Antimony in the New Zealand environment

Dave Craw

Geology Department, University of Otago, Dunedin, New Zealand

Abstract

Sb has similar chemical behaviour to arsenic, in that it has 3+ and 5+ oxidation states, and forms oxyanions in solution. Sb occurs at low background levels in New Zealand rocks (typically 0.01-0.1 mg/kg), distinctly lower than arsenic (2-20 mg/kg). Sb is readily mobilised from background rocks by hydrothermal waters, and some is transported to hot springs and near-surface geothermal systems in the North Island, accompanying As and Hg. Ancient mesothermal vein systems in the South Island also contain variable amounts of Sb, and some minor Sb mining has occurred historically. Sb occurs at elevated levels (typically 10-100 mg/kg), but is subordinate to arsenic, in most mesothermal gold deposits in the South Island. Stibnite (Sb_2S_3) is the most common Sb sulfide mineral, and this mineral commonly occurs with arsenopyrite (FeAsS). Arsenopyrite can have up to % level Sb in solid solution, and stibnite can have % level As in solid solution. Stibnite oxidises to a variety of Sb oxide minerals, principally valentinite ($Sb^{III}_2O_3$) and stibiconite ($Sb^{III}Sb^V_2O_6OH$) under surficial conditions. These oxides are soluble and dissolved Sb up to 50 mg/kg can arise, as $Sb^VO_3^-$ or $Sb^V(OH)_6^-$. Dissolved Sb is readily attenuated by, for example, high surface area iron oxyhydroxide, with empirical K_d of ca. 10^5 L/kg. Without this type of attenuation, elevated dissolved Sb can be traced for kilometres or even hundreds of kilometres from point sources.

1. Introduction

Antimony (Sb) is a Group 15 (old Group VA) metalloid like arsenic, and reputedly has similar toxicity to arsenic in humans because Sb can mimic P chemically. Like arsenic, antimony has been employed extensively for a wide range of uses historically, but those uses are declining because of increasing world-wide environmental and toxicological concerns. Nevertheless, Sb still has a range of common uses in modern society, particularly in manufacture of plastics. This paper summarises some recent work on point sources of Sb in New Zealand, from a principally geological and mineralogical perspective. In these settings, Sb is not strictly a trace element, as it is commonly present in percentage-level amounts. However, studies of Sb at point sources can elucidate the behaviour of Sb in the surficial environment, information that is difficult to obtain from other approaches. Field-based observations are linked to experimental observations where relevant.

2. Sb point sources

Most New Zealand basement rocks have 0.01-0.1 mg/kg Sb, although background Sb may get as high as 1 mg/kg (Pitcairn et al. 2006). This background Sb dissolves readily in hydrothermal waters, and is transported through fractures to the near-surface environment. Hence, Sb is a common component of hot springs and near-surface geothermal systems in the North Island. Modern and Quaternary hot spring systems in Northland have Sb accompanying Hg and As rich deposits (Craw et al. 2000; Wilson et al. 2007). Sb also accompanies As and other metals in the central North Island geothermal systems (Pope et al. 2004; Wilson et al. 2007). Sb is also enriched (typically 10-100 mg/kg) with As in quartz veins (many gold-bearing) deposited in middle to upper crustal levels (mesothermal systems) during the Mesozoic in the South Island basement schists, and in some North Island greywackes. Some Sb mining has occurred historically in the South Island, principally at Endeavour Inlet in the Marlborough Sounds (Wilson et al. 2004a,b). These Sb deposits are also enriched in As.

