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Tripuhyite and schafarzikite: two of the ultimate sinks for antimony in the natural environment

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ABSTRACT

Studies of the stability of the oxides schafarzikite, $FeSb_2O_4$, and tripuhyite, $FeSbO_4$, have been undertaken to clarify the roles these secondary minerals may have in determining the dispersion of antimony in oxidizing environments. Solubilities were determined at 298.15 K in aqueous HNO_3, and these data were used to calculate values of $\Delta G_f^\ominus$ at the same temperature. The derived $\Delta G_f^\ominus$(s, 298.15 K) values for $FeSb_2O_4$ and $FeSbO_4$ are -959.4 ± 4.3 and -836.8 ± 2.2 kJ mol^{-1}, respectively. These results have been compared with electrochemically derived data, extrapolated from 771−981 K. The present study shows conclusively that although the mobility of Sb above the water table is limited by simple Sb(III) and Sb(V) oxides and stibiconite-group minerals, depending upon the prevailing redox potential and pH, tripuhyite is an important ultimate sink for Sb in the supergene environment. It is highly insoluble even in strongly acidic conditions and its anomalous stability at ambient temperatures causes the common mineral goethite, FeOOH, to react to form tripuhyite at activities of $Sb(OH)_5$(aq) as low as 10^{-11}. The comparatively limited numbers of reported occurrences of tripuhyite in the supergene zone are almost certainly due to the fact that its physical properties, especially colour and habit, are remarkably similar to those of goethite. In contrast, the small number of reported occurrences of schafarzikite can be related to its decomposition to tripuhyite as redox potentials rise at the top of the supergene zone and the fact that it decomposes to sénarmontite, Sb_2O_3, in acidic conditions, releasing Fe^{2+} ions into solution. In general, the findings confirm the immobility of Sb in near-surface conditions. Geochemical settings favouring the formation of the above minerals have been assessed using the results of the present study and data from the literature.

KEYWORDS: tripuhyite, schafarzikite, solubility, stability, oxidizing environment, antimony mobility.

Introduction

THE near-surface chemical behaviour of Sb has attracted considerable attention. Antimony is considered to be a toxic heavy metal and this has occasioned many studies aimed at understanding its solubility behaviour in surface waters and how it may be immobilized in the supergene zone. Several recent reviews have highlighted what is and is not known in this connection and point to what remains to be achieved to produce a reliable model for its aqueous geochemistry (Filella and May, 2003; Filella *et al.*, 2002*a*,*b*, 2009). Two key questions emerge: what controls the adsorption and co-precipitation of Sb(V), and what solid phases limit the solubility and mobility of Sb in oxidising environments? Opinion concerning the latter is confused, some authors claiming that Sb is mobile (Vink, 1996; Krupka and Serne, 2002), some the contrary (Wilson *et al.*, 2004), and others noting that little is known about the matter (Filella *et al.*, 2002*a*,*b*). The confusion arises to a large degree from assessments of the solubility of Sb based on Pourbaix diagrams using Sb_2O_5(s) as a proxy for naturally

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occurring secondary Sb(V) minerals (Brookins, 1988; Vink, 1996). This phase does not occur naturally. Studies that address this issue have emerged only recently, and have highlighted the roles that salts of the $Sb(OH)_6^-$ ion and members of the roméite group ($M_xSb_2(O,OH)_7$) such as oxycalcioroméite, $Ca_2Sb_2O_7$, and oxyplumboroméite, $Pb_2Sb_2O_7$, have in controlling the dispersion of Sb in the supergene environment (Diemar *et al*., 2009; Filella *et al*., 2009, Majzlan *et al*., 2011). However, it remains apparent that other mineralogical controls must be more significant than these.

A survey of the literature has revealed two other potentially important phases: tripuhyite, $FeSbO_4$, and schafarzikite, $FeSb_2O_4$. Schafarzikite is known from relatively few localities, but tripuhyite is a rather common secondary Sb mineral (Anthony *et al*., 1997; Berlepsch *et al*., 2003); it also occurs as a primary pegmatite phase. We note in passing that squawcreekite (Foord *et al*., 1991) was shown by Berlepsch *et al*. (2003) and Basso *et al*. (2003) to be identical with tripuhyite and was subsequently discredited. Squawcreekite was originally found as a primary phase at two localities and later reported from another (Cabella *et al*., 2003). High-temperature studies of the formation of tripuhyite and associated solid-solution phenomena have been explored separately by Martinelli *et al*. (2004, 2006).

We have confirmed the occurrence of tripuhyite in every oxidized zone of the many Sb deposits that we have examined in the New England region of New South Wales, Australia (Diemar *et al*., 2009) and in the Pearse deposit at Mineral Hill, New South Wales, where it is abundant. The association of Sb with Fe(III) oxyhydroxides has long been appreciated and adsorption effects that appear to be significant in the immobilization of Sb have been addressed by a number of workers. A recent report summarizes what is known, and points towards the incorporation of Sb(V) in the goethite lattice (Mitsunobu *et al*., 2010, and references therein). However, in our view it is quite likely that the incorporation of Sb(V) in the goethite lattice may also result in the formation of nano-domains of tripuhyite. The very recent study of Majzlan *et al*. (2011) reinforces this view in that, aside from adsorbed Sb, tripuhyite is an important phase in reactive Sb-rich mine wastes at a number of Slovakian deposits. The same authors point out that tripuhyite is easily overlooked as it is visually indistinguishable from goethite or hematite in hand specimen. Furthermore, Mitsunobu *et al*. (2011) identified abundant nano-domains of tripuhyite in soils adjacent to Sb-rich mine tailings.

