Bi-Sb energetics in sulfosalts and sulfides

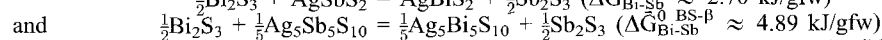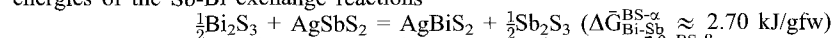S. Ghosal[1] and R. O. Sack[2]*

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ABSTRACT

Experimental brackets (300–450°C) on Sb-Bi partitioning between stibnite-bismuthinites $(Sb,Bi)_2S_3$ and sulfosalts in the $AgSbS_2$–$AgBiS_2$ binary subsystem (α-$Ag(Sb,Bi)S_2$, β-$Ag_5(Sb,Bi)_4^I(Sb,Bi)^{II}S_{10}$) and extant constraints are used to define mixing properties and standard state Gibbs energies of Sb-Bi exchange reactions. They are also used to construct a phase diagram for $Ag(Sb,Bi)S_2$ sulfosalts. We infer that the non-ideality associated with Sb-Bi mixing is largest in minerals of the β-$Ag_5(Sb,Bi)_4^I(Sb,Bi)^{II}S_{10}$ series, and is sufficient to produce miscibility gaps between an ordered intermediate species $Ag_5(Sb)_4^I(Bi)^{II}S_{10}$ and Sb- and Bi-end-members at $T < 240°C$ (measured in terms of symmetric regular-solution-type parameters $\frac{1}{4}W_{Bi-Sb}^{I\beta} = W_{Bi-Sb}^{II\beta} \sim 8.5$ kJ/gfw). The non-ideality associated with the Sb-Bi substitution in stibnite-bismuthinite and α-$Ag(Sb,Bi)S_2$ is $\approx 70\%$ that in the $Ag_5(Sb,Bi)_4^I(Sb,Bi)^{II}S_{10}$ series ($W_{Bi-Sb}^{BS} \approx 12.0$ kJ/gfw; $W_{Bi-Sb}^{\alpha} \approx 6.0$ kJ/gfw). It is insufficient to produce exsolution at temperatures of ore deposition ($T > T_c \approx 88°C$), but most likely is responsible for a preponderance in molar Sb/Bi ratios towards end-member compositions. Finally, positive Gibbs energies of the Sb-Bi exchange reactions
$$\tfrac{1}{2}Bi_2S_3 + AgSbS_2 = AgBiS_2 + \tfrac{1}{2}Sb_2S_3 \ (\Delta\bar{G}_{Bi-Sb}^{BS-\alpha} \approx 2.70 \text{ kJ/gfw})$$
and $\quad \tfrac{1}{2}Bi_2S_3 + \tfrac{1}{5}Ag_5Sb_5S_{10} = \tfrac{1}{5}Ag_5Bi_5S_{10} + \tfrac{1}{2}Sb_2S_3 \ (\Delta\bar{G}_{Bi-Sb}^{0\ BS-\beta} \approx 4.89 \text{ kJ/gfw})$
indicate that Bi is more compatible in stibnite-bismuthinite sulfides than in $Ag(Sb,Bi)S_2$ sulfosalts.

Keywords: bismuthinite-stibnites, $Ag(Sb,Bi)S_2$ sulfosalts, Sb-Bi energetics, ordering and exchange reactions.

Introduction

Antimony- and Bi-rich sulfides and sulfosalts with compositions approximating those in the Ag_2S–Sb_2S_3–Bi_2S_3 system (stibnite-bismuthinites, $(Sb,Bi)_2S_3$; miargyrite, $Ag(Sb,Bi)S_2$, $X_{Bi} \approx 0.0$; aramayoite, $Ag(Sb,Bi)S_2$, $0.17 \leqslant X_{Bi} \leqslant 0.35$; matildite, $Ag(Bi,Sb)S_2$, $X_{Bi} \approx 1.0$) are common constituents in polymetallic hydrothermal sulfide ore deposits of epithermal-mesothermal vein type (e.g. Bartos, 1990; Boldyreva, 1970; Borodayev *et al.*, 1986; Brooker and Jaireth, 1995; Bussell *et al.*, 1990; Ruvalcaba-Ruiz and Thompson, 1988; Czamanske and Hall, 1975; Gibson *et al.*, 1990; Gilmer *et al.*, 1988; Goodell, 1974; Goodell and Petersen, 1974; Gröpper *et al.*, 1991; Hayase,

1955; Jeppson, 1987; Johnson and Meinert, 1994; Kelly and Turneaure, 1970; Lueth, 1988; Lueth *et al.*, 1990; Petersen *et al.*, 1977; Petruk, 1968; Sillitoe *et al.*, 1975; Springer, 1969; Stone, 1959; Turneaure, 1971). Among these minerals, bismuthinite-stibnites exhibit distinct compositional variations along flow paths of mineralizing fluids in ore deposits that are characterized by preponderances of molar Bi/(Bi+Sb) ratios near the end-members, with a conspicuous paucity of intermediate compositions (Fig. 1). Such a pattern of molar semi-metal ratios is suggestive of significant non-ideality of Sb-Bi mixing in bismuthinite-stibnites (e.g. Ghosal and Sack, 1995). Previous workers (e.g. Lueth *et al.*, 1990) have attributed such variations in molar Bi/(Bi+Sb) ratios to a process referred to as 'semi-metal boiling', whereby preferential volatilization of antimony from the ore fluid at a point along the flow path is held responsible for the sudden change
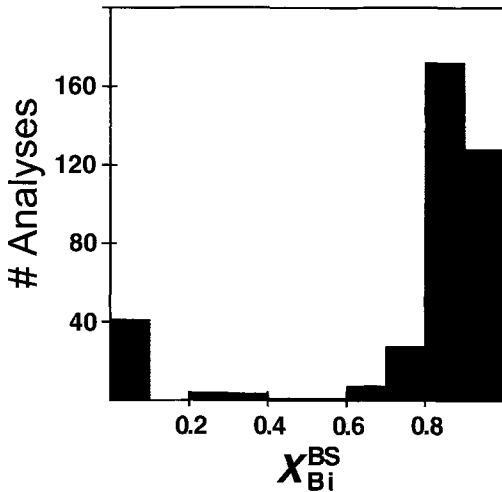
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FIG. 1. Histogram of number of analyses (# Analyses) vs molar Bi/(Bi + Sb) ratios (X_{Bi}^{BS}) of bismuthinite-stibnites taken from compilations of Springer (1969) and Lueth (1988).

in bismuthinite-stibnite Bi/Sb ratios. However, a similar pattern of semi-metal abundance ratios is observed in the argentian sulfosalt pyrargyrite-proustite ($Ag_3(As,Sb)S_3$), and is due to non-ideality of As-Sb mixing (Ghosal and Sack, 1995).

