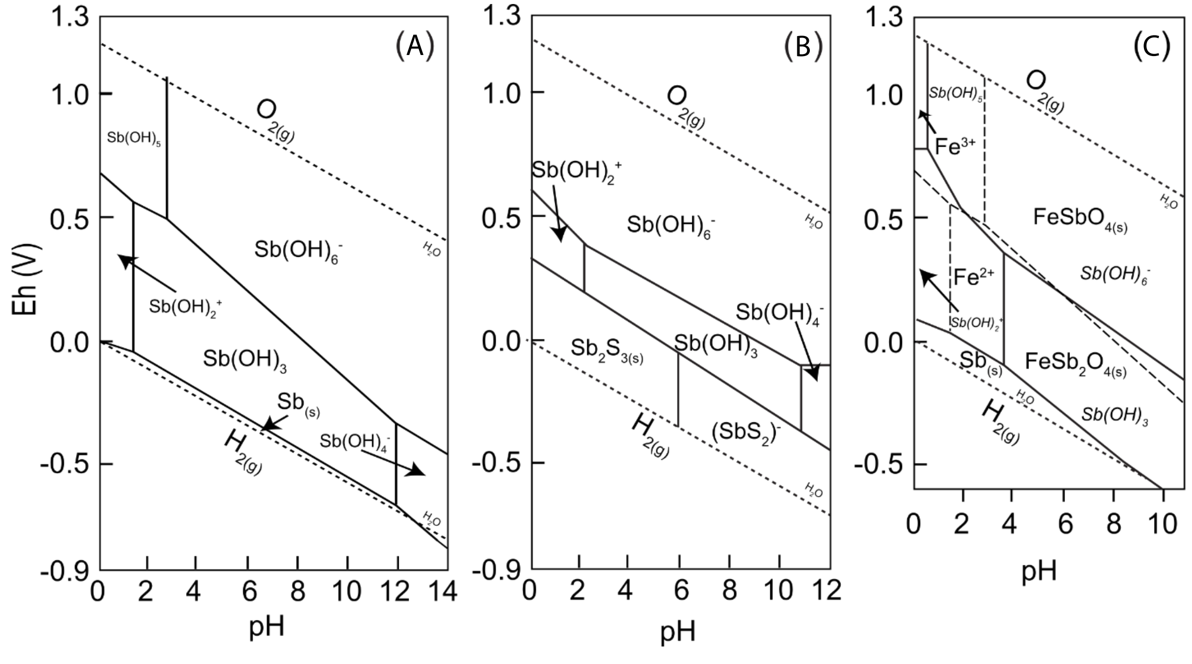

Fig. 1. Eh-pH diagrams for Sb. A. The Sb-O-H system. $\Sigma_{Sb} = 10^{-10}$ mol.l^{-1}, 25ºC. Adapted from Takeno (2005). B. The Sb-S-H_2O system. $\Sigma_{Sb} = 10^{-8}$mol.l^{-1}, $\Sigma_S = 10^{-3}$mol.l^{-1}, 25ºC. Adapted from Filella et al. (2002a, b). C. The Sb-Fe-H_2O system. Σ_{Sb} = 10^{-6} mol.l^{-1}, $\Sigma_{Fe} = 10^{-6}$ mol.l^{-1}, 25ºC. Areas of dissolved Sb species separated by dashed lines, and Sb species shown in italics. Adapted from Leverett et al. (2012).

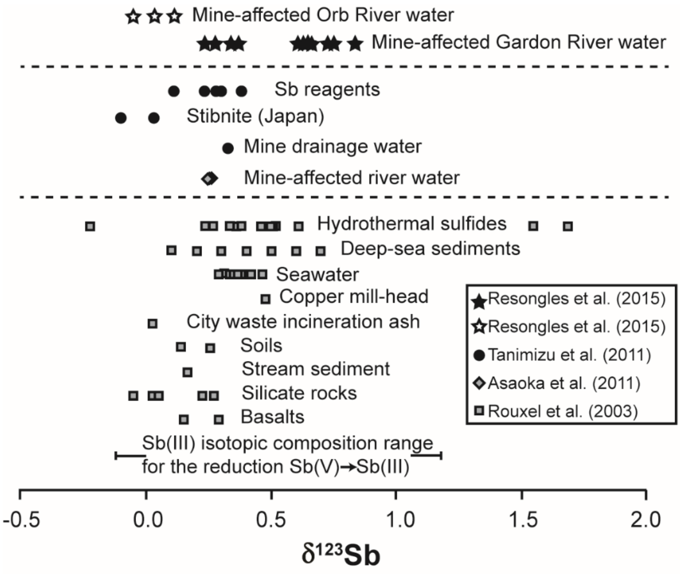

Fig. 2. Antimony isotope composition of geologic and mining-affected materials. Note that the absolute values of δ^{123}Sb cannot be compared across studies separated by dashed lines because the Sb isotope standard used for the δ^{123}Sb calculation is different. Adapted from Resongles et al. (2015), with permission from Elsevier.

oxidative dissolution of Sb_2S_3 and precipitation of Sb(III), Sb(III)-Fe, and Sb(V)-Fe oxides. Although Sb isotopes provide valuable information about geochemical processes, relatively few studies have measured Sb isotope compositions in mining environments.

Sb Deposits and Primary Ore Minerals

Antimony is a chalcophilic element and is often found bound to sulfur (S) in a trivalent state in ore deposits. It tends to be found in elevated concentrations associated with Au and Ag deposits and co-occurring with As, bismouth (Bi), Cu, mercury (Hg), Ni, Pb, selenium (Se), Sn, tellurium (Te), tungsten (W), and Zn, but ore-grade concentrations of Sb are rare (Pirajno, 2010; Schwarz-Schampera, 2014). Antimony may be extracted as the primary commodity, but it is often a by-product in the extraction of another resource. Mining activities targeting other commodities may contain Sb minerals in the waste stream and can cause release of Sb to the environment. Several examples include orogenic-type gold deposits (Druzbicka and Craw, 2013; Fawcett et al., 2015) and tetrahedrite-bearing copper deposits (Borčinová Radková et al., 2017; Majzlan et al., 2018).

The majority of Sb deposits have a hydrothermal origin and are associated with continental plate margins and orogenic belts (Pirajno, 2010; Schwarz-Schampera, 2014). The largest deposits with highest concentrations of Sb occur in carbonate replacement deposits, epithermal Au-Sb vein deposits, and reduced intrusive systems. Primary Sb-producing deposits tend to be simple stibnite deposits, sometimes with co-occurring Au. Complex polymetallic deposits produce Sb mainly as a secondary by-product of mining a primary commodity (Schwarz-Schampera, 2014; Seal et al., 2017).

Nearly 200 Sb minerals are formed by hydrothermal or igneous processes, distinguished here from secondary minerals formed by weathering reactions either in premining oxidation zones or postmining waste (Table 1; Lottermoser, 2010). The most common Sb primary mineral is stibnite. Stibnite can form in veins under a wide range of temperatures accompanied by quartz (SiO_2), arsenopyrite (FeAsS), pyrite (FeS_2), and sulfosalts (Table 1; Obolensky et al., 2007; Schwarz-Schampera, 2014). Most of the primary phases are sulfides and sulfosalts where Sb is a primary component or is a substitute for other metals and metalloids (Table 1). In the crystal structures of sulfosalts tetrahedrite ($Cu_{12}Sb_4S_{13}$), boulangerite ($Pb_5Sb_4S_{11}$), or jamesonite ($PbFeSb_6S_{14}$), Sb occurs with Cu, Pb, Ag, Fe, and As (Moëlo et al., 2008), and S can be replaced by Se or Te (King, 2001; Filippou et al., 2007). Sulfosalts are commonly found in polymetallic hydrothermal veins associated with other sulfides (Chovan et al., 1998; Schwarz-Schampera, 2014). Unless sulfosalts are of economic interest in the deposit, they are rarely reported in mine wastes (Kossoff et al., 2012; Lalinská-Voleková et al., 2012; Borčinová Radková et al., 2017). Primary Sb minerals are almost always associated with As, most commonly in the form of arsenopyrite or tetrahedrite. For this reason, at mine sites where Sb is an environmental concern, As is as well; however, the reverse is not always true.

