

Sphalerite composition in relation to deposition and metamorphism of the Foss stratiform Ba-Zn-Pb deposit, Aberfeldy, Scotland

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ABSTRACT. Sphalerite is a common constituent of the mineralized rocks and host metasediments of the Foss baryte-base metal deposit, located near Aberfeldy in the central Scottish Highlands. Microprobe analyses of sphalerite show a wide range in minor element content (0-17 mol. % FeS, 0-3 mol. % MnS), and sphalerites of contrasting composition are often found in the same rock. This suggests that equilibrium domains in some rocks were minute (< 1 mm), during regional metamorphism. Pressures derived from the selective application of the sphalerite geobarometer are consistent with other mineralogical evidence of peak metamorphic pressures in the range 7-10 kbar, at 540-580 °C. However, there is considerable evidence of partial retrograde re-equilibration of sphalerite, by continued buffering with pyrite + pyrrhotine and by outward diffusion of iron. Marginal depletion of Fe and Mn in sphalerite within coarse carbonate rocks is attributed to partitioning reactions following recrystallization. Sphalerite which has retained its pre-metamorphic composition shows systematic variations in composition through profiles of mineralized beds, which may be related to depositional environments. Bimodal primary compositions can be explained by precipitation of zinc sulphides under the contrasting chemical environments of hydrothermal vents and cooler, exhaled brine layers on the sea floor.

THE Aberfeldy stratiform baryte-base metal deposits, which have been described by Coats *et al.* (1980, 1981), are situated in the central Scottish Highlands (fig. 1). They are contained within steeply inclined metasedimentary rocks of the Middle Dalradian (c. 600 Ma) which were subjected to polyphase deformation and garnet-grade metamorphism during the Grampian Orogeny (Bradbury *et al.*, 1979; Siraparakash, 1982). The deposits have many of the characteristics of the shale-hosted, sedimentary exhalative class of stratiform ore deposits (Large, 1981). They are considered to have formed from metalliferous brines which were expelled into actively developing sedimentary basins during a period of increasing crustal instability (Russell *et al.*, 1981a; Laux *et al.*, in prep.). This paper concerns the sulphide mineralogy of the Foss

deposit, which is the westerly of the two major deposits at Aberfeldy, in both of which sphalerite is widespread and locally abundant.

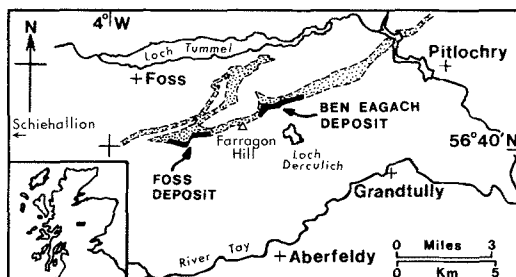


FIG. 1. Map of the central Scottish Highlands showing location of the Aberfeldy deposits. Outcrop of the Ben Eagach Schist is shown by the stippled ornament.

The importance of sphalerite in geological studies derives from its refractory nature, and its capacity to record physical and chemical characteristics of the environment of deposition or metamorphism by changes in minor element composition (Barton, 1970; Scott, 1983). The changing temperature and chemistry of mineralizing solutions has left a delicate record in the growth-banded sphalerite of some vein and Mississippi Valley type deposits (e.g. McLimans *et al.*, 1980). Sequential trends of sphalerite composition have been described from the Kuroko deposits (Urabe, 1974), and from some sedimentary exhalative deposits such as Sullivan (Campbell and Ethier, 1983). The Fe content of sphalerite in equilibrium with pyrite and pyrrhotine has been calibrated as a geobarometer (Scott, 1973; Lusk and Ford, 1981), which has been applied to many metamorphosed sulphide deposits with variable success (Scott, 1976; Plimer, 1980; Hutchison and Scott, 1981).

In this paper, the compositions and textural

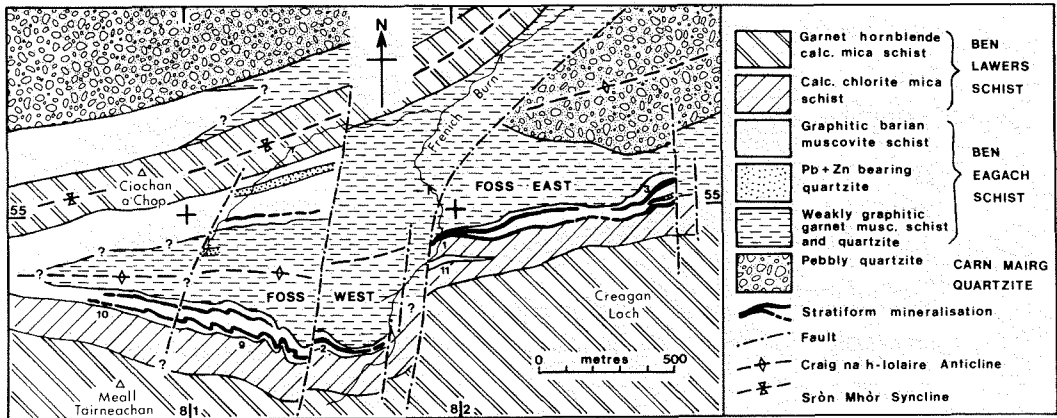


FIG. 2. Geological map of Foss deposit, Aberfeldy, based on maps by Sturt (1961) and Coats *et al.* (1981) and unpublished field maps. IGS borehole sites located by numbers. Grid numbers refer to OS sheet 52.

relationships of sphalerite in the Foss deposit are described, and an attempt is made to distinguish sphalerite compositions of primary origin from those modified by metamorphic processes. Consideration is given to the size of equilibrium domains and the significance of diffusion processes affecting sphalerite during metamorphism. The application of the sphalerite geobarometer is evaluated and results are compared with geothermometric and geobarometric data derived from calcite-dolomite, garnet-hornblende, and cymrite-celsian phase equilibria. The range and spatial distribution of pre-metamorphic sphalerite compositions are discussed and are tentatively related to depositional processes in the mineralizing system.

