

Bismuth sulphosalts within quartz veining hosted by the Loch Shin monzogranite, Scotland

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Abstract

The Loch Shin monzogranite is host to quartz veins bearing the sulphosalts aikinite, hammarite, lindströmite, krupkaite, gladite and pekoite, which belong to the aikinite–bismuthinite series, and represents the first significant occurrence of this series in the United Kingdom. Inclusions of the sulphotelluride tetradymite occur in krupkaite–gladite. Berryite is present as inclusions in chalcopyrite. Electron microprobe analyses reveal a range of compositions in individual crystal masses from hammarite to krupkaite in one sample, and from krupkaite to gladite in a second. Compositions between friedrichite and hammarite and gladite and pekoite are notably absent.

KEYWORDS: Bismuth sulphosalts, aikinite-bismuthinite series, Caledonian intrusives, Loch Shin, Scotland, microprobe data, X-ray powder diffraction.

Mineralization in the Lairg region

THE monzogranite is situated at the SW corner of Loch Shin, approximately 2 km west of the village of Lairg in the Northern Highland Terrane (Fig. 1). It intrudes Moinian psammites of the Morar Division. The psammites have a grey–green colour but are reddened within 5 m of the contact with monzogranite. The Grudie monzogranite crops out approximately 3 km to the SW. These intrusions, and the remainder of the Cromarty Suite of monzogranites (Lowry, 1991), are of Late Caledonian age (post F4 deformation), probably 420–400 Ma (Pidgeon and Aftalion, 1978) although precise age dates are lacking.

Low-grade molybdenite mineralization is sporadically distributed through Moinian and Lewisian rocks in the Loch Shin area, being generally restricted to thin post-foliation quartz \pm fluorite veins and as coatings to joints and

foliation planes in the schists and gneisses. Pyrite, chalcopyrite, and bismuth minerals are also present. Galena, sphalerite and barite tend to form a separate stage of veining and are concentrated along the eastern margin of the Grudie granite (Gallagher, 1970; Gallagher *et al.*, 1974).

Mineralization hosted by the Loch Shin monzogranite. Disseminated mineralization is largely restricted to molybdenite, pyrite and fluorite, sporadically scattered throughout the monzogranite. Molybdenite, chalcopyrite, galena, sphalerite and bismuth minerals as well as pyrite and fluorite are associated with quartz veins in the Shin granite (Gallagher and Smith, 1976) and are thought to have formed soon after intrusion (Lowry, 1991).

This paper reports minerals from two vein sets, the first (LS 1) cropping out within 10 m of the southern contact with Moinian psammites, the second (LS 3) within 20 m of the northern contact (Fig 1). LS 1 is a set of quartz veins which are consistently ~ 1–1.5 cm wide, with pyrite of cubic and subcubic form mainly restricted to the vein margins. Paragenetically it is followed by quartz

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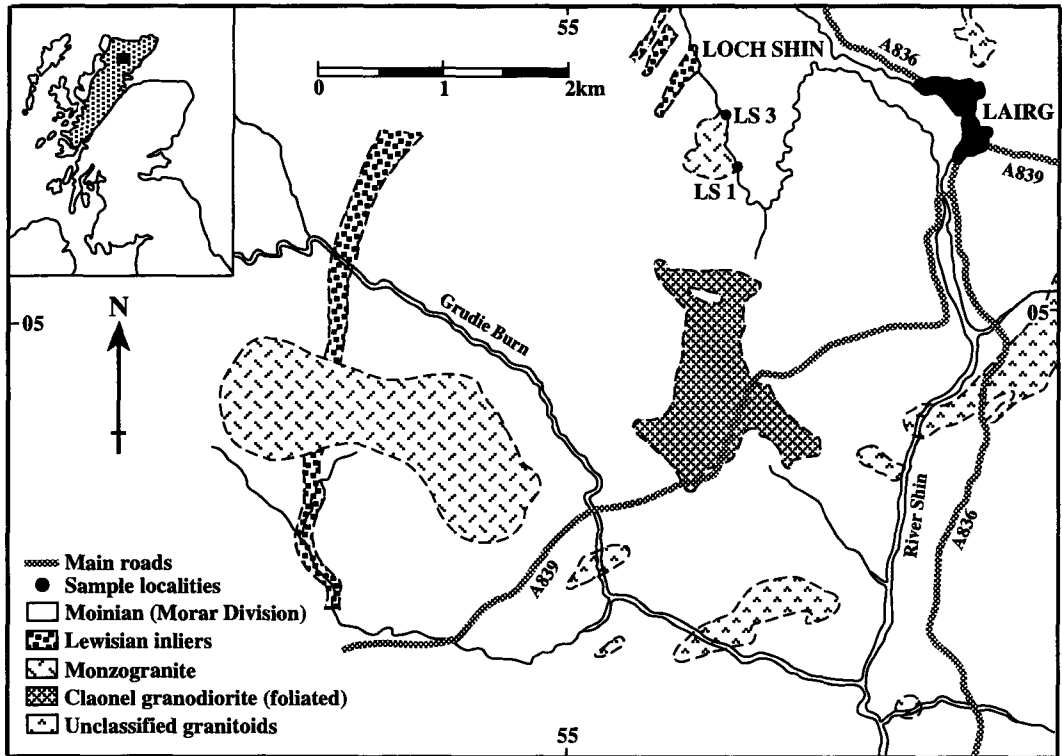


