

## FELBERTALITE AND RELATED BISMUTH SULFOSALTS FROM THE FUNIUSHAN COPPER SKARN DEPOSIT, NANJING, CHINA

GU XIANG-PING<sup>§</sup>, MAKOTO WATANABE, MAKIO OHKAWA, KENICHI HOSHINO  
AND YASUHIRO SHIBATA

*Department of Earth and Planetary Sciences, Hiroshima University, Hiroshima 739-8526, Japan*

CHEN DESONG

*Guilin Research Institute of Geology for Mineral Resources, Guangxi 541004, China*

### ABSTRACT

Electron-microprobe and single-crystal X-ray-diffraction analyses have confirmed the second occurrence of felbertalite in the Funiushan copper skarn deposit, near Nanjing, in eastern China. It can be chemically described as  $\text{Cu}_2\text{Ag}_x\text{Pb}_{6-2x}\text{Bi}_{8+x}(\text{S},\text{Se})_{19}$ , with a wide range of substitution of Bi + Ag for 2Pb, with  $x$  ranging from 0.64 to 1.03 (probably up to 1.33), suggesting the presence of a solid-solution series in felbertalite. The measured unit-cell parameters of a felbertalite grain with a composition of  $\text{Cu}_{2.20}\text{Ag}_{0.70}\text{Pb}_{4.65}\text{Bi}_{8.45}\text{S}_{19.12}$  are:  $a$  27.68(4),  $b$  4.046(1),  $c$  20.67(3) Å,  $\beta$  131.06(8)°, space group  $C2/m$ . A set of phases in the bismuthinite–aikinite series, mostly free of Ag and characterized by intermediate compositions between ideal formulae, were identified with electron-microprobe data. Compositional variations from  $\text{Cu}_{1.80}\text{Pb}_{1.80}\text{Bi}_{2.20}\text{S}_6$ , through  $\text{Cu}_{1.53}\text{Pb}_{1.53}\text{Bi}_{2.47}\text{S}_6$ ,  $\text{Cu}_{1.07}\text{Pb}_{1.07}\text{Bi}_{2.93}\text{S}_6$ ,  $\text{Cu}_{0.73}\text{Pb}_{0.73}\text{Bi}_{3.27}\text{S}_6$ , to  $\text{Cu}_{0.58}\text{Pb}_{0.58}\text{Bi}_{3.42}\text{S}_6$  within a single grain were observed, indicating that an intergrowth of three structural units, *i.e.*, bismuthinite ribbons, krupkaite ribbons and aikinite ribbons, could occur in the progressive exsolution or precipitation of a single phase in the bismuthinite–aikinite series. The exceptionally high contents of Ag (0.76–1.27 wt%) in the phase  $\text{Cu}_{0.83}\text{Ag}_{0.10}\text{Pb}_{0.90}\text{Bi}_{3.13}\text{S}_6$ , presumably corresponding to krupkaite, are noted. Electron-microprobe analyses have also revealed the occurrence of a number of rare minerals, including junöite, unknown  $\text{Cu}_2\text{Ag}_x\text{Pb}_{10-2x}\text{Bi}_{12+x}\text{S}_{29}$  ( $1.23 < x < 1.49$ ), berryite, benjaminite?, schirmerite?, Bi- and Ag-bearing galena, wittichenite and tetradymite. Within the intergrowths of Cu–Ag–Pb–Bi–S(Se,Te) minerals, Te (especially) and Se are preferably partitioned into Ag-bearing phases.

**Keywords:** felbertalite, bismuthinite–aikinite series, bismuth sulfosalts, unknown  $\text{Cu}_2\text{Ag}_x\text{Pb}_{10-2x}\text{Bi}_{12+x}\text{S}_{29}$ , copper skarn, Funiushan, Nanjing, China.

### SOMMAIRE

Nous avons confirmé la présence de la felbertalite dans le gisement de skarn cuprifère de Funiushan, près de Nanjing, dans la partie orientale de la Chine, avec des analyses à la microsonde électronique et par diffraction X sur cristal unique. Il s'agit du deuxième exemple connu. Sa composition peut s'exprimer par la formule  $\text{Cu}_2\text{Ag}_x\text{Pb}_{6-2x}\text{Bi}_{8+x}(\text{S},\text{Se})_{19}$ ; il y a un grand intervalle de substitution de Bi + Ag pour 2Pb, avec  $x$  entre 0.64 et 1.03 (et même probablement jusqu'à 1.33), ce qui indiquerait la présence d'une solution solide dans la felbertalite. Les paramètres réticulaires d'un grain ayant une composition de  $\text{Cu}_{2.20}\text{Ag}_{0.70}\text{Pb}_{4.65}\text{Bi}_{8.45}\text{S}_{19.12}$  sont:  $a$  27.68(4),  $b$  4.046(1),  $c$  20.67(3) Å,  $\beta$  131.06(8)°, groupe spatial  $C2/m$ . Plusieurs phases de la série bismuthinite–aikinite, en général sans Ag et ayant une composition intermédiaire entre les formules idéales, ont été identifiées par microsonde électronique. Les variations en composition, de  $\text{Cu}_{1.80}\text{Pb}_{1.80}\text{Bi}_{2.20}\text{S}_6$ , en passant par  $\text{Cu}_{1.53}\text{Pb}_{1.53}\text{Bi}_{2.47}\text{S}_6$ ,  $\text{Cu}_{1.07}\text{Pb}_{1.07}\text{Bi}_{2.93}\text{S}_6$ ,  $\text{Cu}_{0.73}\text{Pb}_{0.73}\text{Bi}_{3.27}\text{S}_6$ , jusqu'à  $\text{Cu}_{0.58}\text{Pb}_{0.58}\text{Bi}_{3.42}\text{S}_6$ , ont été trouvées à l'intérieur d'un seul grain, indication qu'une intercroissance de trois unités structurales, *c'est-à-dire*, les rubans de bismuthinite, de krupkaïte et d'aikinite, a pu se former au cours de l'exsolution progressive ou de la précipitation d'une seule phase de la série bismuthinite–aikinite. Nous notons les teneurs anormalement élevées d'Ag (0.76–1.27%, par poids) dans la phase  $\text{Cu}_{0.83}\text{Ag}_{0.10}\text{Pb}_{0.90}\text{Bi}_{3.13}\text{S}_6$ , que nous attribuons à la krupkaïte. Les analyses à la microsonde électronique révèlent aussi la présence de plusieurs minéraux rares, par exemple junöite,  $\text{Cu}_2\text{Ag}_x\text{Pb}_{10-2x}\text{Bi}_{12+x}\text{S}_{29}$  ( $1.23 < x < 1.49$ ) méconnu, berryite, benjaminite?, schirmerite?, galène enrichie en Bi et Ag, wittichenite et tétradymite. Dans les intercroissances de minéraux de Cu–Ag–Pb–Bi–S(Se,Te), le Te, particulièrement, et le Se sont préférentiellement répartis dans les phases riches en Ag.

(Traduit par la Rédaction)

**Mots-clés:** felbertalite, série de la bismuthinite–aikinite, sulfosels de bismuth,  $\text{Cu}_2\text{Ag}_x\text{Pb}_{10-2x}\text{Bi}_{12+x}\text{S}_{29}$  méconnu, skarn cuprifère, Funiushan, Nanjing, Chine.

<sup>§</sup> E-mail address: guxp@geol.sci.hiroshima-u.ac.jp

## INTRODUCTION

China is a country rich in bismuth resources, with total recoverable reserves about 481,400 tonnes of metallic bismuth in 1994 (Song 1998). Bismuth sulfosalt minerals are distributed in various types of deposits, including high-temperature hydrothermal W–Bi quartz vein, skarn-type Cu, Pb and Zn deposits, and mesothermal Cu, Pb, Zn and Au–Ag deposits (Liang *et al.* 1981, Hong *et al.* 1982, Ren 1965, 1998). However, detailed mineralogical studies are still quite few, and not in keeping with the rich bismuth resources available for detailed investigation.

