

## CRYSTAL CHEMISTRY AND RE-EXAMINATION OF NOMENCLATURE OF SULFOSALTS IN THE AIKINITE-BISMUTHINITE SERIES

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### ABSTRACT

The six known phases in the aikinite-bismuthinite series, aikinite, hammarite, lindströmite, krupkaite, gladite, and pekoite, were examined using electron microprobe and X-ray precession camera techniques. This study shows that these phases do not have discrete stoichiometric compositions but that limited solid solution exists. The nomenclatures of the sulfosalts in this series (Moore 1967; Syneček & Hybler 1975; Mumme *et al.* 1976) were proposed without complete knowledge of the existence of solid solution. After re-examination of the problems of nomenclature it is concluded that the Moore and Syneček & Hybler classifications, and the name "rezbanyite", should be discarded. It is also concluded that the nomenclature proposed by Mumme *et al.* is valid. However, the known compositional range for each species should be defined as follows: *aikinite*  $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{BiS}_{3-1.5x}$  with  $0 \leq x \leq 0.29$ ; *hammarite*  $\text{Cu}_2\text{Pb}_2\text{Bi}_{4-x}\text{S}_{9-1.5x}$  with  $0.4 \leq x \leq 0.7$ ; *lindströmite*  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ ; *krupkaite*  $\text{CuPbBi}_{3-x}\text{S}_{8-1.5x}$  with  $0 \leq x \leq 0.4$ ; *gladite*  $\text{CuPbBi}_{5-x}\text{S}_{9-1.5x}$  with  $0 \leq x \leq 0.3$ ; *pekoite*, ideal formula  $\text{CuPbBi}_{11}\text{S}_{18}$ , general formula uncertain. In addition, several new localities were found for hammarite, lindströmite, krupkaite, gladite and pekoite.

### SOMMAIRE

Les six phases connues dans la série aikinite-bismuthinite (aikinite, hammarite, lindströmite, krupkaite, gladite et pekoite), après étude à la micros-

de et par diffraction des rayons X, à la chambre de précession s'avèrent être des solutions solides à domaine restreint. Les diverses nomenclatures des sulfosels de cette série (Moore 1967; Syneček & Hybler 1975; Mumme *et al.* 1976) furent proposées dans l'incertitude de l'existence des solutions solides. Un nouvel examen des problèmes de nomenclature conduit à discréditer la classification de Moore et celle de Syneček & Hybler, de même que le nom de "rezbanyite", mais la nomenclature proposée par Mumme *et al.* reste valide. Toutefois, les limites de composition doivent être définies comme suit: *aikinite*  $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{BiS}_{3-1.5x}$ ,  $0 \leq x \leq 0.29$ ; *hammarite*  $\text{Cu}_2\text{Pb}_2\text{Bi}_{4-x}\text{S}_{9-1.5x}$ ,  $0.4 \leq x \leq 0.7$ ; *lindströmite*  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ ; *krupkaite*  $\text{CuPbBi}_{3-x}\text{S}_{8-1.5x}$ ,  $0 \leq x \leq 0.4$ ; *gladite*  $\text{CuPbBi}_{5-x}\text{S}_{9-1.5x}$ ,  $0 \leq x \leq 0.3$ ; *pekoite* formule idéale  $\text{CuPbBi}_{11}\text{S}_{18}$ , formule générale incertaine. On décrit aussi plusieurs gîtes nouveaux de hammarite, lindströmite, krupkaite, gladite et pekoite.

### INTRODUCTION

The sulfosalts (Table 1), aikinite, hammarite, lindströmite, gladite, and rezbanyite in the aikinite-bismuthinite series were described as early as the last century from Gladhammar, Kalmar, Sweden by Lindström (1887-1889), Flink (1910) and Johansson (1924). Each species was defined on the basis of its chemical composition. Due to the similarity in physical properties, X-ray powder diffraction patterns, and continuous varia-

TABLE 1. LITERATURE DATA OF THE AIKINITE DERIVATIVES

Structure cell formula	a Å	b Å	c Å	Space group	Moore's (1967) notation	Synecek & Hybler's (1975) notation	Mumme et al. (1975) nomenclature*
$\text{Cu}_4\text{Pb}_4\text{Bi}_4\text{S}_{12}$	11.32	11.64	4.04	$P\bar{2}1m$	1 <sup>1</sup> -aikinite	1 <sub>4</sub> -aikinite	aikinite
$\text{Cu}_8\text{Pb}_8\text{Bi}_{16}\text{S}_{36}$	33.45	11.58	4.01	$P\bar{2}1m$	3 <sup>2</sup>	3 <sub>8</sub>	hammarite
$\text{Cu}_{12}\text{Pb}_{12}\text{Bi}_{28}\text{S}_{60}$	56.07	11.57	4.01	$Pb2_1m$	5 <sup>3</sup>	5 <sub>12</sub>	lindströmite
$\text{Cu}_2\text{Pb}_2\text{Bi}_6\text{S}_{12}$	11.15	11.51	4.01	$Pb2_1m$	-	1 <sub>2</sub>	krupkaite
$\text{Cu}_4\text{Pb}_4\text{Bi}_{20}\text{S}_{36}$	33.66	11.45	4.02	$P\bar{2}1m$	3 <sup>1</sup>	3 <sub>4</sub>	gladite
$\text{Cu}_2\text{Pb}_2\text{Bi}_{22}\text{S}_{36}$	33.50	11.32	3.99	$Pb2_1m$	-	3 <sub>2</sub> **	pekoite

\* Nomenclature approved by Commission on New Minerals and Mineral Names, I.M.A.

\*\* Was not proposed by Synecek & Hybler.

tion in chemical compositions between aikinite ( $\text{CuPbBi}_3\text{S}_9$ ) and bismuthinite ( $\text{Bi}_2\text{S}_3$ ), Paděra (1956) considered that these minerals existed as solid solutions intermediate to bismuthinite and aikinite, and proposed that the name rezbanyite should be used to represent hammarite, lindströmite, gladite, and all the intermediate members in the series.

On re-examination of the sulfosalts from Gladhammar, Welin (1966) found several phases with stoichiometric compositions between bismuthinite and aikinite, and with unit cells having superstructures of aikinite. The individual superstructure was characterized by the integral multiple of the  $a$ -translation of the unit cell of aikinite. The phases reported were  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$ ,  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$  and  $\text{CuPbBi}_5\text{S}_9$  (Table 1). The stoichiometric compositions and the formation of superstructures indicated that ordered structures, i.e. non-random substitution between Bi and Pb, most likely occurred in this series, and consequently Welin concluded that at least twenty hypothetical phases with different superstructures and stoichiometry could be present in this series.

Due to the close relationship among the superstructures, Welin (1966) suggested that all names, such as lindströmite, hammarite, gladite, and rezbanyite should be disregarded and a new nomenclature should be proposed based on a structural relationship. Thus, on the basis of Welin's superstructures, Moore (1967) proposed a general formula,  $\text{Cu}_x\text{Pb}_x\text{Bi}_{8z-x}\text{S}_{12z}$ , for the phases in this series:  $Z$  represents the integral multiple of the  $a$ -translation in aikinite for the superstructures, and  $x$  was assumed to be a multiple of 4 to satisfy the equipoint requirements for the space groups observed for the aikinite derivatives. Since only four Cu sites (i.e. four tetrahedral interstices) in each bismuthinite cell are available, the condition  $4Z > x$  must be satisfied. Consequently, a classification was proposed on the basis of  $Z^n$ , where  $n = x/4$ , the numbers of lead atoms in the asymmetric unit. Accordingly, gladite ( $\text{CuPbBi}_5\text{S}_9$ ) was named  $3^1$ -aikinite; hammarite ( $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$ ),  $3^2$ -aikinite; and lindströmite ( $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ ),  $5^3$ -aikinite (Table 1).

The discovery of the new minerals krupkaite with the composition  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_{12}$  and unit cell  $Pb2_1m$ ,  $a = 11.15$ ,  $b = 11.51$ ,  $c = 4.01\text{Å}$  (Zak *et al.* 1975; Large & Mumme 1975) and pekoite with the composition  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_{12}$  and unit cell  $Pb2_1m$ ,  $a = 33.50$ ,  $b = 11.32$ ,  $c = 3.99\text{Å}$  (Mumme *et al.* 1976) indicates the failure of Moore's classification. According to Moore, both minerals would have an  $x$  of 2 and  $n$  of  $\frac{1}{2}$ , which is not allowed in his classification. Re-

cently, Synecek & Hybler (1975) proposed a new classification using the same general formula proposed by Moore except that  $x$  can be any value in the interval  $0 \leq x \leq 4Z$ . Accordingly, gladite becomes  $3_4$ -aikinite; aikinite is  $1_4$ -aikinite; hammarite is  $3_3$ -aikinite; and krupkaite is  $1_2$ -aikinite.

