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Evidence for the mechanism of the reaction producing a bournonite–galena symplectite from meneghinite

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Abstract

In vein material from the abandoned copper mine at Dhurode, County Cork, Republic of Ireland, the sulphosalt meneghinite is partly replaced by later minerals, notably a symplectite of galena and bournonite. Mineral analyses and proportions indicate that the bulk Pb/Sb ratio in the symplectite is almost identical to that of the meneghinite. It is inferred that Pb and Sb were the relatively immobile elements whose short-range segregation controlled the scale of symplectite intergrowth, during a diffusive replacement reaction in which Cu and S were added from the vein-forming fluid. This is the second sulphosalt-bearing symplectite for which immobile elements have been identified. In both cases, the inferred replacement reaction causes a volume increase, approximately 15% in the present example.

KEYWORDS: symplectite, meneghinite, bournonite, replacement, Ireland.

Introduction

OPAQUE minerals display a great variety of intergrowths (Ramdohr, 1969). Many of these can be interpreted as symplectites, in which the elongate intergrown minerals were produced from a single precursor mineral by growth approximately perpendicular to a reaction 'front' or interface. The non-random, roughly periodic spacing of rods or lamellae should be explicable in terms of a reaction mechanism. Studying a hornblende–spinel symplectite replacing plagioclase, Mongkoltip and Ashworth (1983) deduced that the texture is produced by short-range segregation of two components in the reaction interface during an open-system replacement reaction. Al_2O_3 and SiO_2 are identified as the immobile components in this and other symplectites whose Al/Si ratio is inherited from reactant plagioclase (Mongkoltip and Ashworth, 1983;

Ashworth and Birdi, 1990). If a non-silicate symplectite has an analogous origin, a slow-diffusing pair of elements should be recognizable by analogous, approximately constant-ratio, behaviour. An interpretation of this kind has been given by Moëlo *et al.* (1988) for a symplectite of jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$) and stibnite, replacing berthierite (FeSb_2S_4). Obvious candidates for interpretation in terms of replacement are opaque-mineral symplectites showing caries texture (Bastin *et al.*, 1931), i.e. embaying the edges of pre-existing grains, towards which they have fairly smooth convex boundaries. These occurrences are texturally analogous to the plagioclase–quartz symplectite, myrmekite, replacing feldspar (e.g. Ashworth, 1986). In this paper we describe a sulphosalt-bearing symplectite of this type, and demonstrate the use of the isocon method (Grant, 1986) in reconstructing the reaction.

Geological setting

The locality is Dhurode (grid reference V 781 306), in the West Carbery mining district of County Cork, Republic of Ireland, where late-Hercynian mineralized veins cut the folded Devonian and Carboniferous rocks of the Munster Basin (Reilly, 1986). The abandoned Dhurode mine produced some 200t of copper ore in the 1840s (Cowman and Reilly, 1988). The veining is poorly exposed, though the surrounding sandstone contains arsenopyrite and small quartz-sulphide veins. For this study, vein material was collected from spoil heaps.

Optical petrography

Although the majority of vein specimens contain complex, coarse-grained copper ore comprising chalcopyrite, bornite, digenite, djurleite, tetrahedrite, enargite-group minerals and wittichenite (with a gangue of quartz, chlorite, calcite and siderite), the two specimens of interest here consist mainly of bournonite and meneghinite. Bournonite is the most abundant mineral and forms mosaics, up to centimetres in diameter, of 100–200 μm diameter crystals with abundant parquet twinning. They enclose the meneghinite as 50–200 μm long euhedral to subhedral crystals, which are frequently associated with galena and native antimony. There are two other main spatial associations in the ore: (a) within the outermost margins of the coarse-grained bournonite, fine-grained bournonite occurs with chalcopyrite, galena and sphalerite, surrounding a tetrahedrite-group mineral with a brown surface colour; (b) the quartz surrounding bournonite contains chalcopyrite and a tetrahedrite-group mineral with a green-grey surface colour, as both coarse intergrowths and discrete crystals, with rare galena and small (40 μm long) arsenopyrite rhombs. Association (b) is similar to those in other Cu-rich veins of the West Carbery district (Ixer, 1990). The quartz-siderite gangue contains angular clasts of fine-grained siliciclastic wallrock that carry discrete, euhedral, zoned and twinned arsenopyrite crystals up to 2 mm long.

