

Mineralization in the Bonser vein, Coniston, English Lake District: mineral assemblages, paragenesis, and formation conditions

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ABSTRACT. The Bonser vein, one of the most productive sources of copper in the English Lake District, contains a mineral assemblage comprising quartz, chlorite, calcite, dolomite, stilpnomelane, magnetite, pyrrhotine, pyrite, marcasite, native bismuth, bismuthinite, laitakarite, joseite, arsenopyrite, chalcopyrite, sphalerite, galena, and cosalite. The phases pyrrhotine, sphalerite, arsenopyrite, laitakarite, joseite, and cosalite were analysed by electron microprobe. The occurrence of laitakarite is the first reported in the British Isles. Textures of the ore and gangue minerals show that the vein minerals were deposited successively in open voids. The sequence of deposition was of quartz forming throughout, early chlorite and stilpnomelane with some dolomite and calcite, magnetite as the earliest opaque phase, followed by arsenopyrite, pyrrhotine, sphalerite, chalcopyrite, pyrite, and marcasite; the bismuth- and lead-bearing minerals were the last to form.

The data on the coexisting phases and their compositions have been used to estimate the temperatures of mineralization and the activities of sulphur and oxygen. Magnetite and arsenopyrite appear to have formed at 350–400°C with a_{S_2} reaching 10^{-12} to 10^{-14} atm. and a_{O_2} around 10^{-24} to 10^{-29} atm. The assemblage of quartz, chlorite, stilpnomelane, calcite, dolomite, pyrrhotine, chalcopyrite, sphalerite, and (late) arsenopyrite was probably deposited at ~240°C, with a_{S_2} decreasing to 10^{-15} to 10^{-16} atm and a_{O_2} to 10^{-38} to 10^{-44} atm. The later minerals probably formed at temperatures as low as 200°C and under similar conditions of sulphur and oxygen activity.

COPPER was mined in the southern part of the English Lake District within an area of approximately 16 km² located to the north of Coniston village. Included in this region are the minor copper trials near Seathwaite Tarn (Stanley and Criddle, 1979) and the more productive

Coniston, Greenburn, and Tilberthwaite mining areas.

The Bonser vein, 2.5 km northwest of Coniston, cuts the Tilberthwaite Tuffs and the Paddy End Rhyolite of the Ordovician Borrowdale Volcanic Group. While the vein is not entirely barren in the tuffs as was suggested by Mitchell (1940), the most favourable host rock is the rhyolite, and the vein appears to die out where it meets strongly cleaved tuffs at its eastern end. Dagger (1977) has noted that the Coniston deposits, including the Bonser vein, occur in a series of conjugate shears, tension fractures, and strike faults, which may have formed during the main phase of folding affecting the rocks in the Caledonian orogenic episode. It also seems likely that many of the fractures could have formed by pressure release after the main period of folding.

Near Levers Water [SD 2810 9930], the Bonser vein trends WNW-ESE but this changes to nearly E-W to the east of Red Dell Beck. At outcrop the vein dips steeply to the south, but Shaw (1970) states that at depth it dips more gently to the north. In places the vein is several metres wide and carried, according to Kendall (1884), 'chalcopyrite equal to a continuous solid rib 8½ inches wide'.

The vein, one of the most productive in the area, has been stoped out over a length of about 0.5 km and to a depth of 375 m from the surface. Mining reached a peak in the last century but came to a halt when the increasing amount of magnetite in the ore caused difficulties in beneficiation. The mine is now flooded up to the Deep Level, but part of it is still accessible by way of the Deep Level crosscut adit [SD 2890 9880]. A small part of the vein remaining in the roof of the Deep Level is

about a metre in width, and is mostly barren quartz containing irregular veinlets of chlorite and a few stringers of chalcopyrite.

Most of the specimens collected from the Bonser vein were obtained from a spoil tip north of the Youth Hostel [SD 2885 9870], which appears to have been used as a dump for the magnetite-rich ore which was difficult to process. Other specimens were obtained from tips around the Old Shaft [SD 2880 9900].

