

GUSTAVITE, A NEW SULPHOSALT MINERAL FROM GREENLAND

S. KARUP-MØLLER

*Falconbridge Nickel Mines Ltd., 2281 Portage Avenue,
Winnipeg 12, Manitoba*

ABSTRACT

Two new sulphosalt minerals found in the cryolite deposit at Ivigtut, southwest Greenland are described as gustavite and phase X. Phase X has exsolved from gustavite and occurs in this mineral as submicroscopic blebs. The two phases show parallel crystallographic alignment. They have orthorhombic symmetry, $Bbmm$, $Bb2_1m$ or $Bbm2$, identical a and c cell dimensions ($13.548 \pm 0.033 \text{ \AA}$ and $4.105 \pm 0.013 \text{ \AA}$ respectively) but slightly different b dimensions ($19.440 \pm 0.026 \text{ \AA}$ and 20.0 \AA). Electron microprobe analyses agree best with the compositions: gustavite = $\text{Bi}_{11}\text{Pb}_5\text{Ag}_3\text{S}_{24}$, phase X = $\text{Bi}_{10}\text{Pb}_7\text{Ag}_2\text{S}_{24}$. Physical and optical data of the two phases are given. The two phases may form members of a solid solution series between $\text{Pb}_3\text{Bi}_2\text{S}_8$ (lillianite) and $\text{AgPbBi}_3\text{S}_6$. Similar cell dimensions and space groups of gustavite, phase X and andorite ($\text{AgPbSb}_3\text{S}_6$) also indicate a solid solutions series.

INTRODUCTION

In 1961 Prof. Pauly found a suite of Bi-Pb-Ag-(Cu)-sulphosalt minerals in the cryolite deposit at Ivigtut, southwest Greenland. Three minerals in the suite, berryite ($\text{Bi}_7\text{Pb}_3\text{Cu}_{3.5}\text{Ag}_{1.5}\text{S}_{10}$), gustavite* ($\text{Bi}_{11}\text{Pb}_5\text{Ag}_3\text{S}_{24}$) and phase X ($\text{Bi}_{10}\text{Pb}_7\text{Ag}_2\text{S}_{24}$), had not previously been described. Phase X occurs as exsolved, submicroscopic blebs in gustavite and both phases were referred to as mineral X in a recent description of berryite (Karup-Møller, 1966). Their mode of occurrence has briefly been described in that paper. A complete mineralogical description of phase X was not possible however, and no name was attached to this phase.

An ore specimen† from the Silver Bell Mine, Red Mountain, Ouray, Colorado, labelled galenobismuthinite is composed of pavonite, bismuthinite and a mineral with the composition $\text{AgPbBi}_3\text{S}_6$ determined by the electron microprobe analyser. This latter mineral is present in amounts insufficient for x-ray examination. On the basis of composition, optical data and etch tests, it is concluded that it is identical to gustavite.

*Named for Gustav Adolf Hageman (1842-1916), chemical engineer of the Cryolite Firm. The name has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

†Borrowed from Dr. Sløver at Bergskolan in Filipstad, Sweden.

A synthetic phase, phase III with the ideal composition $\text{Pb}_3\text{Bi}_2\text{S}_6$ has been described by Otto & Strunz (1968), and a natural phase, lillianite, with the same composition has been reported by Franc *et al.*, (1967). Both phases have identical cell dimensions and are very similar to those of gustavite and phase X. All have the same space group possibilities. The existence of a probable solid solution series between all of these phases, as well as between gustavite and andorite ($\text{AgPbSb}_3\text{S}_6$), is discussed below.

MINERAL DESCRIPTION

Gustavite

Habit. Grains of gustavite are tabular in form (Fig. 3 and Fig. 5) and sometimes slightly bent (Fig. 4). The smaller sized crystals tend to be idiomorphic (Fig. 5 and Fig. 7). Maximum grain size for gustavite is $2 \times 2 \times 0.5$ millimetres with an average size of $1 \times 1 \times 0.25$ millimetres.

Cleavage. Gustavite shows a rare cleavage parallel to the tabular plates.

Twinning. Two different twin laws characterize gustavite. One of these (A) is common, while the other (B) is only present in a restricted number of grains.

(A) Repeated twinning with the composition plane parallel to the tabular plates is present in most of the grains of gustavite. The composition plane is sometimes regularly shaped, in which case it stretches along the entire extension of the plates (Fig. 1). However, the composition plane is usually very irregular in shape with twin individuals having jagged margins (Fig. 6).

(B) Twinning with the composition plane oriented perpendicular to the tabular plates was found to be present in a few grains of gustavite. This composition plane is always regularly developed. Generally, each grain is composed of only two twin individuals, although in one case five were observed (Fig. 2). Grains with this type of twinning are generally slightly bent (Fig. 2 and Fig. 9). This indicates that the twin type could have been caused by deformation during growth of the adjacent mineral grains.

Phase X

Phase X occurs as extremely small particles enclosed in gustavite. These are either evenly distributed or accumulated in bands. Both the ore microscope and the electron microscope were used for studying the relationship between the two phases, with the plastic replica technique of Bradley (1954) being used for the electron microscopic study. This method requires the presence of relief differences between phases and these

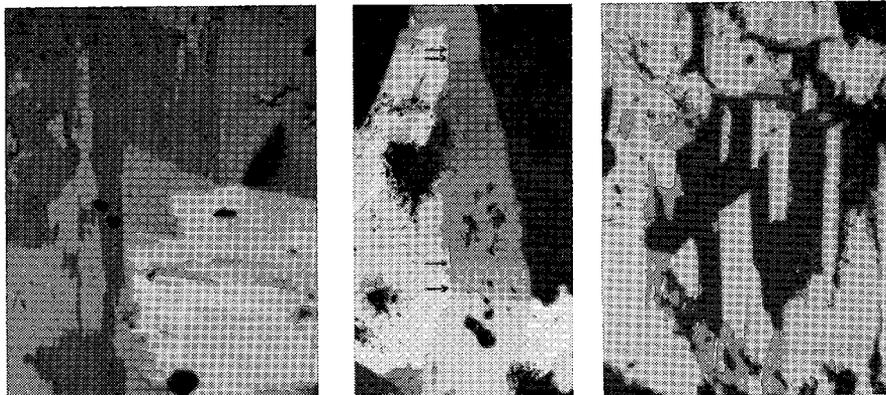


FIG. 1. Three large, differently oriented grains of gustavite (grey and white) showing repeated twinning. The twin individuals are regularly shaped and extend through most of the grains of gustavite. The grains are penetrated by galena (light grey) along their boundaries and cleavage directions.