Crystal structure analyses show that the aikinite structure can be derived from that of bismuthinite by placing Pb at the interior five-coordinated Bi positions in the quadrupole chain, while Cu is added to a tetrahedral interstice. The substitutions cause no major distortion of the bismuthinite arrangement, and the atomic positions in aikinite (Ohmasa & Nowacki 1970a; Kohatsu & Wuensch 1971) remain remarkably similar to those in bismuthinite (Kupcik & Vesela-Novakova 1970).

Ohmasa & Nowacki (1970b) introduced three types of ribbons to interpret the superstructures observed by Welin. The ribbons proposed are (a)  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$ -ribbon, (b)  $\text{Bi}_4\text{S}_6$ -ribbon, and (c)  $\text{CuPbBi}_3\text{S}_8$ -ribbon. The  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$ - and  $\text{Bi}_4\text{S}_6$ -ribbons were known in the structures of aikinite and bismuthinite respectively, and the existence of  $\text{CuPbBi}_3\text{S}_8$ -ribbons was later observed in the structures of krupkaite (Synecek & Hybler 1975; Mumme 1975) and gladite (Kohatsu & Wuensch 1973; Synecek & Hybler 1975). The crystal structures of aikinite, krupkaite, and gladite, as well as the superstructures observed, indicate an ordered distribution of Pb and Cu atoms in the structures.

In an investigation of the minerals in the Cu-Pb-Bi-S system, the present writers have identified all the reported natural phases, including the new mineral pekoite, in the aikinite-bismuthinite series. Instead of stoichiometric compositions suggested by Welin (1966), a limited range of solid solution was found for some of the phases. Since no solid solution of the phases had ever been reported, a detailed study on the chemical compositions and superstructures of the intermediate phases in this series seemed warranted.

#### MATERIALS

Samples labelled as aikinite from world-wide occurrences were obtained from the National Museum of Natural History-Smithsonian Institution, Washington; Geological Survey of Canada, Ottawa; Royal Ontario Museum, Toronto; and several from individuals. The description and source of each sample are listed in Table 2.

Each sample was studied by electron microprobe analyses, by X-ray powder diffraction using Gandolfi and Debye-Scherrer cameras, by

TABLE 2. Descriptions of the Materials Studied

Sample No.	Original Descriptions and Source	Identification
1 and 2	Rezbanyite from Dobsina, Hirshkohlung, Slovakia, Czechoslovakia. Associated with chalcocopyrite, pyrite, bravoite, traces of sphalerite and galena (Smithsonian Institution NMNH R 11076-2).	Aikinite
3	Aikinite from Naica, Mexico. Associated with wollastonite, chalcocopyrite, sphalerite, tennantite, tetradymite, wittichenite, and hodrushite (G.S.C. collection).	Aikinite
4	Aikinite from Berezovsk, Ekatekinborg, Ural (R.O.M. collection).	Aikinite
5	Phenakite with aikinite inclusions from San Miguel di Piracicaba, Brazil (Smithsonian Institution NMNH B 18924).	Aikinite
6	Alaskaite and argentiferous galenobismutite from Nevada, U.S.A. Associated with chalcocopyrite, bismuthinite, and a pavonite-like mineral. (G.S.C. collection).	Hammarite*
7	Aikinite from Silver Miller mine, Cobalt, Ontario (Smithsonian Institution NMNH 106760).	Lindstromite*
8	Aikinite and cosalite from Temiskaming, Quebec (G.S.C. Collection).	Krupkaite*
9	Aikinite in quartz from Cucomungo Canyon, Esmeralda Co., Nevada, U.S.A. (Smithsonian Institution NMNH 120581).	Krupkaite*
10	Aikinite, U.S.S.R. (Smithsonian Institution NMNH C 771).	Krupkaite*
11	Aikinite from Ball's mine, Little Cottonwood district, Utah, U.S.A. (Smithsonian Institution NMNH 105571).	Krupkaite*
12	Aikinite showing exsolution of two aikinite-type phases, from Bernic Lake, Manitoba. Associated with gustavite.	Gladite (blebs)* Pekoite (host)
13	Aikinite showing exsolution of two aikinite type phases, from Brejuin Correis Novos mine, Rio Grande de Norte, Brazil. Associated with native bismuth.	Gladite (blebs)* Pekoite (host)

\* These are new localities for the minerals in the aikinite-bismuthinite series.

X-ray single crystal methods, and by reflected light microscopy and etching tests.

#### CHEMICAL COMPOSITIONS AND X-RAY SINGLE CRYSTAL DATA

Electron microprobe determination of Cu, Pb, Sb, Bi and S were performed at 25 kV with a Material Analysis Company (MAC) Model 400 electron probe using a synthetic  $\text{Cu}_2\text{Pb}_2\text{Bi}_3\text{S}_{7.5}$  prepared by Springer (1971) and an antimonial bismuthinite as standards. The X-ray intensities were corrected for drift, dead time, background, absorption, fluorescence and atomic number using a computer program (Rucklidge & Gasparini 1969). The results are tabulated in Table 3 and plotted in a  $\text{Cu}_2\text{S-PbS-Bi}_2\text{S}_3$  diagram in Figure 1.

The choice of standards for analyses in the aikinite-bismuthinite series is very important. Using a synthetic standard  $\text{Cu}_2\text{Pb}_2\text{Bi}_3\text{S}_{7.5}$ , the Cu/Pb ratio in these phases is close to 1. With standards such as synthetic  $\text{AgBiS}_2$ ,  $\text{PbS}$ , and  $\text{CuS}$ , the Cu/Pb ratio was always  $<1$ , approximately 0.9. Combination of standards such as metallic Cu and Bi,  $\text{PbS}$ , and  $\text{FeS}_2$ , gave the poorest results, both in Cu/Pb and Bi. Therefore, it is likely that any deviation from the ratio 1:1 for Cu:Pb indicates inaccuracy in analysis or is due to interference from exsolved phases or adjacent minerals.

The sixteen analyses show that approximate continuity in compositions exists between aikinite and gladite, at least for compositions corresponding to aikinite and krupkaite. For compositions between gladite and bismuthinite, an exsolution between gladite and pekoite (analyses 12b & 13b) was observed in the samples from Bernic Lake, Manitoba (Fig. 2) and from Rio Grande de Norte, Brazil.

The fragments pre-analyzed by electron microprobe were extracted from the polished sections, identified by Gandolfi X-ray films, and studied by the X-ray precession method using  $\text{MoK}\alpha$  radiation. Two axial directions were precessed for each crystal, and two to three reciprocal layers were taken for each precessed axis. The cell parameters (Table 3) were refined from the X-ray powder data.

All crystals studied show a pronounced common subcell,  $Pbnm$  with  $a' \sim 11.2$ ,  $b' \sim 11.6$ , and  $c' \sim 4.0\text{\AA}$ . The true cell has a space group symmetry either  $Pbnm$  or  $Pb2_1m$ , with  $a$  being a multiple of that of the subcell and  $b$  and  $c$  unchanged.

