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LIVINGSTONITE, $HgSb_4S_8$: SYNTHESIS AND STABILITY

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ABSTRACT

Systematic silica tube experiments have confirmed the composition of livingstonite as $HgSb_4S_8$ and established its maximum thermal stability as 451±3°C. The approximate free energy of formation of livingstonite at 300° and 400°C are calculated from knowledge of the equilibrium S_2 vapor pressure.

Livingstonite, the only reported ternary Hg-Sb-S phase, is a rare sulfosalt mineral that has been the subject of many investigations. The author obtained a small quantity of livingstonite from Dr. Gunnar Kullerud of the Carnegie Institution of Washington, Geophysical Laboratory. Studies of this natural material, which had been collected by Dr. E. G. Zies in 1938 at the type locality of Huitzuco, Mexico, together with synthetic livingstonite are described in this report.

Livingstonite was first recognized as a mineral species by Barcena (1874) in samples from the mercury ores of Huitzuco, Mexico. Natural single crystals from this locality have since been the subjects of several X-ray crystallographic studies (Richmond, 1936; Gorman, 1951; Niizeki and Buerger, 1957; Fabregat, 1966). The composition was long assumed to be $HgSb_4S_7$ ($HgS:2Sb_2S_3$) on the basis of early chemical analyses and the known compositions of other sulfosalt minerals. Pelabon (1905), operating under this assumption, was unable to synthesize a compound of this composition, but did observe eutectic melting relations on the HgS-Sb_2S_3 join at 455°C and 34 weight percent HgS. Niizeki and Buerger (1957) reevaluated the results of previous structural studies, determined that livingstonite is monoclinic (space group $A2/a$ a 30.25, b 4.00, c 21.48 Å, and β 104°12′), and detected more sulfur in the structure than accounted for by the formula $HgSb_4S_7$. Combining their X-ray data with a new chemical analysis they concluded that the true chemical formula is $HgSb_4S_8$ ($HgS/2Sb_2S_3/S$). Fabregat (1966) also examined natural single crystals but determined a slightly different unit cell with the dimensions of a 29.78, b 4.01, c 21.40 Å, and β 104°12′. Learned (1966) reports synthesis of livingstonite crystals from a mixture of HgS, Sb_2S_3 and Na_2S solution at 200°C and 100 bars pressure.

X-ray powder diffraction patterns of natural livingstonite taken during this study contain many reflections not observed by Berry and

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Thompson (1962) and previous workers, but nearly coincide with those obtained by Fabregat (1966). Fabregat (1966), however, employs a different indexing scheme and is not consistent with extinction requirements for the space group *A2/a*. It is possible to index the entire livingstonite pattern obtained in the present study on the basis of Niizeki and Buerger's (1957) unit cell using only permitted reflections. Comparison of the X-ray diffraction patterns of natural livingstonite obtained by Berry and Thompson (1962), Fabregat (1966), and the author and of synthetic $HgSb_4S_8$ are given in Table 1.

Because no data existed regarding the thermal stability of livingstonite heating experiments using evacuated fused quartz tubes were conducted on natural livingstonite. Semi-quantitative electron probe analysis of the livingstonite indicated that the only elements present other than mercury, antimony, and sulfur were iron (less than 0.1%) and lead and arsenic (combined less than 0.3%). These minor element contents are consistent with those found by Niizeki and Buerger (1957) in samples from the same locality. The results of the heating experiments (Table 2a) indicate that the maximum thermal stability, in the presence of an equilibrium vapor is $452 \pm 1°C$.

After the thermal stability of livingstonite was established, synthetic livingstonite was prepared in evacuated silica tube experiments and its thermal stability examined in the pure Hg-Sb-S system. These experiments (Table 2b), prepared with 99.99 percent pure elements, confirm the composition of livingstonite as $HgSb_4S_8$ and demonstrate its maximum thermal stability in the pure system to be $453 \pm 3°C$. Natural and synthetic $HgSb_4S_8$ melt congruently; the liquid formed quenches on cooling to form a dense red glass. The X-ray diffraction pattern of synthetic livingstonite (Table 1, D) is identical with that of natural livingstonite with the exception of one weak reflection (2.26 Å) observed in the natural material. Measured densities of portions of the natural livingstonite (4.8 ± 0.2) and the synthetic livingstonite (4.88 ± 0.02) are consistent with measured and calculated values in the literature.