(Polished section, 45 X, Nicols crossed at 88°).

FIG. 2. Tabular crystal of gustavite with repeated twinning normal to its long dimension. (Arrows at composition planes). Gangue minerals (black) are fluorite (right and left) and topaz (center).

(Polished section, 50 X, Nicols crossed at 75°).

FIG. 3. Tabular shaped grain of gustavite (white). Tabular inclusions of galena (grey) and fluorite (black) are oriented parallel to the host.

(Polished section, 70 X, 1 nicol. Etched 1-2 secs. with conc. HNO₃).

were obtained after treatment of polished sections with concentrated nitric acid for up to 10 seconds. The acid etches phase X, but has no effect on gustavite.

In most of the samples studied, phase X is present as oval shaped blebs with an average size of less than $1/2 \mu$. Generally, the blebs are evenly distributed and aligned parallel to the tabular plates of the host grains (Fig. 13). The proportion of gustavite to phase X is fairly constant, varying from 3:1 to 4:1. An uneven distribution of blebs may also be present (Fig. 7).

In a small number of specimens, phase X appears as lamellae in gustavite (Fig. 9). The lamellae vary in thickness from less than $1/3 \mu$ (Fig. 10) to 5μ (Fig. 14). Electron microscopic study of replica from grains of gustavite with phase X lamellae shows that the lamellae are composed of more or less well defined layers, each consisting of partly intergrown blebs of phase X, which are oriented parallel to each other (Fig. 11, Fig. 12, Fig. 15 and Fig. 16). The lamellae pinch out and disappear close to the grain boundaries of the host (Fig. 9 and Fig. 15). Where the host grains are bent, the enclosed phase X lamellae are also bent (Fig. 9 and Fig. 16).

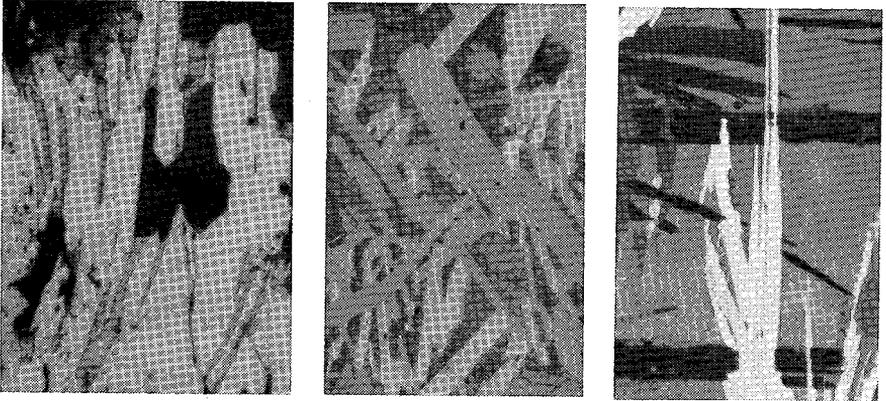


FIG. 4. Slightly bowed and tabular shaped grain of gustavite (white). Grains of galena (grey) are enclosed within and oriented parallel to the gustavite grain. Gangue minerals (black) are fluorite (well defined boundaries) and topaz (irregular boundaries).

(Polished sections. 70 X. 1 nicol. Etched 1-2 secs. with conc. HNO_3).

FIG. 5. Randomly oriented gustavite grains (white) of a smaller size than the average, in a matrix of galena (grey). The grains are idiomorphic against galena.

(Polished section. 80 X. Nicols crossed at 25° . Etched 1-2 secs. with conc. HNO_3).

FIG. 6. Distinctly twinned grain of gustavite (twin type A). The twin individuals show highly jagged margins. Enclosed laths of berryite are in place partially replaced by galena.

(Polished section. 95 X. Nicols crossed at 88°).

Sometimes the lamellae are irregular in shape, being either thick (Fig. 14) or very thin and are generally short. When one lamella pinches out, another is developed. The grain of gustavite illustrated in Fig. 10 contains a very unusual arrangement of phase X lamellae. Bands of very regularly shaped and extremely thin lamellae alternate with bands of more irregular but slightly thicker lamellae. Similar bands observed under the electron microscope are shown on Fig. 12 and Fig. 11 respectively.

Grains of gustavite have been observed to contain both evenly disseminated blebs and blebs arranged in lamellae (Fig. 8).

PHYSICAL PROPERTIES

When phase X is present as thin and closely spaced lamellae in grains of gustavite, no detectable differences in hardness or optics between the two phases can be observed. It is assumed that these properties for the two phases are practically identical. The physical data given below covers both phases, and were determined on grains of gustavite containing evenly distributed phase X blebs.

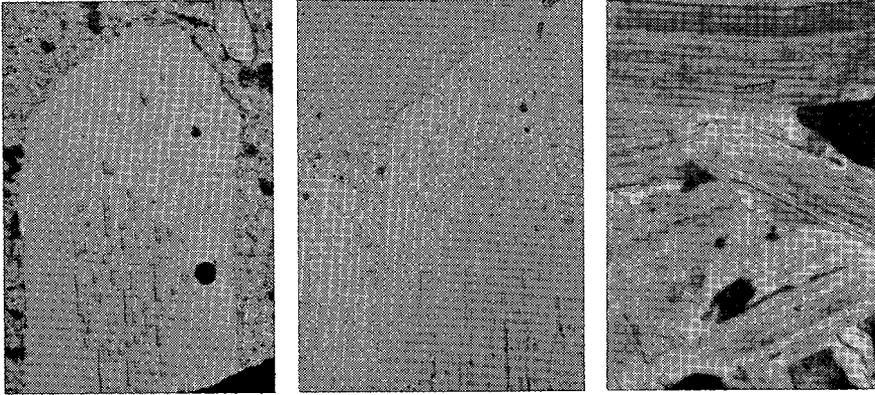


FIG. 7. Idiomorphic grain of gustavite in galena with blebs of phase X present in its central area. The blebs show tendency to lamellar development.
(Electron micrograph, 2080 X. Carbon replica).