#### Aikinite

The mineral in samples No. 1 to 5 has a chemical composition close to  $\text{Cu}_4\text{Pb}_4\text{Bi}_4\text{S}_{12}$ . Its unit cell:  $Pbnm$ ,  $a = 11.3$ ,  $b = 11.6$ , and  $c = 4.0\text{\AA}$ , therefore corresponds to aikinite. (Cu or

TABLE 3. COMPOSITIONAL AND CRYSTAL DATA OF THE SULFOSALTS IN THE AIKINITE-BISMUTHINITE SERIES

Sample No.	Cu	Pb	Bi	Sb	S	Total wt%	Formula*	$a\text{\AA}^{**}$	$b\text{\AA}$	$c\text{\AA}$	Space Group
Aikinite											
1	10.01	33.37	39.46	0.18	17.13	100.15	$\text{Cu}_{0.83}\text{Pb}_{0.85}\text{Bi}_{1.00}\text{S}_{2.81}$	11.33	11.62	4.02	<i>Pbnm</i>
2	9.86	32.55	40.40	0.15	16.78	99.74	$\text{Cu}_{0.81}\text{Pb}_{0.81}\text{Bi}_{1.00}\text{S}_{2.71}$	11.33	11.62	4.02	
3	9.57	31.74	41.37	0.0	17.07	99.75	$\text{Cu}_{0.76}\text{Pb}_{0.77}\text{Bi}_{1.00}\text{S}_{2.67}$	11.33	11.60	4.02	<i>Pbnm</i>
4	9.54	31.68	41.72	0.39	17.15	100.48	$\text{Cu}_{0.74}\text{Pb}_{0.75}\text{Bi}_{1.00}\text{S}_{2.63}$	11.32	11.60	4.01	<i>Pbnm</i>
5	9.36	30.27	42.69	0.28	17.16	99.76	$\text{Cu}_{0.71}\text{Pb}_{0.71}\text{Bi}_{1.00}\text{S}_{2.60}$	11.31	11.60	4.01	<i>Pbnm</i>
Hammarite											
6a	8.43	28.94	46.94	0.0	17.46	101.77	$\text{Cu}_{0.95}\text{Pb}_{1.00}\text{Bi}_{1.61}\text{S}_{3.89}$	-	-	-	
6b	8.07	26.54	48.33	0.0	17.31	100.25	$\text{Cu}_{1.00}\text{Pb}_{1.00}\text{Bi}_{1.80}\text{S}_{4.22}$	33.86	11.56	4.01	<i>Pbnm</i>
Lindströmite											
7	6.90	22.33	53.07	0.44	18.09	100.83	$\text{Cu}_{1.00}\text{Pb}_{1.00}\text{Bi}_{2.39}\text{S}_{5.22}$	56.15	11.56	3.99	<i>Pb2<sub>1</sub>m</i>
Krupkaite											
8	6.05	20.41	55.01	0.0	17.81	99.28	$\text{Cu}_{0.96}\text{Pb}_{1.00}\text{Bi}_{2.66}\text{S}_{5.61}$	11.23	11.56	3.99	<i>Pb2<sub>1</sub>m</i>
9	6.29	21.03	55.80	0.0	17.78	100.90	$\text{Cu}_{0.98}\text{Pb}_{1.00}\text{Bi}_{2.64}\text{S}_{5.50}$	11.22	11.52	3.97	<i>Pb2<sub>1</sub>m</i>
10	6.02	20.08	56.09	0.61	17.69	100.48	$\text{Cu}_{0.98}\text{Pb}_{1.00}\text{Bi}_{2.81}\text{S}_{5.69}$	11.22	11.57	3.99	
11	5.75	19.30	55.72	1.20	17.76	99.73	$\text{Cu}_{0.97}\text{Pb}_{1.00}\text{Bi}_{2.98}\text{S}_{5.96}$	11.17	11.51	3.98	<i>Pb2<sub>1</sub>m</i>
Gladite (blebs in exsolution)											
12a	4.1	13.7	60.1	2.6	18.3	98.8	$\text{Cu}_{0.98}\text{Pb}_{1.00}\text{Bi}_{4.67}\text{S}_{8.63}$	33.50	11.37	3.98	<i>Pbnm</i>
13a	4.37	12.66	65.10	0.0	18.38	100.51	$\text{Cu}_{1.13}\text{Pb}_{1.00}\text{Bi}_{5.10}\text{S}_{9.38}$	33.50	11.37	3.98	<i>Pbnm</i>
Pekoite (host in exsolution)											
12b	0.6	1.1	75.0	3.5	19.0	99.2	$\text{Cu}_{0.05}\text{Pb}_{0.03}\text{Bi}_{2.00}\text{S}_{3.06}$	33.45	11.37	3.98	<i>Pbnm?</i>
13b	0.98	1.07	79.87	0.0	19.03	100.95	$\text{Cu}_{0.08}\text{Pb}_{0.03}\text{Bi}_{2.00}\text{S}_{3.11}$	33.45	11.37	3.98	<i>Pbnm?</i>

\* Sb is included in Bi category.

\*\* The standard deviations of  $a$  parameters for aikinite and krupkaite are 0.00 each; for hammarite, gladite, and pekoite are 0.01; for lindströmite, 0.03. The standard deviations for  $b$  and  $c$  parameters are 0.00.

Pb)/Bi ranges from 0.85 to 0.71, and the cell dimensions decrease slightly with decrease in this ratio. The four tetrahedral cavities in the busmuthinite structure permit a maximum of 4 atoms of Cu or Pb in the aikinite structure. Consequently, the (Pb or Cu)/Bi ratio is limited to  $\leq 1$ , and deviations from 1 indicate vacancies in Cu (or Pb) sites in the structure.

Analysis No. 5 (Table 3) corresponds to Moore's (1967) hypothetical composition  $\text{Cu}_{20}\text{Pb}_{20}\text{Bi}_{28}\text{S}_{72}$ , which is  $6^5$  in his classification and would have  $Z = 6$  (the integral multiple of the  $a$ -translation). Similarly, analysis No. 1 corresponds to  $\text{Cu}_{3.66}\text{Pb}_{3.60}\text{Bi}_{4.34}\text{S}_{12}$  ( $Z = 12$ ), analysis No. 2 to  $\text{Cu}_{3.60}\text{Pb}_{3.60}\text{Bi}_{4.40}\text{S}_{12}$ , ( $Z = 10$ ), and analysis No. 4 to Welin's (1966)  $\text{Cu}_{3.43}\text{Pb}_{3.43}\text{Bi}_{4.57}\text{S}_{12}$  ( $Z = 7$ ). The four phases (Nos. 1, 3, 4, 5) have  $a$  of 11.3Å and no superstructure. Very weak diffuse streaks observed along  $a^*$  on precession photographs of samples No. 3 and 5 are attributed to stacking disorder along this direction.

### Hammarite

The mineral in sample No. 6 has a composition that corresponds to hammarite and has a unit cell: *Pbnm*,  $a = 33.86$ ,  $b = 11.56$ , and  $c$

$= 4.01\text{\AA}$ . The two analyses (Nos. 6a, 6b) from two different grains have Pb/Bi ratios of 0.55 to 0.60. These, as well as Welin's sample RM 24098:1 which is  $\text{Cu}_{2.87}\text{Pb}_{2.78}\text{Bi}_{5.00}\text{S}_{12.28}$  with Pb/Bi 0.55 (or 0.51?) and has a similar unit cell, suggest an ideal formula of  $\text{Cu}_8\text{Pb}_8\text{Bi}_{16}\text{S}_{36}$  for hammarite.

The present data show that the solid solution range of hammarite covers two of Welin's hypothetical compositions,  $\text{Cu}_8\text{Pb}_8\text{Bi}_8\text{S}_{12}$  (with Pb/Bi = 0.60 and  $Z = 4$ ) and  $\text{Cu}_{2.8}\text{Pb}_{2.8}\text{Bi}_{5.2}\text{S}_{12}$  (with Pb/Bi = 0.54 and  $Z = 10$ ).

### Lindströmite

The mineral in sample No. 7 with composition  $\text{Cu}_{1.00}\text{Pb}_{1.00}\text{Bi}_{2.39}\text{S}_{5.22}$  and unit cell *Pb2<sub>1</sub>m*,  $a = 56.15$ ,  $b = 11.56$ ,  $c = 3.99\text{\AA}$  is identical with the lindströmite (RM 24100:3) reported by Welin. The observed Pb/Bi ratios of 0.42 and 0.43 for sample No. 7 and RM 24100:3, respectively, imply that lindströmite most probably is stoichiometric  $\text{Cu}_{12}\text{Pb}_{12}\text{Bi}_{28}\text{S}_{60}$ .