Mineralogy. Wheatley (1971) and Dagger (1977) have given brief descriptions of the mineralogy of the Coniston veins, including the Bonser vein. The mineral assemblage, determined from a study of hand specimens and of thin and polished sections, is quartz, chlorite, calcite, dolomite, stilpnomelane, magnetite, pyrrhotine, pyrite, marcasite, native bismuth, bismuthinite, laitakarite, joseite, arsenopyrite, chalcopyrite, sphalerite, galena, and cosalite. Magnetite is uncommon in Lake District copper veins, and the only other reported occurrences are

at Long Crag [NY 2865 0160] (E. Holland pers. comm.) and Shap (Firman, 1957).

Native bismuth and bismuthinite are relatively abundant in the Bonser vein, particularly in material derived from magnetite-rich parts of the vein. Another phase is consistently associated with these minerals. Its reflectance is slightly higher than that of bismuthinite although considerably lower than that of native bismuth. It appears pale grey in this association and has strong birefractance; the anisotropy is distinct, with rotation tints varying from cream-buff to dark brown. It was not possible to identify the phase by X-ray diffraction owing to its small grain size ($< 50 \mu\text{m}$), but electron probe microanalysis demonstrated the presence of Bi, Pb, Se, S, and minor Te (Table I, 10-16). A small Te-rich area was found which has similar optical properties to the Se-rich phase.

In discussing the bismuth sulphotellurides and bismuth sulphoselenides it is usual to refer to the metal : non-metal ratio $A : X$, where A is Bi, Pb, Sb;

TABLE I. *Electron microprobe data for the Bonser vein*

		wt. %					Total	Specimen no.
		Fe	S					
1	Pyrrhotine	59.6	38.8				98.4	78Co.2.A
		Fe	Zn	S				
2	Sphalerite	7.9	58.5	32.8		99.2	78Co.2.A	
3	Sphalerite	8.3	58.7	32.6		99.6	78Co.2.A	
		Fe	As	S				
4	Arsenopyrite	34.4	44.2	20.2		98.8	78Co.2.A	
5	Arsenopyrite	34.8	43.7	21.4		99.9	78Co.2.A	
6	Arsenopyrite	34.9	44.9	19.6		99.4	Co.2.5	
7	Arsenopyrite	34.8	43.9	20.9		99.6	Co.2.5	
8	Arsenopyrite	33.5	47.1	19.8		100.4	77Co.2.E	
9	Arsenopyrite	33.8	46.3	20.2		100.4	77Co.2.E	
		Bi	Pb	Te	Se	S		
10	Laitakarite	84.0	—	0.6	8.6	6.1	99.3	78Co.2.C
11	Laitakarite	81.8	—	1.2	13.2	3.6	99.8	78Co.2.C
12	Laitakarite	84.4	—	1.0	9.8	5.2	100.4	78Co.2.C
13	Laitakarite	84.4	—	1.2	10.0	5.1	100.8	Co.2.11
14	Laitakarite	82.2	—	1.1	9.0	5.7	98.0	Co.2.11
15	Laitakarite	80.6	6.0	0.2	6.7	7.2	100.7	E.511
16	Laitakarite	82.8	1.9	0.2	7.8	7.1	99.8	E.511
17	Joseite	77.8	—	13.0	2.2	5.9	98.9	78Co.2.C
18	Cosalite	42.4	41.0	—	—	16.3	99.7	Co.2.21

Instrument: Cambridge Instruments Microscan Mk. 5 (except analyses 15 and 16—Mk. 9).

Accelerating voltage: 20 kV.

Radiations: Fe-K α , S-K α , Zn-K α , As-K α , Bi-M α , Pb-L α , Te-L α , Se-L α

Standards: Pure elements, Asp200, troilite, PbSe.

