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## Dispersion of antimony from oxidizing ore deposits\*

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**Abstract:** The solubilities of brandholzite,  $[\text{Mg}(\text{H}_2\text{O})_6][\text{Sb}(\text{OH})_6]_2$ , and bottinoite,  $[\text{Ni}(\text{H}_2\text{O})_6][\text{Sb}(\text{OH})_6]_2$ , at 25 °C in water have been measured. Solubilities are  $1.95(4) \times 10^{-3}$  and  $3.42(11) \times 10^{-4}$  mol dm<sup>-3</sup>, respectively. The incongruent dissolution of romeite,  $\text{Ca}_2\text{Sb}_2\text{O}_7$ , and bindheimite,  $\text{Pb}_2\text{Sb}_2\text{O}_7$ , at 25 °C in 0.100 mol dm<sup>-3</sup> aqueous  $\text{HNO}_3$  was also investigated. Equilibrium dissolved Sb concentrations were  $3.3 \pm 1.0 \times 10^{-7}$  and  $7.7 \pm 2.1 \times 10^{-8}$  mol dm<sup>-3</sup>, respectively. These values have been used to re-evaluate the geochemical mobility of Sb in the supergene environment. It is concluded that the element is geochemically immobile in solution and in soils. This was in part validated by an orientation soil geochemical survey over the Bayley Park prospect near Armidale, New South Wales, Australia. Anomalous soil Sb levels are confined to within 100 m of known stibnite mineralization.

**Keywords:** antimony; bindheimite; bottinoite; brandholzite; exploration geochemistry; mobility; mopungite; romeite; soils; solubility.

## INTRODUCTION

Sulfide and sulfosalt minerals mostly form deep in the Earth at high temperatures and under comparatively reducing conditions. They remain stable as long as they are protected from oxygen but, with few exceptions, sulfides and sulfosalts are intrinsically unstable above the water table and react with oxygen, resulting in higher oxidation states; notably, sulfide is ultimately transformed to sulfate. This general process has a very important consequence with respect to solubility phenomena [1]. Sulfides and sulfosalts are extremely insoluble in water under ambient conditions. However, their oxidized equivalents are much more soluble and are transported in soil and ground water away from their original settings. For geochemical exploration, an understanding of the processes involved in such transport is vital for success and details of the geochemical behavior of a many elements in the supergene zone remains, at best, sketchy.

Our attention has recently focused on the element antimony. A series of comprehensive reviews by Filella et al. [2–5] has done much to increase our understanding of the behavior of Sb in the natural environment, but the geochemistry of Sb in the vicinity of oxidizing primary ores is still poorly understood. Several hundred primary Sb minerals are known, and all are essentially insoluble in water under

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ambient conditions. It is the secondary phases formed under oxidizing conditions that act as metal ion buffers, and control the dispersion of Sb in surface and soil waters. Some 40 such minerals are known [6]; many are rare, but common species have become the focus of study in an effort to elucidate the geochemical behavior of Sb in oxidized settings. Here we report studies of the solubility of several Sb(V) minerals. The results indicate that Sb is much less mobile in the supergene zone than has previously been assumed. Implications for exploration geochemistry using Sb as a pathfinder element are discussed.

## EXPERIMENTAL

Powder X-ray diffraction (XRD) measurements were carried out using a Philips PW1825/20 diffractometer (Ni-filtered Cu  $K\alpha_1$  radiation,  $\lambda = 1.5406 \text{ \AA}$ , 40 kV, 30 mA). Measurements of pH were made using a Radiometer PHM220 apparatus fitted with a combination electrode. Solubilities of brandholzite and bottinoite were determined by atomic absorption spectroscopy (AAS) using a Perkin Elmer Analyst100 spectrophotometer (air-acetylene, 2000 ppm added KCl to control ionization, matched standards). Inductively coupled plasma-mass spectroscopy (ICP-MS) (Sb and Pb) and ICP-optical emission spectroscopy (OES) (Ca) analyses were determined by a NATA-compliant commercial laboratory (LabMark PL, Asquith, Australia). Scanning electron microscopy (SEM) was used to analyze synthetic romeite and bindheimite (JEOL T330, EDS standardless mode, Moran Scientific acquisition, control and processing software, 20 kV, 2 nA).