FIG. 8. Grain of gustavite with phase X showing a transition from areas with even distribution of phase X lamellae into areas containing phase X blebs. The darker grey area is galena. A cubic or pseudocubic mineral enclosed in the galena is probably exsolved argentite.
(Electron micrograph, 1500 X. Carbon replica).

FIG. 9. Randomly oriented grains of gustavite with enclosed lamellae of phase X. The largest of the grains of gustavite is twinned with a composition plane (at the arrow) perpendicular to its tabular plates. Galena is present to a minor extent. Black areas are fluorite.
(Polished section, 50 X, 1 nicol. Etched 1-2 secs. with conc. HNO_3).

Polishing hardness. The polishing hardness of gustavite and phase X is less than that of cosalite and aikinite, but higher than that of galena.

Micro indentation hardness. The micro indentation hardness of five differently oriented and tabular shaped grains was measured. The results obtained are given in Table 1. Grain no. 1 was oriented with its tabular plates perpendicular to the polished surface. Grain no. 5 was oriented parallel to the surface. The other three grains occupied intermediate positions. The grains possess a distinct anisotropy of hardness ($\Delta\text{VHN}_{100g} = 43$).

TABLE 1. MICRO INDENTATION HARDNESS OF GUSTAVITE CONTAINING EVENLY DISTRIBUTED BLEBS OF PHASE X

Grain No.	Number of measurements	Average hardness values	ΔS Standard deviation	Orientation of mineral tablets
1	4	175	14	\perp pol. surf.
2	6	181	14	
3	7	192	8	
4	7	201	9	
5	7	218	4	\parallel pol. surf.

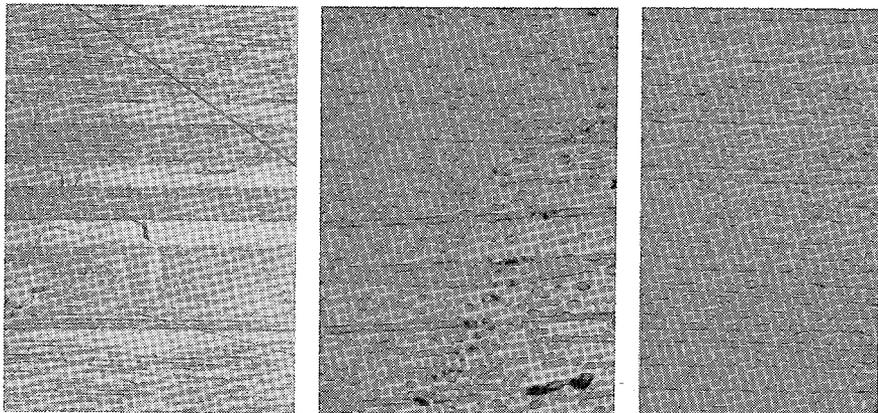


FIG. 10. Grain of gustavite with bands of regularly developed lamellae alternating with bands of irregularly developed lamellae of phase X. This distribution of the lamellae is rare.

(Polished section, 210 X, 1 nicol. Etched 1–2 secs. with conc. HNO_3).

FIG. 11. Irregularly shaped lamellae of phase X in gustavite. The lamellae are composed of oval shaped blebs arranged in parallel rows. In some areas the blebs have coalesced to form continuous strips, while others have remained isolated.

(Electron micrograph, 2920 X. Carbon replica).

FIG. 12. Regular and parallel lamellae of phase X in a grain of gustavite. Each lamella is composed of one layer of partly intergrown blebs of phase X.

(Electron micrograph, 3100 X. Carbon replica).

Reflectivity. The reflectivity of gustavite-phase X compared with that of the minerals associated with the two phases is judged to be higher than that of cosalite but lower than that of aikinite. Reflectivity measurements on two grains gave for $\lambda = 546 \text{ nm}$ 42–46% in air.

Colour and pleochroism. The reflection colours of gustavite-phase X are white to grey-white in both air and oil. The colours are very similar to those of cosalite and galena.

The reflection pleochroism for grains with the tabular plates oriented perpendicular to the surface of the polished section is weak in air but distinct in oil. Grains oriented parallel to the surface show slight to practically no pleochroism.

Anisotropism and anisotropy colours. Gustavite-phase X is weakly anisotropic in air but distinctly anisotropic in oil. The anisotropy effect is more distinct for grains with the tabular plates oriented perpendicular to the surface. The anisotropy effect is less pronounced than that of cosalite and aikinite.

The anisotropy colours are bluish-black close to the extinction position. When the microscope stage is rotated 45° from this position, the colours

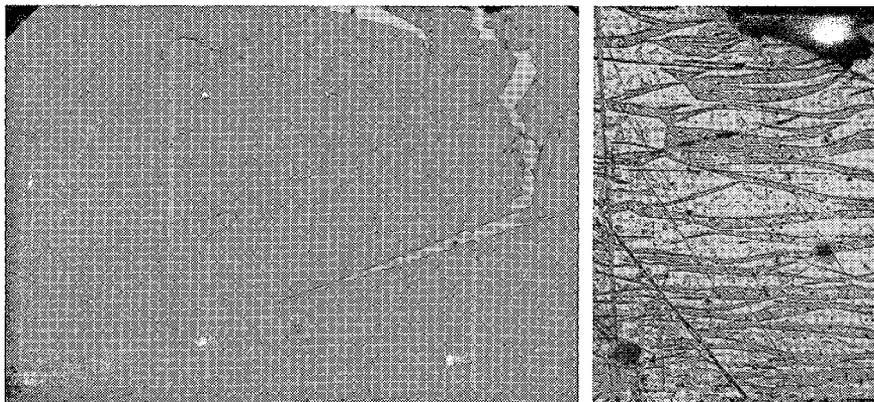


FIG. 13. Randomly oriented grains of gustavite with evenly distributed, oval shaped blebs of phase X. The blebs are aligned parallel to the tabular margins of the host grains. Dark grey areas are galena. A cubic or pseudocubic mineral enclosed in the galena is most likely exsolved argentite. The two small light grey areas without inclusions are topaz. Several polishing scratches (at arrows) cut the gustavite grains. The texture of these is similar to that of the phase X blebs. White areas represent cracks in the carbon replica. (Electron micrograph, 1260 X. Carbon replica).

