



Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand

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Abstract

Antimony (Sb) occurs principally in stibnite (Sb_2S_3) in mesothermal vein deposits hosted in low-grade metamorphic belts of eastern Australia and southern New Zealand. Stibnite is commonly associated with gold. Many deposits have been mined historically, with one large deposit, at Hillgrove, New South Wales, being mined recently. Natural outcrops in the relatively rugged terrains are oxidised under humid to semiarid conditions and stibnite transforms to oxides including valentinite, senarmonite, stibiconite, and rarely cervantite. Oxidation of stibnite and associated arsenopyrite and pyrite causes local acidification; however, acid is readily neutralised by carbonates in mineralised zones and host rocks, and associated waters are near neutral (pH 6–8.5). Stibnite dissolves readily in moderately oxidised waters as SbO_3^- , in conjunction with antimony oxide formation. Experimental stibnite oxidation yielded up to 37 ppm dissolved Sb, and mine and tailings dam waters at Hillgrove have up to 55 ppm dissolved Sb. Natural stibnite can contain >5000 ppm As in solid solution. Dissolution of stibnite, arsenopyrite and arsenian pyrite releases arsenic, and resultant dissolved As concentrations are up to 3.6 ppm (experimental) and up to 7.2 ppm (mine and tailings dam seepages). Mine and tailings discharge waters have elevated Sb and As where they emerge, but attenuation occurs by deposition of the metals onto amorphous iron oxyhydroxides which can contain >10% each of Sb and As. Historic disposal of mineralised waste rock material into the stream system at Hillgrove has caused strong contamination of stream sediments with Sb and As. Equilibration of stream water with contaminated stream sediment, as well as additions from erosion of natural outcrops and mine and tailings dam seepages, has led to the main drainage system (Bakers Creek) containing strongly contaminated water (up to 1.8 mg/l Sb and 0.3 mg/l As) for 20 km until its junction with the Macleay River. Environmentally high values of dissolved Sb (and As), are inevitable in waters associated with mesothermal stibnite (–gold) deposits.

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1. Introduction

Antimony (Sb) is a Group V element that is similar to arsenic in many aspects of chemical behaviour and

toxicity to animals (Gurnani et al., 1994; WHO, 1996; Filella et al., 2002). Likewise, antimony can be absorbed by plants and may be phytotoxic (Foy et al., 1978). Consequently, the presence of elevated levels of antimony in surface and ground waters, and associated stream sediments and soils, may be an issue of environmental concern. Arsenic com-

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monly occurs in the same geochemical environment as antimony; thus, both elements may be anomalous in rocks, soil, stream sediments and waters.

Current Australian drinking water guideline values for Sb and As are 3 and 7 $\mu\text{g/l}$, respectively (NWQMS, 1996). Australian and New Zealand freshwater quality guideline values for Sb are not well established, and currently there is a low reliability trigger value of 9 $\mu\text{g/l}$ for Sb^(III) (NWQMS, 2000). For As, however, trigger values are established for varying levels of protection and for 99% protection, the guideline values are 1 $\mu\text{g/l}$ for As^(III) and 0.8 $\mu\text{g/l}$ for As^(V) (NWQMS, 2000). For stream sediments, interim quality guideline values have been established for Sb at 2 ppm (trigger value) and 25 ppm (high value), and for As at 20 ppm (trigger value) and 70 ppm (high value) (NWQMS, 2000).

Hydrothermally altered and mineralised rocks, and associated veins, constitute the principal source of antimony in the natural environment (Ragaini et al., 1977; Zanzari et al., 1995). A variety of antimony-bearing sulphides, such as stibnite (Sb_2S_3), tetrahydrite ($(\text{Cu,Ag})_{12}\text{Sb}_4\text{S}_{13}$), bournonite (CuPbSbS_3), pyrrargyrite (Ag_3SbS_3), famatinite (Cu_3SbS_4), occurs in epithermal mineralised zones (e.g. Erickson and Cunningham, 1993; Corbett and Leach, 1998) and geothermal systems associated with arc volcanism with amorphous Sb sulphide being precipitated in certain low sulphidation hot spring systems (e.g. Weissberg, 1969). In epithermal settings, antimony is generally an undesirable by-product of precious metal mining, and the antimony-bearing minerals are discharged with mine tailings. Stibnite, however, is most common in mesothermal vein systems hosted in low-grade metamorphic rocks. Here stibnite may be abundant and is commonly associated with elevated contents of As, Au and, locally, Hg and W (e.g. Nesbitt et al., 1989; Williams-Jones and Normand, 1997; Groves et al., 1998). Such deposits provide much of the antimony used for commercial purposes, and in fact may also be exploited for gold. Arsenic is found in solid solution in the above-mentioned minerals, but dominantly occurs as arsenopyrite (FeAsS) and arsenian pyrite (FeS_2 , with up to several wt.% As).

Despite the environmental significance of elevated antimony around mesothermal vein systems, there has been little research into mobilisation of antimony at these sites. This study documents the extent of, and

geochemical controls on, mobilisation. To do this, we use a combination of field examples (Fig. 1A,B), a major mine site and its downstream runoff (Figs. 1A and 2), and simple laboratory experiments. From these different approaches, we define typical mineralogy of stibnite deposits, and the scales of physical and chemical dispersal into the environment. We also include comments on arsenic mobility as arsenic occurs in the same field situations, has similar chemistry, and has significant environmental consequences (Bhumbla and Keefer, 1994).

2. Methods

Mineralogical identifications and mineral textural relationships were determined using hand specimen, light microscopy (thin and polished sections) and X-ray diffraction. Additional mineralogical and geochemical information was obtained by electron microprobe element mapping. These maps were constructed by short (ca. 1 s) semiquantitative analyses with a 2- μm beam, obtained automatically on a grid pattern, 2- μm spacing, across an area of 2×1.8 mm. Each map consists of 225,000 points. Results are contoured (grey-scale; Fig. 3) for relative concentrations of each element. Detection limit is ca. 0.5 wt.% for most elements, and resolution is ca. 2 μm . Analyses were obtained at 25 kV using wavelength dispersion on a JEOL 8600 microprobe.

Stream sediment samples were analysed by ICP-AES (inductively coupled plasma atomic emission spectrometry) at ALS-Chemex, Brisbane, Australia. Sieved sediments ($-180\text{-}\mu\text{m}$ fraction) were digested with concentrated HCl and H_2O_2 at 95 °C. Complexing agents were added and extracted by an organic solvent, with the subsequent centrifuged solution being introduced into the instrument. Detection limits are 0.2 ppm for Sb and 0.1 ppm for As. Duplicate, blank (pure quartz) and laboratory standard samples were analysed routinely for quality control. Stibnite from Otago deposits was analysed by XRF, with detection limits of ca. 5 ppm for Sb and As. Stibnite from Hillgrove was also analysed by proton microprobe at CSIRO Division of Exploration as part of the study of Ashley et al. (2000).