China, Bolivia, Australia, and Russia have the largest resources of Sb, while China, Russia, and Tajikistan are the leading mine producers worldwide (U.S. Geological Survey, 2021). China's largest Sb deposit is a carbonate replacement deposit in Hunan Province (Xikuangshan deposit) and consists of mainly quartz-stibnite and calcite-stibnite mineral assemblages (Seal et al., 2017, and references therein). The Sarylakh and Sentachan deposits in Russia are replacement deposits that contain Au and Sb; the ore is primarily quartz-stibnite. The Bolivian deposits, forming an "antimony belt," are an example of epigenic Au-Sb vein deposits with quartz, stibnite, other sulfides, and sulfosalts present (Seal et al., 2017, and references therein).

Antimony Minerals in Mine Wastes

Extraction and generation of mine waste

Antimony is extracted from the ores by crushing and grinding, followed by a combination of gravity concentration and flotation. Depending on ore grade, Sb oxidation state, and sulfide and oxide content, Sb ores and Sb flotation concentrates are usually recovered using pyrometallurgical techniques for lower grade ores (Anderson, 2012) or hydrometallurgical methods involving the use of alkaline sulfide and acidic chloride systems for higher grade ores containing 45 to 60% Sb (Bhatti et al., 2009; Anderson, 2012). Antimony trioxide (Sb_2O_3) is the most common compound produced. Antimony pentoxide (Sb_2O_5), Na antimonate ($NaSbO_3$), $NaSb(OH)_6$, Sb metal, antimony trichloride ($SbCl_3$), and Pb-Sb alloys are also produced for various purposes (Filella et al., 2002a, and references therein; Schwarz-Schampera, 2014).

Composition of wastes generated by Sb extraction (e.g., waste piles, tailings) depends upon the mineralogy of the deposit type but are often composed of quartz and stibnite, with ancillary minerals such as pyrite and arsenopyrite, and may also contain carbonate minerals, particularly from carbonate replacement deposits. The sulfides have acid-generating potential, but if concentrations of carbonate minerals are sufficient, the waste may have enough acid-neutralizing capacity

Table 1. Examples of Primary and Secondary Sb-Bearing Minerals with Sb as a Major Component in Sb Ores and Mine Wastes

Mineral	Formula	Reference
Sulfides		
Stibnite	Sb_2S_3	Klimko et al. (2011); Kossoff et al. (2012); Borčinová Radková et al. (2020)
Sulfosalts		
Boulangerite	$Pb_5Sb_4S_{11}$	Kossoff et al. (2012); Lalinská-Voleková et al. (2012);
Bornonite	$PbCuSbS_3$	Kossoff et al. (2012)
Frankeiite	$Fe(Pb,Sn)_6Sn_2Sb_2S_{14}$	Kossoff et al. (2012)
Jamesonite	$PbFeSb_6S_{14}$	Lalinská-Voleková et al. (2012); Kossoff et al. (2012)
Potosiite	$Pb_6Sn_3FeSb_3S_{16}$	Kossoff et al. (2012)
Tetrahedrite	$(Cu_{12}Sb_4S_{13})$ or $(Cu,Ag)_{10}(Cu,Zn,Fe,Cd,Hg)_2(Sb,Bi,As)_4S_{13}$	Borčinová Radková et al. (2017); Majzlan et al. (2018)
Zoubekite	$AgPb_4Sb_4S_{10}$	Kossoff et al. (2012)
Oxides		
Brandholzite	$Mg[Sb^{5+}(OH)_6]_2{\bullet}6(H_2O)$	Majzlan et al. (2016); Borčinová Radková et al. (2020)
Cervantite	$Sb^{3+}Sb^{5+}O_4$ orthorombic	Levresse et al. (2012); Lalinská-Voleková et al. (2012)
Clinocervantite	$Sb^{3+}Sb^{5+}O_4$ monoclinic	Courtin Nomade et al. (2012)
Kermesite	Sb_2S_2O	Majzlan et al (2011); Lalinská-Voleková et al. (2012)
Romeite	$Ca_2Sb_2O_7$	
Senarmontite	Sb_2O_3	Ashley et al. (2003); Manaka et al. (2007); Lalinská-Voleková et al. (2012)
Bindheimite	$Pb_2Sb_2O_7$	Szakall et al. (2000); Klimko et al. (2011)
Stibiconite	$Sb^{3+}Sb^{5+}{}_2O_6(OH)$	Ashley et al. (2003); Lalinská-Voleková et al. (2012); Levresse et al. (2012)
Tripuhyite	$FeSbO_4$	Mitsunobu et al. (2011); Courtin-Nomade et al. (2012); Lalinská-Voleková et al. (2012); Borčinová Radková et al. (2017)
Valentinite	Sb_2O_3	Ashley et al. (2003); Courtin-Nomade et al. (2012)
Sulfates		
Peretaite	$CaSb_4O_4(OH)_2(SO_4)_2{\bullet}2(H_2O)$	Majzlan et al. (2016)
Klebelsbergite	$Sb_4O_4(OH)_2(SO_4)$	Majzlan et al. (2016)

to prevent acidic drainage (Seal et al., 2017). Wastes may be exposed to weathering, resulting in changes to the mineral and metal(loid) composition from the primary mineral assemblage.

Secondary minerals in mine wastes

In minimally weathered mine waste, stibnite and other primary minerals are often present. However, stibnite occurs rarely in older mine waste, likely because it is dissolved more rapidly than other sulfides such as arsenopyrite (Klimko et al., 2011; Lalinská-Voleková et al., 2012; Borčinová Radková et al., 2020). About 45 secondary minerals formed by weathering of primary Sb minerals have been described (Roper et al., 2012). The oxidation of Sb sulfide and sulfosalt primary minerals, caused by near-surface exposure, is accelerated by mining activities and may cause Sb to be released to air and water (Craw et al., 2004; Hiller et al., 2012; Majzlan et al., 2016). The example of the oxidation of stibnite in the presence of water can be described as:

$$Sb_2S_3 + 6O_2 + 6H_2O \rightarrow 2Sb(OH)^0_{3(aq)} + 3SO_4^{2-} + 6H^+. \qquad (1)$$

The half-reaction of Sb^{3+} oxidation can be written with as follows:

$$Sb(OH)^0_{3(aq)} + 3H_2O \rightarrow Sb(OH)^-_{6(aq)} + 3H^+ + 2e^- \quad \text{(Filella and May, 2003).} \qquad (2)$$

Accumulation of dissolved Sb can result in the precipitation of secondary Sb-bearing phases. The minerals that form when stibnite is exposed to oxidizing conditions include senarmontite (Sb_2O_3), valentinite (Sb_2O_3), or pyrochlore group Sb minerals (Table 1; Ashley et al., 2003). The sulfoxide kermesite (Sb_2S_2O) can occur as an intermediate phase. These minerals are common in stibnite ore oxidation zones and less commonly found in mine wastes (Roper et al., 2012). Stibiconite ($Sb_3O_6(OH)$) and kermesite often appear as pseudomorphs of stibnite. Secondary bindheimite ($Pb_2Sb_2O_7$) may be present as the weathering product of Pb-Sb sulfides such as tetrahedrite or jamesonite, and co-occurrence of other secondary minerals such as jarosite (e.g., $KFe_3(OH)_6(SO_4)_2$) or cerussite ($PbCO_3$) is common (Szakall et al., 2000). Pyrochlore group minerals (stibiconite, bindheimite ($Pb_2Sb_2O_7$), and romeite ($Ca_2Sb_2O_7$)) occur in oxidation zones of Sb deposits and mine waste (Anthony et al., 1990-2003; Diemar, 2008; Lalinská-Voleková et al., 2012; Borčinová Radková et al., 2017).