Analyses 1-9 are averages of three 10-second spot analyses on each of three different grains. Analyses 10-18 are averages of three 10-second spot analyses on a single grain.

and X is Te, Se, S (Godovikov *et al.*, 1971). In the case of the bismuth sulphoselenide from Coniston, the A:X ratio is nearly 4:3 with A consisting of Bi (Pb was detected in analyses 15 and 16 (Table I)) and X, Se, Te, and S. The phase shows a variable composition between the limits 6.7–13.2 wt. % Se corresponding to formulae of $[Pb_{0.28}Bi_{3.72}]_{\Sigma 4.00}[S_{2.16}Se_{0.82}Te_{0.02}]_{\Sigma 3.00}$ and $Bi_{4.08}[S_{1.17}Se_{1.74}Te_{0.09}]_{\Sigma 3.00}$ respectively. This is consistent with the mineral described by Berry and Thompson (1962) as 'selenjoseite', and name which Berry (1963) suggested should be dropped in favour of laitakarite, previously described by Vormaa (1960) from Orjäärvi, Finland. The analysis given by Vormaa (1960) is 78.3 wt. % Bi, 15.5 % Se, 3.3 % S, this is close to analysis 11 (Table I) and consistent with a chemical formula of Bi_4Se_2S or $Bi_4(Se,S)_3$. The Bonser vein analyses are closer to those reported for laitakarite than they are to analyses reported for the only other similar known mineral, ikonolite (Kato, 1959), which has a S:Se ratio of 92:8 with only a few % Se. Vormaa (1960) suggested that the selenium end-member of the Bi_4Se_3 – Bi_4S_3 solid-solution series be named laitakarite and the sulphur end-member, ikonolite.

Analysis of one of the associated phases with similar optical properties to laitakarite showed a high Te content and an A:X ratio of about 3.5:3 (Table I, 17), compatible with this mineral being a slightly bismuth-deficient joseite. It is similar to an analysis by Peacock (1941) of a phase which he classified as joseite and which contained 79.2 wt. % Bi; 15.9 % Te; 1.5 % Se; and 3.2 % S.

Comparison of X-ray data for pyrrhotine from the Bonser vein with the data reported by Morimoto *et al.* (1975) showed that the pyrrhotine is monoclinic and, following Wuensch's (1963) nomenclature, of type 2A, 2B, 4C. The composition ($Fe_{0.88}S$; Table I, 1) determined by electron probe microanalysis confirms that the pyrrhotine is monoclinic (Scott and Kissin, 1973; Kissin, 1974). The absence of any intergrown hexagonal pyrrhotine was verified by etching tests.

Arsenopyrite occurs in one specimen as small euhedral grains in pyrrhotine and was shown to contain about 44 wt. %. As when analysed by electron microprobe using Kretschmar's Asp200 standard. Analyses 4 and 5 (Table I) are from different areas of this specimen. Similar analyses were obtained from a different specimen with larger grains of arsenopyrite which have a slightly arsenic-rich core (Table I, analysis 6 represents core zones and analysis 7 marginal zones). Euhedral arsenopyrite in cleaved and altered tuffs had higher As contents of ~46 wt. % (Table I, analyses 8 and 9 are core and margin respectively). Analyses of arsenopyrite in a number of other specimens fell

into the two compositional types represented by analyses 4–9.

Sphalerite coexisting with pyrrhotine has 13.6–14.4 mole % FeS (Table I, 2–3). The presence of stilpnomelane, a complex hydrated aluminosilicate of Mg and Fe which was first recorded from the Bonser vein by Russell (1925), was confirmed in this study by its optical characteristics and by X-ray diffraction. Cosalite ($Pb_{1.9}Bi_{2.0}S_5$) (Table I, 18) was identified on the basis of its optical characteristics and its composition. It was found in one polished section as an anhedral inclusion in galena.

Paragenesis. The sequence of formation of the minerals occurring in the Bonser vein, as deduced from a study of hand specimens and sections, is illustrated in fig. 1.



FIG. 1. Paragenetic diagram for the Bonser vein.

Fracturing and brecciation of the country rocks adjacent to the Bonser vein appears to be less extensive than that associated with many of the Lake District veins, and especially the nearby Paddy End vein. Angular fragments of tuffaceous country rock are included in the vein, although thin sections show them to be little altered, with only minor silicification present in addition to the chloritization produced by the regional metamorphism. In hand specimen, many of the textures suggest that the vein minerals were deposited successively in open voids and that only minor fracturing occurred during, and possibly after, mineralization.