During a mineralogical investigations of the ores from the Funiushan copper skarn deposit, Nanjing, China, a suite of Cu–Ag–Pb–Bi–S–Se–Te minerals were identified by ore microscopy and electron-probe micro-analysis (EPMA). Among these, the presence of feibertalite was confirmed by single-crystal X-ray diffraction. New information on minerals in this assemblage was obtained, though most of the phases still need confirmation by X-ray diffraction. We report here the occurrences of these minerals with an emphasis on feibertalite and the bismuthinite–aikinite series.

## GEOLOGICAL SETTING AND SAMPLE DESCRIPTION

The Funiushan copper deposit, located about 26 km east of Nanjing City, Jiangsu Province in eastern China (Fig.1), is genetically related to the Funiushan granodiorite complex, which covers an area about 4.5 km<sup>2</sup>. The intrusive complex consists of porphyritic granodiorite, granodiorite porphyry, quartz dioritic porphyry and quartz syenite porphyry. According to Ye (1999), two stages of intrusion occurred in the Yanshanian Period, the earlier porphyritic granodiorite and granodiorite porphyry being followed by quartz diorite porphyry and quartz syenite porphyry. The Rb–Sr isochron age of the granodiorite porphyry was reported to be  $111 \pm 1$  Ma with an initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of  $0.7058 \pm 0001$  (Ye 1999).

Skarn rocks occur at the contact of the Yanshanian intrusive rocks and Upper Devonian quartz sandstone and slate hornfels. No apparent spatial relation is observed between the skarn and the Upper Devonian carbonate rocks.

The copper orebodies, striking NE or EW, occur in association with skarn or skarn hornfels and locally are hosted in the sandstone of the Wutong Group of the

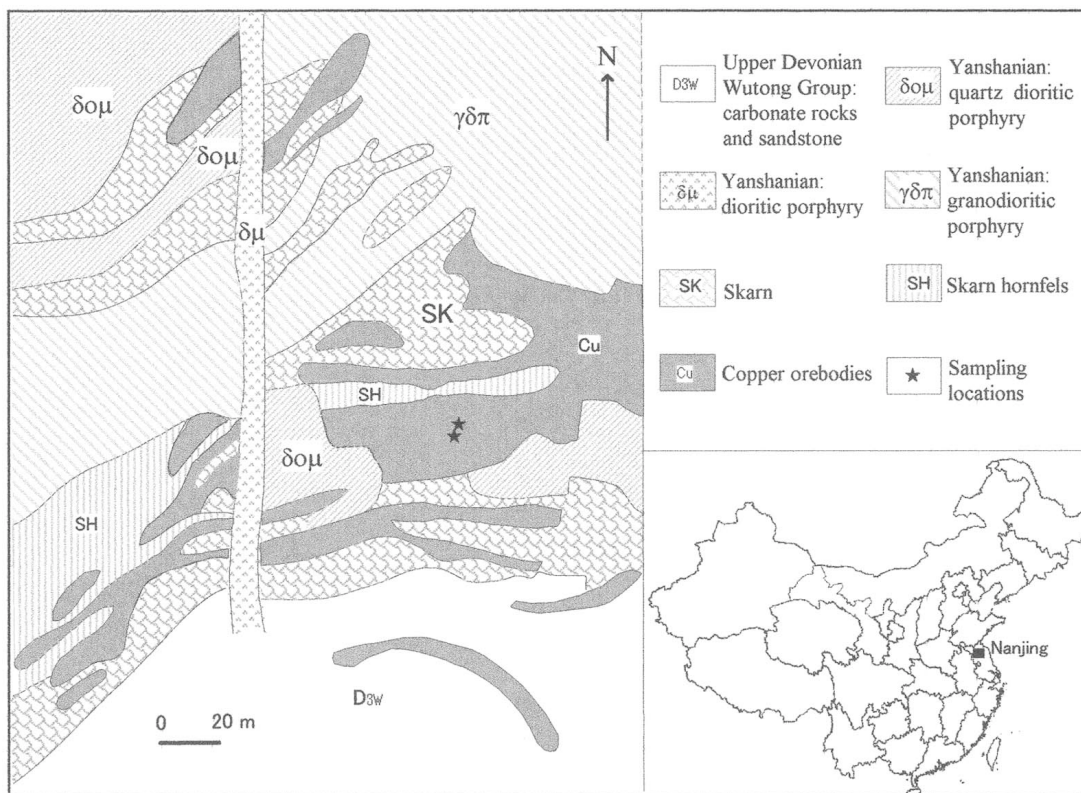


FIG. 1. Geological map and sampling locations on the +60 m level of the Funiushan skarn copper deposit (after Zhang 1998).

Upper Devonian System (Fig. 1). Total copper metal reserves of the deposit are estimated to be less than 100,000 tonnes, almost exhausted by now. Ore minerals are mainly pyrite and chalcopyrite, with minor amounts of pyrrhotite, siegenite, sphalerite and galena. Trace Au–Ag alloy also is present in association with siegenite and chalcopyrite. The gangue minerals include mainly andraditic garnet, carbonate and quartz. The average grade of ores on the +30 m and +60 m levels is: 1.08% Cu, 0.66% Zn, 50 ppm Pb, <100 ppm Bi, 60 ppm Co, 40 ppm Ni, 21 ppm Se, 3.5 ppm Te, 0.35 ppm Au and 11.5 ppm Ag.

Three out of 60 samples, collected at every 5 to 10 m on the +60 m level, were found to contain an abundance of bismuth sulfosalt minerals. The samples are mainly composed of chalcopyrite (20 vol.%), pyrite (5 vol.%) and minor sphalerite, galena and siegenite. Hematite is commonly observed to enclose and replace bismuth sulfosalt minerals. Gangue minerals are dominated by andradite (>70 vol.%) in grains that are concentrically zoned, with small amounts of quartz. Bismuth sulfosalt minerals, easily recognizable in polished sections by their gray-white color, occur as acicular aggregates or irregular grains up to  $5 \times 0.3$  mm in size. They are usually disseminated in intergranular spaces among andradite grains or along chalcopyrite grains. Back-scattered electron (BSE) images (Figs. 2, 3) reveal intimate intergrowths of Cu–Ag–Pb–Bi–S–Se–Te minerals, indistinguishable under the microscope. Textural relationships indicate that bismuth sulfosalts formed later than andradite, pyrite and most of the chalcopyrite, sphalerite and siegenite.

#### ANALYTICAL METHODS

Polished sections containing bismuth sulfosalt minerals were carefully examined under the microscope. Their chemical compositions were established with a JEOL JCMA–733II electron-microprobe analyzer. The operating conditions were as follows: accelerating voltage 25 kV, probe current 12–15 nA, and beam diameter 5  $\mu$ m. The spectral lines of  $SK\alpha$ ,  $CuK\alpha$ ,  $FeK\alpha$ ,  $SeL\alpha$ ,  $AgL\alpha$ ,  $PbM\alpha$ ,  $BiM\alpha$ ,  $SbM\alpha$  and  $TeM\alpha$  were used. Synthetic pure materials of Te, Bi, Ag, Se, Sb and synthetic  $CuFeS_2$  and  $PbS$  were used as standards. The results were corrected on-line (ZAF).

Under the microscope, most of the Cu–Ag–Pb–Bi sulfosalts show similar features, *i.e.*, gray-white to yellowish white color, weak to clear birefractance and anisotropism. They are closely intergrown and difficult to distinguish from each other. Therefore, great attention was paid to back-scattered electron (BSE) images in order to distinguish the various phases in their intimate intergrowths and to ensure the selection of homogeneous areas for analytical work.

One grain of felbertalite in the polished section, about  $400 \times 200 \mu\text{m}^2$  in size (Fig. 2a), was removed from its andradite host and broken into several smaller

grains. A rectangular crystal,  $50 \times 150 \times 190 \mu\text{m}^3$  in dimension, was mounted on fine glass capillary with epoxy. The intensity data were collected on a RIGAKU AFC–7R four-circle diffractometer with graphite-monochromatized  $MoK\alpha$  radiation (60 kv, 250 mA). A total of 4196 reflections were observed. The cell dimensions were determined by a least-squares method using 25 reflections. Detailed structural data will be published elsewhere.