FIG. 1. Geological map of the Lairg region showing sample localities hosted by the Loch Shin monzogranite (adapted from Gallagher *et al.*, 1974; Gallagher and Smith, 1976; and BGS 1:50000 (Scotland) Geological Sheet 102. The map of Scotland inset includes the Lairg region in black. The grey shaded area is the Northern Highland Terrane bounded by the Moine Thrust and the Great Glen Fault.

and then masses, up to 1 cm across, of aikinite (CuPbBiS_3)–bismuthinite (Bi_2S_3) series minerals, sometimes overgrowing pyrite and intergrown with quartz. Occasionally these minerals show a platy structure, typical of this series (Pring, 1989). Rare patches of intergrown sphalerite, chalcopyrite and galena are interstitial to quartz (Fig. 2).

LS 3 is an anastomosing zone of grey quartz approximately 1.8 m wide over 12.5 m of exposed strike (Gallagher *et al.*, 1974), containing 0.57% Cu, 0.05% Pb, 4200 p.p.m. Bi and enrichments of Ag and Cd (Gallagher and Smith, 1976). Sulphides tend to be concentrated in the central part of the vein which is approximately 0.75 m wide. Pyrite cubes are again the earliest crystallizing phase (Fig. 3). Chalcopyrite, which in some areas forms coarse intergrowths with sphalerite, aikinite and galena, is the dominant sulphide phase, often containing inclusions of galena and bismuth sulphosalts. Most galena is interstitial to quartz and probably represents the final sulphide phase to crystallize.

Wallrock alteration adjacent to the quartz veins involves a reddening of the monzogranite for up to 2 cm out from the vein margin. In these zones biotite is replaced by muscovite and hematite, and plagioclase and K-feldspar have a cloudy red-brown appearance. These have been microclinized and dusted with fine hematite.

Mineralization: temperatures of formation. Temperatures of formation have been estimated using fluid inclusion homogenizations, sulphur isotopic equilibrium pairs and sulphide mineral stabilities (Lowry, 1991). The presence of striated pyrite cubes suggests that during early stages of mineralization the fluid temperature was between 300 and 450°C with low degrees of sulphur supersaturation (Murowchick and Barnes, 1987). Electron microprobe analysis of sphalerite indicates a range of 0.45–2.9 mole% FeS. Sphalerite is not considered to co-exist with pyrite, but lies within the chalcopyrite stability field and is thus restricted at low pressure to a maximum temperature of ~ 370°C for the lowest Fe

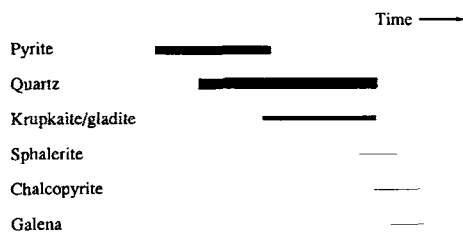


FIG. 2. Paragenesis of quartz-sulphide veins at location LS 1. Line widths indicate relative abundances.

content (see Scott and Kissin, 1973; Scott, 1983). Bismuth metal and covellite form at the margins of chalcopyrite crystals. Bismuth may be a breakdown product of Bi-sulphosalts which probably formed at temperatures in excess of the maximum stability of bismuth (271.5°C, Barton and Skinner, 1979), but it is also a minor constituent of the chalcopyrite and could be released when the chalcopyrite is broken down to covellite. Primary aqueous fluid inclusions homogenise in the range 228–377°C, but may need to be corrected for pressure. Therefore it is proposed that most of the primary mineralization occurred over the temperature range 270–400°C.

