

## Skinnerite, $\text{Cu}_3\text{SbS}_3$ , A New Sulfosalt from the Ilímaussaq Alkaline Intrusion, South Greenland<sup>1</sup>

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### Abstract

A new mineral, skinnerite ( $\text{Cu}_3\text{SbS}_3$  with minor amounts of silver), is identical with synthetic  $\text{Cu}_3\text{SbS}_3$  (the B' phase of Skinner, Luce, and Makovicky, 1972). A reversible phase transformation takes place in both materials at about 122°C. The high temperature modification (B) is orthorhombic ( $a = 7.81 \text{ \AA}$ ,  $b = 10.25 \text{ \AA}$ ,  $c = 6.61 \text{ \AA}$ , space group  $Pnma$ ,  $Z = 4$ ); the low temperature modification (B') is monoclinic ( $a = 7.81 \text{ \AA}$ ,  $b = 10.25 \text{ \AA}$ ,  $c = 13.27 \text{ \AA}$ ,  $\beta = 90^\circ 21'$ , space group  $P2_1/c$ ,  $Z = 8$ ). The latter becomes polysynthetically twinned on (001). Optical data, microindentation hardness, etching results, and Guinier powder data are listed. Skinnerite occurs intergrown with senarmonite, valentinite, native antimony, tetrahedrite, chalcocite, galena, and traces of loellingite. These minerals form ore aggregates less than 1 cm in size disseminated in analcime-natrolite veins cutting naujaite rocks in the southern part of the Ilímaussaq intrusion. The geological and mineralogical evidence indicates that the ore aggregates crystallized at about 400°C from metal-rich residual magmatic fluids markedly deficient in sulfur.

### Introduction

During the 1972 field season a mineralogically unique Cu-Sb mineralization was discovered in the Ilímaussaq alkaline intrusion in South Greenland. One of the minerals present was recognized as being a natural analogue of the low temperature synthetic phase  $\text{Cu}_3\text{SbS}_3$  described by Skinner, Luce, and Makovicky (1972). The occurrence yielded only small amounts of the new mineral so that descriptive data obtained from the synthetic and natural material were cross-checked and combined, once the identity of the two was established. The synthetic material used comes from the original work by Skinner *et al* (1972).

The name *skinnerite* is in honor of Professor Brian J. Skinner, Department of Geology and Geophysics, Yale University, who worked out the phase relations in the system Cu-Sb-S, including detailed descriptions of those for synthetic  $\text{Cu}_3\text{SbS}_3$ . The name was approved by the IMA Commission for

New Minerals and Mineral Names in July 1973. The type material is kept at the Mineralogical Museum, University of Copenhagen, Denmark, file no. 1973.421.

### Mineral Description

Skinnerite occurs as small irregular grains (average size 0.1 mm) in fine-grained sulfide-oxide aggregates (Figs. 1 and 2) embedded in analcime-natrolite veins which cut the naujaite rocks of the Ilímaussaq intrusion.

The chemical composition of skinnerite was established on the basis of 15 microprobe analyses of the natural material. They are summarized in Table 1. The Hitachi microprobe model MS-5 of the Institute of Mineralogy, Copenhagen, was used (acceleration voltage of 30 kV, take-off angle of 42.5°). Standards were pure Cu, Sb, Ag, and natural PbS. Matrix corrections were made using a program written by Springer (1967). The compositional ranges, expressed as the calculated standard deviations in Table 1, are all within instrumental errors and cannot be interpreted as compositional

<sup>1</sup> Contribution to the Mineralogy of Ilímaussaq No. 33.