#### RESULTS

##### *Felbertalite*

Felbertalite, the bismuth sulfosalt most commonly encountered in the deposit, in domains 30  $\mu$ m to 1.5 mm in size, usually forms acicular or granular intergrowths with aikinite and friedrichite in an intergranular position among grains of andradite or along grains of chalcopyrite (Figs. 2a–f).

Results of electron-microprobe analyses on 19 grains of felbertalite associated with aikinite and friedrichite are presented in Table 1. The results agree well with the formula  $Cu_2Ag_xPb_{6-2x}Bi_{8+x}(S,Se)_{19}$ , with  $x$  ranging from 0.64 to 1.03, except for an excess of 0.18–0.49 Cu per formula. Two additional grains, one associated with berryite and wittichenite (no. e14 and e09 in Table 1, Fig. 3a) and another with pekoite, benjaminite and tetradymite (no. c31 and e36 in Table 1, Fig. 3b), have even higher Ag content, with  $x$  equal to 1.12 and 1.33 atoms per formula unit (*apfu*).

One grain with  $x$  equal to 0.70 (Fig. 2a) was confirmed by single-crystal X-ray diffraction to have space group  $C2/m$ ,  $a$  27.68(4),  $b$  4.046(1),  $c$  20.67(3) Å,  $\beta$  131.06(8)°, which is in good agreement with the findings of Topa *et al.* (2000) determined on holotype felbertalite (Topa *et al.* 2001).

Felbertalite was recently discovered from Felbertal, Austria (Topa *et al.* 2000, 2001, Grice & Ferraris 2000). The structural formula is  $Cu_2Pb_6Bi_8S_{19}$  composed of *en échelon* staggered fragments of  $(100)_{PbS}$  layers alternating with periodically sheared  $(111)_{PbS}$  layers two octahedra thick (Topa *et al.* 2000). The compositional data from the type locality (E. Makovicky, pers. commun.) and Spain (Marcoux *et al.* 1996) show that felbertalite contains a small amount of silver as a result of the substitution  $Ag + Bi = 2Pb$  in  $(111)_{PbS}$  layers, yielding a general formula  $Cu_2Ag_xPb_{6-2x}Bi_{8+x}(S,Se)_{19}$ , with  $x$  ranging from 0 to 0.79. Nevertheless, a wide range of solid-solution substitution has not been reported to date. As shown by the compositions of felbertalite from the Funiushan copper deposit, up to three-fourth of the Pb in  $(111)_{PbS}$  layers may be replaced by Ag + Bi, with  $x$  ranging from 0.64 to 1.33.

We note that an excess of Cu (0.18–0.49, average 0.28 *apfu*) occurs in the formula in samples of felbertalite from the Funiushan deposit. Excess Cu was also observed in some lillianite homologues (Cook

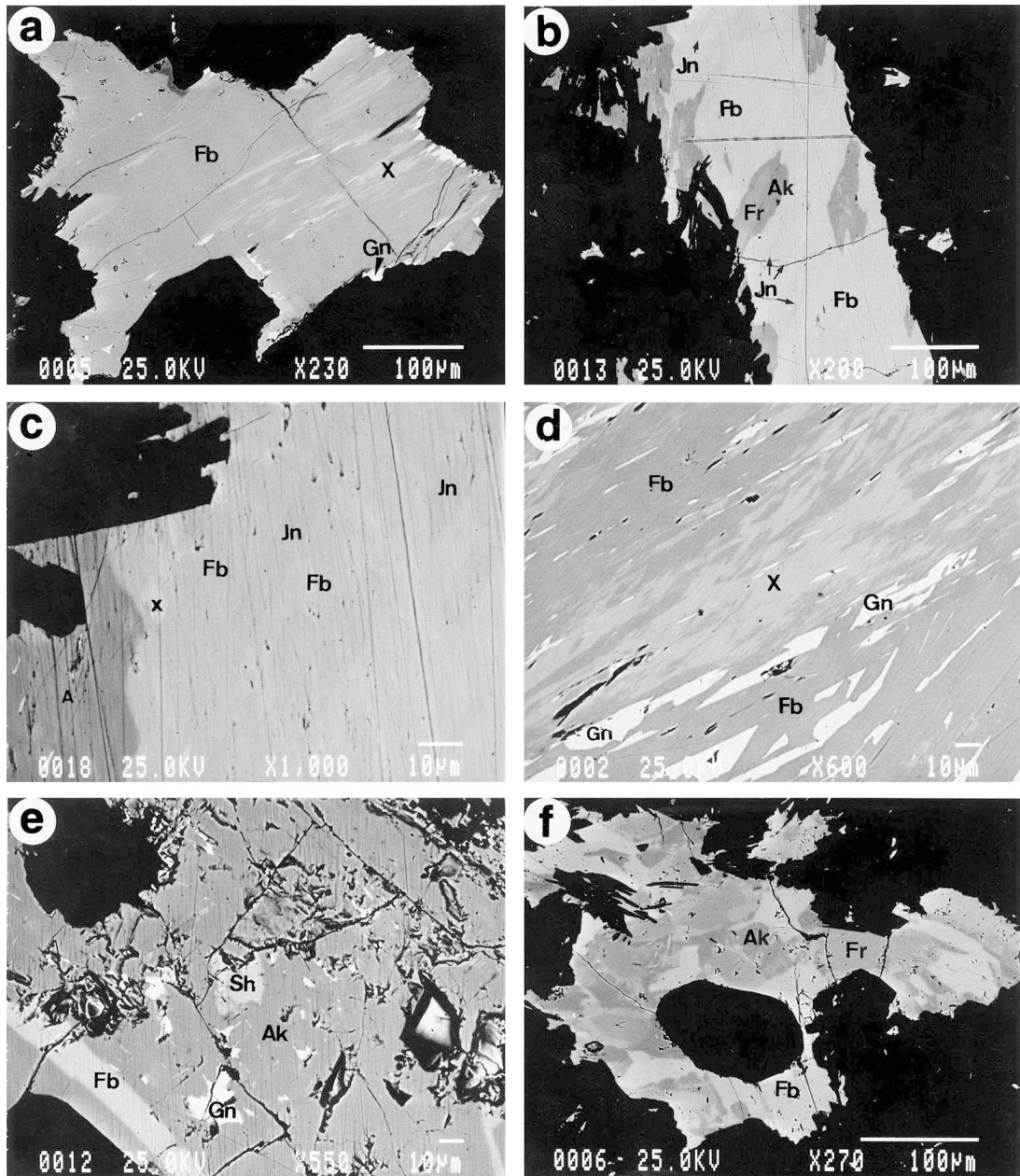


FIG. 2. Back-scattered electron images of bismuth sulfosalts. a. Felbertalite (Fb) and exsolution patches of unknown  $\text{Cu}_2\text{Ag}_x\text{Pb}_{10-2}\text{Bi}_{12+x}\text{S}_{29}$  (X) and Bi- and Ag-bearing galena (Gn). b. Exsolution lamellae of junoite (Jn) in felbertalite (Fb) in association with aikinite (Ak) and friedrichite (Fr). c. Enlargement of part of b to show exsolution lamellae of junoite (Jn) in felbertalite (Fb) in association with aikinite (Ak). d. Oriented exsolution-induced lamellae of unknown  $\text{Cu}_2\text{Ag}_x\text{Pb}_{10-2}\text{Bi}_{12+x}\text{S}_{29}$  (X) and Bi- and Ag-bearing galena (Gn) in felbertalite (Fb). e. Mineral association of aikinite (Ak), felbertalite (Fb), Bi- and Ag-bearing galena (Gn) and schirmerite? (Sh). f. Complex intergrowth of felbertalite (Fb), friedrichite (Fr) and aikinite (Ak).