Iron (oxyhydr)oxides and Fe oxyhydroxysulfates are commonly observed around mine sites and may sequester aqueous Sb in surface mine drainage and tailings pore waters by adsorbing or incorporating Sb (Craw et al., 2004; Majzlan et al., 2007). Antimony can be taken up by low pH minerals like jarosite and schwertmannite ($Fe_8O_8(OH)_6(SO_4)$, Fe minerals such as ferrihydrite ($Fe(OH)_3$) that form at higher pH, and goethite (FeOOH), which forms at wide range of pH (Bigham et al., 1996; Manaka et al., 2007; Courtin-Nomade et al., 2012; Table 2). The Sb concentration in jarosite from contaminated tailings can be as high as 5.9 ± 2.1 wt % (Courtin-Nomade et al., 2012), whereas lower amounts of Sb (0.045 wt %) were reported in schwertmannite by Manaka et al. (2007). Ferrihydrite and goethite identified in mine wastes from stibnite mining contain Sb concentrations of approximately 3 to 4 wt % (Lalinská-Voleková et al., 2012), and values up to 14 wt % have been reported (Courtin-Nomade at al., 2012), higher than the Sb concentrations in Fe oxyhydroxysulfates (jarosite,

Table 2. Antimony Concentrations in Sb Secondary Minerals in Mine Wastes

Mineral	Stoichiometry	Sb content (wt %) in natural samples	Type of mine waste	Reference
Sb adsorbed HFO	$Fe_2O_3.0.5(H_2O)$	0.2-2.03, 1.2 (mine drainage), 13.91(tailings)	Mine drainage, tailings	Courtin-Nomade et al. (2012); Majzlan et al. (2011); Lalinská-Voleková et al. (2012)
Sb adsorbed goethite	FeO(OH)	14 (tailings),0.015 (mine drainage)	Mine drainage, tailings	Courtin-Nomade et al. (2012); Manaka et al. (2007)
Sb adsorbed jarosite	$KFe_3(OH)_6(SO_4)_2$	5.9 ± 2.1	Tailings	Courtin-Nomade et al. (2012)
Sb adsorbed schwertmannite	$Fe_{16}O_{16}(OH)_{12}(SO_4)_2$	0.045	Mine drainage	Manaka et al. (2007)
Sb adsorbed hematite	Fe_2O_3	up to 3	Tailings roaster products	Courtin-Nomade et al. (2012) Fawcett and Jamieson (2011)
Sb adsorbed maghemite	Fe_2O_3	up to 1.4	Roaster products	Fawcett and Jamieson (2011)
Tripuhyite	$FeSb_2O_4$	29.65-45.57(soil), 15.94-50.83(tailings)	Tailings, soil, waste rock resulted from stibnite and tetrahedrite mining	Mitsunobu et al. (2011); Courtin-Nomade et al. (2012); Lalinská-Voleková et al. (2012)
Pyrochlore group minerals	CaSb5+2O5(OH)2 (example of hydroxocalcioroméite)	41.07-44.69 (tailings), 16.55 (waste rock), 42.7 (smelting slags)	Tailings, tetrahedrite waste rock, smelting slags	Klimko et al. (2011); Courtin-Nomade et al. (2012); Borčinová Radková et al. (2017)
Senarmontite	Sb_2O_3	n.a.	Coatings on stibnite - waste rock piles, smelting slags, soils	Manaka et al. (2007); Lalinská-Voleková et al. (2012) (Fig. 5D)
Valentinite	Sb_2O_3	n.a.	Smelting slags	Courtin-Nomade et al. (2012)
Brandholzite	$Mg[Sb(OH)_6]_2 \bullet 6(H_2O)$	41.64-42.18 (underground mine), 45.75-50.69 (tailings)	Abandoned stibnite mines - massive, covering underground mine surfaces, neutral pH tailings	Majzlan et al. (2016); Borčinová Radková et al. (2017)
Klebelsbergite	$Sb_4O_4(OH)_2(SO_4)$	59.74-62.68	Acidic pH-weathering of stibnite and pyrite, no carbonates, underground adits	Majzlan et al. (2016)
Peretaite	$CaSb_4O_4(OH)_2(SO_4)_2 \bullet 2(H_2O)$	56.05-56.6	Acidic pH, underground adits-simultaneous weathering of pyrite and stibnite	Majzlan et al. (2016)

schwertmannite). Fe (oxyhydr)oxides can adsorb or incorporate very high As >20 and Sb >1.5 wt % (Haffert et al., 2010; Hiller et al., 2012) in waters discharged from mine adits and tailings impoundments.

Iron (oxyhydr)oxide coatings formed from oxidation of primary sulfide in tailings and waste rock can influence Sb mobility. For example, oxidation rims on pyrite and arsenopyrite in tailings composed of Fe (oxyhydr)oxides such as goethite may retain high concentration of Sb leached initially from stibnite (Fig. 3C, Majzlan et al., 2011; Lalinská-Voleková et al., 2012). Antimony concentrations as high as 5.69 wt % were reported in oxidation rims in arsenopyrite (Lalinská-Voleková et al., 2012). In the tailings at the Beaver Brook mine (Canada), the oxidation rims on arsenopyrite showed even higher Sb amounts of 3.8 to 11.3 wt % Sb (Fig. 3F, Borčinová Radková et al., 2020).

Secondary Sb minerals have been rarely reported. However, recent studies show that their occurrence may be more common than was previously thought. Tripuhyite ($FeSbO_4$) has been observed at some Sb contaminated sites (Fig. 3A, Lalinská-Voleková et al., 2012). Natural tripuhyites show widely varying Fe/Sb ratios (Lalinská -Voleková et al., 2012; Table 2). Tripuhyite is the end-product of secondary weathering reactions and is sparingly soluble (Majzlan et al., 2011; Lalinská- Voleková et al., 2012; Leverett et al., 2012). As such, several authors (e.g., Kossoff et al., 2015; Multani et al., 2017) have proposed that it could be used for remediation and recovery of Sb in mine wastes. There is no information about kinetics of tripuhyite formation. However, recently deposited tailings (<10 yrs) at Beaver Brook mine contain a tripuhyite-like phase with Sb ranging from 6.7 to 37.8 wt % (avg 21.7 wt %, Fig. 3H, Borčinová Radková et al., 2020).

Another example of secondary Sb phases is the mineral brandholzite ($Mg[Sb(OH)_6]_2 \cdot 6H_2O$), which has been described as a precipitate formed from pH neutral waters in abandoned stibnite mines (Sejkora et al., 2010; Majzlan et al., 2016). The ephemeral occurrence of brandholzite in recently deposited tailings resulting from stibnite mining was observed by Borčinová Radková et al. (2020; Fig. 3E). In the tailings described by Borčinová Radková et al. (2020), brandholzite was observed only in near-surface tailings sampled during dry weather and appeared absent in the same tailings sampled after several days of rain. Because of the high solubility of brandholzite, this may be an important but ephemeral, underreported source of dissolved Sb in mine waste.

Antimony-sulfate secondary minerals can also form upon oxidation of stibnite and other sulfides. In the study by Majzlan et al. (2016), phases such klebelsbergite ($Sb_4O_4(OH)_2(SO_4)$) and peretaite ($CaSb_4O_4(OH)_2(SO_4)_2 \bullet 2(H_2O)$; Table 1) were reported in underground mines in Slovakia. These Sb(III) sulfates form from locally acidic waters caused by pyrite dissolution, where Sb is supplied by stibnite weathering. In the waste rock piles of a copper mine in Slovakia where tetrahedrite was the ore mineral, Sb was hosted in tripuhyite, pyrochlore-like phases, and a µXRD amorphous phase, which also contained Fe, As, and Cu (Figs. 3G, 4C; Borčinová Radková et al., 2017; Majzlan et al., 2018). Antimony-bearing secondary minerals from the romeite group (Table 1) have been reported also