The thermodynamic stabilities of tripuhyite and schafarzikite based on electrochemical measurements at 771−981 K have been reported by Swaminathan and Sreedharan (2003). Extrapolation to 298 K gives data that indicate that goethite will react to form these phases at activities of $Sb(OH)_5^o(aq)$ as low as 10^{-18}. At first sight this conclusion appears untenable and therefore we have recently determined $\Delta G_r^\ominus(298.15\text{ K})$ for the minerals using solution methods and found that our value for schafarzikite is in agreement with that extrapolated from the data of Swaminathan and Sreedharan (2003) (within error), and that our value for tripuhyite is only 40 kJ mol^{-1} less than the extrapolated value. These extraordinary findings show that both minerals exert very significant controls on the dispersion of Sb in the natural environment and they may, in conjunction with adsorption phenomena, control dissolved Sb levels in surface waters. The results of these studies are reported below.

Experimental

X-ray powder diffraction studies were carried out using a Philips PW1825/20 powder diffractometer (using Ni-filtered Cu$K\alpha_1$ radiation, λ = 1.5406 Å at 40 kV, 30 mA). The solubility of schafarzikite was determined by atomic absorption spectrometry (AAS) using a Perkin Elmer AAnalyst100 spectrophotometer (air-acetylene with 2000 ppm added KCl to control ionization, and matched standards). The solubility of tripuhyite was determined by inductively coupled plasma mass spectrometry (ICP-MS) for Sb at a NATA-compliant commercial laboratory (LabMark PL, Asquith, Australia). Measurements of pH were made using a Radiometer PHM220 apparatus fitted with a combination electrode.

Syntheses

Tripuhyite was synthesized following the method of Martinelli *et al*. (2002). The oxides Sb_2O_3 (4.9983 g, 0.017 mol) and Fe_2O_3 (2.7390 g, 0.017 mol) were thoroughly mixed by mortar and pestle before being placed in a fused silica boat and heated in a Raemus tube furnace open to the atmosphere at 1246±10 K for 12 h to give a dark brown, crystalline product. The product was soaked in aqueous 0.1 M HNO_3 for 48 h, collected at the pump, washed with water and then with acetone, and sucked dry. The yield was essentially quantitative. Powder X-ray diffractometry (XRD) (Table 1) showed the mineral to be of high purity, no other phases being detected. Refinement of the data using *LAPOD* (Langford, 1973) gave a = 4.6374(2), c = 3.0749(2) Å, which are in excellent agreement with the values of Foord *et al*. (1991) and Berlepsch *et al*. (2003).

Schafarzikite was synthesized following the method of Chater *et al*. (1985). Previously ground Sb_2O_3 (8.7456 g, 0.03 mol) and Fe_2O_3 (1.5969 g, 0.01 mol), and Fe powder (0.5584 g, 0.01 mol) were added to a sample container and mixed by rolling for 1 week to produce as homogeneous a mixture as possible. This mixture was sealed under vacuum in a Pyrex reaction tube to provide the environment required for the reaction to proceed stoichiometrically in the absence of atmospheric oxygen. For safety reasons the sealed reaction tube was placed inside a steel pipe fitted with threaded end-caps; it was heated to 773±10 K for 10 days. After allowing the apparatus to slowly cool to room temperature, the reaction tube was carefully opened and the dark reddish brown product removed. Powder XRD analysis confirmed that the yield was essentially quantitative, no phase other than schafarzikite being detected. The XRD data (Table 1) were indexed in line with the single-crystal X-ray structure (Fischer and Pertlik, 1975) and refined as above to give a = 8.620(1), c = 5.919(2) Å, which are in excellent agreement with the values of Sejkora *et al*. (2007) and Fischer and Pertlik (1975).

Solubility studies

Preliminary studies showed that tripuhyite dissolves congruently in 0.2 M HNO_3. Acid-washed tripuhyite (~0.1 g) was added to a series of 500 cm^3 conical Quickfit flasks together with 50.00 cm^3 of standardized 0.195 M aqueous HNO_3. The flasks were sealed and left to equilibrate at 25±0.2ºC in a temperature-controlled water bath. A

TABLE 1. Powder X-ray data for synthetic tripuhyite and schafarzikite.

Tripuhyite			Schafarzikite		
h k l	d_{obs} (Å)	d_{calc} (Å)	*h k l*	d_{obs} (Å)	d_{calc} (Å)
1 1 0	3.2796	3.2792	1 1 0	6.1080	6.0950
1 0 1	2.5625	2.5627	2 0 0	4.3143	4.3098
2 0 0	2.3185	2.3187	2 1 0	3.8637	3.8548
1 1 1	2.2425	2.2430	2 1 1	3.2316	3.2302
2 1 0	2.0735	2.0739	2 2 0	3.0467	3.0475
2 1 1	1.7193	1.7194	0 0 2	2.9598	2.9597
2 2 0	1.6395	1.6396	3 1 0	2.7256	2.7258
0 0 2	1.5376	1.5375	1 1 2	2.6636	2.6624
3 1 0	1.4665	1.4665	2 0 2	2.4400	2.4398
1 1 2	1.3920	1.3921	2 1 2	2.3458	2.3476
3 0 1	1.3813	1.3811	4 0 0	2.1524	2.1549
			4 1 0	2.0903	2.0906
			3 3 0	2.0317	2.0317
			4 0 1	2.0253	2.0249
			3 1 2	2.0057	2.0050
			4 1 1	1.9710	1.9712
			4 2 0	1.9272	1.9274
			2 1 3	1.7568	1.7564
			4 0 2	1.7416	1.7421
			4 1 2	1.7058	1.7076
			3 3 2	1.6756	1.6750
			5 2 1	1.5453	1.5451
			4 4 0	1.5243	1.5237
			5 1 2	1.4682	1.4679

separate solution was monitored periodically for pH but virtually no change was detected. After 40 days, the solutions were filtered (0.2 μm Millipore) and dissolved Sb was determined by ICP-MS. Even at this concentration of HNO_3, tripuhyite is quite insoluble.