The preceding data combined with that from additional experiments, not listed, and thermochemical calculations (data from Dr. Paul Barton, personal communication 1969) on the reaction:

$$3Hg + Sb_2S_3 = 3HgS + 2Sb$$

indicate that the compositions of stable mineral assemblages in the Hg—Sb—S between 25° and 450°C are: $Hg+Sb+Sb_2S_3$; $Hg+Sb_2S_3+HgS$; $HgS+Sb_2S_3+HgSb_4S_8$; $HgS+HgSb_4S_8+S$(liq. or solid); and $Sb_2S_3+HgSb_4S_8+S$(liq. or solid).

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR LIVINGSTONITE

		A		B		C		D	
hkl	*d* Å (calc.)	*d* Å	*I.*	*d* Å	*I.*	*d* Å	*I.*	*d* Å	*I.*
002	10.41	—	—	10.47	5	10.54	4	10.46	3
402	5.40	—	—	5.39	2	5.41	2	5.34	1
004	5.21	5.16	4	5.20	10	5.23	10	5.20	10
$\bar{4}04$	4.84	4.87	1	4.86	2	4.87	1	4.83	1
404	3.83	—	—	3.83	3	3.83	5	3.81	5
211 $\bar{8}02$	3.76 3.75	3.74	7	3.76	2	3.77	2	3.75	2
800	3.67	—	—	3.66	1	3.67	1	3.64	½
$\bar{4}06$ 006	3.48 3.47	3.48	7	3.49	8	3.49	8	3.47	8
213 $\bar{4}13$	3.28 3.29	3.28	1	3.29	1	3.29	½	3.31	1
511 802	3.20 3.22	—	—	3.22	1	3.22	1	3.27	1
611 $\bar{6}13$	3.00 3.01	3.00	10	3.01	2	3.01	4	2.99	2
015 806	2.89 2.90	—	—	—	—	2.89	1	2.88	½
406	2.88	2.87	1	2.87	3	2.88	5	2.85	6
613 $\bar{6}15$	2.68 2.69	2.67	3	2.69	1	2.69	1	2.68	½
715 008 811	2.59 2.60 2.62	—	—	2.60	2	2.61	1	2.59	4
12.0.2	2.52	2.49	½	2.51	1	2.52	1	2.51	½
$\bar{8}08$ 12.0.0	2.42 2.44	2.42	3	2.42	1	2.44	1	2.43	2
$\overline{12}.0.6$ 408 217	2.28 2.28 2.29	2.28	6	2.28	4	2.28	7	2.27	6
806 $\overline{10}.1.5$	2.259 2.257	—	—	2.252	1	2.257	1	—	—

A. Berry and Thompson (1962).
B. Fabregat (1966).
C. Natural, this study.
D. $HgSb_4S_8$, synthetic, this study.

TABLE 1.—(*Continued*)

		A		B		C		D	
hkl	*d* Å (calc.)	*d* Å	*I.*	*d* Å	*I.*	*d* Å	*I.*	*d* Å	*I.*
$\bar{4}.1.10$ $\overline{11}.1.5$ 917	2.146 2.148 2.137	—	—	2.14	1	2.14	1	2.14	2
517 0.0.10 $\overline{10}.1.6$	2.07 2.08 2.06	—	—	2.08	5	2.08	5	2.07	5
$\bar{8}.0.10$ $\bar{2}19$ 1.0.10	2.04 2.04 2.04	2.04	2	2.04	2	2.04	2	2.03	2
019 020	2.00 2.00	1.989	2	1.997	1	2.002	½	1.995	½
		—	—	—	—	1.937	½	1.927	½
		—	—	1.895	1	1.899	1	1.898	1
		1.881	3	1.880	1	1.884	2	1.877	3
		1.845	3	1.845	1	1.848	1	1.841	½
		—	—	—	—	1.798	1	1.792	½
		—	—	1.752	2	—	—	—	—
		—	—	1.739	2	1.741	3	1.737	1
		1.734	5	1.731	2	1.733	3	1.728	2
		1.647	½	—	—	1.649	½	1.635	1

