

LINDSTRÖMITE FROM COBALT, ONTARIO

ALLAN PRING¹

Department of Mineralogy, South Australian Museum, North Terrace, Adelaide, South Australia 5000, Australia

BENJAMIN A. GRGURIC

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

ALAN J. CRIDDLE

Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

ABSTRACT

The results of the characterization of a well-ordered lindströmite from the Drummond mine (also known as the Silver Miller mine), 3 km southeast of Cobalt, Ontario are reported. Chemical analyses by electron microprobe gave the composition $\text{Cu}_{2.70}\text{Pb}_{2.80}\text{Bi}_{7.18}\text{Sb}_{0.09}\text{S}_{15}$, intermediate between the ideal composition of lindströmite $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ and of krupkaite $\text{CuPbBi}_3\text{S}_6$. Least-squares refinement of the powder X-ray-diffraction pattern gave an orthorhombic cell, $a = 55.99(3)$, $b = 11.549(3)$, $c = 4.010(1)$ Å, which is within error limits of the cell given for lindströmite from the type locality, Gladhammar, Sweden. The optical properties in reflected light and the indentation hardness are reported, and were found to be very similar to those of krupkaite and hammarite. It is not possible to distinguish among intermediate members of the bismuthinite – aikinite series on the basis of their optical properties or indentation hardness. Electron-diffraction patterns reveal a well-ordered $5a$ superlattice of the bismuthinite parent cell, the superlattice reflections are sharp, and there is no evidence of streaking along a^* . High-resolution images show the perfectly ordered nature of the structure. The nature of compositional ordering processes in these bismuthinite – aikinite minerals is discussed.

Keywords: lindströmite, bismuthinite – aikinite series, supercell ordering, transmission electron microscopy, Cobalt, Ontario.

SOMMAIRE

Nous présentons les résultats d'une caractérisation d'un échantillon de lindströmite bien ordonnée provenant de la mine Drummond (aussi appelée mine Silver Miller), située à 3 km au sud-est de Cobalt, en Ontario. Les analyses chimiques obtenues par microsonde électronique donnent la composition $\text{Cu}_{2.70}\text{Pb}_{2.80}\text{Bi}_{7.18}\text{Sb}_{0.09}\text{S}_{15}$, intermédiaire entre la composition idéale de la lindströmite, $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$, et celle de la krupkaïte, $\text{CuPbBi}_3\text{S}_6$. Un affinement par moindres carrés des données de diffraction X sur poudre indique une maille orthorhombique, a 55.99(3), b 11.549(3), c 4.010(1) Å, qui est celle de la lindströmite de la localité type, Gladhammar, en Suède, compte tenu des erreurs expérimentales. Nous décrivons les propriétés optiques en lumière réfléchie, ainsi que la dureté mesurée par indentation. Les résultats sont très semblables à ceux pour la krupkaïte et la hammarite. Il s'avère impossible de distinguer parmi les membres intermédiaires du groupe de la bismuthinite – aikinite par leurs propriétés optiques ou leur dureté à l'indentation. Les clichés de diffraction d'électrons révèlent une surstructure bien ordonnée ayant une périodicité $5a$ par rapport à la maille de la bismuthinite; les réflexions dues à la surstructure sont au point, et non floues, et nous ne voyons aucun signe d'étirement le long de a^* . Les images de la structure à haute résolution illustrent le degré d'ordre élevé de la structure. Nous évaluons les processus de mise en ordre dans la série bismuthinite – aikinite.

(Traduit par la Rédaction)

Mots-clés: lindströmite, série bismuthinite – aikinite, mise en ordre, surstructure, microscopie électronique par transmission, Cobalt, Ontario.

¹ E-mail address: pring@geology.adelaide.edu.au

INTRODUCTION

Lindströmite, $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$, is an ordered intermediate member of the bismuthinite – aikinite group, a homeotypic series between Bi_2S_3 and CuPbBiS_3 . Homogeneous specimens of the supercell minerals of the bismuthinite – aikinite series are rare, and we have undertaken a detailed study of the lindströmite in order to fully characterize this mineral. This study was also undertaken to investigate the nature of ordering processes in these minerals. In a broader context, such ordering reactions are of interest because they involve a continuum of states of order, from short-range Pb–Bi ordering to large-scale exsolution. The kinetics of order – disorder transitions and of exsolution are fundamentally different. Exsolution requires the transport of ions over long distances and is diffusion-controlled, whereas order – disorder transformations are short range in nature, involving the interchange of ions between neighboring sites, and are generally treated in terms of phase transitions.

BACKGROUND INFORMATION

Lindströmite was originally described by Johansson (1924) from Gladhammar, southeastern Sweden; the mineral was assigned the composition $\text{CuPbBi}_3\text{S}_6$. Welin (1966) re-examined Johansson's type material and noted that it is somewhat inhomogeneous, with some crystals consisting of an intergrowth of two compositionally similar minerals, the major phase having a composition close to $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ and a structure based on a $5a$ supercell of bismuthinite. The description of a new mineral, krupkaite, $\text{CuPbBi}_3\text{S}_6$, which has a simple ordered structure derived from bismuthinite (Žák *et al.* 1974, Syneček & Hybler 1974, Mumme 1975), precipitated a review of the nomenclature of the bismuthinite – aikinite group. Lindströmite was formally redefined with the composition $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ (Mumme *et al.* 1975). The structure of lindströmite was determined by Horiuchi & Wuensch (1977) with a crystal from Johansson's type material. They confirmed that the structure is an ordered $5a$ supercell of bismuthinite in which the ordered substitution of Pb for Bi is coupled with the insertion of Cu into adjacent tetrahedral sites. The structures of the intermediate bismuthinite – aikinite minerals also can be viewed as being an intergrowth of ribbons of an end member, either bismuthinite (B ribbons) or aikinite (A ribbons), with the middle member krupkaite (K ribbons). The ribbons are half the width of the unit cell along b , and so lindströmite can be viewed as an intergrowth of $8K + 2A$ ribbons. In order to refine the crystal structure, Horiuchi & Wuensch (1977) had to assume the presence of some krupkaite exsolved within the crystal selected. Pring & Hyde (1987) examined fragments from the type specimen by high-resolution transmission electron microscopy (HRTEM) and found it to be structurally rather inhomogeneous. It