A powder XRD examination of the products of the reaction of schafarzikite with aqueous 0.1 M HNO_3 showed that it dissolves incongruently according to equation 1:

$$FeSb_2O_4(s) + 2H^+(aq) \rightleftharpoons Sb_2O_3(s,\ \text{sénarmontite}) + Fe^{2+}(aq) + H_2O(l) \quad (1)$$

Appropriate reaction conditions were chosen such that equilibrium would be reached with both schafarzikite and sénarmontite present in the solid state. Schafarzikite (~0.1 g) was added to a series of 500 cm^3 conical Quickfit flasks with 50.00 cm^3 of standardized 0.100 M aqueous HNO_3. The flasks were sealed and left to equilibrate at 25±0.2ºC in a temperature-controlled water bath. A separate solution was monitored periodically for dissolved Fe using AAS and pH until no change in concentrations were detected (~1 week). After 38 days, the pH of each resulting solution was measured and the solutions filtered as above. Filtrates were diluted by 1:40 using aqueous 0.1 M HNO_3 and analysed by AAS for total dissolved Fe(II).

Results and discussion

Solubility data for tripuhyite and schafarzikite are listed in Tables 2 and 3, respectively. For the congruent dissolution of the mineral according to equation 2, the stability of tripuhyite at 298.15 K may be calculated using the relationship $[Fe^{3+}]_{TOT} = [Sb^{5+}]_{TOT}$.

$$FeSbO_4(s) + H_2O(l) + 3H^+(aq) \rightleftharpoons Fe^{3+}(aq) + Sb(OH)_5^o(aq) \quad (2)$$

A comment is warranted here on the speciation of Fe^{3+} and Sb^{5+} in the experimental conditions in the solution experiments. The hydrolysis of Fe^{3+} has been discussed by Baes and Mesmer (1976) and it is evident that the only solution species of any possible significance at the pH values given in Table 2 are $Fe^{3+}(aq)$ and $FeOH^{2+}(aq)$. A reliable lg *K* value for equation 3:

$$Fe^{3+}(aq) + H_2O(l) \rightleftharpoons FeOH^{2+}(aq) + H^+(aq) \quad (3)$$

was recently reported by Stefánsson and Seward (2008): lg $K(298.15\ K) = -2.18\pm0.01$ at an ionic strength, *I*, of 0 mol dm^{-3}. Correction to I = 0.1946 mol dm^{-3} (the ionic strength of the equilibrium HNO_3 solutions) using the method of Baes and Mesmer (1976), gives a lg $K(298.15\ K)$ value of −2.61. Substitution in equation 3 indicates negligible hydrolysis in the experimental solutions. For antimony the only solution species that are potentially important are $Sb(OH)_5^o(aq)$ and $Sb(OH)_6^-(aq)$. These are related according to equation 4:

$$Sb(OH)_5^o(aq) + H_2O(l) \rightleftharpoons Sb(OH)_6^-(aq) + H^+(aq) \quad (4)$$

A reliable lg *K* value for equation 4 was recently reported by Accornero *et al.* (2008): lg $K(298.15\ K) = -2.848$ at $I = 0$. Correction to I = 0.1946 mol dm^{-3} yields lg $K(298.15\ K) = -2.535$ and substitution indicates the presence of negligible amounts of $Sb(OH)_6^-(aq)$ in these solutions.

Individual ion activity coefficients were calculated using the Davis extension of the Debye–Hückel equation for 298.15 K: lg γ =

TABLE 2. Final Sb^{5+} concentrations for filtrates obtained from the dissolution of tripuhyite in 0.195 M HNO_3 at 298.15 K and measured equilibrium pH values.

Solution	[Sb] (ppm)	[Sb] (mol dm^{-3})	pH
1	0.130	1.068×10^{-6}	0.536
2	0.094	7.720×10^{-7}	0.538
3	0.088	7.227×10^{-7}	0.536
4	0.110	9.034×10^{-7}	0.540
5	0.160	1.314×10^{-6}	0.540
Mean	0.1164	9.52×10^{-7}	0.538
Error	±0.029		±0.002

TABLE 3. Final Fe^{2+} concentrations for filtrates obtained from the dissolution of schafarzikite in 0.100 M HNO_3 at 298.15 K, and equilibrium pH values.