Relative ages of most minerals cannot be determined, but meneghinite and the brown tetrahedrite-group mineral are early members of their respective associations. The tetrahedrite-group mineral is replaced by bournonite intergrown with chalcopyrite, sphalerite and galena. We are here concerned with the bournonite-galena symplectite which occurs as partial rims and patches (up to $450 \times 300 \mu\text{m}$) embaying the meneghinite (Fig. 1a). Near the embayed men-

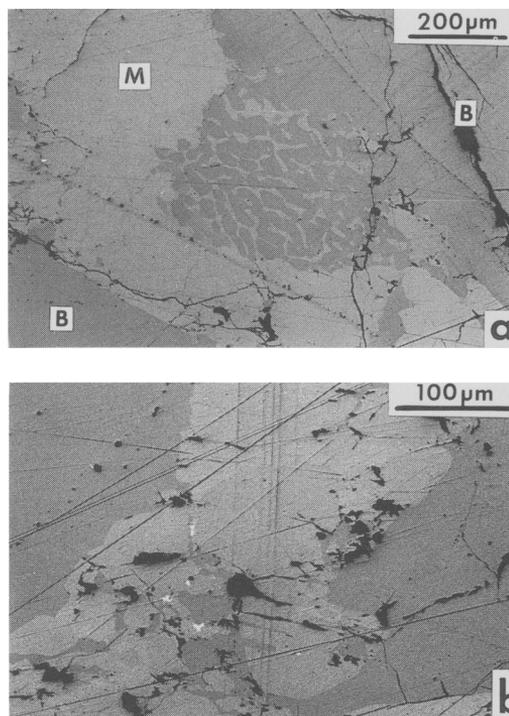


FIG. 1. Photomicrographs in reflected light. (a) The symplectite of bournonite and galena, showing coarse texture against a large meneghinite grain (M) in coarse bournonite (B). Partially crossed polars. (b) Meneghinite with bournonite on cleavage planes and grain boundaries, associated with small grains of native antimony (bright). Plane polarised light.

eghinite, and in optical continuity with it, are inclusions of meneghinite within the symplectite galena. Some symplectite occurrences are not in contact with meneghinite within the plane of section; instead they are surrounded by coarse bournonite. In addition to the main symplectite, thin veinlets of fine-grained bournonite and galena with rare native antimony penetrate meneghinite along its grain boundaries and (010) cleavage (Fig. 1b).

Mineral compositions and proportions

Meneghinite and bournonite were analysed by wavelength-dispersive electron microprobe. Representative analyses are presented in Table 1; average recalculations (with ranges from 5 analyses of each mineral) are given in Table 2 and plotted in Fig. 2. Galena, in which only Pb and S were detected, is taken to be pure PbS. The sulphosalts are close to the ideal formulae,

Table 1. Electron microprobe analyses.

	meneghinite ^a	bournonite in symplectite ^b	coarse bournonite ^b
Cu	1.35	13.29	12.80
Pb	61.52	42.02	42.47
Sb	19.34	24.24	24.26
Bi	0.29	0.15	0.20
S	17.12	18.94	18.88
Total	99.61	98.65	98.62

^a Microscan V (Aston University): 20 kV, 50 nA.

^b Camebax (University of Manchester): 20 kV, 30 nA.

CuPbSbS₃ (bournonite) and CuPb₁₃Sb₇S₂₄ (meneghinite). They appear to have slight metal excesses relative to sulphur (Table 2). This may be an artefact of incipient sulphur loss in the electron beam (though use of a defocused beam made no discernible difference). The data are taken at face value in subsequent calculations (Table 2, Fig. 3a); if ideal formulae were used, the changes would be negligible. The slight sulphur deficiency is ignored in plotting the PbS-Cu₂S-Sb₂S₃ diagram (Fig. 2).