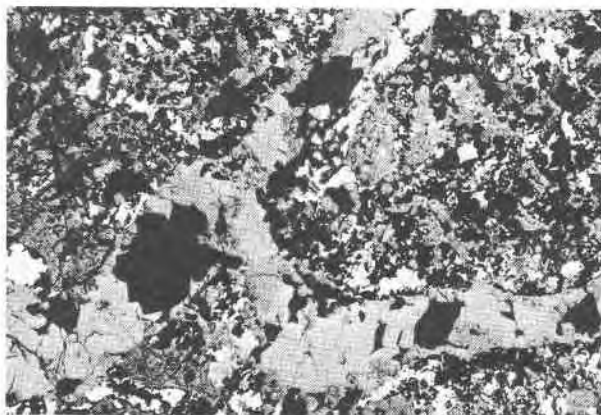


FIG. 1. Section of the mineral aggregate composed of senarmontite (black) and valentinite (dark gray) with isolated grains of native antimony (white) and the skinnerite-tetrahedrite intergrowth (light gray). The cross-cutting veins contain valentinite (dark gray), tetrahedrite (gray), and skinnerite (light gray). 45  $\times$ , oil immersion, one nicol.

variations of different mineral grains. On the basis of the analyses the empirical formula for skinnerite,  $\text{Cu}_{3.0}\text{Ag}_{0.1}\text{Sb}_{1.0}\text{S}_{2.9}$ , was obtained, which is very close to the ideal formula,  $\text{Cu}_3\text{SbS}_3$ . The latter has been well established for the synthetic material by Skinner, Luce, and Makovicky (1972), who also report a small compositional range of  $\text{Cu}_3\text{SbS}_3$  along the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  join at 500°C. Hall (1972) reports extensive solid solution of Ag in synthetic  $\text{Cu}_3\text{SbS}_3$  although he does not give exact compositions of his products.

In reflected light skinnerite is light bluish gray. Reflectance pleochroism is weak in air, weak to

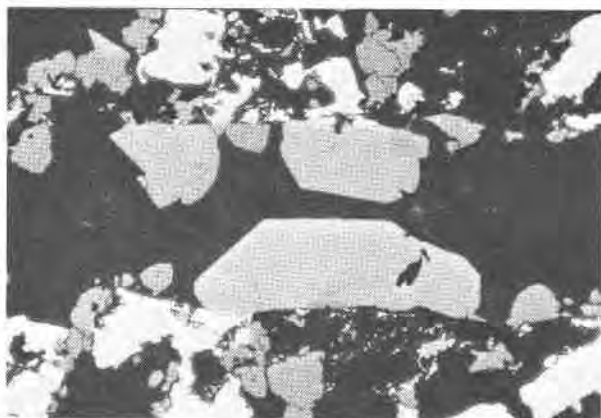


FIG. 2. Vein with crystals of skinnerite (white) and considerably smaller crystals of tetrahedrite (light gray) enclosed in valentinite (dark gray). 270  $\times$ , oil immersion, one nicol.

TABLE 1. Results of Microprobe Analyses on Skinnerite

	Wt. %		Mol. ratio
Ag	2.01	esd 0.45	0.077
Cu	46.08	0.51	2.998
Sb	29.06	0.74	0.987
S	22.79	0.34	2.938
Total	99.94		7.000

distinct in oil. Anisotropy is distinct in air, distinct to strong in oil with colors from pale purple to grayish yellow. Deep red internal reflections are commonly observed in air and are very pronounced in oil. Reflectance measurements were made by Drs. J. Besterio and A. López-Solar in the laboratory of Professor M. Font-Altaba, Department of Crystallography and Mineralogy, Barcelona. Results are plotted in Figure 3, and the values at the four principal wavelengths are listed in Table 2. The instrument and method used are described by Simpson and López-Solar (1973). The micro-indentation hardness ( $\text{VHN}_{50g}$ ) is 148-166 (Instrument DURIMET, Leitz). Etching tests (one minute) gave negative results with the following reagents: HCl (1:1),  $\text{HNO}_3$  (1:1), KOH (40 percent),  $\text{FeCl}_3$  (20 percent),  $\text{HgCl}_2$  (5 percent) and KCN (20 percent).