1997) and jaskolskiite and titaite (Moëlo *et al.* 1995). In the experiments of Mariolacos (1979) and Sugaki *et al.* (1986), the "AG" phase  $\text{Cu}_{12}\text{Pb}_{25}\text{Bi}_{38}\text{S}_{88}$  (or  $\text{Cu}_{2.56}\text{Pb}_{5.33}\text{Bi}_{8.12}\text{S}_{18.77}$  based on  $\text{Cu} + \text{Pb} + \text{Bi} = 16$ ), a possible synthetic equivalent of felbertalite, also showed excess Cu compared to  $\text{Cu}_2\text{Pb}_6\text{Bi}_8\text{S}_{19}$ , which is unlikely to be attributable to the substitution of 2Pb by Cu + Bi. It seems that in the Funiushan samples, excess Cu may be involved in the substitutions of  $\text{Ag} + \text{Cu}_{\text{interstitial}}$  for Pb,  $\text{Cu} + \text{Cu}_{\text{interstitial}}$  for Pb and, less probably,  $\text{Cu} + 2\text{Cu}_{\text{interstitial}}$  for Bi.

#### The bismuthinite–aikinite series

Minerals in the bismuthinite–aikinite series, usually constituting complex solid-solution intergrowths from 20  $\mu\text{m}$  to more than 1 mm in size, are commonly seen in association with felbertalite (Figs. 2a–f), benjaminite and Bi- and Ag-bearing galena (Figs. 2e, 3b, 3d–f). Their compositions are plotted linearly on the bismuthinite–aikinite join characterized by Cu equal to Pb, mostly located between the ideal compositions of indi-

vidual minerals in this series (Fig. 4). According to the general formula  $\text{Cu}_x\text{Pb}_x\text{Bi}_{4-x}\text{S}_6$  proposed by Žák (1980), the corresponding values of  $x$  are calculated to be between 1.90 and 0.17, as shown in Table 2. In the range of  $x$  from 1.90 to 1.53, two distinct phases can be distinguished from textural evidence in BSE images (Figs. 2b, f, 3c), one with  $x$  from 1.90 to 1.76 corresponding to aikinite, another with  $x$  from 1.74 to 1.53 corresponding to friedrichite. Similarly, two phases can be distinguished in the range of  $x$  from 0.41 to 0.17, one with  $x$  from 0.41 to 0.31 corresponding to pekoite and another with  $x$  from 0.28 to 0.17 probably corresponding to Pb(Cu)-bearing bismuthinite (Fig. 3f). We note that compositional variations from  $x = 1.80$  to 0.58 are observed from the margin to the core of a single grain (Fig. 3c), in which five compositional phases were distinguished according to the BSE image, with  $x$  respectively around 1.80, 1.53, 1.07, 0.71–0.75 (average 0.73) and 0.58. The grains associated with pekoite or wittichenite (Figs. 3a, d), 30 to 200  $\mu\text{m}$  in diameter, have compositions with  $x$  from 0.94 to 0.88, presumably of krupkaite, which, in contrast to other Ag-free

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES AND SINGLE-CRYSTAL X-RAY DIFFRACTION OF FELBERTALITE FROM THE FUNIUSHAN COPPER SKARN DEPOSIT

	Weight %										<i>apfu</i> based on $\Sigma\text{cations} = 16$						Associated minerals	
	Bi	Sb	Ag	Cu	Fe	Pb	Se	Te	S	Total	Cu	Ag	Bi+ Sb	Pb+ Fe	S+Se +Te	Pb+ 2Ag		Bi- Ag
d36	49.22	0	1.93	3.87	0	27.23	1.3	0.29	16.45	100.29	2.19	0.64	8.45	4.72	19.08	6.00	7.81	frd–gn
d22	49.56	0.04	1.95	3.97	0	25.45	1.3	0.29	16.32	98.88	2.27	0.66	8.62	4.46	19.15	5.78	7.96	frd–gn
f01	49.54	0.03	2.03	3.83	0	26.25	1.44	0.44	16.36	99.92	2.18	0.68	8.57	4.57	19.2	5.93	7.89	aik–x–gn
f10*	49.67	0.03	2.13	3.94	0	27.14	1.38	0.46	16.59	101.34	2.20	0.70	8.45	4.65	19.12	6.05	7.75	aik–x–gn
d34	49.40	0	2.17	4.26	0.11	25.48	1.49	0.39	16.57	99.86	2.39	0.72	8.5	4.42	19.22	5.86	7.78	aik–frd
d56	50.02	0	2.21	3.92	0.03	24.18	1.49	0.39	16.49	98.73	2.25	0.75	8.75	4.27	19.54	5.77	8.00	aik–frd–jnt–x
f05	50.67	0	2.28	4.05	0	25.84	1.65	0.43	16.37	101.29	2.26	0.75	8.58	4.41	18.93	5.91	7.83	aik–x–gn
d24	50.94	0.01	2.30	4.02	0.03	24.55	1.37	0.35	16.98	100.54	2.26	0.76	8.74	4.25	19.66	5.77	7.98	frd
e54	49.50	0.01	2.29	3.99	0	25.65	1.35	0.41	16.33	99.51	2.26	0.76	8.52	4.45	19.05	5.97	7.76	frd–jnt–x
d23	50.95	0	2.30	3.99	0.01	23.89	1.3	0.4	16.44	99.26	2.26	0.77	8.80	4.16	19.21	5.70	8.03	frd–gn
d40	50.01	0.01	2.34	4.03	0.01	24.63	1.51	0.44	16.3	99.28	2.29	0.78	8.64	4.29	19.16	5.85	7.86	frd–jnt
d37	50.59	0.01	2.34	4	0.02	23.06	1.45	0.33	16.52	98.32	2.3	0.79	8.85	4.07	19.56	5.65	8.06	aik–frd–jnt
d25	51.11	0.03	2.69	3.93	0	23.89	1.46	0.40	16.46	99.97	2.21	0.89	8.77	4.13	19.16	5.91	7.88	frd
f08	51.68	0.01	2.85	4.07	0.02	23.47	1.44	0.42	16.84	100.79	2.27	0.94	8.78	4.02	19.37	5.90	7.84	aik
f15	51.76	0	2.97	4.21	0.77	23.20	1.49	0.51	16.4	101.31	2.27	0.94	8.95	4.07	19.56	5.95	8.01	aik–frd
d54	51.10	0	2.90	3.99	0.18	24.26	1.52	0.42	16.22	100.6	2.21	0.95	8.72	4.18	18.6	6.08	7.77	aik–jnt–x
d43	51.99	0.02	2.95	4.07	0	22.71	1.91	0.48	16.17	100.29	2.28	0.97	8.85	3.90	18.94	5.84	7.88	aik
f12	52.34	0	2.98	4.25	0.10	22.65	2.05	0.63	16.05	101.05	2.35	0.97	8.85	3.87	18.64	5.81	7.88	aik–frd
e56	52.00	0.02	3.11	4.13	0.04	21.33	1.94	0.55	16.27	99.37	2.33	1.03	8.95	3.70	19.22	5.76	7.92	frd
e14	53.22	0	3.43	4.49	0.25	19.28	2.98	0.62	15.58	99.86	2.49	1.12	9.12	3.35	18.59	5.59	8.00	wtc–ber
e09	52.78	0	3.66	4.27	0.55	19.13	2.88	0.64	15.73	99.64	2.36	1.19	9.04	3.41	18.67	5.79	7.85	wtc–ber
c31	55.73		3.92	4.21		17.71	2.47	0.65	16.31	100.99	2.33	1.28	9.38	3.01	19.17	5.57	8.10	pek–bnj
e36	55.48	0.04	4.04	4.22	0.01	16.98	2.45	0.57	16.19	99.98	2.35	1.33	9.42	2.91	19.14	5.57	8.09	pek–bnj

Unit-cell data for felbertalite  $[\text{Cu}_{2.20}\text{Ag}_{0.70}\text{Pb}_{4.65}\text{Bi}_{8.45}(\text{S}, \text{Se}, \text{Te})_{19.12}]$  from the Funiushan deposit: space group  $C2/m$ ,  $a$  27.68,  $b$  4.046,  $c$  20.67 Å,  $\beta$  131.06°. Unit-cell data for felbertalite  $[\text{Cu}_2\text{Pb}_2\text{Bi}_8\text{S}_{16}]$  from Felbertal, Austria (Topa *et al.* 2000): space group  $C2/m$ ,  $a$  27.64,  $b$  4.05,  $c$  20.74 Å,  $\beta$  131.26°. \* The grain confirmed by single-crystal X-ray diffraction. *apfu*: atoms per formula unit. Blank space: no analysis made. Symbols: aik: aikinite, bnj: benjaminite, ber: berryite, frd: friedrichite, gn: galena, jnt: junonite, pek: pekoite, wtc: wittichenite, x: unknown  $\text{Cu}_2\text{Ag}_2\text{Pb}_{10-2}\text{Bi}_{12-x}\text{S}_{29}$ .

