

Stabilities of byströmite, MgSb_2O_6 , ordoñezite, ZnSb_2O_6 and rosiaite, PbSb_2O_6 , and their possible roles in limiting antimony mobility in the supergene zone

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ABSTRACT

In order to clarify the roles that secondary minerals may have in determining the extent of dispersion of Sb in the supergene environment, syntheses and stability studies of the Sb(V) oxides byströmite, MgSb_2O_6 , ordoñezite, ZnSb_2O_6 and rosiaite, PbSb_2O_6 , have been undertaken. Solubilities in aqueous HNO_3 were determined at 298.2 K and the data obtained used to calculate values of ΔG_f^\ominus at the same temperature. The derived ΔG_f^\ominus (s, 298.2 K) values for MgSb_2O_6 ($-1554.1 \pm 3.6 \text{ kJ mol}^{-1}$), ZnSb_2O_6 ($-1257.0 \pm 2.6 \text{ kJ mol}^{-1}$) and PbSb_2O_6 ($-1154.2 \pm 2.6 \text{ kJ mol}^{-1}$) have been used in subsequent calculations to determine their relative stabilities and relationships with other secondary Sb minerals.

KEYWORDS: byströmite, ordoñezite, rosiaite, antimony, solubility, mobility, chemical mineralogy, supergene zone.

Introduction

OUR understanding of the mobility of Sb in oxidizing environments has been highlighted in a number of recent reviews (Filella *et al.*, 2002*a,b*, 2009; Filella and May, 2003; Filella and Williams, 2012; Roper *et al.*, 2012). These, together with the findings of Leverett *et al.* (2012), who described tripuhyite, FeSbO_4 , to be one of the ultimate mineralogical sinks for Sb in the supergene environment, indicate that Sb is very immobile with respect to chemical dispersion. This conclusion is in accord with the studies reported by a series of other workers (Majzlan *et al.*, 2011; Courtin-Nomade *et al.*, 2012; Mitsunobu *et al.*, 2010, 2011, 2013). Of the 200 primary Sb minerals that exist all are essentially insoluble in water. Upon exposure to near-surface conditions at ambient temperatures however, the primary phases are unstable and react to form

secondary minerals with appreciably greater solubilities. Nevertheless, although a clearer understanding of Sb mobility has been gained, solubility and thermochemical data for many of the secondary Sb minerals are still inadequate or not available. It has been noted (Roper *et al.*, 2012) that a complete understanding of the roles that secondary Sb minerals play in the dispersion of Sb in oxidizing environments is crucial to understanding the true nature of Sb mobility.

Minerals containing Sb(V) are of particular importance as it is commonly incorporated in tripuhyite and the very stable minerals of the roméite group, $\text{M}_x\text{Sb}_2(\text{O},\text{OH})_7$, rely on this species. Interest extends to brandholzite, $\text{Mg}[\text{Sb}(\text{OH})_6]_2 \cdot 6\text{H}_2\text{O}$, as a possible hydrated precursor to the rare secondary phase byströmite, MgSb_2O_6 , and the stoichiometrically related minerals ordoñezite, ZnSb_2O_6 and rosiaite, PbSb_2O_6 . Although these minerals have been reported to occur in only a few deposits, they may well have been consistently overlooked, as has been pointed out for tripuhyite and schafarzi-

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kite, FeSb_2O_4 (Leverett *et al.*, 2012). Byströmite is known from three occurrences. In the La Fortuna and San Jose mines, El Antimonio, Mexico, it was noted to be associated intimately with roméite-group minerals. Mason and Vitaliano (1952) noted that some stibiconite, $(\text{Sb,Ca})\text{Sb}_2(\text{O,OH})_7$, was always present even in the purest samples. Ordoñezite also occurs in the La Fortuna mine (Mason and Vitaliano, 1952). Aside from the Mexican deposits, byströmite is known only from the Silberne Rose mine, Brandholz, Germany, where it is associated with roméite-group minerals and brandholzite. Little is known about the mode of formation of byströmite, but its synthesis and crystal structure have been known for some time (Byström *et al.*, 1941; Kasenov *et al.*, 1996). Mason and Vitaliano (1952) proposed that byströmite originated from metasomatic action of magnesium-bearing solutions on stibiconite which was supported by the comparatively local distribution of byströmite at El Antimonio, occurring in only a few veins. However, it is almost certainly secondary in origin, undoubtedly for the Silberne Rose mine where it is associated with a suite of common secondary Sb minerals (Meier, 1995). Of significant mineralogical interest is the potential solid solution between byströmite and ordoñezite and its implications for the stability of brandholzite. Byströmite and ordoñezite are isomorphous, space group $P4_2/mnm$ with $a = 4.68, 4.668(2)$ and $c = 9.21, 9.269(6)$ Å, respectively (Byström *et al.*, 1941; Ercit *et al.*, 2002).