### Crystallography

Single crystal studies and Guinier data show the complete identity of natural and synthetic skinnerite. Both display the B-to-B' phase transformation described first by Skinner, Luce, and Makovicky (1972).

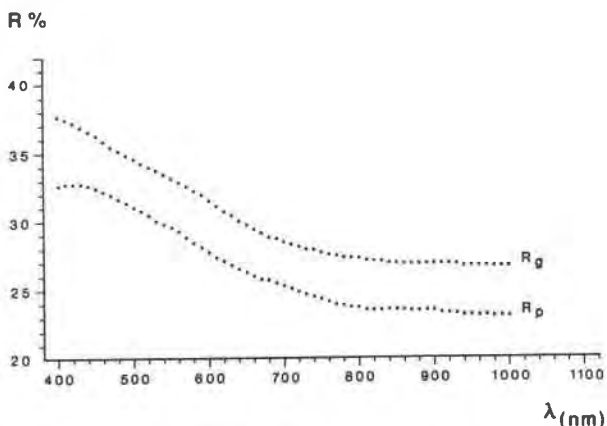


FIG. 3. Reflectivity dispersion curves of skinnerite.

The low temperature modification of  $\text{Cu}_3\text{SbS}_3$  is monoclinic, space group  $P2_1/c$ , with  $a = 7.815 \pm 0.001 \text{ \AA}$ ,  $b = 10.252 \pm 0.003 \text{ \AA}$ ,  $c = 13.270 \pm 0.002 \text{ \AA}$ ,  $\beta = 90^\circ 21' \pm 1'$ . Lattice constants were refined from Guinier data taken at room temperature from the synthetic material, using a computer program written by E. Leonardsen, Institute of Mineralogy, University of Copenhagen. Weissenberg data from a crystal of natural skinnerite show the presence of submicroscopic twinning on (001), identical with the submicroscopic to microscopic twinning found in synthetic crystals. In the latter it results from a high-to-low reversible phase transformation of the B to B' form which takes place at  $122^\circ$  (Makovicky and Skinner, 1972). At least the pure synthetic  $\text{Cu}_3\text{SbS}_3$  is in the metastable portion of its existence range at this temperature (Skinner, Luce, and Makovicky, 1972). The synthetic unquenchable high-temperature form (phase B) of  $\text{Cu}_3\text{SbS}_3$  is orthorhombic, space group  $Pnma$  (preferred to  $Pn2_1a$  both on the basis of the structure investigation now in progress and on the symmetry relationships of the high and low forms). Its lattice constants, based on Weissenberg data at  $150^\circ\text{C}$  (Makovicky and Skinner, 1972), are:  $a = 7.81 \text{ \AA}$ ,  $b = 10.25 \text{ \AA}$ ,  $c = 6.61 \text{ \AA}$ . The structure investigation indicates  $Z = 4 \text{ Cu}_3\text{SbS}_3$  for the high temperature form, implying  $Z = 8$  for the low temperature B' modification. The phase-transformation origin of the twinning in the natural material, with the volume ratio of the two orientations  $\approx 1:1$ , was corroborated by heating a crystal of natural skinnerite mounted on a Weissenberg apparatus equipped with a heating head. In spite of the small size of the crystal, the reversible monoclinic to orthorhombic (B'  $\leftrightarrow$  B) transformation could be clearly determined to lie between  $115$  and  $125^\circ\text{C}$ .

TABLE 2. Reflectance Measurements in Air on One Skinnerite Grain, Showing Maximum Anisotropism by Crossed Nicols.

$\lambda$ (nm)	481	546	589	644
$R_p$	31.5	29.5	28.0	26.3
$R_g$	35.0	33.1	31.8	29.8

Powder diffraction patterns of synthetic and natural skinnerite at room temperature (the phase B') were taken on a Guinier-Hägg camera using the  $\text{CuK}\alpha_1$  radiation and quartz powder as standard. This technique resolved the very closely situated  $hkl$  and  $hk\bar{l}$  lines, which usually coalesce when standard powder techniques are used (Skinner, Luce, and Makovicky, 1972; Godovikov, Ilyasheva, and Nenasheva, 1971), and allowed further refinement of the lattice constants of the low-temperature form. Although pure natural material was available only in minor amounts, its Guinier pattern contained all the important lines of the synthetic analogue.

