MINERALOGICAL NOTES

MINERALOGICAL MAGAZINE, DECEMBER 1993, VOL 57, PP. 751–755

First occurrences of matildite ($AgBiS_2$) associated with Caledonian intrusives in Scotland

MATILDITE has been identified during an investigation of Late Caledonian granitoid-related mineralisation in northern Britain (Lowry, 1991). It occurs in quartz veins at the NW contact between the Fleet granite and greywackes at Talnotry, which is ~5 km NE of Newton Stewart in the Southern Uplands. It also occurs in quartz veins at the eastern margin of the Ratagain Complex, which is located on the south side of Loch Duich, ~10 km east of Glenelg in the Northern Highlands. These represent the first reported occurrences of this mineral in Scotland. Elsewhere in Great Britain, matildite has previously been reported from Cornwall (Stanley, pers. comm.). The mineral was identified by microprobe analysis (Table 1) and confirmed by optical examination (e.g. yellow–green colour next to galena).

Previous work at Talnotry, including microprobe analysis, has concentrated on a sulphide segregation at the base of a diorite sheet approxi-

TABLE 1: Representative electron microprobe analyses (in wt.%) for intergrown galena and matildite from Talnotry, and for galena, matildite and Phase A sulphosalt from Invershiel. Figures in brackets in the second row indicate the number of analyses made on that mineral. Analyses were performed using a JEOL JCXA-733 electron probe microanalyser in wavelength dispersion mode. The standards used were Ag_2Te, PbS and pure metals (Ag, Bi, Cd, Cu, Fe). Points were analysed using a beam of 20 kV, current of 30 nA and 2 μm spot size.

DEPOSIT	TALNOTRY				RATAGAIN		
MINERAL	Galena (5)	Matildite (22) Low Ag	High Ag	Mean	Phase A (4)	Product A (5) (Matildite)	Product B (2) (Galena)
Ag	1.26	23.26	25.70	24.41	15.74	26.06	1.77
Cu							0.13
Pb	82.35		0.25	0.04	30.57	0.66	78.31
Bi	3.05	59.52	57.39	58.43	38.48	57.52	5.02
Fe	0.14						
Cd		0.07		0.07			
Te		0.24	0.32	0.17			
S	13.59	17.13	16.84	16.92	15.01	16.11	12.76
Total	100.39	100.22	100.50	100.07	99.80	100.35	97.09

Mineral Formulae:

Talnotry matildite - $Ag_{0.87}Bi_{1.06}S_2$

Ratagain Phase A - $Ag_{0.93}Pb_{0.95}Bi_{1.18}S_3$ or $Ag_{5.58}Pb_{5.70}Bi_{7.08}S_{18}$

Ratagain matildite - $Ag_{0.96}Pb_{0.01}Bi_{1.10}S_2$

mately 250 m NW of the granite (see Stanley *et al.*, 1987, for details). The matildite was found intergrown with galena in a 1 m-wide quartz vein at the contact between coarse-grained biotite granite and hornfelsed greywacke (Cook, 1976) on the south side of Palnure Burn (NX 4815 7017). Matildite segregations are found within five galena masses from the single polished section analysed (Fig. 1). They contain on average 0.17 wt.% Te and <0.2 wt.% Pb (Table 1). The mean Bi content of 58.6 wt.% is higher than the expected stoichiometric content of 54.9 wt.% and the mean Ag content of ~25.5 wt.% is lower than the ideal 28.3 wt.% Ag (Fig. 3). Galena contains 0.9–1.4 wt.% Ag and 2.2–3.5 wt.% Bi.

The matildite at Ratagain was located in a vein from the main road cutting at Invershiel (NG 9378 1980) where the monzonite is in contact with Moinian metasediments in the vicinity of the Strathconon Fault. Quartz veins hosted by the Ratagain monzonite have previously been studied by Alderton (1986; 1988) but matildite was not reported. Within one vein intersection at the Invershiel occurrence, two euhedral crystals have been identified enclosed within a mass of Bi- and Ag-bearing galena more than 3 mm across. While keeping its original crystal shape this phase has undergone almost complete breakdown in a very patchy manner (Fig. 2) to galena with up to 6.2 wt.% Bi and 2.5 wt.% Ag, and matildite with <1.5 wt.% Pb. Analyses of an extremely fine-grained intergrowth or intermediate phase (Phase A, medium grey using backscattered electron imaging—BSEI), could partly reflect the composition of the precursor phase with the mean formula $Ag_{0.93}Pb_{0.95}Bi_{1.18}S_3$ (Table 1, Fig. 3). This does not correspond to a known mineral phase, partly reflecting the extremely fine-grained intergrowths and the limitations of spot size. The closest named minerals are eskimoite ($Ag_7Pb_{10}Bi_{15}S_{36}$) and schirmerite ($Ag_3Pb_6Bi_7S_{18}$) (see Foord *et al.*, 1988). The analyses presented here are relatively enriched in Ag by comparison with these compositions, but fall between the ourayite S.S. (Fig. 3; Foord and Shawe, 1989) and those reported by Bortnikov *et al.*, (1987) which lie close to the galena–matildite join and include $AgPbBiS_3$.