Geology

The Foss deposit, which has a strike-length of about 2 km and an explored depth of 300 m, extends between the northern slopes of Meall Tairneachan and Creagan Loch (fig. 2). The mineralization occurs as multiple sheets or lenses within graphitic and calcareous mica schists of the Ben Eagach Schist formation, and the mineralized zone ranges from about 30 m to over 200 m in true thickness. It is terminated to the east by a N.-S. fault zone, and plunges to the west in the core of the Craig na h'Iolaire Anticline (Sturt, 1961).

Although potentially a source of industrial baryte, much of the mineralization consists of carbonate, quartz, and barium-silicate lithologies which are variably enriched in base-metal sulphides. Rapid lateral facies variations within both mineralized horizons and metasediments, and localized structural attenuation associated with folding, are features of the deposit (Swenson *et al.*, 1981).

However, closely spaced drillholes have allowed the correlation of individual horizons (Laux *et al.*, in prep. and unpublished work). Stratigraphic correlation has been assisted by the recognition of thin (2 cm–2 m) metabasic layers of probable tuffaceous origin, which are closely associated with several of the mineralized horizons.

Thickness and facies variations and the local occurrence of synsedimentary breccias suggest a genetic relationship between the distribution of mineralization and penecontemporaneous faulting. Growth faults were active elsewhere in the Dalradian basin in the late Proterozoic–early Cambrian (Anderton, 1979) and are a characteristic feature associated with sedimentary exhalative deposits (Large, 1981). These faults may have acted as conduits for mineralizing brines which were expelled into the marine basin, possibly by means of seismic pumping (Sibson *et al.*, 1975). It is envisaged that baryte was deposited in relatively shallow, oxygenated parts of the basin, while sulphides accumulated on the downthrown sides of postulated growth faults where pooling of the brines inhibited mixing with sea-water sulphate (Moles, 1982, and Laux *et al.*, in prep.). As cross-cutting mineralization (of pre-metamorphic origin) and alteration pipes are absent from below the stratiform horizons at the present level of exposure, the deposits may be classified as distal (Large, 1981; Plimer, 1979).

Sulphide mineralogy

In the Aberfeldy deposits, sphalerite is the second most abundant sulphide mineral after pyrite; galena and pyrrhotine are less abundant, and chalcocopyrite occurs in trace amounts. Although widespread in both the mineralized rocks and host metasediments,

sphalerite is seldom a major constituent. In sulphidic bands, the sphalerite content occasionally increases to > 50 % over intervals of 1–20 cm. Sphalerite more frequently occurs as disseminated grains, or as tenuous laminae which are parallel to the lithological layering. Fine sedimentary layering has generally been preserved in lithologies which are rich in quartz, barium feldspars, baryte, and carbonates, whereas micaceous rocks are usually highly schistose. Remobilization of sulphides, along high-angle cleavage planes or into veinlets and segregations, is generally minor and localized in extent, except in some mineralized carbonate rocks where breccia textures have developed.

Sphalerite grains range in shape from equant and subhedral to highly irregular and embayed. Grain size ranges from 0.03 to 3 mm corresponding to a similar range in the host rocks. Individual crystals may reach 2 cm in veins and segregations. Small sphalerite grains are often encapsulated by pyrite, which often forms discrete rounded to euhedral cubic porphyroblasts. Sphalerite grains of differing colour often occur in the same rock, and visible zoning of sphalerite is sometimes observed in transmitted light. Microprobe analyses have confirmed that these variations in colour correspond to variations in the minor element contents of sphalerite. This allows a visual estimate to be made of the abundance of particular compositions (Fe-rich or Fe-poor) in polished thin sections. A variety of textural and compositional relationships in sphalerite-bearing assemblages are illustrated in figs. 3–8, and are described in detail below.

Irregular or rectangular-shaped grains of pyrrhotine are common in graphitic schist and dolomitic celsian rocks, but pyrrhotine is rare in baryte rock. Pyrrhotine commonly coexists with sphalerite and galena, and is often associated with minor chalcopyrite. The occurrence of pyrrhotine in certain metabasic lithologies suggests that reactions involving Fe–Mg silicates may have generated some pyrrhotine during metamorphism, but massive bands formed of pyrrhotine are undoubtedly primary in origin. No evidence of pyrrhotine replacing pyrite has been observed, but in many rocks some or all of the pyrrhotine has been pseudomorphed by pyrite and marcasite. The porous structure or 'bird's-eye' texture of secondary pyrite distinguishes it from the pre-existing, well-crystallized pyrite. This replacement of pyrrhotine is clearly post-tectonic and some has resulted from supergene alteration. From the drillcore samples examined, it is estimated that pyrite has replaced roughly 20 % of the pyrrhotine originally present.

Pyrrhotine occasionally occurs as small inclusions in ferroan sphalerite, which may be crystallographically orientated (fig. 7a). Depletion in the

Fe content of the host sphalerite around these orientated inclusions suggests that this pyrrhotine formed by exsolution from the sphalerite. Chalcopyrite is more common as inclusions in sphalerite, and has been observed in sphalerites of a wide range of compositions. Chalcopyrite inclusions, which are usually equant and can reach 30 μm in diameter, may be randomly dispersed, orientated along crystallographic planes, or concentrated towards the centres of host sphalerite grains. Although some chalcopyrite may have been exsolved from sphalerite (Wiggins and Craig, 1980), the abundance of inclusions (often about 5 % by volume) suggests that the chalcopyrite originated as a primary two-phase intergrowth which was recrystallized during metamorphism (Hutchison and Scott, 1981).

Sphalerite analyses. Analyses were performed on a Cambridge Instruments Microscan Mk. 5 electron microprobe at Edinburgh University. The wavelength dispersive technique was employed, with an accelerating voltage of 20 KeV, a probe current (measured at the Faraday Cage) of 30 nA, and an electron beam diameter of 1 μm . Metal standards were used for Zn, Fe, Mn, Cu, and Cd, and a pyrite standard was used for sulphur. Data reduction was performed by an on-line computer using the ZAF correction procedures of Sweatman and Long (1969). Under the analytical conditions employed, detection limits were 0.03 wt. % for iron and 0.02 wt. % for manganese, and precision for iron was usually better than ± 1 % of the wt. % Fe present for sphalerites with > 6 wt. % Fe (= 10 mol. % FeS).