## Syntheses

### *Bottinoite and brandholzite*

An aqueous  $0.100 \text{ mol dm}^{-3}$  solution of  $\text{Sb(OH)}_6^-$  solution was made by refluxing  $\text{KSb(OH)}_6(\text{s})$  in water for 2 h. A small amount of undissolved material was separated by decantation. Aliquots of the above solution were mixed with  $0.100 \text{ mol dm}^{-3}$  aqueous solutions of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$  or  $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$  at a mol ratio of Sb:Mg,Ni equal to 2:1. In both cases, X-ray amorphous precipitates formed immediately and the mixtures were left to stand at room temperature. In the case of the Mg preparation, squat, hexagonal prisms of brandholzite,  $[\text{Mg(H}_2\text{O)}_6][\text{Sb(OH)}_6]_2(\text{s})$ , up to 1 mm in size, were obtained overnight. The product was left to age further for 1 month, washed by decantation, collected at the pump, washed with water and acetone, sucked dry, then finally dried in an oven at  $40^\circ\text{C}$ . In the Ni case, a few crystals could be seen in the precipitate after 24 h. The precipitate was left to age during one month, when it had converted to pale green, hexagonal plates of bottinoite,  $[\text{Ni(H}_2\text{O)}_6][\text{Sb(OH)}_6]_2(\text{s})$ . The product was isolated as above. Yields of brandholzite and bottinoite were  $>90\%$ . XRD measurements showed that the minerals were not contaminated with any other detectable phases. Traces were indexed and unit cell data refined using LAPODC [7]. For brandholzite and bottinoite, both cells were hexagonal with  $a = 16.124(1)$ ,  $c = 9.874(1)$ , and  $a = 16.070(2)$ ,  $c = 9.800(1) \text{ \AA}$ , respectively. These values compare excellently with those reported earlier [8,9].

### *Romeite and bindheimite*

Aqueous  $0.100 \text{ M}$  solutions of  $\text{PbNO}_3(\text{s})$  or  $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s})$  were mixed with the above solution of  $\text{Sb(OH)}_6^-$  at Sb:Pb,Ca mol ratios of 1:1 or 1:2. In all cases, white, flocculant precipitates were obtained and remained X-ray amorphous at room temperature for more than 2 months. To accelerate the aging, the mixtures were refluxed. After 1 h, dense precipitates were obtained (white for the Ca salts and pale yellow to tan in color for the Pb salts). The mixtures were refluxed for a further 11 h, and the resulting precipitates were separated by centrifugation and decantation. Products were washed several times with water, then acetone, and dried in the oven at  $40^\circ\text{C}$ . Yields were essentially quantitative. Powder XRD showed that all species had the pyrochlore structure (stibiconite group) and SEM analyses indicated that the solids had Sb:M ( $M = \text{Ca, Pb}$ ) ratios corresponding to those used in the synthesis. Thus, the com-

positions  $MSb_2O_5(OH)_2$  and  $M_2Sb_2O_7$  ( $M = Ca, Pb$ ) were obtained. XRD traces were indexed by analogy to other stibiconite group minerals and unit cell data refined using LAPODC [7].  $CaSb_2O_5(OH)_2$ ,  $Ca_2Sb_2O_7$ ,  $PbSb_2O_5(OH)_2$ , and  $Pb_2Sb_2O_7$  gave  $a = 10.277(2)$ ,  $10.289(2)$ ,  $10.417(2)$ , and  $10.452(6)$  Å, respectively, in excellent agreement with literature values [6].