Water samples obtained in the field were collected in 500-ml acid-washed plastic bottles and acidified on

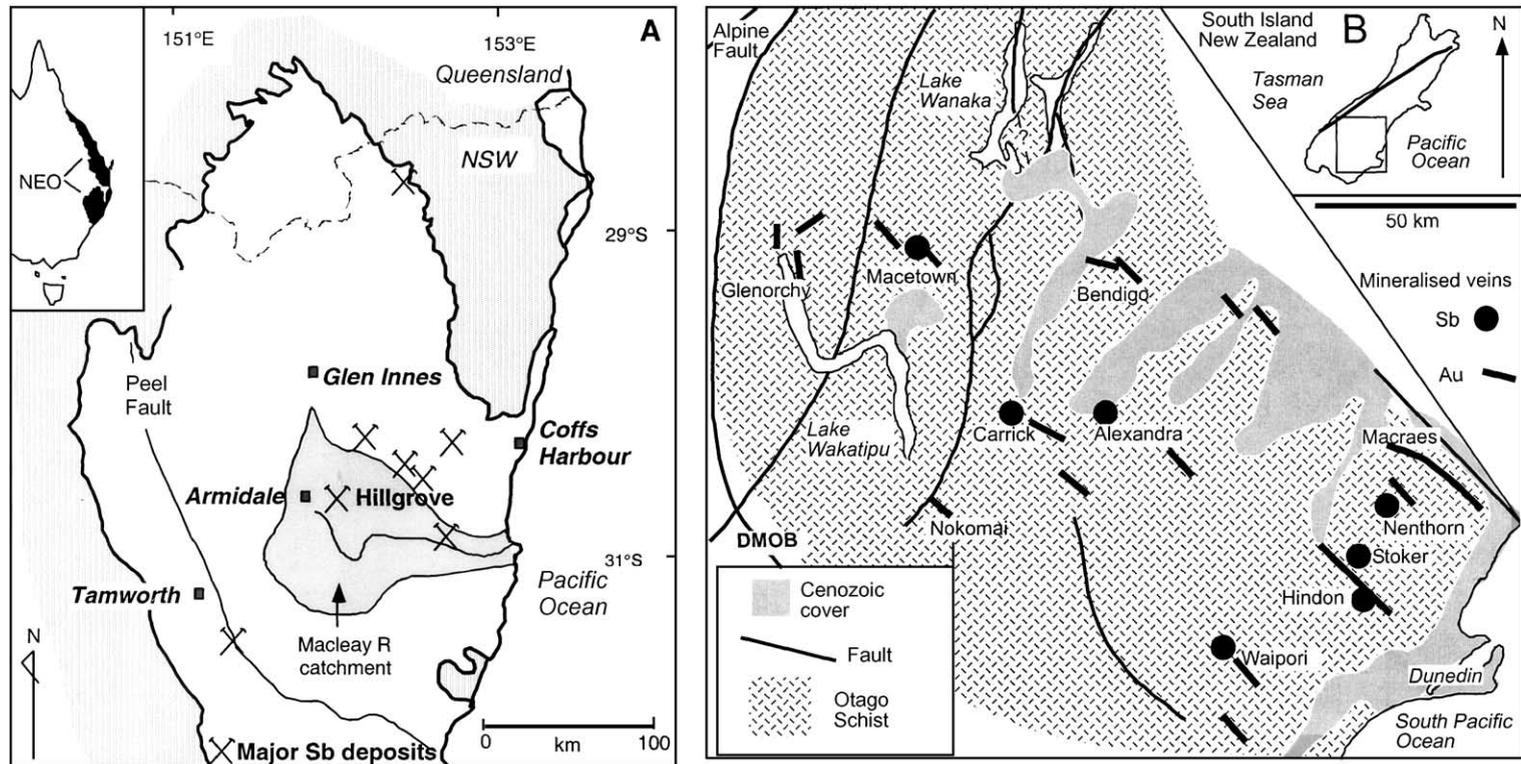


Fig. 1. (A) Map of southern part of the New England Orogen with locations of Hillgrove and other mesothermal Sb-bearing deposits, and the Macleay River catchment. (B) Summary geological map of Otago Schist vein systems (after Williams, 1974) showing stibnite localities in relation to mesothermal gold deposits.

site with 2 ml 1 M nitric acid. Experimental waters were separated from their experimental cells into acid-cleaned glass tubes and dispatched immediately to the laboratory. All waters were filtered (0.45 µm) before analysis. Water analyses were obtained by ICPMS (inductively coupled plasma mass spectrometry) at ALS-Chemex (0.001 mg/l detection limit for As and Sb), and Hill Laboratories, Hamilton, New Zealand (detection limit 0.0002 mg/l for Sb and 0.001 mg/l for As). Duplicate and blank water samples were analysed at these laboratories for quality control. Uncertainties associated with analyses are contained within the size of the symbols in all plots in this paper.

3. Mesothermal stibnite vein systems

Mesothermal vein systems occur worldwide in low-grade metamorphic belts. Vein systems are dominated by quartz and carbonates, with subordinate pyrite and arsenopyrite. They are commonly important sources of gold, both in the free form and encapsulated (chemically and in particulate form) in the sulphides (e.g. Nesbitt, 1991; Groves et al., 1998; Goldfarb et al., 2001). Locally, veins contain disseminated to massive stibnite on the centimetre to metre scale (e.g. Williams-Jones and Normand, 1997). In this study, we focus on mineralised vein systems of the low-grade metamorphic terranes of the New England Orogen in northern New South Wales, Australia (e.g. Barnes et al., 1988; Boyle, 1990; Ashley et al., 1996; Stroud et al., 1999) and the Otago Schist of southern New Zealand (Williams, 1974; Ashley and Craw, 1995). In both terranes, stibnite-bearing veins commonly accompany gold-bearing veins. The terranes currently have a humid to semiarid climate, with limited lithic soil development. Many deposits occur in areas of steep topography and consequently, mechanical erosion of material into stream systems is typical.

Several hundred Sb and Sb–Au vein deposits occur in the New England Orogen in northeastern New South Wales, commonly in clusters (Barnes et al., 1988; Stroud et al., 1999) (Fig. 1A). The most important deposits occur in the Hillgrove district (Figs. 1A and 2), where Au and Sb have been mined intermittently since 1877. Numerous vein systems have been mined recently at Hillgrove and total recorded production is now in excess of 60,000 t stibnite concentrate

and 25 t Au from several million tonnes of ore mined (Ashley et al., 2000). Mineralisation at Hillgrove occupies steeply dipping vein and hydrothermal breccia systems, hosted in metamorphosed quartzofeldspathic sedimentary rocks and granitoids. The veins are dominated by quartz and stibnite, with smaller volumes of carbonates and minor to trace amounts of gold–electrum, arsenopyrite, aurostibite, scheelite and base metal sulphides. The immediate host rock is hydrothermally altered and mineralised; typically it contains Au-bearing arsenopyrite and arsenian pyrite, ankeritic carbonate, sericite and quartz. Although most As in the ore occurs in arsenopyrite and arsenian pyrite, stibnite contains up to 5620 ppm As (Ashley et al., 2000). Several tens of thousands of tonnes of ore have been processed annually and for the past 25 years concentrator tailings have been impounded in a large dam. However, in pre-1920 mining at Hillgrove, several million tonnes of waste rock and mill tailings were disposed of into the Bakers Creek drainage system, a significant sub-catchment of the Macleay River, itself one of the major coastal river systems in northern NSW (Fig. 2). The Hillgrove mineral field is mostly within the steep headwater gorges of Bakers Creek, a region of accelerated natural erosion and high-energy stream environment.