Only very weak streaky reflections were observed for the superlattice on the single crystal photographs. However, the reflections clearly indicate a unit cell with  $a = 5a'$ , and the space group

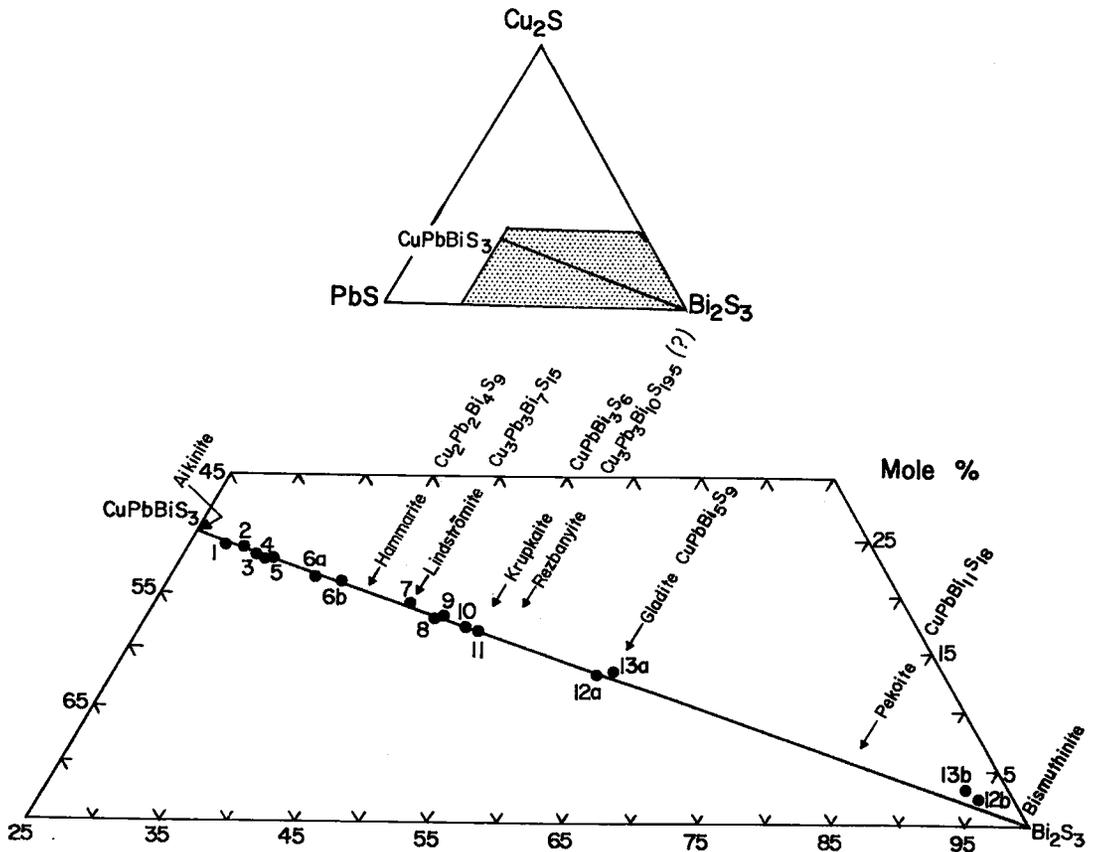


FIG. 1. The distribution of the sulfosalts studied in the  $\text{Cu}_2\text{S-PbS-Bi}_2\text{S}_3$  diagram.

*Pb<sub>2</sub>m*. The hypothetical phase with identical composition and cell dimensions, but with space group *Pbnm* (Synecek & Hybler 1975), was not found.

#### *Krupkaite*

The mineral in samples No. 8 to No. 11 has a general composition  $\text{Cu}_2\text{Pb}_2\text{Bi}_6\text{S}_{12}$  with unit cell: *Pb<sub>2</sub>m*  $a \sim 11.2$ ,  $b \sim 11.5$ ,  $c \sim 3.99\text{Å}$ , corresponding to the krupkaite described by Zak *et al.* (1975) and Synecek & Hybler (1975). Pb/Bi ranges from 0.37 to 0.33, and cell dimensions decrease with decreasing Pb/Bi ratio.

The hypothetical phase  $\text{Cu}_4\text{Pb}_4\text{Bi}_{12}\text{S}_{24}$ , with space group *Pb<sub>2</sub>m* and  $Z = 2$  (Moore 1967; Synecek & Hybler 1975) has not been found in nature.

#### *Gladite*

Samples Nos. 12 and 13 have two exsolved phases (Fig. 2) whose compositions (Nos. 12a, 13a) are identical to that of gladite ( $\text{Cu}_4\text{Pb}_4\text{Bi}_{20}\text{S}_{36}$ ,

Welin 1966; Synecek & Hybler 1975). Their Pb/Bi ratios are both about 0.21.

X-ray single crystal work on fragments, each consisting mainly of an exsolved bleb, gave *Pbnm*,  $a = 33.50$ ,  $b = 11.37$ ,  $c = 3.98\text{Å}$ , thus confirming their identification as gladite.

#### *Pekoite*

The host grains of the exsolutions have compositions (No. 12b, 13b) very close to bismuthinite but with minor amounts of Cu and Pb. X-ray single crystal work of several fragments revealed only one unit cell: *Pbnm*,  $a = 33.45$ ,  $b = 11.37$ ,  $c = 3.98\text{Å}$ .

Exsolution among aikinite phases has been reported by Welin (1966), Ramdohr (1960, p. 187), and Correia Neves *et al.* (1974). Large & Mumme (1975) reported several aikinite exsolutions (No. 1 host and No. 2 bleb; No. 3 host and 4 bleb; No. 5 host; No. 6 host; Fig. 3) from the Juno mine, Tennant Creek, Australia. These exsolution pairs have Pb/Bi ratios of: 0.06 (host crystals) and 0.18 (bleb); 0.04 (host) and 0.21

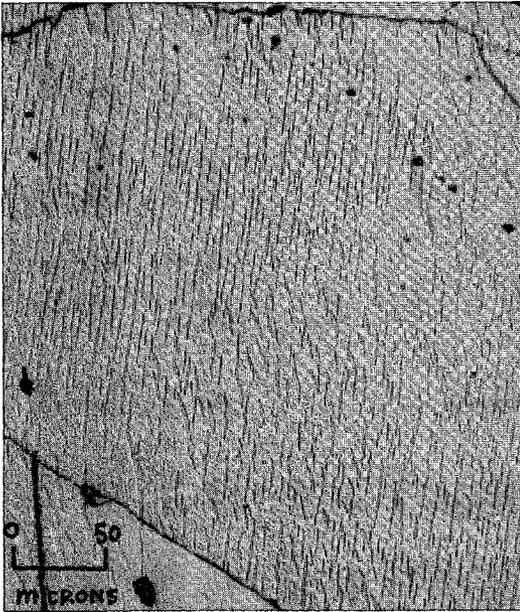


FIG. 2. Exsolution of gladite (blebs, heavily etched) and pekoite (host, lightly etched) from Bernic Lake, Manitoba. Etched with  $\text{HNO}_3$  1:1 for 60 seconds.

(bleb); 0.08 (host); and 0.10 (host). It is obvious that the exsolved blebs are gladite, whereas Pb/Bi in the second phase (host) ranges from 0.04 to 0.10. This second phase is pekoite,  $\text{Cu}_2\text{Pb}_2\text{Bi}_{22}(\text{S},\text{Se})_{38}$ ,  $Pb_{21}m$ ,  $a = 33.744$ ,  $b = 11.472$ ,  $c = 4.016\text{\AA}$  (Mumme *et al.* 1976). The low-Se phase of this mineral was reported to have  $a = 33.504$ ,  $b = 11.322$ ,  $c = 3.987\text{\AA}$ .

Experimental work by Springer (1971) indicated that a complete solid solution exists between aikinite and bismuthinite above  $300^\circ\text{C}$ . The exsolution in the natural material suggests that a miscibility gap exists between gladite and a more Bi-rich aikinite phase. The gap may form below  $300^\circ\text{C}$ .

The exsolutions of the two aikinite phases from Bernic Lake, Manitoba (No. 12), from Rio Grande de Norte, Brazil (No. 13), and those from the Juno mine all may be of the same type. That is, they are exsolutions of gladite and pekoite wherein a high Pb/Bi phase exsolves with a low Pb/Bi phase. Composition differences among the exsolved phases may indicate that the exsolution processes were in some way quenched at different temperatures during the geological evolution. The exsolved pairs from Bernic Lake, or Rio Grande de Norte, with the highest and lowest Pb/Bi values for gladite and pekoite respectively, most probably have reached equi-

ilibrium; the exsolved pair from Juno mine with Pb/Bi lowest for gladite and highest for pekoite may have been quenched at a higher temperature. The wide compositional range of pekoite perhaps indicates a shallow slope of the solvus (Fig. 4).

#### X-RAY POWDER DIFFRACTION DATA AND PHYSICAL PROPERTIES

All the sulfosalts in the aikinite-bismuthinite series have a pronounced common substructure which resembles the structure of bismuthinite, and all have similar X-ray powder diffraction patterns. Although intensities and  $d$ -values gradually change with composition variation, powder X-ray diffraction data do not uniquely characterize the individual species in the series.

