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The stability of the rare sodium antimonate, brizziite, and it’s role in Sb mobility

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ABSTRACT

Synthesis and solubility studies of brizziite, $NaSbO_3$, have been undertaken to determine the possible role of this rare secondary phase in the immobilization of Sb under supergene conditions and the conditions responsible for its formation in the supergene zone. Solubility studies were undertaken at $T = 298.15$ K. A value of ΔG_f°) ($NaSbO_3$, s, 298.15 K) = –806.66 ± 1.4 kJ mol^{-1} was derived. Calculations involving tripuhyite, $FeSbO_4$, byströmite, $MgSb_2O_6$, ordoñezite, $ZnSb_2O_6$ and rosiaite, $PbSb_2O_6$, show that brizziite is a thermodynamically stable phase only at negligible activities of Pb^{2+}(aq) at high pH and high salinity. Calculations involving mopungite $Na[Sb(OH)_6]$ combined with reported mineral associations suggest that mopungite is the thermodynamically unstable precursor to brizziite and its presence in natural settings must be due to kinetic stability. This explains why brizziite is such a rare secondary phase and therefore why it cannot exert any significant influence on the dispersion of Sb in the supergene environment.

Keywords: brizziite, antimony, solubility, stability, chemical mineralogy, supergene zone.

Introduction

As a part of a series of investigations of the solubility and stability of secondary Sb minerals, the rare mineral brizziite, $NaSbO_3$, has been examined in connection with the relationships of this rare phase with a number of more common secondary Sb minerals, thus allowing assessment of brizziite’s contribution to Sb dispersion in the supergene zone. Brizziite is known only from the Cetine mine, Tuscany, Italy, where it occurs as an alteration product of stibnite, Sb_2S_3, in a silicified limestone (Olmi and Sabelli, 1994). Reported associations are with stibiconite, $Sb^{3+}Sb_2^{5+}O_6(OH)$, mopungite, $NaSb(OH)_6$(s), ceteinite, $(K,Na)_{3-x}(Sb_2O_3)_3(SbS_3)_2(OH)_x\cdot 2.4H_2O$ and senarmontite, Sb_2O_3(s). However, the relationship of brizziite with mopungite, and further ceteinite–ottensite, is of particular interest. At the type locality, Green prospect, Lake district, Nevada, mopungite, $NaSb(OH)_6$(s), was found as an alteration product of stibnite with the more common secondary phases stibiconite, romeite, senarmontite and tripuhyite (Williams, 1985). A review of the literature displays similar mineral associations from several deposits in Tuscany, Italy. Le Cetine mine (Brizzi *et al.*, 1988; Preite, 1992), the Pereta Mine (Marzoni Fecia Di Cossato *et al.*, 1987) and the Tafone mine (Meli, 1999) all have reported associations of mopungite with cetineite and senarmontite. Brizzi and Meli (1990) also reported mopungite from La Selva Mine, Tuscany, Italy in a siliceous matrix containing metallic Sb. The chemical similiarities of brizziite and mopungite suggest a potential kinetic stability for one of the phases at ambient temperatures, similar to recent findings concerning byströmite and brandholzite, $Mg[Sb(OH)_6]_2\cdot 6H_2O$, (Roper *et al.*, 2014). The investigation of this possibility is reported below.

Experimental

Synthesis of brizziite

Brizziite was synthesized following the procedure of Ramirez-Meneses *et al.* (2007). Stoichiometric

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ratios (1:1) of Na_2CO_3 (4.3757 g, 0.0413 mol) and Sb_2O_3 (12.0400 g, 0.0413 mol) were mixed thoroughly using a mortar and pestle. Some 2.5 g of the mixture were placed in a fused silica boat and heated in a tube furnace at 1033 K ± 10 K for 120 hours. After cooling to room temperature, the product was obtained as a white crystalline powder, which was placed in aqueous 0.05 M Na_2CO_3 for 24 hours to dissolve any residual starting materials. The precipitate was then collected on GF/F grade filter paper, rinsed with water then acetone, and sucked dry.