Antimony deposits in the Otago Schist (Fig. 1B) are much smaller than Hillgrove and no mining is occurring at present. Deposits were explored and/or exploited from shallow surface workings developed at surface outcrops, many of which are still exposed. Vein systems are typically less than 1 m across and consist of massive stibnite intergrown with quartz, locally cementing hydrothermal breccias. Calcite and/or siderite accompany the stibnite in the veins, and in veinlets (cm-to-mm scale) in the adjacent host schist. Pyrite occurs with most stibnite deposits, but arsenopyrite is rare. Stibnite contains up to 100 ppm As in solid solution.

The widespread occurrence of carbonate minerals in the mineralised veins and adjacent rocks is characteristic of mesothermal deposits in both the New England Orogen and Otago terranes. In addition, the host schist in Otago commonly contains calcite as a metamorphic mineral. The carbonate minerals are volumetrically more abundant than sulphides on the 10-m scale around all deposits; as a consequence, no significant acidification of surface or ground waters

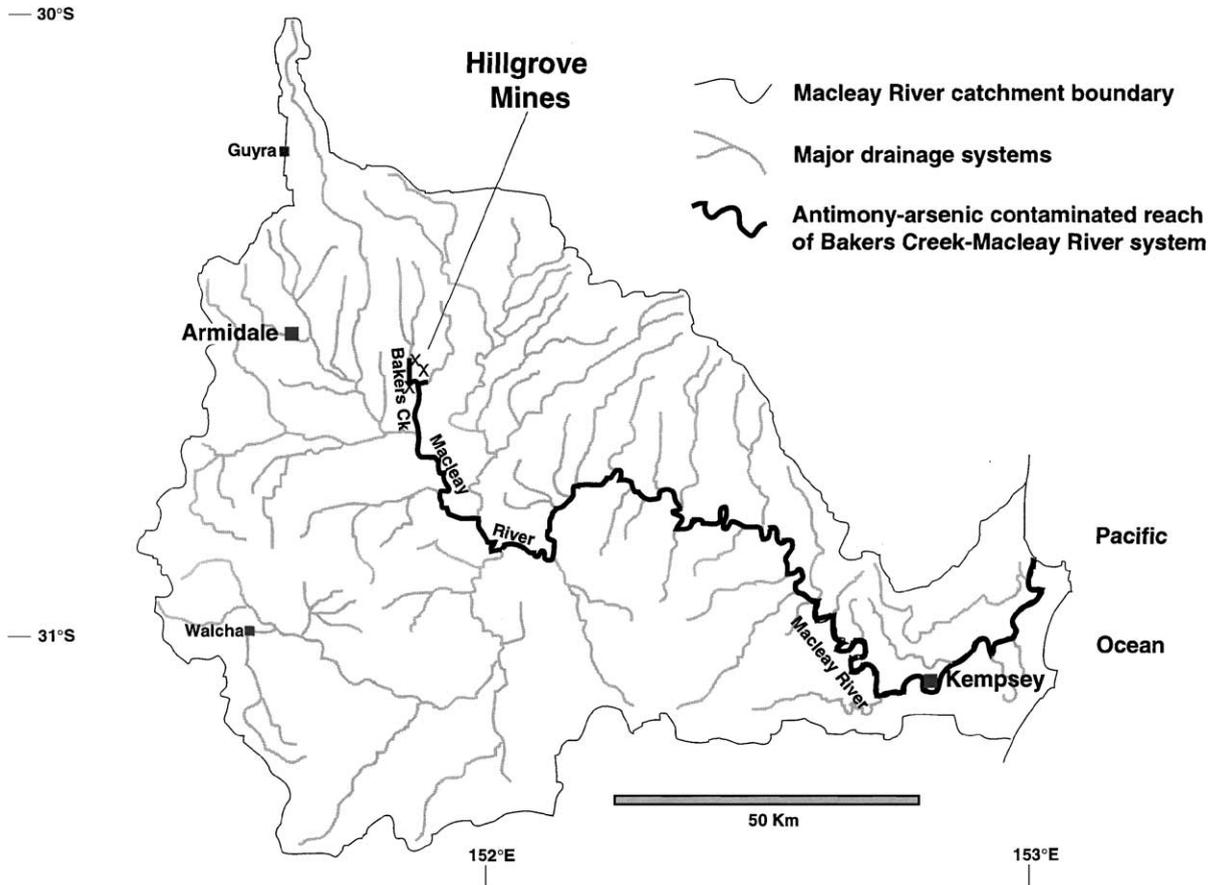


Fig. 2. Map of Macleay River catchment with location of Hillgrove mines and contaminated reach of the Bakers Creek–Macleay River system.

occurs during weathering of the deposits in situ or in mine wastes. Any sulphuric acid generated by oxidation of, e.g. pyrite, is essentially instantaneously neutralised by the abundant carbonate (Craw, 2000). Surface and near-surface waters emanating from Sb mines and mineralised rocks in New England Orogen and Otago typically have pH values between 6 and 8, and Eh between 0 and +400 mV.

4. Stibnite decomposition

4.1. Natural outcrops

Stibnite outcrops in both NEO and Otago typically contain a white coating of stibiconite ($\text{Sb}_3\text{O}_6[\text{OH}]$), although the steep terrain and active streams locally

result in fresh stibnite in outcrop and in stream cobbles at Hillgrove. The stibiconite coating can be up to 3-cm thick, and occurs on exposed surfaces and fracture walls in most outcrops. Some stibiconite appears to replace stibnite, and ragged relic stibnite patches occur within stibiconite crusts. Thin (mm scale) veinlets of stibiconite penetrate into otherwise fresh stibnite deeper in the outcrops.

The white crusts on stibnite also contain valentinite and senarmonite, with yellow-brown goethite (Gilligan et al., 1992; Ashley and Craw, 1995). Jarosite occurs with goethite in the Carrick deposit of Otago (Ashley and Craw, 1995), and Gilligan et al. (1992) report cervantite and scorodite as oxidation products of stibnite–arsenopyrite-bearing veins at Hillgrove.

Freshly broken stibnite is shiny with a metallic lustre, but this lustre disappears within weeks as a dull

tarnish develops. The mineralogical nature of this tarnish is not known, but some Sb oxide is probable. The oxide-covered outcrop occurrences may be a result of the same process operating over geological time.

4.2. Hillgrove concentrator tailings

Bulk concentrator tailings at Hillgrove total ~ 1 million tonnes averaging 0.48% Sb and 0.2% As and contain about 1 wt.% residual sulphides (range ~ 0.2–5%), with stibnite, arsenopyrite and pyrite being present and the remainder comprising silicates and carbonates (Weir, 1998). Sulphides occur as discrete grains and in composites with the gangue phases. Tailings material is deposited via pipeline to a dam and occurs as silt to sand-sized sediments up to 20-m thick. Although carbonates in the tailings offer buffering potential against the formation of acid mine drainage, acid production potential tests conducted by Weir (1998) indicated that between 1 and 14 kg of acid per tonne of tailings could result from complete oxidation.