consists of a disordered intergrowth of krupkaite and aikinite ribbons occurring together with regions of well-ordered krupkaite, hammarite and lindströmite. Pring (1989) showed that many natural compositions in the bismuthinite – aikinite series consist of disordered intergrowths as well as the ordered intermediate minerals. That is, a number of different structural states (states of order) are possible for the same composition. Earlier, Harris & Chen (1976) had established the extent of compositional variation in the bismuthinite – aikinite series. In their study, they noted a second occurrence of lindströmite from the Silver Miller mine, Cobalt, Ontario. Pring (1989) re-examined many of the specimens examined by Harris & Chen (1976) and found the Silver Miller mine lindströmite to be very well ordered.

OCCURRENCE

Two specimens of lindströmite were examined in this study: U.S. National Museum of Natural History #106760 and Harvard Mineralogical Museum #119763. Both specimens were originally obtained by these museums from Mr. W.W. Pinch. The locality given for both is the Silver Miller mine, Coleman Township, Timiskaming District, Ontario, Canada. Silver Miller Mines Ltd. was incorporated in 1946 and owned many mines in the Cobalt – Gowganda area. It has not been possible to establish unequivocally from which mine these samples were obtained. Enquiries to the Canadian Museum of Nature (CMN), which now holds the Pinch collection, revealed that the collection contains four specimens of lindströmite from the Cobalt area. For three of the specimens, the original Pinch labels gave the locality as the "Silver Miller mine"; however, during cataloguing at the CMN, this was clarified to be the Drummond mine, 3 km southeast of Cobalt, a mine owned and operated by Silver Miller Mines Ltd. The Drummond mine dates from the early part of the century and was worked by a number of companies prior to being taken over by Silver Miller Mines Ltd. in the 1960s. The major ore minerals in the deposit are native silver and skutterudite, with minor chalcopyrite, sphalerite, galena, pyrite and nickeline hosted in systems of calcite veins. Lindströmite is associated with laths of native bismuth and, in some cases, with minor amounts of chalcopyrite in mineralized veins a few mm thick in a graywacke matrix. The fourth Pinch specimen is from the Agnico mine, 7 km northeast of Cobalt, and is similar in appearance to the specimens from the Drummond mine. An account of the geology of these mines is given by Sergiades (1968), whereas Berry (1971) presented an overview of the mineralogy and geology of the silver deposits in the Cobalt – Gowganda region. It seems most likely that the lindströmite specimens examined in this study came from either the Drummond mine or the Agnico mine, and the mineral textures are consistent with crystallization at temperatures below the melting point of Bi (below 270°C).

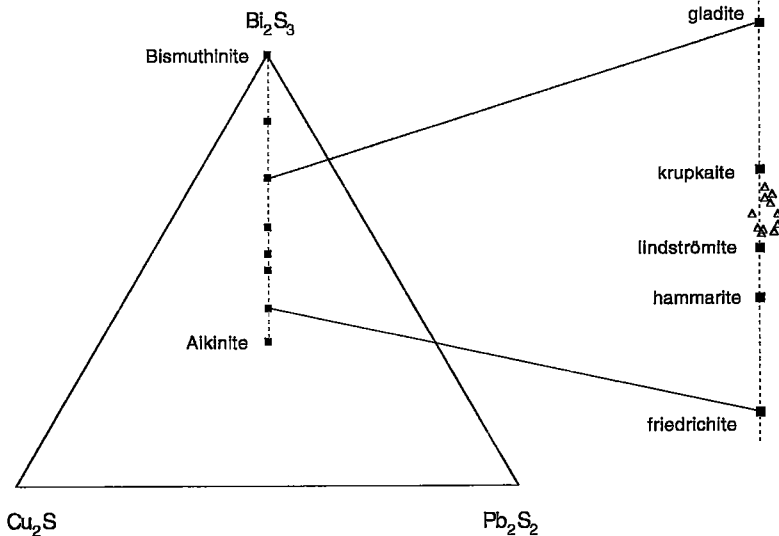


FIG. 1. Plot of electron-microprobe data for the "Silver Miller mine" lindströmite; the compositions lie between lindströmite and krupkaite.