The physical properties of the phases change gradually along the series, but all phases are very similar in reflected light. For example, aikinite is creamy white to pale brownish (in air) with distinct or strong bireflection and distinct anisotropism; bismuthinite is slightly greyish or bluish, with fair or distinct bireflection and very strong anisotropism. Krupkaite is greyish white in air, and has a pale brownish tint as compared with the bluish tint of bismuthinite. Aikinite is usually granular and fractures, whereas bismuthinite has better cleavage, has straight cracks, and is lath-like.

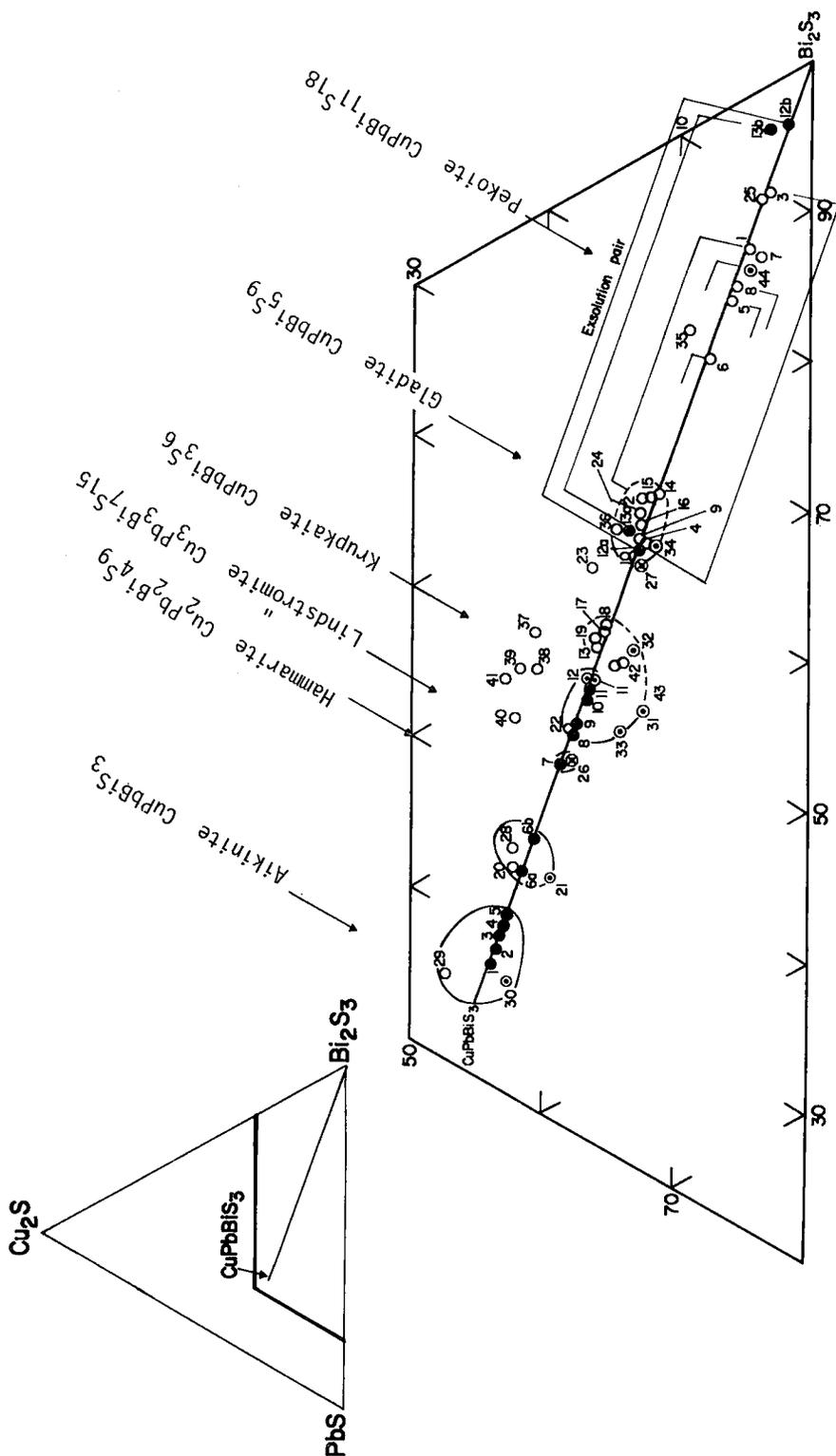
$\text{HNO}_3$  (1:1) etches easily with effervescence and blackens the surface of all phases in the series. The light brown stain from  $\text{FeCl}_3$  usually distinguishes the members of the aikinite series from bismuthinite.

Reflectances were determined with a Leitz MPE microscope photometer using a calibrated silicon standard (N 2538.42, issued by I.M.A. Commission on Ore Microscopy). Microhardness values were determined with a Leitz Durimet hardness tester. Results for both are given in Table 4.

The calculated densities for the phases in this series range from 7.1 for aikinite to 6.8  $\text{g}/\text{cm}^3$  for pekoite. Measured values obtained with a Berman balance are 6.91 for aikinite, 7.10 for lindströmite, and 6.89  $\text{g}/\text{cm}^3$  for krupkaite. These and data reported in the literature (Fig. 5) indicate a gradual decrease in density from aikinite to bismuthinite.

#### NOMENCLATURE

Six phases,  $\text{CuPbBi}_3\text{S}_8$ ,  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_8$ ,  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ ,  $\text{CuPbBi}_5\text{S}_8$ ,  $\text{CuPbBi}_5\text{S}_8$ , and  $\text{CuPbBi}_{11}\text{S}_{18}$  are currently known as minerals in the aikinite-bismuthinite series. These are recognized as



Mole %

Fig. 3 Some compositions of sulfosalts in the aikinite-bismuthinite series. ● This study (1-13, numbers correspond to those in Table 2). The following are analyses from the literature: ⊙ probe analyses with X-ray single crystal data; ⊗ spectrographic analysis with X-ray single crystal data; ○ probe analyses only; 1-12 Large & Mumme (1975), 13-19 Borodaev & Mozgova (1971), 20-27 Melin (1966), 28-29 Povilyaitis *et al.* (1969), 30 Ohmura & Nowacki (1970a), 31-33 Zak *et al.* (1975), 34 Synecek & Hybler (1975), 35-43 Nicolau & Hakli (1970), 44 Mumme *et al.* (1975).

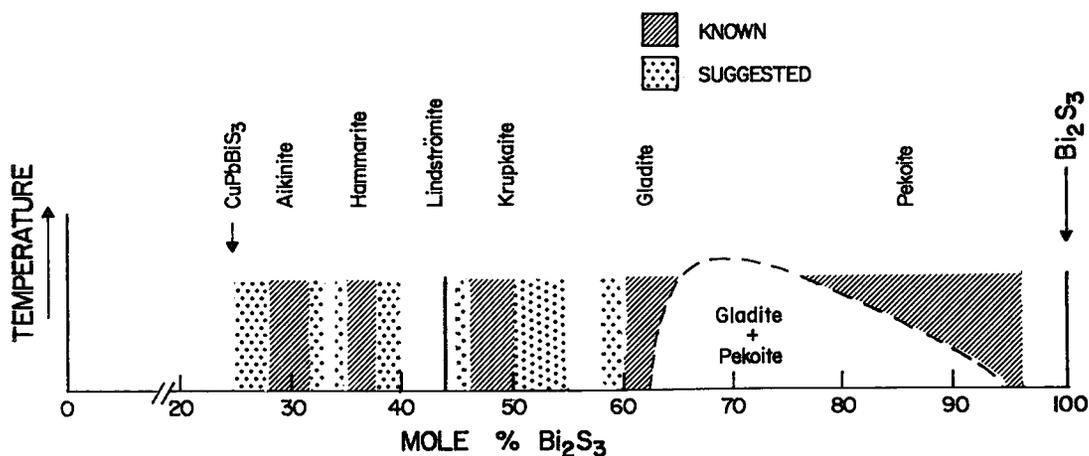


FIG. 4. The known compositional ranges, in terms of mole %  $\text{Bi}_2\text{S}_3$  in the  $\text{Cu}_{12}\text{S-PbS-Bi}_2\text{S}_3$  system, of the sulfosalts and the miscibility gap observed in the aikinite-bismuthinite series.

ordered phases with stoichiometric compositions for which Mumme *et al.* (1976) proposed the names aikinite, hammarite, lindströmite, krupkaite, gladite, and pekoite, respectively (Table 1). Because Pb tends to order into the maximum number of  $\text{Bi}_2\text{S}_3$ -ribbons and form the  $\text{CuPbBi}_3\text{S}_6$ -ribbons, as in the structures of krupkaite, pekoite, and gladite, Mumme *et al.* suggested that Moore's classification should not be retained.