The Zn analogue of brandholzite has never been reported to occur naturally, although the Ni^{2+} analogue, bottinoite, is well known. Solubility data for both brandholzite and bottinoite were determined by Deimar *et al.* (2009), who concluded that the minerals' rarity was probably due to their appreciable solubilities combined with the tendency of larger cations to preferentially form pyrochlore-type roméite-group minerals. Brandholzite has been reported only twice. At the type locality, the Silberne Rose mine, it is an alteration product of stibnite (Friedrich *et al.*, 2003). It also occurs in the Křižnica mine, Slovak Republic, which carries a complex primary Sb assemblage (Sejkora *et al.*, 2007). Here, brandholzite is commonly associated with pyrite, stibnite, sénarmonite, roméite-group minerals, gypsum, native sulfur and Sb-rich Fe(III) oxyhydroxides.

At the type locality, the Santin mine, Guanajuato, Mexico, ordoñezite occurs in highly altered veins carrying cassiterite (Switzer and

Foshag, 1955) and Ercit *et al.* (2002) noted the same association at Sapioris, Durango, Mexico. The remaining five reported localities for the mineral carry common assemblages of secondary oxidized Sb minerals, specifically roméite-group minerals. Ordoñezite is associated with zapatalite, $\text{Cu}_3\text{Al}_4(\text{PO}_4)_3(\text{OH})_9 \cdot 4\text{H}_2\text{O}$ and chenevixite, $\text{Cu}_2\text{Fe}_2(\text{AsO}_4)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$, in the La Fortuna mine (Mason and Vitaliano, 1952). This is the only reported occurrence in which both byströmite and ordoñezite appear in the same assemblage, and thus specific conditions or mineralizing events must dictate their formation. Ordoñezite has also been reported from a number of deposits associated with common secondary Sb minerals (Schmutz *et al.*, 1986; Pawlowski, 1991; Schnorrer-Köhler, 1986; Northrop, 1996; Vajdak, 2008).

Despite the fact that the Pb member of the roméite group, bindheimite, is a very common secondary mineral, rosielite is known from several deposits. Its synthesis and crystal structure were known prior to it being recognized as a natural mineral. Rosielite is not isomorphous with byströmite and ordoñezite and is hexagonal, space group $P\bar{3}1m$, $a = 5.295(1)$ and $c = 5.372(1)$ Å (Hill, 1987). It was described originally as a mineral from the Tafone mine, Manciano, Italy (Basso *et al.*, 1996), where it is associated with a suite of commonly occurring secondary minerals, notably with bindheimite. Similar associations are noted at the Bwlch mine, Deganwy, Wales (Meli, 1999; Ryback and Francis, 2001). In the Clara mine, Oberwolfach, Germany and the Monte Avanza mine, Forni Avoltri, Italy, rosielite is described as an alteration product of tetrahedrite (Blass and Graf, 1997; Dondi *et al.*, 1995) and associations of more exotic species, namely the secondary Cu-Sb minerals camerolaite, $\text{Cu}_4\text{Al}_2[\text{HSbO}_4, \text{SO}_4](\text{OH})_{10}(\text{CO}_3) \cdot 2\text{H}_2\text{O}$, chalcophyllite, $\text{Cu}_{18}\text{Al}_2(\text{AsO}_4)_4(\text{SO}_4)_3(\text{OH})_{24} \cdot 36\text{H}_2\text{O}$ and cualstibite, $\text{Cu}_2\text{Al}[\text{Sb}(\text{OH})_6](\text{OH})_6$, at Monte Avanza appear to be related directly to the oxidation of primary tetrahedrite as the source of Sb.

Conditions of formation for byströmite, ordoñezite and rosielite appear to be characteristic of the particular deposit type and/or mineralizing event, and their possible control on supergene Sb mobility is apparent from their strict localization in the deposits mentioned above. Here we report syntheses, solution and stability studies of byströmite, ordoñezite and rosielite, together with derived values of $\Delta G_f^\circ(\text{s}, 298.2 \text{ K})$ for the

minerals. Although synthetic pathways have been known for some time (Bystrom *et al.*, 1941; Hill, 1987), the only thermochemical data available in the literature are those of Kasenov *et al.*, (1996) who reported experimental measurements of the heat capacities of a series of alkaline earth antimonates and used these to derive S° (298.2 K) data. In addition, estimates of ΔH_f° (298.2 K) were obtained by comparison to analogous arsenates. These were used to calculate $\Delta G_f^{\circ}(\text{MgSb}_2\text{O}_6, \text{s}, 298.2 \text{ K}) = -1468.5 \text{ kJ mol}^{-1}$. Nevertheless, it does appear that while the heat capacity data are sound, there is some doubt concerning the methods used to derive ΔH_f° data, and thus a reinvestigation of the thermochemical data for byströmite has been undertaken. The results have been used to extend a geochemical model for Sb behaviour in the supergene zone in the vicinity of oxidizing Sb deposits.