CHEMICAL ANALYSIS

Chemical analyses were performed using a Cameca SX-50 electron microprobe at the University of Cambridge. Beam current and accelerating voltage were set at 50 nA and 12 kV, respectively. The standards used for the wavelength-dispersion analyses were synthetic PbS for Pb and S, Bi_2S_3 for Bi, and Cu and Sb metals. Analysis of the associated native bismuth showed it to be essentially pure. The results of the analyses are summarized in Table 1 and plotted in Figure 1. The mean result of the seven analyses gives a formula $\text{Cu}_{2.70}\text{Pb}_{2.80}\text{Bi}_{7.18}\text{Sb}_{0.09}\text{S}_{15}$ (calculated on the basis of 15 S atoms), which is near that reported for the Silver Miller mine lindströmite by Harris & Chen (1976), $\text{Cu}_{2.87}\text{Pb}_{2.87}\text{Bi}_{6.87}\text{S}_{15}$, and the composition documented for the type locality by Welin (1966),

$\text{Cu}_{2.67}\text{Pb}_{2.79}\text{Bi}_{6.63}\text{S}_{15}$. Whereas all of these formulae approximate to the ideal composition $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ (for lindströmite $x = 0.6$), none are in exact agreement. Harris & Chen (1976) noted the difficulties in obtaining accurate compositions of bismuthinite – aikinite minerals. In their case, the total of large cations (Bi + Pb + Sb) is low compared to the ideal formula (9.72 *versus* 10). There is a similar problem for the results of Welin (1966), in which the Cu:Pb ratio is less than 1. Our material shows a slight excess in large cations (10.07) and a Cu:Pb ratio slightly less than 1. We believe that deviations from the ideal stoichiometry are probably associated with the ZAF correction routines and the choice of standards. Harris & Chen (1976) noted the importance of choosing appropriate standards in obtaining accurate analyses (they used a synthetic compound of composition $\text{Cu}_2\text{Pb}_2\text{Bi}_3\text{S}_{7.5}$). They also concluded that any deviation from the ratio 1:1 for Cu:Pb indicates inaccuracy in the analysis, or interference from exsolved phases or adjacent minerals, rather than a breakdown in the coupled substitution of Cu + Pb by Bi. There is no evidence of exsolved phases in the Silver Miller mine lindströmite. We considered employing the synthetic hammarite prepared by Pring (1995) as a standard. This material, however, is slightly inhomogeneous. We believe that the Silver Miller mine lindströmite is probably closer to the ideal composition than the analytical results indicate.

TABLE 1. SUMMARY OF ELECTRON-MICROPROBE DATA FOR LINDSTRÖMITE

Sample	SM1	SM2	SM3	SM4	SM5	SM6	SM7	Mean	H & C	We	Theo
Cu wt%	5.90	5.81	6.53	6.58	6.02	6.63	6.28	6.25	6.90	6.5	6.92
Pb	20.10	20.75	21.77	20.59	20.39	21.93	22.54	21.15	22.33	22.1	22.57
Bi	56.12	55.36	53.82	55.03	55.43	53.59	53.36	54.67	53.07	53.0	53.04
Sb	0.32	0.34	0.42	0.35	0.38	0.48	0.42	0.39	0.44	-	-
S	17.57	17.66	17.46	17.38	17.62	17.44	17.46	17.51	18.09	18.4	17.47
Total	100.00	99.93	99.99	99.93	99.85	100.07	100.05	99.97	100.83	100	100

SM 1: $\text{Cu}_{2.56}\text{Pb}_{2.66}\text{Bi}_{7.33}\text{Sb}_{0.07}\text{S}_{15}$
 SM 2: $\text{Cu}_{2.69}\text{Pb}_{2.73}\text{Bi}_{7.21}\text{Sb}_{0.08}\text{S}_{15}$
 SM 3: $\text{Cu}_{2.83}\text{Pb}_{2.89}\text{Bi}_{7.06}\text{Sb}_{0.11}\text{S}_{15}$
 SM 4: $\text{Cu}_{2.87}\text{Pb}_{2.75}\text{Bi}_{7.28}\text{Sb}_{0.08}\text{S}_{15}$
 SM 5: $\text{Cu}_{2.65}\text{Pb}_{2.66}\text{Bi}_{7.25}\text{Sb}_{0.09}\text{S}_{15}$
 SM 6: $\text{Cu}_{2.88}\text{Pb}_{2.92}\text{Bi}_{7.07}\text{Sb}_{0.11}\text{S}_{15}$
 SM 7: $\text{Cu}_{2.77}\text{Pb}_{2.99}\text{Bi}_{7.03}\text{Sb}_{0.11}\text{S}_{15}$
 H & C: Harris & Chen (1976), $\text{Cu}_{2.87}\text{Pb}_{2.87}\text{Bi}_{6.87}\text{S}_{15}$
 We: Welin (1966), $\text{Cu}_{2.67}\text{Pb}_{2.79}\text{Bi}_{6.63}\text{S}_{15}$
 Theo: theoretical

POWDER X-RAY DIFFRACTION

The powder X-ray diffraction pattern was recorded using a 100 mm diameter Guinier – Hägg camera with $\text{CrK}\alpha$ radiation; Si was used as an internal standard. No