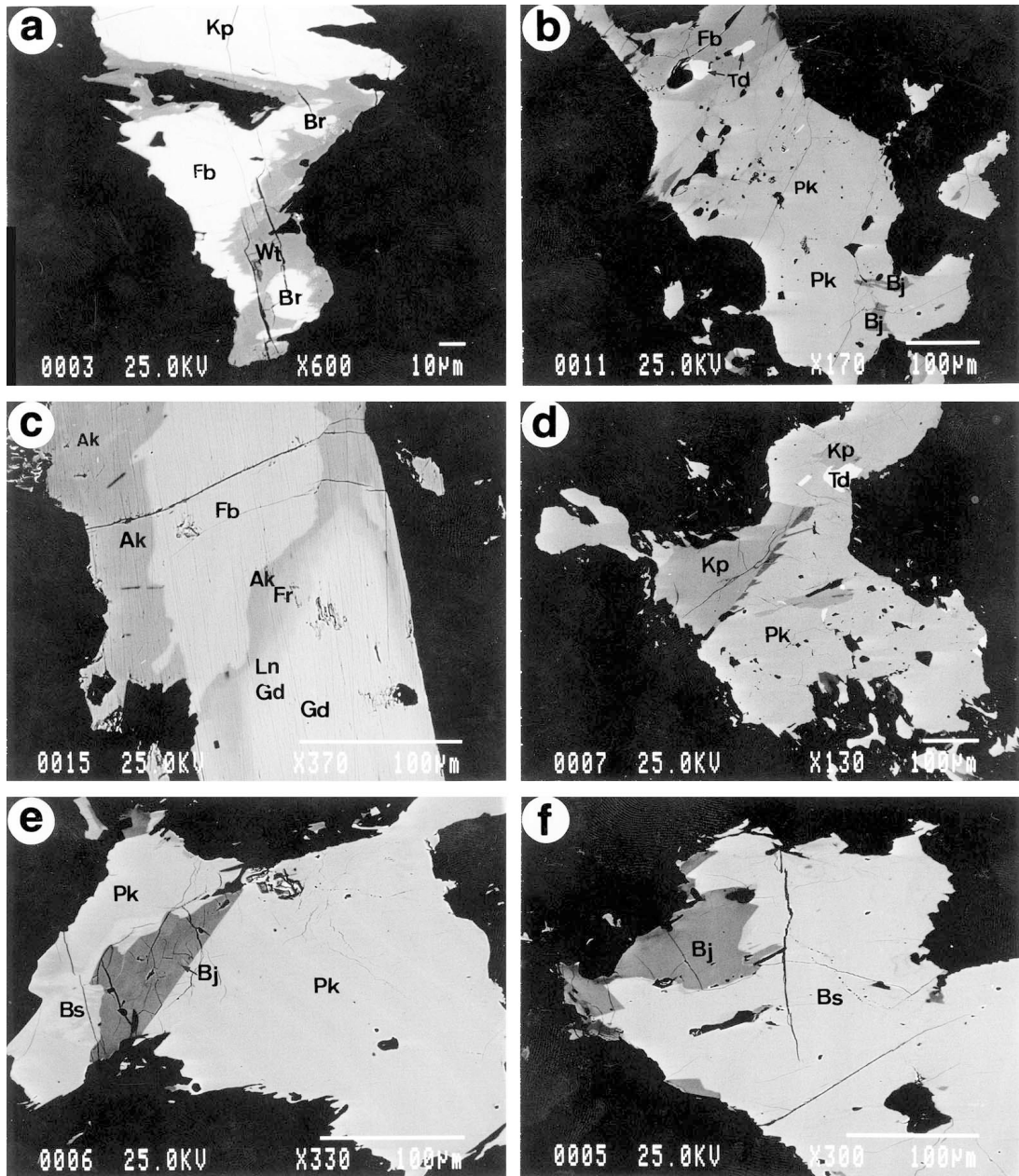


FIG. 3. Back-scattered electron images of bismuth sulfosalts. a. Mineral association of felbertalite (Fb,  $1.12 < x < 1.19$ ) and berrylite (Br) and krupkaite? (Kp) surrounded by wittichenite ribbon (Wt), with compositional zoning. b. Mineral association of pekoite (Pk), felbertalite (Fb,  $1.28 < x < 1.33$ ), tetradymite (Td) and benjaminite? (Bj). c. Compositional zoning in a single grain from aikinite (Ak,  $x = 1.80$ ), friedrichite (Fr,  $x = 1.53$ ), lindstromite (Ln,  $x = 1.07$ ), gladite? (Gd,  $0.75 < x < 0.58$ ). Aikinite (Ak) shares common boundary with felbertalite (Fb). d. Mineral association of krupkaite? (Kp), pekoite (Pk) and tetradymite (Td). e. Mineral association of benjaminite? (Bj), pekoite (Pk) and Pb- and Cu-bearing bismuthinite (Bs). f. Mineral association of benjaminite? (Bj) and Pb- and Cu-bearing bismuthinite (Bs).