Quartz is the major gangue phase and was deposited periodically throughout the mineralization. Much of it is milky vein quartz, but some is euhedral. Chlorite is abundant and mostly early, forming botryoidal masses and smaller elongate grains. Stilpnomelane, in fine acicular crystals (<200 μ m) and matted aggregates (<1 mm), overgrows chlorite and also occurs in interstitial areas in magnetite. Calcite and dolomite are also considered to be mainly early, with dolomite the later of the two minerals. A later carbonate stage infills vugs in the quartz vein.

Magnetite was the first ore mineral deposited and it shows two habits. One is of bladed, and in some instances radiating, grains (< 2 mm) which are commonly associated with quartz, calcite, and chlorite; the other is of a more massive variety which is anhedral to subhedral. This uncharacteristic lack of crystal form shown by the magnetite may be explained by interpreting the textures as magnetite pseudomorphing an earlier phase such as hematite. Magnetite of a similar type occurs together with hematite, which it partially replaces, in material from the Long Crag vein, some 2.5 km due north of the Bonser vein.

Arsenopyrite occurs as large, fractured, euhedral or subhedral grains. Early arsenopyrite occurring as euhedral, commonly zoned, rhombs has in some instances penetrated into the cleaved and altered tuffs. In the main vein material, it is associated with pyrrhotine as small included rhombs (< 20 μm), and is also associated with chalcopyrite and sphalerite.

Pyrrhotine is not abundant in the ore-bearing specimens. It is later than magnetite and contains inclusions of arsenopyrite, sphalerite, and chalcopyrite. Pyrrhotine occurs as large anhedral grains (< 100 μm) in aggregates forming areas up to 10 mm across, and has been replaced by marcasite and pyrite.

Chalcopyrite occurs in massive form as stringers in the main quartz vein, or as anhedral inclusions (< 100 μm) in sphalerite, pyrrhotine, and bismuthinite. Sphalerite inclusions in pyrrhotine (< 50 μm) are generally associated with chalcopyrite and, in some specimens, the chalcopyrite forms a thin (< 20 μm) margin between the sphalerite and pyrrhotine.

Pyrite occurs with both pyrrhotine and magnetite but is later than both of these minerals. It replaces pyrrhotine and magnetite at grain boundaries to a limited extent and forms a skeletal development along calcite cleavages. Botryoidal chlorite is overgrown by pyrite euhedra (< 1 mm) while larger (< 3 mm) pyrite dodecahedra are found as inclusions in quartz.

Bismuthinite forms inclusions in pyrite and occurs along fractures in quartz. In the latter case, the grain size may be quite coarse (< 1 mm) and aggregates may form extensive areas associated with chlorite, chalcopyrite, and native bismuth. A silicate, possibly chlorite, elongate and rectangular in section grows along bismuthinite cleavage planes in some specimens. Bismuthinite has been replaced by laitakarite, which occurs as aggregates (< 50 μm) of small anhedral grains (< 10 μm), with a few minute grains of joesite.

Native bismuth is less common than bismuthinite as inclusions in pyrite and is generally interstitial,

forming areas up to several millimetres across. It is associated with bismuthinite and laitakarite.

Galena was the last sulphide formed and occurs in association with late sphalerite and chalcopyrite, one specimen having minute inclusions of bismuth and also larger (< 100 μm) inclusions of cosalite.

In summary, it may be said that the mineralization was mainly continuous, with little fracturing occurring within the vein during mineral deposition, and relatively minor replacement of the earlier minerals taking place.

Age of mineralization. K–Ar isotopic age determinations on wall-rock chlorites and illites by Ineson and Mitchell (1974) have given an age of 383 Ma for a spoil heap sample from the Bonser vein. For the Coniston area as a whole, a mean age of 388 Ma and a range of 367–402 Ma (from five samples) was obtained, and it was suggested that the youngest of these values might be spurious because of minor argon loss. These results are interpreted as suggesting that emplacement or remobilization of the ores into their present position occurred at some time in the Devonian. A Devonian age for the mineralization is in agreement with the field evidence, which shows that the Coniston veins were unaffected by either the folding or the regional metamorphism resulting from the Caledonian earth movements (since no deformation or remobilization of the ores has apparently taken place).

