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Siegenite-bearing assemblages found at the Great Orme Mine, Llandudno, North Wales

R. A. Ixer

School of Earth Sciences,
University of Birmingham,
Edgbaston, Birmingham, B15 2TT

C. J. Stanley

Department of Mineralogy,
Natural History Museum,
London, SW7 5BD

DESPITE the well known presence of siegenite and other thiospinels in the Mississippi Valley-type ores of the Southeast Missouri Lead District, U.S.A. (Hagni, 1986) and the ubiquitous presence of iron–nickel–cobalt-bearing sulphides from all of the Mississippi Valley-type deposits of Britain (Brown *et al.*, 1987; Ixer and Vaughan, 1993) no thiospinels have been recorded from British Mississippi Valley-type orefields other than a 'linnaeite' collected from the spoil heaps associated with the Great Orme Mines, Llandudno (Bevins, 1994). Siegenite is, however, reported from South Wales (Bevins and Horák, 1985) and Central Wales (Mason, 1995) but in both cases is associated with non-carbonate hosted mineralization.

The North Wales 'linnaeite' specimen (National Museum of Wales specimen NMW 83.41G. M1489) has been investigated as part of a programme to characterize the ores of the Great Orme Mine especially those that may have been exploited in the Bronze Age.

The Great Orme Mine (SH772831) lies above and to the west of Llandudno, Gwynedd. Here epigenetic copper mineralization cuts Asbian carbonates and belongs to the copper-dolomite class of deposits despite falling within the western extremity of the Northeast Wales Orefield, one of Britain's Mississippi Valley-type orefields. Indeed, this copper mineralization is the first example of the copper-dolomite association to be recorded from

Great Britain. Within the mine area, copper ores accompanied by minor lead and trace amounts of cobalt and nickel mineralization, have been exploited for at least four millenia, approximately 1880 BC–1880 AD (Dutton *et al.*, 1994). Notwithstanding the longevity of the mining activity descriptions of the ores are sparse and scant. The presence of chalcopyrite as the main copper-bearing sulphide with malachite, azurite, cuprite, tenorite and native copper as secondary phases, and minor amounts of galena have been noted (Dewey and Eastwood, 1925; Lewis, 1990; Jenkins and Lewis, 1991). A brief, preliminary description of the ores and their mineralogies is given in Ixer, 1994, and Joel *et al.*, 1996.

Parnell (1988) described chalcopyrite, malachite and saddle dolomite from the nearby Ty Gwyn Mine (SH782829) together with hydrocarbons containing cobaltian niccolite $(Ni_{0.82}Co_{0.18})_{0.95}As$ and Eakin (in Bevins, 1994) noted gersdorffite (also associated with hydrocarbons) from the Great Ormes Head.

Methods

Representative material from the full range of wallrocks and rock types were collected from surface spoil and *in situ* underground workings supplemented by material from the National Museum of Wales and Great Orme Mines Ltd. Routine transmitted and reflected light petrography supplemented by X-ray diffraction and cathodoluminescence were performed. Electron microprobe analyses on siegenite were performed using a Cameca X50 employing an accelerating voltage of 20 kV with pure elements and FeS standards.

Copper-dolomite association ores

Close to the mine coarse-grained limestones and finer grained argillaceous bioclastic limestone, interbedded with shale/mudstone horizons and rare sandstone units, are cut by a number of sub-parallel, high angle, north-south trending faults. Adjacent to these faults the limestones have suffered extensive dolomitization and the resultant dolostones carry the copper mineralization.

The ores are dolomite-altered chalcopyrite–calcite–malachite-rich and are present within very vughy coarse-grained dolostones. In these ores saddle dolomite crystals are overgrown by coarse-grained untwinned chalcopyrite intergrown with minor, euhedral, unzoned pyrite and marcasite to form veins and vugh-infills up to centimetres in diameter. The primary sulphides show alteration to banded limonite accompanied by thin rims of digenite, djurleite, spionkopite, covelline and trace amounts of photosensitive silver-bearing minerals. At least three generations of supergene calcite can be distinguished by cathodoluminescence. These calcite generations are interbanded with botryoidal limonite, accompanied by native copper, cuprite, tenorite, spionkopite, malachite and manganese minerals plus hydrocarbons. Lead, zinc, cobalt and nickel-bearing minerals are absent from this ore.