## Solubility studies

### *Bottinoite and brandholzite*

Bottinoite or brandholzite (ca. 0.2 g) was added to 100 cm<sup>3</sup> of water in sealed conical Quickfit flasks and left to equilibrate at  $25 \pm 0.2$  °C in a thermostatted water bath. Separate solutions were monitored periodically for dissolved Ni or Mg until no change in concentration was detected (ca. 1 week). After 30 days, the pH of the solutions was measured and the solutions filtered (0.2 µm) and analyzed by AAS for Ni or Mg. Separate experiments (XRD) showed that bottinoite and brandholzite dissolve congruently in water. A separate batch of solubility experiments was run using 0.100 mol dm<sup>-3</sup> KNO<sub>3</sub> as background electrolyte.

### *Romeite and bindheimite*

Accurate amounts of bindheimite or romeite ( $M_2Sb_2O_7$ , 0.5 g) were placed in sealed conical Quickfit flasks together with 100.000 g of 0.0100 M aqueous HNO<sub>3</sub> and left to equilibrate at  $25 \pm 0.2$  °C in a thermostatted water bath. Separate solutions were monitored periodically for pH until no change was detected (ca. 1 day). After 14 days, the final pH values were recorded and the solutions filtered as above. Dissolved Ca, Pb, and Sb concentrations were then determined by ICP methods.

## Field studies

Soil samples (B horizon) in the vicinity of the Bayley Park Sb prospect near Armidale, NSW, Australia (AGM 55 grid reference 56J 03914E 66244N; see below) were sieved (–1.25 mm), dried and analyzed for a suite of elements, including Sb, by a NATA-compliant commercial laboratory, Australian Laboratory Services PL, Brisbane, Australia.

## RESULTS AND DISCUSSION

### Solution geochemistry

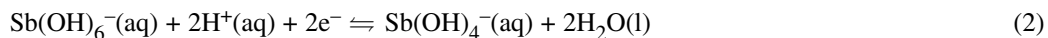
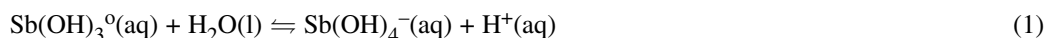
Previous attempts to describe the basic geochemical behavior of Sb have adopted the classical Pourbaix diagram approach. The first such report was published more than 50 years ago [10], and subsequent modifications have attempted to refine Pourbaix's original description [11,12]. All of these descriptions have suffered the lack of reliable values for the thermochemical properties of many of the species that were incorporated in calculations. In particular, reliable values of  $\Delta G_f^\circ$  for cervantite,  $Sb_2O_4$ , senarmonite and valentinite, dimorphs of composition  $Sb_2O_3$ , were either not available or overlooked. Fortunately, this deficiency has now been rectified [13,14]. An enduring problem, however, concerns the fact that the geochemical behavior of Sb under oxidizing conditions has been interpreted on the basis of the solubility of  $Sb_2O_5(s)$ . Baes and Mesmer [15] derived a value for  $\lg K_{S10}$  of –3.7 at 25 °C, based on earlier solubility studies [16]. Later workers reported solubility data for  $Sb_2O_5$  that were consistent with the above value [17,18]. Coupled with a value for  $\Delta G_f^\circ(Sb_2O_5, s, 298.15 \text{ K})$  [19], Sb has been thought to be easily dispersed in the natural environment. Thus, Vink [12] noted the "...relatively high mobility of antimony under oxidizing conditions, be it acidic or alkaline", a remark echoed elsewhere in that Sb is "...relatively mobile in the environment, especially under oxic conditions" [20]. Other comments on the matter have been more cautious or contradictory. Filella et al. [2] suggested that "...little is known about the environmental mobility of antimony..."; Wilson et al. [21], in a study of a

contaminated smelter site, concluded that "...antimony is not readily mobilised into the environment...".