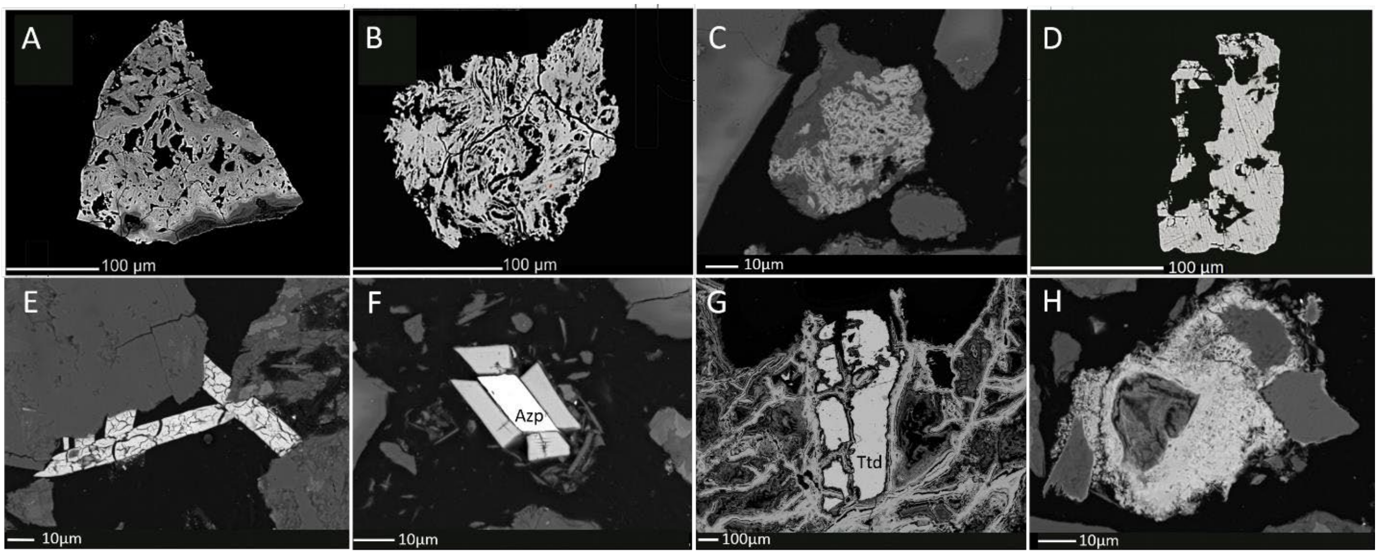

Fig. 3. Backscattered electron images (BSE) of Sb secondary minerals in mine waste. A. Tripuhyite grain with disrupted, zonal texture, tailings from Pezinok Sb-Au deposit, Slovakia. B. Sb-Ca mineral with the pyrochlore structure with Sb up to 52.90 wt %, Fe up to 21.22 wt %, and Ca up to 7.40 wt % from Au-Sb deposit Medzibrod, Slovakia. C. Porous goethite with 0.9% Sb from Beaver Brook tailings. D. Sénarmontite from soil contaminated by Sb mining from Dubrava Sb deposit, Slovakia. E. Tabular crystals of brandholzite with 49.2% Sb from Beaver Brook Sb tailings, Newfoundland. F. Fe oxides with 9.2% Sb forming rim on arsenopyrite (Azp) from Beaver Brook Sb tailings, Newfoundland. G. Roméite and tripuhyite forming veinlets as tetrahedrite (Ttd) oxidation products from the Cu-Ag historic mine site Špania Dolina-Piesky. H. Trypuhyite-like Sb-Fe oxide with 21.3% Sb with needle-shaped micron-size crystals precipitated around gangue minerals from Beaver Brook Sb tailings, Newfoundland. A. B. and D. taken from Lalinská-Voleková et al. (2012), reproduced with permission. G taken from Borčinová Radková et al. (2017), reproduced with permission. C. E. F. and H. taken from Borčinová Radková et al. (2017), reproduced with permission.

Fig. 4. Three examples of Sb mining sites. A. Tailings at currently operating Beaver Brook antimony mine, Newfoundland, deposited in 2012. The most common Sb host in tailings is stibnite and Sb concentrations in tailings are up to 8 200 mg kg^{-1}. B. Agnes adit outflow at Poproč Au-Sb deposit in Slovakia. The mine was closed in 1965. Antimony is hosted by Fe (oxyhydr)oxides and is released in water with Sb content up to 380 ug/L in outflow and Sb (>1,200 mg kg $^{-1}$ in Fe (oxyhydr)oxides. C. Weathered tetrahedrite-rich waste (containing tetrahedrite relics, tripuhyite, romeite) from the historic Ag deposit Špania Dolina Piesky in Slovakia. Photos (A) and (C) taken by Anežka Borčinová Radková and photo (B) by Heather Jamieson.

from tailings or slag residues (Fig. 3; Klimko et al., 2011; Courtin-Nomade et al., 2012).

The study of mine waste resulting from Au ore roasting at the Giant mine, Yellowknife, Canada, showed that Sb minerals identified in primary ore (in the form of sulfosalts and stibnite) were completely transformed during the roasting process (Fawcett and Jamieson, 2011). The ore roasting produced volatile Sb, which was incorporated in roaster-generated maghemite (g-Fe_2O_3) and hematite (Fe_2O_3; max Sb 1.4 wt %, Fawcett and Jamieson, 2011) and forms an apparently near-continuous solid solution between Sb_2O_3 and As_2O_3 (Schuh, 2019). Courtin Nomade et al. (2012) reported well-crystalline romeite (42.7% Sb), senarmontite (Sb_2O_3), valentinite (Sb_2O_3), cervantite (Sb_2O_4) or clinocervantite (Sb_2O_4), tripuhyite (avg 26.2 wt % Sb), hematite, and goethite (avg 7.4 wt % Sb) in Sb-bearing smelting slags resulted from Sb-bearing ores (mostly containing stibnite) at Massive Central, France.

Arsenic can also be released from sulfide or sulfosalt minerals under oxidizing conditions. Similar to Sb, As mobility can be attenuated by adsorption to and substitution in iron (oxyhydr)oxides. An arsenic analog of the relatively insoluble anhydrous mineral tripuhyite (Kossoff et al., 2015) is a commonly found mineral in mine waste scorodite ($FeAsO_4 \times 2H_2O$). A number of highly soluble arsenates such as roesslerite and brassite are the analogs to the highly soluble Mg-Sb hydroxides like brandholzite (Majzlan et al., 2016; Borčinová Radková at al., 2020).

Under reducing conditions in sulfur-rich environments, As can precipitate as a sulfide including realgar (AsS) and orpiment (As_2S_3; e.g., Schuh et al., 2018; Miller et al., 2019). The formation of Sb(III) sulfide phases would be expected under analogous Sb-rich, reducing conditions. However, secondary Sb sulfides have not been reported from mine waste. At lower concentrations, As can be incorporated in Fe-S phases, which may also be the case for Sb, although there is little information about the incorporation of Sb in sulfide minerals.

Determining the mobility (ease of release from its solid sources into water or pore solutions) of Sb at a particular site is complex and ultimately depends upon the complex geochemistry, mineralogy, and biology of Sb. Vink (1996) and Krupka and Serne (2002) suggested that Sb is relatively mobile in the weathering environment. These suggestions have been challenged by other studies (Diemar et al., 2009; Filella et al., 2009; Majzlan et al., 2011; Leverett et al., 2012) that consider Sb to be quite immobile in near-surface surroundings. Majzlan et al. (2016) concluded that the reason for the contradictory information is the different stability of Sb-hosting minerals. Antimony can be mobile in near-surface environments at some contaminated sites because primary or secondary Sb minerals are not in equilibrium with surrounding conditions, and their dissolution is promoted.

The thermodynamic data are available for some of the minerals found in mine waste but are not included in geochemical modeling software databases included with PHREEQC, Geochemist's Workbench, and other modeling software packages. The data for tripuhyite and schafarzikite are available in Leverett et al. (2012), bystromite in Roper et al. (2015a), brandholzite and mopungite in Diemar et al. (2009), and kleberzbergite in Roper et al. (2015b). The calculations of these data are for well-crystallized, bulk, and stoichiometric samples. The nature of mine waste samples is usually poorly crystalline, fine-grained, and often nonstoichiometric, and the variation of thermodynamic data is hard to estimate (Majzlan et al., 2016).