The matildite and galena at Talnotry are paragentically late and postdate a shearing event. Fluid inclusion homogenisations in host vein quartz suggest temperatures below 235 °C for the late fluids (Lowry, 1991). The euhedral sulphosalts and enclosing galena at Invershiel are part of the main sulphide precipitating event and predate shearing and sulphate infiltration. Sulphur iso-

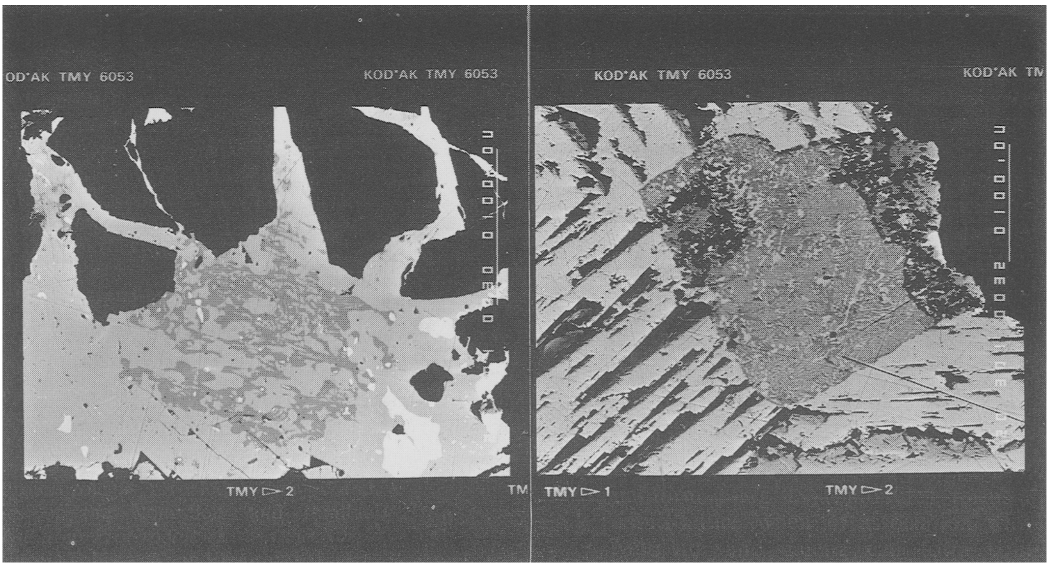

FIG. 1. (*left*) Intergrowth of matildite (dark grey) and galena (light grey) within quartz veining at the Fleet granite contact at Talnotry. Native bismuth crystals (white) are present in galena which brecciates arsenopyrite (black). (BSE image-scale bar = 100 μm). FIG. 2. (*right*) Subhedral Ag–Bi–Pb sulphosalt overgrown by galena within quartz veining at Invershiel. The sulphosalt has decomposed or exsolved to form galena (white), matildite (dark grey) and a grey phase which could be finely intergrown galena and matildite, but having a composition close to that of the precursor mineral (BSE image-scale bar = 100 μm).