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

Solubility of brizziite

Solubility studies were undertaken in sealed 250 cm^3 conical Quickfit^R flasks in a 25.0±0.2°C thermostatted water bath. Measurements of pH were made using a Radiometer ION450 apparatus fitted with a combination electrode calibrated as per the manufacturer's instructions.

For the congruent dissolution of brizziite, the carbonate-washed product (~0.1 g) was added to a conical flask with 100.00 cm^3 of standardized aqueous 0.0497 M Na_2CO_3. The flasks were left for 6 weeks whilst a paired flask was being monitored periodically for pH (~1 week) until no change was detected.

Equilibrium was achieved after 3 weeks but flasks were left longer to ensure no further changes occurred. Solutions were filtered using Whatman^R GF/F grade filter paper and the filtrates collected in clean PET bottles. Dissolved Sb concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) using matched standards.

Results and discussion

Synthesis of brizziite

High purity, single phase samples of brizziite were obtained in essentially quantitative yield using the methods described by Ramirez-Meneses *et al.* (2007). Unit-cell parameters for brizziite refined using *LAPOD* (Langford, 1973) were $a = 5.294(1)$, $c = 15.949(3)$ Å, and agree well with those reported by Wang *et al.* (1994), $a = 5.2901$, $c = 15.9260$ Å.

Solubility of brizziite

After equilibration in 0.0497 M Na_2CO_3, some solid brizziite remained and no other phase was detected by post-solubility powder X-ray diffraction (PXRD) analysis. Thus, for the purpose of solubility calculations we consider brizziite to dissolve congruently. Dissolved concentrations of Sb(V) determined by ICP-MS are reported in Table 1. The congruent dissolution can be expressed by equation 1.

$$\mathrm{NaSbO_3(s) + 3H_2O(l) \rightleftharpoons Sb(OH)_6^-(aq) + Na^+(aq)} \qquad (1)$$

The pH at equilibrium (10.890) was used in the determination of solution speciation using *COMICS*. A reliable lg K value for equation 2 of lg K(298.15 K) = –2.72 at $I = 0$ mol dm^{-3} was reported recently by Accornero *et al.* (2008). Correction to $I =$ 0.1491 mol dm^{-3} by the method of Baes and Mesmer (1976), yields lg K(298.15 K) = –2.601. Substitution into equation 2 indicates only $Sb(OH)_6^-(aq)$ under the experimental conditions employed. For equation 3 a reliable lg K value of lg K(298.15 K) = –14.2 at $I = 0$ mol dm^{-3} was reported by Baes and Mesmer (1976). Correction to $I = 0.1491$ mol dm^{-3} yields lg K(298.15 K) = –14.32. Thus negligible $NaOH^0(aq)$ is present. For equation 4 a reliable lg K value of lg K(298.15 K) = –3.67 at $I = 0$ mol dm^{-3} was also reported by Baes and Mesmer (1976). Correction to $I = 0.1491$ mol dm^{-3} yields lg K(298.15 K) = –4.026, indicating that, as expected, $CO_3^{2-}(aq)$ is the only significant carbonate species in solution at the pH used for the

TABLE 1. Dissolved metal concentrations for brizziite equilibrations.

Solution	[Sb]/ppm	[Sb]/mol dm^{-3}	pH
1	0.42	3.449×10^{-6}	10.880
2	0.41	3.367×10^{-6}	10.896
3	0.47	3.860×10^{-6}	10.885
4	0.39	3.203×10^{-6}	10.880
5	0.41	3.367×10^{-6}	10.899
Mean	0.42	3.449×10^{-6}	10.890
Error	±0.04	$\pm 3.29 \times 10^{-7}$	±0.010

TABLE 2. Thermodynamic quantities (ΔG_f^o) used in the calculations ($T = 298.15$ K).