Microprobe analyses were obtained from the polished thin (c. 30 μm) sections used for transmitted and reflected light observations. The iron content of Foss sphalerite varies from 0.0 to 17.0 mol. % FeS, which corresponds to a range in appearance from colourless, through yellow and orange, to dark red in transmitted light. The Mn content is low in most Fe-rich sphalerite (> 10 mol. % FeS) but ranges up to 2.7 mol. % MnS in Fe-poor sphalerite (see Coats *et al.*, 1980). Fe-poor, Mn-rich sphalerite is grey in transmitted light. These relationships between sphalerite composition and colour are similar to those noted by Page and Watson (1976).

A small amount (0.1–0.3 wt. %) of Cd was detected in many sphalerites, but Sb was below detection limits (c. 0.05 wt. %) in most analyses. Cu was detected in trace amounts (up to 0.14 wt. %) in some sphalerites, but microscopic chalcopyrite inclusions account for the higher apparent Cu contents in some analyses of inclusion-rich sphalerite. The metal : sulphur ratio of sphalerite confirms that it is stoichiometric (Zn,Fe,Mn)S, within the limits of analytical precision (± 0.3 % of the amount present for sulphur).

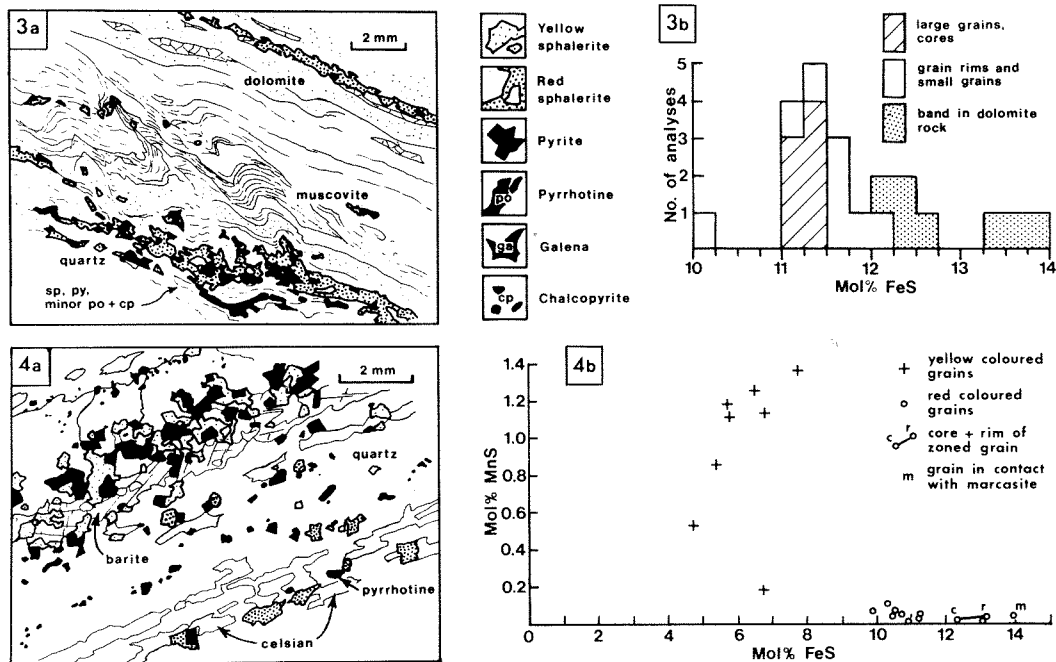
Textural and compositional relationships. Six samples which illustrate a range in textural and compositional relationships between sphalerite and associated phases, and which contain features crucial to their interpretation, are now described in some detail. Information on these samples is summarized in Table I and in figs. 3–8.

TABLE I. Summary of textural and chemical features of sphalerite-bearing rock samples described in the text

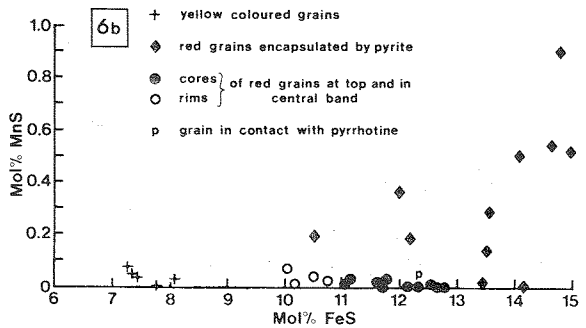
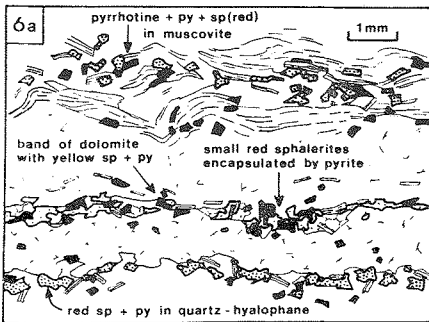
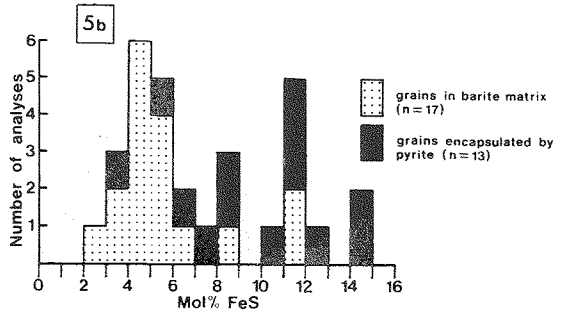
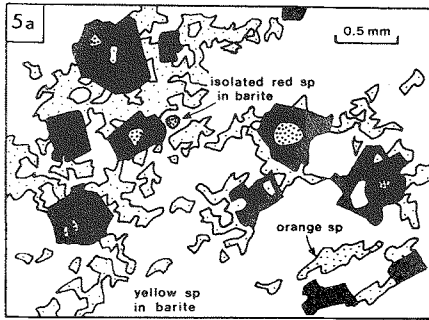
Fig.	Sample*	Lithology	Sulphide assemblage	No. of analyses	Range in mol. % FeS	Range in mol. % MnS	Interpretation
3	705-9	Graphitic musc. qtz. dol. schist	py + po + sp, minor ga, cp	22	10-14	0-0.1	Buffered, in part retrogressive
4	80-30A	Pyritic qtz. celsian rock	py + sp; py + po + sp, retro. mar	20	5-14	0-1.3	Primary (Fe-poor) + buffered (Fe-rich)
5	705-20	Sulphidic baryte rock	py + sp, minor ga	30	3-15	0-0.2	Primary, bimodal
6	429-8	Qtz. musc. dol. hyalophane metachert	py + sp; py + po + sp, minor ga, cp	30	7-15	0-0.9	Primary, bimodal + locally buffered
7	202-3	Muscovitic quartzite with sulphide lenses	py + po + sp + ga + cp; retrograde po, py + mar	38	11-17	0-0.1	Retrogressively buffered with annealed cp intergrowth
8	705-21	Coarse sp. celsian dolomite rock	sp; sp + py, minor ga	20	2-14	0-0.3	Diffusion zoned: loss of Fe + Mn to carbonate