Fresh tailings are grey, with millimetre-scale dark streaks reflecting beds richer in sulphides. The material is porous and permeable and residual processing water rapidly drains from the surface. Hence, some oxidation of tailings can occur before burial by later discharges and are manifest by transient, thin efflorescent coatings of soluble sulphate minerals (e.g. thenardite, Na_2SO_4 ; konyaite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$). This oxidation is limited, as burial normally occurs within weeks or at most months. We have obtained samples of relatively oxidised tailings that were exposed on the dam margin for several years. These samples show the most extreme oxidation likely to occur at this site. The oxidised tailings are stained brown by a near-pervasive pigment of iron oxyhydroxide. The stain covers almost all grains, including silicates, with a submicron scale coating. The stain is most pronounced in sulphide-rich layers, especially on pyrite grains, from which the stain is mostly derived. Irregular plumes of brown stain extend from these layers into adjacent sulphide-poor layers. Reflected light examination shows that most sulphide grain edges, including pyrite, are sharp and little corroded by oxidation that has affected the outer edge of grains on the micron scale only. Microprobe element maps of a portion of oxidised tailings show

the relative distribution of elements from the sulphides (Fig. 3A–D). Distribution of pyrite, arsenopyrite and stibnite, mainly concentrated in thin layers, is shown with the S, Fe, Sb and As maps (Fig. 3A–D), particularly near the bottom of each map. The iron map shows the more pronounced redistribution of iron during oxidation as diffuse areas, mainly to top and right of the map (some areas arrowed in Fig. 3B). In addition, there appears to have been redistribution of antimony, as some high antimony areas in Fig. 3C occur, where sulphur is relatively low (arrowed areas, Fig. 3C).

4.3. Hillgrove mine waters

Most water from the tailings dam at Hillgrove is recycled through the processing plant and only a very small proportion escapes via seepage through a series of toe dams. However, there are several current and historic mine adits through which metal-rich waters are escaping into the Bakers Creek system. Tailings dam (surface and seepage) and mine waters have pH values of 6.2–8.5 and contain up to 55 mg/l Sb and 7.2 mg/l As (Fig. 4A), and 366–3530 mg/l SO_4 . X-ray amorphous iron oxyhydroxide is precipitating where seeps emerge from the tailings dam and from a few of the mine adits. Dried flocculant precipitates contain up to 11.2% Sb and 10.3% As (but with varying Sb/As), and it is assumed that Sb and As are adsorbed onto the iron oxyhydroxide (cf. Mok and Wai, 1994; Craw and Chappell, 2000). No discrete Sb or As phase was detected by heating the precipitates to 500 °C.

4.4. Water and sediment downstream of Hillgrove

Recent mining and processing operations at Hillgrove essentially allow no entry of solid waste into the Bakers Creek system. However, based on the flow and compositions of mine seepage waters, Ashley and Graham (2001) estimated that ~ 1.9 t Sb and ~ 0.19 t As enter the streams in solution annually. The historic disposal of solid mine wastes into the Bakers Creek system has led, however, to very high Sb and As contents of stream sediments. Upstream of Hillgrove, Bakers Creek contains near-background contents of Sb and As (regional backgrounds for the Macleay River catchment were determined as 1 ppm

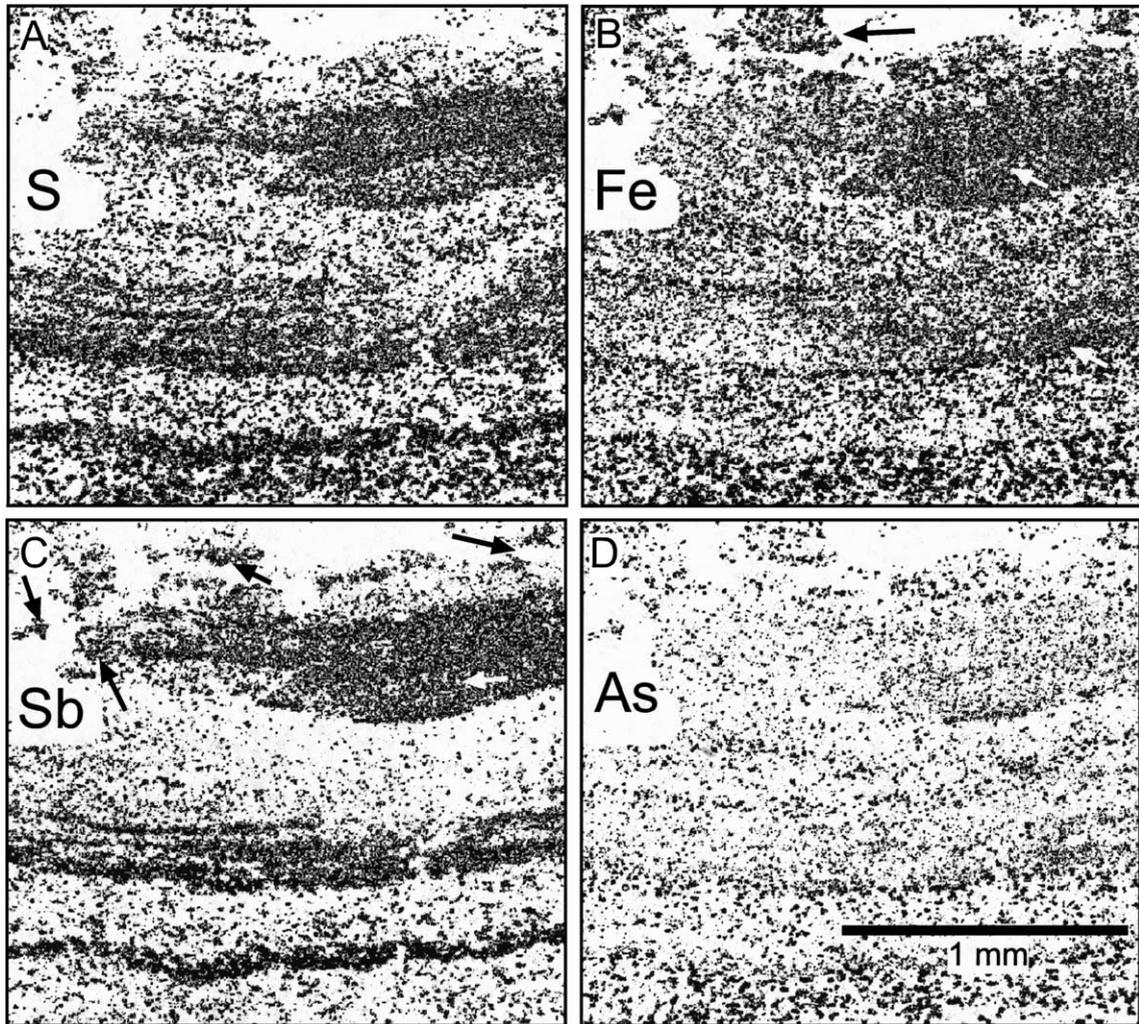


Fig. 3. Microprobe element maps of Hillgrove antimony mine tailings, constructed by methods described in the text. (A) Sulphur distribution in the tailings, showing the bedding of sulphide-rich tailings sediments. (B) Iron map, with some examples of secondary iron deposition indicated (black and white arrows). (C) Antimony map, dominated by stibnite bedding (especially in lower part) with some secondary antimony deposition zones indicated (black arrows). (D) Distribution of arsenic in the tailings.