The volume proportions of minerals in the symplectite were measured by digitizing enlarged photomicrographs of the area shown in Fig. 1a, four times, with results shown in Table 2. Combining these with the recalculated analyses and literature data on unit-cell volume (Table 2) gives the estimated bulk composition of the symplectite.

The Pb/Sb ratio of the symplectite (1.93 ± 0.03) is nearly equal to that of the meneghinite (1.89 ± 0.02). The effect is illustrated in terms of the PbS-Cu₂S-Sb₂S₃ system in Fig. 2. No other pair of elements shows such a relation. This is clearly seen in the isocon diagram (Fig. 3a), in which a pair of elements whose concentration-ratio is the same in parent and product define a straight line (isocon) emanating from the origin.

Interpretation

The textures show that the symplectite has formed from meneghinite. Meneghinite patches in symplectitic galena are interpreted as relicts, and the fine-grained bournonite-galena (\pm trace amounts of native antimony) association on grain boundaries and cleavages is interpreted as the product of a reaction similar to the symplectite-forming one but with a less simple mechanism.

Broadly two hypotheses can be proposed: exsolution and replacement. Exsolution from cooling meneghinite seems possible since Hoda and Chang (1975) synthesized a wide solid-solution range at 300 to 500 °C (Fig. 2). However,

we reject the exsolution hypotheses on two grounds:

(a) There is too much symplectite to be consistent with the limited solid-solution range (towards the symplectite composition) in high-temperature meneghinite (Fig. 2). Though the patchiness of symplectite development precludes quantitative measurement of the extent of reaction, it is clear that some meneghinite grains are extensively embayed. Symplectite patches surrounded by bournonite are thought to represent *complete* reaction, within the plane of section.

(b) A constant Pb/Sb ratio has no special significance in relating low-temperature, near-ideal meneghinite to compositions in the high-temperature field. A high-temperature meneghinite is not constrained to lie near the constant Pb/Sb line in Fig. 2, so closed-system exsolution need not follow this line, whereas constant Pb/Sb is easily explained by the hypothesis of replacement of near-ideal meneghinite, as follows.

In a replacement process, there is transport on a scale larger than the reacting system, but some more local effect is necessary to produce a symplectitic texture. The latter can be attributed to diffusion control if two constituents are approximately conserved, defining an isocon. Thus Pb and Sb are indicated as these immobile species in the present case. The system was open to other elements (Cu and S).

Similar interpretations have been offered, without quantitative evidence, for other intergrowths containing sulphosalts. For example, Ramdohr (1969) suggested that 'myrmekitic' intergrowths of meneghinite, bournonite, chalcopyrite and sphalerite formed by breakdown of a tetrahedrite-group mineral with addition of Pb. (This occurrence is unlike ours, in which meneghinite is spatially separate from the chalcopyrite-bournonite-galena-sphalerite intergrowths replacing tetrahedrite.) To our knowledge, the only previous quantitative study is that of Moölo *et al.* (1988), who showed that a jamesonite-stibnite symplectite could be derived from berthierite by addition of Pb and loss of Fe.

The isocon diagram (Fig. 3) is an aid in reconstructing open-system reactions. The slope of the isocon line defines the mass change (Grant, 1986) which, in our atomic-percentage context, is the change in total number of atoms. The data indicate a slope of 0.83 ± 0.02 (underlined results in right-hand column of Table 2). Since the adopted formulae for meneghinite and symplectite (Table 2) contain 45.6 and 48.7 atoms respectively, a slope of 0.83 indicates that one formula unit of meneghinite has reacted to (45.6/