In situ galena ores

Galena is rare at the Great Orme Mines but centimetre-diameter crystals occur along a fault/joint plane cutting fine-grained dolostones. Small, 5–60 μm diameter, pyrite, nickeloan pyrite, marcasite, millerite and chalcopyrite crystals are present within galena but sulphosalts are absent. Galena is altered initially to thin rims of digenite and djurleite followed by spionkopite and covelline and then to banded cerussite. Late-stage voids are infilled by malachite and calcite. The mineralization is similar to that found in the rest of the Northeast Wales Orefield (Ixer and Vaughan, 1993).

Siegenite-bearing ores

Rarely, hand specimens collected from the spoil heaps consist of a second and distinctly different ore assemblage. This assemblage is polymetallic and associated with fine-grained argillaceous dolostones that show widespread dedolomitization. Here, the ore minerals are disseminated throughout the dolostone rather than infilling visible void spaces. The clay component comprises kaolinite, minor detrital quartz and TiO_2 minerals plus pyrite, chalcopyrite and strongly zoned nickeloan/cobaltian pyrite. Within the carbonate component fine-grained saddle dolomite is replaced by calcite and the junction is marked by discontinuous veinlets of chalcopyrite and pyrite but mainly by a subhedral to euhedral, up to 5 μm in diameter, white, cubic, high reflectance phase with the optical properties of gersdorffite/cobaltite. Elsewhere this phase forms 2–5 μm diameter grains that infill small void spaces or forms inclusions in galena and chalcopyrite, or forms 2–10 μm pentagonal dodecahedral cores surrounded by a 2 μm wide lilac-coloured zone within the earliest generation of pyrite, itself forming euhedral crystals up to 40 μm in diameter. The same generation of pyrite encloses 2–5 μm cores of lilac-coloured pyrite.

Pale pink twinned, euhedral to subhedral siegenite crystals, 20 to 250 μm in size, grow out from discontinuous veinlets of pyrite, chalcopyrite and gersdorffite into small void spaces or into clear, coarse-grained calcite. Siegenite is shattered and is enclosed and cemented by late coarse-grained pyrite and twinned marcasite so forming aggregates up to millimetres across or it forms euhedral cuboctahedral crystals rarely up to 4 mm in diameter (specimen NMW 83.41G.M1489), that enclose minor amounts of chalcopyrite. Microprobe analyses of these large siegenite crystals (Table 1) show them to be restricted in composition from $(Co_{1.84}Ni_{1.18}Cu_{0.05}Fe_{0.02})S_4$ to $(Co_{1.69}Ni_{1.30}Fe_{0.06}Cu_{0.04})S_4$ and with up to 1.08 wt.% Cu; 1.01 wt.% Fe; 0.17 wt.% As and 0.09 wt.% Sb. The mean composition (n = 19) is $(Co_{1.77}Ni_{1.24}Cu_{0.05}Fe_{0.04})S_4$.

The main generation of chalcopyrite forms up to 200 μm diameter euhedral crystals and occupies a similar paragenetic position to that of siegenite. It is the most abundant phase and encloses iron-nickel-cobalt sulphides, galena and trace amounts of 2–30 μm tennantite and up to 60 μm diameter aggregates of pale honey-coloured inclusion-free sphalerite that infills voids between chalcopyrite crystals.

Galena forms euhedral to anhedral crystals up to centimetres in length that enclose gersdorffite, iron-cobalt-nickel sulphides plus very rare tennantite and sphalerite up to 10 μm across. It is free of any other inclusions. The paragenetic position of galena is difficult to determine especially its relationship with the main generation of chalcopyrite. Much galena is intergrown with chalcopyrite and appears to be replaced along its cleavage by the copper-iron sulphide and by late stage pyrite and marcasite. Unzoned pyrite and marcasite enclosing all other phases are the final primary sulphides.

Supergene alteration of the primary phases is minor but the iron-nickel-cobalt sulphides are altered to limonite, chalcopyrite is pseudomorphed by malachite and limonite, and galena by cerussite.

Discussion

Siegenite is present in Wales in three quite different mineral associations and as Table 1 shows they are each compositionally distinctive.

Siegenite forms part of a widespread association of millerite, galena sphalerite, chalcopyrite and organic matter within voids in clay-ironstone nodules from the South Wales Coalfield (Bevins and Horák, 1985). It has a mean composition of $Co_{1.30}Ni_{1.60}Fe_{0.09}Cu_{0.02})S_4$ and hence is nickel-rich but cobalt-poor when compared with the siegenite analyses from the Carboniferous rocks of North Wales which have a mean of $(Co_{1.77}Ni_{1.21}Cu_{0.05}Fe_{0.04})S_4$ and where millerite is absent from the assemblage.