* Samples from Creagan Loch (Foss East) except 429-8, from Meall Tairneachan (Foss West) (see fig. 2). All samples except for 80-30A are from drillcore.

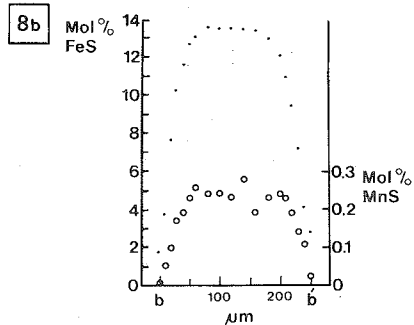
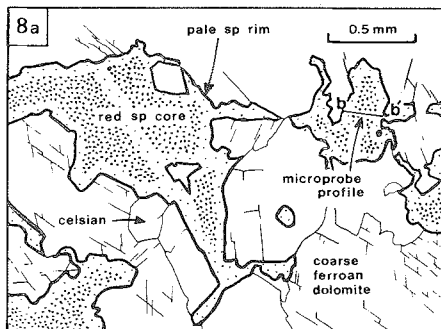
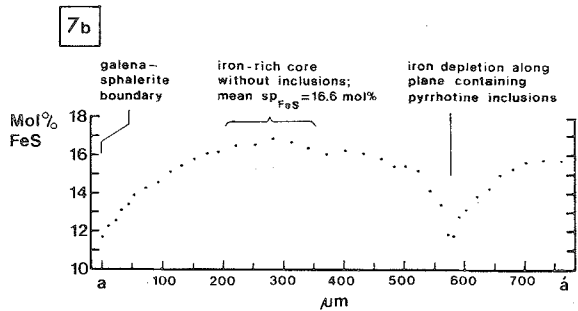
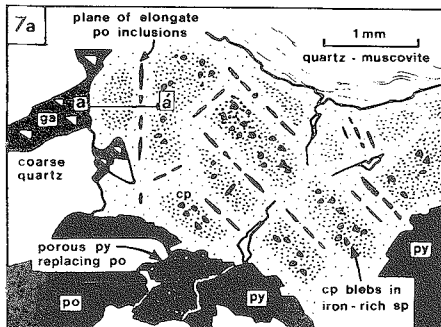
Abbreviations: py, pyrite; po, pyrrhotine; sp, sphalerite; ga, galena; cp, chalcopyrite; mar, marcasite.



FIGS. 3 and 4. (a) line drawings from polished thin sections (PTS). FIG. 3. Sample 705-9: (b) histogram of mol. % FeS for twenty-two sphalerite analyses. FIG. 4. Sample 80-30A: (b) plot of mol. % MnS vs. mol. % FeS for twenty sphalerite grains.



FIGS. 5 and 6. (a) line drawings from PTS. FIG. 5. Sample 705-20: (b) histogram of mol. % FeS for 30 sphalerite grains. FIG. 6. Sample 429-8: (b) plot of mol. % MnS vs. mol. % FeS for thirty sphalerite grains.



FIGS. 7 and 8. (a) line drawings from PTS. FIG. 7. Sample 202-3: (b) microprobe profile of FeS-content of sphalerite along line a-a'. FIG. 8. Sample 705-21: (b) microprobe profile of Fe (●) and manganese (○) contents of sphalerite along line b-b'.

Fig. 3a illustrates a sample of graphitic, calcareous metasediment in which sedimentary layering is expressed by variations in the proportions of muscovite to dolomite and quartz. Laminae of sphalerite + pyrite, with minor associated pyrrhotine and galena, parallel this layering, but are partly disrupted by small-scale folding and strain-slip cleavage oblique to the layering. The porous texture of some of the pyrite indicates that much of the pyrrhotine coexisting with the sphalerite during metamorphism has been replaced by secondary pyrite. All of the sphalerite is red in transmitted light, and microprobe analyses (fig. 3b) show a range in iron content from 10–14 mol. %, with a modal composition of 11.4 mol. % FeS. The central parts of coarser crystals of sphalerite contain less Fe than both the rims of these crystals and small grains, and sphalerite contained in a dolomitic band is relatively Fe-rich.