In this study, we conducted experiments to characterize Sb-Bi partitioning between bismuthinite-stibnites and solid solutions near the $AgSbS_2$-$AgBiS_2$ binary at 300, 350, 400 and 450°C. We have used these brackets, as well as available constraints on phase equilibria in the $AgSbS_2$-$AgBiS_2$ subsystem (Keighin and Honea, 1969; Chang et al., 1977; Van Hook, 1960), to determine the non-idealities of Sb-Bi mixing in sulfides and sulfosalts in the $AgSbS_2$-$AgBiS_2$-Sb_2S_3-Bi_2S_3 quadrilateral subsystem. We also construct a T-X diagram for the $AgSbS_2$-$AgBiS_2$ binary (Fig. 3) consistent with extant constraints on miscibility gaps and two-phase regions.

Systematics

Stibnite-bismuthinites (*Pbnm*; Klein and Hurlbut Jr., 1971) exhibit complete solid solubility in Sb-Bi at temperatures $\geqslant 200°C$ (Springer and LaFlamme, 1971). The minerals approximating the $AgSbS_2$-$AgBiS_2$ binary subsystem, miargyrite, aramayoite, and matildite, exhibit limited solid solution at temperatures of ore deposition

(~200–300°C). However, at higher temperatures (~380°C, $AgSbS_2$, Keighin and Honea (1969); 195°C, $AgBiS_2$, Van Hook, (1960)) they undergo polymorphic transitions to a galena-like face-centred cubic structure which forms an isomorphous series across the $AgSbS_2$-$AgBiS_2$ binary join (e.g. Graham, 1951). The structures of all three low-temperature polymorphs are similar, being based on a galena-like layering of alternate S and Ag-Sb-Bi layers of atoms, and can be described in terms of pseudo-cubic sublattices with near-identical cell-edge lengths (Graham, 1951). More recent structure refinements of the low-temperature forms (Knowles, 1964; Mullen and Nowacki, 1974) describe statistical super-structures based on rock-salt-type substructures that differ from earlier structural estimations in their finer details, but these details are suspect because of the high R values in their calculations (12–13%) and because of the difficulty in distinguishing between Ag and Sb atoms by X-ray analysis deriving from their similar scattering properties (Knowles, 1964). The Ag and semi-metal atoms in the low-temperature structures are ordered into separate sites, resulting in a lowering of symmetry with respect to the high-temperature cubic structure (Graham, 1951). Additionally, the semi-metals atoms in the aramayoite (~$Ag_5Sb_4BiS_{10}$, Chang et al., 1977) structure appear to exhibit long-range ordering into two types of semi-metal sites. Based on arguments derived from analysis of the phase equilibria (e.g. Fig. 3), we have assumed that end-member 'aramayoite' has the formula $Ag_5Sb_4BiS_{10}$ rather than the formula $Ag_6Sb_5BiS_{12}$ suggested by Graham (1951). In contrast, the high-temperature cubic polymorph has a completely disordered arrangement of the Ag, Sb and Bi atoms within the metal–semi-metal layer (Graham, 1951). The close similarity between the low-temperature structures is consistent with their treatment as a continuous solid solution (referred to as β-$Ag_5(Sb,Bi)_5S_{10}$ in this study), with immiscibility and the existence of a strongly ordered compound on the $AgSbS_2$-$AgBiS_2$ binary join (i.e. aramayoite; $Ag_5Sb_4BiS_{10}$) narrowing the ranges of Sb-Bi solubility at the temperatures of deposition. This low-temperature (non-cubic) solid solution inverts to the high-temperature (cubic) solid solution (referred to as α-$Ag(Sb,Bi)S_2$) at temperatures of 195–380°C, with the inversion involving a complete disordering of the Ag, Sb and Bi atoms (Graham, 1951).

Experimental

The Sb-Bi exchange experiments (evacuated silica tubes; 300−450°C) were conducted between bismuthinite-stibnites and solid solutions in the AgSbS$_2$-AgBiS$_2$ subsystem. The starting materials were synthesized from stoichiometric proportions of the pure elements (99.999% Ag shot, 99.999% Sb ingot, 99.9995% S pieces, 99.999% Bi ingot) which were heated in evacuated silica tubes to temperatures above the liquidus. The melts were then quenched and annealed at a temperature (500°C) below the solidus (519−801°C) for 1−2 weeks. Quenched products were characterized with a CAMECA SX-50 electron microprobe and a SIEMENS D500 X-ray diffractometer. Phases in the AgSbS$_2$-AgBiS$_2$ subsystem homogenized after one such run. However, the bismuthinite-stibnites used in this study had to be re-ground and re-annealed three times (1−2 weeks for each run) to attain homogeneity in these products, contrary to the claims of earlier workers (Springer and Laflamme, 1971) that homogeneity could be achieved at 500°C in a few days. The exchange experiments were conducted as described in Ghosal and Sack (1995), with tiny grains of solid solutions in the AgSbS$_2$-AgBiS$_2$ system immersed in substantially larger volumes of finely ground bismuthinite-stibnite in each experiment (Table 1). The experiments were annealed at 300−450°C for 2−4 months and then quenched. The quenched products were mounted in cold-setting epoxy and then polished using 3 μ alumina powder and 1 μ diamond paste. The final composition of the Ag(Sb,Bi)S$_2$ grain was analysed using a CAMECA SX-50 electron microprobe (20 kV, 10 na, 1−10 μ beam-size). The standards used were synthetic AgSbS$_2$ (Ag, Sb, S) and AgBiS$_2$ (Bi). The analytical precision of the analyses ($\sqrt{N}/N$; N = counts), determined from Poisson statistics of counts on standards, was <0.5% for all elements. Based on microprobe analyses of internal standards, we believe that analyses are accurate to better than $\pm 2\%$ for elements present in concentrations >3 wt%.