Experimental

Syntheses

Byströmite and ordoñezite were synthesized following the method of Bystrom *et al.* (1941). Stoichiometric ratios (1:1) of Sb_2O_3 (5.8301 g, 0.02 mol) and MgO (0.8062 g, 0.02 mol), and Sb_2O_3 (5.8300 g, 0.02 mol) and ZnO (1.6279 g, 0.02 mol) for byströmite and ordoñezite, respectively, were mixed thoroughly by grinding. The mixtures were placed in a fused silica boat and heated in a tube furnace open to the atmosphere at $1273 \pm 10 \text{ K}$ for 48 h. The samples were then removed and reground before being placed back in the fused silica boat and heated at the same temperature for another 48 h to ensure complete reaction. The product obtained in both cases was a pale grey, crystalline powder. The product was suspended in aqueous 0.1 M HNO_3 at room temperature for 24 h to dissolve any residual starting materials. It was then collected at the pump, washed with water then acetone and sucked dry.

Rosiaite was synthesized following the procedure outlined by Hill (1987). Stoichiometric ratios (1:1) of PbO (2.2316 g, 0.01 mol) and Sb_2O_3 (2.9154 g, 0.01 mol) were mixed thoroughly by grinding, placed in a fused silica boat and heated in a tube furnace open to the atmosphere at $1125 \text{ K} \pm 10 \text{ K}$ for 24 h. The sample was removed and reground before being heated at the same temperature for 7 days. The product obtained was an off-white crystalline powder and was isolated as described above.

Powder X-ray diffraction (XRD) studies of the products were carried out using a Philips PW1825/20 powder diffractometer (Ni-filtered $\text{CuK}\alpha_1$ radiation, $\lambda = 1.5406 \text{ \AA}$, 40 kV, 30 mA). Traces were produced between 5 and $70^\circ 2\theta$, with a step size of 0.02° and a rate of $1.2^\circ \text{ min}^{-1}$. Diffraction Technology Data processing software (*Traces Version 6*) and JCPDS-ICDD data base files were used to identify the phases produced.

Solubility studies

Solubility studies were undertaken using sealed 250 cm^3 conical Quickfit^R flasks maintained at $25.0 \pm 0.2^\circ\text{C}$ in a thermostatted water bath. Measurements of pH were made using a Radiometer PHM220 apparatus fitted with a combination electrode. Subsequent analyses showed that all three minerals dissolve congruently in aqueous HNO_3 . The minerals ($\sim 0.1 \text{ g}$) were added to a series of conical flasks containing 100 cm^3 of standardized HNO_3 ; 0.1053 M for byströmite and ordoñezite, and 0.0988 M for rosiaite. The flasks were left for 14 weeks during which time the pH of a paired flask was monitored periodically until no change was detected. In all cases, equilibrium was achieved after 5 weeks. Resulting solutions were filtered through a Whatman^R GF/F fibreglass filter and collected in clean PET bottles. Dissolved Mg/Sb, Zn/Sb and Pb/Sb concentrations were determined using ICP-MS with matched standards.

Results and discussion

Syntheses

High-purity samples of byströmite, ordoñezite and rosiaite were obtained in essentially quantitative yield. Powder XRD gave no evidence for any contaminating phase. Unit-cell parameters were refined using the program *LAPOD* (Langford, 1973) and gave $a = 4.664(3)$, $c = 9.261(8) \text{ \AA}$ for byströmite, $a = 4.632(1)$, $c = 9.206(3) \text{ \AA}$ for ordoñezite and $a = 5.297(1)$, $c = 5.372(1) \text{ \AA}$ for rosiaite. These results are in excellent agreement with those reported elsewhere (Byström *et al.*, 1941; Hill, 1987; Ercit *et al.*, 2002).

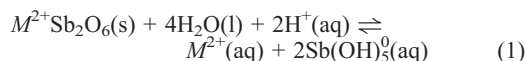
Solution studies

Solubility data for the three minerals are reported in Table 1. All three phases are comparatively insoluble and dissolve congruently in aqueous

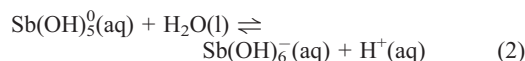
TABLE 1. Equilibrium solubilities and pH values for the mineral dissolution experiments at 298.2 K.

Dissolution of byströmite in aqueous 0.1053 M HNO ₃ (<i>n</i> = 6)			
Mean [MgSb ₂ O ₆]/ 10 ⁻⁴ mol dm ⁻³	Range [MgSb ₂ O ₆]/ 10 ⁻⁴ mol dm ⁻³	Mean pH	Range pH
2.20 ± 0.18	2.14–2.38	1.134 ± 0.005	1.130–1.139
Dissolution of ordoñezite in aqueous 0.1053 M HNO ₃ (<i>n</i> = 6)			
Mean [ZnSb ₂ O ₆]/ 10 ⁻⁵ mol dm ⁻³	Range [ZnSb ₂ O ₆]/ 10 ⁻⁵ mol dm ⁻³	Mean pH	Range pH
5.16 ± 0.68	4.68–5.85	1.134 ± 0.002	1.133–1.136
Dissolution of rosiäite in aqueous 0.0996 M HNO ₃ (<i>n</i> = 4)			
Mean [PbSb ₂ O ₆]/ 10 ⁻⁶ mol dm ⁻³	Range [PbSb ₂ O ₆]/ 10 ⁻⁶ mol dm ⁻³	Mean pH	Range pH
6.01 ± 1.55	5.09–7.56	0.860 ± 0.006	0.857–0.866

HNO₃. The dissolution of the minerals is expressed in equation 1, where $M^{2+} = \text{Mg}^{2+}$, Zn^{2+} , Pb^{2+} .