Relationship of mineralization to the Lake District granite batholith. The K–Ar ages for the copper mineralization are close to the Lower Devonian ages obtained for some of the Lake District granites by Brown *et al.* (1964). There is no evidence for granite near the surface beneath the Coniston area, and the nearest exposed granite to the Coniston deposits, the Eskdale Granite, lies some 8 km to the northwest, and was dated at 429 ± 9 Ma by Rundle (1979). Whereas Bott (1974) had suggested from the interpretation of gravity data that the exposed granites in the Lake District were connected at depth, Rundle argued that the Eskdale Granite was a separate and much earlier intrusion, and that the main batholithic granite was emplaced in end-Silurian times beneath the Eskdale mass. The Coniston veins lie above the southern margin of the proposed granite batholith.

Estimates of the temperature and depth of mineralization. If mineralization took place during the Devonian, then an estimated depth of cover might be 7–9 km, made up of 0–2 km Devonian, 6 km Silurian (Rickards, 1978), and 1 km Ordovician (Mitchell, 1940) strata.

The geothermal gradient in the Earth's crust varies from approximately 10°C/km in stable cratonic regions, to about 50°C/km in active

orogenic belts (Smith, 1963); a mean or normal gradient is generally taken to be between 20°C/km and 35°C/km. Miyashiro (1973) suggested that the temperature gradient in an area during low grade regional metamorphism (as suffered by the Lake District during the Caledonian orogeny) is at least 25°C/km. Estimates of the wall-rock temperature for the Bonser vein vary from 175 to 225°C (at 7 and 9 km respectively), assuming a geothermal gradient of 25°C/km; and 245 to 315°C (at 7 and 9 km respectively) with a geothermal gradient of 35°C/km. It is possible that even higher temperatures existed during the early stages of mineralization due to the additional temperature gradient established by the recently emplaced granite bodies nearby.

Mineralogical indicators of the conditions of mineralization. Combining the paragenetic interpretation with published thermochemical data for coexisting minerals, estimates can be made of conditions in the Bonser vein during mineralization. The stability of some individual minerals is important. For example, cosalite, a late mineral associated with galena in the Bonser vein, has a stability limit of 425°C (Craig, 1967); native bismuth almost certainly formed below its melting point of 271.5°C, as it shows evidence neither of crystallization from a melt nor of subsequent melting. Klement *et al.* (1963) report a lowering of native bismuth's melting point of 7.6°C per kbar of total pressure; consequently, still lower maximum temperatures may be considered for its formation. If a purely hydrostatic load is assumed (100 bars/km) then the pressure at the time of mineralization was 700–900 bars (using the estimates of depth given previously); if a purely lithostatic load is assumed (250 bars/km) then the pressure was 1750–2250 bars. These estimates give maximum temperatures of ~265°C (for hydrostatic load) and ~255°C (for a lithostatic load) for the formation of native bismuth in the Bonser vein. Monoclinic pyrrhotine cannot have formed above 248°C (Scott and Kissin, 1973) unless by inversion from a higher-temperature hexagonal form. Such an inversion is thought improbable in this instance, since the monoclinic pyrrhotine is homogeneous. Sphalerite inclusions in monoclinic pyrrhotine have a composition of 13.6–14.4 mole % FeS (Table I, 2–3), and could have formed in equilibrium at temperatures of less than 248–5°C according to the speculative low-temperature phase diagram of Scott and Kissin (1973).