Experimental results

The results of the Sb-Bi exchange experiments between bismuthinite-stibnites and solid solutions in the AgSbS$_2$-AgBiS$_2$ subsystem (i.e. α- and β-Ag(Sb,Bi)S$_2$) at 300 and 450°C (Table 1) are plotted as brackets on the apparent configurational

energy of the exchange reaction RTlnK_D

$$\text{(where } \text{RTln}K_D = \frac{(1 - X_{\text{Bi}}^{\Phi})}{X_{\text{Bi}}^{\Phi}} \frac{X_{\text{Bi}}^{\text{BS}}}{(1 - X_{\text{Bi}}^{\text{BS}})}\text{)};$$

where $\Phi \equiv$ α- or β-Ag(Sb,Bi)S$_2$; BS $\equiv$ bismuthinite-stibnite) against molar Bi/(Bi + Sb) ratios in bismuthinite-stibnite (Fig. 2). The reversal brackets on RTlnK_D for the α-Ag(Sb,Bi)S$_2$ solution indicate limited partitioning of Sb and Bi between α-Ag(Sb,Bi)S$_2$ and bismuthinite-stibnites for $X_{\text{Bi}}^{\text{BS}} \leqslant 0.5$ at 450°C, and $\geqslant 0.6$ at 300°C. In contrast, the
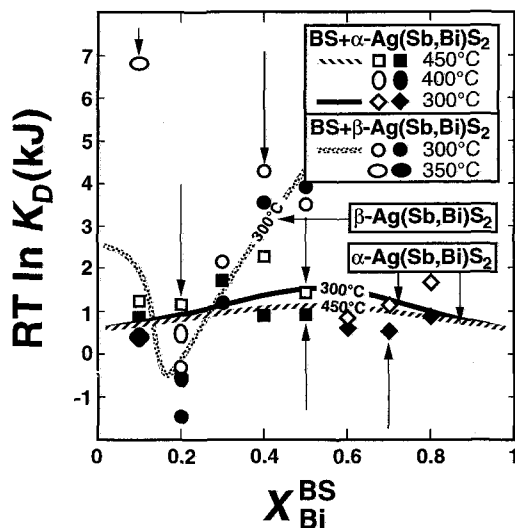

FIG. 2. Apparent configurational Gibbs energies

$$(\text{RTln}K_D; \quad K_D = \frac{(1 - X_{\text{Bi}}^{\Phi})}{X_{\text{Bi}}^{\Phi}} \frac{X_{\text{Bi}}^{\text{BS}}}{(1 - X_{\text{Bi}}^{\text{BS}})};)$$

of Sb-Bi exchange reactions between bismutinite-stibnites (BS) and α- and β-Ag(Sb,Bi)S$_2$ solid solutions (Φ) as functions of the molar Bi/(Bi+Sb) ratios of bismutinite-stibnites ($X_{\text{Bi}}^{\text{BS}}$). Empty and filled *squares*, *ellipses* with vertical major axes and *rhombi* represent 450, 400 and 300°C brackets on Sb-Bi partitioning between bismutinite-stibnites and α-Ag(Sb,Bi)S$_2$ solid solutions (*empty* symbols represent brackets for which RTlnK_D decreased during experiment). *Circles* and *ellipses* with horizontal major axes represent 300 and 350°C brackets on Sb-Bi partitioning between bismuti-nite-stibnites and β-Ag(Sb,Bi)S$_2$ solid solutions. Labelled curves give values of RTlnK_D calculated using equations 7 and 13 for the parameters given in Table 2. Arrows indicate direction of change in RTlnK_D during the experiments.
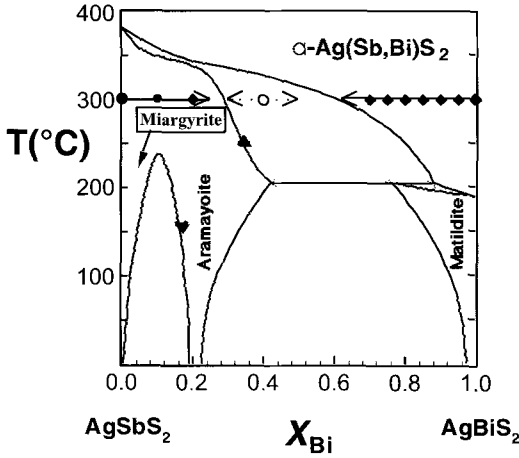
FIG. 3. Temperature-composition $(T–X)$ diagram for the AgSbS$_2$-AgBiS$_2$ subsystem. Filled *rhombi* represent mixtures that homogenized on annealing (Chang *et al.*, 1977). Empty *circle* represents an initial homogeneous composition that unmixed on annealing (this study); filled *circles* represent compositions that remained homogeneous during annealing. *Arrows* represent brackets on the two-phase region between α- and β-Ag(Sb,Bi)S$_2$. Upright and inverted triangles represent natural aramayoite compositions reported by Borodayev *et al.* (1986; $X_{Bi} \approx 0.35$, $T \approx 250°C$) and Graham (1951; $X_{bi} \approx 0.17$, $T > 150°C$ as required by the phase diagram) respectively.

partitioning between bismuthinite-stibnites and the β-Ag(Sb,Bi)S$_2$ solution is strongly dependent on the composition of bismuthinite-stibnite, with $0.2 \leqslant X_{Bi}^{BS} \leqslant 0.5$ at 300°C. The experiments also demonstrate that the α-Ag(Sb,Bi)S$_2$ solution does not coexist stably with bismuthinite-stibnites with $X_{Bi}^{BS} \geqslant 0.6$ at 450°C and $\geqslant 0.9$ at 300°C, as the α-Ag(Sb,Bi)S$_2$ compositions in these experiments undergo partial breakdown to pavonite (AgBi$_3$S$_5$). In addition, our experiments indicate that a single α- or β-Ag(Sb,Bi)S$_2$ solution with $X_{Bi} = 0.4$ is not stable at 300°C, as homogeneous grains with that initial composition unmixed into α- and β-Ag(Sb,Bi)S$_2$ solutions with $X_{Bi}^{BS} \geqslant 0.5$ and $X_{Bi}^{BS} \leqslant 0.3$ respectively (Fig. 3).