The pH at equilibrium (1.134, Mg^{2+} and Zn^{2+} ; 0.860, Pb^{2+}) was used in the determination of ion-speciation patterns using the program *COMICS* (Perrin and Sayce, 1967). A reliable $\lg K$ value for equation 2 at 298.2 K of -2.848 at $I = 0$ was reported recently by Accornero *et al.* (2008). Correction to $I = 0.1053$ mol dm⁻³ (Mg^{2+} and Zn^{2+} runs) and 0.0996 mol dm⁻³ (Pb^{2+}) by the method of Baes and Mesmer (1976), yields $\lg K(298.2 \text{ K}) = -2.611$ and -2.613 , respectively. From these data, the concentrations of $\text{Sb}(\text{OH})_5^0(\text{aq})$ are 2.204×10^{-4} , 4.993×10^{-5} and 5.904×10^{-6} mol dm⁻³ for the Mg^{2+} , Zn^{2+} and Pb^{2+} mineral solutions, respectively. Negligible amounts of $\text{Sb}(\text{OH})_6^-(\text{aq})$ are present in solution.



The speciation of Mg^{2+} and Zn^{2+} is straightforward, both presenting in free ionic form; concentrations of hydrolysed species are negligible at the given values of pH and thus the concentrations of $\text{Mg}^{2+}(\text{aq})$ and $\text{Zn}^{2+}(\text{aq})$ are 1.102×10^{-4} and 2.497×10^{-5} mol dm⁻³ for the solutions containing byströmite and ordoñezite, respectively. The speciation of Pb^{2+} presents as two significant species, $\text{Pb}^{2+}(\text{aq})$ and $\text{PbNO}_3^+(\text{aq})$. A reliable $\lg K$ value of $\lg K(298.2 \text{ K}) = 1.17$ at $I = 0$ was reported by Smith and Martell (1976) for equation 3. Correction to $I = 0.0996$ mol dm⁻³

by the method of Baes and Mesmer (1976), yields $\lg K(298.2 \text{ K}) = 0.850$. From this, for the equilibrated solution containing rosiäite, concentrations of $\text{Pb}^{2+}(\text{aq})$ and $\text{PbNO}_3^+(\text{aq})$ are 1.741×10^{-6} and 1.227×10^{-6} mol dm⁻³, respectively, were obtained.



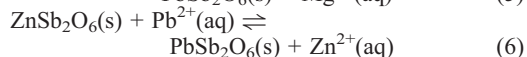
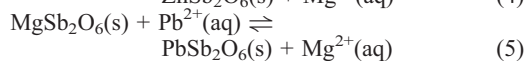
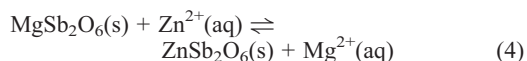
Individual ion activity coefficients were calculated using the Davis extension of the Debye-Hückel equation at 298.2 K, $\lg \gamma = -0.5085z^2(\sqrt{I}/(1+\sqrt{I}) - 0.3I)$. For byströmite and ordoñezite, $I = 0.1053$ mol dm⁻³, $\gamma^{2+} = 0.37$ and $\gamma^{\pm} = 0.78$. For rosiäite, at $I = 0.0996$ mol dm⁻³, $\gamma^{2+} = 0.37$ and $\gamma^{\pm} = 0.78$. In all instances, γ^0 is taken to be unity. These results were used to calculate $\lg K$ values for equation 1 of -9.44 ± 0.10 , -11.37 ± 0.10 and -14.92 ± 0.10 for the Mg^{2+} , Zn^{2+} and Pb^{2+} minerals, respectively, and associated values of ΔG_r^0 . Values of $\Delta G_r^0(298.2)$ for $\text{Mg}^{2+}(\text{aq})$, $\text{Zn}^{2+}(\text{aq})$, $\text{Pb}^{2+}(\text{aq})$, $\text{Sb}(\text{OH})_5^0(\text{aq})$ and $\text{H}_2\text{O}(\text{l})$ listed in Table 2 then gave $\Delta G_r^0(\text{MgSb}_2\text{O}_6, \text{s}, 298.2 \text{ K}) = -1554.1 \pm 3.6$ kJ mol⁻¹, $\Delta G_r^0(\text{ZnSb}_2\text{O}_6, \text{s}, 298.2 \text{ K}) = -1257.0 \pm 2.6$ kJ mol⁻¹ and $\Delta G_r^0(\text{PbSb}_2\text{O}_6, \text{s}, 298.2 \text{ K}) = -1154.2 \pm 2.6$ kJ mol⁻¹. Estimated errors take into account the analytical error of the solubility experiments and errors quoted for the thermochemical data used, including an estimated error of ± 1.0 kJ mol⁻¹ for $\Delta G_r^0(\text{Sb}(\text{OH})_5^0, \text{aq}, 298.2 \text{ K})$ (Roper *et al.*, 2012). It is noted that the derived value of byströmite by Kasenov *et al.*, (1996) and the value derived herein differ by some 86 kJ mol⁻¹, and this is attributed to the estimations used by Kasenov *et al.* (1996) to derive ΔH_f^0 for the mineral. This approach is