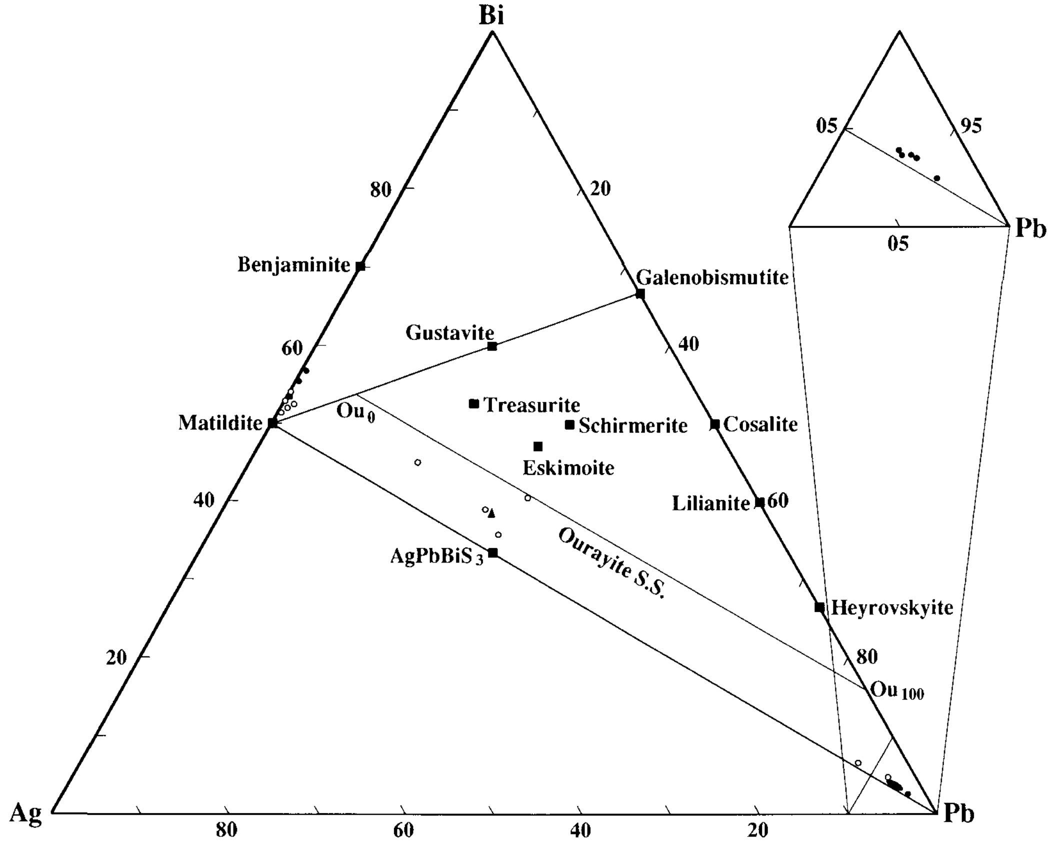

FIG. 3. Microprobe analyses from Talnotry and Invershiel showing the atomic proportions for minerals in the ternary Ag–Pb–Bi system. Idealised mineral compositions (filled squares) from Foord *et al.* (1988). Open circles = Ratagain analyses, filled triangle = mean of Phase A analyses, filled circles = Talnotry analyses.

tope geothermometry and fluid inclusion homogenisations in associated vein quartz suggest that the main sulphide forming event spanned a range of temperatures from 260–300 °C (Lowry, 1991). These estimated temperatures for the two vein systems can be related to the phase relations in the Ag–Pb–Bi–S system. $AgBiS_2$ has two forms. The high temperature cubic form, α-$AgBiS_2$ (schapbachite, Hey, 1982) is stable between ~215 °C and ~560 °C (Barton, 1979) and forms a solid solution with PbS (Chang *et al.*, 1988). The low-temperature (<215 °C, Craig, 1967), hexagonal form, β-$AgBiS_2$ (matildite), forms a pseudo-cubic lattice when in association with galena. Matildite and galena can form contemporaneously when temperatures of the precipitating fluid are below 215 °C, or can form as decomposition products of a high-temperature PbS-αAgB-iS_2 solid-solution series mineral (Karup-Moller and Pauli, 1979). This is in agreement with the formation of the Talnotry matildite below 235 °C producing the lattice with galena shown in Fig. 1, and the unstable precursor solid solution sulphosalt at Invershiel forming above 260 °C, but then decomposing or exsolving to galena and matildite below 215 °C.

Acknowledgements. This work was carried out while the author was in receipt of a University of St. Andrews Research Scholarship. Donald Herd is thanked for help with the preparation of microprobe analytical software for sulphide analyses and BSEI photography. The manuscript has been greatly improved by the helpful comments of Dave Alderton, Richard Pattrick, Ed Stephens and two anonymous referees.

References

Alderton, D. H. M. (1986) Hessite and electrum from the Ratagain intrusion, north-west Scotland. *Mineral. Mag.*, **50**, 179.

——(1988) Ag–Au–Te mineralisation in the Ratagain complex, northwest Scotland. *Trans. Instn. Min. Metall.* (*Sect. B*), **97**, B171–80.

Barton, P. B. Jr. (1979) Sulphide mineral stabilities. Ch. 7. In *Geochemistry of hydrothermal ore deposits*, 2nd ed. (Barnes, H. L., ed.) Wiley & Sons (New York), 278–403.

Bortnikov, N. S., Laputina, L. P. and Safonov, Y. G. (1987) New mineral group of the system Ag–Pb–B–S from the Kanimansur ore field, Karamazar. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.*, **292**, 124–7.

Chang, L. L. Y., Wu, D. and Knowles, C. R. (1988) Phase relations in the system Ag_2S–Cu_2S–PbS–Bi_2S_3. *Econ. Geol.*, **83**, 405–18.