Thermodynamic formulation

The molar Gibbs energy of a solid solution Φ can be described in terms of its configurational $(-T\bar{S}^{IC\ \Phi})$ and non-configurational (or vibrational; $\bar{G}^{*\Phi}$) components,

$$\bar{G}^{\Phi} = \bar{G}^{*\Phi} - T\bar{S}^{IC\ \Phi} \quad (1)$$

For bismuthinite-stibnite (BS; (Sb,Bi)$_2$S$_3$), the Gibbs energy can be adequately described with a symmetric regular solution model. In this model, the vibrational Gibbs energy is given by the expression

$$\bar{G}^{*BS} = \bar{G}_{Sb_2S_3}^{0\ BS}(1 - X_{Bi}^{BS}) + \bar{G}_{Bi_2S_3}^{0\ BS}X_{Bi}^{BS} + W_{Bi-Sb}^{BS}X_{Bi}^{BS}(1 - X_{Bi}^{BS}) \quad (2)$$

and the configurational component is formulated based on an assumption of random mixing of Sb and Bi on the semi-metal site with a multiplicity of two in the (Sb,Bi)$_2$S$_3$ formula unit,

$$\bar{S}^{IC\ BS} = -2R[X_{Bi}^{BS}\ \ln X_{Bi}^{BS} + (1 - X_{Bi}^{BS})\ \ln(1 - X_{Bi}^{BS}) \quad (3)$$

A symmetric regular solution model may also be used to describe the Gibbs energy of the α-Ag(Sb,Bi)S$_2$ solid solution, with a vibrational component

$$\bar{G}^{*\alpha} = \bar{G}_{AgSbS_2}^{*\ \alpha}(1 - X_{Bi}^{\alpha}) + \bar{G}_{AgBiS_2}^{*\ \alpha}X_{Bi}^{\alpha} + W_{Bi-Sb}^{\alpha}X_{Bi}^{\alpha}(1 - X_{Bi}^{\alpha}) \quad (4)$$

and a configurational component that assumes random mixing of Ag, Sb and Bi on the two cation sites with exactly 50% of the sites being occupied by Ag atoms,

$$\bar{S}^{IC\ \alpha} = -2R[\tfrac{1}{2}\ln\tfrac{1}{2} + \tfrac{1}{2}X_{Bi}^{\alpha}\ \ln\tfrac{1}{2}X_{Bi}^{\alpha} + \tfrac{1}{2}(1 - X_{Bi}^{\alpha})\ \ln\tfrac{1}{2}(1 - X_{Bi}^{\alpha})] \quad (5)$$

The exchange reaction between bismuthinite-stibnite and the α-Ag(Sb,Bi)S$_2$ solid solution

$$\tfrac{1}{2}Bi_2S_3 + AgSbS_2 = AgBiS_2 + \tfrac{1}{2}Sb_2S_3 \quad (6)$$

can be formulated as

$$RT\ \ln\left[\frac{(1-X_{Bi}^{\alpha})X_{Bi}^{BS}}{X_{Bi}^{\alpha}(1-X_{Bi}^{BS})}\right] + \tfrac{1}{2}W_{Bi-Sb}^{BS}(1 - 2X_{Bi}^{BS}) = \Delta\bar{G}_{BiSb}^{0\ BS-\alpha} + W_{Bi-Sb}^{\alpha}(1 - 2X_{Bi}^{\alpha}) \quad (7)$$

where

$$\Delta\bar{G}_{BiSb}^{0\ BS-\alpha} = (\Delta\bar{G}_{AgBiS_2}^{*\ \alpha} - \bar{G}_{AgSbS_2}^{*\ \alpha}) - \tfrac{1}{2}(\bar{G}_{Bi_2S_3}^{0\ BS} - \bar{G}_{Sb_2S_3}^{0\ BS}) \quad (8)$$

In formulating the Gibbs energy of the β-Ag(Sb,Bi)S$_2$ phases (i.e. miargyrite, Ag$_5$Sb$_5$S$_{10}$; aramayoite, Ag$_5$Sb$_4$BiS$_{10}$; matildite, Ag$_5$Bi$_5$S$_{10}$), we assume that these phases display pronounced long-range ordering of Sb and Bi atoms between two non-equivalent

TABLE 1. Results of exchange experiments between bismuthinite-stibnite and miargyrite-matildite at 300–450°C (Key: BS = bismuthinite-stibnite; MM = miargyrite-matildite)