3. Sb minerals

Stibnite (Sb_2S_3) is the most common Sb sulphide mineral precipitated in subsurface hydrothermal systems. Stibnite is commonly accompanied by arsenopyrite (FeAsS) in these settings. Arsenopyrite is typically enriched in Sb (thousands of mg/kg) in solid solution, even if no stibnite is present. Likewise, stibnite almost always has abundant (up to 5 wt%) As in solid solution. Stibnite oxidizes rapidly (days or weeks) under surficial conditions to a variety of Sb oxide minerals (Fig. 1). Valentinite and senarmontite are Sb^{3+} oxides ($Sb^{III}_2O_3$) and stibiconite is a mixed Sb^{3+} and Sb^{5+} oxide ($Sb^{III}Sb^V_2O_6OH$) (Fig. 1).
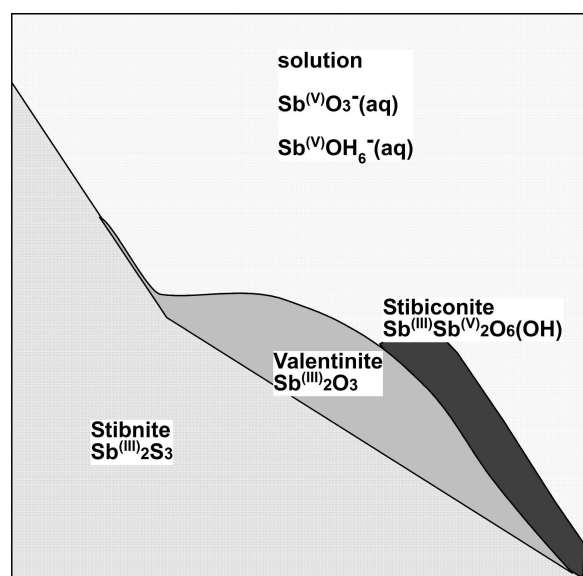

Figure 1. Sketch to show relationships between principal Sb minerals. Stibnite (lower left) is the most common Sb sulfide, and this oxidises in the surficial environment to valentinite (or senarmontite) and stibiconite. Modified from Ashley et al. (2003).

4. Sb solubility and mobility

Stibnite and the oxides readily dissolve under surficial conditions. Dissolved Sb^{5+} species ($Sb^VO_3^-$ or $Sb^V(OH)_6^-$) are soluble (up to 50 mg/L; Fig. 2; Ashley et al. 2003). These high levels of dissolved Sb are observed in experiments (Fig. 2), in the field at an active Sb mine site in Australia (Ashley et al. 2003), and are in accord with theromodynamic calculations (Fig. 2).
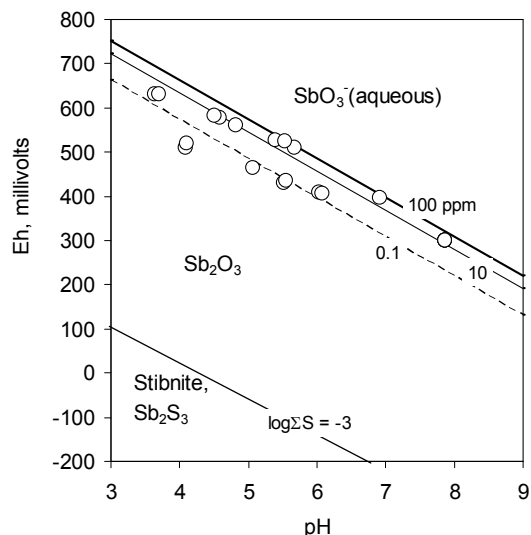

Figure 2. Redox-pH relationships of Sb minerals. Open circles are from test-tube stibnite solution experiments, and these are imposed on a theoretical Eh-pH diagram calculated from established thermodynamic data. Contours of solubility of SbO_3^- (aq) were calculated from thermodynamic data, and the experimental data broadly coincide with these contours. Modified from Ashley et al. (2003).

Dissolved Sb and dissolved As are commonly at similar concentrations in antimony mines (Ashley et al. 2003; Wilson et al. 2004b). At gold mines, where Sb is subordinate to As in ore, As dominates over Sb in solution (Craw et al. 2004; Hewlett et al. 2005). This dominance of As over Sb persists to plants growing on mine wastes (Fig. 3).
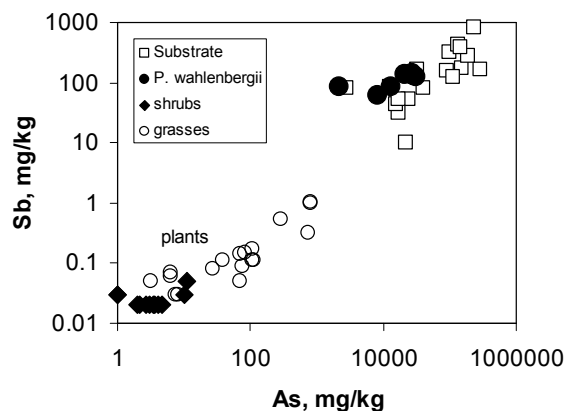

Figure 3. Relative amounts of As and Sb in substrates and plants in Reefton mining areas. Modified from Craw et al. (2007).