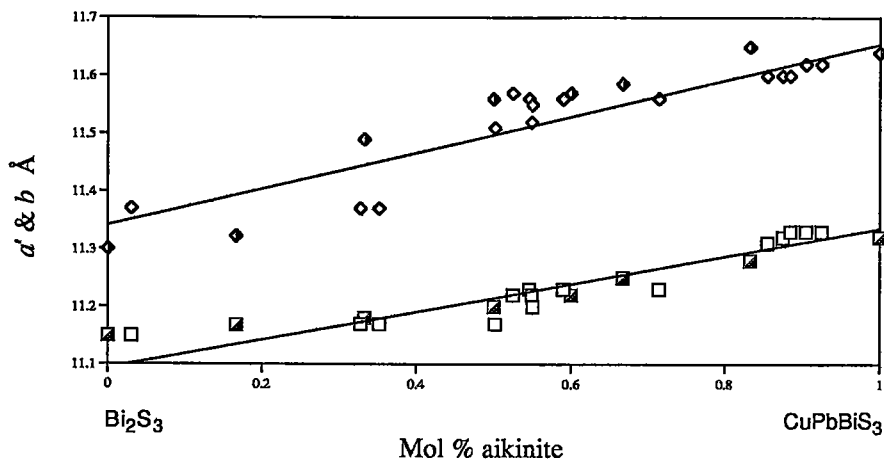


FIG. 2. Plot of the a' and b cell parameters for minerals of the bismuthinite – aikinite group. Open symbols: Harris & Chen (1976), half shade: end members (Pring 1989), shaded: lindströmite (this work), squares: a' , diamonds: b .

superlattice reflections were observed, but the subcell reflections of bismuthinite are strong and sharp. The pattern was indexed by reference to the ICDD powder diffraction data for krupkaite (file 30–490), and the subcell parameters were refined by least-squares methods. The parameters for the orthorhombic subcell are a' 11.198(3), b 11.549(3), c 4.010(1) Å, giving a supercell with $a = 5a' = 55.99(3)$ Å. These can be compared with the values reported by Harris & Chen (1976): a 56.15(3), b 11.56(0), c 3.99(0) Å, and by Horiuchi & Wuensch (1977): a 56.115(4), b 11.5695(8), c 4.001(5) Å. All three cells fall within error parameters, and any difference is not statistically significant. Figure 2 shows a plot of a and b cell parameters against composition; the data are taken from Harris & Chen (1976) and crystal-structure reports. The parameters show an approximately linear relationship with composition. The scatter in values, particularly in the region between 0.5 and 0.7 aikinite, may reflect uncertainties in compositional data for some samples or, possibly, a variation in the state of order, spontaneous strain associated with cation ordering, for various compositions. It is clear that simply refining the cell parameters for a bismuthinite – aikinite mineral will only enable the approximate composition to be determined.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

A 7 mg piece was extracted from a polished mount using a dental drill, and a DSC scan was recorded in an attempt to locate a thermal anomaly that could be due to the (Cu,Pb)–Bi disordering reaction. The DSC scan was recorded using a Perkin – Elmer DSC–7 instrument and a heating rate of 10°C/min. No such thermal anomaly was found. A sharp endothermic peak, at approximately

270°C, is due to the melting of native bismuth, a contaminating phase in the lindströmite (Fig. 3). The melting point of members of the bismuthinite – aikinite series decreases from 763°C for bismuthinite to 467°C for aikinite (Springer 1971). No thermal anomaly was noted in DTA studies across the composition field by Springer (1971).

OPTICAL PROPERTIES

In reflected plane-polarized light, lindströmite is moderately reflecting, with a white to gray bireflectance. It is not pleochroic. Between crossed polars, the anisotropy is distinct, but the rotation tints are somber: at 45° from extinction, it is a light metallic fawn in color, and the sequence of tints is brown to gray to brown-gray to fawn. With polars uncrossed by 3°, the tints are much brighter and range from olive to purple brown to a clear light fawn to a purplish light gray. All of these effects are enhanced when the mineral is immersed in oil.

Reflectance measurements were made on a freshly (diamond) polished section of lindströmite with a Zeiss MPM800 microscope spectrophotometer. The standard used was WTiC (no. 314). Air and oil objectives ($\times 20$) had their full numerical apertures reduced for measurement to 0.20 (by closure of the illuminator aperture diaphragm). The data in Table 2 are the mean values from ten scans on the most bireflectant grain of the mineral observed in the polished section. Check measurements were made on other grains, but all were less bireflectant and within the quoted range. Most of the grains have straight extinction, but the extinction of two grains was found to be undulose; these grains showed slightly higher bireflectance. The spectra in both media for the

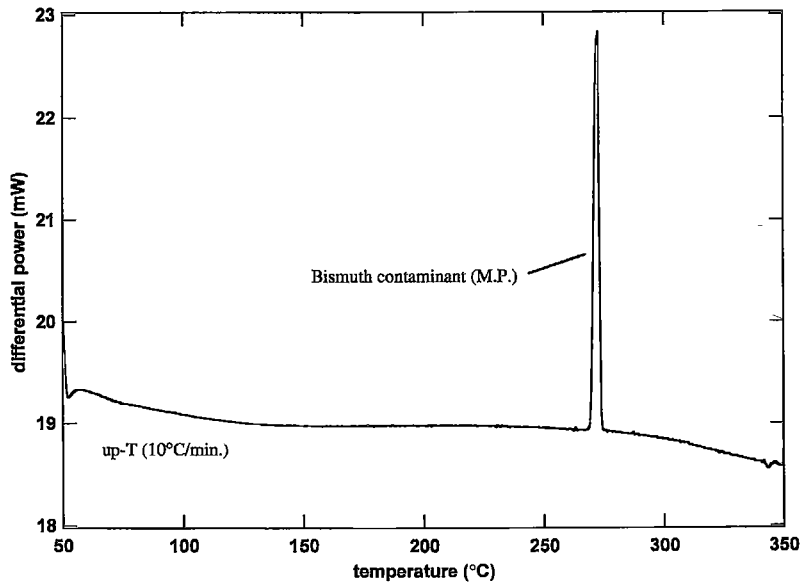


FIG. 3. DSC scan for lindströmite. Note that the large peak at 270°C is due to melting of inclusions of bismuth. No thermal anomalies due to disordering are apparent.