| Label | Temp (°C) | Time (h) | Initial X_{Bi} | | # pts | Final composition of miargyrite-matildites (weight percentages, standard deviations(σ) and X_{Bi}) | | | | | | | | | X_{Bi} |
			BS	MM		Ag	σ	Sb	σ	Bi	σ	S	σ	Total	
04971-11	450	1584	0.1	0.0	5	33.42	0.30	39.04	0.11	6.08	0.21	21.73	0.21	100.3	0.083
04971-12	450	1584	0.1	0.1	5	33.13	0.35	38.56	0.69	6.39	0.20	21.56	0.16	99.64	0.088
04971-21	450	1584	0.2	0.0	5	32.65	0.53	33.76	0.26	11.96	0.30	21.58	0.19	99.94	0.171
04971-31	450	1584	0.3	0.1	5	31.30	0.47	30.26	0.28	15.77	0.26	20.28	0.29	97.61	0.233
04971-33	450	1584	0.3	0.3	5	31.91	0.27	29.88	0.34	16.56	0.46	20.66	0.20	99.01	0.244
04971-42	450	1584	0.4	0.3	5	30.97	0.37	26.27	0.33	23.02	0.30	20.59	0.58	100.9	0.338
04971-43	450	1584	0.4	0.4	5	30.85	0.40	24.91	0.24	24.55	0.33	20.54	0.14	100.9	0.365
04971-51	450	1584	0.5	0.3	2	28.00	1.39	21.68	0.24	28.61	0.23	20.20	0.10	98.49	0.435
04971-53	450	1584	0.5	0.5	1	29.48	–	20.14	–	30.08	–	19.57	–	99.27	0.465
02982-11	400	1512	0.1	0.0	1	36.11	–	38.82	–	4.70	–	21.38	–	101.1	0.066
02982-12	400	1512	0.1	0.1	1	35.38	–	36.97	–	6.70	–	21.37	–	100.4	0.095
02982-21	400	1512	0.2	0.1	1	35.11	–	33.37	–	13.12	–	21.08	–	102.7	0.186
02982-23	400	1512	0.2	0.3	1	35.35	–	31.63	–	15.13	–	21.06	–	103.2	0.218
02983-11	350	1176	0.1	0.0	1	36.14	–	39.31	–	1.99	–	21.90	–	99.34	0.029
02983-13	350	1176	0.1	0.2	1	35.76	–	34.74	–	6.81	–	20.78	–	98.09	0.103
02983-21	350	1176	0.2	0.1	1	34.27	–	31.97	–	12.72	–	20.71	–	99.68	0.188
02983-23	350	1176	0.2	0.3	1	33.51	–	31.11	–	13.63	–	20.95	–	99.2	0.203
04974-23	300	3720	0.2	0.2	1	33.84	–	30.56	–	14.02	–	19.83	–	98.24	0.211
04974-24	300	3720	0.2	0.3	1	38.76	–	26.62	–	15.68	–	20.12	–	101.2	0.255
04974-32	300	3720	0.3	0.2	1	33.85	–	31.07	–	14.57	–	20.70	–	100.2	0.215
04974-33	300	3720	0.3	0.3	1	33.35	–	26.70	–	19.43	–	20.42	–	99.89	0.249
04974-41	300	3720	0.4	0.2	1	33.90	–	30.61	–	14.19	–	20.76	–	99.46	0.213
04974-42	300	3720	0.4	0.3	1	35.16	–	29.42	–	16.02	–	20.86	–	101.5	0.241
04974-51	300	3720	0.5	0.3	1	33.80	–	26.30	–	21.65	–	20.24	–	102.0	0.324
04974-52	300	3720	0.5	0.4	1	33.35	–	25.73	–	19.44	–	20.43	–	98.95	0.306
04974-62	300	3720	0.6	0.5	1	31.21	–	16.19	–	35.00	–	19.06	–	101.5	0.558
04974-63	300	3720	0.6	0.6	1	30.49	–	15.06	–	33.87	–	19.72	–	99.14	0.567
04974-72	300	3720	0.7	0.6	1	30.95	–	12.62	–	39.73	–	18.79	–	102.1	0.647
04974-73	300	3720	0.7	0.7	1	30.08	–	11.05	–	39.51	–	18.47	–	99.11	0.676
04974-82	300	3720	0.8	0.7	1	28.19	–	8.61	–	41.71	–	17.45	–	95.96	0.738
04974-83	300	3720	0.8	0.8	1	29.81	–	7.64	–	43.32	–	17.60	–	98.36	0.768

TABLE 2. Thermodynamic mixing parameters and energies of transitions and exchange reactions in bismuthinite-stibnite and α- and β-Ag(Sb,Bi)S₂. (Key: BS = bismuthinite-stibnite; β = β-Ag(Sb, Bi)S₂; α = α-Ag(Sb, Bi)S₂)

Name of solid solution	Parameter	Description	kJ/gfw
(Bi,Sb)₂S₃ (bismuthinite-stibnite)	$W_{Bi\text{-}Sb}^{BS}$	Margules-type parameter describing non-ideality of Bi-Sb mixing	12.0 ± 2.0
α-Ag(Sb,Bi)S₂	$W_{Bi\text{-}Sb}^{\alpha}$	Margules-type parameter describing non-ideality of Bi-Sb mixing	6.0 ± 1.0
β-Ag(Sb,Bi)S₂			
Ordering reaction $\frac{3}{5}Ag_5Sb_5S_{10} + Ag_5Bi_4SbS_{10} = \frac{8}{5}Ag_5Bi_5S_{10} + Ag_5Sb_4BiS_{10}$	$\Delta\bar{H}_s^{0\ \beta} = \bar{H}_{Ag_5Sb_4BiS_{10}}^{0\ \beta} + \frac{3}{5}\bar{H}_{Ag_5Bi_5S_{10}}^{0\ \beta} - \bar{H}_{Ag_5Bi_4SbS_{10}}^{0\ \beta} - \frac{3}{5}\bar{H}_{Ag_5Sb_5S_{10}}^{0\ \beta}$	Enthalpy of ordering reaction	−11.0 ± 1.0
	$\Delta\bar{S}_s^{0\ \beta} = \bar{S}_{Ag_5Sb_4BiS_{10}}^{0\ \beta} + \frac{3}{5}\bar{S}_{Ag_5Bi_5S_{10}}^{0\ \beta} - \bar{S}_{Ag_5Bi_4SbS_{10}}^{0\ \beta} - \frac{3}{5}\bar{S}_{Ag_5Sb_5S_{10}}^{0\ \beta}$	Entropy of ordering reaction	0.0
	$\Delta\bar{G}_s^{0\ \beta} = \Delta\bar{H}_s^{0\ \beta} - T\Delta\bar{S}_s^{\ \beta}$	Gibbs energy of ordering reaction	−11.0 ± 1.0
Reciprocal reaction $Ag_5Sb_5S_{10} + Ag_5Bi_5S_{10} = Ag_5Sb_4BiS_{10} + Ag_5Bi_4SbS_{10}$	$\Delta\bar{H}_x^{0\ \beta} = \bar{H}_{Ag_5Sb_4BiS_{10}}^{0\ \beta} + \bar{H}_{Ag_5Bi_4SbS_{10}}^{0\ \beta} - \bar{H}_{Ag_5Sb_5S_{10}}^{0\ \beta} - \bar{H}_{Ag_5Bi_5S_{10}}^{0\ \beta}$	Enthalpy of reciprocal reaction	0.0
	$\Delta\bar{S}_x^{0\ \beta} = \bar{S}_{Ag_5Sb_4BiS_{10}}^{0\ \beta} + \bar{S}_{Ag_5Bi_4SbS_{10}}^{0\ \beta} - \bar{S}_{Ag_5Sb_5S_{10}}^{0\ \beta} - \bar{S}_{Ag_5Bi_5S_{10}}^{0\ \beta}$	Entropy of reciprocal reaction	0.0
	$\Delta\bar{G}_s^{0\ \beta} = \Delta\bar{H}_s^{0\ \beta} - T\Delta\bar{S}_s^{\ \beta}$	Gibbs energy of reciprocal reaction	0.0

TABLE 2. (contd.)