The high-to-low phase transformation of  $\text{Cu}_3\text{SbS}_3$  involves doubling of the  $c$  axis and appearance of a very slight monoclinic deformation ( $21'$  of arc), connected with an extensive symmetry degradation as illustrated in Figure 4 (Makovicky and Skinner, 1972). The intensities of new reflections arising from the doubling of the  $c$  axis, are medium to weak. The  $0kl$  reflections with  $l = 2n$ , however, correspond to the  $0kl$  reflections of the high-temperature form and nearly preserve the original  $n$ -glide extinction scheme. Consequently, all  $0kl$  reflections with  $l$  even of the B' phase with  $k + \frac{1}{2}l = 2n + 1$  are very weak. Similarly, of those  $hk0$  reflections which are systematically absent in

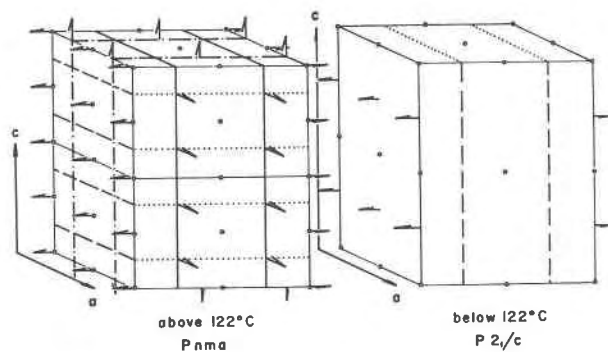


FIG. 4. Relationships between the unit cells and symmetry elements of the high-temperature (left) and low-temperature (right) modifications of skinnerite.

the B phase as a consequence of the  $a$ -glide plane, only several weak-to-extremely-weak reflections (150, 1.11.0, 330, 340, and 350) appear in the monoclinic B' form. This indicates that the distortions in the low temperature form nearly preserve the  $a$ - and  $n$ -glide configurations of the structural elements in a subcell with the dimensions of the elements in the substructure with a subcell equal to the original high-temperature unit cell.

The extinction violations due to double diffraction were eliminated by comparing the single crystal photographs of skinnerite taken with Cu and Mo radiations.

The twinning on (001) always present in the low-temperature form leads to an angular difference of only  $42'$  between the  $a^*$  orientations of the twin lamellae. The latter led Godovikov, Ilyasheva, and Nenasheva (1971) to describe the low temperature form of  $\text{Cu}_3\text{SbS}_3$  erroneously as orthorhombic and to regard it as fully analogous to wittichenite,  $\text{Cu}_3\text{BiS}_3$ . Their conclusions were further propagated by Hall (1972). The complete identity of our and Godovikov's (1971)  $d$ -values precludes existence of two different modifications of  $\text{Cu}_3\text{SbS}_3$  in this case.

The kinship between  $\text{Cu}_3\text{SbS}_3$  and  $\text{Cu}_3\text{BiS}_3$  is