most bireflectant grain of lindströmite in the polished section (Fig. 4) are compared with those of aikinite, hammarite, krupkaite and bismuthinite (taken from Criddle & Stanley 1993). As is well known, the reflectance spectra in the visible region for sulfosalts of similar composition are themselves similar. Though there are differences in dispersion between all of them, in general, reflectance is not diagnostic of these species. In effect, the dispersion of their reflectance and magnitude of their bireflectance, for the most anisotropic grains, may well be characteristic, but in a general section, where the anisotropy of individual grains may vary from zero to the maximum for the species, all that can realistically be said is that the mineral is likely to be one of the group of lead - bismuth sulfosalts. The

lindströmite spectra in Figure 4 are quite similar to those of krupkaite, and the bireflectance of both minerals is greater than that of hammarite. All of them are considerably less bireflectant than bismuthinite. The greater bireflectance and the difference in the dispersion of the reflectance make it easy to distinguish bismuthinite from the intermediate members of the series to aikinite.

MEASUREMENTS OF INDENTATION HARDNESS

Measurements of micro-indentation hardness were made with a Leitz Durimet Hardness tester (with a Vickers diamond) at a loading of 100 pond. Ten indentations were made, all of which were slightly fractured, five had perfect outlines, five concave; VHN_{100} is in the range 118–197 (mean 170). These values are compared in Table 3 with those for aikinite and bismuthinite (Uytenbogaardt & Burke 1971) and krupkaite and hammarite (Criddle & Stanley 1993). The mean values in brackets were calculated from the range quoted by

TABLE 2. SPECULAR REFLECTANCE DATA FOR LINDSTRÖMITE IN AIR AND IN OIL

λ nm	R_1	R_2	mR_1	mR_2	λ nm	R_1	R_2	mR_1	mR_2
400	38.3%	46.0%	24.0%	29.9%	560	38.5%	46.4%	23.5%	30.7%
420	38.6	45.7	24.1	29.9	580	38.6	46.5	23.3	30.6
440	38.7	45.5	24.2	29.9	589	38.5	46.3	23.3	30.5
460	38.8	45.45	24.2	30.0	600	38.3	46.0	23.3	30.3
470	38.8	45.6	24.2	30.0	620	38.2	45.8	23.1	30.0
480	38.9	45.8	24.1	30.2	640	38.0	45.6	23.0	29.8
500	38.9	46.1	23.9	30.3	650	37.8	45.4	22.7	29.55
520	38.8	46.2	23.9	30.5	660	37.6	45.2	22.5	29.3
540	38.6	46.35	23.75	30.6	680	37.2	44.9	22.3	29.05
546	38.6	46.4	23.7	30.6	700	36.85	44.2	22.1	28.5

Zeiss oil, $N_D = 1.515$.

TABLE 3. VHN VALUES FOR LINDSTRÖMITE AND OTHER BISMUTHINITE - AIKINITE MINERALS

	VHN (pond)	range	mean
aikinite	100	165 - 227	(196)
bismuthinite	100	67 - 216	(142)
hammarite	50	224 - 264	243
krupkaite	100	148 - 188	165
lindströmite	100	118 - 197	170

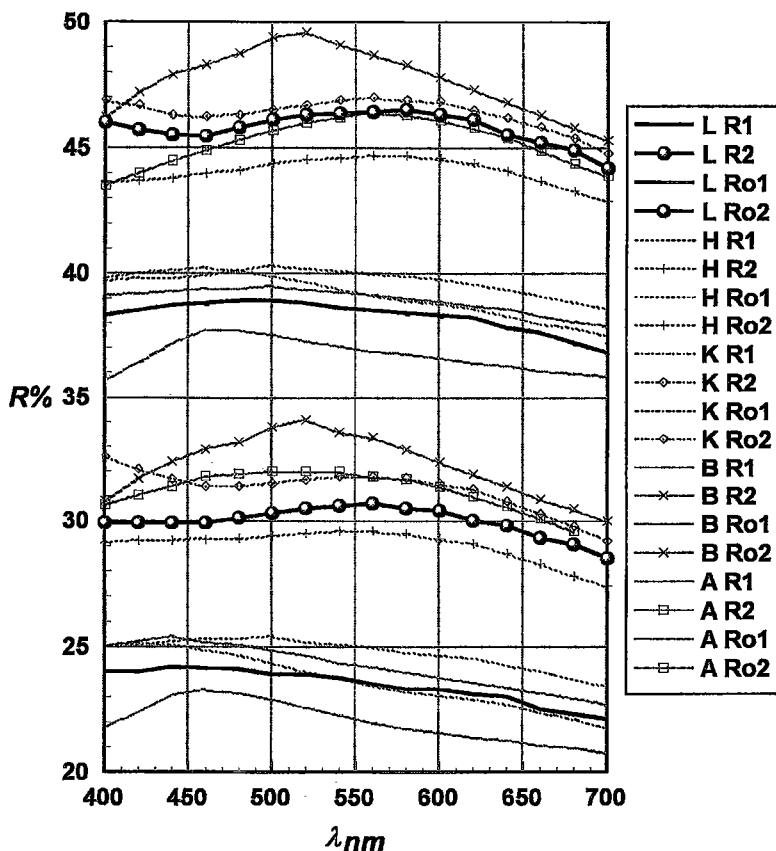


FIG. 4. Comparison of reflectance spectra for lindströmite and for selected other members of the bismuthinite - aikinite series. Lindströmite, *L*, hammarite, *H*, krupkaite, *K*, bismuthinite, *B*, and aikinite, *A*. The data for hammarite, krupkaite, bismuthinite and aikinite are taken from Criddle & Stanley (1993).