$W^{I,\beta}_{Bi-Sb}$	Margules-type parameter describing non-ideality of Bi-Sb mixing on site I	34.0 ± 4.0
$W^{II,\beta}_{Bi-Sb}$	Margules-type parameter describing non-ideality of Bi-Sb mixing on site II	8.5 ± 1.0
$\beta \to \alpha$		
$\Delta \bar{H}^{0\ \beta \to \alpha}_{AgSbS_2}$	Enthalpy of transition for Sb-end-member	7.53
$\Delta \bar{S}^{0\ \beta \to \alpha}_{AgSbS_2}$	Entropy of transition for Sb-end-member	0.0115
$\Delta \bar{H}^{0\ \beta \to \alpha}_{AgBiS_2}$	Enthalpy of transition for Bi-end-member	5.34
$\Delta \bar{S}^{0\ \beta \to \alpha}_{AgBiS_2}$	Entropy of transition for Bi-end-member	0.0115
Energies of exchange reaction		
$\Delta \bar{G}^{0,\ BS-\alpha}_{BiSb}$	Energy of exchange reaction between bismuthinite-stibnite and α-AgSbS$_2$ (Equation 8)	2.70 ± 0.10
$\Delta \bar{G}^{0,\ BS-\beta}_{Bi-Sb}$	Energy of exchange reaction between bismuthinite-stibnite and β-AgSbS$_2$ (Equation 14)	4.89 ± 0.10

semi-metal sites (I and II) which occur in a ratio of multiplicities of 4:1. A formula unit based on 10 S atoms is chosen for the β-Ag(Sb,Bi)S$_2$ solid solution to simplify the formulation of the model for the Gibbs energy, and, the species Ag$_5$(Sb)$_4^I$(Bi)^{II}S$_{10}$ represents a fully ordered 'aramayoite' component that is stable at low temperatures. Molar compositional and ordering variables may be defined as

$$X_{Bi}^\beta = Bi/(Bi + Sb)$$

and

$$s^\beta = X_{Bi}^{II\,\beta} - X_{Bi}^{I\,\beta} \qquad (9)$$

The vibrational component of the Gibbs energy of β-Ag(Sb,Bi)S$_2$ solid solutions can be adequately expressed as a second-order Taylor's expansion in these compositional and ordering variables:

$$\bar{G}*^\beta = g_o + g_x(X_{Bi}^\beta) + g_s(s^\beta) + g_{xx}(X_{Bi}^\beta)^2 + \\ g_{ss}\,(s^\beta)^2 + g_{xs}(X_{Bi}^\beta)(s^\beta), \qquad (10)$$
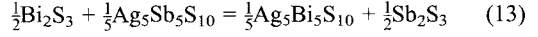
Following procedures outlined elsewhere (e.g. Sack, 1992) the coefficients in equation 10 may be ready related to end-member energies ($\bar{G}_{Ag_5Sb_5S_{10}}^{0\,\beta}$, $\bar{G}_{Ag_5Bi_5S_{10}}^{0\,\beta}$), energies of ordering and reciprocal reactions ($\Delta\bar{G}_s^{0\,G\beta}$ and $\Delta\bar{G}_x^{0\,G\beta}$; Table 2), and symmetric Margules-type parameters describing non-idealities of Sb-Bi mixing on sites I and II ($W_{Bi-Sb}^{I\,\beta}$ and $W_{Bi-Sb}^{II\,\beta}$; Table 2):

$$\bar{G}*^\beta = \bar{G}_{Ag_5Sb_5S_{10}}^{0\,\beta}(1 - X_{Bi}^\beta) + \bar{G}_{Ag_5Bi_5S_{10}}^{0\,\beta}X_{Bi}^\beta + \\ (\Delta\bar{G}_x^{0\,\beta} + W_{Bi-Sb}^{I\,\beta} + W_{Bi-Sb}^{II\,\beta})(X_{Bi}^\beta)(1 - X_{Bi}^\beta) + \\ (\tfrac{3}{10}\Delta\bar{G}_x^{0\,\beta} + \tfrac{1}{2}\Delta\bar{G}_s^{0\,\beta} - \tfrac{1}{5}W_{Bi-Sb}^{I\,\beta} + \tfrac{4}{5}W_{Bi-Sb}^{II\,\beta})(s^\beta) + \\ (\tfrac{4}{25}\Delta\bar{G}_x^{0\,\beta} - \tfrac{1}{25}W_{Bi-Sb}^{I\,\beta} - \tfrac{16}{25}W_{Bi-Sb}^{II\,\beta})(s^\beta)^2 + \\ (-\tfrac{3}{5}\Delta\bar{G}_x^{0\,\beta} + \tfrac{2}{5}W_{Bi-Sb}^{I\,\beta} - \tfrac{8}{5}W_{Bi-Sb}^{II\,\beta})(X_{Bi}^\beta)(s^\beta) \qquad (11)$$

For the molar configurational entropy of the β-Ag(Sb,Bi)S$_2$ solid solution we may write the following formulation based on the assumption that Sb and Bi display long-range nonconvergent ordering between sites I and II (e.g. Harlov and Sack, 1994).

$$\bar{S}^{IC\,\beta} = -R[4(1 - X_{Bi}^\beta + \tfrac{1}{5}s^\beta)\ln(1 - X_{Bi}^\beta + \tfrac{1}{5}s^\beta) + \\ 4(X_{Bi}^\beta - \tfrac{1}{5}s^\beta)\ln(X_{Bi}^\beta - \tfrac{1}{5}s^\beta) + \\ (1 - X_{Bi}^\beta - \tfrac{4}{5}s^\beta)\ln(1 - X_{Bi}^\beta - \tfrac{4}{5}s^\beta) + \\ (X_{Bi}^\beta + \tfrac{4}{5}s^\beta)\ln(X_{Bi}^\beta + \tfrac{4}{5}s^\beta) \qquad (12)$$