STABILITIES OF BYSTRÖMITE, ORDOÑEZITE AND ROSIAITE

TABLE 2. Thermodynamic quantities used in the calculations (298.2 K).

		$\Delta G_f^\ominus/\text{kJ mol}^{-1}$	Reference
Byströmite	MgSb ₂ O ₆ (s)	-1468.5	Kasenov <i>et al.</i> (1996)
	MgSb ₂ O ₆ (s)	-1554.1 ±3.6	<i>this study</i>
Ordonezite	ZnSb ₂ O ₆ (s)	-1257.0 ±2.6	<i>this study</i>
Rosiaite	PbSb ₂ O ₆ (s)	-1154.2 ±2.6	<i>this study</i>
Brandholzite	Mg[Sb(OH) ₆] ₂ ·6H ₂ O	-4358.4 ±3.4	Diemar <i>et al.</i> (2009)
Tripuhyite	FeSbO ₄ (s)	-836.8 ±2.2	Leverett <i>et al.</i> (2012)
Goethite	FeOOH(s)	-488.6 ±1.7	Parker and Khodakovskii (1995)
	H ₂ O(l)	-237.1 ±0.1	Cox <i>et al.</i> (1989)
	Mg ²⁺ (aq)	-455.4 ±0.6	Cox <i>et al.</i> (1989)
	Zn ²⁺ (aq)	-147.3 ±0.2	Cox <i>et al.</i> (1989)
	Pb ²⁺ (aq)	-24.2 ±0.2	Cox <i>et al.</i> (1989)
	Sb(OH) ₃ (aq)	-996.6 ±1.0	Roper <i>et al.</i> (2012)

clearly not precise enough. The value determined in this study has been adopted for all calculations regarding byströmite.



Relationships between byströmite, ordoñezite and rosiaite are described by equations 4–6, for which $\Delta G_r^\ominus(298.2 \text{ K}) = -11.0, -31.3$ and

$-20.3 \text{ kJ mol}^{-1}$ and correspond to $\lg K$ values of +1.93, +5.53 and +3.60, highlighting the increase in stability attributed to the replacement of the cation in the M^{2+} site by Mg, Zn and Pb, successively. Thus, thermodynamic stability increases in the order $\text{Mg} < \text{Zn} < \text{Pb}$, with an inherent structure change in rosiaite, presumably to accommodate the larger cation in the lattice. The boundary conditions for the transformation of one mineral into another is shown in Fig. 1.

In natural settings, byströmite would be a product of the oxidation of sénarmonite/valentinite, Sb₂O₃, or cervantite, Sb₂O₄, in a

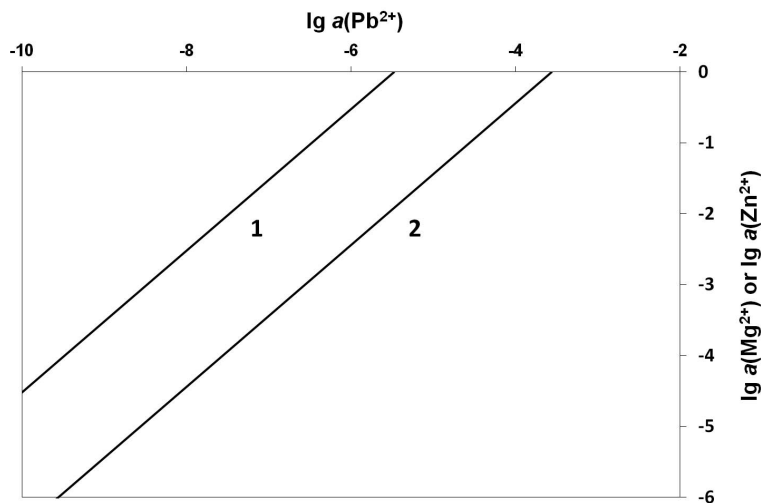


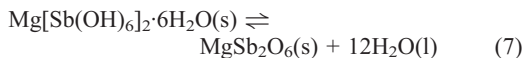
FIG. 1. Relationships of the $M^{2+}\text{Sb}_2\text{O}_6$ phases, as a function of $\lg a(\text{Pb}^{2+})$ vs. $\lg a(\text{Mg}^{2+})$ or $\lg a(\text{Zn}^{2+})$. Boundary conditions are for (1) $\text{PbSb}_2\text{O}_6 - \text{MgSb}_2\text{O}_6$ and (2) $\text{PbSb}_2\text{O}_6 - \text{ZnSb}_2\text{O}_6$. In both cases the stability field of PbSb_2O_6 lies to the right of the boundary.