Cook, D. R. (1976) *The geology of the Cairnsmore of Fleet granite and its environs, SW Scotland*. Ph.D. thesis (unpubl.), University of St. Andrews.

Craig, J. R. (1967) Phase relations and mineral assemblages in the Ag–Bi–Pb–S system. *Mineral. Dep.*, **1**, 278–306.

Foord, E. E. and Shawe, D. R. (1989) The Pb–Bi–Ag–Cu–(Hg) chemistry of galena and some associated sulphosalts: A review and some new data from Colorado, California and Pennsylvania. *Can. Mineral.*, **27**, 363–82.

——Shawe, D. R., and Conklin, N. M. (1988) Coexisting galena, Pb_{ss} and sulphosalts: Evidence for multiple episodes of mineralisation in the Round Mountain and Manhattan gold districts, Nevada. Ibid., **26**, 355–76.

Hey, M. H. (1982) International Mineralogical Association: Commission on New Minerals and Mineral Names. *Mineral. Mag.*, **46**, 513–4.

Karup-Moller, S. and Pauli, H. (1979) Galena and associated ore minerals from the cryolite at Ivigtut, South Greenland. *Medd. Gronland. Geosci.*, **2**, 1–25.

Lowry, D. (1991) *The genesis of Late Caledonian granitoid-related mineralisation in Northern Britain*. Ph.D. thesis (unpubl.), University of St. Andrews.

Stanley, C. J., Symes, R. F., and Jones, G. C. (1987) Nickel-copper mineralisation at Talnotry, Newton Stewart, Scotland. *Mineral. Petrol.*, **37**, 293–313.

KEYWORDS: matildite, Caledonian intrusive, Scotland, microprobe data

*D. LOWRY

*Department of Geography and Geology,
University of St. Andrews,
Fife KY16 9ST, UK.*

*Current address: *Department of Geology,
Royal Holloway University of London,
Egham,
Surrey TW20 0EX.*

[*Manuscript received 20 October 1992:
revised 23 February 1993*]

Namibite from Buckbarrow Beck, Cumbria: the first British occurrence

A NARROW quartz–chalcopyrite–scheelite vein, which cuts the granodiorite of the Eskdale intrusion, at Buckbarrow Beck [SD 1367 9097] west Cumbria, is remarkable for the common occurrence within it of the rare supergene minerals russellite, bismutoferrite and cuprotungsite (Young, 1985; Young *et al.*, 1986; 1991). Recent examination of veinstone obtained from the outcrop has revealed the presence of several further rare supergene species, including namibite, reported here, for the first time, from Britain. Identification was by X-ray powder photography. No chemical analyses have been undertaken.

Namibite ($CuBi_2VO_6$) has hitherto been known only from its type locality at Khorixas, Namibia (von Knorring and Sahama, 1981). Buckbarrow Beck is only the second confirmed occurrence of the species. At Buckbarrow Beck namibite (XE752*) occurs, rarely, as very dark green, roughly spherical masses up to about 1.5 mm across. In some instances these exhibit an internal sheaf-like, platy, crystalline texture and smooth to drusy external surfaces. The mineral occurs both alone and in small cavities with quartz veinstone and accompanied by bismutite, bismutoferrite, eulytite and mixite.

Eulytite ($Bi_4(SiO_4)_3$) (XE744) is common on several samples of iron-stained quartz veinstone. It occurs both as colourless to honey-yellow complex tetrahedra, up to 0.5 mm across, and as spherical aggregates up to 2.0 mm across in which concentric colour banding is locally conspicuous. In Britain, eulytite has previously been recorded only from Southwick Cliffs, near Dalbeattie, Dumfries and Galloway Region (Macpherson and Livingstone, 1981, p. 21).

Mixite ($BiCu_6AsO_4)_3(OH)_6.3H_2O$) (XE753) is a common associate of eulytite and namibite at Buckbarrow Beck. It typically occurs as pale turquoise to almost white acicular crystals which commonly form fibrous aggregates encrusting or filling small cavities in quartz veinstone. The only previously published references to mixite from Britain are those of Miller and Taylor (1966) who recorded it from trhe Dalbeattie area, S.W. Scotland and of Embrey (1977, p. LX) who reported its likely occurrence on specimens collected by A. W. G. Kingsbury from Wheal Owles, St. Just, Cornwall.

The abundance of bismuth-bearing supergene minerals in the oxidised outcrop of the Buckbarrow Beck vein strongly suggests that bismuth minerals may comprise an important part of the hypogene assemblage at depth. A small, but significant, concentration of vanadium-bearing minerals is suggested by the presence both of vanadium in the russellite from this locality

* BGS X-ray number.