Sb and 7.5 ppm As by Ashley and Graham, 2001). Through the Hillgrove mining area (about 5 km), Bakers Creek and tributaries contain 80–4640 ppm Sb and 102–1490 ppm As in stream sediments. Values only decrease to 190–250 ppm Sb and 90–170 ppm As in the next 20 km downstream to the junction with the Macleay River. All of the stream sediment values in Bakers Creek downstream of Hillgrove greatly exceed current sediment quality guide-

line values for Sb and also significantly exceed them for As (cf. NWQMS, 2000).

The Macleay River displays a gradual decay of stream sediment Sb and As values from the Bakers Creek junction (156 ppm Sb, 89 ppm As) for 280 km to the Pacific Ocean (Fig. 2); however, the last 50-km floodplain reach of the Macleay retains an average Sb value of 8 ppm ($8 \times$ background) and an average As value of 11 ppm ($1.5 \times$ background). Ashley and

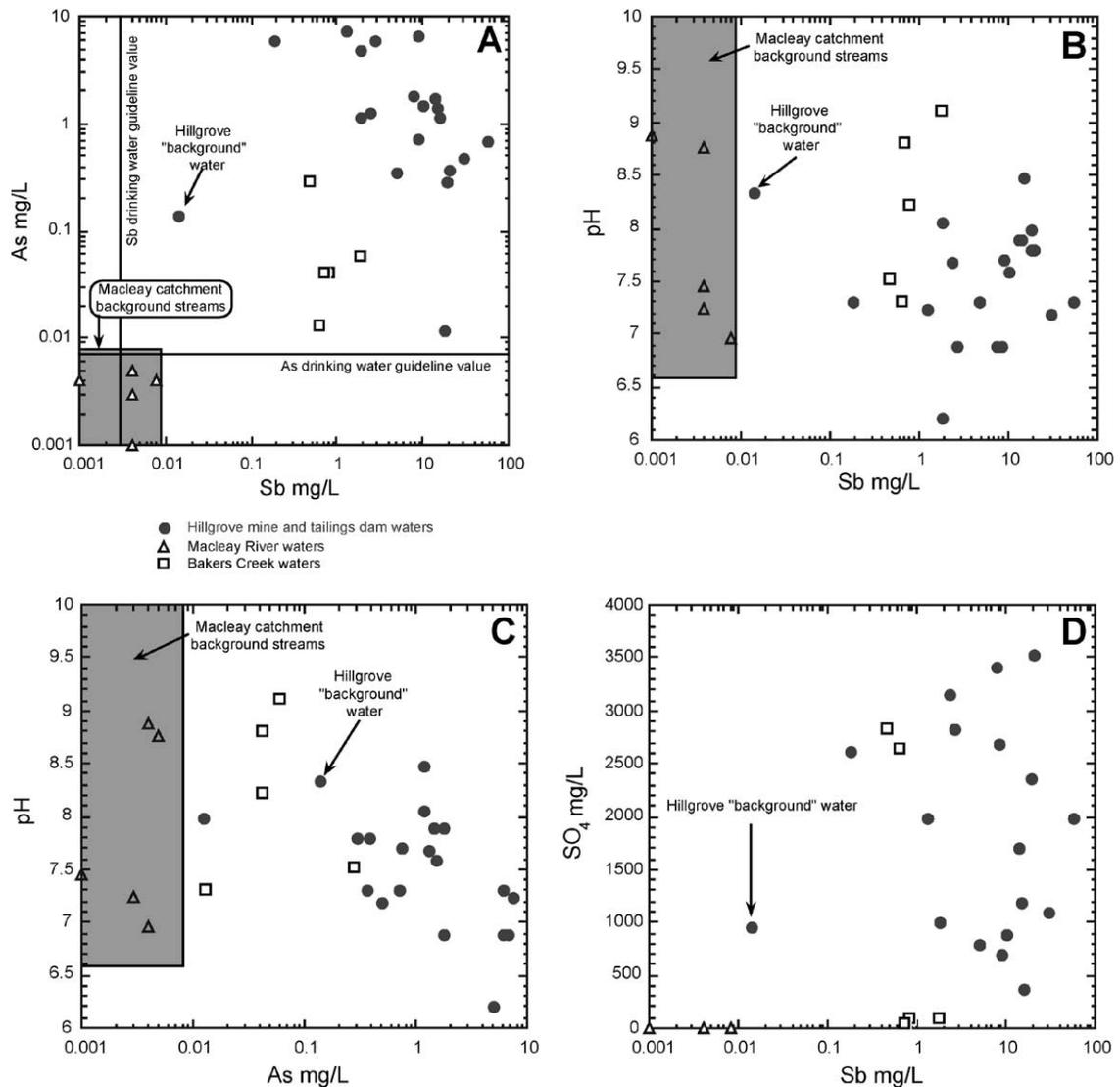


Fig. 4. Antimony, arsenic, sulphate and pH values in mine and stream waters from Hillgrove (mine seepages and tailings dam), Bakers Creek and Macleay River, with drinking water guideline values for Sb and As (NWQMS, 1996). Regional background Sb and As values determined for the Macleay catchment are 0.002 mg/l Sb and 0.003 mg/l As (Ashley and Graham, 2001). (A) log Sb mg/l vs. log As mg/l; (B) log Sb mg/l vs. pH; (C) log As mg/l vs. pH; and (D) log Sb mg/l vs. log SO₄ mg/l.

Graham (2001) estimated from compositions and volumes of contaminated sediment that approximately 3300 t of Sb are resident in the Bakers Creek–Macleay River system, with >90% of this being as clastic sediment derived from solid mine waste at Hillgrove.

Water quality in Bakers Creek has been severely compromised between Hillgrove and the junction with the Macleay River. Antimony values range between

470 and 1800 µg/l and As values are between 13 and 285 µg/l, with Sb exceeding drinking water quality guidelines by at least two orders of magnitude in places (Fig. 4A). However, downstream in the Macleay River the respective values approach the regional catchment backgrounds of 0.002 mg/l Sb and 0.003 mg/l As (Fig. 4A) established for these elements (Ashley and Graham, 2001).