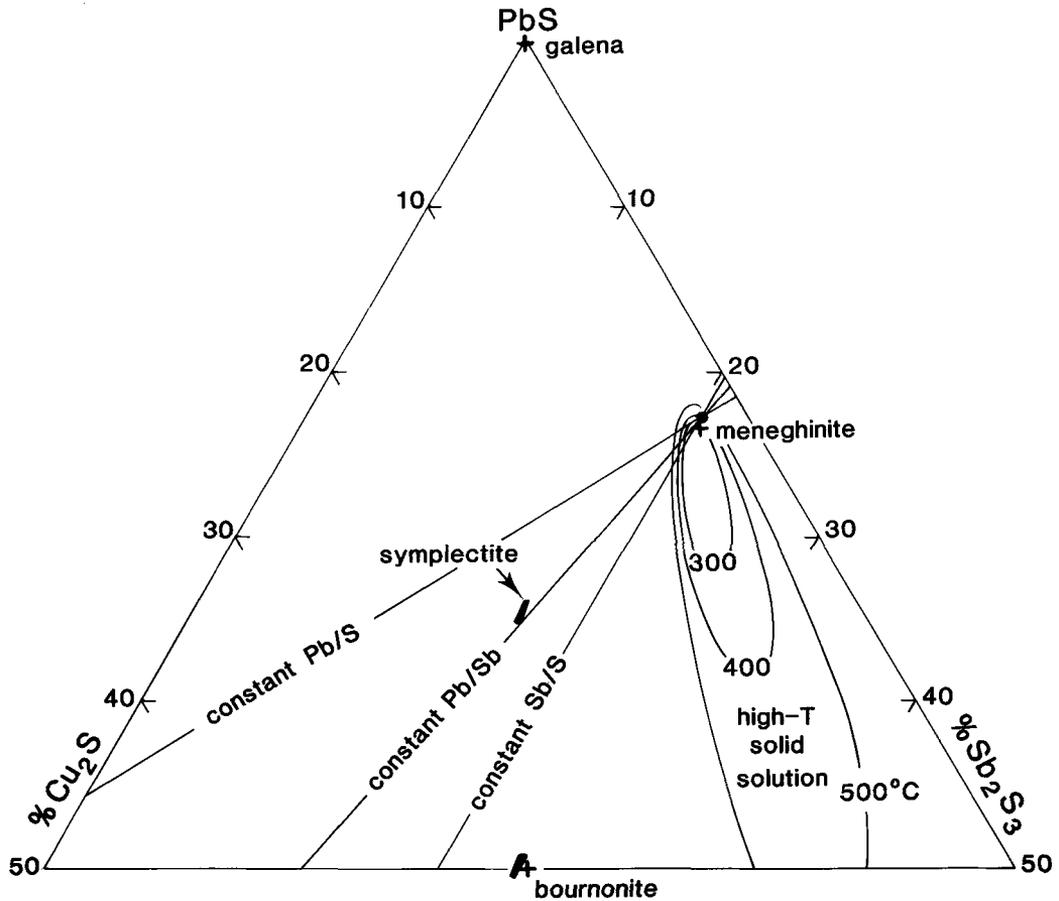


FIG. 2. Compositional relations represented in the PbS-rich part of the system PbS-Cu₂S-Sb₂S₃. Crosses are ideal mineral compositions. Black areas represent the range in the present data for bournonite, meneghinite and symplectite. For three element pairs, lines of constant atomic-percentage ratio are drawn through the meneghinite composition. Also shown are the approximate solid-solution fields of meneghinite at 300, 400 and 500 °C from Hoda and Chang (1975).

Table 2. Summary of quantitative data.

	meneghinite	bournonite	galena	symplectite		
Volume % in symplectite:	-	74.3 ± 0.5	25.7 ± 0.5			
Volume per 24 S atoms (Å ³):	1128.4 ^a	1111.6 ^b	1255.2 ^b			
% in symplectite on 24-S basis:	-	76.6 ± 0.5	23.4 ± 0.5			
Analyses recalculated to 24 sulphur atoms:						
	Cu	0.99 ± 0.07	8.45 ± 0.24	-	6.47 ± 0.28	
	Pb	13.47 ± 0.13	8.33 ± 0.05	24	11.99 ± 0.14	
	Sb	7.13 ± 0.03	8.12 ± 0.02	-	6.22 ± 0.06	
Atom %:					ratio	
	Cu	2.2 ± 0.1	17.3 ± 0.5	50	13.3 ± 0.6	6.1 ± 0.5
	Pb	29.5 ± 0.2	17.0 ± 0.2	50.0	24.7 ± 0.2	0.834 ± 0.015
	Sb	15.6 ± 0.1	16.6 ± 0.1	-	12.8 ± 0.1	0.820 ± 0.012
	S	52.6 ± 0.2	49.1 ± 0.3	50.0	49.3 ± 0.2	0.938 ± 0.008

^aEuler and Hellner (1960)

^bJCPDS (1980).