system containing Mg^{2+} and significantly depleted in not only Zn^{2+} and Pb^{2+} , but also Ca^{2+} and Fe^{3+} , which serve to stabilize roméite-group minerals and triphuyite. A similar situation therefore presents for the formation of ordoñezite, which requires near exhaustion of aqueous Pb^{2+} and a relatively concentrated Zn^{2+} solution to form. It is thus concluded that byströmite is most likely to form in systems essentially free of both Pb and Zn. Thus, at El Antimonio where both byströmite and ordoñezite have been reported, although not in direct association, there are two explanations. Ordoñezite formed originally in a localized environment from a solution where $a(\text{Zn}^{2+}) > 10^{-5}$, or byströmite reacted to form ordoñezite in the presence of a Zn-rich solution. The lack of association of these two phases at the locality suggests that a localized environment contributed to the formation of ordoñezite.

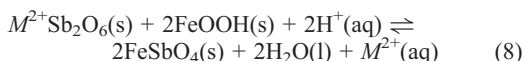
The situation with rosiaite is more complex. The stable roméite-group mineral bindheimite is easily made from solutions of Pb^{2+} and $\text{Sb}(\text{OH})_6^-$ (Diemar *et al.*, 2009). Thus the question arises as to why rosiaite did not form? At this stage we are not in a position to provide an answer until a reliable stability constant for bindheimite has been determined. However, the apparent rarity of rosiaite in contrast with bindheimite suggests that the former may be metastable. Investigations are underway in our laboratory to elucidate the

solubility behaviour of the roméite group of minerals.

Note the relationship of byströmite with brandholzite, as expressed by equation 7. We reiterate that at the type locality both minerals are present.



Using the derived ΔG_f^\ominus value reported by Diemar *et al.* (2009) for brandholzite, $\Delta G_f^\ominus(\text{Mg}[\text{Sb}(\text{OH})_6]_2 \cdot 6\text{H}_2\text{O}, \text{s}, 298.2 \text{ K}) = -4358.4 \pm 3.4 \text{ kJ mol}^{-1}$, $\Delta G_f^\ominus(298.2 \text{ K})$ for equation 7 is $-23.76 \text{ kJ mol}^{-1}$. Thus, the thermodynamically stable phase at 298.2 K is byströmite and kinetic effects must account for the few reported occurrences of brandholzite, unless the stabilities of one or both of the minerals are influenced profoundly by temperature. Diemar *et al.* (2009) found no evidence whatsoever for the formation of byströmite and we see no evidence for the formation of brandholzite in the experiments described above. It may be simply the case that the rate of transformation of brandholzite to byströmite is very slow at 298.2 K.



Finally, any influence that byströmite, ordoñezite or rosiaite might have on the mobility of Sb, must be viewed against the possible formation of

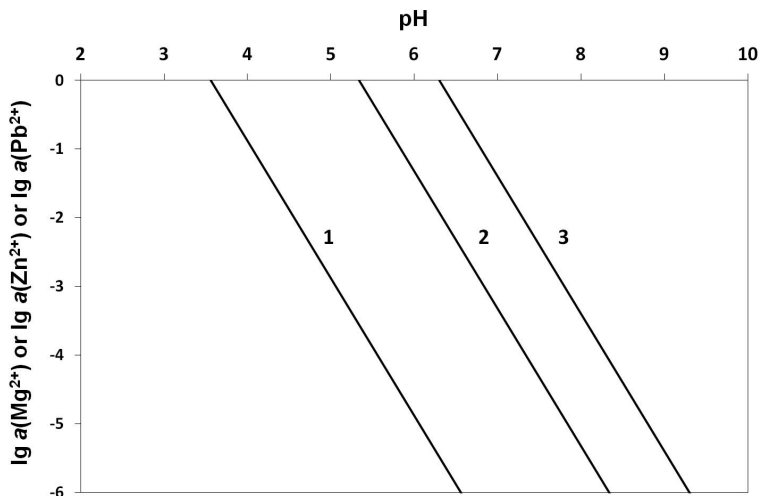


FIG. 2. Relationships of the $\text{M}^{2+}\text{Sb}_2\text{O}_6$ phases with triphuyite and goethite as a function of pH. Boundary conditions are for equation 8: (1) $\text{FeSbO}_4 - \text{PbSb}_2\text{O}_6 + \text{FeOOH}$; (2) $\text{FeSbO}_4 - \text{ZnSb}_2\text{O}_6 + \text{FeOOH}$; (3) $\text{FeSbO}_4 - \text{MgSb}_2\text{O}_6 + \text{FeOOH}$. The triphuyite field lies to the left of each line.