Table 1 summarizes the species recognized in

this series, and the nomenclatures most commonly used in the literature. The following problems warrant further discussion.

#### Rezbanyite

Rezbanyite is the oldest name used for a mineral representing an intermediate phase in the aikinite-bismuthinite series. The original formula of Frenzel,  $\text{Pb}_4\text{Bi}_{10}\text{S}_{18}$ , (in Dana 1892, p.

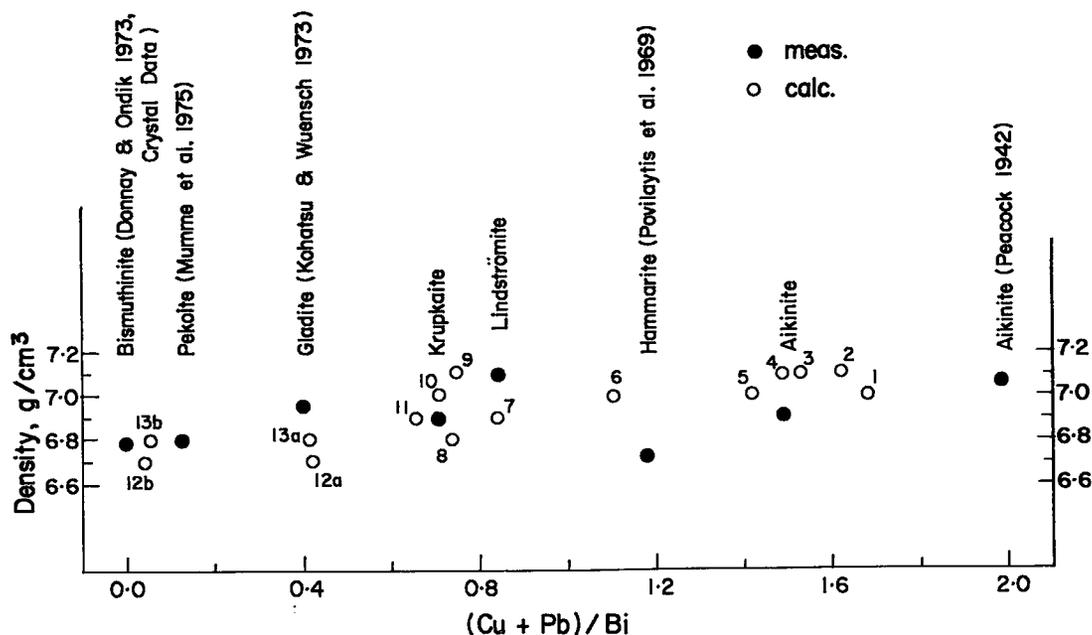


FIG. 5. The measured and calculated densities for the sulfosalts in the aikinite-bismuthinite series. Specimen numbers are listed in Table 2.

TABLE 4. REFLECTANCE AND MICRO-INDENTATION HARDNESS

Sample No.	Wavelength								Micro-Indentation Hardness	
	470 nm		546 nm		589 nm		650 nm		(kg/mm <sup>2</sup> ) Range	VHN, Av. <sup>50g</sup>
	Range	Av.	Range	Av.	Range	Av.	Range	Av.		
1	41.6-48.2	43.9	40.0-48.0	43.5	39.4-47.0	42.9	38.4-45.2	42.0	177-230	199
3	40.9-47.4	44.6	40.2-46.9	43.7	38.5-46.3	42.4	39.2-45.9	42.7	248-250	249
4	42.2-46.6	44.5	40.7-45.6	43.1	39.7-45.3	42.6	40.2-45.4	43.0	195-210	202
5	40.7-46.3	43.2	39.4-44.7	42.2	38.7-43.8	41.5	37.4-43.5	40.6	-	-
6	43.0-47.2	45.6	41.5-46.2	44.6	40.7-46.0	44.0	40.6-45.0	43.5	174-183	180
7	42.6-47.6	45.1	41.0-46.2	43.9	40.7-46.5	43.7	39.7-45.9	42.9	247-265	255
8	39.6-46.0	42.5	38.2-43.6	41.1	38.2-43.9	40.8	36.4-43.3	40.0	202-225	212
9	40.8-46.9	44.2	40.8-45.8	43.2	40.7-45.7	43.1	39.6-44.9	42.4	213-245	223
10	39.9-46.7	43.8	38.1-45.3	42.2	37.3-45.3	41.8	36.7-45.1	41.2	208-231	229
11	40.5-45.0	42.6	38.7-43.6	41.1	37.9-42.9	40.6	37.4-42.4	39.6	194-219	208

111) was derived from analyses made on impure material, probably largely cosalite, from Rezbanya, Hungary. From another reported occurrence of rezbanyite at Vaskö, Hungary, Kock (in Palache *et al.* 1944) derived the formula  $Pb_2Cu_2Bi_{10}S_{19}$ . Paděra *et al.* (1955) suggested that the formula for rezbanyite is  $Cu_3Pb_3Bi_{10}S_{19.5}$ . Because of the similarity of physical properties and X-ray powder patterns among the phases in the aikinite-bismuthinite series, Paděra (1956) concluded that a complete solid solution existed, and that rezbanyite should be used to represent all the intermediate members.

Afanaseva & Vyal'sor (1971) used the name rezbanyite for a mineral from the Kafan deposit, USSR. Their composition,  $Cu_{1.34}Pb_{1.86}Bi_{10.14}S_{12}$ , corresponding to  $Cu_2Pb_3Bi_{10}S_{19}$ , is commonly used for rezbanyite in the literature even though rezbanyite is usually described as a member in the aikinite-bismuthinite series. Moreover, minerals identified as rezbanyite have been found to consist of several species, such as gladite (RM 24097 by Welin 1966), and aikinite (No. 1 in this study).

#### Synecek & Hybler's classifications

Synecek & Hybler (1975), using the same general formula proposed by Moore (1967), proposed a new classification in terms of  $Z_x$  where  $0 \leq x \leq 4Z$ . By operating the  $n$ -guide plane, with systematic restriction of some of the symmetry operators, on the basic bismuthinite (or aikinite) structure, they correlated the space group symmetry of each superstructure with the  $Z$  and  $x$ . As noted by Synecek & Hybler,  $Z_x$  can be common to several different phases in the aikinite-bismuthinite series. For example,  $S_{12}$  defines only the cell dimensions; the space group symmetry can be either  $Pbnm$  or  $Pb2_1m$ , and is therefore

not necessarily that of lindströmite. Similarly, a mineral with the composition  $CuPbBi_8S_8$  in the asymmetric unit can be either krupkaite (i.e. 1<sub>2</sub>) or the hypothetical phase 2<sub>4</sub> with the same space group symmetry.

#### Range of solid solution

The results of the present study show that limited ranges of solid solutions exist in the aikinite-bismuthinite series, at least for some of the intermediate members. Although solid solutions were also considered by Paděra (1956) and Kupcik *et al.* (1969), their conclusions were not accepted by Welin (1966) because of the lack of single crystal data to support their arguments. Although Welin's analyses also indicated possible solid solution, the three phases he studied by the single crystal method were stoichiometric. Consequently, Welin derived twenty theoretical phases which allowed almost no range of solid solution for the aikinite-bismuthinite series. Moore (1967) and Synecek & Hybler (1975) subsequently proposed the classifications which dealt mainly with these theoretical phases, and which could accommodate only the stoichiometric compositions. The possibility of a limited amount of disorder of some atoms among the structural sites available was pointed out by Mumme (1975), who also established that up to 20% of the Cu atoms in the krupkaite structure were disordered.

Figure 3 shows the compositions of the phases in the aikinite-bismuthinite series observed in this study, as well as the electron probe analyses reported by Large & Mumme (1975), Borodaev & Mozgowa (1971), Welin (1966), Povialytis *et al.* (1969), Ohmasa & Nowacki (1970a), Zak *et al.* (1975), Synecek & Hybler (1975), and Nicolaou & Hakli (1970). The phases confirmed by

X-ray single crystal work are indicated.