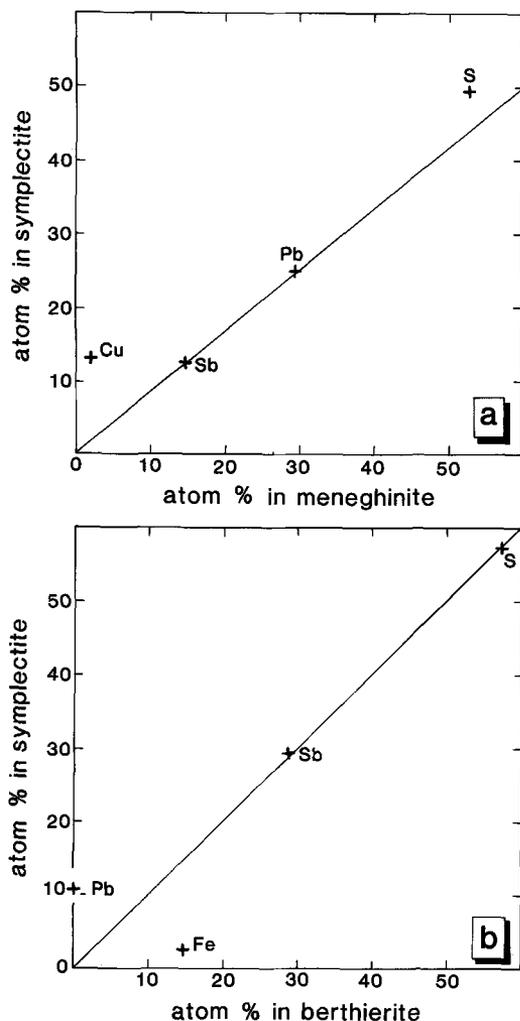
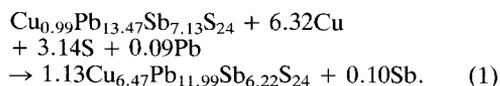


FIG. 3. Isocon diagrams (Grant, 1986) for (a) the present symplectite compared with meneghinite, and (b) the symplectite of Moëlo *et al.* (1988) compared with berthierite.

48.7)/0.83 = 1.13 units of symplectite. The overall reaction is thus estimated as



The open-system behaviour here is essentially addition of Cu_2S , in contrast to the reaction studied by Moëlo *et al.* (1988), with an isocon slope near unity (Fig. 3b), in which the metasomatism is essentially an atom-for-atom exchange of Pb for Fe. It is noteworthy that both reactions

involve a volume increase, approximately 10% in the case of Moëlo *et al.* (1988) and 14.7% calculated for reaction (1) using volume data in Table 2. In many silicate reactions producing layered coronas, formation of a symplectite layer involves a volume increase but this is compensated by a decrease elsewhere in the corona (e.g. Mongkoltip and Ashworth, 1983). There is no obvious complementary reaction in the present case. Moëlo *et al.* (1988) inferred a reaction simultaneous with their symplectite-forming one, and causing complementary volume loss by dissolution of material in the hydrothermal, mineralizing fluid. In vein-style fluid-rock interaction generally, there is obviously more scope for volume change by dissolution and precipitation than in the metamorphic environments producing the silicate coronas, though it is possible that volume-change constraints influenced the patchy distribution of the symplectite.

Discussion

The bournonite-galena symplectite is attributed to relative immobility of Pb and Sb during the open-system replacement of meneghinite. Segregation of two elements in the reaction interface is a diffusive process, and transport of the more mobile Cu and S through the growing symplectite to the interface was probably also by grain-boundary diffusion, analogously to the transport mechanism in silicate corona formation (Ashworth and Birdi, 1990). An obvious difference from the silicate examples is the interaction with a vein-forming fluid, which not only made possible a local volume increase but presumably also supplied the Cu and S. Thus the reaction illustrates the interplay of diffusion and fluid advection during mineralization.