Uytenbogaardt and Burke, the others are the mean values from the complete range of measured indentations. As can be seen, it is not possible to distinguish these minerals one from another on the basis of their hardness.

ELECTRON MICROSCOPY

Material was prepared for electron microscopy by grinding under acetone in an agate mortar. The fragments were dispersed from suspension onto Cu grids coated with holey carbon support films. Electron-diffraction patterns and high-resolution images were obtained using a JEOL 200 CX transmission electron microscope fitted with a specially modified side entry $\pm 15^\circ$ double-tilt goniometer. The optical parameters for this instrument are $C_s = 0.41$ mm, $C_c = 0.90$ mm, and at 200 kV the point-to-point resolution is 1.8 Å and the Scherzer defocus Δf is equal to -393 Å.

Figure 5 shows the electron-diffraction pattern, [001] zone, of the Silver Miller mine lindströmite. The diffraction patterns reveals a well-ordered $5a$ superlattice, the superlattice reflections are sharp, and there is no evidence of streaking along a^* , in contrast to some of the patterns shown in Pring (1989, 1995). Note the distribution of the intensities of the superlattice reflections; the first and fourth satellite reflections are significantly stronger than the second and third reflections. The high-resolution images (Fig. 6) show the well-ordered nature of the structure. Note also the considerable changes in lattice motif and contrast with thickness; the supercell repeat is more prominent in the thicker parts of the crystal fragment shown in Figure 6b, which is slightly tilted off-zone. In the thicker parts of the image shown in Figure 6a, the contrast appears to show a $3 + 2$ subcell pattern of ordering, whereas in the thinner region, the sequence appears to be $4 + 1$. But it should be noted that image contrast changes continuously

with thickness, and interpretation of the exact nature of the ordering scheme on the basis of these data is not possible.

All fragments of lindströmite that could be tilted onto the [001] zone were found to show a similar high degree of order to that illustrated in Figures 5 and 6. The Silver Miller mine lindströmite is well ordered and devoid of evidence for exsolution lamellae or "stacking disorder", as had been reported by Pring & Hyde (1987) for lindströmite from the type locality, and by Pring (1989) for other members of the bismuthinite – aikinite series.

At the edge of the crystals shown in Figure 6, there is a second phase. We believe that this phase is due to the partial decomposition of the crystal in the electron beam. Electron-diffraction patterns reveal that the dark patches at the edge of the crystal are a phase with a PbS-like structure in the [110] orientation. The composition of the phase could not be determined, but it could be a Cu analogue of a matildite – galena solid solution ($\text{Pb}_{0.33}\text{Cu}_{0.33}\text{Bi}_{0.33}\text{S}$). This phase exsolved topotactically (all patches at the crystal edge appear to be in the same orientation: Fig. 7). The proposed reaction is $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15} \rightarrow \text{Pb}_3\text{Cu}_3\text{Bi}_3\text{S}_9 + 2\text{Bi}_2\text{S}_3$. This reaction occurs slowly due to beam heating at temperatures of the order of 200°C under the high vacuum conditions of the HRTEM column and represents a decomposition rather than an ordering reaction.

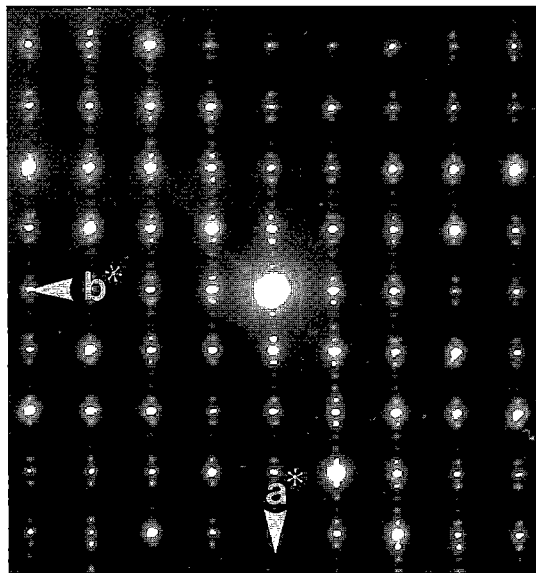


FIG. 5. Electron-diffraction pattern for lindströmite down the [001] zone. Note the strong sharp superlattice reflections due to a $5a$ supercell of the bismuthinite cell.

DISCUSSION

It is clear from the optical and microhardness data that it is not possible to differentiate among the intermediate members of the bismuthinite – aikinite series on the basis of their physical properties. Nor is it easy using electron-microprobe data, given the difficulty in obtaining accurate analyses. In any case, the analytical data only provide the position within the compositional field, not information on the state of order. Unfortunately superlattice reflections are not readily observed in X-ray powder diffraction, and thus this method cannot be used to establish the state of order; refinement of the cell parameters will give only an approximate indication of composition. The easiest method with which to establish the state of order is electron diffraction and high-resolution imaging. The period and sharpness of superlattice reflections provide a good indication of the state of order of the various compositional ribbons and, with high-resolution images, the state of order is directly observable. Unfortunately, very accurate calibration of the camera length for electron-diffraction patterns is difficult to achieve, which makes it difficult to determine the repeat distances accurately. A further problem is that the series forms a chemical continuum, which makes it impossible to obtain accurate chemical data by simultaneous EDS analyses in the TEM. In consequence, accurate characterization of a bismuthinite – aikinite mineral is achievable only by a combination of the following techniques: TEM, powder X-ray diffraction and electron-microprobe analyses.