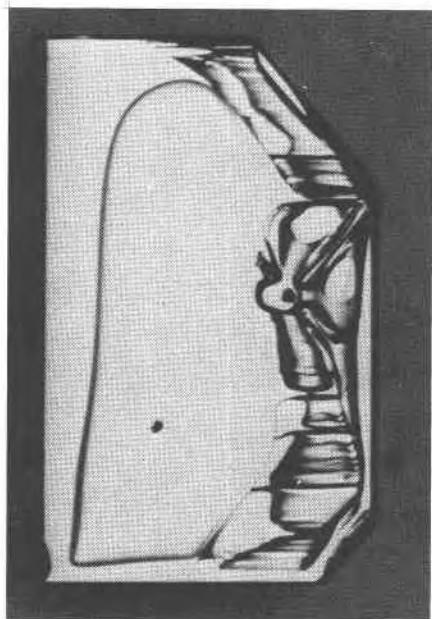


FIG. 5. Crystal (0.9 mm long) of synthetic skinnerite grown from a sulfide vapor phase at  $400^\circ\text{C}$ . Elongation parallel to the  $a$  axis. Crystal is tabular on  $\{010\}$ , but partly displays skeletal growth.

revealed by the similarities of all three lattice dimensions of the high temperature form of skinnerite to those of wittichenite (Nuffield, 1947). The low temperature forms of these two minerals have profoundly different space groups,  $P2_1/c$  vs  $P2_12_12_1$ . Wittichenite has recently been found to possess a high-to-low phase transformation somewhat similar to that of skinnerite (Makovicky and Makovicky, unpublished data). Through complicated reversible changes confined between  $118^\circ\text{C}$  and  $\approx 150^\circ\text{C}$ , the low temperature form of wittichenite ( $P2_12_12_1$ ) converts into the high temperature form. The latter preserves the unit cell vectors of the low form but assumes the same Laue symmetry as the high temperature form of  $\text{Cu}_3\text{SbS}_3$ . Based upon the observed changes in symmetry, the known structural characteristics of the high temperature form of  $\text{Cu}_3\text{SbS}_3$  (Makovicky and Skinner, 1972) and of the low temperature form of wittichenite (Matzat, 1972; Kocman and Nuffield, 1973), it is assumed that the phase transformations in both minerals are connected with a transition of copper atoms from fixed to mobile states (Makovicky and Skinner, unpublished data). This will also cause their equal statistical distribution over previously unequally populated structural positions. Although Sb substitution for Bi in  $\text{Cu}_3\text{BiS}_3$  may exceed 50 atomic percent at  $375^\circ\text{C}$ , the solubility of Bi in  $\text{Cu}_3\text{SbS}_3$  at  $375^\circ\text{C}$  is less than 10 percent (Skinner and Makovicky, unpublished data). In spite of the overall similarity of the high temperature structures of wittichenite and skinnerite, we have to assume that the geometrical differences between them (caused primarily by slightly different shapes and sizes of Bi-S and Sb-S coordination pyramids) are large enough to cause the immiscibility gap, the differences in their phase transformations, and the different structures of the two low temperature forms.

The morphology of the crystals of synthetic  $\text{Cu}_3\text{SbS}_3$ , grown either from sulfide vapor or in hydrothermal solutions (4 M KCl and 4 M  $\text{NH}_4\text{Cl}$  solutions at  $375^\circ\text{C}$ , 2000 bars) (Makovicky and Skinner, 1972), conforms with the orthorhombic symmetry of the B modification. Such crystals are flattened to tabular on  $\{010\}$  and slightly elongated in the  $[100]$  direction. The orthorhombic crystal forms present were determined from measured photomicrographs and are, in the order of prominence,  $\{010\}$ ,  $\{101\}$ ,  $\{011\}$ ,  $\{001\}$ ,  $\{100\}$ , and  $\{111\}$  (Fig. 5). Interfacial angles of the natural material, obtained

from photomicrographs such as Figure 2, suggest that the habit of natural crystals is essentially determined by the same forms.

Only the thinnest tabular crystals of synthetic skinnerite (thickness  $\approx 0.003$  mm) are sufficiently transparent to reveal the fine polysynthetic twinning parallel to (001), resulting from the  $B \rightarrow B'$  phase transformation. The monoclinic extinction angle relative to the  $a$ -axis is  $5^\circ 30'$ . The microscopic lamellae often become too fine to be discerned optically and only the single crystal photographs show that such crystals are also twinned as described above. The very deep red color of skinnerite does not allow the observation of any internal details of its grains in thin sections of the natural material.