The data indicate that extensive solid solution is present in aikinite, hammarite, krupkaite, and gladite, and that pekoite exsolved in gladite has a wide range of composition which closely approaches that of bismuthinite. The known compositional range for each phase and the hypothetical miscibility gap between gladite and pekoite are indicated in Figure 4.

### CONCLUSIONS

(1) No unique crystal-chemical data can be attributed to rezbanyite, which should be discredited.

(2) The Syneck & Hybler (1975) classification should be abandoned.

(3) Names proposed by Mumme *et al.* (1976), i.e. aikinite, hammarite, lindströmite, krupkaite, gladite, pekoite, and bismuthinite as members of the aikinite-bismuthinite series, are valid. However, the known compositional range for each species should be indicated as follows:

- (a) *aikinite*: ideal formula  $\text{CuPbBi}_3\text{S}_6$ , general formula  $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{3-x}\text{S}_{6-1.5x}$  where  $0 \leq x \leq 0.29$ .
- (b) *hammarite*: ideal formula  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_8$ , general formula  $\text{Cu}_2\text{Pb}_2\text{Bi}_{4-x}\text{S}_{8-1.5x}$  where  $0.4 \leq x \leq 0.7$ .
- (c) *lindströmite*: stoichiometric formula  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ .
- (d) *krupkaite*: ideal formula  $\text{CuPbBi}_3\text{S}_6$ , general formula  $\text{CuPbBi}_{3-x}\text{S}_{6-1.5x}$  where  $0 \leq x \leq 0.4$ .

(e) *gladite*: ideal formula  $\text{CuPbBi}_3\text{S}_6$ , general formula  $\text{CuPbBi}_{3-x}\text{S}_{6-1.5x}$  where  $0 \leq x \leq 0.3$ .

(f) *pekoite*: ideal formula  $\text{CuPbBi}_{11}\text{S}_{18}$ , general formula uncertain.

(g) *bismuthinite*: ideal formula  $\text{Bi}_2\text{S}_3$ , with possible minor substitution of Cu and Pb.

The details of the crystal chemical properties of the species are discussed as follows and are summarized in Table 5.

### Aikinite

The compositions of grains confirmed by single crystal data (Fig. 3) show a range of solid solution from 27 to 32 mole %  $\text{Bi}_2\text{S}_3$  along the  $\text{CuPbBi}_3\text{S}_6$ - $\text{Bi}_2\text{S}_3$  join. Ohmasa & Nowacki (1970a) have shown by crystal structure analysis that aikinite has an ideal composition of  $\text{Cu}_4\text{Pb}_4\text{Bi}_4\text{S}_{12}$ ; therefore, it is concluded that composition varies at least from 25 to 32 mole %  $\text{Bi}_2\text{S}_3$ . Because the structural sites available require that the Cu (or Pb)/Bi not exceed 1, a general formula  $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{3-x}\text{S}_{6-1.5x}$  is proposed, where  $0 \leq x \leq 0.29$ . However, if disorder is permitted for Pb and Bi, the general formula will be  $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1+x}\text{S}_6$ , where  $0 \leq x \leq 0.17$ .

Aikinite contains only  $\text{Cu}_2\text{Pb}_2\text{Bi}_2\text{S}_6$ -ribbons in the structure (Ohmasa & Nowacki 1970a; Kohatsu & Wuensch 1971), and has the space group symmetry *Pbnm* with  $a \sim 11.33$ ,  $b \sim 11.61$ ,  $c \sim 4.02\text{Å}$ .

TABLE 5. CRYSTAL-CHEMICAL DATA OF THE KNOWN MINERAL SPECIES IN THE AIKINITE-BISMUTHINITE SERIES

Mineral <sup>†</sup>	Composition (Known)	a(Å)	b(Å)	c(Å)	Space group	Unit cell content	Structure elements
Aikinite	$\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{3-x}\text{S}_{6-1.5x}$ $0 \leq x \leq 0.29$	11.33	11.61	4.02	<i>Pbnm</i>	4	$\text{Cu}_2\text{Pb}_2\text{Bi}_2\text{S}_6$ -ribbon
Hammarite	$\text{Cu}_2\text{Pb}_2\text{Bi}_{4-x}\text{S}_{8-1.5x}$ $0.4 \leq x \leq 0.7$	3x11.29	11.56	4.01	<i>Pbnm</i>	4	*
Lindströmite	$\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$	5x11.23	11.56	3.99	<i>Pb2_1m</i>	4	*
Krupkaite	$\text{CuPbBi}_{3-x}\text{S}_{6-1.5x}$ $0 \leq x \leq 0.4$	11.22	11.55	3.99	<i>Pb2_1m</i>	2	$\text{CuPbBi}_3\text{S}_6$ -ribbon
Gladite	$\text{CuPbBi}_{3-x}\text{S}_{6-1.5x}$ $0 \leq x \leq 0.3$	3x11.17	11.37	3.98	<i>Pbnm</i>	4	One $\text{Bi}_4\text{S}_6$ +two $\text{CuPbBi}_3\text{S}_6$ -ribbon
Pekoite	$\text{CuPbBi}_{11}\text{S}_{18}$	3x11.17	11.32	3.99	<i>Pb2_1m</i>	2	Two $\text{Bi}_4\text{S}_6$ +one $\text{CuPbBi}_3\text{S}_6$ -ribbon
Bismuthinite	$\text{Bi}_2\text{S}_3$	11.12	11.25	3.97	<i>Pbnm</i>	4	$\text{Bi}_4\text{S}_6$ -ribbon

\* Possibly consists of  $\text{Cu}_2\text{Pb}_2\text{Bi}_2\text{S}_6$ -and  $\text{CuPbBi}_3\text{S}_6$ -ribbons (Ohmasa & Nowacki 1970b).

† Nomenclature follows Mumme *et al.* (1975).

### Hammarite

Microprobe analyses and single crystal data show a compositional range from 35 to 38 mole %  $\text{Bi}_2\text{S}_3$  along the  $\text{CuPbBi}_3\text{S}_6\text{-Bi}_2\text{S}_3$  join. The composition corresponds to  $0.4 \leq x \leq 0.7$  in the formula  $\text{Cu}_2\text{Pb}_2\text{Bi}_{4-2x}\text{S}_{9-1.5x}$ .

Hammarite has the space group symmetry  $Pbnm$  with  $a = 33.86$ ,  $b = 11.56$ ,  $c = 4.01 \text{ \AA}$ . The crystal structure possibly consists of  $\text{Cu}_2\text{Pb}$ ,  $\text{Bi}_2\text{S}_6$  and  $\text{CuPbBi}_3\text{S}_6$ -ribbons (Ohmasa & Nowacki 1970b).

### Lindströmite

The analyses (Fig. 3) indicate that lindströmite may be stoichiometric  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ . Its unit cell is  $Pb2_1m$ ,  $a = 56.15$ ,  $b = 11.56$ ,  $c = 3.99 \text{ \AA}$ . The structure may consist of  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_6$  and  $\text{CuPbBi}_3\text{S}_6$ -ribbons (Ohmasa & Nowacki 1970b).

### Krupkaite

Compositions of grains confirmed by single crystal data range from 46 to 50 mole %  $\text{Bi}_2\text{S}_3$  along the  $\text{CuPbBi}_3\text{S}_6\text{-Bi}_2\text{S}_3$  join. The compositions correspond to  $0 \leq x \leq 0.4$  in the formula  $\text{CuPb}_{1-2x}\text{Bi}_{3+x}\text{S}_{6-1.5x}$ . Several analyses close to that of krupkaite, but without confirmatory single crystal data, have been reported (Fig. 3). These, if valid, and the original krupkaite analysis (Zak *et al.* 1975), indicate a range from 46 to 55 mole %  $\text{Bi}_2\text{S}_3$ . This suggests that there may be substantial disorder between Pb and Bi, and indicates a general formula  $\text{Cu}_{1-2x}\text{Pb}_{1+x}\text{Bi}_{3+x}\text{S}_6$ , where  $-0.13 \leq x \leq 0.14$ .

Krupkaite has only  $\text{CuPbBi}_3\text{S}_6$ -ribbons in the structure (Synecek & Hybler 1975; Mumme 1975), and has a unit cell:  $Pb2_1m$ ,  $a \sim 11.22$ ,  $b \sim 11.55$ ,  $c \sim 3.99 \text{ \AA}$ .