Solution	[Fe] (ppm)	[Fe] (mol dm^{-3})	pH
1	126	2.256×10^{-3}	0.868
2	130	2.328×10^{-3}	0.872
3	133	2.382×10^{-3}	0.870
Mean	129.7	2.322×10^{-3}	0.870
Error	±3.3	6.322×10^{-5}	±0.002

$-0.5085z^2(\sqrt{I}/(1+\sqrt{I}) - 0.3I)$. For I = 0.1947 mol dm^{-3}, $\gamma^{3\pm}$ = 0.074 and $\gamma^{\pm}$ = 0.748; γ^{o} is taken to be unity. The activity of H^+(aq), $a(H^+)$, in 0.195 M HNO_3 was calculated and corresponding activities $a(Fe^{3+})$ and $a(Sb(OH)_5^o)$ calculated from the solubility data. This yields a value of lg K for equation 2 of −10.68±0.10. With $\Delta G_f^\ominus(Fe^{3+}$, aq, 298.15 K) = −16.28±1.1 kJ mol^{-1} (Parker and Khodakovskii, 1995), $\Delta G_f^\ominus(H_2O$, l, 298.15 K) = −237.1±0.1 kJ mol^{-1} (Robie and Hemingway, 1995) and $\Delta G_f^\ominus(Sb(OH)_5^o$, aq, 298.15 K) = −996.6 kJ mol^{-1} (see Appendix) this yields a value for $\Delta G_r^\ominus$(298.15 K) of +60.97 kJ mol^{-1} for equation 1, and thus $\Delta G_f^\ominus(FeSbO_4$, s, 298.15 K) = −836.8±2.2 kJ mol^{-1}. The estimated error takes into account the analytical error of the solubility experiments, errors quoted for the thermochemical data used, and an estimated error of ±1.0 kJ mol^{-1} for $\Delta G_f^\ominus(Sb(OH)_5^o$, aq, 298.15 K).

A different approach was adopted to estimate $\Delta G_f^\ominus(FeSb_2O_4$, s, 298.15 K) in that solubility experiments were designed such that schafarzikite and sénarmontite were present as solid phases at equilibrium. Thus thermochemical values were calculated with respect to equation 5:

$$FeSb_2O_4(s) + 2H^+(aq) \rightleftharpoons Fe^{2+}(aq) + Sb_2O_3(s) + H_2O(l) \quad (5)$$

Hydrolysis of Fe^{2+}(aq) at the pH and total $[Fe^{2+}]$ values listed in Table 3 is not detectable (Baes and Mesmer, 1976) and similar calculations to those outlined above indicate that the $a(Sb(OH)_2^+)$ may be neglected. The data listed in Table 3 lead to I = 0.102 mol dm^{-3}, $\gamma^{2\pm}$ = 0.3709; $\gamma^{\pm}$ = 0.7804, and thus K for equation 5 is 0.155±0.004. Using $\Delta G_f^\ominus(Fe^{2+}$, aq, 298.15 K) = −90.0±2.0 kJ mol^{-1} (Robie and Hemingway, 1995), $\Delta G_f^\ominus(H_2O$, l, 298.15 K) as given above and $\Delta G_f^\ominus(Sb_2O_3$, s, sénarmontite, 298.15 K) = −633.2±2.1 kJ mol^{-1} (see Appendix) leads to $\Delta G_f^\ominus(FeSb_2O_4$, s, 298.15 K) = −959.4±4.3 kJ mol^{-1}.

It was noted above that if the high temperature data reported by Swaminathan and Sreedharan (2003) for tripuhyite and schafarzikite could be reliably extrapolated to 298.15 K some remarkable consequences would ensue. Their relationship $\Delta G_f^\ominus(FeSb_2O_4$, s) = −1068.7 + 0.3561$T$(K) ±3.5 kJ mol^{-1} gives $\Delta G_f^\ominus$(298.15 K) = −962.5±3.5 kJ mol^{-1} for schafarzikite which is the same, within experimental error, as the value derived in this study. Their relationship $\Delta G_f^\ominus(FeSbO_4$, s) = −976.9 + 0.3289$T$ (K) ±5.5 kJ mol^{-1} gives $\Delta G_f^\ominus$(298.15 K) = −878.8±5.5 kJ mol^{-1} for tripuhyite. The value determined in this study is 40 kJ mol^{-1} different to the extrapolated value, but this is perfectly reasonable given the 470 K difference in temperature between the two sets of experimental data. These findings are extraordinary.

The equilibria between tripuhyite, schafarzikite can be represented by the equations:

$$FeSbO_4(s) + 3H_2O(l) \rightleftharpoons FeOOH(s) + Sb(OH)_5^o(aq) \quad (6)$$

$$FeOOH(s) + 2Sb(OH)_3^o(aq) + H^+(aq) + e^- \rightleftharpoons FeSb_2O_4(s) + 4H_2O(l) \quad (7)$$

At 298.15 K, lg K = lg $a(Sb(OH)_5^o)$ = −11.0 for equation 6, and it is inescapable that the ubiquitous Fe(III) mineral goethite is thermodynamically unstable with respect to tripuhyite at vanishingly small activities of Sb(V) in aqueous solution. The value of lg $a(Sb(OH)_5^o)$ = −11.0 corresponds to a few parts per trillion dissolved Sb. Therefore tripuhyite must be one of the ultimate mineralogical sinks for Sb in the supergene environment.