5. Experimental studies

5.1. Dissolution of stibnite

Laboratory experiments were designed to investigate the amount of antimony likely to dissolve from stibnite. For the experiments, stibnite from the Stoker deposit in Otago (Fig. 1B) was used. This stibnite contains 75 ppm As in solid solution, and scattered quartz inclusions, but is otherwise clean coarse-grained (cm scale) material. Stibnite was crushed and sieved to extract two size fractions: coarse (>1 mm) and fine (<180 μm). Ten grams of coarse or fine stibnite were placed into two sets of 10 glass tubes with screw lids. Five of the coarse and fine stibnite-containing tubes were filled to overflowing with 30-ml tap water and the lids were screwed on and sealed with parafilm to limit oxygen access. The remaining tubes were filled with 15-ml tap water and the lids loosely screwed on to allow oxidising conditions. The tubes were kept at 18–20 °C during storage in the dark for up to 11 months. A set of four samples (sealed coarse and fine; unsealed coarse and fine) was opened after 122, 241, 302 and 347 days, and water was extracted for analysis for pH,

Table 1
Experimental results for dissolution of Otago (Stoker) stibnite

Material	Date	pH	Eh (mV)	Sb (mg/l)	As (mg/l)
Coarse unsealed	01 Nov 1999	7.9	299.2	0.0	0.0
	02 Mar 2000	5.5	429.8	24.5	1.7
	29 Jun 2000	5.1	464.1	10.3	3.5
	29 Aug 2000	3.6	630.7	11.2	2.6
	14 Oct 2000	3.7	630.1	5.9	3.6
Fine unsealed	01 Nov 1999	7.9	299.2	0.0	0.0
	02 Mar 2000	4.1	510.8	37.3	3.2
	29 Jun 2000	4.1	519.3	14.8	1.6
	29 Aug 2000	4.8	561.8	15.0	1.5
	14 Oct 2000	4.6	578.2	6.8	1.0
Coarse sealed	01 Nov 1999	7.9	299.2	0.0	0.0
	02 Mar 2000	6.0	408.4	22.3	0.9
	29 Jun 2000	5.6	434.8	25.1	0.7
	29 Aug 2000	5.4	527.0	21.3	0.8
	14 Oct 2000	4.5	583.4	15.7	1.2
Fine sealed	01 Nov 1999	7.9	299.2	0.0	0.0
	02 Mar 2000	6.9	397.5	26.5	1.7
	29 Jun 2000	6.1	405.1	24.3	2.3
	29 Aug 2000	5.7	511.3	25.3	2.8
	14 Oct 2000	5.5	524.5	18.7	2.3

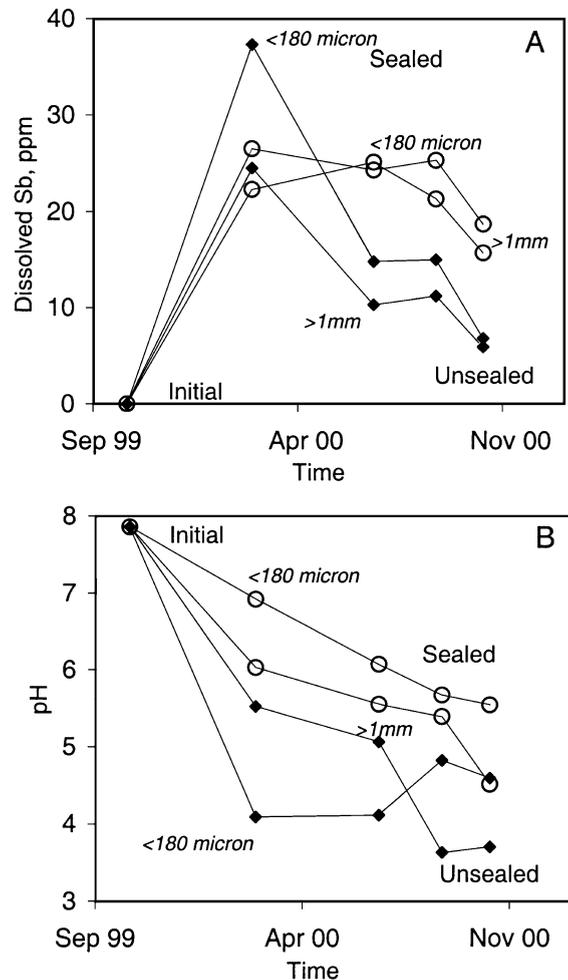


Fig. 5. Experimental dissolution of Otago stibnite (see text and Table 1 for details). ○=sealed experiments; ◆=unsealed experiments. (A) Variations in dissolved Sb with time. (B) Variations of experimental pH with time.

oxidation potential, and Sb and As contents. Results are summarised in Table 1 and Fig. 5.

The amount of dissolved Sb had reached in excess of 20 mg/l after the first 4 months (Fig. 5A). After this initial high level, dissolved Sb generally dropped with time. The unsealed samples showed the most dramatic changes, especially the fine-grained experiment, which peaked with dissolved Sb of 37 mg/l and ended with 7 mg/l dissolved Sb (Fig. 5A). The pH of the experiments began at 7.9 and evolved to distinctly more acid conditions with time (Fig. 5B). Again, the unsealed

samples were the most reactive, with pH lowering to ca. 4 (Fig. 5B). Hence, the highest Sb contents were generally found with the highest pH, with only one clear exception, the most reactive fine stibnite sample (Table 1; Fig. 5A,B).

At the same time as Sb was being dissolved, significant amounts of As were also being released and dissolved (Table 1). The unsealed experiments yielded highest dissolved As, up to 3.5 mg/l (Table 1). There is no clear relationship between pH and dissolved As, or between dissolved Sb and dissolved As, although the most reactive (fine, unsealed) experiment yielded one of the higher dissolved As concentrations (Table 1).

5.2. Dissolution of Sb and As from contaminated stream sediments

Following acquisition of stream sediment and water analytical results from Bakers Creek and the Macleay River, we performed an experiment to assess the solubilities of Sb and As in typical stream water. Hundred gram aliquots of five uncrushed stream sediment samples, with Sb and As contents ranging from background to highly contaminated, as well as a sample of stibnite concentrate from the Hillgrove mine (Table 2), were equilibrated with 1 l of “background” stream water for 32 days in unstoppered flasks. The experiment was aimed at simulating a stream environment where uncontaminated stream water passed over/through contaminated stream sediments. The stream water used for the experiment contained <0.001 mg/l

Sb and 0.002 mg/l As and had a pH of 7.1, with low total dissolved solids (<150 mg/l). During the experiment, average temperature remained at ~ 20 °C, the sample flasks were shaken and pH monitored daily. After 32 days, each solution was filtered and analysed for Sb and As.

Results (Table 2) show that with increasing amounts of Sb and As in stream sediment, an increasing amount of Sb and As were leached and went into solution. However, equilibration with the stibnite concentrate (66% Sb, 0.15% As) did not result in further increase; in fact, the solubilities dropped, perhaps as a result of saturation. In the experiment with the stibnite concentrate, a faint white suspension formed and this was assumed to be a form of Sb oxide. During all sample equilibrations, pH values remained relatively constant and in the range 6.6–8.2. The Sb/As value of the solution was commonly higher (~ 1.1–21 times) than in the solid sample, implying a greater solubility of Sb than As under the conditions of the experiment.

6. Discussion

6.1. Deposition of Sb oxides

Observations of natural outcrop specimens of stibnite deposits show that antimony oxides form commonly in nature over geological time scales. Some observations from this study also show that antimony oxides form on shorter time scales that are of significance to environmental studies.

Deposition of antimony oxides as a cement in mine tailings is suspected from observations of oxidised tailings samples. It is not possible to resolve microscopically any cementation of the tailings by secondary minerals, as the brown staining obscures details. However, microprobe maps show up some separation of Sb from S and loss of distinct Sb-rich bedding in places (Fig. 3A,C). This suggests that there has been secondary deposition of antimony oxide in the tailings on a time scale of weeks or months, although we cannot identify the exact species.