The quartz celsian rock illustrated in fig. 4a contains trace (< 1%) pyrrhotine in addition to disseminated pyrite and sphalerite. All three sulphides are occasionally in mutual contact, but most of the sphalerite occurs as isolated grains and aggregates with pyrite. Much of this sphalerite is yellow-orange in colour, but grains which are in mutual contact with pyrrhotine (\pm pyrite) are red. Isolated grains of sphalerite (or of sphalerite + pyrite) within a few millimetres of pyrrhotine are also red in colour. Two analysed grains of sphalerite in mutual contact with pyrrhotine + pyrite contain 11.2 and 10.8 mol. % FeS, and other red-coloured grains in the vicinity of pyrrhotine range from 9.9 to 13.0 mol. % FeS (fig. 4b). One grain containing 14 mol. % FeS adjoins marcasite of supergene origin. Yellow-coloured sphalerites contain 5–7 mol. % FeS, and in contrast to the red sphalerites, are variably enriched in manganese up to 1.3 mol. % MnS.

The textures portrayed in fig. 5a are typical of sulphide-rich baryte layers which commonly occur near to the stratigraphic base of the lower baryte horizon in Foss East. Pyrrhotine is absent from these rocks. Pyrite forms subhedral crystals up to 2 mm in diameter, which often enclose one or several grains of sphalerite. Encapsulated sphalerites may exceptionally attain > 200 μ m in diameter but are usually much smaller. Sphalerite surrounding the pyrites may be highly irregular in shape and intergrown with baryte, or (in other rocks) the sphalerite forms a continuous matrix enclosing crystals of pyrite. A large proportion of the sphalerite (typically > 90%) is yellow in colour corresponding to a relatively low Fe content, but many of the encapsulated grains are red and Fe-rich (fig. 5b). A few isolated orange and red coloured grains also occur in the baryte matrix. In

a similar rock to the one illustrated, discrete sphalerite grains of contrasting colour and composition are in mutual grain contact, but this occurrence is exceptional. However, pyrite crystals often enclose several sphalerite grains of contrasting composition.

A sample of laminated quartz–muscovite–hyalophane metachert, which forms the hanging wall to the upper baryte horizon in Foss West, is illustrated in fig. 6a. Red-coloured sphalerite, containing 10.0–12.7 mol. % FeS, occurs as disseminated grains, some of which are in contact with pyrrhotine + pyrite, in crenulated muscovite-rich rock at the top of the field of view. Sphalerite of similar composition, associated with pyrite and muscovite (but not with pyrrhotine), also forms a thin band in hyalophane rock near the bottom of the illustration. In the centre is another thin band of sphalerite which is orange-yellow in colour and contains 7–8 mol. % FeS. Disseminated yellow sphalerite of this composition occurs together with pyrite elsewhere in the sample where pyrrhotine is absent. Small, red-coloured sphalerite grains are encapsulated in pyrite crystals associated with both red and yellow bands of sphalerite and elsewhere in the sample. These sphalerites are distinctive in that they contain appreciable manganese (up to 0.9 mol. % MnS), and up to 15 mol. % FeS (fig. 6b).

Strongly zoned sphalerite crystals are illustrated in figs. 7 and 8, but on detailed examination these are seen to have major differences. The large sphalerite crystal of fig. 7a is associated with coarse pyrite, pyrrhotine (partly replaced by porous pyrite) and galena. Equant chalcocopyrite blebs populate dark red cores of the sphalerite crystal in which the Fe content is 15.5–17.0 mol. % FeS. More transparent sphalerite containing 11.5–12.2 mol. % FeS occurs at the margins of the crystal, and also along intersecting crystallographic planes containing planar inclusions of pyrrhotine and chalcocopyrite. Usually pyrrhotine and chalcocopyrite form separate, parallel grains (typically 5 \times 50 μ m in size) in these Fe-depleted zones, but occasionally chalcocopyrite mantles pyrrhotine inclusions.

The highly irregular and embayed form of sphalerite shown in fig. 8a is typical of carbonate mineralization in which sedimentary layering has been obliterated by recrystallization during metamorphism. The sphalerite shows pronounced depletion in both Fe and Mn towards grain rims and along internal cracks and cleavage planes. Small grains (< 100 μ m) are pale-coloured, whereas the central areas of larger grains or aggregates are orange-red and differ in Fe content by up to 12 mol. % FeS from the rims (fig. 8b). In other examples to the one illustrated, each sphalerite grain or aggregate is homogeneous in colour and

composition, but the Fe content appears to increase in direct proportion to grain size.

Interpretation. Several general observations which emerge from the foregoing detailed descriptions are critical to the interpretation of textural and compositional relationships of sphalerite in the Foss deposit.

(1) Sphalerite which is in grain contact or in close association with pyrrhotine (or pyrite pseudomorphs of pyrrhotine) is invariably red-coloured and ferroan (> 10 mol. % FeS). Such sphalerite is also usually Mn-poor.

(2) Sphalerite occurring as isolated grains or coexisting with pyrite, but not in the immediate vicinity of pyrrhotine, has a wide range in compositions from Fe-poor to Fe-rich. Overall, Mn and Fe contents are not systematically related, but in individual samples compositional grouping of sphalerite may be based on variations in both Fe and Mn (e.g. figs. 4b and 6b).

(3) Bands of massive sphalerite and individual disseminated grains are usually homogeneous, but adjacent grains or bands may differ in composition. Sphalerite hosted by recrystallized carbonate rock is often strongly zoned, and zoned sphalerite also occurs in coarse sulphide rocks bearing evidence of retrograde alteration. The zonation is diffuse rather than abrupt or oscillatory, and is usually an outward decrease in Fe (and Mn) content.

It is apparent from these observations that equilibrium domains have been minute in some rocks despite the effects of regional metamorphism. At least some of the observed variation in sphalerite composition within and between samples appears to have been inherited from the time of deposition. Several processes can be distinguished which have erased or modified original sphalerite compositions during metamorphism. These are: (a) buffering of the Fe content of sphalerite coexisting with pyrrhotine + pyrite; (b) homogenization of individual grains or of massive bands of sphalerite by intracrystalline diffusion; (c) partitioning of Fe and Mn between sphalerite and carbonate or other sulphide phases; and (d) exsolution and retrograde alteration of sphalerite assemblages.

The background to the use of the sphalerite geobarometer and its application to the Foss deposit are considered first. After other processes which have modified original sphalerite compositions are considered, it is then possible to discuss the significance of primary sphalerite compositions and their stratigraphic variation.