Sb can be traced downstream from Sb-rich point sources for many kilometres (Fig. 4). This long-distance signature is partly a result of transport of dissolved Sb without attenuation, and partly a result of ongoing dissolution of Sb-rich solid debris that has been physically transported downstream (Ashley et al. 2003, 2006; Wilson et al. 2004a,b). In addition, the flux of Sb increases downstream of mine sites because of aggregation of natural groundwaters that have passed through Sb-rich rocks in the vicinity of mines (Wilson et al. 2004b; Ashley et al. 2006). This natural enrichment in Sb in these areas dominates over mine-related Sb discharges (Fig. 4; Wilson et al. 2004b).
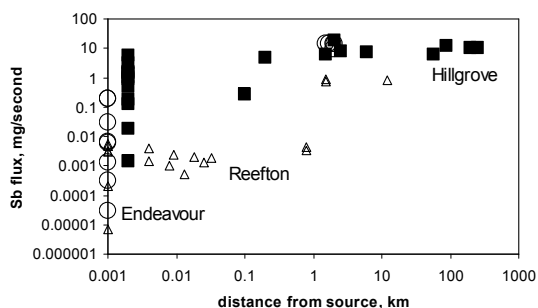

Figure 4. Flux of dissolved Sb from mine site point sources. Hillgrove (New South Wales; black squares) is an active Sb mine; Reefton (open triangles) and Endeavour (open circles) are historic South Island mines. Modified from Ashley et al. (2006).

5. Sb adsorption and attenuation

Dissolved Sb is readily attenuated by high surface area material, especially iron oxy-hydroxide (Wilson et al. 2004a; McComb et al. 2007). Field measurements of Sb in coexisting mine waters and underlying iron oxyhydroxide precipitates at Reefton (West Coast of South Island) suggest an empirical K_d of up to ca. 10^5 L/kg for Sb (Fig. 5). This K_d is similar to that observed for As at the same sites (Fig. 5). The abundance of iron oxyhydroxide at Reefton ensures that dissolved Sb immediately downstream of the mine is attenuated by adsorption, and is lower than, for example, the active Hillgrove Sb mine (NSW) (Fig. 4; Ashley et al. 2003, 2006). However, attenuation by adsorption

is pH-dependent (McComb et al. 2007). Since dissolved Sb occurs as an oxyanion, adsorption to iron oxyhydroxide is most effective under low pH conditions, and desorption will occur if the pH is raised to alkaline conditions (Fig. 6; McComb et al. 2007).
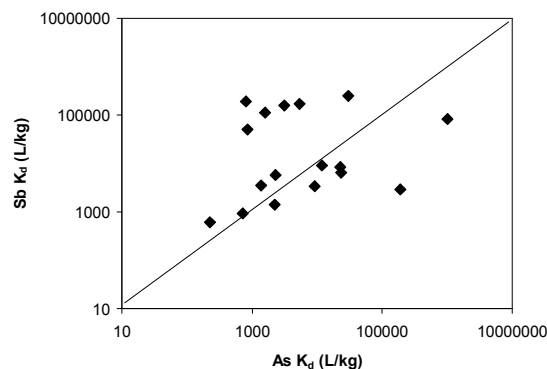