The aikinite-bismuthinite series

The individual minerals of this series have only been characterized following re-examination of material from Gladhammar, Sweden, by Welin (1966). Aikinite, hammarite, lindströmite, gladite and bismuthinite were originally identified toward the end of the last century. Additional members of the series have been identified more recently: namely krupkaite (Zak *et al.*, 1975; Large and Mumme, 1975); pekoite (Mumme *et al.*, 1976); and friedrichite (Chen *et al.*, 1978).

The aikinite-bismuthinite series structures are based on the type structure of meneghinite and the end member formulae $Z_{2N}S_{2N+2}$ and $X_2^{+}Y_2^{2+}Z_2^{3+}S_{2N+2}$, where X, Y, and Z are metal cations and S is sulphur. For this series the value of N is 2 (Makovicky, 1985). For this reason the number of cations of X and Y should always be equal, thus arriving at the general formula for the series of $Cu_xPb_xBi_{12-x}S_{18}$ (Mumme and Watts, 1976) where $x = 0$ for bismuthinite, 1 for pekoite, 2 for gladite, 3 for krupkaite, 3.6 for lindströmite, 4 for hammarite, 5 for friedrichite and 6 for aikinite (Table 1). These compositions represent ordered structure units (Pring and Hyde, 1987). The general formula is not appropriate for

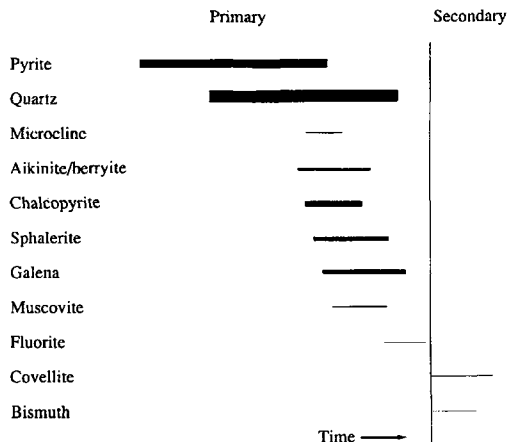


FIG. 3. Paragenesis of quartz-sulphide veins at location LS 3. Line widths indicate relative abundances.

lindströmite, although it is definitely a member of this series (Horiuchi and Wuensch, 1977). Its unit cell is a 56.11, b 11.57, c 4.00 Å, which is a $5a$ supercell (Pring and Hyde, 1987) consisting of krupkaite and aikinite in the ratio 4:1. Other intermediate members of the series have a $3a$ supercell (see Table 1).

The aikinite-bismuthinite series has been described in terms of a complete solid solution series (Harris and Chen, 1976; Chang *et al.*, 1988) or individual members formed by the intergrowth of A + K or K + B ribbons (Pring, 1989; Table 1), where A = aikinite, B = bismuthinite and K = krupkaite. Pring and Hyde (1987) suggest that both solid solution and the disordered intergrowth of ordered structure units may operate in the formation of natural specimens. Extensive compositional fields have been reported in natural specimens of krupkaite ($Cu_{1-x}Pb_{1-x}Bi_{3+x}S_{18}$ where $-0.13 \leq x \leq 0.14$), which could result from the disordered intergrowth of compositionally distinct ribbons of aikinite, krupkaite and bismuthinite (Zak, 1980) rather than solid solution (i.e. disordered intergrowth of the ordered structure units). The complete compositional range has only been achieved in synthetic studies (e.g. Springer, 1971; Mumme and Watts, 1976).

Other occurrences of minerals from this series include Juno Mine, Tennant Creek, Australia (notable for krupkaite; Mumme, 1975), Dobsina, USSR (krupkaite; Zak and Hybler, 1981), the Habach Valley, Salzburg (friedrichite; Chen *et al.*, 1978), Outlaw Prospect, Nevada (Foord *et al.*,

TABLE 1. Characteristics of the aikinite-bismuthinite series minerals. General formulae from Mumme and Watts (1976). The ribbon structures were derived from Pring (1989), although aikinite, krupkaite and bismuthinite have been normalised to six ribbons for ease of comparison with the intermediate compositions which have a 3z supercell. Lindströmrite is shown as a ten ribbon intergrowth (Pring and Hyde, 1989) because it has a 5a supercell.