The calculated density of the monoclinic form of  $\text{Cu}_3\text{SbS}_3$  is  $5.10$  g/cm<sup>3</sup>. Neither the impure fine-grained natural material nor the synthetic crystals, full of fluid and/or gas inclusions, were suitable for a reliable density measurement.

#### Mode of Occurrence

Skinnerite occurs in a complex of analcime-natrolite veins situated in naujaites of the southern part of the Ilímaussaq intrusion, the description of which is now in preparation (by S. Karup-Møller). They are located on a mountain plateau approximately 1 km inland and to the north-east of the head of the fiord Kangerdluarssuk. Thus far the mineral association containing skinnerite has been found only in a small group of large angular boulders embedded in the less than 2 m thick blanket of till covering the area. Their size, shape, and distribution indicate that they were probably separated from nearby, unexposed mineral veins. Similar veins in surrounding bedrock outcrops contain one or several of the following minerals: natrolite, analcime, ussingite, sodalite, feldspars, aegirine, and arfvedsonite, associated with a number of rare minerals present in small amounts. In one of these veins Cu-Sb mineralization, different from that of the skinnerite-bearing vein material and briefly described below, was identified.

The silicate minerals of the boulders consist of coarse-grained, dull-gray analcime ( $\approx 90$  percent) containing coarse-crystalline natrolite and minor amounts of fine-grained albite, aegirine, arfvedsonite, and altered steenstrupine. The ore aggregates form isolated and sharply outlined bodies less than 1 cm in size. The bodies are irregularly shaped when surrounded by fine-grained silicate masses, or partly

TABLE 3. Powder Diffraction Patterns of the Low Temperature Form of Synthetic and Natural Skinnerite.

Synthetic $\text{Cu}_3\text{SbS}_3$			Natural skinnerite	
$d_{hkl}$	l	hkl	$d_{hkl}$	l
5.62	4	111		
5.57	1	01 $\bar{2}$ , (012)		
5.13	1	020		
5.06	3	102, 10 $\bar{2}$		
4.533	5	112, 11 $\bar{2}$	4.548	1
4.075	2	022		
3.911	8	200	3.910	6
3.603	3	122, 12 $\bar{2}$ , 113		
3.518	4	211, 21 $\bar{1}$		
3.317	5	004		(overlap with quartz)
3.208	7	21 $\bar{2}$	3.210	4
3.192	7	212	3.155	4
3.105	6	220	3.111	6
3.061	6	104, 123	3.054	4
3.048	7	104, 131		
3.033	7	032, 22 $\bar{1}$	3.048	7
2.933	5	114		
2.921	5	114	2.929	2
2.830	10	132, 13 $\bar{2}$	2.831	10
2.810	3	222, 213, 22 $\bar{2}$		
2.785	6	024		
2.628	9	124	2.628	4
2.619	9	124	2.622	4
2.570	5	230, 015		
2.560	4	040	2.563	3
2.547	3	133		
2.537	4	223, 204		
2.4780	7	311, 31 $\bar{1}$	2.482	2
2.4595	4	214		
2.4495	4	214		
2.3980	5	232	2.395	1
2.3646	4	312		
2.3562	2	312	2.359	1
2.2904	5	321		
2.1991	5	313		
2.1905	5	313		
2.1636	4	016		
2.1518	3	215	2.152	5
2.1395	3	215		
2.0554	5	304		
2.0430	5	304, 24 $\bar{2}$		
2.0368	5	242, 234		
2.0132	4	314		
2.0031	4	—		
1.9587	5	151, 15 $\bar{1}$		
1.9180	5	410, (206)		
1.9068	5	324		
1.8979	7	324, 152, 21 $\bar{6}$		
1.8781	1	402, 333		
1.8639	1	017, (402, 333)	2.864 (B)	1
1.8569	5	036		(a number of un-
1.8135	5	11 $\bar{7}$ , 34 $\bar{1}$ , 117, 250		measurably weak
1.8059	9	136, 136, 226, 341		lines follow)
1.7633	5	422, 413, 342		
1.7589	5	422, 413, 342		
1.7500	7	252, 25 $\bar{2}$ , 334		
1.7074	5	060		
1.7016	1	154, 154		
1.6967	4	430		
1.6910	1	423, 306		
1.6733	4	236		
1.6027	3	344		
1.5967	2	344, 351, 35 $\bar{1}$		
1.5777	5	028		
1.5650	5	352, 260		
1.5299	2	—		
1.5241	3	208		
1.5074	2	425, 336		
1.5015	5	056, 425		
1.4893	7	164, 164		