In central Wales siegenite is intergrown with cobaltian pentlandite as part of a polymetallic, minor gold-bearing sulphide assemblage cutting Lower Palaeozoic rocks (Mason, 1995). Here it has a mean composition of $(Co_{0.95}Ni_{1.53}Fe_{0.56})S_4$ and hence is iron-rich and cobalt-poor compared with either stoichiometric siegenite or siegenites from the Carboniferous rocks of Wales.

The copper ores within vughy dolostones at the Great Orme and Ty Gwyn Mines (Parnell, 1988) are

TABLE 1. Analyses of Welsh siegenite (all data in wt.%)

Specimen No.	Co	Ni	Fe	Cu	As	Sb	S	Total	Formula
Great Orme									
83.41G.M1489	34.04	23.18	0.66	0.87	0.05	0.05	41.03	99.88	$(Co_{1.81}Ni_{1.23}Fe_{0.04}Cu_{0.04})S_4$
83.41G.M1489	34.86	22.27	0.38	1.08	0.01	0.04	41.34	99.98	$(Co_{1.84}Ni_{1.18}Cu_{0.05}Fe_{0.02})S_4$
83.41G.M1489	34.02	23.34	0.60	0.90	0.17	0.06	41.54	100.63	$(Co_{1.78}Ni_{1.23}Cu_{0.04}Fe_{0.03})S_4$
83.41G.M1489	32.15	24.67	1.01	0.79	0.09	0.00	41.36	100.07	$(Co_{1.69}Ni_{1.30}Fe_{0.06}Cu_{0.04})S_4$
83.41G.M1489	33.34	23.78	0.71	0.86	0.02	0.00	41.24	99.95	$(Co_{1.76}Ni_{1.26}Fe_{0.04}Cu_{0.04})S_4$
Central Wales Orefield									
Erglodd Mine	16.60	31.90	9.63	n.a.	n.a.	n.a.	41.80	99.93	$(Co_{0.88}Ni_{1.66}Fe_{0.52})S_4$
Erglodd Mine	18.51	27.19	12.11	n.a.	n.a.	n.a.	41.75	99.27	$(Co_{0.95}Ni_{1.42}Fe_{0.67})S_4$
Coveden Mine	19.30	28.60	8.99	n.a.	n.a.	n.a.	41.50	98.39	$(Co_{1.02}Ni_{1.52}Fe_{0.49})S_4$
South Wales Coalfield									
83.42G.M3									$(Co_{1.31}Ni_{1.59}Fe_{0.08}Cu_{0.03})S_4$
83.42G.M3									$(Co_{1.32}Ni_{1.57}Fe_{0.09}Cu_{0.02})S_4$
37.239G.R1									$(Co_{1.26}Ni_{1.65}Fe_{0.09})S_4$

Great Orme analyses are all from one specimen but different analyses.

Analysis S. Wales Coalfield from Bevins *et al.* (1985); Central Wales Orefield from Mason (1995)

n.a. not analysed

the result of a simple, primary dolomite-sulphide mineralization followed by multiple generations of supergene enrichment. The presence of saddle dolomite, chalcopyrite, minor pyrite and marcasite and the paucity of galena and absence of sphalerite separate these ores from the galena-sphalerite dominated Mississippi Valley-type ores of the Northeast Wales Orefield (Ixer and Vaughan, 1993). Rather these ores belong to the world-wide copper-dolomite association. These deposits, found in association with evaporites, hydrocarbons and Mississippi Valley deposits, are interpreted as being formed by fluids expelled during late-stage basin dewatering and hence later than their associated Mississippi Valley type ores (Andrew, 1993).

However, *in situ* Mississippi Valley-type style ores belonging to the main mineralization of the Northeast Wales Orefield do occur at the Great Orme Mines, albeit as a single galena-bearing vein cutting fine dolostones. The presence of minor amounts of chalcopyrite and Co-Ni-bearing pyrite is characteristic, although that of millerite is unusual for these ores.

The polymetallic siegenite-bearing assemblages collected from the spoil, although chalcopyrite-rich and associated with baroque dolomites show greater affinities in their mineralogy to British Mississippi Valley-type ores than to the copper-dolomite association. This is exemplified by the presence of galena, minor sphalerite, trace amounts of tennantite plus Co-Ni-bearing pyrite, siegenite and gersdorffite. In addition the textural relationships of galena-chalcopyrite and tennantite are very similar to those described from assemblages seen at Clevedon, Avon, mineralization associated with the Mendip Orefield (Ixer *et al.*, 1993).