Further information on temperatures and sulphur activities at the time of ore deposition may be obtained using Kretschmar and Scott's (1976) arsenopyrite geothermometer. Bonser vein arsenopyrites were analysed using Kretschmar's Asp200

probe standard. Different specimens showed slight compositional variation; none, however, was found to contain cobalt or any other detectable impurity which might affect the application of the geothermometer. The highest As contents were from early euhedral arsenopyrites which formed in the silicified and chloritized country rock of cleaved tuffs (Table I, 8–9). Later arsenopyrites occur in pyrrhotine and chalcopyrite and have a lower As content. Both generations of arsenopyrite are compositionally zoned with a higher As content in the core than in the rim, with the exception of the small arsenopyrite euhedra in pyrrhotine which are not zoned, the two analyses from different areas (Table I, 4–5) showing only minor compositional variation. Kretschmar and Scott's (1976) arsenopyrite geothermometer should only be applied when the arsenopyrite was formed in equilibrium with an a_{S_2} -dependent assemblage, and, while the early arsenopyrite may not have been in equilibrium with such an assemblage, the small arsenopyrite euhedra in pyrrhotine almost certainly fulfil these conditions.

The relevant arsenopyrite sulphidation curves were plotted on a sulphur activity–temperature diagram (fig. 2) extrapolating Kretschmar and Scott's (1976) curves to somewhat lower temperatures than 300°C. A number of other sulphidation curves were also plotted on this diagram and, in addition, the magnetite/hematite stability fields were plotted at 350°C and 400°C with their respective oxygen activities. In order to obtain estimates of oxygen activity in the vein, a sulphur activity against oxygen activity diagram was constructed (fig. 3) in a manner similar to that described by Holland (1959, 1965) to show the stability fields for various mineral species in the assemblage at temperatures of 250°C and 350°C. Thermodynamic data have also been taken from Barton and Skinner (1967, 1979) using sulphidation curves obtained from several sources.

There is no definite 'fixed point' in the a_{S_2} -temperature diagram (fig. 2) for the early magnetite mineralization in the Bonser vein. Early arsenopyrite with 34.1 at. % As cannot have formed below temperatures of about 330°C at $a_{S_2} \sim 10^{-13}$ atm. (see fig. 2). Outer zones of this early arsenopyrite (33.4 at. % As) could have formed above 290°C at $a_{S_2} \sim 10^{-14}$ atm. Some doubt exists however, as to whether this arsenopyrite is from an a_{S_2} -buffered assemblage, and so these minimum temperatures must be regarded with a degree of caution. The paragenetic relations of this early arsenopyrite are unclear but it probably formed later than the magnetite (which pseudomorphs hematite). At 350°C hematite is a stable phase only with $a_{O_2} > 10^{-25.4}$ atm. (see fig. 2) and magnetite could