The insolubility of tripuhyite may be attributed to a remarkably stable lattice and this finds echoes in a different environment. The facile syntheses of tripuhyite and schafarzikite at elevated temperatures make it readily apparent why tripuhyite is also found as a high temperature mineral in pegmatites and in certain hydrothermal cassiterite deposits that are antimony rich and sulfur poor (Hussak and Prior, 1897; Mason and Vitaliano, 1953; Foord *et al.*, 1991). This echoes the comparatively common occurrence of stibiobetafite, $(Ca,Sb)_2(Ti,Nb,Ta)(O,OH)_7$, stibiocolumbite, $Sb(Nb,Ta)O_4$, stibiomicrolite, $(Sb,Ca,Na)_2(Ta,Nb)O_7$, stibiotantalite, $Sb(Ta,Nb)O_4$, and stibivanite, Sb_2VO_5, in similar settings (Anthony *et al.*, 1997). In terms of the stability of tripuhyite in the supergene environment, it is particularly noteworthy that the mineral was first described from alluvial deposits derived from the weathering of pegmatites (Hussak and Prior, 1897) that had been in contact with water for thousands to millions of years. It is a very refractory phase at ambient conditions. It is also well known as a supergene mineral in oxidizing, Sb-rich ore systems. The suggestion that schafarzikite may also occur as a primary high-temperature phase (Sejkora *et al.*, 2007) is intriguing, and also in line with the synthesis of the mineral. Schafarzikite is also anomalously stable except in acidic conditions. For equation 7, $E^\ominus$ = +1.35 V and for values of $a(Sb(OH)_3^o)$ associated with the presence of sénarmontite, goethite reacts to form schafarzikite at lower redox potentials where tripuhyite is unstable. In connection with the formation of schafarzikite it is of note that the few localities from which it is reported are either hosted by carbonate rocks (Orlandi and Dini, 2004; Sejkora *et al*., 2004; Coppola *et al*., 2009) or contain significant amounts of carbonate minerals in the gangue (Robinson and Normand, 1996; Philippo and Hanson, 2007). Carbonates would buffer mineralizing groundwaters to pH values of approximately 7 to 8. The gangue associations of the Drew Hill sulfide prospect, Maine, USA are not known (Robinson and King, 1991).

To illustrate some of the relationships outlined above, a Pourbaix diagram has been constructed for total dissolved Sb and total dissolved Fe = 10^{-6} mol dm^{-3} at 298.15 K (Fig. 1). *For the chosen values*, no other secondary Sb mineral plots on the field.

Given the abundance of Fe(III) in oxidized zones, an important question arises. Why are there any other secondary Sb minerals at all? In part, the answer to this question comes from the fact that deeper in the oxidized zone, approaching the water table, redox potentials fall (Williams, 1990) and Sb(III) is stabilized with respect to Sb(V); Fe(II) ultimately becomes stable. It is thus evident that kinetic phenomena must be taken into account. That is to say, just how fast does $Sb(OH)_5^0$ react with goethite to form tripuhyite? In this connection, one important field observation is to hand (Diemar *et al*., 2009). At the Bayley Park prospect near Hillgrove, New South Wales, an unusual gossan cap to an oxidized, fault-hosted stibnite deposit was noted. Bright orange 'goethite' after stibnite and pyrite was found lining cavities in quartz. Standardless SEM EDS analyses of the 'goethite' gave major Fe and Sb and trace amounts of Si. However, powder X-ray measurements on

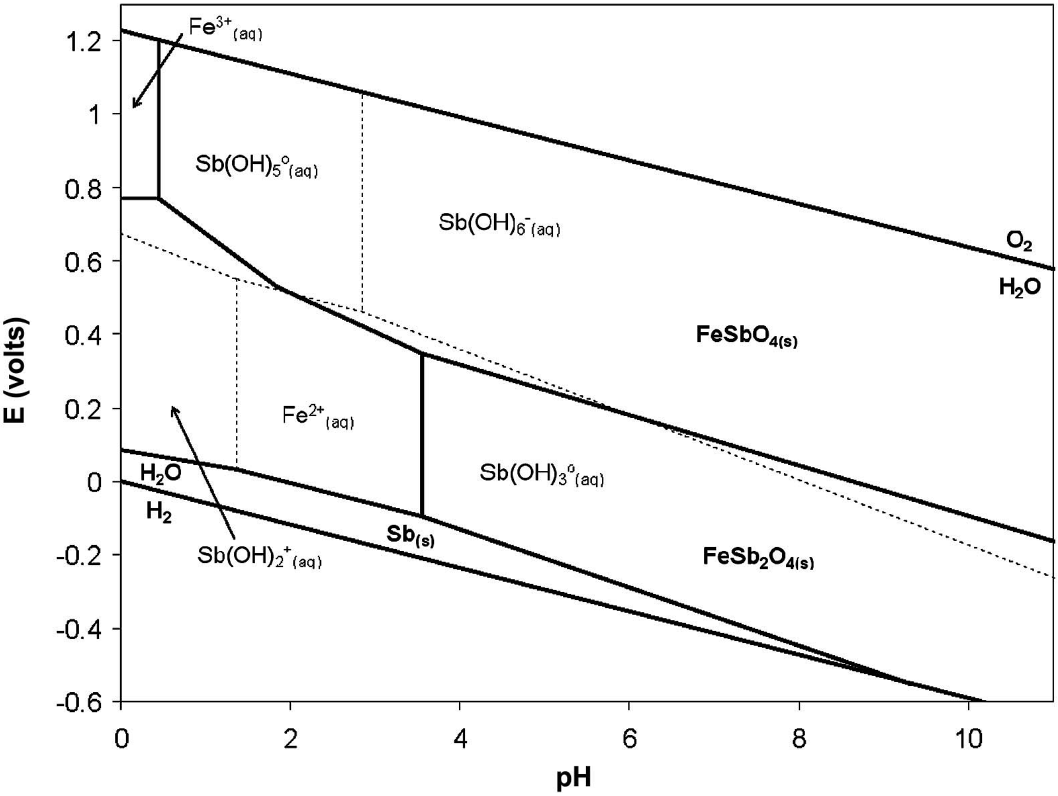

FIG. 1. Pourbaix diagram displaying stability fields of schafarzikite and tripuhyite with respect to dissolved iron species, calculated at 298.15 K and total dissolved concentrations of Sb and Fe of 10^{-6} mol dm^{-3} (bold lines). Areas of predominance of dissolved Sb species are separated by dashed lines.

the same material showed that the Fe- and Sb-bearing material was X-ray amorphous and the only crystalline phase that could be identified was quartz. Therefore it is evident that the transformation of goethite to tripuhyite in the presence of dissolved Sb may be quite slow. This in turn means that many secondary Sb mineral assemblages must be metastable in nature.