The classical model of diffusion in sulphides, whereby mobile cations move through a rigid sulphur lattice (Birchenall, 1974) is not applicable here because sulphur was fast-diffusing. This is perhaps not surprising, in view of the complexity of sulphosalt structures (Makovicky, 1989) and the disordered nature of the grain-boundary diffusion channels relative to a perfect crystal. It is interesting that different behaviour is shown by the same elements in this reaction and that of Moëlo *et al.* (1988). Sulphur, mobile in the present case, is immobile in the other; Pb *vice versa* (Fig. 3). Two symplectites are a small sample, but already it seems that diffusion behaviour is more complex than in the silicate analogues, where the common symplectites so far studied are all controlled by the same pair of elements: Al and Si (Ashworth and Birdi, 1990).

It is hoped that future research on opaque-mineral reactions may reveal some pattern in the identity of immobile elements as a function of petrogenetic environment.

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References

- Ashworth, J. R. (1986) Myrmekite replacing albite in prograde metamorphism. *Am. Mineral.*, **71**, 895–9.
- and Birdi, J. J. (1990) Diffusion modelling of coronas around olivine in an open system. *Geochim. Cosmochim. Acta*, **54**, 2389–401.
- Bastin, E. S., Graton, L. C., Lindgren, W., Newhouse, W. H., Schwartz, G. M. and Short, M. N. (1931) Criteria of age relations of minerals. With especial reference to polished sections of ores. *Econ. Geol.*, **26**, 561–610.
- Birchennall, C. E. (1974) Diffusion in sulfides. In *Geochemical transport and kinetics* (Hofmann, A. W., Giletti, B. J., Yoder, H. S. Jr. and Yund, R. A., eds.), Carnegie Institution of Washington Publication 634, 53–9.
- Cowman, D. and Reilly, T. A. (1988) *The abandoned mines of West Carbery. Promoters, adventurers, and miners*. Geological Survey of Ireland, 177 pp.
- Euler, R. and Hellner, E. (1960) Über komplex zusammengesetzte sulfidische Erze VI. Zur Kristallstruktur des Meneghinits, $\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}$. *Zeits. Kristallogr.*, **113**, 345–72.
- Grant, J. A. (1986) The isocon diagram—a simple solution to Gresens' equation for metasomatic alteration. *Econ. Geol.*, **81**, 1976–82.
- Hoda, S. N. and Chang, L. L. Y. (1975) Phase relations in the pseudo-ternary system $\text{PbS}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ and the synthesis of meneghinite. *Can. Mineral.*, **13**, 388–93.
- Ixer, R. A. (1990) *Atlas of opaque and ore minerals in their associations*. Open University Press, Milton Keynes, 208 pp.
- Joint Committee on Powder Diffraction Standards (1980) Mineral powder diffraction file.
- Makovicky, E. (1989) Modular classification of sulphosalts—current status. Definition and application of homologous series. *Neues Jahrb. Mineral. Abh.*, **160**, 269–97.
- Moëlo, Y. Robert, J.-F., and Picot, P. (1988) Symplectite jamesonite–stibine de la mine d'antimoine de Fecunda (district du Val de Ribes, Pyrénées catalanes). *Bull. Minéral.*, **111**, 451–5.
- Mongkoltip, P. and Ashworth, J. R. (1983) Quantitative estimation of an open-system symplectite-forming reaction: restricted diffusion of Al and Si in coronas around olivine. *J. Petrol.*, **24**, 635–61.
- Ramdohr, P. (1969) *The ore minerals and their intergrowths*. English 1st Ed. Pergamon, Oxford, 1174 pp.
- Reilly, T. A. (1986) A review of vein mineralization in SW County Cork, Ireland. In *Geology and genesis of mineral deposits in Ireland* (Andrew, C. J., Crowe, R. W. A., Finlay, S., Pennell, W. M., and Pyne, J. F., eds.), Irish Association for Economic Geology, Dublin, 513–44.

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