The challenge for future mine waste remediation processes is to determine a way that Sb could reach equilibrium in solid form after exposing contaminated waste to surface conditions. This can be reached either by adjusting the conditions so that the primary form remains stable (e.g., placing stibnite waste in reducing conditions to prevent oxidation) or to enhance the conditions for secondary minerals to form and remain stable. Even if the secondary minerals are formed, they may not remove enough Sb from water and further remediation action may be required. In mine drainage where Fe input to the mine water is low, Sb can be more mobile (Craw et al., 2004). An example is the Beaver Brook Sb mine in Newfoundland, Canada, where slower Fe sulfide oxidation and relatively fast stibnite oxidation do not promote sufficient Fe supply in mine water to precipitate secondary phases. In this case, the input of Fe in mine drainage may be desirable in specific cases to limit Sb mobility in water (Borčinová Radková et al., 2020).

Sb Concentrations in Mine Wastes, Mining-Affected Waters, Soils, and River Sediments

The abundance of Sb in the Earth's crust reported is 0.3 mg/kg (Wedepohl, 1995; Reimann et al., 2010) and 0.5 mg/kg (Yaroshevsky, 2006). In most cases, the measured Sb concentration in uncontaminated waters is <1 µg/L, with the exception of hot springs where it can sometimes get close to 500 mg/L. The lowest reported aqueous concentrations of Sb (200 ng/L) are those in seawater (Filella et al., 2002a, and references therein). Antimony concentrations in mine tailings are moderate to very high compared to crustal abundance (145–176,700 mg/kg), as are mining-affected soils and river sediments (2–80,200 mg/kg and 2-7,230 mg/kg; Table 3).

Examples of Sb concentrations in mining-affected waters are shown in Table 3 and images of Sb-containing mine sites in Canada and Slovakia are shown in Figure 4. Concentrations of mining-affected rivers, groundwaters, other surface waters, waste-rock and adit discharges, surface water on tailings, and tailings pore waters range from <0.001 to 55.0 mg/L (Table 3), with the lowest concentrations found in surface waters (e.g., Hiller et al., 2012) and the highest in tailings pore water (e.g., Ritchie et al., 2013). Some studies have shown that natural attenuation, via dilution and/or sorption of Sb onto phases such as Fe (oxyhydr)oxides, reduces aqueous Sb concentrations downstream of tailings dams (Wilson et al., 2004a; Fľaková et al., 2012). In similar systems where adsorption does not occur due to the lack of suitable substrates, aqueous Sb concentrations remain high downstream of mine waste sources (Wilson et al., 2004b). In cases where adsorption does not attenuate Sb, fluxes of Sb from catchments can be high (Wilson et al., 2004b).

Antimony and As often occur together in mine wastes, and only when Sb is the main commodity does the concentration of Sb exceed As in the mine waste (e.g., Hiller et al., 2012). Otherwise, As typically exceeds Sb concentration in both solid and liquid mine waste by a factor of 10 or more (e.g., Hiller et al., 2012; Fawcett et al., 2015; Mbadugha et al., 2020).

Microbiology of Sb in Mine-Impacted Water and Mine Waste

Microorganisms in the mining environment play an important role in biogeochemical transformations of Sb. Even though Sb is a nonessential element, reduction, oxidation, and methylation of Sb can be mediated by microorganisms for detoxification and cell growth. A better understanding of the role that microorganisms play in biogeochemical cycling can improve mine site management and assist in the development of bioremediation strategies for Sb-impacted environments. The oxidation state of Sb affects the precipitation of secondary minerals and the toxicity of Sb to aquatic micro- and macroorganisms. This section describes the mechanisms of microbially controlled Sb transformations and microbial activity relevant to mine sites and remediation design.

Microbial Sb oxidation, reduction, and formation of organoantimonials

By chemical analogy, Sb, like As, is generally toxic to cells due to the chemical affinity for thiol groups in proteins, which can interfere with folding and function. Antimonate is also linked to increased transcription of pathways related to oxidative stress (Abin and Hollibaugh, 2019). Because it is not an essential nutrient, there are no known specialized transporters for Sb(III) or Sb(V) in bacteria (Li et al., 2016). Antimonite can enter cells through aquaglyceroporins in a number of or-

Table 3. Selected Sb Concentrations of Mine Tailings, Mining-Affected Soils, River Sediments, and Waters

Mine tailings (mg kg^{-1})	Soils (mg kg^{-1})	River sediments (mg kg^{-1})	Water (mg L^{-1})	Type of mine	Reference
	2–21,600 = 293 (*n* = 893)	2–840 = 45.2 (*n* = 29)	<0.002-0.798 (*n* = 25)	W-Au-Sb	Carvalho et al. (2009)
160–1,800		Up to 461	Tailings ponds 0.146-1.62 (*n* = 6);	Au	Fawcett et al. (2015); Bailey (2017)

			adits 0.046-0.645, = 0.280 (*n* = 3);
			tailings pore water 0.018-7.50, = 1.117 (*n* = 8);
			groundwater from base of tailings 0.750-7.75 (*n* = 2);
			mixed ground and surface water 0.139-0.90, =1.325 (*n* = 3);
			creek water 0.004-0.045, =0.032 (*n* = 32);
				Sb	Fľaková et al. (2012)

			untreated mine water 2.22-13.93	Sb	Li et al. (2016)
		6.6–7,230 (*n* = 51)	Surface waters <0.0003-0.72 (*n* = 51); tailings pore water 55.0 (*n* = 1)	Sb	Ritchie et al. (2013)
34,600–176,700 (*n* = 6)	smelter soil 80,200 (*n* = 1)	18–243 (*n* = 6)	River waters 0.014-0.030 (*n* = 6)	Sb	Wilson et al. (2004a)
16.9–9,861 (*n* = 12)	2.0–9,619 (*n* = 42)	11–1,360 (*n* = 29)	Rivers, waste rock and adit discharges, tailings <0.001-9.3 (*n* = 65)	Sb	Hiller et al. (2012)
684–17,196 (*n* = 50)	141–8,733 (*n* = 78)		Rivers, ponds, reservoirs, paddy fields 0.01-0.14 (*n* = 75)	Sb	Fu et al. (2016)
6,796–13,743 (*n* = 13)			Groundwater 0.0007-0.0022 (*n* = 3); tailings water 1.645 (*n* = 1)	Sb	Levresse et al. (2012)
	11.89–336.2			As-Cu-Pb-Sb	Flynn et al. (2003)
723 ± 63 (*n* = 30)	1.23±0.62 (*n* = 6)			Ag-Sn	Kossoff et al. (2012)
203–2,513 (*n* = 18)	583–953 (*n* = 6)			Cu	Anawar et al. (2011)
	28–15,112 (*n* = 15)			Sb	Baroni et al. (2000)

960–8200 (*n* = 8)			Tailings pore water 2.01-26.4 (*n* = 2);
			tailings ponds 12-26.1 (*n* = 2);
			stream water 8.6 (*n* = 1);
				Sb	Borčinová Radková et al. (2020)

Notes: Values shown are ranges or single analyses with mean values ($\bar{x}$); "*n*" refers to number of samples analyzed ganisms (Meng et al., 2004; Porquet and Filella, 2007). The mechanism for Sb(V) transport into the interior of a cell is not known but may be related to the phosphate transport system that also incidentally carries As(V) (Li et al., 2016). Transport of Sb(III) out of a cell (efflux or extrusion) has been found to occur via several transport systems, including proteins coded by the *ars* genes that can also transport As(III) (Meng et al., 2004). Reduction and transport of Sb(III) out of a cell is an effective detoxification strategy for As resistance.

Antimonate reduction can also be used by cells for dissimilatory growth under anaerobic conditions. Enrichment cultures in the laboratory have demonstrated that a bacterial consortium can grow on antimonite as the terminal electron acceptor (TEA) in the presence of organic carbon (lactate and acetate; Kulp et al., 2013; Abin and Hollibaugh, 2014), H_2 gas (Lai et al., 2016), methane (Lai et al., 2018), and even by directly using electrons from an electrode (Nguyen et al., 2019). The enrichment cultures of Kulp et al. (2013) were grown from a neutral-pH Sb mine (Stibnite mine, Idaho) and a suburban lake near San Francisco, California, on antimonite, indicating that the ability for organisms to reduce Sb(V) may be widespread. In addition, the cultures were not able to grow autotrophically, unlike cultures grown by Lai et al. (2016), suggesting that there may be multiple microbial pathways. Additional evidence for widespread ability to reduce Sb(V) heterotrophically comes from pure cultures of a *Bacillales* strain (Abin and Hollibaugh, 2013) and a *Sinorhizobium* strain (Nguyen and Lee, 2014) isolated from Mono Lake (California) and a contaminated industrial site (Korea), respectively, via enrichment cultures. Mineral precipitates formed in laboratory studies consisted of either Sb_2O_3 or Sb_2S_3, if grown in the presence of sulfate and sulfate-reducing bacteria (Abin and Hollibaugh, 2013; Kulp et al., 2013; Wang et al., 2018; Zhu et al., 2018). Recent studies of the genetics of Sb reduction highlight the importance of a family of dimethyl sulfoxide reductase enzymes that are present in a phylogenetically diverse group of organisms (Shi et al., 2019).