FIG. 14. Unusually thick and irregularly shaped lamellae of phase X (dark grey) in a grain of gustavite (light grey). Minor PbS is present. Black area is fluorite. (Polished section, 225 X, 1 nicol. Etched 1–2 secs. with conc. HNO_3).

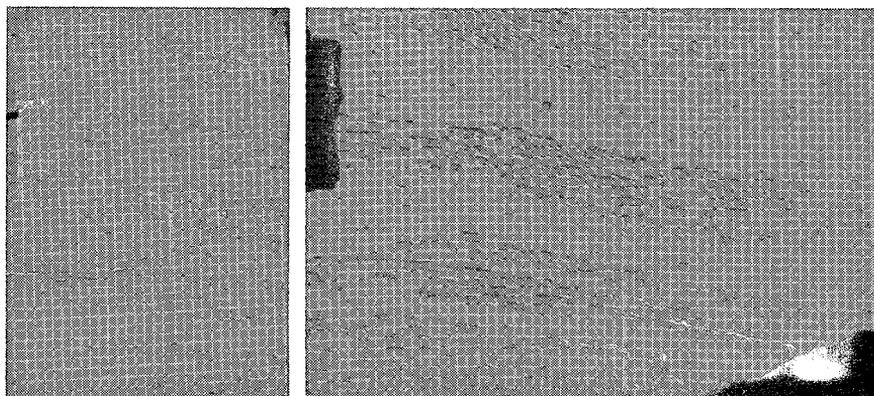


FIG. 15. Parallel lamellae of phase X in a grain of gustavite. Each lamella is composed of blebs of phase X arranged in several more or less distinctive layers. The lamellae pinch out and disappear at some distance from the host grain boundaries. The white area represent a crack in the carbon replica. (Electron micrograph, 1280 X. Carbon replica).

FIG. 16. Parallel lamellae of phase X in a grain of gustavite. The lamellae are slightly bent. Each lamellae is composed of blebs arranged in layers. (Electron micrograph, 3870 X. Carbon replica).

become greyish-white to cream. The colours are the same in air and in oil, but more distinct in oil.

Etch results. Gustavite is not etched with concentrated nitric acid after treatment for up to 10 seconds. Phase X is strongly etched and assumes a greyish colour. Gustavite and phase X were not etched after treatment for one minute with the following reagents: HCl (1HCl:1 H₂O); HNO₃ (1HNO₃:1 H₂O); KCN (20% solution by weight); KOH (40% solution by weight) and FeCl₃ (20% solution by weight).

X-RAY INVESTIGATIONS

The Weissenberg zero layer of a gustavite fragment with submicroscopic, evenly distributed phase X blebs is shown on Fig. 17. Reflections on Weissenberg films of the zero layer and of layer lines of higher order gradually split up into two reflections with increasing values of k only. A similar effect was also observed on precession diagrams taken of the cleavage fragment. Thus, two lattices aligned in a parallel fashion are present, and the fragment investigated therefore consists of two phases as already assumed. The reflections of the one lattice are approximately four times as strong as the same reflections of the other. Since the quantitative relationship between gustavite and phase X is about 3:1 to 4:1, it is concluded that the lattice of gustavite has produced the stronger intensity reflections and the lattice of phase X the weaker reflections.

Weissenberg diagrams show that the blebs of phase X in a grain of gustavite have parallel orientation. The two phases show orthorhombic symmetry, with identical a and c dimensions but differing slightly in b values (0.5 Å).

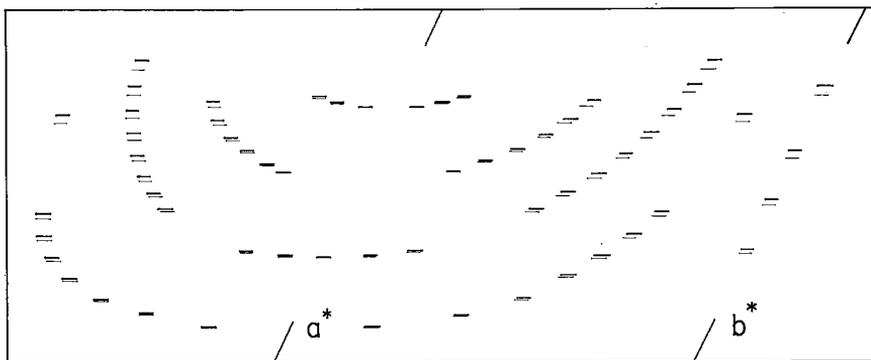


FIG. 17. Tracing of Weissenberg diagram—zero level. (Co-radiation). Thick, upper lines are gustavite α -reflections, thin lines phase X α -reflections. All β -reflections have been omitted. Separation of the reflections takes place with increasing values of k only.

On the rotation diagram, a layer line with weak intensity reflections is present between the zero layer and the first layer line. A superstructure is therefore present. From the Weissenberg diagram of this layer line, it is evident that the lattice of gustavite possesses the superstructure, and a doubling of the a and c values has taken place.

Reflection takes place when the following rules are satisfied:

$$\begin{aligned} (hkl) \quad h + l &= 2n \\ (0kl) \quad k &= 2n \end{aligned}$$

This leads to the following possible space groups: $Bbmm$, $Bb2_1m$ and $Bbm2$.

Guinier powder films were indexed using information obtained from the Weissenberg diagrams. Results are given in Table 2. Line nos. 1–28 are gustavite lines. Of these, nos. 20–28 are caused by the superstructure of the lattice.

The dimensions of the unit cell of gustavite were determined by the "least-squares method", the calculations being carried out on a GIER digital computer. The following cell dimensions were obtained:

$$\begin{aligned} a &= 13.548 \pm 0.033 \text{ \AA} \\ b &= 19.449 \pm 0.026 \text{ \AA} \\ c &= 4.105 \pm 0.013 \text{ \AA} \end{aligned}$$

Only one line, no. 29 could be attributed to phase X. The reason for the apparent absence of phase X lines is not clear. One possible explanation is the small grain size of the blebs. However, this is not an entirely satisfactory explanation, since phase X is clearly defined on the Weissenberg photographs.