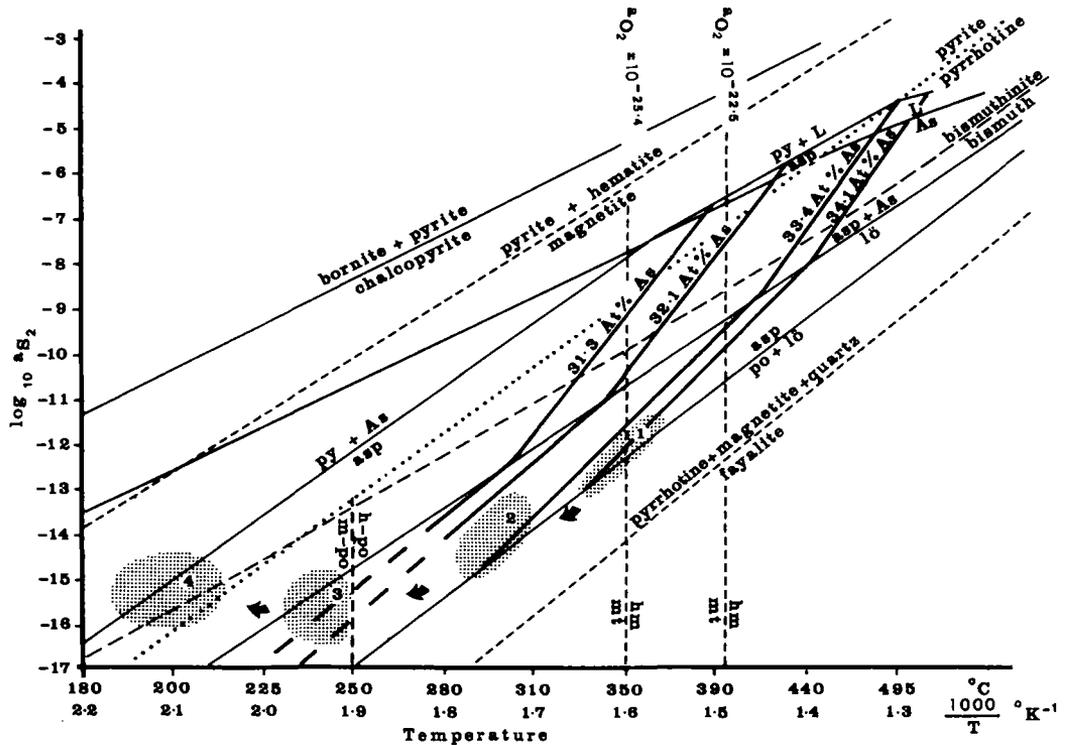


Fig. 2. a_{S_2} - T diagram. Stippled areas 1-4 represent the likely changes in temperature and composition of the ore fluids during mineralization of the Bonser vein (sulphidation curves taken from various sources, see Barton and Skinner, 1967, 1979).

pseudomorph it provided that the a_{O_2} dropped either below $10^{-25.4}$ atm. at 350°C or below $10^{-32.4}$ atm. at 250°C (see fig. 3). Several interpretations are possible, but despite the problems of 'fixing' the early mineralization it is thought that area A (fig. 3) and areas 1 and 2 (fig. 2) provide reasonable estimates of formation conditions. It is possible that the early hematite mineralization formed in an environment with considerably lower sulphur activities than those shown on the diagrams.

For the main stage of sulphide mineralization, the absence of the assemblage bornite-pyrite limits the area of interest in the a_{S_2} -temperature diagram to the chalcopyrite stability field. This area is further restricted by the presence of pyrrhotine, magnetite, and quartz in the assemblage rather than fayalite (see fig. 2). Monoclinic pyrrhotine, with late arsenopyrite, sphalerite, chalcopyrite, quartz, calcite/dolomite, and chlorite, cannot have formed above 250°C (Kissin, 1974). Sphalerite (13.6-14.4 mole % FeS) may have formed in equilibrium with monoclinic pyrrhotine at temperatures below

$245-8^\circ\text{C}$ (Scott and Kissin, 1973). It is assumed that the small arsenopyrite euhedra enclosed in pyrrhotine were deposited simultaneously along with some of the chalcopyrite and sphalerite in the assemblage. Area 3 (fig. 2) is thought best to represent conditions for the deposition of minerals at this stage of the paragenetic sequence, at 240°C and with $a_{S_2} \sim 10^{-16}$ atm. Lower temperatures and therefore lower sulphur activities (due to the shape of the arsenopyrite 31.3 at. % As and 32.1 at. % As stability curves) are also possible, but are thought unlikely, there being no evidence for any significant deviation from the curve indicated by areas 1-4 (fig. 2).

Stability fields at 250°C and 350°C have been constructed on the a_{S_2} - a_{O_2} diagram (fig. 3) and it is now possible to fit the data obtained from the a_{S_2} -temperature diagram (fig. 2) to this. Magnetite, a somewhat refractory mineral, shows very little evidence of having been replaced by pyrrhotine and this is taken to indicate that the composition of the mineral-bearing fluids, during the deposition of pyrrhotine, was not far removed from the