Sphalerite geobarometry

The amount of FeS in solid solution in sphalerite (sp_{FeS}) is a function of temperature, pressure, and

FeS activity (a_{FeS}). Barton and Toulmin (1966) and Scott and Barnes (1971) have shown that sp_{FeS} is a function only of pressure in the range 254–550 °C, provided that the a_{FeS} is buffered by coexisting pyrite + hexagonal 1C pyrrhotine. Under these conditions, sphalerite has a fixed FeS content of 20.8 mol. % at 1 bar, but with increasing pressure sp_{FeS} decreases progressively. This compositional change has been calibrated as a geobarometer to 10 kbar by Scott (1973), Lusk and Ford (1978), and Hutchison and Scott (1981) (fig. 9). Above 550 °C, sp_{FeS} varies with both temperature and pressure, but at high pressures the temperature-independent field extends above 600 °C.

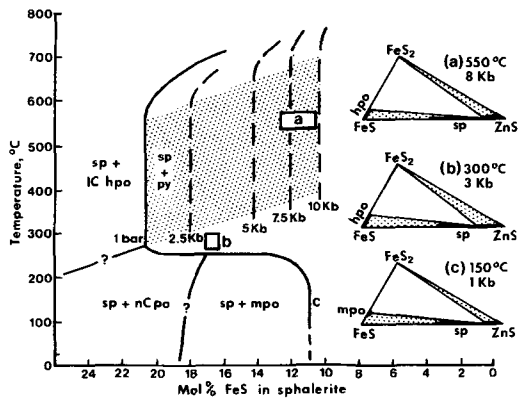


FIG. 9. T - X projection of the FeS-ZnS-S system showing the sphalerite + pyrrhotine + pyrite solvus at 1 bar (heavy line), and at higher pressures (broken lines). Stippled area is the temperature-independent field in which the sphalerite-pyrite-hexagonal-pyrrhotine barometer can be applied. Modified from Scott and Barnes (1971), Scott (1973), Scott and Kissin (1973), and Lusk and Ford (1978). Box labelled a indicates estimated peak P , T conditions at Aberfeldy, box labelled b indicates retrograde conditions deduced from sample 202-3 (see text). Inset: isothermal sections of the condensed system FeS-FeS₂-ZnS at points a, b, and c.

Below 254 °C (at 1 bar), 1C pyrrhotine undergoes structural and compositional changes, and monoclinic 4C pyrrhotine becomes stable in the assemblage pyrrhotine-pyrite-sphalerite. Low-temperature re-equilibration of sphalerite in this assemblage results in a marked decrease in sp_{FeS} . Scott and Kissin (1973) and Groves *et al.* (1975) have found convincing evidence of a largely temperature-independent monoclinic pyrrhotine-pyrite-sphalerite solvus corresponding to about 10.5 and 12.0 mol. % FeS in sphalerite (fig. 9, point c).

Tests with magnetic colloid and XRD tracings have shown that in all samples from Foss that were

examined, the pyrrhotine is monoclinic. However, estimates of peak metamorphic conditions in the Aberfeldy area are well in excess of 300 °C (Table II) and therefore hexagonal 1C pyrrhotine would have been stable during metamorphism. Before applying the sphalerite geobarometer, textural and geochemical evidence of retrograde alteration of sphalerite compositions must be thoroughly examined.

Retrograde re-equilibration. Evidence for low-temperature (< 250 °C) reactions involving sphalerite and monoclinic pyrrhotine include the exsolution of pyrrhotine from ferroan sphalerite and the depletion in sp_{FeS} adjacent to pyrite and pyrrhotine. Both features are illustrated by the sphalerite in fig. 7a. Re-equilibration of this sphalerite crystal with monoclinic pyrrhotine + pyrite, achieved in part by the exsolution of pyrrhotine, has clearly not gone to completion and the Fe-rich cores are relicts from buffering reactions with coexisting hexagonal pyrrhotine + pyrite.

The Fe content of these relict cores allows an estimation to be made of the confining pressure at the point in the cooling history below which hexagonal pyrrhotine was no longer stable. Inserting the mean of five analyses (16.6 mol. % FeS; fig. 7b) into the equation of Hutchison and Scott (1981) gives a pressure of 3.1 ± 0.3 kbar. The hexagonal pyrrhotine-monoclinic pyrrhotine transition, and therefore the horizontal limb of the solvus in the Zn-Fe-S system (fig. 9), may be displaced to higher temperatures due to the effect of confining pressure. This has not been determined, but an upper limit of 300 °C at 3.4 kbar can be interpolated from the experimental data of Scott (1973). Therefore it may be postulated that, at some time during uplift, the rock mass enclosing the Foss deposit passed through the P - T area of 3.1 ± 0.3 kbar and 260–300 °C (fig. 10).

A record of metamorphic conditions during uplift has been preserved in this sphalerite crystal (fig. 7a) because of its large size and incomplete re-equilibration at low temperatures. Of critical importance is the ability to distinguish between small, unzoned sphalerites which have been buffered by monoclinic pyrrhotine + pyrite at low temperatures (< 250 °C), and sphalerite which (although currently in the same assemblage), has retained the equilibrium composition generated by buffering with hexagonal pyrrhotine + pyrite at about 9 kbar, since in both cases the sphalerite will contain about 11 mol. % FeS (fig. 9). Features which allow the recognition of sphalerites of this composition which have been involved in low-temperature reactions, are:

(a) Zoning or heterogeneity, and the presence of exsolved pyrrhotine.

(b) The presence of chalcopyrite inclusions, which appear to promote retrograde reactions (see Doctor, 1980; Hutchison and Scott, 1981).

(c) The association with retrograde metamorphic or supergene phases particularly marcasite and pyrite pseudomorphs of pyrrhotine, and retrograde chlorite and siderite, which indicate the passage of late metamorphic or meteoric fluids.