The white suspension observed in the experiment with a Hillgrove stibnite concentrate (above) suggests that Sb oxide forms readily. This suspension is visible because the experiment was agitated daily. The experiments with Otago stibnite were not agitated,

Table 2

Results of equilibration for 32 days at ~ 20 °C of uncontaminated stream water with background and contaminated stream sediments, and a Hillgrove stibnite concentrate

Sample	Concentration (ppm)		Sb/As ratio	Solution (mg/l)		Sb/As ratio
	Sb	As		Sb	As	
MYSS332	0.7	6.7	0.1	0.006	0.006	1.0
MYSS441	28.9	20.2	1.4	0.025	0.007	3.6
MYSS248	156	89	1.8	0.31	0.08	3.9
MYSS53	636	159	4.0	3.9	0.045	86.7
MYSS56	4640	517	9.0	6.0	0.1	60
Stibnite concentrate	660,000	1500	440	5.2	0.011	473

Sample MYSS332 contains regional background values of As and Sb, whereas sample MYSS56 is highly contaminated.

and the water remained clear. The Otago stibnite used in the pure stibnite experiments has 75 ppm As, so dissolution of 1 mg/l Sb from the stibnite should release 75×10^{-6} mg/l As. This is four to five orders of magnitude less than the 1–3 mg/l observed in most experiments. The high dissolved As content of the experimental waters may therefore be indicative of even larger amounts of stibnite dissolution than the dissolved Sb suggests. If so, deposition of antimony may be occurring, presumably in oxide form (see above). There is no firm evidence for oxide deposition on the remaining stibnite grains or the container. However, the high surface area of the crushed stibnite means that submicron scale deposition of oxides, equivalent to surface tarnish, may have occurred on the stibnite.

Antimony-rich waters are discharging from the mine tailings, and some Sb is being deposited, with As, among amorphous iron oxyhydroxide precipitates (above). Adsorption of both Sb and As by iron oxyhydroxide is a common phenomenon, but the observed Sb and As contents of seepage deposits (up to 11.2% Sb, 10.3% As) are higher than expected for adsorption alone (typically a few tens or hundreds of ppm; Thanabalasingam and Pickering, 1990; Bowell, 1994; Belzile et al., 2001; Roddick-Lanzilotta et al., 2002). Hence, some deposition of Sb and As oxide(s) with the iron oxyhydroxide is suspected although this material remains X-ray amorphous up to 500 °C (heating to 1000 °C for 1 day caused complete dehydration and crystallisation of hematite, claudetite (As_2O_3) and a Sb_2O_4 phase). This deposition assists in attenuation of the water contamination plume.

6.2. Theoretical antimony mobility

Speciation of dissolved antimony in nature is not well understood (Filella et al., 2002), especially that of $\text{Sb}^{(\text{V})}$. Evaluation of available thermodynamic data by Vink (1996) suggests that $\text{Sb}^{(\text{V})}$ commonly exists in nature as SbO_3^- , rather than a solid, Sb_2O_5 . The latter form is relatively insoluble, with associated dissolved Sb below 0.1 mg/l (ca. 10^{-6} mol/kg) in solution. Vink (1996) suggests that field occurrences of Sb minerals imply greater dissolved Sb mobility, with which we concur on the basis of our field observations and experiments (above). Hence, the following discussion follows Vink's (1996) analysis. This discussion is

hampered by the lack of thermodynamic data for stibiconite, and we restrict discussion to relationships between stibnite, Sb_2O_3 (valentinite or senarmonite) and SbO_3^- ions in solution. We also avoid cervantite, which is rare in the deposits studied. The chemical system relevant to this work is depicted in cartoon form in Fig. 6, which shows relative spatial relationships between stibnite and its oxidation products.

Dissolution of stibnite in oxidised circumneutral natural waters can occur by two principal pathways: direct oxidative dissolution to $\text{Sb}^{(\text{V})}\text{O}_3^-$ (Eq. (1), Fig. 6) or formation of an $\text{Sb}^{(\text{III})}$ oxide intermediate by replacement or incongruent dissolution, which then partially dissolves and oxidises to $\text{Sb}^{(\text{V})}\text{O}_3^-$ ions (Fig. 6, Eqs. (2) and (3)). The oxide intermediate may be a very thin coating, as deduced from observations and experimental work (above), and this is depicted as a thin oxide sliver on stibnite in Fig. 6. Stibiconite may be an additional intermediate oxidation stage (Fig. 6). Both Eqs. (1) and (2) (Fig. 6) result in formation of sulphate ions and acidification of solutions. The acidification of the experimental solutions (above) is a result of this sulphate formation. In mesothermal stibnite deposits, however, this acid is generally neutralised immediately by the abundant carbonate

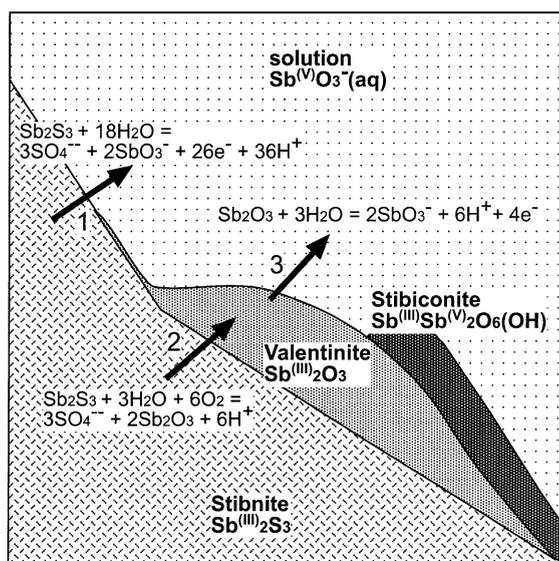


Fig. 6. Cartoon showing spatial relationships among stibnite, secondary antimony oxides, and antimony in solution in an oxidised surficial environment, with relevant chemical equations linking the different Sb species.

present (above). Rare occurrences of cervantite may indicate localised acidification (Vink, 1996), as may jarosite occurrences (above) in muscovite-bearing systems.