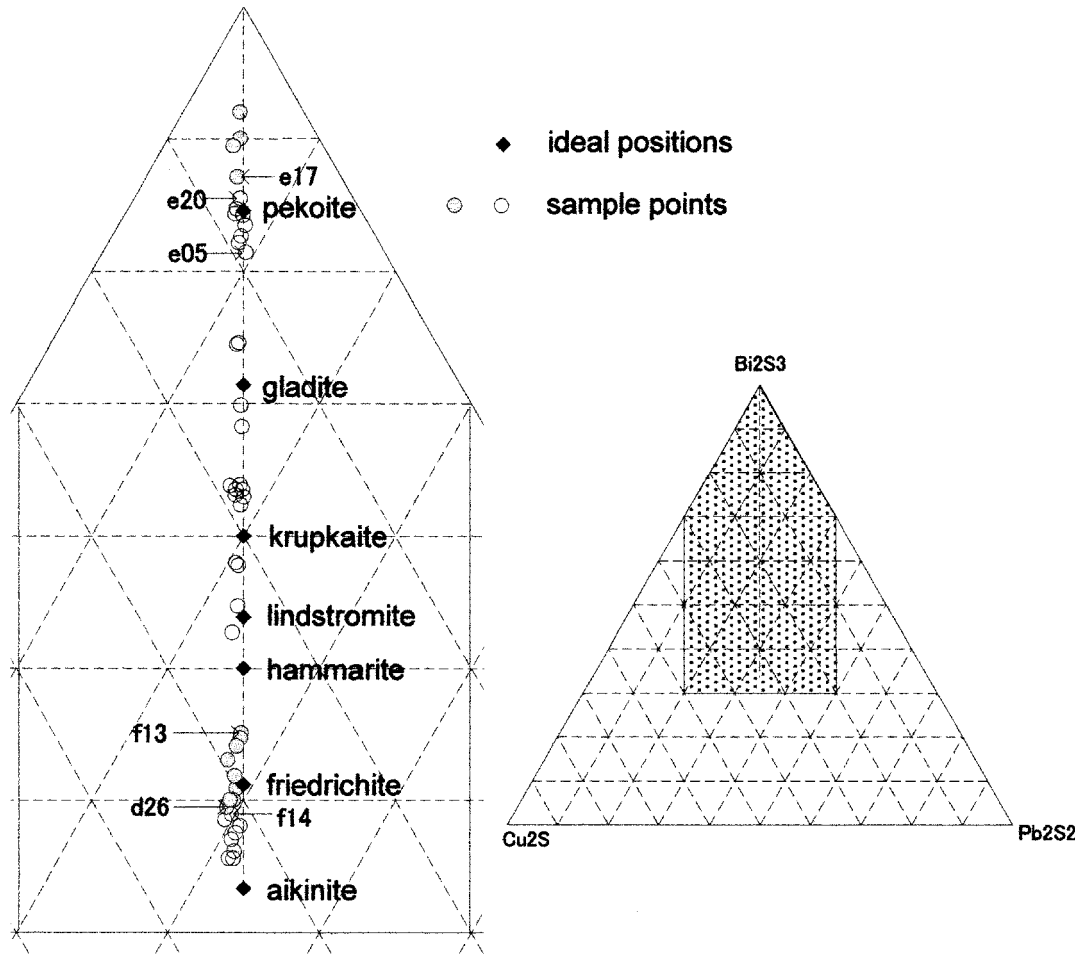


FIG. 4. The compositions of bismuthinite–aikinite series plotted in the system  $\text{Cu}_2\text{S}–\text{Pb}_2\text{S}_2–\text{Bi}_2\text{S}_3$ .

phases in the bismuthinite–aikinite series, contains noticeable amounts of Ag (Table 2).

The compositions of members of the bismuthinite–aikinite series have been documented in numerous papers (*e.g.*, Ciobanu & Cook 2000, Cook 1997, Marcoux *et al.* 1996, Lowry *et al.* 1994, Mozgova *et al.* 1990, Large & Mumme 1975). Most of the data are distributed in the range from aikinite to gladite, but the field between pekoite and bismuthinite is still poorly constrained. Structural refinements have shown that minerals of this series are composed of three basic structural units, *i.e.*, the bismuthinite ribbon, the krupkaite ribbon and the aikinite ribbon (*e.g.*, Harris & Chen 1976, Kohatsu & Wuensch 1976, Mumme & Watts 1976). On the basis of the structural units, several methods were proposed to represent the crystal chemistry of the

bismuthinite–aikinite series (*e.g.*, Žák 1980, Makovicky & Makovicky 1978, Mumme & Watts 1976). Makovicky & Makovicky (1978) proposed the general formula  $\text{Cu}_x\text{Pb}_y\text{Bi}_{8-(x+y)/2}\text{S}_{12}$  in order to express the percentage of the krupkaite ribbons  $n_k$  as  $[100 - 25(x + y) - 100]$ , which is calculated for the samples studied and shown in Table 2. Žák (1980) summarized the properties of 21 possible discrete phases in the bismuthinite–aikinite series and suggested the general formula  $\text{Cu}_x\text{Pb}_y\text{Bi}_{4-z}\text{S}_6$ , in which  $x = (K + 2A)/z$  or 0–2 for ordered or disordered phases, where K and A are coefficients of krupkaite and aikinite ribbons, and  $z$  is the multiple of  $a_0$  of bismuthinite. High-resolution transmission electron microscopy (HRTEM) studies by Pring (1989, 1995) and Pring & Hyde (1987) showed that the compositional variations in the bismuthinite–aikinite series are caused

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF MINERALS OF THE BISMUTHINITE-AIKINITE SERIES FROM THE FUNIUSHAN COPPER SKARN DEPOSIT

No.	weight %										x*	n <sub>mp</sub> * %	
	Bi	Sb	Ag	Cu	Fe	Pb	Se	Te	S	Total			
aik	d31	38.36	0.02	0.03	10.78	0.01	33.70	0.92	0.05	16.50	100.37	1.90	10.00
	f06	38.58	0	0	10.92	0	33.47	0.78	0.04	16.76	100.55	1.90	10.20
	f09	39.26	0.02	0.01	10.76	0	33.75	0.69	0	17.31	101.80	1.88	12.35
	d42	39.62	0	0.01	10.53	0.03	32.60	0.68	0.02	16.45	99.94	1.84	16.00
	d39	40.80	0	0	10.53	0.02	33.12	0.70	0	16.67	101.83	1.82	18.20
	d44**	41.00	0	0	10.24	0.02	32.83	0.57	0	16.71	101.37	1.80	20.47
	d32	40.94	0	0.07	10.32	0.04	31.13	0.75	0	17.08	100.34	1.78	22.30
	f14	41.69	0	0	10.20	0	31.52	0.61	0	16.95	100.95	1.76	24.29
fdr	d26	42.38	0.01	0.02	10.23	0	31.04	0.55	0.04	16.86	101.12	1.74	26.45
	d27	41.55	0	0	9.69	0.01	30.17	0.62	0	16.97	99.00	1.71	28.66
	e55	42.25	0	0	9.93	0.02	30.42	0.53	0	17.01	100.15	1.71	28.69
	d29	42.85	0.02	0.08	9.52	0	30.20	0.58	0.04	16.96	100.26	1.68	32.31
	d38	43.40	0	0	9.50	0.19	29.42	0.56	0.03	16.92	100.01	1.65	35.27
	d41	44.20	0	0.03	9.23	0.05	27.92	0.61	0	16.83	98.87	1.59	40.64
	d48	45.81	0	0	9.06	0.11	28.37	0.55	0	16.85	100.75	1.56	44.38
	d45**	46.47	0.03	0	8.85	0.04	28.36	0.64	0.02	16.87	101.29	1.53	46.91
	f13	46.47	0	0	8.87	0.31	28.01	0.56	0.01	17.03	101.25	1.53	47.47
	Ind?	ff01	52.53		0	7.40		22.66	0.69	0.16	16.97	100.42	1.24
ff02		54.14		0	6.94		21.85	0.67	0.10	16.98	100.68	1.17	80.50
d46**		55.70	0	0	6.30	0.01	19.87	0.91	0	17.21	100.00	1.07	92.85
d49**		55.61	0.05	0	6.31	0.05	19.49	0.82	0.07	17.32	99.71	1.07	93.45
krp?	e11	58.59	0	0.89	5.02	0.29	17.16	2.53	0.34	16.22	101.05	0.94	93.52
	e04	58.77	0.03	0.76	4.83	0.03	17.15	2.41	0.38	16.42	100.77	0.91	91.07
	e06	58.88	0	0.97	4.82	0.03	16.55	2.54	0.33	16.32	100.43	0.91	90.53
	e03	59.49	0	0.80	4.75	0	16.88	2.48	0.40	16.18	100.97	0.89	89.30
	e26	59.10	0.05	1.16	4.64	0.02	16.35	2.19	0.37	16.23	100.09	0.89	89.27
	e27	59.50	0	1.27	4.64	0	15.92	2.11	0.40	16.37	100.21	0.88	88.41
	e01	59.00	0.02	0.91	4.61	0	16.35	2.20	0.32	16.49	99.89	0.88	88.22
	gld?	d52**	63.11	0.04	0	4.50	0.02	14.42	0.84	0.01	17.40	100.34	0.75
d51**		64.30	0.05	0	4.28	0.01	13.58	0.97	0.01	17.45	100.64	0.71	70.97
d47**		65.73	0.04	0.04	3.52	0.02	10.74	0.98	0.02	17.64	98.73	0.58	58.47
d50**		66.19	0.03	0	3.51	0.01	10.88	0.93	0	17.93	99.47	0.58	58.15
pek	e05	71.33	0	0	2.45	0.10	8.04	1.86	0	17.89	101.67	0.41	41.01
	e19	70.86	0.10	0.03	2.41	0	7.36	1.51	0.05	17.49	99.81	0.39	39.15
	e25	71.14	0.10	0	2.32	0.01	7.26	1.49	0	17.16	99.46	0.38	37.95
	e35	71.34	0.11	0	2.12	0.02	7.04	1.66	0.01	17.84	100.17	0.36	35.94
	e02	72.59	0	0	2.09	0.17	6.43	1.50	0	17.56	100.33	0.34	34.28
	e34	71.73	0.08	0.03	2.15	0	6.11	1.84	0.05	17.71	99.70	0.34	33.87
	c32	72.42	0.15	0.01	2.01	0	6.09	1.79	0.10	18.21	100.77	0.33	33.03
	e20	73.51	0.02	0	1.95	0.10	5.81	1.41	0	17.60	100.40	0.31	31.20
bmt	e17	74.05	0.13	0.03	1.76	0	5.09	1.68	0	17.54	100.27	0.28	27.50
	e22	76.51	0.10	0.15	1.46	0.07	3.77	1.25	0.06	17.91	101.27	0.22	22.22
	e16	76.18	0.21	0.02	1.33	0	4.00	1.53	0.06	17.57	100.91	0.21	20.93
	e15	76.47	0.16	0	1.07	0	3.09	1.53	0.11	17.09	99.51	0.17	16.53

\* x: calculated values according to the general formula  $Cu_xPb_{1-x}Bi_{1-x}S_6$  (Zák 1980); n<sub>mp</sub>: calculated percentages of the krukpaite ribbon, according to Makovický & Makovický (1978).