Microbial Sb(III) oxidation may be very important in controlling the mobility of Sb in Sb(III)-rich environments, such as mine tailings piles, where reduced Sb may be present in relict ore minerals. Once oxidized, Sb(V) may be more likely to be mobilized into water or sequestered in secondary minerals, as discussed in “Secondary minerals in mine wastes.” Generally, oxidation of aqueous Sb(III) by atmospheric O_2 in the absence of light is kinetically limited at circumneutral pH (Leuz and Johnson, 2005), but microorganisms can accelerate the rate of oxidation by many orders of magnitude, either via direct enzymatic oxidation or by oxidizing Fe(II) to Fe(III), which then reacts abiotically (Asta et al., 2012). The physiological impetus for oxidation may be detoxification or chemoautotrophic growth, although more information is needed on the biological mechanisms (Li et al., 2016). There appear to be multiple cellular pathways for Sb oxidation. An antimonite oxidase (*anoA*) has been identified and found to be widely distributed but is not the only pathway (Li et al., 2015). An intracellular H_2O_2 pathway has also been found to oxidize Sb(III) in addition to direct enzymatic oxidation (Li et al., 2017). In addition, some organisms are limited to aerobic Sb(III) oxidation, while others can employ both aerobic and anaerobic (e.g., nitrate as terminal electron acceptor) pathways (Nguyen et al., 2017, Loni et al., 2020). There have been more studies characterizing the phylogeny of organisms that can perform Sb(III) oxidation than Sb(V) reduction. Many organisms that have been observed in culture to oxidize Sb(III) can also oxidize As(III) (Lehr et al., 2007; Terry et al., 2015; Wang et al., 2015). Bacteria may preferentially oxidize As, Sb, or oxidize both As and Sb simultaneously, depending upon the organic carbon substrate and the organism (Nguyen et al., 2017; Lu et al., 2018). In addition, enrichment cultures grown from sediments collected at the same mine site (Idaho) exhibited the ability to reduce Sb(V) or oxidize Sb(III), depending upon redox conditions (Kulp et al., 2013; Terry et al., 2015), suggesting that the potential for both oxidation and reduction exists in the microbial consortia. Bacteria also play an important role in the dissolution of Sb-bearing solids, including stibnite, by enhancing the dissolution of Sb and facilitating complete oxidation of aqueous Sb(III) to Sb(V) (Loni et al., 2020).

Antimony biomethylation appears to be predominantly a bacterial and fungal process and can occur under aerobic or anaerobic conditions (Filella et al., 2007; Filella, 2010; Wilson et al., 2010, and references therein). Production of organoantimonials is hypothesized to be driven by decreased reactivity and toxicity of methylated Sb species, providing an alternative detoxification mechanism, although the cellular mechanism is still unknown and the fortuitous methylation of Sb cannot be excluded. Organoantimonial species are generally thought to mimic methylated arsenic species, with mono-, di-, and trimethyl Sb species possible (Bentley and Chasteen, 2002). Concerns about accurate preservation and measurement of organo-Sb(V), Sb(III), and Sb(-III) compounds are well founded, given the analytical challenges present with these species (Dodd et al., 1996); a similar issue exists with arsenic species, although more analytical information is present on organoarsenicals than organoantimonials (Campbell and Nordstrom, 2014). Some methylated Sb species, such as trimethylantimonite and methylstibnine, are volatile and may present a different kind of human exposure risk via inhalation. Work with a fungus, *Scopulariopsis brevicaulis*, has shown that di- and tri-methylstibnite can accumulate in aerobic culture and that the pathway is similar to that of arsenic methylation (Craig et al., 1999; Andrewes et al., 2000a).

Many of the common organisms and enzymatic pathways of Sb transformation have yet to be fully investigated. Due to the chemical similarity of As and Sb, it is often assumed that the same enzymatic pathways are active for both elements. Although this assumption is sometimes true, the rate and extent of microbial transformations do not necessarily directly translate from As to Sb. For example, Terry et al. (2015) isolated several bacterial strains from neutral-pH mine sediments (Idaho) that can oxidize both As(III) and Sb(III), but appear to exhibit an Sb(III)-specific enzymatic pathway that is homologous but not identical to the genes used for As(III) oxidation. Similarly, genetic studies with a pure strain of *Agrobacterium tumefaciens* showed that Sb(III) oxidation occurred by a different pathway than As(III) oxidation (Lehr et al., 2007). Whether Sb(III) oxidation pathways are specific to Sb(III) or can cometabolize other elements is undetermined (Li et al., 2015). While expulsion pathways are the same for As(III) and Sb(III), the regulation and oxidation of these species proceeds by different mechanisms (Wang et al., 2015). In addition, because As and Sb commonly co-occur in mine wastes, the presence of arsenic may affect the microbial transformations of Sb (and vice versa). In enrichment cultures from mine sediments amended with acetate, Sb(V), and As(V), reduction of Sb(V) was inhibited by the presence of As(V), which was reduced preferentially (Kulp et al., 2013). Fungal biomethylation of As(III) was inhibited by Sb(III) but not Sb(V) (Andrewes et al., 2000b). Clearly, more research into the pathways of Sb metabolism is needed to fully understand microbial transformations of Sb in the environment.

Microbial diversity at mine sites

Compared to As, much less information is available on the microbial diversity present at Sb-rich mine sites. Microbial community structure (16S rRNA gene sequencing) was evaluated at an As- and Sb-rich tailings site and a stream affected by the mine drainage in southwest China (Sun et al., 2016a; Xiao et al., 2016). At the site, the water was neutral pH, and As and Sb were associated with iron sulfide and iron oxide phases. The microbial community was fairly diverse, and although there were a number of uncultured organisms with unknown function, several sulfur- and iron-oxidizing organisms were identified, including common acidophilic organisms such as *Acidithiobacillus ferrooxidans*. Both heterotrophic and chemotrophic metabolisms were present. Deeper in the tailings, where anaerobic or microanaerobic conditions may exist, sulfate- and metal-reducing organisms were identified, suggesting that metal and sulfur cycling was occurring in the tailings. However, whether Sb redox cycling was also occurring in the tailings was unknown. In soils contaminated by Sb from a shooting range in Switzerland, wet-dry cycling of the soils in the field and in laboratory microcosms changed the oxidation state and mobility of Sb (Hockmann et al., 2014, 2015). Upon wetting of the soil, anaerobic conditions promoted the microbial reduction of Sb(V) to Sb(III). Antimonite was sequestered by adsorption on iron oxides until reductive dissolution of the iron oxides mobilized aqueous Sb(III). In soils collected from the region surrounding the Xikuangshang mine (China), the bacterial, archaeal, and fungal community composition was primarily controlled by soil pH (pH 4-8) and correlated with total Sb and As concentrations (Wang et al., 2016, Wang et al., 2018). Highly elevated As and Sb concentrations tend to decrease microbial diversity and exert selective pressure toward tolerant organisms (Sun et al., 2017).