In general, for any composition in the bismuthinite – aikinite series there are three or four possible structural states:

1. Complete solid-solution, where the Pb is randomly substituted for Bi on the $M2$ sites, and Cu is disordered over the available tetrahedral sites (Fig. 8).
2. Ordering of the Pb–Bi and Cu into A , K or B ribbons and the disordered intergrowth of these ribbons.
3. Disordered intergrowth of A , K or B ribbons with ordered ribbons of the higher (or supercell) members of the series, such as slabs of hammarite within a krupkaite matrix.
4. Fully ordered intergrowth of polysomatic ribbons, such as in lindströmite ($8K + 2A$), where the composition matches that of a supercell member. However, for a supercell composition and period, there are a number of possible ordered arrangements of ribbons, some of which have the same symmetry.

The structure of lindströmite determined by Horiuchi & Wuensch (1977) is only a two-dimensional refinement; they worked on a projection down [001]. They noted that there were 110 possible schemes of order for the arrangement of the 6 Cu atoms in the 10 possible sites (in the acentric structure). By ingenious computing methods, all possible schemes of order were evaluated, and the centric model for the structure (Fig. 8) was

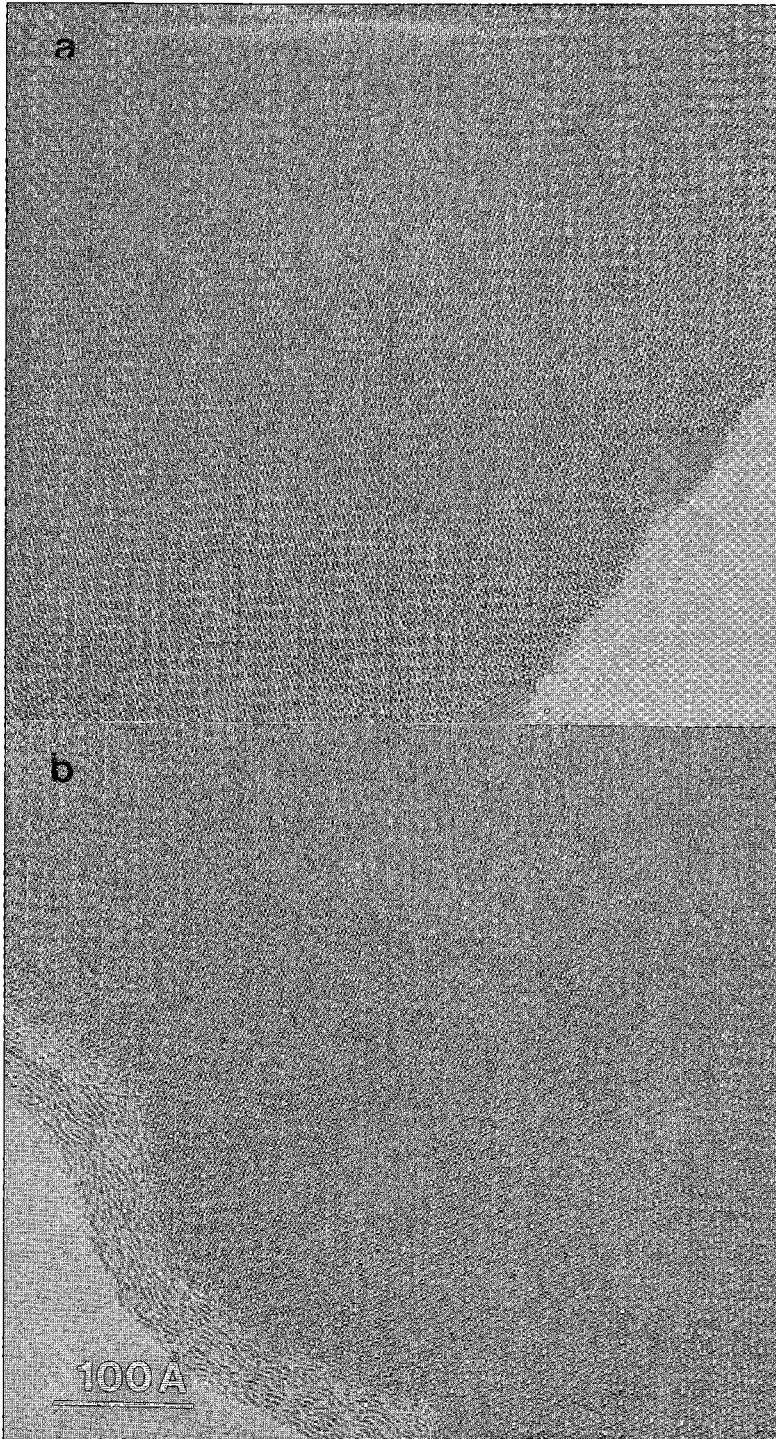


FIG. 6. Images of lindströmite down [001] zone, showing the well-ordered supercell. Note the changes in image detail and apparent degree of order with thickness. (a) A well-aligned image, (b) an image taken with the beam slightly off-tilt, which enhances the contrast differences in the ordered structure.