The Sb-Bi exchange reaction between bismuthinite-stibnite and the β-Ag(Sb,Bi)S$_2$ solid solution

$$\tfrac{1}{2}Bi_2S_3 + \tfrac{1}{5}Ag_5Sb_5S_{10} = \tfrac{1}{5}Ag_5Bi_5S_{10} + \tfrac{1}{2}Sb_2S_3 \qquad (13)$$

can thus be described as

$$RT \ln\left[\left\{\frac{(1 - X_{Bi}^\beta + \tfrac{1}{5}s^\beta)^4(1 - X_{Bi}^\beta - \tfrac{4}{5}s^\beta)}{(X_{Bi}^\beta - \tfrac{1}{5}s^\beta)^4(X_{Bi}^\beta + \tfrac{4}{5}s^\beta)}\right\}^{1/5}\frac{X_{Bi}^{BS}}{(1 - X_{Bi}^{BS})}\right] - \\ \Delta\bar{G}_{BiSb}^{0\,BS-\beta} + \tfrac{1}{2}W_{Bi-Sb}^{BS}(1 - 2X_{Bi}^{BS}) = \\ \tfrac{1}{5}(\Delta\bar{G}_x^{0\,\beta} + W_{Bi-Sb}^{I\,\beta} + W_{Bi-Sb}^{II\,\beta})(1 - 2X_{Bi}^\beta) + \\ \tfrac{1}{25}(-3\Delta\bar{G}_x^{0\,\beta} + 2W_{Bi-Sb}^{I\,\beta} - 8W_{Bi-Sb}^{II\,\beta})(s^\beta) \qquad (14)$$

where

$$\Delta\bar{G}_{BiSb}^{0\,BS-\beta} = \tfrac{1}{5}(\bar{G}_{Ag_5Bi_5S_{10}}^{0\,\beta} - \bar{G}_{Ag_5Sb_5S_{10}}^{0\,\beta}) - \\ \tfrac{1}{2}(\bar{G}_{Ag_5Sb_5S_{10}}^{0\,BS} - \bar{G}_{Sb_2S_3}^{0\,BS}) = \\ \Delta\bar{G}_{BiSb}^{0\,BS-\alpha} + \Delta\bar{G}_{AgSbS_2}^{0\,\beta\to\alpha} - \Delta\bar{G}_{AgBiS_2}^{0\,\beta\to\alpha} \qquad (15)$$

The value of s^β for a given X_{Bi}^β and T can be determined by applying the condition of homogeneous equilibrium to the Gibbs energy of the solid solution

$$(\partial\bar{G}/\partial s^\beta) = 0 \qquad (16)$$

which gives us the equation

$$RT \ln\left[\frac{(X_{Bi}^\beta - \tfrac{1}{5}s^\beta)(1 - X_{Bi}^\beta - \tfrac{4}{5}s^\beta)}{(1 - X_{Bi}^\beta + \tfrac{1}{5}s^\beta)(X_{Bi}^\beta + \tfrac{4}{5}s^\beta)}\right] = \\ (\tfrac{3}{8}\Delta\bar{G}_x^{0\,\beta} + \tfrac{5}{8}\Delta\bar{G}_s^{0\,\beta} - \tfrac{1}{4}W_{Bi-Sb}^{I\,\beta} + W_{Bi-Sb}^{II\,\beta}) + \\ (\tfrac{2}{5}\Delta\bar{G}_x^{0\,\beta} - \tfrac{1}{10}W_{Bi-Sb}^{I\,\beta} - \tfrac{8}{5}W_{Bi-Sb}^{II\,\beta})(s^\beta) + \\ (-\tfrac{3}{4}\Delta\bar{G}_x^{0\,\beta} + \tfrac{1}{2}W_{Bi-Sb}^{I\,\beta} - 2W_{Bi-Sb}^{II\,\beta})(X_{Bi}^\beta) \qquad (17)$$

Finally, the condition of equilibrium for the Sb-Bi exchange reaction between the α- and β-Ag(Sb,Bi)S$_2$ solid solutions,

$$AgBiS_2 + \tfrac{1}{5}Ag_5Sb_5S_{10} = \tfrac{1}{5}Ag_5Bi_5S_{10} + AgSbS_2 \qquad (18)$$
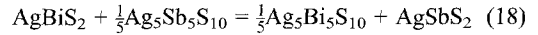
may be derived by subtracting equation 7 from 14.

$$RT \ln\left[\left\{\frac{(1 - X_{Bi}^\beta + \tfrac{1}{5}s^\beta)^4(1 - X_{Bi}^\beta - \tfrac{4}{5}s^\beta)}{(X_{Bi}^\beta - \tfrac{1}{5}s^\beta)^4(X_{Bi}^\beta + \tfrac{4}{5}s^\beta)}\right\}^{1/5}\frac{X_{Bi}^\alpha}{(1 - X_{Bi}^\alpha)}\right] + \\ \Delta\bar{G}_{AgBiS_2}^{0\,\beta\to\alpha} - \Delta\bar{G}_{AgSbS_2}^{0\,\beta\to\alpha} + W_{Bi-Sb}^\alpha(1 - 2X_{Bi}^\alpha) = \\ \tfrac{1}{5}(\Delta\bar{G}_x^{0\,\beta} + W_{Bi-Sb}^{I\,\beta} + W_{Bi-Sb}^{II\,\beta})(1 - 2X_{Bi}^\beta) + \\ \tfrac{1}{25}(-3\Delta\bar{G}_x^{0\,\beta} + 2W_{Bi-Sb}^{I\,\beta} - 8W_{Bi-Sb}^{II\,\beta})(s^\beta) \qquad (19)$$

Calibration of thermodynamic models

In conjunction with constraints on the transition temperatures between the α- and β-Ag(Sb,Bi)S$_2$ solutions, and bounds on the width of their two-