Bioreactors and bioleaching

Bioleaching has been extensively studied as a method to passively mine economically viable metals from sulfide ores. Because Sb is a chalcophilic element, like As, it commonly co-occurs with metals such as copper, silver, gold, nickel, zinc, and other elements. Bioleaching typically occurs under acidic conditions and relies upon sulfide mineral oxidation by acidophilic iron- and sulfur-oxidizing organisms. In batch bioleaching experiments designed to leach zinc from waste products of copper smelting using *Acidithiobacillus ferrooxidans* and its *Acidiphilium* symbiote, Klink et al. (2016) found that greater than 2 mg/L Sb was leached into solution, primarily as Sb(V), while arsenic reached concentrations of greater than 12 mg/L, but was dominantly As(III). Similarly, enrichment cultures from Sb-rich ore (Olympiadinskoe deposit, Russia) were able to oxidize and mobilize Sb from the stibnite-rich ore (Tsaplina et al., 2010, 2014). This suggests either direct enzymatic oxidation of Sb(III) or indirect oxidation via aqueous Fe(III). Clearly, the pathways of Sb(V) and As(V) oxidation under bioleaching conditions are controlled by different factors, and more research is needed to fully understand what controls metalloid oxidation under these conditions.

Under reducing conditions in sulfur-rich conditions, as can be found in tailings piles, it is expected that reduced Sb(III)-sulfide solid phases will form, providing a limitation to Sb(III) mobility. This reaction has been harnessed in sulfate-reducing bioreactors to immobilize a number of elements, including Sb (Li et al., 2016; Sun et al., 2016b; Zhang et al., 2016). The ability of sulfate-reducing bacteria to reduce Sb(V) is not known, but it is possible that abiotic reactions with dissolved sulfide and precipitation as Sb_2S_3 is common in bioreactors that specifically select for sulfate-reducing bacteria (Zhang et al., 2016). While bioreactors seem to be a promising bioremediation technology, more research is needed on the biogeochemistry of Sb in these systems.

In mine waste situations where both As and Sb are present in relatively high concentrations, particular waste from Sb mining and processing, it is advisable to examine As and Sb behavior carefully to limit aqueous concentrations and optimize remediation.

Bioavailability, Bioaccumulation, Bioaccessibility, and Regulation of Sb

The focus on Sb as a potentially toxic compound has increased over the last decade, and its toxicity is thought to be similar to that of As (Kabata-Pendias and Pendias, 1984; Gebel, 1997; Smichowski, 2008). As a carcinogen, Sb is one of the priority pollutants of interest by the Canadian Council of Ministers of the Environment, the Environmental Protection Agency of United States and the European Union (Council of the European Communities, 1998; Canadian Council of Ministers of the Environment, 2003; Environmental Protection Agency of the United States, 2018). When considering the environmental impact of mine waste, reference is typically made to maximum permitted levels of elements in specified media. The risk to human and wildlife health associated with Sb in mine waste involves assessing exposure via drinking Sb-contaminated water, ingesting Sb from soil (particularly common in babies or young children), breathing Sb in dust, or exposure via dermal contact.

Bioaccumulation, bioavailability, and bioaccessibility

Bioaccumulation of Sb in microbial and multicellular organisms is important to understand for ecosystem health. In general, little information is available. A few studies suggest that algae and plants may take up Sb when elevated concentrations are present in water or soil (Filella et al., 2007; He, 2007; Dovick et al., 2015). Adsorption and biomineralization onto biomass have not been well characterized and may be quite variable. One notable exception is in a geothermal system (Waiotapu, New Zealand) where the presence of reduced sulfur, Sb, As, and silica created a biomineralized shell around microbes (Phoenix et al., 2005). In a study of mining-impacted water (Idaho), Sb and As were found to bioprecipitate in microbial/algal mats and to bioaccumulate in tadpoles ingesting the algae, but there was no biomagnification up the food chain (macroinvertebrates and fish; Dovick et al., 2015). However, the tadpoles accumulated some of the highest As and Sb concentrations reported for living vertebrates, and they exhibited some sublethal effects, including delayed development and decreased size at metamorphosis (Dovick et al., 2020).

Although Sb concentrations in mine-affected soils and river sediments are elevated above crustal abundance (Table 3), they are reported to have relatively low bioavailability (Casado et al., 2007; Levresse et al., 2012; Fu et al., 2016). This is reflected by low Sb concentrations in plants growing in mining-affected soils (Table 4), even if these concentrations are higher than that of a global "reference plant" (0.10 mg/kg; Markert, 1992). In addition, Tschan et al. (2009), in a review of literature on the plant-soil-antimony system, showed that Sb uptake depended on the plant species and characteristics of the study site. Using H_2O, NH_4NO_3, ethylenediaminetetraacetic acid (EDTA), and acetic acid extractions, they demonstrated that the extractable Sb concentrations in soils correlated with the amount of Sb taken up in the plants, which can be high (up to 1,000 mg/kg; Fig. 5). Plants growing in tailings, in particular, show very high Sb concentrations (e.g., the roots and basal leaves of *Plantago lanceolate* contain up to 1,150 and 569 mg/kg by growing in abandoned Sb tailings in Turkey; Baroni et al., 2000). Levresse et al. (2012) suggested that the amount of Sb taken up by plants growing in mining-affected substrates depends on the Sb speciation, its degree of dissolution in water, and the efficiency of plant uptake.

For human health, the bioaccessibility of Sb in solid materials, including mine waste, depends on the solubility of Sb-bearing phases in bodily fluids, and therefore on the mineralogical compositions of the wastes (Plumlee and Morman, 2011). The total concentrations, which are in many cases the only available data from Sb-contaminated mine waste sites, typically give no indication of bioaccessibility and therefore assessments may lead to overestimation of risks. Mine wastes containing low concentrations of potentially toxic contaminants associated with unstable mineral phases represent more serious risk to the environment than tailings with high contents of contaminants in the form of minerals, which are inert in near-surface environments. For example, Flynn et al. (2003) demonstrated that Sb is biologically unavailable over a wide range of pH at former mining and smelting sites in the UK despite the high total Sb concentrations reaching up to 700 mg/kg. Even higher Sb concentrations (up to 3,061 mg/kg) were measured in agricultural soils located close to mining and smelting areas near Xikuanghsan, China (Li et al., 2014). Although these concentrations greatly exceed Sb regulatory limits for agricultural soils (36 mg/kg; Chang et al., 2002), less than 30% of the total Sb has been reported to be bioaccessible (Li et al., 2014). As is the case for other elements such as As and Pb, the challenge is to find a universally acceptable method of bioavailability assessment (Bagherifam et al., 2019).

Table 4. Selected Sb Concentrations of Mining-Affected Plants

Plants (mg kg^{-1})	Ore deposit type	Reference
Leaf and tuber vegetables and fruit 1.13–91.0 (n = 183)	Carbonate replacement deposit, Xikuangshan Sb mine, China	Fu et al. (2016)
Achillea ageratum Roots 0.25–28.15 (n = 6) Shoots 0.19–14.98 (n = 4) Basal leaves 1.06–33.23 (n = 6)	Limestone-hosted quartz-carbonate-stibnite vein, Tuscany	Baroni et al. (2000)
Plantago lanceolate Roots 10.37–1150.31 (n = 5) Basal leaves 28.45–569.34 (n = 5)		
Silene vulgaris Roots 13.75–249.52 (n = 4) Shoots 17.61–1163.81 (n = 4) Basal leaves 19.45–853.75 (n = 4)		
Bubblejaceae Buddleja Leaf 3.67–7.31 (n = 2) Stem 0.97–6.93 (n = 2)	Carbonate replacement deposits Wadley mining district, San Luis Potosí, Mexico	Levresse et al. (2012)
Pinaceae Pinus Leaf 2.55–15.61 (n = 2) Stem 8.36–11.02 (n = 2) Root 14.83 (n = 1)		

Governmental regulations of Sb

The main environmental concern relating to Sb is its concentration in waters. The limit of concentrations in drinking water is even lower (0.005 mg/L) than that of As (0.01 mg/L) according to European Union drinking-water standards (Council of the European Communities, 1998) and China drinking-water standards (China Drinking Water Standard, 2007). The drinking-water limit for Sb is slightly higher in the United States and Canada with a value of 0.006 mg/L (Health Canada, 2014; U.S. Environmental Protection Agency, 2018).