angular when they fill the cavities among large subhedral natrolite crystals. The ore minerals (Fig. 1) represent a fairly uniform, fine-grained mixture of anhedral grains of valentinite (40 percent, visual estimation from polished sections), senarmontite (30 percent), skinnerite (10 percent), tetrahedrite (10 percent; electron microprobe analyses yielded the composition  $\text{Ag}_{0.3}\text{Cu}_{11.4}\text{Sb}_{4.4}\text{Fe}_{0.6}\text{S}_{12.6}$ ), native antimony (5 percent), chalcostibite (1 percent), galena (1 percent), loellingite ( $\ll 0.1$  percent), and silicate components (3 percent). These aggregates are cut by irregular coarser-grained veinlets containing valentinite and all the Cu-Sb sulfides just mentioned (with native antimony and senarmontite absent, Fig. 1, 2). The veinlets do not reach the boundaries of the aggregates and represent the last stage of their crystallization. The sulfide-oxide aggregates are sometimes outlined by a narrow rim of either skinnerite or valentinite. A detailed description of the individual members of the sulfide-oxide association is given elsewhere (Karup-Møller, in preparation).

### Discussion

Experimental studies (Skinner, Luce, and Makovicky, 1972) revealed that  $\text{Cu}_3\text{SbS}_3$  is stable in the condensed Cu-Sb-S system in the temperature interval from 359° to 607°C. Below 359°C this phase decomposes into a mixture of native antimony, chalcostibite, and tetrahedrite. We do not expect that the minor amounts of silver in the natural phase will substantially change these limiting temperatures. The annealing experiments by Hall (1972), in which he obtained  $(\text{Cu},\text{Ag})_3\text{SbS}_3$ , were not carried out below 400°C.

The skinnerite-bearing veins and related silicate veins lie in naujaite, only a short distance from a lujavrite body intrusive into naujaite. They are considered to be crystallization products of the water-rich magmatic fluids which developed during the final stages of the crystallization of lujavrite magma. Sørensen (1962) assumes that the latter consolidated at temperatures close to 400°C and at a pressure of about 2000 bars. A temperature of consolidation between 400° and 500°C was proposed by Piotrowsky and Edgar (1970) on the basis of their experimental results. At another locality within the Ilímaussaq massif north of the bay Tuperssuatsiait, similar Cu-Sb-sulfide and -oxide minerals were found in a lujavrite vein where local concentration of coarse natrolite has taken place (Karup-Møller, in preparation). Here the large

natrolite crystals occur either directly embedded in lujavrite, or lujavrite fills the interstices between them. Thus, the conditions of formation of the sulfide-oxide minerals can be estimated as approximately 400°C and a few thousand bars, lying within the experimental stability limits for pure skinnerite. Attempts to confirm the temperature of formation using fluid inclusions in associated silicate minerals failed because inclusions suitable for homogenization runs were not found.