Mineral	Composition	General Formula $Cu_xPb_xBi_{12-x}S_{18}$	Ribbon structure	Ideal formula (wt.%)			Molecular proportions (%)			Molecular composition			Cation proportions (%)		
				Cu	Pb	Bi	S	Cu_2S	PbS	Bi_2S_3	Cu_2S	2PbS	Bi_2S_3	Cu	Pb
Aikinite	CuPbBiS ₃	$Cu_6Pb_6Bi_6S_{18}$	6A	11.03	35.98	36.29	16.70	25	50	25	Cu_2S . 2PbS. Bi_2S_3	33.3	33.3	33.3	
Friedrichite	$Cu_2Pb_2Bi_7S_{18}$	$Cu_3Pb_5Bi_7S_{18}$	4A + 2K	9.36	30.53	43.11	17.00	22.73	45.45	31.82	Cu_2S . 2PbS. 1.4 Bi_2S_3	29.41	29.41	41.18	
Hammarite	$Cu_2Pb_2Bi_4S_9$	$Cu_4Pb_4Bi_8S_{18}$	2A + 4K	7.63	24.87	50.18	17.32	20	40	40	Cu_2S . 2PbS. 2 Bi_2S_3	25	25	50	
Lindströmrite	$Cu_3Pb_3Bi_7S_{15}$	$Cu_{3.6}Pb_{3.6}Bi_{8.4}S_{18}$	2A + 8K	6.92	22.55	53.08	17.45	18.76	37.52	43.71	Cu_2S . 2PbS. 2.33 Bi_2S_3	23.08	23.08	53.84	
Krupkaite	CuPbBi ₃ S ₆	$Cu_3Pb_3Bi_9S_{18}$	6K	5.83	19.00	57.52	17.65	16.67	33.33	50	Cu_2S . 2PbS. 3 Bi_2S_3	20	20	60	
Gladite	CuPbBi ₅ S ₉	$Cu_2Pb_2Bi_{10}S_{18}$	4K + 2B	3.96	12.91	65.14	17.99	12.5	25	62.5	Cu_2S . 2PbS. 5 Bi_2S_3	14.29	14.29	71.43	
Pekoite	$CuPbBi_{11}S_{18}$	$CuPbBi_{11}S_{18}$	2K + 4B	2.02	6.58	73.06	18.34	7.14	14.29	78.57	Cu_2S . 2PbS. 11 Bi_2S_3	7.69	7.69	84.62	
Bismuthinite	Bi ₂ S ₃	$Bi_{12}S_{18}$	6B	0	0	81.29	18.71	0	0	100	Bi_2S_3	0	0	100	

TABLE 2. Representative electron microprobe analyses for vein mineralization hosted by the Loch Shin monzogranite. Figures in brackets in the second column indicate the number of samples analysed.