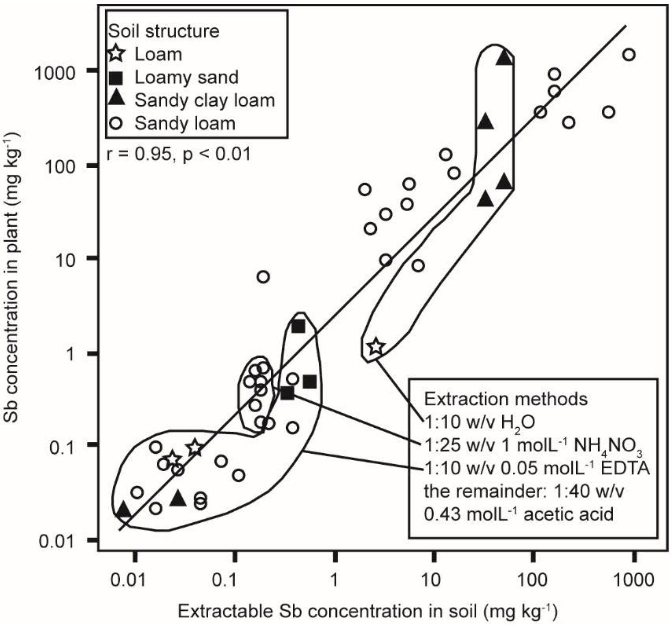

Fig. 5. Relationship between soluble Sb concentrations of field-contaminated soils and Sb in plants grown in these soils, based on data in Baroni et al. (2000), Hammel et al. (2000), Pratas et al. (2005), Dominguez et al. (2008), Rached-Mosbah et al. (1992), Murciego et al. (2007), De Gregori et al. (2001, 2003, 2004). The points represent averages of replicate samples or pot trials. Regression was performed on the log-transformed data. Adapted with the permission of the Mineralogical Society of Great Britain and Ireland from a paper by Tschan et al. (2009).

The lowest limits for Sb in drinking water are those given by the Australian and Japanese governments with values of 0.003 and 0.002 mg/L, respectively. The World Health Organization (2004) recommends Sb in drinking water at a maximum level of 0.02 mg/L (Table 5).

Currently, in many countries there are no limits for Sb in mine effluents, and limits instead are decided on a case-by-case basis in discharge permit. Both Sb and As are carcinogenic metalloids but regulations for Sb are relatively few. This may be because conventional wisdom is that they behave similarly and since usually As is present in greater concentrations and is regulated, any remediation that deals with As will take care of Sb cleanup as well. Additionally, generally less information is available about Sb toxicity to inform regulatory standards. Antimony is toxic to aquatic organisms and its toxicity depends on oxidation state. Sb(III) is not always more toxic than Sb(V), and most of the toxicity studies are focused on Sb(III) exposure despite the predominant exposure to Sb(V) in the near-surface environment. The aquatic species such as amphibians and macroinvertebrates show higher sensitivity to Sb compared to fish and bacteria. However, there is a large variation in individual responses reported in different studies (Obiakor et al., 2017).

The consequences of missing guidelines for mine effluents are that either Sb is unregulated or the low limits for Sb concentrations in drinking water are used. Guidelines for Sb in soil have different values between countries and regions (Wilson et al., 2010). For example, the toxicity guideline for Sb concentration in soil for residential areas is 10 mg/kg in Italy (Carlon, 2007), 20 mg/kg in Canada (Canadian Council of Ministers of the Environment, 2018), and 40 mg/kg in Czech Republic (Carlon, 2007). The limits are higher for industrial areas: 30 mg/kg in Italy, 40 mg/kg in Canada, and 80 mg/kg in Czech Republic (Carlon, 2007; Canadian Council of Ministers of the Environment, 2018). The tolerable daily intake (TDI; a dose below which no adverse effects will occur) is set at 6 µg/kg of Sb of body weight per day (World Health Organization, 2003). In the recent work by Bagherifam et al. (2019), five common soil and sediment toxicity guidelines set by the United States, Canada, Australia, the Netherlands, and Finland and their derivation methods were compared. More consistent guidelines for environmental risk assessment could help to minimize the effects of Sb-contaminated soils to the environment in some cases; however, because of site-specific properties (e.g., mobility or environmental availability of Sb, groundwater depth, soil properties), differences in geographic and sociocultural factors (such as social behavior and land use), the potential for universal guidelines is low (Bagherifam et al., 2019).

Only some countries have legislation for Sb maximum concentrations in sediments. For example, the maximum permissible Sb concentration in sediment in the Netherlands is 14 mg/kg (Crommentuijn et al., 2000). The Australian and New Zealand guidelines for fresh and marine water quality (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, 2000) provides two values in guidelines for Sb in sediments: 2 and 25 mg/kg, below which biological effects would rarely and possibly occur, respectively.

Smelting and refining operations can also be a source of atmospheric Sb pollution. The limits on allowable emissions are variable by country. As an example, the Ontario Ministry of Environment in the ambient air-quality criteria lists 25 µg/m^3 of Sb (in 24 h avg time) as the maximum allowable concentration in air (Ontario Ministry of the Environment and Climate Change, 2016).

Conclusions

This work summarizes current information about geochemistry, mineralogy, and microbiology of Sb in mine waste. During the last decade, research has been considerable on the concentrations and distribution of Sb in different media related to mine waste. The process of stibnite and sulfosalts weathering by near-surface exposure is accelerated by mining activities and causes Sb to be released into water systems and redistributed among secondary minerals forming in mine waste. Recent work (e.g., Majzlan et al., 2016) suggests there are more Sb-bearing minerals in mine waste to be discovered and their role in Sb mobility yet to be described. Because no complex thermodynamic data for some of the Sb-containing secondary phases (e.g., pyrochlores) are available, it is crucial that further research in this area is undertaken. Such data would

Table 5. Regulatory Values for Concentrations of Antimony and Arsenic in Waters, Effluents, and Soil

Parameter	Drinking water (mg/l)				Protection of aquatic life (mg/l)	Metal mining effluent (mg/l)				Soil (mg/kg)		
						Canada[6]						
	USA[1] Canada[2]	Europe[3]	China	Australia[4]	Canada[5]	Maximum authorized: monthly mean	Maximum authorized: composite sample	Maximum authorized: grab sample		Canada[7]	Czech Republic[8]	Italy[8]
Antimony	0.006	0.005	0.005	0.003	n.a.	n.a.	n.a.	n.a.	Residential areas	20	40	10
									Industrial areas	40	80	30
Arsenic	0.01	0.01	0.01	0.007	0.005	0.5	0.75	1	Residential areas	12	70	20
									Industrial areas	12	140	50

Notes: n.a. = not available; [1]U.S. Environmental Protection Agency (2006); [2]Environment Canada and Health Canada (2014); [3]Council of the European Communities (1998); [4]Australian Drinking Water Guidelines (2004); [5]Canadian Council of Ministers of the Environment (1997); [6]MMER (2002); [7]Canadian Council of Ministers of the Environment (2018a); [8]Council of the European Communities (2007) provide a base for more accurate geochemical modeling. In addition, because some of the historic mine sites contain high Sb concentration in tailings and waste rock, the potential of Sb recovery remains to be explored. Studies focused on Sb influence on ecosystem and human health could serve as a base for missing regulations, especially mine-effluent Sb limits. Additional information about microbial diversity at Sb mine sites, how these organisms affect Sb cycling and mobility, and whether they can be used in bioremediation and biomining would also be beneficial.

Acknowledgments

All authors thank colleagues and students with whom they have enjoyed working on antimony over many years. We also thank JM, AM, and SJW for their insight and suggestions provided in their invaluable reviews. Anežka Borčinová Radková acknowledges funding from the Society of Economic Geologists Canada Foundation via the Student Research Grant Program and from the Mineralogical Association of Canada research grant. Heather Jamieson acknowledges funding from NSERC (Natural Sciences and Engineering Research Council) Discovery Grant. Kate Campbell acknowledges funding from the U.S. Geological Survey (USGS) Minerals Resources Program and the U.S. Geological Survey Environmental Health Toxics Substances Hydrology Program. Karen Hudson-Edwards acknowledges funding from the UK Natural Environment Research Council and the National Basic Research Program of China, the UK Science and Technology Facilities Council for beamtime at the Diamond Light Source, and the Natural History Museum, London, for a CASE studentship award to D. Kossoff. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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