Stibnite is not thermodynamically stable at surface temperatures except under very reducing conditions and/or high dissolved sulphur concentrations not normally found in surface waters (Fig. 7A; Vink,

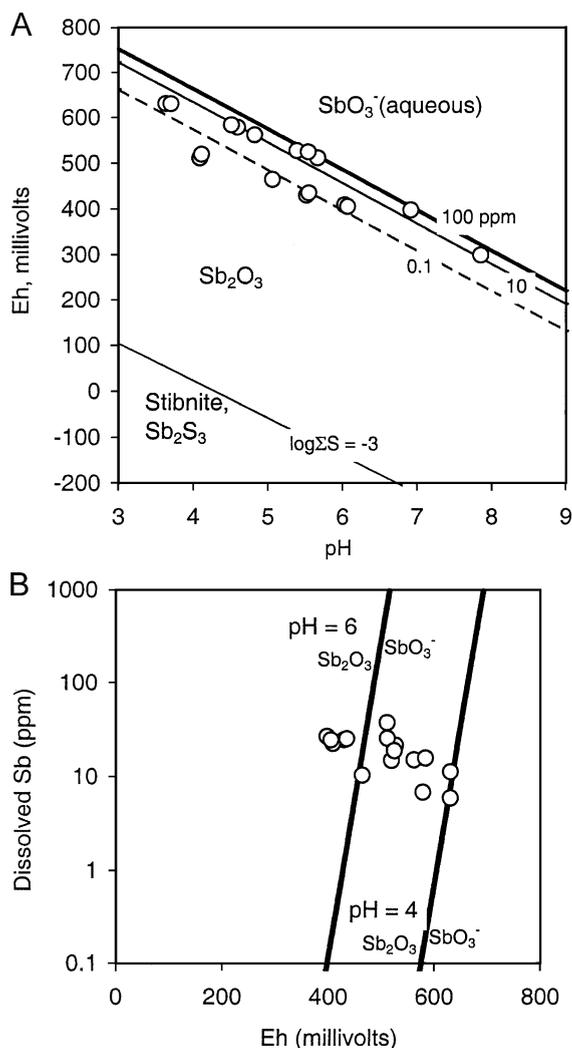


Fig. 7. Theoretical solubility of common Sb oxide valentinite (Sb_2O_3), with experimental data from dissolution of Otago stibnite (Table 1). (A) Eh–pH diagram calculated from thermodynamic data tabulated by Vink (1996), including use of Barin’s (1989) data for valentinite. (B) Variation of dissolved Sb with redox potential at constant pH of 6 and 4, calculated from the same data as in A.

1996). Equilibrium formation of Sb_2O_3 from stibnite (Eq. (2), Fig. 6) also occurs under relatively reducing conditions (Fig. 7A). No net dissolution of antimony is required for Eq. (2) (Fig. 6). Hence, dissolution of stibnite (Eq. (1), Fig. 6) is a disequilibrium process, and is not reversible in natural surface waters.

Eq. (3) (Fig. 6) is representative of equilibrium between antimony oxide and dissolved antimony, rather than disequilibrium dissolution of stibnite (Eq. (1)). Determination of the Eh–pH conditions for this equilibrium reaction to occur to any detectable extent requires knowledge of thermodynamic data for Sb_2O_3 phases, and there is considerable disagreement over these data (Vink, 1996). We have constructed the boundaries between Sb_2O_3 and dissolved SbO_3^- in Fig. 7A using Barin’s (1989) value of ΔG° for Sb_2O_3 of -356.2 kcal/mol. Boundaries for 0.1, 10 and 100 mg/l dissolved antimony were calculated for Eq. (3) (Fig. 6), and plotted in Fig. 7A. The latter two boundaries are most relevant to our experimental and field observations (above), where dissolved Sb concentrations up to 37 mg/l (laboratory) and 55 mg/l (field) occur during Sb oxidation. Our experimental data for dissolution of stibnite (Table 1) are plotted in Fig. 7A for comparison, and fall close to the relevant calculated boundaries, with minor scatter. On this basis we support use of Barin’s (1989) thermodynamic data for valentinite, rather than Vink’s (1996) arbitrary value of ΔG° for Sb_2O_3 of -320 kcal/mol. However, the problem of defining the stability field of cervantite, as highlighted by Vink (1996), still remains.

The amount of dissolved antimony theoretically resulting from Eq. (3) (Fig. 6) is strongly dependent on the redox conditions of the solution. This is emphasised in Fig. 7B, calculated from the same thermodynamic data as Fig. 7A (Barin, 1989; Vink, 1996). For a constant pH solution, the amount of dissolved Sb in equilibrium with Sb_2O_3 minerals changes by an order of magnitude with each 100 mV change in redox potential, and dissolved Sb of >1000 mg/l is theoretically possible in oxidised waters (Fig. 7B). Circumneutral data from our experiments (Table 1) represent common natural redox conditions in mesothermal deposits, and the more acid experiments (down to pH near 4; above) may represent local and temporary extreme acidification in these deposits. It is notable that the theoretical solubility of stibnite (Fig. 7A,B) agrees well with (a) the laboratory exper-

imental results on pure Otago stibnite, (b) simple equilibration experiments with contaminated stream sediments and (c) actual solubilities measured from field samples at Hillgrove.

7. Conclusions

Stibnite in mesothermal antimony deposits in humid to semiarid climates alters to various antimony oxides during oxidation at the Earth's surface. These oxides include valentinite, senarmonite, and stibiconite, and more rarely, cervantite. Formation of these oxides is accompanied by high dissolved Sb (tens of mg/l) in equilibrium with the oxides. These dissolution reactions happen rapidly (days/weeks) in laboratory experiments and mine tailings, and probably in stream sediments as well. Field and experimental observations of dissolved antimony and associated mineralogy support Vink's (1996) contention that antimony is mobile as an $\text{Sb}^{(\text{V})}$ species under common environmental conditions. Antimony mobility in the environment is moderated by deposition of antimony oxides locally, but these are soluble and can be redissolved.

Mesothermal stibnite contains arsenic in solid solution, from tens to thousands of ppm, and this arsenic is released into the environment when the stibnite, and commonly associated arsenopyrite and arsenian pyrite, dissolves. Experimental work suggests that the dissolved As can remain in solution (up to 3 mg/l), while Sb oxides are precipitated. However, substantial As and Sb are deposited with precipitating amorphous iron oxyhydroxides from waters seeping from stibnite-bearing mine tailings.

Historical disposal of Sb–As-mineralised mine waste, together with dissolved Sb and As inputs from mine waters and erosion of natural mineralised outcrops at Hillgrove, New South Wales, has released Sb and As into streams. Antimony concentrations are up to 55 mg/l in mine waters, and up to 1.8 mg/l in stream waters immediately downstream of the mines. Highly contaminated stream sediments release Sb and As into solution in near-neutral stream water. The Sb (–As) stream sediment dispersion can be traced for 300 km down the Macleay River system to the Pacific Ocean. Dissolved Sb concentrations measured in stream waters exceed current Australian drinking water quality guideline values by at least two orders of magnitude for

20 km downstream of Hillgrove. Likewise, As is also elevated in the same waters (up to 285 $\mu\text{g/l}$), and exceeds water quality guideline values by up to $40 \times$ (Fig. 4A). The elevated Sb and As in distal waters are most likely derived from dissolution of metals from contaminated stream sediments although some contribution from mine seepage waters is plausible.

Substantial Sb and As are likely to go into solution at mineralised sites (e.g. mesothermal Sb, Sb–Au and epithermal precious metal systems containing Sb), where Sb and As are abundant. Acidification is unnecessary for their solubility, and pH values may remain near neutral. Oxidising conditions clearly favour high Sb solubility, probably as $\text{Sb}^{(\text{V})}$. More reducing conditions lower Sb solubility. The actual measured field and experimental solubilities of Sb are considerable (up to tens of mg/l), such that water quality guideline values are greatly exceeded. There is potential for Sb and associated As to have significant negative effects on stream and riparian ecosystems due to diminution of water quality and the potential for Sb and As to be continually liberated from contaminated stream sediments.

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