### Gladite

Microprobe analyses together with single crystal data show a compositional range from 60 to 63 mole %  $\text{Bi}_2\text{S}_3$ , corresponding to  $0 \leq x \leq 0.3$  in  $\text{CuPbBi}_{5-2x}\text{S}_{8-1.5x}$ . If the analyses, unconfirmed by single crystal data, from the exsolved blebs are also taken into account, the compositional range extends to 65 mole %  $\text{Bi}_2\text{S}_3$ .

The structure consists of  $\text{Bi}_4\text{S}_6$  and  $\text{CuPbBi}_3\text{S}_6$ -ribbons in a ratio of 1:2 (Kohatsu & Wuensch 1973; Synecek & Hybler 1975). The unit cell has the symmetry  $Pbnm$  with  $a \sim 33.50$ ,  $b \sim 11.37$ ,  $c \sim 3.98 \text{ \AA}$ .

### Pekoite

Pekoite was only found as exsolved grains in gladite. The composition range, from 76 to 95

mole %  $\text{Bi}_2\text{S}_3$ , is unusually large; the true compositional range is uncertain.

Pekoite described by Mumme *et al.* (1976) has the composition  $\text{Cu}_2\text{Pb}_2\text{Bi}_{22}\text{S}_{36}$  and a unit cell:  $Pb2_1m$ ,  $a = 33.50$ ,  $b = 11.32$ ,  $c = 3.99 \text{ \AA}$ . The structure consists of  $\text{CuPbBi}_3\text{S}_6$  and  $\text{Bi}_4\text{S}_6$ -ribbons in a ratio of 1:2.

### Bismuthinite

Bismuthinite, ideally  $\text{Bi}_2\text{S}_3$ , may contain minor Cu and Pb. The mineral is characterized by the presence of  $\text{Bi}_4\text{S}_6$ -ribbons (Kupcik & Vesela-Novakova 1970) and has a unit cell:  $Pbnm$ ,  $a = 11.12$ ,  $b = 11.25$ ,  $c = 3.97 \text{ \AA}$ .

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### REFERENCES

- AFANASEVA, E. L. & VYAL'SOR, L. N. (1971): Rez-banyite from chalcopyrite ores of Kafan deposit (Armenian SSR). *Izv. Vyssh. Ucheb. Zaved. Geol. Razved.* 14(4), 35-41.
- BORODAEV, YU. S. & MOZGOWA, N. N. (1971): Electron microprobe study of micro-intergrowths in sulfosalts. *Vop. Odnorodnosti Neodnorodnosti Mineral.*, 118-126.
- , ——— & VYAL'SOR, L. N. (1970): Bismuthinite-aikinite isomorphous series. *Moscow Univ. Vestn. Geol.* 1, 18-33.
- CORREIA NEVES, J. M., LOPES NUNES, J. E., SAHAMA, T. G., LEHTINEN, M. & KNORRING, O. V. (1974): Bismuth and antimony minerals in the granite pegmatites of northern Mozambique. *Rev. Cienc. Geol.* 7, 1-37.
- DONNAY, J. D. H. & ONDIK, H. M. (1973): *Crystal Data — Determinative Tables*, 2. U.S. Dep. Commerce, Nat. Bur. Stand. & J.C.P.D.S.
- FLINK, G. (1910): Bidrag till Sveriges mineralogi. *Arkiv Kemi Mineral. Geol.* 3, 1-166.

- JOHANSSON, K. (1924): Bidrag till Gladhammar-gruvornas mineralogi. *Arkiv Kemi Mineral. Geol.* 9, 1-22.
- KOHATSU, I. & WUENSCH, B. J. (1971): The crystal structure of aikinite,  $\text{PbCuBiS}_3$ . *Acta Cryst.* B27, 1245-1252.
- & ——— (1973): The crystal structure of gladite,  $\text{PbCuBi}_3\text{S}_6$ . *Amer. Mineral.* 58, 1098 (Abstr.).
- KUPCIK, V. & VESELA-NOVAKOVA, L. (1970): The crystal structure of bismuthinite redetermined. *Tschermaks Mineral. Petrogr. Mitt.* 14, 55-58.
- & SCHNEIDER, A. & VARCEK, C. (1969): Chemistry of some bisulfosalts from the Slovak ore mountains (CSSR). *Neues Jahrb. Mineral. Monatsh.* No. 10, 445-454.
- LARGE, R. R. & MUMME, W. G. (1975): Junoite, "wittite", and related seleniferous bismuth sulfosalts from Juno Mine, Northern Territory, Australia. *Econ. Geol.* 70, 369-383.
- LINDSTRÖM, G. (1887): Om förekomsten av wismuthmineral vid Gladhammar. *Geol. Fören. Förh.* 9, 523-528.
- (1889): Ytterligare om wismuthmineral från Gladhammar. *Geol. Fören. Förh.* 11, 171-172.
- MOORE, P. B. (1967): A classification of sulfosalt structures derived from the structure of aikinite. *Amer. Mineral.* 52, 1874-1876.
- MUMME, W. G. (1975): The crystal structure of krupkaite,  $\text{CuPbBi}_3\text{S}_6$ , from the Juno Mine at Tennant Creek, Northern Territory, Australia. *Amer. Mineral.* 60, 300-308.
- WELIN, E. & WUENSCH, B. J. (1976): Crystal chemistry and proposed nomenclature for sulfosalts intermediate in the system bismuthinite-aikinite ( $\text{Bi}_2\text{S}_3$ - $\text{CuPbBiS}_3$ ). *Amer. Mineral.* 61, 15-20 (preprint 1975).
- NICOLAOU, M. & HAKLI, T. A. (1970): The presence of aikinite in the Aberdeen area of the Kirki Mine, western Thrace, Greece. *Bull. Geol. Soc. Finland* 42, 53-55.
- OHMASA, M. & NOWACKI, W. (1970a): A redetermination of the crystal structure of aikinite ( $\text{BiS}_2/\text{S}/\text{Cu}^{\text{IV}}\text{Pb}^{\text{VI}}$ ). *Z. Krist.* 132, 71-86.
- & ——— (1970b): Note on the space group and on the structure of aikinite derivatives. *Neues Jahrb. Mineral. Monatsh.* No. 4, 158-162.
- PADERA, K. (1956): The revision of minerals of the bismuthinite and aikinite group. *Chemie der Erde* 18, 14-18.
- , BOUSKA, V. & PELIKAN, J. (1955): Rez-banyit aus Dobsina in der Ostlowakei, CSR. *Chemie der Erde* 17, 329-340.
- PALACHE, C., BERMAN, H. & FRONDEL, C. (1944): *The System of Mineralogy* 1, 7th ed. John Wiley & Sons, New York.
- PEACOCK, M. A. (1942): Studies of mineral sulphosalts: VI-Aikinite. *Univ. Toronto Studies Geol. Ser.* 47, 63-69.
- POVILAYTIS, M. M., MOZGOWA, N. N., BORODAEV, YU. S., SENDEROVA, V. M. & RONAMI, G. N. (1969): The first find of hammarite in the USSR. *Dokl. Akad. Nauk SSSR* 187, 124-127.
- RAMDOHR, P. (1969): *The Ore Minerals and Their Intergrowths*. 3rd. ed. (Engl. transl.) Pergamon, Oxford.
- RUCKLIDGE, J. C. & GASPARRINI, E. L. (1969): Electron microprobe analytical data reduction (EMPADR VII). *Dept. Geol. Univ. Toronto*.
- SPRINGER, G. (1971): The synthetic solid-solution series  $\text{Bi}_2\text{S}_3$ - $\text{BiCuPbS}_3$  (bismuthinite-aikinite). *Neues Jahrb. Mineral. Monatsh.* No. 1, 19-24.
- SYNECEK, V. & HYBLER, J. (1975): The crystal structure of krupkaite,  $\text{CuPbBi}_3\text{S}_6$ , and of gladite,  $\text{CuPbBi}_3\text{S}_6$ , and the classification of superstructures in the bismuthinite-aikinite group. *Neues Jahrb. Mineral. Monatsh.* No. 12, 541-560.
- WELIN, E. (1966): Notes on the mineralogy of Sweden, 5. Bismuth-bearing sulphosalts from Gladhammar, a revision. *Arkiv Mineral. Geol.* 4, 377-386.
- ZAK, L., SYNECEK, V. & HYBLER, J. (1975): Krupkaite,  $\text{CuPbBi}_3\text{S}_6$ , a new mineral of the bismuthinite-aikinite group. *Neues Jahrb. Mineral. Monatsh.* No. 12, 553-541.

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