One key to the rationalization of these observations is that solutions of Sb(V), prepared by acidifying or ion-exchanging solutions of  $\text{KSb}(\text{OH})_6$  (as used in the above-mentioned solubility studies) or hydrolysis of  $\text{SbCl}_5$  are metastable at ambient temperatures, except at very low concentrations. This was indeed alluded to by Baes and Mesmer [15], and carefully considered in a recent determination of the temperature-dependence of the  $\text{p}K_a$  of  $\text{Sb}(\text{OH})_5^0(\text{aq})$  [22]. While aqueous solutions of  $\text{KSb}(\text{OH})_6$  with concentrations of the order of  $0.1 \text{ mol dm}^{-3}$  appear to be stable for protracted periods at  $25^\circ\text{C}$ , their proton-exchanged equivalents are not and white precipitates of "antimonic acid",  $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  are obtained over hours to days, depending upon the temperature. A number of synthetic antimonic acids are known, but the phase prepared as described above is cubic and has the pyrochlore structure with  $1 \leq n \leq 4$ . The stoichiometry  $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  is better recast as  $(\text{H}_3\text{O}^+)_2\text{Sb}_2\text{O}_5(\text{OH})_2$  for  $n = 4$ , indicating the presence of hydronium ions and protonation of the oxide lattice. These parameters vary with pH and extent of desiccation. England et al. [23] passed a solution of  $\text{KSb}(\text{OH})_6$  in boiling water through an ion exchange column in the  $\text{H}^+$  form and obtained  $\text{HSbO}_3 \cdot 2\text{H}_2\text{O}$  by aging the solution at  $80^\circ\text{C}$  for 4 days. Its structure was solved with  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  occupying sites  $16d$  and  $8b$  (50 and 100 % occupied, respectively) in the archetypal perovskite lattice. It was also shown that the phase synthesized by aging acidified (HCl) precipitates at room temperature [24] was identical in nature. Lower hydrates exhibit a subtly different pyrochlore-type structure. Riviere et al. [25] followed the cation exchange route outlined above using aqueous solutions of  $\text{KSb}(\text{OH})_6$  at  $0^\circ\text{C}$ , then evaporated the filtrate to dryness to yield  $\text{HSbO}_3 \cdot 0.5\text{H}_2\text{O}$ . Refinement of powder diffraction data showed the Sb and O atoms at the usual  $16c$  and  $48f$  sites, respectively, but with  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  occupying the  $32e$  site with reduced occupancy. This structure was confirmed in a neutron diffraction study of a partially deuterated analog [26].

The geochemical significance of the above is profound. Once formed, the pyrochlore is very insoluble in acid or base and acts as a cation exchanger [23–26, and references therein]. The most commonly found secondary Sb minerals are formed in this way. These include stibiconite,  $\text{Sb}^{3+}\text{Sb}_2\text{O}_6\text{OH}$ , romeite,  $\text{Ca}_2\text{Sb}_2\text{O}_7$ , and bindheimite,  $\text{Pb}_2\text{Sb}_2\text{O}_7$  (ideal stoichiometries are given, but naturally occurring materials are always highly defective and multiple solid solution is common). Cations smaller than  $\text{Ca}^{2+}$  or  $\text{Pb}^{2+}$  give other species including the layered hexagonal phases bottinoite and brandholzite [8,9] or mopungite,  $\text{Na}[\text{Sb}(\text{OH})_6]$  (tetragonal,  $a = 7.994$ ,  $c = 7.859 \text{ \AA}$  [27]). While  $\text{K}[\text{Sb}(\text{OH})_6]$  is quite soluble in water at  $25^\circ\text{C}$  (see Experimental section), concentrations of  $\text{K}^+$  in groundwaters are usually very low in comparison to  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  [28]. Salts of these ions and of  $\text{Ni}^{2+}$  are rather less soluble than  $\text{K}[\text{Sb}(\text{OH})_6]$  at ambient temperatures. For the thermochemical data concerning these salts as discussed below, the following derivations should be noted.

First, a reliable value for  $\Delta G_f^\circ[\text{Sb}(\text{OH})_3^0, \text{aq}, 298.15 \text{ K}]$  of  $-644.4 \pm 1.1 \text{ kJ mol}^{-1}$  is available, based on the careful solubility work of Zotov et al. [14]. Similarly, a recent, critical experimental study by Zakaznova-Herzog and Seward [29] reviewing all previous work and gave  $\lg K = -11.82 \pm 0.02$  at  $298.15 \text{ K}$  for eq. 1.