Byströmite	$MgSb_2O_6(s)$	–1554.1 ± 3.6	Roper *et al.* (2014)
Ordoñezite	$ZnSb_2O_6(s)$	–1257.0 ± 2.6	Roper *et al.* (2014)
Rosiaite	$PbSb_2O_6(s)$	–1154.2 ± 2.6	Roper *et al.* (2014)
Mopungite	$Na[Sb(OH)_6](s)$	–1508.5	Blandamer *et al.* (1974)
Brizziite	$NaSbO_3(s)$	–806.38 ± 1.4	this study
Tripuhyite	$FeSbO_4(s)$	–836.8 ± 2.2	Leverett *et al.* (2012)
	$H_2O(l)$	–237.1 ± 0.1	Cox *et al.* (1989)
	$Na^+(aq)$	–261.5 ± 0.1	Cox *et al.* (1989)
	$Mg^{2+}(aq)$	–455.4 ± 0.6	Cox *et al.* (1989)
	$Zn^{2+}(aq)$	–147.3 ± 0.2	Cox *et al.* (1989)
	$Pb^{2+}(aq)$	–24.2 ± 0.2	Cox *et al.* (1989)
	$Sb(OH)_5^o(aq)$	–996.6	Roper *et al.* (2012)
	$Sb(OH)_6^-(aq)$	–1218.2	Roper *et al.* (2012)

equilibration runs.

$$Sb(OH)_5^0(aq) + H_2O(l) \rightleftharpoons Sb(OH)_6^-(aq) + H^+(aq) \qquad (2)$$

$$Na^+(aq) + H_2O(l) \rightleftharpoons NaOH^0(aq) + H^+(aq) \qquad (3)$$

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \qquad (4)$$

Individual ion activity coefficients were calculated using the Davis extension of the Debye-Hückel equation for 298.15 K, $\lg \gamma = –0.5085z^2(\sqrt{I}/(1+\sqrt{I}) – 0.3I)$. For $I = 0.1491$ mol dm^{-3}, $\gamma^{2\pm} = 0.335$ and $\gamma^{\pm} = 0.761$; γ^o is taken to be unity. The activities of $a(Sb(OH)_6^-)$ and $a(Na^+)$ were calculated from the solubility data, yielding a value of lg K for equation 1 of –6.70 ± 0.10 corresponding to $\Delta G_r^o = 38.26 \pm 1.1$ kJ. Use of the appropriate data in Table 2 for equation 1 give $\Delta G_f^o(NaSbO_3$, s, 298.15 K$) = –806.66 \pm 2.5$ 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 $\Delta G_f^o(Sb(OH)_6^-$, aq, 298.15 K).

$$NaSbO_3(s) + 3H_2O(l) \rightleftharpoons Na\left[Sb(OH)_6\right](s) \qquad (5)$$

The relationship of brizziite and mopungite can be described by equation 5. We reiterate that only the single known locality of brizziite reports an association of the two minerals, but mopungite is also reported from a further six localities. The association highlights the likelihood of kinetic effects being important for their coexistence.

Using the derived ΔG_f^o value reported by Blandamer *et al.* (1974) for mopungite, $\Delta G_f^o(Na[Sb(OH)_6]$, s, 298.2 K$) = –1508.5$ kJ mol^{-1}, ΔG_r^o(298.2 K) for equation 5 is + 9.46 kJ. Thus, the thermodynamically stable phase at 298.2 K is brizziite and kinetic effects must account for the existence of mopungite, unless the stabilities of one or both of the minerals are influenced profoundly by temperature. In line with our previous findings of the Mg antimonate phases brandholzite and byströmite (Roper *et al.*, 2014), it must simply be the case that the rate of transformation of mopungite to brizziite is very slow at 298.2 K. The lack of brizziite in any of the six remaining localities hosting mopungite supports this notion.

$$2NaSbO_3(s) + M^{2+}(aq) \rightleftharpoons M^{2+}Sb_2O_6(s) + 2Na^+(aq) \qquad (6)$$