Equilibrium domains and retrograde diffusion. Sulphide-rich rocks from the Foss deposit which contain major amounts of pyrrhotine (frequently associated with minor chalcopyrite) are seldom suitable for deriving peak pressure estimates because of the high incidence of retrograde re-equilibration of sulphides in such rocks. Disseminated sphalerite in competent lithologies such as baryte rock and quartz metachert, in which pyrite is common but pyrrhotine is comparatively rare, has a greater tendency to retain compositions generated by prograde buffering reactions. In such cases, sphalerites in grain contact with pyrrhotine + pyrite are similar in colour and composition to nearby isolated sphalerite (\pm pyrite) grains, but at a greater distance from the pyrrhotine, sphalerite grains differ in composition and have apparently remained unaffected by buffering reactions during metamorphism (e.g. figs. 4 and 6). These observations suggest that an interstitial fluid phase in the immediate vicinity of pyrrhotine + pyrite was buffered with respect to a_{FeS} , and that this fluid provided the transport medium for enrichment in sp_{FeS} .

The rock volume, or equilibrium domain, within which disseminated sphalerite has been buffered by interstitial fluid in equilibrium with one or more grains of pyrrhotine (+ pyrite) ranges from less than 1 mm³ (e.g. sample 80-30A) to at least the size of a hand specimen, and is possibly on the scale of metres in schistose lithologies. In well-banded rocks, buffered equilibrium domains may be planar in shape, particularly where banding is defined by variations in mica content (e.g. sample 429-8). In other rocks, the shape of buffered equilibrium domains relate to cross-cutting veinlets. Characteristically, equilibrium volumes are sharply defined and grains as little as 30 μ m apart, at the boundary of a fluid-buffered domain, may differ greatly in colour and composition.

Two independent processes appear to have affected sphalerite compositions subsequent to equilibration during climactic metamorphism. These are: (1) Partial down-pressure re-equilibration of sphalerite (particularly if in grain contact with pyrrhotine), resulting in an increase in sp_{FeS} (e.g. sample 705-9). (2) Outward diffusion and depletion in sp_{FeS} in small (< 100 μ m diameter) grains and in the rims of larger grains. This depletion is typically

in the order of 0.5–2.0 mol. % FeS, but may exceed 10 mol. % FeS in carbonate-hosted sphalerite (e.g. sample 705-21). Outward diffusion of FeS in sphalerite has previously been invoked by Barton and Skinner (1979) to explain anomalous high-pressure estimates from sphalerite immediately adjacent to pyrrhotine. In the Foss deposit, outward diffusion of FeS in sphalerite (to varying extents) seems to be widespread, and is not restricted to mutual grain boundaries with pyrrhotine.

As these processes have opposing effects on sphalerite composition, the application of the sphalerite geobarometer using the mean of a number of analyses of sphalerites which show evidence of having been buffered by pyrite + hexagonal pyrrhotine, need not necessarily yield peak metamorphic pressures. The centres of relatively large (> 100 μm) sphalerite grains within fluid-buffered equilibrium domains (but not always in contact with pyrrhotine) are taken as the most suitable compositions for geobarometry. These compositions (taken from 705-9, 80-30A, 429-8, and other samples) range from 10.4 to 12.7 mol. % FeS, from which pressures of 9.7–6.9 kbar are calculated using the equation of Hutchison and Scott (1981) (fig. 10).

Comparison of silicate and sphalerite geobarometers. Estimates of peak metamorphic pressures in the Aberfeldy area from several silicate geobarometers (Table II), compare favourably with pressures in excess of 7 kbar suggested by the selective application of the sphalerite geobarometer.

Aluminosilicate-bearing rocks have not been found in the vicinity of the deposit, but kyanite is recorded by Sivaprakash (1982) from Grandtully (about 6 km to the SE), and by Wells and Richardson (1979) from Schiehallion (about 10 km to the W.; see fig. 1). Recent recalculations of the plagioclase–garnet–kyanite–quartz equilibrium (Newton and Haselton, 1981) suggest that the pressures derived by these authors may be several (1–3) kilobars too high.

Metamorphic temperatures derived from calcite–dolomite geothermometry by Sivaprakash (1982) and from unpublished data, range from 550 to 420 °C, which suggests that retrograde re-equilibration of carbonates is common. The temperature range 540–580 °C derived from garnet–biotite and garnet–hornblende geothermometry, is regarded as representative of peak metamorphic temperatures. Temperatures in this range are also indicated by $\delta^{34}\text{S}$ fractionations between some coexisting sulphide and sulphide–baryte pairs (Willan and Coleman, 1981, and unpublished work).

Further petrological work has supported the suggestion by Fortey and Beddoe-Stephens (1982) that much of the celsian occurring at Aberfeldy was formed by the post-deformational replacement of the platy mineral, cymrite, by the reaction:

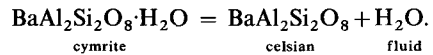


TABLE II. *Estimates of metamorphic temperatures and pressures in the Aberfeldy area*

Author	Area	Mineral equilibria	T °C	P kbar
Wells and Richardson (1979)	Schiehallion (Dalradian)	Plag-gt-ky-qtz Garnet-biotite ^a	560 ± 50	12 ± 1.5
Wells (1979)	Schiehallion (Moine)	Hb-plag-qtz-gt-ep Garnet-biotite ^a Gt-hornblende		
Sivaprakash (1982)	Aberfeldy-Grandtully	Plag-gt-ky-qtz Ep-gt-plag-qtz Garnet-biotite ^a	500–580	10 ± 1 8–10
Moles (1983) and unpublished data	Foss deposit, Aberfeldy	Calcite-dolomite ^b Gt-hornblende ^c Calcite-dolomite ^b Cymrite-celsian ^d Sph-py-po	420–550 540–580 480–530	> 7.0* 8.5 ± 1.5 6.8 ± 0.3 6.1 ± 0.1
Willan (1980, 1981)	Aberfeldy deposits	Sph-py-po		
Willan and Coleman (1981)	Aberfeldy deposits	$\delta^{34}\text{S}$ of sulphide and baryte pairs	550 ± 50	

* at $T = 540$ °C (see text).

Calibrations used: ^a Ferry and Spear (1978); ^b Bickle and Powell (1977); ^c Graham and Powell (in prep.);

^d Nitsch (1980).