No superstructure of phase X was found, and the superstructure of gustavite is very weak. Since reflections from phase X are approximately four times less intense than the corresponding reflections from gustavite, it is doubtful whether a superstructure of phase X could be recognized on an x -ray film.

The cell dimensions for phase X are:

$$\begin{aligned} a &= 13.548 \text{ \AA} \\ b &= 20.0 \text{ \AA} \\ c &= 4.105 \text{ \AA} \end{aligned}$$

The a and c values, based on Guinier data, are identical with those of gustavite. The last value is based on Weissenberg data.

Two lines, nos. 30 and 31 could not be identified.

Reflections on the Guinier films were generally diffuse, and a number of films were taken before satisfactory results could be obtained.

TABLE 2. GUSTAVITE: X-RAY POWDER DATA

Gustavite, Phase X*				Phase III* Otto & Strunz (1968)		
No.	<i>I</i>	<i>d</i> (meas.)	<i>hkl</i>	<i>I</i>	<i>d</i> (meas.)	<i>hkl</i>
1	1	9.846	020			
2	2	6.381	210			
3	1	5.565	220			
4	1	4.705	230			
5	5	3.977	240	4	4.10	240
6	2	3.844	111	2	3.934	101
7	8	3.640	121	1	3.880	111
8	8	3.401	400	4	3.678	121
9	8	3.376	250	10	3.523	250
10	10	3.363	131	7	3.419	131
11	5	3.326	410	3	3.384	400
12	1	3.237	060	3	3.326	410
13	3	3.190	420	1	3.211	420
14	3	3.068	141	3	3.128	141
15	2	3.033	301	3	3.060	260
16	10	2.996	311	6	3.005	311
17	5	2.911	260			
18	10	2.895	321	8	2.913	321
19	8	2.751	331	6	2.778	331
20	2	6.130	1/2, 2, 1/2			
21	1	5.806	3/2, 1, 1/2			
22	3	3.721	5/2, 3, 1/2			
23	3	3.516	7/2, 0, 1/2			
24	2	3.590	1/2, 5, 1/2			
25	4	3.304	5/2, 4, 1/2			
26	2	3.282	3/2, 5, 1/2			
27	4	2.953	5/2, 5, 1/2			
28	2	2.804	9/2, 1, 1/2			
29	3	3.477	205.			
30	3	3.592				
31	1	3.551				

*Guinier powder data on gustavite (lines nos. 1-28) and phase X (line no. 29). Lines nos. 30-31 are unidentified. (CuK α_1).

†Guinier powder data on phase III by Otto and Strunz (1968). $a = 13.522$ Å, $b = 20.608$ Å and $c = 4.112$ Å. (CuK α_1).

A phase III (Pb₃Bi₂S₈) which has the same space group possibilities and very similar cell dimensions as gustavite and phase X has been synthesized by Otto & Strunz (1968). The x-ray data on this phase are given in Table 2.

ELECTRON MICROPROBE ANALYSES

The nature of gustavite and phase X and intimate intergrowth of this material with galena prevents its isolation for chemical analyses. The chemical compositions of gustavite and phase X were thus determined using an electron microprobe.

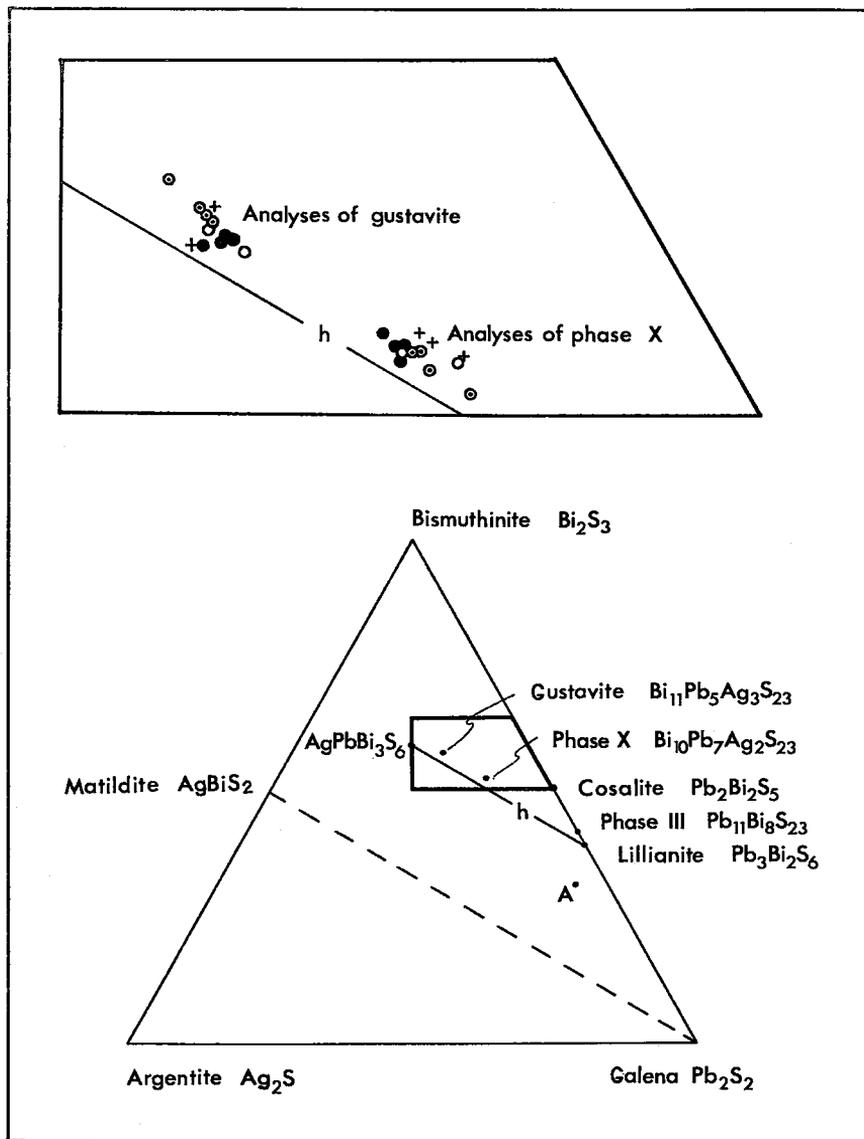


FIG. 18. Diagram showing results of electron microprobe analyses. The symbols (cross full circle, circle with dot and open circle) represent analyses on phase X lamellae and corresponding intermittent areas in each of four analyzed gustavite grains. "A" refer to sulphosalt mineral described by Kupcik *et al.*, (1961).