phase loop, we may develop a calibration for the parameters describing Sb-Bi mixing in bismuthinite-stibnite and α- and β-Ag(Sb,Bi)S_2 based on analysis of our brackets on Sb-Bi partitioning. The parameters are tightly bound, if it is assumed that the standard state Gibbs energies of the Sb-Bi exchange reactions (Eqns 8, 15) are independent of temperature (e.g. Sack and Ghiorso, 1989; Harlov and Sack, 1994). As a first approximation, we may also assume that the entropy of the ordering reaction ($\Delta\bar{S}_s^{0\ \beta}$),and the enthalpy and entropy of the reciprocal reaction ($\Delta\bar{H}_x^{0\ \beta}$, $\Delta\bar{S}_x^{0\ \beta}$), for the β-Ag(Sb,Bi)S_2 solid solution are zero (Table 2). Finally, we may assume that the entropy changes of the $\beta\rightarrow\alpha$ transitions are entirely due to the configurational effect of the complete disordering of Ag, Sb and Bi between the metal and semi-metal sites that are distinct in the low-temperature ordered (β) structure (e.g. Graham, 1951). For this assumption, the entropies of the $\beta\rightarrow\alpha$ transitions in the AgSbS$_2$ and AgBiS$_2$ end-members ($\Delta\bar{S}_{AgSbS_2}^{0\ \beta\rightarrow\alpha}$, $\Delta\bar{S}_{AgBiS_2}^{0\ \beta\rightarrow\alpha}$) are 2Rln2 per formula unit, and values of $\Delta\bar{H}^{0\ \beta\rightarrow\alpha}$ for these transitions (determined from the relation $\Delta\bar{H}^{0\ \beta\rightarrow\alpha} = T\ \Delta\bar{S}^{0\ \beta\rightarrow\alpha}$; $T \approx 380°C$ for AgSbS$_2$; 190°C for AgBiS$_2$) are consistent with the calorimetric determinations of Bryndzia and Kleppa (1989). With these assumptions and the requirement that $W_{Bi-Sb}^{BS} \leqslant 14.0$ kJ/gfw (bismuthinite-stibnites exhibit continuous solid solubility at temperatures $\geqslant 200°C$; Springer and Laflamme, 1971), we may readily develop a calibration for the condition of equilibrium of the Sb-Bi exchange reaction between bismuthinite-stibnite and the α-Ag(Sb,Bi)S_2 solid solution (Equation 7) that satisfies our brackets on Sb-Bi partitioning between these phases at 300–450°C (Fig. 2), provided $W_{Bi-Sb}^{BS} \approx W_{Bi-Sb}^{\alpha}$, $\Delta\bar{G}_{Bi-Sb}^{0\ BS-\alpha} \approx 2.6–3.2$ kJ/gfw.

Examination of the conditions of Bi-Sb exchange equilibrium between bismuthinite-stibnite and β-Ag(Sb,Bi)S_2 (Equation 14), and between coexisting α- and β-Ag(Sb,Bi)S_2 (Equation 18), allows the value of W_{Bi-Sb}^{BS} to be refined, and values of $W_{Bi-Sb}^{II\ \beta}$ (assumed to be equal to 4W) and $\Delta\bar{H}_s^{0\ \beta}$ to be determined (Table 2). The strong composition dependence on the apparent Gibbs energy of the Sb-Bi exchange reaction between bismuthinite-stibnite and β-Ag(Sb,Bi)S_2 can only be satisfied if $\frac{1}{4}W_{Bi-Sb}^{I\ \beta}$ ($= W_{Bi-Sb}^{II\ \beta}$) is greater than $\frac{1}{2}W_{Bi-Sb}^{BS}$ by at least 2 kJ/gfw, and if the standard state Gibbs energy of the reaction

$$\tfrac{3}{5}Ag_5Sb_5S_{10} + Ag_5(Bi)_4^I(Sb)^{II}S_{10} =$$
$$\tfrac{3}{5}Ag_5Bi_5S_{10} + Ag_5(Sb)_4^I(Bi)^{II}S_{10}$$
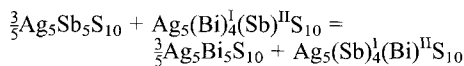
is strongly negative (i.e. $\Delta\bar{H}_s^{0\ \beta} < -10$ kJ/gfw). Values of $W_{Bi-Sb}^{BS} > 14.0$ kJ/gfw require values of $\frac{1}{4}W_{Bi-Sb}^{I\beta}$ and $W_{Bi-Sb}^{II\beta}$ (>9.5 kJ/gfw) that are also unrealistically large, predicting miscibility gaps between miargyrite and aramayoite, and between aramayoite and matildite too extensive to satisfy experimental and natural constraints, respectively. For example, values of $W_{Bi-Sb}^{II\ \beta} > 9.5$ kJ/gfw require miscibility gaps to appear at $T > 300°C$ ($X_{Bi} \approx 0.10$), but in our experiments, Ag(Sb,Bi)S_2 grains of this composition were stable to annealing for 4 months at 300°C. Equivalent values for $\frac{1}{4}W_{Bi-Sb}^{I\ \beta}$ require miscibility gaps between aramayoite and matildite too extensive to accommodate the natural aramayoite composition reported by Borodayev et al. (1986; $X_{Bi} \approx 0.35$; Fig. 3).

At the opposite extreme, the assumption of ideal mixing in bismuthinite-stibnite ($W_{Bi-Sb}^{BS} = 0.0$), values of $\frac{1}{4}W_{Bi-Sb}^{I\ \beta}$ and $W_{Bi-Sb}^{II\ \beta}$ of at least 6.0 kJ/gfw are required. Calibrations predicted on this assumption may be considered problematic because of the large implied differ-ence in non-ideality of Sb-Bi substitution in solutions with similar structures. We therefore adopt the calibration for parameters given in Table 2 for a value of W_{Bi-Sb}^{BS} of 12.0 ± 2.0 kJ/gfw, to achieve maximal correspon-dence between the models and experimental data, as well as be consistent with the premise that the energetic consequences of Sb-Bi substitution should not be grossly different in materials with similar structures. The calibrated parameters are used in constructing a phase diagram for the AgSbS$_2$-AgBiS$_2$ binary subsystem (Fig. 3), and the resulting calculated miscibility gaps between the β-Ag(Sb,Bi)S_2 sulfosalts, miargyrite, aramayoite and matildite, are consistent with phase assemblages and compositions observed in nature.

Conclusions

Antimony-bismuth mixing in sulfides and argen-tian sulfosalts is significantly non-ideal, in accordance with similar non-idealities exhibited by their As-Sb counterparts (Ghosal and Sack, 1995). Bismuthinite-stibnites ($W_{Bi-Sb}^{BS} \approx 12.0$ kJ/gfw) are predicted to exsolve at temperatures $\leqslant 88°C$, consistent with their exhibiting contin-uous solid solution in hydrothermal ore deposits ($T \approx 150–350°C$), but exhibiting preponderances in molar ratios towards the end-members (Lueth, 1988; Fig. 1). The non-idealities in disordered

Sb-Bi sulfides and sulfosalts are found to be less than that of their As-Sb counterparts, with the exception of ordered compounds (Table 2; Ghosal and Sack, 1995), and this can be attributed to the lesser relative size difference between Sb and Bi atoms, causing smaller strain effects.

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