tripuhyite (Leverett *et al.*, 2012). Relationships of these phases can be described by equation 8, where $M^{2+} = \text{Mg}^{2+}$, Zn^{2+} or Pb^{2+} . Using the ΔG_f^\ominus values for goethite and tripuhyite given in Table 2, equation 8 yields $\Delta G_f^\ominus(298.2 \text{ K})$ values of -72.0 , -61.0 and $-40.7 \text{ kJ mol}^{-1}$, corresponding to $\lg K = +12.6$, $+10.7$ and $+7.1$ for the Mg^{2+} , Zn^{2+} and Pb^{2+} congeners, respectively. Relative stabilities of the minerals are depicted in Fig. 2. Under conditions generally occurring in natural settings, rosiaite may exert a significant control on Sb mobility under circumneutral pH conditions. However, it is impossible to conceive natural conditions that would render ordoñezite or byströmite thermodynamically stable with respect to tripuhyite. Ultimately, they must be metastable, transient under ambient conditions, and their existence dependent on the rate of nucleation of tripuhyite. Conversely, conditions of formation of rosiaite and goethite with respect to tripuhyite at 298.2 K (pH 6; $\lg a(\text{Pb}^{2+}) > -6$) are such that the formation of rosiaite in natural settings is achievable under the conditions described and over the normal pH range of the natural environment. Again, however, its role in limiting chemical dispersion of Sb in the supergene zone will depend on its own stability with respect to that of bindheimite.

This study has established the conditions under which the rare minerals byströmite, ordoñezite and rosiaite can form under ambient conditions in the oxidized zones of Sb-bearing deposits. Rather special solution conditions must be observed for them to be stable phases and thus it is improbable that they can exert any significant effect, in relation to other secondary Sb species, in the immobilization of Sb in the supergene environment. This conclusion is significant to the extent that it provides a more refined focus on other secondary Sb phases that do play more important roles in buffering dissolved Sb species in solution.

References

- Accornero, M., Marini, L. and Lelli, M. (2008) The dissociation constant of antimonic acid at 10–40°C. *Journal of Solution Chemistry*, **37**, 785–800.
- Baes, C.F., Jr and Mesmer, R.E. (1976) *The Hydrolysis of Cations*. Wiley Interscience, New York.
- Basso, R., Lucchetti, G., Zefiro, L. and Palenzona, A. (1996) Rosiaite, PbSb_2O_6 , a new mineral from the Cetine mine, Siena, Italy. *European Journal of Mineralogy*, **8**, 487–492.
- Blass, G. and Graf, H.W. (1997) Neue Mineralienfunde und Bestimmungen (17). *Mineralien Welt*, **8(2)**, 16–19.
- Byström, A., Hök, B. and Mason, B. (1941) The crystal structure of zinc metantimonate and similar compounds. *Arkiv for Kemi, Mineralogi och Geologi*, **15B**, 1–8.
- Courtin-Nomade, A., Rakotoarisoa, O., Bril, H., Grybos, M., Forestier, L., Foucher, F. and Kunz, M. (2012) Weathering of Sb-rich mining and smelting residues: insight in solid speciation and soil bacteria toxicity. *Chemie der Erde – Geochemistry*, **72 (sup. 4)**, 29–39.
- Cox, J.D., Wagman, D.D. and Medvedev, V.A. (1989) *CODATA Key Values for Thermodynamics*. Hemisphere Press, New York.
- Diemar, G.A., Filella, M., Leverett, P. and Williams, P.A. (2009) Dispersion of antimony from oxidizing ore deposits. *Pure and Applied Chemistry*, **81**, 1547–1553.
- Dondi, M., Palenzona, A. and Puggioli, G. (1995) La mine de Mt Avanza, Forni Avoltri (Udine). *Rivista Mineralogica Italiana*, **19**, 125–136.
- Ercit, T.S., Foord, E.E. and Fitzpatrick, J.J. (2002) Ordoñezite from the Theodoso Soto mine, Sapioris, Durango, Mexico: new data and structure refinement. *The Canadian Mineralogist*, **40**, 1207–1210.
- Filella, M. and May, P.M. (2003) Computer simulation of the low-molecular-weight inorganic species distribution of antimony(III) and antimony(V) in natural waters. *Geochimica et Cosmochimica Acta*, **67**, 4013–4031.
- Filella, M. and Williams, P.A. (2012) Antimony interactions with heterogeneous complexants in waters, sediments and soils: a review of binding data for homologous compounds. *Chemie der Erde*, **72S4**, 49–65.
- Filella, M., Belzile, N. and Chen, Y.-W. (2002a) Antimony in the environment: a review focused on natural waters I. Occurrence. *Earth Science Reviews*, **57**, 125–176.
- Filella, M., Belzile, N. and Chen, Y.-W. (2002b) Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry. *Earth Science Reviews*, **59**, 265–285.
- Filella, M., Williams, P.A. and Belzile, N. (2009) Antimony in the environment: knowns and unknowns. *Environmental Chemistry*, **6**, 95–105.
- Friedrich, A., Mazzi, F., Wildner, M. and Tillmanns, E. (2003) Addendum: isotypism of $\text{Co}(\text{H}_2\text{O})_6[\text{Sb}(\text{OH})_6]_2$ with brandholzite and bottinoite. *American Mineralogist*, **88**, 462–463.
- Hill, R.J. (1987) Structure of PbSb_2O_6 and its relationship to the crystal chemistry of PbO_2 in antimonial lead-acid batteries. *Journal of Solid State Chemistry*, **71**, 12–18.
- Kasenov, B.K., Mukhanova, M.A., Kasenova, S.B. and