Electron microprobe analyses were carried out on four grains of gustavite containing unusually thick lamellae of phase X. For each grain 2-4

TABLE 3. MICROPROBE ANALYSES ON ONE GUSTAVITE GRAIN AND ENCLOSED PHASE X LAMELLAE

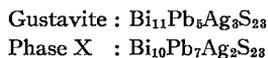
Element	Gustavite analyses		Phase X analyses	
	Wt. %	Mol. %	Wt. %	Mol. %
Ag	7.39	7.11	4.33	4.31
Pb	22.82	11.49	32.17	16.70
Bi	51.15	25.60	44.95	23.17
S	17.13	55.80	16.60	55.80
Total	98.49	100.00	98.05	100.00
Ag	7.37	7.08	5.41	5.28
Pb	22.00	11.04	31.08	15.82
Bi	51.71	25.73	46.69	23.52
S	17.27	56.25	16.83	55.83
Total	98.35	100.00	100.01	100.00

lamellae and a corresponding number of inter lamellar areas were analysed. The results obtained are plotted in Fig. 18. The analyses of one mineral grain (plotted as circles in Fig. 18) are listed in Table 3. (The analyses of all four mineral grains are too voluminous to justify tabulation). A traverse across one of the analyzed mineral grains yields the results shown in Fig. 19. The distribution of the three metals present (Pb, Bi, and Ag) in phase X lamellae and the intervening areas of gustavite is evident from the Figure. Cu is present in amounts less than 0.2%.

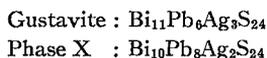
The sulphur values were only determined for two grains and are 1-2 mol.% below the calculated stoichiometric values. This discrepancy is considered to result from error on the sulphur determinations, rather than on those of the metals.

The analyses were carried out on microprobe ARL Model EMX and standard material was sulphur in pyrite, native Pb, Bi and Ag. The data were processed using a program written by Rucklidge (1967).

Formulae based on the analyses of the three metals and on the stoichiometrically calculated sulphur are as follows:



These formulae are not compatible with the size of the unit cells and space group requirements. The only acceptable compositions are:



The probable explanation for the obvious differences between the two sets of formulae is discussed below.

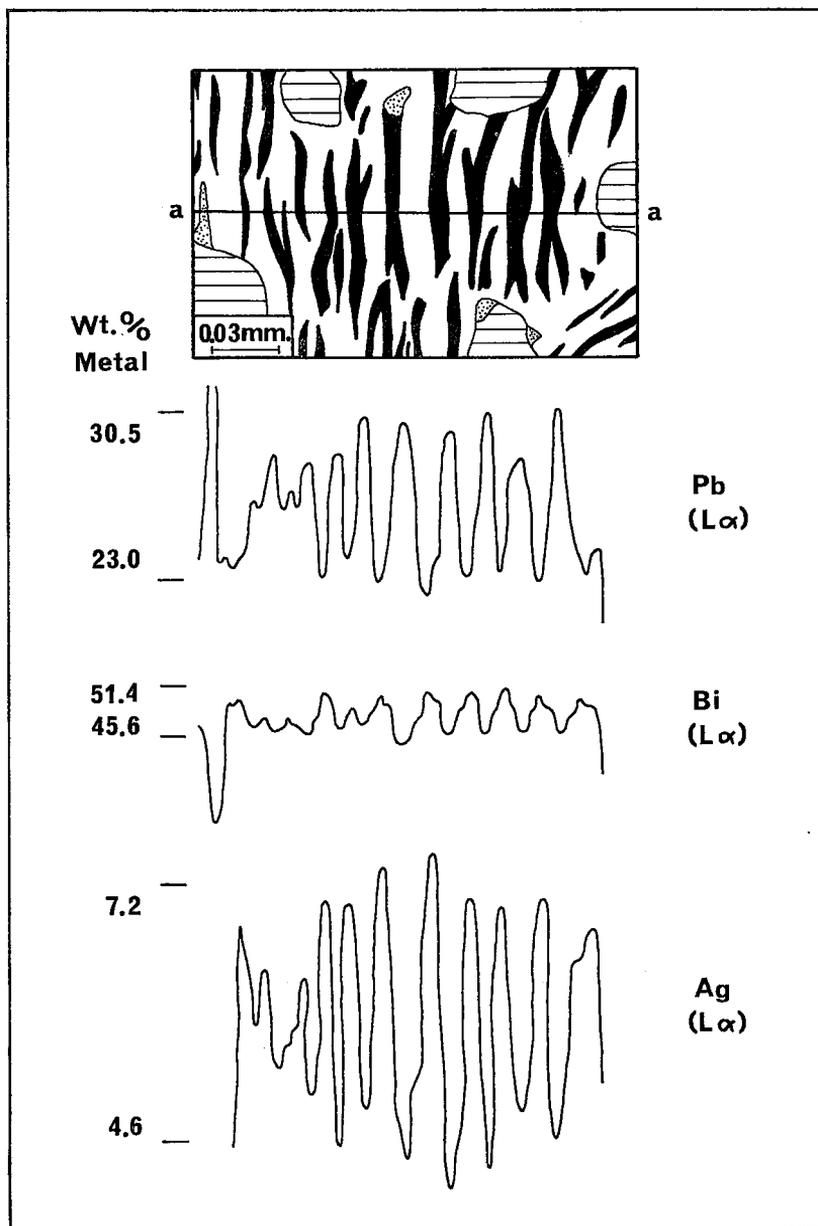


FIG. 19. Profiles of PbL α , BiL α , and AgL α x-ray intensities along the line a-a shown in the sketch. Irregular thick lamellae of phase X in a grain of gustavite. Dotted area is galena, hatched area fluorite.