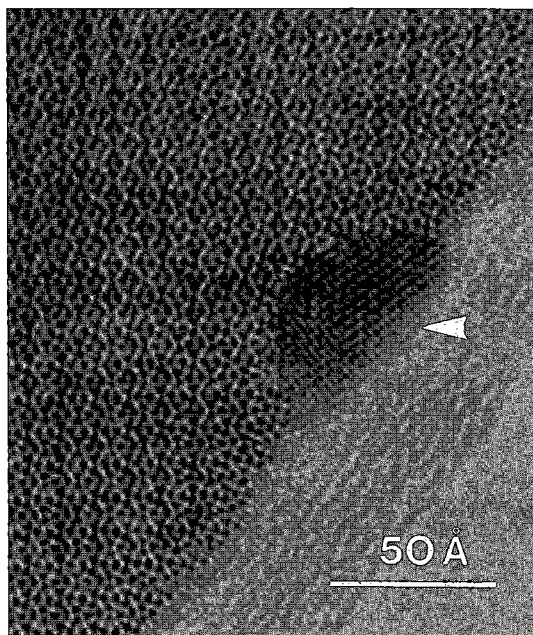


FIG. 7. Lattice image showing the decomposition of lindströmite at the edge of the crystal. The crystal slowly decomposes in the electron beam. The decomposition product has a PbS-like structure (in the [110] orientation) and is believed to be the Cu analogue of matildite. The decomposition results in a shift in composition toward bismuthinite.

selected as the most likely. However, given that they were working in projection, with visually estimated film data, from a crystal known to contain some exsolved krupkaite, there remains some uncertainty as to whether the structure is correct (final $R = 16.3\%$). Variations of contrast in the HRTEM image shown in Figure 6a suggest a simple scheme of order based on the regular intergrowth of one unit cell of aikinite with four unit cells of krupkaite, giving a 56 Å repeat. The centric

structure proposed by Horiuchi & Wuensch (1977) has a $1/2 a_{\text{lind}}$ (23 Å) subrepeat that is not evident in the images in Figure 6. It is not possible, however, to reach any firm conclusions about the scheme of order owing to the thickness of the crystal (>100 Å), too great to test any of the structural models by image simulation with the multislice method. There are also uncertainties in attempting to interpret the images due to the effects of beam tilt (image detail is very sensitive to the effects of any slight misalignment in the illumination direction) (Smith & Barry 1989).

It is by no means certain that the lindströmite samples from Gladhammar and Cobalt would necessarily have exactly the same supercell pattern of order. Pring (1995) followed the progress of supercell ordering in the bismuthinite – aikinite minerals *via* a series of long-term annealing experiments and showed that well-ordered “hammarite” could be prepared by annealing the appropriate stoichiometry at 225°C for 56 months. However, this synthetic hammarite was found to have a different ordered arrangement of *A* and *K* units compared with the hammarite from the Gladhammar deposit. Pring (1995) also showed that a partially ordered 5a supercell phase in the series could be prepared after 24 months annealing at 225°C, and that ordering also takes place at 175°C and probably at lower temperatures. It is reasonable to suppose from these long-term annealing experiments that such temperatures and times are easily achieved in nature. So most natural members of the bismuthinite – aikinite series should be well ordered into mixtures of *A*, *K* and *B* ribbons. The occurrence in nature of a highly ordered supercell phase in the bismuthinite – aikinite series depends on the composition of the mineral assemblage and geological history. The fact that the “Silver Miller mine” lindströmite occurs with native bismuth suggests that S fugacity is a critical factor in this occurrence. A higher S fugacity would increase the mole fraction of Bi_2S_3 at the expense of native Bi, and would push the lindströmite composition toward that of krupkaite. The native Bi occurs as laths and anhedral grains up to 1 mm intergrown with

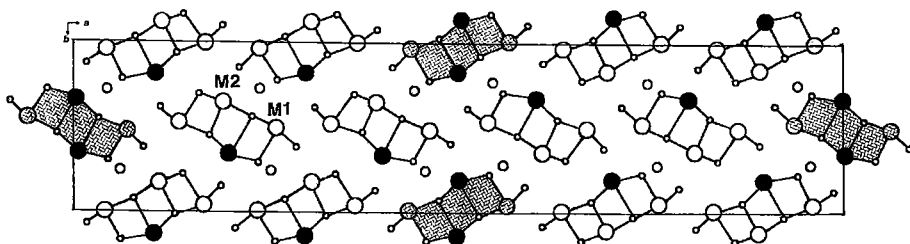


FIG. 8. Schematic diagram of the lindströmite structure projected down [001], showing the ordered intergrowth of eight ribbons of krupkaite and two ribbons of aikinite (shaded), based on the results of Horiuchi & Wuensch (1977). The *M1* and *M2* sites are indicated. In ordered members of the bismuthinite – aikinite series, Pb is ordered at the *M2* sites, and Cu, at the adjacent tetrahedral sites. Small circles represent S, medium circles, Cu, open large circles, Bi, and filled large circles, Pb.

lindströmite, which suggests a temperature of formation below the melting point of Bi.

The temperature of the order – disorder transition could not be established in this study, but on the basis of the annealing experiments of Pring (1995), we believe that the transition takes place at between 250 and 300°C. The melting of native bismuth in the lindströmite specimens may have obscured any thermal anomaly associated with this transition.

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