Figure 5. Empirical distribution constants for Sb adsorbed to iron oxyhydroxide and dissolved, compared to arsenic. K_d calculated from waters and precipitates outside historical Reefton mines. Modified from Craw et al. (2004).
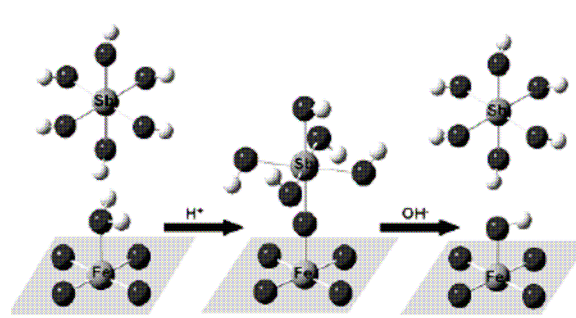

Figure 6. Model of adsorption (left and centre) and desorption (right) of dissolved $Sb(OH)_6^-$ to iron oxyhydroxide. Initial adsorption is under acid conditions; desorption is under alkaline conditions. From McComb et al. (2007).

6. Conclusions

Antimony behaves in a similar manner to arsenic in the environment, and the two elements are commonly found together in point sources and in downstream waters. Both Sb and As are readily dissolved as oxyanions, and these oxyanions are readily adsorbed and attenuated in the presence of iron oxyhydroxide, especially under low pH conditions. Sb will probably never be as

much of a chemical "bogey-man" as is arsenic today, but Sb is gaining increasing publicity as its toxicity becomes better understood. Sb has received little publicity compared to arsenic in the past, and Sb is not commonly analysed in environmental evaluations. However, the close chemical similarity between Sb and As throughout the geological environment means that wherever arsenic is present at elevated levels, Sb can be expected as well, albeit at lower levels (typically 0.1-0.01 of As levels).

Acknowledgments

References

Ashley PM, Craw D, Graham, BP and Chappell, DA 2003. Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand. *Journal of Geochemical Exploration 77:* 1-14.

Ashley PM, Craw D, Tighe MK and Wilson NJ 2006. Magnitudes, spatial scales and processes of environmental antimony mobility from orogenic gold-antimony mineral deposits, Australasia. *Environmental Geology* 51: 499-508.

Craw D, Chappell D and Reay A 2000. Environmental mercury and arsenic sources in fossil hydrothermal systems, Northland, New Zealand. *Environmental Geology* 39: 875-887.

Craw D, Wilson N and Ashley PM 2004. Geochemical controls on the environmental mobility of Sb and As at mesothermal antimony and gold deposits. *Transactions, Institute of Mining & Metallurgy, Applied Earth Sciences* 113: B3-B10.

Craw D., Rufaut CG, Haffert L and Paterson LA. 2007. Plant colonization and arsenic uptake on high arsenic mine wastes, New Zealand. *Water, Air and Soil Pollution* 179: 351-364.

Hewlett L, Craw D and Black A. 2005. Comparison of arsenic and trace metal contents of discharges from adjacent coal and gold mines, Reefton, New Zealand. *Marine and Freshwater Research* 56: 983-995.

McComb K, Craw D and McQuillan J 2007 ATR-IR spectroscopic study of antimonite adsorption to iron oxide. *Langmuir* 23: 12125-12130.

Pitcairn IK, Teagle DAH, Craw D, Olivo GR, Kerrich R and Brewer TS 2006. Sources of metals and fluids in orogenic gold deposits: insights from the Otago and Alpine Schists, New Zealand. *Economic Geology* 101: 1525-1546.

Pope JG, McConchie DM, Clark MD and Brown KL 2004. Diurnal variations in the chemistry of geothermal fluids after discharge, Champagne Pool, Waiotapu, New Zealand. *Chemical Geology* 203: 253-272.

Wilson NJ, Craw D and Hunter KA, 2004a. Antimony distribution and environmental mobility at an historic antimony smelter site, New Zealand. *Environmental Pollution* 129: 257-266.

Wilson NJ, Craw D and Hunter K 2004b. Contributions of discharges from a historic antimony mine to metalloid content of river waters, Marlborough, New Zealand. *Journal of Geochemical Exploration* 84: 127-139.

Wilson NJ, Webster-Brown JG and Brown KL 2007. Controls on stibnite precipitation at two New Zealand geothermal power stations. Geothermics 36: 330-347.