\*\* Analyses performed on the same grains, which show compositional zoning.

Blank space: no analysis was made. Symbols: aik: aikinite, bmt: bismuthinite, fdr: friedrichite, gld: gladiate, hmr: hammarite, krp: krukpaite, Ind: lindströmite, pek: pekoite.

by ordered or disordered intergrowth of three structural units (B, K and A) related to cooling rate. Synthetic phases, as well as natural phases, reveal that Ag contents are very low in the bismuthinite-aikinite series (Chang *et al.* 1988).

In light of the above studies, the compositional variations of the bismuthinite-aikinite series from the

Funiushan deposit may be attributed to various intergrowths of three ordered structural ribbons. The compositional changes from  $x = 1.80$  to 0.58 within a single grain indicate that all three of the structural units may have been involved in the progressive exsolution or precipitation of a single phase. On the other hand, the exceptionally high Ag contents (0.76–1.27 wt.%) of the



phase with  $x = 0.94$  to  $0.88$  probably indicate a structural variant different from the three structural ribbons, for which an X-ray diffraction study is needed.

### Junoite

Junoite was found to occur as oriented exsolution-induced lamellae about  $8 \mu\text{m}$  in width in felbertalite (Figs. 2b, c). Two analyses showed that it is poor in Ag but richer in Pb than felbertalite (Table 3), suggesting a more limited substitution of Ag + Bi for 2Pb. The formula is close to  $\text{Cu}_2\text{Pb}_3\text{Bi}_8\text{S}_{16}$ , comparable to those of Large & Mumme (1975) and Pringle & Thorpe (1980), except for minor excess Cu. The presence of exsolution lamellae of junosite in a felbertalite host (Figs. 2b, c) indicates the similarity of their crystal structures, since both form part of the junosite-felbertalite homologous series, chemically characterized by  $\text{Cu}_2\text{Pb}_{3N}\text{Bi}_8\text{S}_{13+3N}$  (Topa *et al.* 2000, Mumme 1980).

### Unknown phase $\text{Cu}_2\text{Ag}_x\text{Pb}_{10-2x}\text{Bi}_{12+x}\text{S}_{29}$

This phase occurs as oriented patches within felbertalite (Figs. 2a, d). Three electron-microprobe analyses gave an average formula  $\text{Cu}_{2.06}\text{Ag}_{1.34}\text{Bi}_{13.29}\text{Pb}_{7.34}\text{S}_{29.51}$  based on 24 cations (Table 3). It seems that Cu is essential and that Ag substitutes for Pb according to  $\text{Ag} + \text{Bi} = 2\text{Pb}$ , which yields a general formula  $\text{Cu}_2\text{Ag}_x\text{Pb}_{10-2x}\text{Bi}_{12+x}\text{S}_{29}$ , with  $x$  ranging from 1.23 to 1.49. The Ag-free end member is  $\text{Cu}_2\text{Pb}_{10}\text{Bi}_{12}\text{S}_{29}$ .

### Berryite

This phase occurs as irregular grains, 10 to  $25 \mu\text{m}$  in size, associated with felbertalite and Ag-bearing wittichenite (Fig. 3a). Chemically, it lies in the compositional range of berryite reported from other localities (Lowry *et al.* 1994, Cook 1997, Borodaev & Mozgova

TABLE 3. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF Cu–Ag–Pb–Bi–S(Se,Te) MINERALS ASSOCIATED WITH FELBERTALITE AND MINERALS OF THE BISMUTHINITE–AIKINITE SERIES IN THE FUNIUSHAN COPPER SKARN DEPOSIT

		weight %										<i>apfu</i> *				
		Bi	Sb	Ag	Cu	Fe	Pb	Se	Te	S	Total	Cu	Ag	Bi+Sb	Pb+Fe	S+Te
junoite	d55	56.57	0.05	0.61	4.70	0.05	18.83	1.40	0.26	17.18	99.63	2.17	0.17	7.99	2.68	16.32
	d57	55.53	0.01	1.14	4.59	0	19.34	1.32	0.21	17.14	99.27	2.13	0.31	7.82	2.75	16.26
unknown phase	d53	48.66	0	2.86	2.42	0.19	26.37	2.12	0.40	15.90	98.92	2.13	1.49	13.05	7.33	29.48
	f02	49.94	0	2.37	2.38	0	27.11	1.57	0.53	16.20	100.09	2.09	1.23	13.36	7.32	29.59
	f11	50.23	0.03	2.56	2.26	0.02	28.07	1.67	0.49	16.34	101.67	1.96	1.30	13.27	7.47	29.45
berryite	e12	47.67	0	6.43	7.27	0.36	19.96	2.86	0.05	15.37	99.95	3.47	1.81	7.12	2.93	15.67
	e29	46.19	0	6.95	7.59	0.35	19.10	2.86	0.45	15.63	99.12	3.59	1.94	6.84	2.77	15.86
	e30	45.41	0	7.75	7.74	0.41	19.50	2.77	0.94	15.57	100.09	3.63	2.14	6.69	2.80	15.73
benjaminite?	e18	64.54	0	9.95	3.14	0.02	3.69	2.01	0.46	16.60	100.40	1.09	2.03	6.79	0.39	12.00
	e23	65.02	0	9.13	3.54	0	3.25	2.55	0.44	16.61	100.53	1.21	1.83	6.74	0.34	12.00
	e24	64.54	0	10.19	3.33	0.02	2.20	2.04	0.30	16.96	99.58	1.13	2.03	6.66	0.23	12.00
	e28	63.26	0	10.64	3.04	0.04	4.01	3.02	0.46	16.02	100.48	1.06	2.18	6.73	0.44	12.00
	c33	66.16		7.09	3.36		4.45	2.11	0.20	17.66	101.04	1.10	1.36	6.56	0.44	12.00
	e32	64.77	0	8.41	3.30	0.02	3.92	2.10	0.17	17.21	99.91	1.10	1.66	6.60	0.41	12.00
	e33	61.88	0	10.04	3.26	0.10	4.80	2.19	0.18	16.98	99.42	1.10	2.00	6.40	0.52	12.00
schirmerite?	d30	51.52	0.02	7.89	1.12	0.05	20.30	2.52	0.24	15.69	99.33	0.61	2.51	8.51	3.38	18.00
galena	f04	4.85	0	1.29	0.10	0.03	82.20	1.41	0.16	12.72	102.77	0.02	0.03	0.06	0.89	0.97
	d33	4.96	0.02	1.59	0.60	0.02	78.44	3.16	0.20	11.91	100.89	0.02	0.03	0.05	0.90	0.99
	d35	4.40	0	1.44	0.40	0	80.77	1.14	0.09	13.17	101.41	0.01	0.02	0.06	0.91	0.96
wittichenite	e07	41.63	0	3.10	32.47	0.49	1.21	2.75	0.51	16.96	99.10	2.71	0.15	1.10	0.05	3.01
	e08	40.89	0	1.59	35.12	0.51	2.01	1.47	0.24	17.98	99.81	2.83	0.08	1.00	0.09	2.97
tetradymite	c30	60.52		0.11	0.08		0	2.49	32.46	4.37	100.04	$\text{Bi}_{2.03}\text{Se}_{0.22}\text{Te}_{1.78}\text{S}_{0.96}$				

\* Calculations based on a total of 13 cations for junosite, 24 cations for the unknown phase, 31 atoms for berryite, 12 anions atoms for benjaminite?, 18 anions for schirmerite?, 1 cation for galena, 4 cations for wittichenite, and 5 atoms for tetradymite. Blank space: no analysis was done. *apfu*: atoms per formula unit.