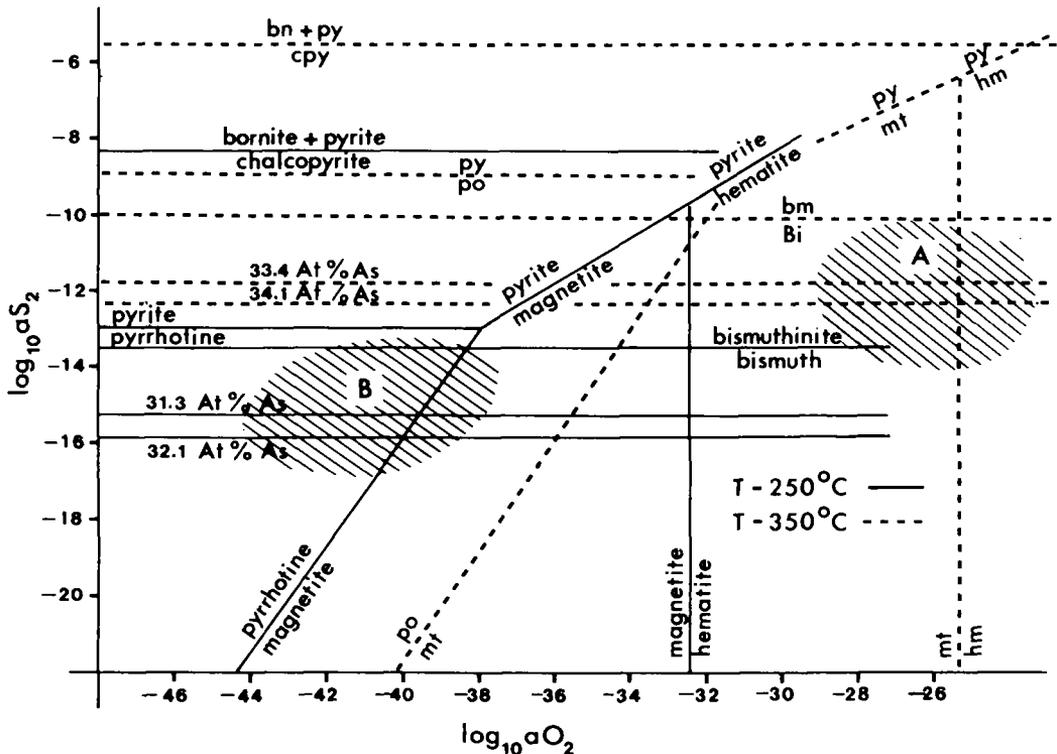


FIG. 3. a_{S_2} - a_{O_2} diagram. Areas A and B represent possible conditions of mineralization at 350 and 250°C respectively.

magnetite stability field. Area B (fig. 3) has therefore been positioned to overlap slightly the magnetite stability field and incorporate the arsenopyrite (31.3 at. % As and 32.1 at. % As), and pyrrhotine stability fields. The oxygen activity of area B is from $\sim 10^{-38}$ atm. to $\sim 10^{-44}$ atm. with $a_{S_2} \sim 10^{-14}$ to 10^{-16} atm.

Although bismuth and bismuthinite are commonly associated with magnetite, they are thought to be later and probably to have formed at the same time as pyrite. There is no evidence of their being associated with pyrrhotine, so the proposed path (Areas 1-4 fig. 2), illustrating the changes in fluid composition during mineralization, does not include the bismuth-bismuthinite-pyrite-pyrrhotine invariant point at 235°C and $a_{S_2} \sim 10^{-14}$ atm. Pyrrhotine has been replaced by marcasite and pyrite and this must have taken place when the sulphur activity increased or the temperature decreased, such that the pyrite/pyrrhotine sulphidation curve was crossed and pyrrhotine was no longer stable. Area 4 (fig. 2), at $\sim 200^\circ\text{C}$ and $a_{S_2} \sim 10^{-15}$ atm., incorporating the bismuth/bismuthinite sulphidation curve in the pyrite stability field, may represent the formation condi-

tions of the later mineralization, although Bente (1982) gives a temperature of $135^\circ\text{C} (\pm 30^\circ\text{C})$ for bismuthinite formation in the Bonser vein on the basis of S isotope fractionation data. The bismuth sulphoselenide, laitakarite, and bismuth sulphotelluride, joseite, may have formed under similar conditions. Late galena and cosalite could have formed subsequently at lower temperatures but similar sulphur activities.

The temperatures indicated from this interpretation of the mineralogical data fall within a slightly higher range than the estimates of wall-rock temperature. It is suggested that the Bonser vein formed by the successive deposition of minerals from solution as a consequence of cooling of the mineralizing fluids, possibly by contact with wall-rocks of lower temperature

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