The relationships of brizziite with bystromite, ordoñezite and rosiaite are described by equation 6 where $M^{2+} = Mg^{2+}$, Zn^{2+} or Pb^{2+} respectively. Using the appropriate data from Table 2 gives ΔG_r^o values of –8.38, –19.38 and –39.68 kJ and subsequent lg K values of + 1.47, +3.39 and + 6.95 for $M^{2+} = Mg^{2+}$, Zn^{2+} or Pb^{2+} respectively. In accordance with equation 6, when Na^+(aq) activity $= 10^{-0.5}$ the formation of brizziite requires activities of Mg^{2+}, Zn^{2+} and Pb^{2+} less than $10^{-2.47}$, $10^{-4.39}$ and $10^{-7.95}$, respectively, to transform brizziite to the divalent metal antimonates. Thus, the rarity of brizziite is readily explained. Competing cations must be essentially absent from mineralizing solutions, save for Mg^{2+}(aq). This is certainly the case for Pb^{2+}(aq) (Roper *et al.*, 2014). Furthermore, local Ca^{2+}(aq) concentrations would need to be quite low to prevent the formation of minerals of the roméite group, such as $Ca_2Sb_2O_7$, and at lower pH values than used in the solution experiments,

Fe^{3+}(aq) must be negligible to prevent the formation of tripuhyite, $FeSbO_4$ (Leverett *et al.* 2012).

A definite relationship exists between brizziite/mopungite and the roméite group of minerals, reported commonly as associated phases in the deposits listed above. However, due to lack of reliable thermochemical data for the end-members of the roméitegroup details of chemical relationships remain sketchy. It is also worth noting that in initial dissolution experiments 0.1 M HNO_3 was employed and this resulted in incongruent dissolution of brizziite and the formation of phases with the pyrochlore structure (roméite group), as determined by PXRD. It thus appears that pH values somewhat >7 are also necessary for the formation of either brizziite or mopungite.

Some further comment on associated phases is warranted here. It is likely that the oxidation of ottensite, a sodium-bearing thioantimonate(III) of formula $(Na,K)_3Sb_6(SbS_3)O_9{\cdot}3H_2O$, gives rise to mopungite under oxidizing conditions, with brizziite eventuating, based on the rate of transformation kinetics. This suggestion is supported by the noted intimate association of ottensite and mopungite (Origlieri *et al*., 2007) combined with rapid and localized oxidation characteristic of stibnite. The association therefore is likely to be an indicator of lower redox potentials than those which must have prevailed at Green prospect, Nevada, USA; here Williams (1985) reported associations with senarmontite, stibiconite, roméite and tripuhyite. Furthermore, the majority of deposits which carry mopungite also have an association with cetineite in the absence of the roméite-group minerals. Ottensite, the Na-analogue of cetineite, was described only recently (Sejkora and Hyršl, 2007) and as such we suggest that reported associations of mopungite and cetineite may have overlooked in some cases the presence of ottensite. This is supported by the noted association of mopungite with cetineite from a number of Tuscan deposits, namely the Pereta mine (Marzoni Fecia Di Cossato *et al*., 1987), Le Cetine Mine (Brizzi *et al*., 1988; Preite, 1992) and the Tafone mine, (Meli, 1999). The only reported Sb-bearing associate of mopungite at La Selva Mine, Tuscany, Italy, is native antimony (Brizzi and Meli, 1990). In this case, either sample volumes were too small to identify any other Sb phases, or prevailing chemical conditions favoured only the formation of mopungite. It is interesting to note that of the two reported occurrences of mopungite at Le Cetine mine, neither noted the presence of brizziite. However, Le Cetine Mine is the type locality for brizziite, and Olmi and Sabelli (1994) reported it to be associated with mopungite, stibiconite, cetineite and senarmontite; this adding significant weight to the suggested kinetic stability of mopungite.

Syntheses for ottensite and a number of other synthetic analogues of the cetineite group (Sabelli *et al*., 1988; Wang and Liebau, 1998; Wang and Liebau, 1999) have been reported yielding single crystals. Replication of these syntheses indeed produced ottensite, however, this phase typically formed only a minor portion of mixtures containing a host of other Sb minerals as well as a number of unidentifiable phases by PXRD. As such, the products were deemed unsuitable for solubility experiments.

Brizziite is considerably rare due not only to the highly restricted conditions which serve to stabilize it, but also because of the kinetic stability of its hydrated precursor mopungite. We must conclude that brizziite has no significant impact on Sb mobility under typical conditions which persist in the oxidized zones of Sb-bearing ores.

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