A second question then arises as to why tripuhyite and schafarzikite may have been overlooked in the past. The only conclusion that can be drawn is that the physical properties of tripuhyite (colour and habit) make visual identifications very difficult as it is hard to differentiate it from goethite or fine-grained hematite, minerals that are always associated with oxidized assemblages. This has already been noted by Majzlan *et al*. (2011). X-ray diffraction or other appropriate analytical methods must be used to identify tripuhyite, as has been shown by recent studies of a number of deposits in the New England region of New South Wales (Diemar *et al*., 2009), the Pearse prospect at Mineral Hill, New South Wales (P.A. Williams, unpublished data) and oxidized Sb-rich ores and tailings from deposits near Dúbrava, Slovakia (Klimko *et al*., 2010) and elsewhere in Slovakia (Majzlan *et al*., 2011). The recent discovery of nano-domains of tripuhyite in soils adjacent to Sb-rich mine tailings by Mitsunobu *et al*. (2011) illustrates just how elusive these minerals may be.

Conclusions

Tripuhyite has been shown to be one of the ultimate mineralogical sinks for Sb in the oxidized, supergene environment at redox potentials higher than those that stabilize schafarzikite. These findings build on the work of Diemar *et al*. (2009), who concluded that Sb was relatively immobile in the supergene zone. Other work remains to be carried out with respect to the Fe-bearing phases. It would be of interest to examine the adsorption of $Sb(OH)_6^-$ on goethite and amorphous Fe(III) oxyhydroxides and to study the kinetics of the transformation to tripuhyite. The recent findings concerning microscopic particles of 'non-stoichiometric' tripuhyite in a number of deposits (Klimko *et al*., 2010; Majzlan *et al*., 2011) and naturally occurring nano-domains of the mineral in soils (Mitsunobu *et al*., 2011) suggest that it would be profitable to explore solubility phenomena of these phases separately. Experimental work along these lines has begun in these laboratories and will be reported in due course.

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Appendix

In order to derive the thermodynamic data reported above and the stability field boundaries, a choice of stability constants and associated thermochemical quantities must be made. It is necessary and appropriate to set these out here so that other workers in the field can make appropriate adjustments to their own databases. Antimony species are discussed below. Values of $\Delta G_f^\ominus$ at 298.15 K for $H_2O(l)$ and $Fe^{2+}(aq)$ used in the calculations are those of Robie and Hemingway (1995); those of $Fe^{3+}(aq)$ and FeOOH(s, goethite) are taken from Parker and Khodakovskii (1995).

Stability relationships for dissolved species

The hydrolysis of Sb(III) in aqueous solution is remarkably simple. Baes and Mesmer (1976) summarized the data available at the time, pointing out that the solubility of $Sb_2O_3(s)$ can be adequately accounted for by the species $Sb(OH)_2^+(aq)$, $Sb(OH)_3^o(aq)$ and $Sb(OH)_4^-(aq)$ over the pH range from 0 to 14. It was also noted that less hydrolysed species could only exist in very acidic solutions and that polymer formation is insignificant at Sb(III) concentrations less than 0.1 M. Data reported subsequently are in excellent agreement with those of earlier workers. The solubility of orthorhombic $Sb_2O_3(s)$, equation A1, at 298.15 K was reported by Gayer and Garrett (1952) with lg $K = -4.28\pm0.08$. Solubility data for equation A1 spanning the range $278 \leqslant T \leqslant 398$ K (Schulze, 1883; Gayer and Garrett, 1952; Zotov *et al*., 2003) give a satisfactory Arrhenius plot and the value of Gayer and Garrett (1952) is adopted here. Sénarmontite, cubic $Sb_2O_3(s)$, is the thermodynamically stable polymorph of Sb_2O_3 and Zotov *et al*. (2003) derived the relationship lg $K = -2165.7/T + 2.28$ for equation A2 over the range $378 \leqslant T \leqslant 698$ K from solubility data. Extrapolation to 298.15 K gives lg $K = -4.98$.

$$0.5Sb_2O_3(\text{valentinite, orthorhombic, s}) + 1.5H_2O(l) \rightleftharpoons Sb(OH)_3^o(aq) \quad (A1)$$

$$0.5Sb_2O_3(\text{sénarmontite, cubic, s}) + 1.5H_2O(l) \rightleftharpoons Sb(OH)_3^o(aq) \quad (A2)$$

Filella and May (2003) estimated lg K values of -4.23 and -4.64 for equations A1 and A2, respectively. Given the strategy they adopted, these values are in very good agreement with those derived from solubility measurements. A reliable value for $\Delta G_f^\ominus(Sb(OH)_3^o$, aq, 298.15 K) of -644.4 ± 1.1 kJ mol^{-1} is based on the careful solubility work of Zotov *et al*. (2003). Baes and Mesmer (1976) used the solubility data of Gayer and Garrett (1952) and Mishra and Gupta (1968) to calculate equilibrium constants for equations A3 and A4 noting that the value for the former was consistent with the work of Schuhmann (1924). However, Mishra and Gupta (1968) conducted their experiments at 23ºC.

$$Sb(OH)_3^o(aq) + H^+(aq) \rightleftharpoons H_2O(l) + Sb(OH)_2^+(aq) \quad (A3)$$

$$Sb(OH)_3^o(aq) + H_2O(l) \rightleftharpoons Sb(OH)_4^-(aq) + H^+(aq) \quad (A4)$$