Thus,  $\Delta G_f^\circ[\text{Sb}(\text{OH})_4^-, \text{aq}, 298.15 \text{ K}]$  is calculated as  $-814.0 \text{ kJ mol}^{-1}$ . Past [30] reported  $E^\circ = +0.363 \text{ V}$  at  $298.15 \text{ K}$  for the reaction given in eq. 2, based on electrochemical measurements in aqueous KOH solutions reported by Grube and Schweigardt [31] and, combined, this gives a value of  $\Delta G_f^\circ[\text{Sb}(\text{OH})_6^-, \text{aq}, 298.15 \text{ K}]$  equal to  $-1218.2 \text{ kJ mol}^{-1}$ . It is difficult to attribute an error to this quantity, and we have arbitrarily assigned it a value of  $\pm 1.0 \text{ kJ mol}^{-1}$  in our further calculations. The true value may well be larger, but this has no bearing on the conclusions that are drawn, based solely on solubility data and not on derived thermochemical quantities. Otherwise, all other  $\Delta G_f^\circ$  data at  $298.15 \text{ K}$  are taken from Robie and Hemingway [32].

Blandamer et al. [33] reported the solubility of mopungite solubility as  $3.18 \pm 0.2 \times 10^{-3} \text{ mol dm}^{-3}$  at 25 °C. Assuming negligible hydrolysis of the  $\text{Na}^+$  ion and concentration of  $\text{Sb}(\text{OH})_5^0$ , at this temperature  $K_{\text{sol}} = 8.89 \times 10^{-6}$  and  $\Delta G_f^\circ(\text{mopungite}, \text{s}, 298.15 \text{ K}) = -1508.5 \pm 1.4 \text{ kJ mol}^{-1}$ . Here and elsewhere, ion activity coefficients have been calculated using the equation  $\lg \gamma = -Az^2/[I(1 + I) - 0.3I]$ .

From our experiments, the solubility of brandholzite in water is  $1.95(4) \times 10^{-3} \text{ mol dm}^{-3}$  at 25 °C [ $n = 4$ ; pH = 6.12(8);  $I = 5.85(4) \times 10^{-3}$ ;  $\gamma^{2\pm} = 0.723$ ;  $\gamma^\pm = 0.922$ ], and this yields  $K_{\text{sol}} = 1.82 \pm 0.15 \times 10^{-8}$  and  $\Delta G_f^\circ(\text{brandholzite}, \text{s}, 298.15 \text{ K}) = -4358.4 \pm 3.4 \text{ kJ mol}^{-1}$ . Similarly, the solubility of bottinoite in water is  $3.42(11) \times 10^{-4} \text{ mol dm}^{-3}$  at 25 °C [ $n = 4$ ; pH = 5.80(6);  $I = 1.03(11) \times 10^{-3}$ ;  $\gamma^{2\pm} = 0.866$ ;  $\gamma^\pm = 0.965$ ], and this yields  $K_{\text{sol}} = 1.29 \pm 0.13 \times 10^{-10}$  and  $\Delta G_f^\circ(\text{bottinoite}, \text{s}, 298.15 \text{ K}) = -3961.1 \pm 3.7 \text{ kJ mol}^{-1}$ . It should be noted that at the pH values given above, the concentrations of hydrolyzed  $\text{Ni}^{2+}(\text{aq})$  species and  $\text{Sb}(\text{OH})_5^0(\text{aq})$  can be neglected in the calculations [32,34]. In aqueous  $0.100 \text{ mol dm}^{-3} \text{ KNO}_3$ , the solubilities of brandholzite and bottinoite at 25 °C were found to be  $2.44(15) \times 10^{-3}$  [ $n = 4$ ; pH = 5.82(3)] and  $5.49(8) \times 10^{-4}$  [ $n = 4$ ; pH = 5.72(32)], respectively. Use of the same method as above to calculate activity coefficients at  $I = 0.1$  gives  $K_{\text{sol}}$  values of  $1.33 \times 10^{-8}$  and  $1.51 \times 10^{-10}$ , for brandholzite and bottinoite, respectively. These are comparable to the values found in water alone, but it is evident that the empirical method used for calculation of activity coefficients cannot be relied upon under these conditions.