Differential thermal analysis of HgS in the presence of Sb_2S_3 yielded an inversion temperature of 345±5°C which is identical with the 344±2°C obtained by Dickson and Tunell (1959).

Prior to realization of the sulfur-rich composition of livingstonite, there was considerable speculation concerning conditions necessary for its formation. Data now available indicate that livingstonite can only form in ores containing mercury and antimony which are deposited in, or are post depositionally subjected to, sulfur vapor pressures or activities greater than those present on the $HgS-Sb_2S_3$ join (ie greater than the mercury sulfidation curve). This is consistent with Tunell's (1964, and personal communication 1969) observations that native sulfur has been present at the time of livingstonite deposition in all confirmed occurrences. In order to further define the minimum sulfur vapor pressure or activity necessary, two experiments were conducted in which grains of copper were physically separated from an assemblage of $HgSb_4S_8+HgS+Sb_2S_3$ but were free to react with the vapor over the assemblage. In

TABLE 2. HEATING EXPERIMENTS

a: Experiments with natural livingstonite

Temp., °C	time, hr.	products
455	1	melt[a]
453	$\frac{1}{2}$	melt[a]
451	1	livingstonite
450	12	livingstonite

b: Experiments with synthetic livingstonite

Composition	Temp., °C	time, days	products
$HgSb_4S_7$	400	150	metacinnabar+stibnite
$HgSb_4S_8$	400	150	livingstonite
$HgSb_4S_8$	400	5	livingstonite
$HgSb_4S_8$	456	$\frac{1}{2}$ hr.	melt[a]
$HgSb_4S_8$	451	2 hr.	livingstonite
$HgSb_4S_8$	448	17	livingstonite

[a] The liquid phase formed on melting of livingstonite quenches to form a dark reddish glass with a density of 4.52 ± 0.04 gm/cm^3.

these experiments ($\frac{1}{2}$ hour at 400° and 1 hour at 300°C) the copper reacted with the sulfur in the vapor to form a composition between Cu_2S and Cu_9S_5 but did not form CuS. The results of the experiments indicate that the partial pressure of S_2 over the $HgSb_4S_8+HgS+Sb_2S_3$ assemblage is less than that of the Cu_9S_5 sulfidation curve. A similar experiment using a small amount of NiS in place of the Cu resulted in the formation of NiS_2 at 400°C, and thus indicates that the partial pressure of S_2 must be greater than the NiS sulfidation curve at 400°C. No sign of reaction of mercury or antimony with the Cu or NiS was observed in any of the experiments. Knowledge of the partial pressure of S_2 over the above mentioned assemblage permits an order of magnitude calculation of the free energy of formation of $HgSb_4S_8$. Dr. Paul Barton, who is presently in the process of evaluating the thermodynamic data for the sulfidation reactions of HgS and Sb_2S_3, has kindly provided the latest free energy data for the antimony and mercury sulfides. These data, with the limiting values of P_{S2}($10^{-10.7}$ to $10^{-5.5}$atm at 300°C and $10^{-6.0}$ to $10^{-2.9}$atm at 400°C), have been used in the equation:

$$HgS + 2Sb_2S_3 + \tfrac{1}{2}S_2 = HgSb_4S_8$$

to calculate the free energy of formation of $HgSb_4S_8$ as between -127.4 and -120.5 kcal at 300°C and between -108.1 and -103.3 kcal at 400°C. The uncertainties of these values due to uncertainties associated with the reactants are about 3.5 kcal. Refinement of the free energy values for the reactants and S_2 partial pressures will permit a more accurate calculation.

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