Values of lg K at 298.15 K for equations A3 and A4 are 1.41 and -11.82, respectively. Filella and May (2003) used an alternate strategy (May and Murray, 2000) to calculate corresponding values of 1.371 and -11.70, which are in good agreement with the above (note that there is an apparent sign error in their paper for the former). A recent experimental study by Zakaznova-Herzog and Seward (2006) confirms the above values with lg K at 298.15 K for (A3) and (A4) being 1.38 ± 0.01 and -11.82 ± 0.02, respectively. These values are adopted here. Equations A3 and A4 can be combined with $\Delta G_f^\ominus(Sb(OH)_3^o$, aq, 298.15 K) to give $\Delta G_f^\ominus$(298.15 K) values for the species $Sb(OH)_2^+(aq)$ and $Sb(OH)_4^-(aq)$ of -415.2 and -814.0 kJ mol^{-1}, respectively.

Data for less hydrolysed species of Sb(III), including $Sb_2(OH)_2^{4+}$, have also been calculated by Filella and May (2003) with accuracies stated to be difficult to estimate but typically 1 or 2 orders of magnitude worse than the stated precision to 4 significant figures. Sample calculations are useful to assess the potential importance of these species in geochemical settings. Appropriate constants given above can be used to derive equilibrium constants at 298.15 K for equations A5 to A7:

$$Sb(OH)_2^+(aq) + H^+(aq) \rightleftharpoons H_2O(l) + SbOH^{2+}(aq) \quad \lg K = 0.19 \quad (A5)$$

$$Sb^{3+}(aq) + H_2O(l) \rightleftharpoons SbOH^{2+}(aq) + H^+(aq) \quad \lg K = 1.21 \quad (A6)$$

$$2Sb(OH)_3^o(aq) + 4H^+(aq) \rightleftharpoons 4H_2O(l) + Sb_2(OH)_2^{4+}(aq) \quad \lg K = 3.545 \quad (A7)$$

With respect to monomeric species, their relative predominance can be simply assessed by reference to the magnitude of lg K. If $a(SbOH^{2+})$

= $a(\mathrm{Sb(OH)}_2^+)$ the pH = 0.19, and if $a(\mathrm{Sb}^{3+})$ = $a(\mathrm{SbOH}^{2+})$ the pH = −1.21. The predominance of $\mathrm{Sb_2(OH)}_2^{4+}$(aq) *vs.* $\mathrm{Sb(OH)}_3^{\mathrm{o}}$(aq) also depends upon concentrations of dissolved Sb(III). In this case, if $a(\mathrm{Sb_2(OH)}_2^{4+}) = a(\mathrm{Sb(OH)}_3^{\mathrm{o}})$ with assigned values of 10^{-5}, 10^{-3} and 10^{-1}, the pH is equal to −2.14, −1.64 and −1.14, respectively. Thus Sb^{3+}(aq) and $\mathrm{Sb_2(OH)}_2^{4+}$(aq) can only be present to any significant extent in extremely acid conditions such that negative values of pH prevail. These values can be achieved in poorly buffered oxidizing sulfide ore bodies (Williams, 1990; Nordstrom *et al.*, 2000), and thus SbOH^{2+}(aq) may be of limited significance in such settings, but only in very acidic conditions.

With respect to Sb(V), Past (1985) reported $E^{\ominus}$ = +0.363 V at 298.15 K for the reaction given in equation A8, based on electrochemical measurements in aqueous KOH solutions reported by Grube and Schweigardt (1923). Using the data above gives a value of $\Delta G_\mathrm{f}^{\ominus}(\mathrm{Sb(OH)}_6^-$, aq, 298.15 K) = −1218.2 kJ mol^{-1}. The first experimental study of the hydrolysis of Sb(V) in the literature, to our knowledge, is that of Lefebvre and Maria (1963). Baes and Mesmer (1976) recalculated their data to yield a value of lg *K*(298.15 K) = −2.72 for equation A9. This has been quoted repeatedly by subsequent workers and can be used to derive $\Delta G_\mathrm{f}^{\ominus}(\mathrm{Sb(OH)}_5^{\mathrm{o}}$, aq, 298.15 K) = −996.6 kJ mol^{-1}. The above calculations are entirely consistent with a recent study by Accornero *et al.* (2008), who found lg *K*(298.15 K) = −2.848 for equation A9.

$$\mathrm{Sb(OH)}_6^-(\mathrm{aq}) + 2\mathrm{H}^+(\mathrm{aq}) + 2e^- \rightleftharpoons \mathrm{Sb(OH)}_4^-(\mathrm{aq}) + 2\mathrm{H_2O(l)} \qquad (\mathrm{A8})$$

$$\mathrm{Sb(OH)}_5^{\mathrm{o}}(\mathrm{aq}) + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{Sb(OH)}_6^-(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq}) \qquad (\mathrm{A9})$$