At 25 °C, the solubilities of the minerals follow the series mopungite > brandholzite > bottinoite, but all three have appreciable solubility. This is in line with the rarity of mopungite and brandholzite (6 and 2 reported localities). Nevertheless, bottinoite is known from some 30 deposits world-wide (tabulated on <www.mindat.org>) and this at first glance may be surprising. However, this nickel antimonate mineral is invariably found as an oxidation product of ullmannite,  $\text{NiSbS}$  [6, and tabulated on <www.mindat.org>], and as ullmannite is oxidized by thin surface layers of oxygen-bearing solutions, the formation of bottinoite can be viewed as a mineralogical and geochemical inevitability. Oxidation products will ultimately be  $\text{Ni}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Sb}(\text{OH})_5$  or  $\text{Sb}(\text{OH})_6^-$  and the simultaneous generation of  $\text{Ni}^{2+}$  and  $\text{Sb}(\text{OH})_6^-$  will lead to the crystallization of bottinoite, given the apparent instability and great rarity of secondary Sb sulfate minerals [6]. It is further noted that mopungite, brandholzite, and bottinoite are unstable in the presence of appreciable amounts of  $\text{Ca}^{2+}$ , a common ion in ground waters, or  $\text{Pb}^{2+}$ , present in an oxidizing assemblage containing, in addition to primary Sb minerals, galena,  $\text{PbS}$ , or Pb-bearing sulfosalts. This is borne out by our measurements of the solubilities of  $\text{Ca}_2\text{Sb}_2\text{O}_7$  and  $\text{Pb}_2\text{Sb}_2\text{O}_7$ .

As noted above, we can find no evidence for the formation of the crystalline salts  $[\text{Ca}(\text{H}_2\text{O})_6][\text{Sb}(\text{OH})_6]_2(\text{s})$  and  $[\text{Pb}(\text{H}_2\text{O})_6][\text{Sb}(\text{OH})_6]_2(\text{s})$ , species that would be analogous to brandholzite and bottinoite. In contrast, Johnson et al. [35] reported in passing solubility products for both salts. At 25 °C,  $K_{\text{sol}}$  values of  $10^{-12.55}$  and  $10^{-11.02}$  were given for  $\text{Ca}(\text{H}_2\text{O})_6[\text{Sb}(\text{OH})_6]_2$  and  $[\text{Pb}(\text{H}_2\text{O})_6][\text{Sb}(\text{OH})_6]_2$ , respectively. These correspond to respective solubilities of about  $6.5 \times 10^{-5}$  and  $2.1 \times 10^{-4} \text{ mol dm}^{-3}$ , indicating that they are reasonably soluble phases. We are obliged to infer that these quantities refer in fact to the upper limits of the solubilities of the X-ray amorphous phases and correspond to dissolved Sb levels of 10 ppm for the Ca salt and 32 ppm for the Pb salt. If this were the case, the conclusion that Sb is relatively mobile in the supergene zone would be logical. Our solubility experiments, however, render such a conclusion untenable.

At 25 °C,  $\text{Pb}_2\text{Sb}_2\text{O}_7$  equilibrated with  $0.0100 \text{ mol dm}^{-3} \text{ HNO}_3$  gives a final pH of  $2.05 \pm 0.05$  ( $n = 6$ ), total dissolved Pb equal to  $4.12 \pm 0.13 \times 10^{-5} \text{ mol dm}^{-3}$  (ca. 8.5 ppm) and total dissolved Sb equal to  $7.7 \pm 2.1 \times 10^{-8} \text{ mol dm}^{-3}$  (ca. 9.3 ppb).  $\text{Ca}_2\text{Sb}_2\text{O}_7$ . Similarly,  $\text{Ca}_2\text{Sb}_2\text{O}_7$  equilibrated with  $0.0100 \text{ mol dm}^{-3} \text{ HNO}_3$  gives a final pH of  $2.23 \pm 0.01$  ( $n = 6$ ), total dissolved Ca equal to  $2.11 \pm 0.05 \times 10^{-3} \text{ mol dm}^{-3}$  (ca. 85 ppm) and total dissolved Sb equal to  $3.3 \pm 1.0 \times 10^{-7} \text{ mol dm}^{-3}$  (ca. 40 ppb). The results reflect the facts noted above that the salts act as cation exchangers and dissolve incongruently. Most significantly, the dissolved Sb concentrations are about three orders of magnitude smaller than