1971, Nuffield & Harris 1966). On the basis of 31 atoms in total, the results show an excess in Cu + Ag and a deficiency in Pb with respect to  $(\text{Cu,Ag})_5\text{Pb}_3\text{Bi}_7\text{S}_{16}$ . The chemical compositions of berryite are still poorly constrained. The type material was defined as  $(\text{Cu,Ag})_3\text{Pb}_2\text{Bi}_5\text{S}_{11}$ , with a Cu:Ag ratio between 1.4 and 2.4 (Nuffield & Harris 1966), whereas accumulated data show it to be closer to  $(\text{Cu,Ag})_5\text{Pb}_3\text{Bi}_7\text{S}_{16}$  (Borodaev & Mozgova 1971, Lowry *et al.* 1994, Cook 1997). The compositional data available invariably show the presence of appreciable amounts of both Cu and Ag. No significant correlation seems to exist between Cu and Ag. Neither Ag-free nor Cu-free end members have been reported. Thus, the role of Cu and Ag in the structure still needs further study.

#### *Benjaminite?*

This phase occurs as irregular grains, 10–80  $\mu\text{m}$  in size, associated with pekoite and Pb(Cu)-bearing bismuthinite (Figs. 3b, e, f). It contains constant Cu but variable Bi, Pb and Ag. No significant correlation was observed among these elements. The  $(\text{Bi} + \text{Pb})/(\text{Cu} + \text{Ag})$  values vary between 3 and 2. The compositions lie in the compositional ranges of benjaminite, pavonite and even makovickyite (Chang *et al.* 1988, Žák *et al.* 1994). We have ascribed it to benjaminite on the basis of the formula  $\text{Ag}_{3.43-(x+y)}\text{Cu}_{y+(n+1)z}\text{Pb}_{2x}\text{Bi}_{6.85-(x+z)}\text{S}_{12}$  proposed by Chang *et al.* (1988). Our calculations show that  $z$  is near 0 and Pb may be involved in the substitutions of  $\text{Pb} = \text{Ag} + \square$  and  $\text{Cu}_{\text{interstitial}} + \text{Pb} = \text{Bi}$  in addition to  $2\text{Pb} = \text{Ag} + \text{Bi}$ . On the other hand, the constant levels of Cu may indicate that Cu occupies a unique position in the structure.

#### *Schirmerite?*

This phase was found to occur as a small grain about 12  $\mu\text{m}$  in diameter in aikinite (Fig. 2e). The electron-microprobe results show it to lie in the compositional field of schirmerite ( $\text{Ag}_3\text{Pb}_3\text{Bi}_6\text{S}_{18}$ – $\text{Ag}_3\text{Pb}_6\text{Bi}_7\text{S}_{18}$ ) (Makovicky & Karup-Møller 1977).

#### *Bi- and Ag-bearing galena*

This phase commonly occurs as oriented blebs within felbortalite (Figs. 2a, d) or irregular grains in aikinite and friedrichite (Fig. 2e). Electron-microprobe analyses of three grains show that it contains Bi (4.40–4.85 wt%), Ag (1.29–1.59%) and Cu (0.1–0.6%) (Table 3), evidence of the coupled substitution  $\text{Ag}(\text{Cu}) + \text{Bi} = 2\text{Pb}$ . Minerals of similar compositions, with the Bi and Ag contents up to 8.4 and 3.75 wt%, have been reported from several other localities and were referred to as galena–matildite solid-solution (*e.g.*, Cook 1997, Foord & Shawe 1989).

#### *Wittichenite*

Wittichenite occurs as thin bands, 8 to 20  $\mu\text{m}$  wide, surrounding other Cu–Ag–Pb–Bi–S(Se,Te) minerals (Fig. 3a). Two compositional variations of wittichenite are distinguished in the BSE image (Fig. 3a), one richer in Ag (3.10 wt%) and the other poorer in Ag (1.59 wt%), Minor Pb (1.21–2.01 wt%) also is present. Synthetic wittichenite is known to show solid solution from  $\text{Cu}_3\text{BiS}_3$  to  $\text{Cu}_{2.5}\text{Ag}_{0.5}\text{BiS}_3$  without appreciable substitutions involving Bi and Pb (Chang *et al.* 1988).

#### *Tetradymite*

Tetradymite occurs as subhedral grains 10 to 50  $\mu\text{m}$  in size, associated with felbortalite and the bismuthinite–aikinite series (Figs. 3b, d). It contains Se (2.49 wt%), but is notably free of Pb.

### CONCLUDING REMARKS

Electron-microprobe analysis and single-crystal X-ray diffraction have confirmed the presence of felbortalite in the Funiushan copper skarn deposit, which in fact is the second locality for this species. Its compositional data show a wide range of coupled substitution according to  $\text{Bi} + \text{Ag} = 2\text{Pb}$  in the  $(111)_{\text{PbS}}$  layers of the crystal structure (Topa *et al.* 2000), yielding a general formula of felbortalite,  $\text{Cu}_2\text{Ag}_x\text{Pb}_{6-2x}\text{Bi}_{8+x}(\text{S,Se})_{19}$ , with  $x$  ranging from 0.64 to 1.33. In comparison, the low contents of silver in exsolution lamellae of junosite within the felbortalite host may indicate a restricted substitution according to  $\text{Bi} + \text{Ag} = 2\text{Pb}$  in the  $(111)_{\text{PbS}}$  layers of single octahedra in the structure of junosite.

In the intergrowths of bismuth sulfosalts in the Funiushan deposit, two groups of minerals may be classified according to their Ag and Te contents. One is the bismuthinite–aikinite series, mostly free of Ag and Te and compositionally intermediate between the ideal compositions of the individual minerals already defined in this series. The other, containing variable contents of Ag and Te, includes felbortalite, junosite, benjaminite?, schirmerite?, berryite, galena and wittichenite. Se is preferably partitioned in the Ag-bearing phases.

As shown in the experiments on the system  $\text{Cu}_2\text{S}$ – $\text{PbS}$ – $\text{Bi}_2\text{S}_3$  (*e.g.*, Chang *et al.* 1988), the bismuthinite–aikinite series forms a complete solid-solution above 300°C but exsolves into several individual phases. This fact may be applied in interpreting the temperature of formation of the bismuth sulfosalts in the Funiushan deposit. The complex intergrowth and commonly seen exsolution textures among the bismuth sulfosalts tend to indicate that the initial solid phases were formed at temperatures above 300°C and experienced exsolution at lower temperatures. The compositional zoning in a

single grain, from  $\text{Cu}_{0.58}\text{Pb}_{0.58}\text{Bi}_{3.42}\text{S}_6$  (gladite?), through  $\text{Cu}_{0.73}\text{Pb}_{0.73}\text{Bi}_{3.27}\text{S}_6$ ,  $\text{Cu}_{1.07}\text{Pb}_{1.07}\text{Bi}_{2.93}\text{S}_6$  (lindströmite?) and  $\text{Cu}_{1.53}\text{Pb}_{1.53}\text{Bi}_{2.47}\text{S}_6$  (friedrichite), to  $\text{Cu}_{1.80}\text{Pb}_{1.80}\text{Bi}_{2.20}\text{S}_6$  (aikinite), may be attributed to the progressive exsolution as temperature decreased below 300°C.

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