The textural evidence and the mode of occurrence of the sulfide-oxide aggregates at both localities suggest that the aggregates represent the final crystallization stages of the injected vein material. The water-rich metal-bearing residual fluids, possibly immiscible with the silicate part of the vein material, congregated as the silicate minerals crystallized. It should be noted that the corresponding portion of the dry, condensed Cu-Sb-S system is well below the solidus surface at the above temperatures. Although a crystallization sequence can be observed, notably the early precipitation of galena and antimony with their subsequent partial resorption, the major part of the ore minerals at the Kangerdluarssuk locality crystallized penecontemporaneously, yielding the uniform, fine-grained aggregates of sulfides in the oxide matrix. Both the resorption processes and the presence of valentinite instead of antimony in the latest oxide-sulfide veins suggest that oxygen fugacity was increasing as the crystallization of the ore minerals progressed. The mineral assemblage shows that the entire ore precipitation process was determined by a concentration of sulfur low in respect to both the oxygen and the metal concentrations.

With the cooling history of the late magmatic injections of the Ilímaussaq massif unknown, preservation of skinnerite below its lower stability limit of 359°C (Skinner, Luce, and Makovicky, 1972) may be explained either by a favorable ratio of cooling rate to decomposition rate, or by a sufficient stabilization of the skinnerite structure by the small amounts of silver present.

As already mentioned, the senarmontite-valentinite-skinerite-tetrahedrite-antimony-chalcostibite association at Kangerdluarssuk represents only one of several small copper-antimony mineralization occurrences disseminated throughout the Ilímaussaq massif. The mineralization at the bay Tuperssuatsiait contains, in the order of importance, valentinite, senarmontite, Fe-tetrahedrite, Ag-tetrahedrite, native antimony, and minor amounts of famatinite,

argentite, and polybasite. While the general sequence of crystallization and resorption resembles that at Kangerdluarssuk, no skinnerite has been found at the bay Tuperssuatsiait. The major host silicate minerals are natrolite and sodalite. At three Cu-Sb localities of the Ilímaussaq intrusion cuprostibite,  $\text{Cu}_2\text{Sb}$ , occurs. In the exposed analcime veins at Kangerdluarssuk, at a distance of 20 m from the skinnerite locality, cuprostibite represents the main ore mineral with only very small amounts of dyscrasite, allargentum, loellingite, galena, and sphalerite (Karup-Møller *et al*, in preparation). At two other localities cuprostibite is associated with rare thallium minerals (chalcothallite and rohaite) and with the more common sulfides—chalcocite, digenite, galena, and sphalerite (Sørensen *et al*, 1969; Engell *et al*, 1971; Semenov *et al*, 1966; Karup-Møller *et al*, in preparation).

All the Cu-Sb ore occurrences of the Ilímaussaq massif project into the low-sulfur portion of the Cu-Sb-S subsystem of the quaternary Cu-Sb-S-O phase system, namely within the broad zone of compositions stretching between the region of cuprostibite ( $\text{Cu}_2\text{Sb}$ ) and the region of tetrahedrite. The explanation of the low sulfur fugacity in the late magmatic stage of agpaitic nepheline syenites was discussed by Kogarko (1974). The high sodium and chlorine content of the Ilímaussaq intrusion promoted the formation of sodalite (hackmanite) in its naujaite stage. The concentration of sulfur in sodalite has reduced its accumulation in the late magmatic fluids, causing an unusually high accumulation of chalcophile elements in the rock-forming silicates (Gerasimovsky, 1969) as well as the small extent of the ore mineralization and its unusual character. The latter was determined by the remaining amounts of sulfur and oxygen which varied considerably on a local scale, even between nearby vein systems.

The skinnerite-bearing and the related ore mineral associations represent a unique ore type falling into a rarely frequented portion of the Cu-Sb-S phase system. This ore type may be attributed to special conditions within the agpaitic, alkaline, Ilímaussaq intrusion that produced a low sulfur fugacity of the residual fluids.

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The interest and advice of Professor H. Sørensen and Dr. K. Brooks, University of Copenhagen, are acknowledged. Drs. J. Besterio and A. López-Soler, University of Barcelona, kindly carried out the reflectance measurements.

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