Sample No.	Mineral	Cu	Ag	Pb	Bi	Fe	Cd	Sb	S	Te	Total	Composition	General formula	Molecular props (%) Cu ₂ S PbS Bi ₂ S ₃		
LS 1C	HAMMARITE/KRUPKAITE (29)															
	Low Bi (hammarite)	7.72	25.29	50.11					17.61		100.73	Cu _{1.99} Pb ₂ Bi _{3.92} S ₉	Cu _{3.98} Pb ₄ Bi _{7.84} S ₁₈	20.08	40.36	39.56
	Lindströmite	6.70	22.35	52.92					17.20		99.17	Cu _{2.95} Pb _{3.01} Bi _{7.08} S ₁₅	Cu _{3.54} Pb _{3.61} Bi _{8.50} S ₁₈	18.39	37.52	44.09
		6.34	21.12	55.48					17.31		100.25	Cu _{2.77} Pb _{2.83} Bi _{7.36} S ₁₅	Cu _{3.32} Pb _{3.40} Bi _{8.83} S ₁₈	17.56	35.84	46.60
	High Bi (krupkaite)	5.91	19.23	58.03					17.78		100.95	CuPbBi _{3.56}	Cu ₃ Pb ₃ Bi _{9.518}	16.69	33.39	49.92
LS 1B	KRUPKAITE/GLADITE (26)															
	Low Bi (krupkaite)	5.52	17.76	58.42					17.86		100.02	Cu _{0.94} Pb _{0.96} Bi _{3.56}	Cu _{2.82} Pb _{2.88} Bi _{9.518}	16.01	32.68	51.31
		4.87	16.39	60.77					17.54		99.57	Cu _{0.84} Pb _{0.87} Bi _{3.1986}	Cu _{2.52} Pb _{2.61} Bi _{9.57} S ₁₈	14.59	30.08	55.33
		4.52	14.58	62.74					17.77		99.62	Cu _{1.15} Pb _{1.14} Bi _{4.88} S ₉	Cu _{2.30} Pb _{2.28} Bi _{9.76} S ₁₈	13.87	27.47	58.66
	High Bi (gladite)	4.04	13.23	65.22					17.89		100.38	Cu _{1.03} Pb _{1.03} Bi _{5.03} S ₉	Cu _{2.06} Pb _{2.06} Bi _{10.06} S ₁₈	12.69	25.38	61.93
	PEKOITE	1.94	6.19	72.58					18.34		98.85	Cu _{0.96} Pb _{0.94} Bi _{11.03} S ₁₈	Cu _{0.96} Pb _{0.94} Bi _{11.03} S ₁₈	6.93	13.59	79.48
	TETRADYMIT (2)	0.24	59.13				0.34	0.17	4.12	36.05	100.05	Bi ₂ Te ₂ S				
LS 3A1	AIKINITE															
	Low Bi	11.23		35.67	36.11	0.36			16.93		100.30	Cu _{1.01} Pb _{0.98} Bi _{10.98} S ₃	Cu _{3.03} Pb _{2.94} Bi _{2.94} S ₁₈	25.56	49.63	24.81
	High Bi	11.15	0.11	34.73	37.98				16.70		100.67	Cu _{1.01} Pb _{0.96} Bi _{1.04} S ₃	Cu _{3.03} Pb _{2.88} Bi _{3.12} S ₁₈	25.42	48.43	26.15
	Mean (8) (± SD)	10.59 (0.79)		35.19 (1.11)	37.52 (0.76)	0.17 (0.20)			16.70 (0.27)		100.17	Cu _{0.96} Pb _{0.98} Bi _{1.04} S ₃	Cu _{2.88} Pb _{2.94} Bi _{3.12} S ₁₈	24.26	49.50	26.24
LS 3A4	AIKINITE															
	Low Bi	10.49		35.21	37.16				16.79		99.65	Cu _{0.94} Pb _{0.97} Bi _{1.02} S ₃	Cu _{2.82} Pb _{2.91} Bi _{3.06} S ₁₈	24.23	49.75	26.12
	High Bi	9.66		33.60	40.30				16.79		100.35	Cu _{0.87} Pb _{0.93} Bi _{1.11} S ₃	Cu _{2.61} Pb _{2.73} Bi _{3.33} S ₁₈	22.76	48.43	28.81
	Mean (9) (± SD)	10.36 (0.33)		34.98 (0.68)	38.51 (1.05)				16.68 (0.20)		100.53	Cu _{0.94} Pb _{0.97} Bi _{1.06} S ₃	Cu _{2.82} Pb _{2.91} Bi _{3.18} S ₁₈	23.89	49.26	26.85
LS 3A1	BERRYITE															
	Maximum Ag	6.44	7.47	20.24	49.02				16.95		100.12	Cu _{3.1} Ag _{2.1} Pb ₂ Bi _{7.1} S ₁₆				
	Minimum Ag	8.44	5.48	23.56	44.31	1.16			16.90		99.85	Cu ₄ Ag _{1.8} Pb _{3.5} Bi _{6.4} S ₁₆				
	Mean (7) (± SD)	7.43 (0.72)	6.90 (0.66)	20.81 (1.28)	47.43 (1.60)	0.84 (0.44)			16.95 (0.14)		100.36	Cu _{3.5} Ag _{1.9} Pb _{2.3} Bi _{6.5} S ₁₆				