Although it has not been possible, so far, to show that the siegenite-bearing ores were mined at the Great Orme Mines, they are hosted by dolomitized Carboniferous Limestone and so belong to the Northeast Wales Orefield. Indeed during the nineteenth century small, irregular pockets of cobalt- and nickel-bearing (up to 4.5% Co and Ni) oxidized iron ores were mined from the orefield (Foster, 1882; Warren *et al.*, 1984). These ores may have been the result of the oxidation of siegenite-bearing assemblages similar to those described here.

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Solid solution among members of the aenigmatite group

B. B. Jensen

Mineralogical-Geological Museum,
Oslo University,
Sars Gate 1,
N-0562 Oslo 5,
Norway

SEVERAL minerals exist which are very closely related to aenigmatite in terms of chemistry, structure and mode of occurrence. This contribution offers a new explanation for the lack of solid solution between aenigmatite and other members of the group.

Aenigmatite has the end member formula $Na_2TiFe_5^{2+}Si_6O_{20}$. It is considered to be isostructural with the following minerals which have the same stoichiometry ($M_{14}O_{20}$) and together constitute the aenigmatite group:-

Krinovite	$Na_2Cr_2Mg_4Si_6O_{20}$
Wilkinsonite	$Na_2Fe_2^{3+}Fe_4^{2+}Si_6O_{20}$
Høgtuvaite	$(Ca,Na)_2(Fe^{2+},Fe^{3+},Ti,Mg,Mn,Sn)_6$ $(Si,Be,Al)_6O_{20}$
Welshite	$Ca_2SbFe^{3+}Mg_4Be_2Si_4O_{20}$
Rhönite	$Ca_2(Ti,Fe^{3+},Fe^{2+},Mg)_6Al_3Si_3O_{20}$
Serendibite	$Ca_2Al_3Mg_3B_{1.5}Al_{1.5}Si_3O_{20}$
Dorrite	$Ca_2Fe_4^{3+}Mg_2Al_6O_{20}$

(The synthetic material baikovite $Ca_2Ti^{4+}Ti_2^{3+}Mg_3Al_4Si_2O_{20}$ can be added to this list.)

The structure of the chain silicate aenigmatite is well studied and complex. The co-ordination is $A_2^{VIII}B_6^{VI}X_6^{IV}O_{20}$ with two structurally different *A* positions, seven *B* positions and six *X* positions (Cannillo *et al.*, 1971). Structural studies indicate the same co-ordinations for krinovite (Bonaccorsi *et al.*, 1989) and rhönite (Bonaccorsi *et al.*, 1990) although the latter has a more distorted *A* site co-ordination polyhedron, serendibite (Van Derveer *et al.*, 1993) is only seven co-ordinated at *A*. A closely related structure is sapphirine where the stoichiometry is the same but both *A* and *B* cations are six co-ordinated (Merlino, 1980). A number of synthetic phases have been prepared which have the aenigmatite structure-type: SFCA (SiFeCaAl) described by Hamilton *et al.* (1989); CSVA (CaSiVAl) described by Arakcheeva and Ivanov (1993); CaAl-ferrite (Arakcheeva, 1994); and NaMgFe-germanate (Barbier, 1995). No detailed structural data are available for the minerals wilkinsonite, høgtuvaite, welshite or dorrite.

The main chemical differences between members of the group are: (*a*) The predominance of either Na or Ca in the *A* position; (*b*) Very different cations in the six co-ordinated position. (All contain both small high valency cations and larger divalent cations in the *B* sites, but in different proportions.)

Three of these minerals occur in magmatic environments and might be expected to form solid solution series; they are aenigmatite, rhönite and wilkinsonite. However, the large number of analyses available for aenigmatite show only small departures from the ideal formula. (Larsen, 1977; Mahood and Stimac, 1990; Bonaccorsi *et al.*, 1990).

There is general agreement that a miscibility gap occurs between aenigmatite and rhönite (Yagi, 1953; Grünhagen and Seck, 1972; Johnston and Stout, 1985) and an intergrowth of rhönite/aenigmatite has been reported (Yagi, 1953). Mumme (1988) was the first to suggest that it was the substitution of Ca for