DENSITY AND CELL CONTENT

Gustavite and phase X could not be isolated for density determination. The density was therefore estimated by comparison with that of minerals chemically similar to the two phases. From the values in Table 4, the density is estimated to be approximately 7 g/cm³. Assuming $Z = 1$, the calculated densities for gustavite and phase X would be 7.01 and 6.98 respectively. The calculations are based on the "ideal" formulae for the two phases.

TABLE 4. DENSITY OF DIFFERENT
SULPHOSALT MINERALS

Galenobismutite (PbBi ₂ S ₄)	: 7.19 g/cm ³
Cosalite (Pb ₂ Bi ₂ S ₆)	: 7.19 g/cm ³
Aikinite (PbCuBiS ₃)	: 7.22 g/cm ³

ORIGIN OF GUSTAVITE AND PHASE X

The microscopic relationship between gustavite and phase X suggests a typical exsolution texture. The even distribution of phase X blebs in grains of gustavite (Fig. 13) indicates that migration of atoms has not taken place over distances greater than 1–5 μ . All phase X reflections on Weissenberg diagrams have intensities which are less than the corresponding gustavite reflections. The relative difference in intensities is constant and lies between 3 and 4. This together with the very similar cell dimensions shows, that the structure of the two phases must be similar. The intensity of the reflections, caused mainly by the heavy metal atoms is a function of the atomic numbers of these and of their position in the crystal lattice. The metal positions are controlled by the S-framework and the metal atoms can be considered to occupy "holes" in this (Hellner 1958). The similar structure of the two phases shows that the arrangement of S-atoms and metal positions must be the same for the two phases. However, according to the electron microprobe analyses, some identical metal positions of the two lattices are occupied by different metal atoms. The different proportions of Pb and Bi in the unit cell will not cause noticeable differences in reflection intensities on Weissenberg films due to their very similar atomic numbers (82 and 83 respectively). Slight differences in intensity of reflections might be expected to result from different content of the lighter Ag atoms (atomic number = 47). Such differences might show up by quantitative intensity measurements on Weissenberg films.

It appears reasonable to conclude that the mineral phase before exsolution had the same S-arrangement as is now present in gustavite and

phase X. As a result of exsolution, some of the metal atoms were re-arranged, this being accompanied by a slight change in the b -dimension of the crystal lattice and may also have originated the superstructure of gustavite.

THE POSSIBILITY OF A SOLID SOLUTION SERIES IN THE
SYSTEM $\text{Ag}_2\text{S}-\text{PbS}-\text{Bi}_2\text{S}_3$ WITH LILLIANITE ($\text{Pb}_3\text{Bi}_2\text{S}_6$) AND
GUSTAVITE ($\text{AgPbBi}_3\text{S}_6$) AS POSSIBLE END MEMBERS

Otto & Strunz (1968) have synthesized five phases within the system $\text{PbS}-\text{Bi}_2\text{S}_3$. One of these (Phase III, Fig. 18) has x -ray crystallographic data very similar to those of gustavite and phase X, (Table 2) and all have the same space group possibilities. Phase III has a composition very close to that of lillianite (Fig. 18). All lillianites described prior to 1959 have been discredited in that detailed mineralogical studies have shown them to represent intergrowths of known sulphosalt minerals (Ramdohr, 1960). Ontoev (1959) has described a mineral with lillianite composition but has not determined the cell dimensions. Syritso & Senderova (1964) have also described a mineral with lillianite composition. Kupcik *et al.* (1961) report a mineral with a similar composition except for the presence of some Ag, (plotted as A in Fig. 18). Neither of the two latter minerals have cell dimensions close to those of phase III. Otto & Strunz referred to a lecture given by Franc *et al.* (1967) who reported finding a mineral with lillianite composition and cell dimensions similar to those of phase III. The space group possibilities are identical.

Based on analytical data the formulae of phase III, gustavite and phase X are not compatible with space group requirements and unit cell volumes. Otto & Strunz (1968) assume that the only reasonable formula for phase III would be $\text{Pb}_3\text{Bi}_2\text{S}_6$, and have determined the crystal structure for phase III on this assumption. The difference in composition of phase III and $\text{Pb}_3\text{Bi}_2\text{S}_6$ is considered due to substitution of Pb^{++} for Bi^{+++} , which should result in unoccupied metal positions in the crystal lattice, provided that stoichiometric balance is maintained. Consequently they give the formulae for phase III as $(3\text{Pb}_{1-x}\text{Bi}_{2x/3}\text{S} \cdot \text{Bi}_2\text{S}_3)$. On the basis of their analytical results phase III should contain 0.24 unoccupied metal positions per unit cell. They have confirmed this figure by density determinations.

An analogous approach to the two different formulae of gustavite and phase X given above would yield 0.24 unoccupied metal positions per unit cell. It is coincidental that this value for gustavite and phase X is identical to that for phase III, in that Salanci (1965) has synthesized a

phase III whose composition would give 0.80 empty metal positions per unit cell.

Assuming that no substitution of Pb^{++} for Bi^{+++} in any of the above three phases has taken place, their composition will all lie on line h in Fig. 18. This line joins lillianite ($Pb_3Bi_2S_6$) with the gustavite phase ($AgPbBi_3S_6$) from the Silver Bell Mine in Colorado and is parallel with the PbS - $AgBiS_2$ join. The composition of any one phase on the tie line h can be derived from another on this line, using the equation: $2Pb^{++} \leftrightarrow Bi^{+++} + Ag^+$. This chemical relationship and the very similar crystallographic data of the various phases suggests that a solid solution series exists between lillianite and gustavite. An almost identical solid solution series between $Pb_3Bi_2S_6$ and $(Ag, Cu)PbBi_3S_6$ has been suggested by Godovikov (1966). Synthetic work on the phase relations within the system Ag - Pb - Bi - S by Craig (1967) has failed to provide evidence of solid solution series in the system other than that between galena (PbS) and matildite ($AgBiS_2$) as first described by Ramdohr (1938). The postulated solid solution series resembles that between galena and matildite in the following respects:

1. In both series, the substitution of metal atoms is controlled by the equation: $2Pb^{++} \leftrightarrow Bi^{+++} + Ag^+$.
2. The volume of the unit cell of members decreases with increasing content of Ag^+ and Bi^{+++} .