- Mustafin, E.S. (1996) The thermodynamic properties of the alkaline-earth metal antimonates. *Russian Journal of Physical Chemistry*, **70**, 18–20.
- Langford, J.I. (1973) Least-squares refinement of cell dimensions from powder data by Cohen's method. *Journal of Applied Crystallography*, **6**, 190–196.
- Leverett, P., Reynolds, J.K., Roper, A.J. and Williams, P.A. (2012) Tripuyhite and schafarzikite: two of the ultimate sinks for antimony in the natural environment. *Mineralogical Magazine*, **76**, 891–902.
- Mason, B. and Vitaliano, C.J. (1952) Byströmite, magnesium antimonate, a new mineral. *American Mineralogist*, **37**, 53–57.
- Majzlan, J., Lalinská, B., Chovan, M., Bläss, U., Brecht, B., Göttlicher, J., Steininger, R., Hug, K., Ziegler, S. and Gescher, J. (2011) A mineralogical, geochemical, and microbiological assessment of the antimony- and arsenic-rich neutral mine drainage tailings near Pezinok, Slovakia. *American Mineralogist*, **96**, 1–13.
- Meier, S. (1995) *Mineralfundstellen im Fichtelgebirge*. Eigenverlag, Marktredwitz, Germany.
- Meli, R. (1999) I minerali delle discariche e delle scorie del Fosso del Tafone (Grosseto). *Rivista Mineralogica Italiana*, **23**, 187–191.
- Mitsunobu, S., Takahashi, Y., Terada, Y. and Sakata, M. (2010) Antimony(V) incorporation into synthetic ferrihydrite, goethite, and natural iron oxyhydroxides. *Environmental Science & Technology*, **44**, 3712–3718.
- Mitsunobu, S., Takahashi, Y., Utsunomiya, S., Matthew, A.M., Terada, Y., Iwamura, T. and Sakata, M. (2011) Identification and characterization nanosized tripuyhite in soil near Sb mine tailing. *American Mineralogist*, **96**, 1171–118.
- Mitsunobu, S., Muramatsu, C., Watanabe, K. and Sakata, M. (2013) Behavior of antimony(V) during the transformation of ferrihydrite and its environmental implications. *Environmental Science & Technology*, **47**, 9660–9667.
- Northrop, S.A. (1996) *Minerals of New Mexico*, third edition, revised by F.A. LaBuzza. University of New Mexico Press, Albuquerque, USA.
- Parker, V.B. and Khodakovskii, I.L. (1995) Thermodynamic properties of the aqueous ions (2+ and 3+) of iron and the key compounds of iron. *Journal of Physical and Chemical Reference Data*, **24**, 1699–1745.
- Pawłowski, D. (1991) *Mineralfundstellen im Sauerland*. Weise Verlag, Munich, Germany.
- Perrin, D.D. and Sayce, I.G. (1967) Computer calculation of equilibrium concentrations in mixtures of metal ions and complexing species. *Talanta*, **14**, 833–842.
- Roper, A.J., Williams, P.A. and Fillela, M. (2012) Secondary antimony minerals: Phases that control the dispersion of antimony in the supergene zone. *Chemie der Erde*, **72S4**, 9–14.
- Ryback, G. and Francis, J.G. (2001) Rosiaite from Bwlch mine, Deganwy, Conwy, Wales. *Journal of the Russell Society*, **7**, 88.
- Schmutz, L., Bachmann, A., Eichen, R., Rüegg, H.-R. and Vogel, C. (1986) Antimonmineralien aus dem Malcantone-Tal. Vorkommen und Ausbildung. *Schweizer Strahler*, **7**, 249–289.
- Schnorrer-Köhler, G. (1986) Neue Minerale von der Schlackenhalde der ehemaligen Zinkhütte Genna in Letmathe/Sauerland. *Aufschluss*, **37(2)**, 55–67.
- Sejkora, J., Ozdín, D., Vitáloš, J., Tuček, P., Čejka, J. and Dud'á, R. (2007) Schafarzikite from the type locality Pernek (Malé Karpaty Mountains, Slovak Republic) revisited. *European Journal of Mineralogy*, **19**, 419–427.
- Smith, R.M. and Martell, A.E. (1976) *Critical Stability Constants. Volume 4. Inorganic Complexes*. Plenum Press, New York.
- Switzer, G. and Foshag, W.F. (1955) Ordoñezite, zinc antimonate, a new mineral from Guanajuato, Mexico. *American Mineralogist*, **40**, 64–69.
- Vajdak, J. (2008) New mineral finds in 2007. *Mineral News*, **24**, 14–15.