It is known that Sb(V) hydrolyses at low pH to give high molecular weight polymeric species. Nevertheless, for the data reported in the substantive section of this paper and subsequent calculations, total Sb(V) concentrations are so low that polymeric ions may be ignored (Baes and Mesmer, 1976). Thus the only other species that might be important at very low pH is $\mathrm{Sb(OH)}_4^+$(aq). Filella and May (2003) calculated lg *K* = 24.61 for equation A10 at 298.15 K. From this, $\Delta G_\mathrm{f}^{\ominus}(\mathrm{Sb(OH)}_4^+$, aq, 298.15 K) = −741.0 kJ mol^{-1}. Equation A11 can now be evaluated. With $\Delta G_\mathrm{f}^{\ominus}(\mathrm{Sb(OH)}_5^{\mathrm{o}}$, aq, 298.15 K) = −996.6 kJ mol^{-1}, lg *K* = −3.24. A sample calculation based on this value is instructive in terms of the potential predominance of $\mathrm{Sb(OH)}_4^+$(aq) in solution. For $a(\mathrm{Sb(OH)}_4^+) = a(\mathrm{Sb(OH)}_5^{\mathrm{o}})$ and assuming $a(\mathrm{H_2O})$ = 1, $a(\mathrm{H}^+) = 10^{3.24}$. In other words $a(\mathrm{Sb(OH)}_4^+)$ can only assume any significance at very negative pH values. Such values are rarely met in the natural environment. Thus, as indicated by Baes and Mesmer (1976), the hydrolysis of Sb(V) in dilute solution is adequately accounted for by the two species $\mathrm{Sb(OH)}_5^{\mathrm{o}}$(aq) and $\mathrm{Sb(OH)}_6^-$(aq) over the entire pH range normally encountered in geochemical systems.

$$\mathrm{Sb(OH)}_4^+(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq}) + 2e^- \rightleftharpoons \mathrm{Sb(OH)}_3^{\mathrm{o}}(\mathrm{aq}) + \mathrm{H_2O(l)} \qquad (\mathrm{A10})$$

$$\mathrm{Sb(OH)}_5^{\mathrm{o}}(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq}) \rightleftharpoons \mathrm{Sb(OH)}_4^+(\mathrm{aq}) + \mathrm{H_2O(l)} \qquad (\mathrm{A11})$$

Stability relationships for solid phases

For some time the value $\Delta G_\mathrm{f}^{\ominus}(\mathrm{Sb_2O_3}$, s, valentinite, 298.15 K) = −626.4±3.0 kJ mol^{-1} has been accepted as being the most accurate (Wagman *et al.*, 1982) and this may be compared quite favourably with the more recent results of Zotov *et al.* (2003). These workers derived $\Delta G_\mathrm{f}^{\ominus}(\mathrm{Sb_2O_3}$, s, valentinite, 298.15 K) = −625.9±2.1 kJ mol^{-1} and $\Delta G_\mathrm{f}^{\ominus}(\mathrm{Sb_2O_3}$, s, sénarmontite, 298.15 K) = −633.2±2.1 kJ mol^{-1}; these values are adopted here. Free energy of formation data for valentinite and sénarmontite listed by Barin (1989) are clearly in error, as noted by Vink (1996).

The situation with respect to cervantite, α-$\mathrm{Sb_2O_4}$, is somewhat more problematic. The generally accepted $\Delta G_\mathrm{f}^{\ominus}(\mathrm{Sb_2O_4}$, s, cervantite, 298.15 K) is −795.8 kJ mol^{-1} (Wagman *et al.*, 1982), but a range of values is found in the literature. Filella and May (2003) derived a value that is comparable with that given by Wagman *et al.* (1982) but the cycle of calculation is in part dependent upon the latter value itself. Two equations used in the calculation (A12 and A13) are based on the compilation of Past (1985), who noted that the standard electrode potentials were calculated from free energies and not experimental data.

$$2\mathrm{Sb_2O_4(s)} + 4\mathrm{H}^+(\mathrm{aq}) + 4e^- \rightleftharpoons \mathrm{Sb_4O_6(s)} + 2\mathrm{H_2O(l)} \qquad E^{\ominus} = 0.342\ \mathrm{V} \qquad (\mathrm{A12})$$

$$\mathrm{Sb_2O_5(s)} + 2\mathrm{H}^+(\mathrm{aq}) + 2e^- \rightleftharpoons \mathrm{Sb_2O_4(s)} + \mathrm{H_2O(l)} \qquad E^{\ominus} = 1.055\ \mathrm{V} \qquad (\mathrm{A13})$$

$$\mathrm{Sb_2O_3(s)\ (valentinite)} + 0.5\mathrm{O_2(g)} \rightleftharpoons \mathrm{Sb_2O_4(s)\ (cervantite)} \qquad (\mathrm{A14})$$

Shortly thereafter, Pankajavalli and Sreedharan (1987) reported experimental electrochemical data for the reaction given in equation A14, measured from 525 to 828 K. Extrapolation of their data gives $\Delta G_f^\ominus$(Sb$_2$O$_4$, s, cervantite, 298.15 K) = −754.5±1.61 kJ mol^{-1}, a result clearly at odds with the above. At first, one cannot be certain of whether the discrepancy is simply the result of extrapolation of high temperature data to 298.15 K or whether the derived value is the more accurate one. For this reason a series of separate calculations has been carried out. The Eh−pH boundaries calculated using the value of Wagman *et al*. (1982) give a very restricted stability field for sénarmontite and this is inconsistent with its common occurrence in the oxidized zones of Sb-rich orebodies. Use of the data of Pankajavalli and Sreedharan (1987) extends the stability field of sénarmontite, and is in agreement with its widespread occurrence. The published solubilities of cervantite (Konopik and Zwiauer, 1952) are consistent with the value of Pankajavalli and Sreedharan (1987), and not with that of Wagman *et al*. (1982). Thus it is apparent that the former must be more accurate, and it has been adopted here.

No reliable thermochemical data exist in the literature for members of the roméite group (Atencio *et al*., 2010). Nevertheless, Diemar *et al*. (2009) have reported limited solubility data for oxycalcioroméite, $Ca_2Sb_2O_7$, and oxyplumboroméite, $Pb_2Sb_2O_7$.