The name gustavite has been given to the phase from Ivigtut. This phase and phase X appear to represent intermediate members of the solid solution series and should have no individual names. It is suggested that the name gustavite should be restricted to the end-member of the solid solution series, thus avoiding unnecessary mineral names. On the basis of the data presented above this end member composition would be $AgPbBi_3S_6$. However, future investigations on both natural and artificial phases may extend the solid solution series all the way to $Ag_3Bi_7S_{12}$ on the join Ag_2S - Bi_2S_3 .

GUSTAVITE, PHASE X AND LILLIANITE AS POSSIBLE MEMBERS OF THE MINERAL GROUP ANDORITE, RAMDOHRITE AND FIZELYITE

X-ray data and cell content of andorite ($Pb_4Ag_4Sb_{12}S_{24}$), ramdohrite ($Pb_6Ag_4Sb_{10}S_{23}$) and fizelyite ($Pb_7Ag_3Sb_{10}S_{23.5}$) suggest a very close mineralogical relationship between these and gustavite, phase X and lillianite. Cell dimensions of the three sulphosalt minerals were determined by Nuffield (1945). Later Donnay & Donnay (1954) examined andorite and found two varieties which occur intergrown with each other.

These two phases have identical pseudocells with $a = 13.03 \text{ \AA}$, $b = 19.15 \text{ \AA}$ and $c = 4.29 \text{ \AA}$, and identical space group possibilities $Bbmm$, $Bb2_1m$ and $Bbm2$. For andorite IV the c -dimension has increased by a factor of 4, for andorite VI by a factor of 6. Ramdohrite was found to be identical with andorite IV. Though the c -dimension of fizelyite is double that of the pseudocell, it was found that the mineral could not be classified as andorite II.

The very similar cell dimensions and identical space group possibilities of phase III, gustavite and phase X with those of the andorite pseudocell indicates that substitution of Sb^{+++} for Bi^{+++} is a possibility.

Donnay & Donnay (1954) were not able to separate andorite IV and andorite VI for chemical analyses. Determination of their chemical composition should now be possible by using the electron microprobe analyser. It will then be known if the two andorites form members of a solid solution series between "falkmannite ($\text{Pb}_3\text{Sb}_2\text{S}_6$)" and andorite ($\text{AgPbSb}_3\text{S}_6$). Such a solid solution series would then be isostructural with that between lillianite and gustavite.

Experimental work should solve the substitutional relationship between the various phases as well as the stability fields of these.

ACKNOWLEDGEMENTS

Prof. H. Pauly of the Technical University of Denmark supplied the ore samples and engaged in many fruitful discussions. Cand. polyt. M. Danø and cand. mag. E. Bang both of the University of Copenhagen and by Prof. C. Kankergaard-Møller, University of Odense, helped the author with the x -ray investigations. The author is indebted to Dr. J. Rucklidge, University of Toronto, who carried out the electron microprobe analyses, to Dr. Bowie, London, who carried out the reflectivity measurements and to Dr. H. Micheelsen, University of Copenhagen, who introduced the author to the electron microscopic study of ore specimens.

Dr. C. Coats, Falconbridge Nickel Mines Ltd., very kindly corrected the English of the manuscript.

REFERENCES

- BRADLEY, D. E. (1954): Evaporated carbon films for use in electron microscopy. *Brit. J. Appl. Phys.*, **5**, 65-66.
- CRAIG, J. R. (1967): Phase relations and mineral assemblages in the Ag-Bi-Pb-S system. *Mineralium Deposita*, **1**, 278-306.
- DONNAY, J. D. H. & DONNAY, G. (1954): Syntactic intergrowth in the andorite series. *Amer. Mineral.* **39**, 161-171.

- FRANC, L., KUPCIK, V. & MAKOVICKY, E. (1967): Unpublished manuscript presented at a crystallographic meeting in Bonn, Germany.
- GODOVIKOV, A. A. (1966). On the role of copper and silver in lead-bismuth sulphosalts. *Unpublished manuscript presented at a meeting of the International Mineralogical Association at Cambridge, England.*
- HELLNER, E. (1958): A structural scheme for sulphide minerals. *Jour. Geol.* **66**, 503–525.
- KARUP-MØLLER, S. (1966): Berryite from Greenland. *Can. Mineral.*, **8**, 414–423.
- KUPCIK, V., MATHERNY, M. & VARCEK, C. (1961): Príspevok k problemu štruktúry mineralu "lillianit". *Geol. Sbor. Sloven. AK, V.R.*, **12**, 1, 103–111.
- NUFFIELD, E. W. (1945): Studies of mineral sulpho-salts: X-Andorite, ramdohrite and fizelyite. *Trans. Roy. Soc. Canada Ser. III* **39**, 41–49.
- ONTOEV, D. O. (1959): Lillianite of the Bokuinsk deposit and conditions of its formation. *Doklady Akad. Nauk SSSR* **126**, 856–859.
- OTTO, H. H. & STRUNZ, H. (1968): Zur Kristallchemie synthetischer Blei-Wismut-Spiessglanze. *N. Jb. Miner. Abh.*, **108**, 1–19.
- RAMDOHR, P. (1938): Über Schapbachite, Matildite und den Silber- und Wismutgehalt mancher Bleiglanze. *Sitzungsber. der Preuss. Akad. Wiss., Phys.- Math. Kl.* 71–91.
- (1960): *Die Erzminerale und ihre Verwachsungen*. Akademie Verlag, Berlin, Germany.
- RUCKLIDGE, J. (1967): A computer program for processing microprobe data. *Jour. Geol.* **55**, 126.
- SALANCI, B. (1965): Untersuchungen am System $\text{Bi}_3\text{S}_2\text{-PbS}$. *N. Jb. Miner. Mh.* 384–388.
- SYRITSO, L. F. & SENDEROVA, V. M. (1964): The problem of lillianite, *Zapiski Vses. Mineralog. Obsch.*, **93**, 468–471.

Manuscript received April 18, 1969, emended July 2, 1969