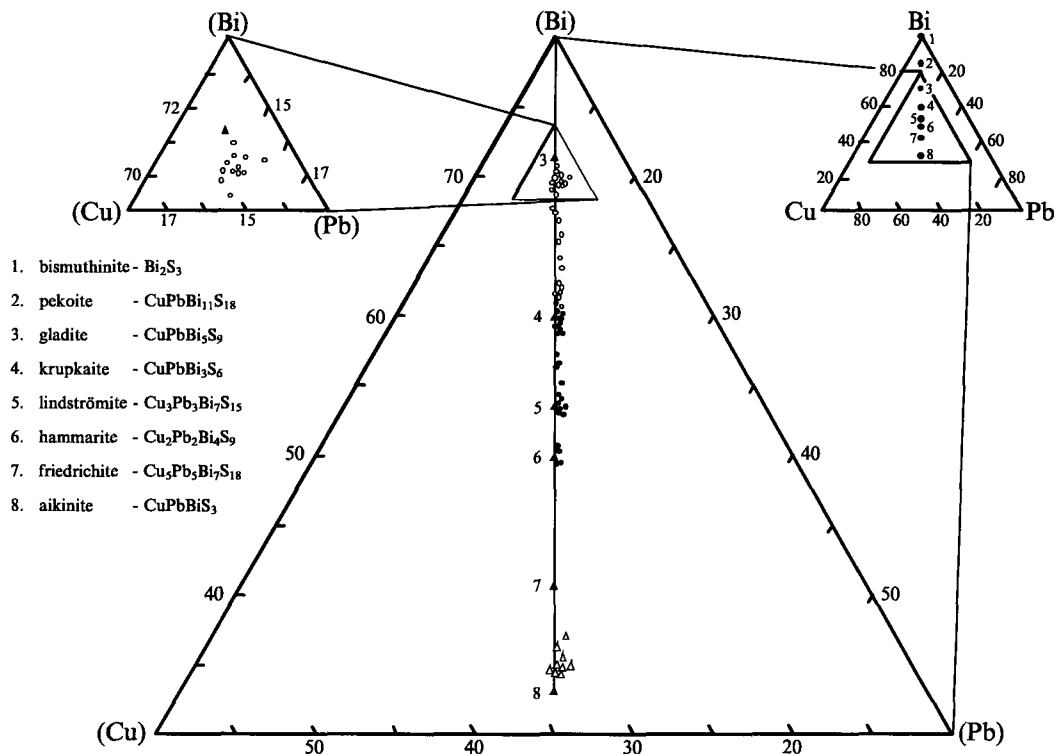


FIG. 4. Microprobe analyses from samples LS 1B, 1C and 3A4 (Loch Shin) showing the atomic properties for minerals of the aikinite–bismuthinite series in the Cu–Pb–Bi ternary system. Mineral formulae from Harris and Chen (1976) and Chen *et al.*, (1978). Open circles – LS 1B, filled circles – LS 1C, open triangles – LS 3A4.

1988), the Montezuma District, Colorado (Foord and Shawe, 1989) and Goldmine River, Ireland (Ixer *et al.*, 1990).

Electron microprobe analysis of bismuth sulphosalts and sulphotellurides

The analyses were performed in the Department of Geology at St. Andrews University using a JEOL JXA-733 electron probe microanalyser in wavelength dispersive mode. The standards used were Ag_2Te (Te), PbS (Pb and S), and pure metals (Ag, Bi, Cd, Cu, Fe and Zn). The lines analysed and crystals used were as follows: L.I.F. — Zn-K α , Cu-K α , Fe-K α , Bi-L α ; P.E.T. — S-K α , Te-L α , Ag-L α , Pb-M α , Cd-L β . Points were analysed using a beam of 20 kV, a current of 30 nA and count times for both standards and unknowns of 30 seconds for peaks and 15 seconds for background. An un rastered beam was employed with an analysing

area (spot size) of $\sim 2 \mu\text{m}^2$. Although PbS was used as the standard for Pb and S, and pure metal for Cu, rather than a synthetic aikinite–bismuthinite series mineral, the Cu/Pb ratios for the analyses of compositions between hammarite and gladite are 0.98 to 1.00, close to stoichiometry. In aikinite analyses the ratio varied from 0.94 to 1.05.

Two polished sections were analysed from veins at locality LS1 (Table 2). The bismuth sulphosalt in LS 1C corresponds to a range of formulae from $\text{Cu}_{2.02}\text{Pb}_{2.06}\text{Bi}_{3.97}\text{S}_9$, close to hammarite ($\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$), to $\text{Cu}_{0.95}\text{Pb}_{0.97}\text{Bi}_{2.96}\text{S}_6$ (krupkaite). It is an homogeneous-looking phase, both optically and using backscattered electron imaging (BSEI), with no inclusions. Some analyses correspond to lindströmite ($\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$). The sulphosalt in LS 1B corresponds to a range of formulae from $\text{Cu}_{0.94}\text{Pb}_{0.96}\text{Bi}_3\text{S}_6$, close to krupkaite ($\text{CuPbBi}_3\text{S}_6$), to $\text{Cu}_{1.04}\text{Pb}_{1.05}\text{Bi}_{4.99}\text{S}_9$, corresponding closely to gladite ($\text{CuPbBi}_5\text{S}_9$). Using BSEI, slightly brighter patches within this mineral