those predicted by Johnson et al. [35], and the conclusion must be drawn that Sb is indeed quite immobile in solution in the supergene zone. This is exactly what was anticipated in that previous thoughts on the matter rested on the erroneous assumption that  $\text{Sb}_2\text{O}_3(\text{s})$  could be used as a proxy for modeling the solution behavior of Sb in the oxidized environment.

The above predictions made on the basis of simple solubility experiments are reinforced by what is known in terms of mineral assemblages and relationships in the oxidized zones of Sb-bearing ore bodies. Only a handful of secondary Sb minerals occur commonly, and they comprise kermesite,  $\text{Sb}_2\text{S}_2\text{O}$ , the dimorphs valentinite and senarmontite,  $\text{Sb}_2\text{O}_3$ , cervantite  $\text{Sb}_2\text{O}_4$ , tripuhyite,  $\text{FeSbO}_4$  and three members of the stibiconite group, bindheimite, romeite, and stibiconite [6]. It is remarkable that oxidation of stibnite,  $\text{Sb}_2\text{S}_3$ , always leads to assemblages of these common minerals in the immediate proximity of their primary precursors and pseudomorphs of them after stibnite are very common. With respect to field studies carried out in conjunction with the solubility work, we have had occasion to characterize the secondary Sb mineralogy of four deposits (Bayley Park prospect, Conningdale mine, Fishers Sb mine, Sunlight lode) in the Hillgrove area of New South Wales [36] and the Razorback mine near Mudgee, New South Wales [37]. In all cases, primary Sb mineralization consists of stibnite. Kermesite pseudomorphs after stibnite were observed at the Conningdale mine. Otherwise, small amounts of senarmontite and cervantite were found coating the surface of partially altered stibnite, and overlying this were pseudomorphs of stibiconite group minerals (stibiconite and romeite); the latter also formed pseudomorphs after stibnite in some specimens. Adjacent to these minerals, small wart-like masses of brown tripuhyite were identified by XRD at the Conningdale mine and the Bayley Park prospect. The extent of migration of the bulk of the Sb in these deposits could be measured in millimetres, and mineral occurrences and parageneses are consistent both with the solubility results described above and the progressive oxidation of Sb(III) to Sb(V).

### Bayley Park soil geochemistry

In light of the conclusion that Sb is quite immobile in the weathering environment, a soil geochemistry orientation survey was conducted over the Bayley Park prospect as part of a validation of predictions concerning the use of soil Sb analyses in the exploration context. The prospect occurs in gently sloping country and is comparatively free of contamination by earlier mining operations. The sole workings over a 500-m strike length consist of an old, back-filled shaft, a prospecting shaft some 15 m deep dating from 1971, and four shallow (0.5 m) prospecting pits. The mineralization is hosted in a subvertical fault filled with brecciated metasediments and stibnite cemented by quartz. Arsenopyrite is reported to be present in the primary ore [36], but none was found in the field. Soil cover is thin, typically less than 0.2 m.

The geochemical soil anomaly associated with deposit the shear zone reached Sb levels of about 150 ppm and delineated the NW–SE shear zone perfectly. Of particular interest was the fact that soil Sb levels had dropped to about 10 ppm within 50 of the known mineralization and reached background levels (typically <4 ppm) within about another 50 m. The survey clearly showed that anomalous Sb levels are confined to the immediate vicinity of the oxidizing lode and are consistent with the view of Wilson et al. [21] that the chemical mobility of Sb in soils is quite limited. It is thus concluded that the use of Sb in geochemical exploration in the area is useful to pinpoint potentially mineralized zones. However, the orientation study, resting on the solubility experiments described, suggests that Sb may not be of any use as a pathfinder element in regional geochemical surveys.

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