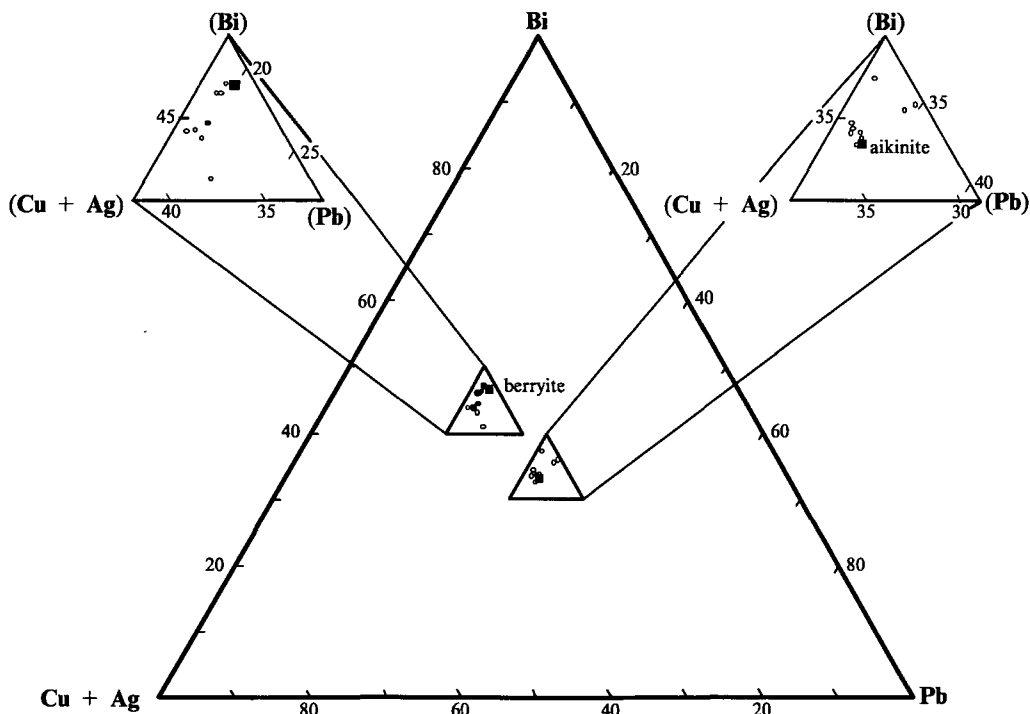


FIG. 5. Microprobe analyses from samples LS 3A1 (Loch Shin) showing the atomic proportions for aikinite in the Cu-Pb-Bi ternary system and berryite in the (Cu + Ag)-Pb-Bi system. Ideal aikinite and berryite points are from Foord *et al.*, (1988). Filled circle — average of all berryite analyses.

have formulae close to pekoite ($\text{CuPbBi}_{11}\text{S}_{18}$). Such exsolution of pekoite from gladite was also noted by Mumme and Watts (1976). Much brighter inclusions, 5–20 μm in diameter, within the gladite are bismuth sulphotellurides with a formula of $\text{Bi}_{2.2}\text{Te}_{2.2}\text{S}$, close to idealized tetradymite ($\text{Bi}_2\text{Te}_2\text{S}$).

Most of the new analyses of the aikinite-bismuthinite series minerals are concentrated close to krupkaite, lindströmite, hammarite and gladite, and have the krupkaite (K) structure dominant over the bismuthinite (B) and aikinite (A) cell structures (Pring, 1989). All compositions between hammarite ($4\text{K} + 2\text{A}$) and gladite ($4\text{K} + 2\text{B}$) are represented by two apparently homogeneous masses in BSEI. While the hammarite, lindströmite and gladite may represent ordered mixed layer growth of aikinite and krupkaite, or krupkaite and bismuthinite ribbons, respectively, the intermediate analyses may represent dominantly disordered intergrowths of the ordered

structures (krupkaite, lindströmite and hammarite, or krupkaite and gladite). Compositions between friedrichite and hammarite, or gladite and pekoite, i.e. $3\text{A} + 3\text{K}$ or $3\text{K} + 3\text{B}$ ribbon structures, were not recorded in the present study and have not been reported from any natural specimens (eg. Chen *et al.*, 1978). The range of analyses is indicated on Fig. 4 for the Cu-Pb-Bi ternary system.

Aikinite was analysed in two sections from locality LS 3 (Table 2) and ranges in composition from near end-member aikinite compositions to those approaching friedrichite ($\text{Cu}_5\text{Pb}_5\text{Bi}_7\text{S}_{18}$, Chen *et al.*, 1978; Fig. 4). There are minor variations in Cu and Bi content between the two vein samples, though Pb is relatively constant. The aikinite in LS 3A1 is intergrown with galena, chalcopyrite and sphalerite in masses up to 1 cm across. In section LS 3A4 it is present as inclusions up to 100 μm in diameter in chalcopyrite, along with an additional sulphosalt containing ~ 17.5

wt.% S, 7.5 wt.% Cu, 6.8 wt.% Ag, 20.5 wt.% Pb and 47.5 wt.% Bi (Fig. 5, Table 2). The formula $\text{Cu}_{3.5}\text{Ag}_2\text{Pb}_3\text{Bi}_7\text{S}_{16}$ corresponds most closely to berryite ($\text{Cu}_{3.5}\text{Ag}_{1.5}\text{Pb}_3\text{Bi}_7\text{S}_{16}$), or Phase VIII ($\text{Cu}_3\text{Ag}_2\text{Pb}_3\text{Bi}_7\text{S}_{16}$) of Boradaev and Mozgova (1971) out of all the bismuth sulphosalts reported by Chang *et al.*, (1988). It is thought to be part of the benjaminite ($[\text{CuAg}]_3[\text{PbBi}]_7\text{S}_{12}$) solid solution series from $\text{Ag}_2\text{Bi}_4\text{S}_7$ into the four-fold system to $\sim \text{Cu}_{4.6}\text{Ag}_2\text{Pb}_{2.2}\text{Bi}_{4.4}\text{S}_{12}$ (Chang *et al.*, 1988). Based on the number of molecules, the proportions of the four end members are 19.16% Cu_2S , 10.40% Ag_2S , 32.84% PbS and 37.60% Bi_2S_3 ($7\text{Cu}_2\text{S}\cdot 3.8\text{Ag}_2\text{S}\cdot 12\text{PbS}\cdot 13.7\text{Bi}_2\text{S}_3$), compared to 19.44% Cu_2S , 8.33% Ag_2S , 33.33% PbS and 38.90% Bi_2S_3 ($7\text{Cu}_2\text{S}\cdot 3\text{Ag}_2\text{S}\cdot 12\text{PbS}\cdot 14\text{Bi}_2\text{S}_3$) for ideal berryite. The main variation is the higher Ag and lower Bi content of the new analyses.

X-ray powder diffractometry of krupkaite and gladite

X-ray powder diffractometry was carried out on a pure mineral separate of the bismuth sulphosalt from LS 1 in the Department of Mineralogy at the Natural History Museum, London. The identities of gladite and krupkaite were confirmed and are included as data cards 200 and 302, respectively, in the Quantitative Data File for Ore Minerals (3rd Ed.) (Criddle and Stanley, 1993). The XRD data for these sulphosalts correspond to powder diffraction files in JCPDS: PDF 29-562 for gladite and PDF 30-490 for krupkaite. A summary of the unit cell parameters for this mineral series is provided by Makovicky (1985).

Summary

(1) The presence of the minerals aikinite, hammarite, lindströmite, krupkaite, gladite and pekoite of the aikinite-bismuthinite series has been inferred from microprobe analyses of minerals associated with quartz veins hosted by the Loch Shin monzogranite. The identification of krupkaite and gladite has been confirmed by X-ray powder diffraction. Berryite and tetradymite compositions have also been noted as inclusions in chalcopyrite and krupkaite, respectively. This deposit represents the first significant occurrence of any of these minerals in the United Kingdom.

(2) A range of compositions in individual crystal masses from hammarite (4K + 2A) to krupkaite (6K), or from krupkaite to gladite (4K + 2B) has been recorded, the krupkaite composition representing maximum Bi content in one sample and minimum Bi content in the second. This suggests that the material is heterogeneous on

the unit cell level, consisting of the ordered structures krupkaite, lindströmite and hammarite in one sample, and krupkaite and gladite in a second, but with some disordered intergrowth of the ordered structures represented by the intermediate analyses.

(3) Aikinite compositions range from close to the end-member (6A) and approach those of friedrichite (4A + 2K). Bismuthinite (6B) does not occur in the Loch Shin veins, but pekoite (4B + 2K) is a rare phase exsolved from gladite. Substitution of Cu and Pb for Bi in bismuthinite toward pekoite has been noted from other mineral localities in Northern Britain, notably from the granitoids at Shap, Northern England, and Cairngaroch Bay, SW Scotland (Lowry, 1991).

(4) Compositions between friedrichite and hammarite, and gladite and pekoite were notably absent in the present study. All other compositions in the series have been found in natural specimens, the present study covering most of these.

Acknowledgements

This work was carried out while D.L. was in receipt of a University of St. Andrews research scholarship. Dave Alderton, Rob Bowell, Bob Symes and two anonymous referees are thanked for their helpful comments on the manuscript.

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[Manuscript received 20 October 1992:
revised 2 June 1993]