Cymrite relics have been found in many celsian-bearing rocks, and the presence of aligned inclusions of quartz, rutile, and sulphides in coarse celsian rock suggests the replacement of a folded cymrite fabric. The reaction has been calibrated experimentally by Nitsch (1980) and further experimental work is in progress (Moles, 1983) to ascertain the displacement of the reaction curve by substitution of (K + Si) for (Ba + Al) in both cymrite and celsian (cf. Reinecke, 1982). Using the pure end-member calibration of Nitsch (fig. 10), a minimum pressure of 7 kbar at $T = 540^\circ\text{C}$ is indicated by the reaction.

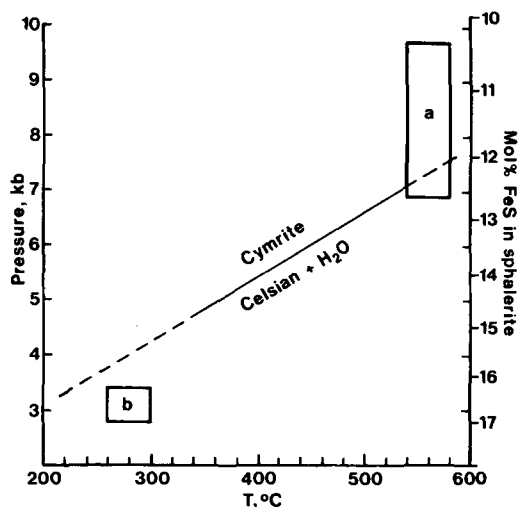


FIG. 10. The equilibrium curve for the reaction, cymrite = celsian + H_2O , from Nitsch (1980). Mol. % FeS scale refers to sphalerite buffered by pyrite + hexagonal pyrrhotine (fig. 9). Boxes labelled a and b correspond to those in fig. 9 and represent estimates of peak and retrograde P , T conditions in the Foss deposit.

The widespread replacement of cymrite in the Aberfeldy deposits suggests that lithostatic pressures were decreasing and/or temperatures were increasing in the area after the development of tectonic fabrics (Moles, 1983). Annealing and continued re-equilibration of sphalerites buffered by pyrrhotine + pyrite during this period may account for some of the spread in pressures derived by sphalerite geobarometry. Previously published results from the application of the sphalerite geobarometer at Aberfeldy (Willan, 1980, 1981; Table II) appear to be underestimates. Willan used a small number of sphalerite grains stated to be in mutual contact with pyrite + pyrrhotine and lacking evidence of retrograde alteration. Unfortunately, the

detailed textural relationships of these sphalerites are not described.

Primary sphalerite compositions

Depositional growth zoning in sphalerite, characterized by abrupt and often oscillatory variations in minor element content, has been observed in several non-metamorphosed stratabound base-metal deposits, such as McArthur River (Croxford and Jephcott, 1972) and Bleiberg, Austria (Schroll *et al.*, 1983), and in Mississippi Valley type deposits (McLimans *et al.*, 1980). However, sphalerite zonation of this type is absent at Aberfeldy, and it is inferred that depositional growth zoning, if originally present in the sphalerite, has been erased by recrystallization and intracrystalline diffusion during prograde metamorphism (Barton, 1970).

The presence of encapsulated sphalerites of contrasting composition may provide evidence for the homogenization of the matrix sphalerite in massive sulphide rocks. In rocks containing disseminated sphalerite with a bimodal distribution of compositions, some sphalerite grains of intermediate composition (fig. 5b) may have formed by the coalescence of several grains of end-member composition. Coalescence during grain coarsening may account for the scarcity of mutual grain contacts between sphalerites of contrasting composition.

Partitioning of minor elements between sphalerite and coexisting phases during metamorphism must also be considered as a mechanism by which primary sphalerite compositions may have been modified. Marginal depletion in the Fe and Mn contents of sphalerite in a matrix of recrystallized carbonate, has been described above (fig. 8). Cathodoluminescence studies have revealed striking oscillatory zonation patterns, which correspond to variations in Fe and Mn concentrations determined on the microprobe, in coarsely recrystallized dolomite and calcite. The association of zoned sphalerite with recrystallized carbonate suggests that Fe and Mn have diffused out of the sphalerite and entered the carbonate matrix during metamorphism. Preferential partitioning of zinc from the matrix into the sphalerite may also have occurred, but the zinc content of carbonates is below detection limit on the microprobe. Diffusion profiles in sphalerite have often been frozen in (fig. 8b), but in some carbonate rocks individual sphalerite grains appear to have homogenized after marginal depletion in Fe and Mn, resulting in a positive correlation between grain size and minor element content.

Encapsulated sphalerites are often enriched in Mn in comparison with sphalerites of similar Fe

content in the matrix. This may be of primary origin, or could be due to a preferential partitioning of manganese into sphalerite from the surrounding pyrite during metamorphism. Campbell and Ethier (1983) have demonstrated a positive correlation between the manganese contents of coexisting sphalerite, pyrite and pyrrhotine in a laminated sulphide rock from the Sullivan deposit. In the Foss deposit, the manganese contents of iron sulphides are very low (Willan, 1980), and the grain size of encapsulated sphalerites does not appear to correlate with the degree of manganese enrichment. Therefore, pyrite-sphalerite partitioning of Mn (and Fe) has probably not affected primary sphalerite compositions. Buffering of sp_{FeS} by fluids in equilibrium with pyrite + pyrrhotine appears to result in the depletion of sp_{MnS} (e.g. sample 80-30A, fig. 4), but the reason for this is not clear.

In summary, the following criteria allow the selection of primary sphalerite compositions which are least likely to have been modified during metamorphism:

(1) The absence of adjoining or nearby pyrrhotine (or retrograde marcasite and pyrite pseudomorphs of pyrrhotine).

(2) The occurrence of sphalerite as small disseminated grains rather than as a continuous matrix.

(3) The absence of zoning, or of a strong positive correlation between grain size and minor element content (particularly if the matrix is recrystallized carbonate rock).

(4) The occurrence of matrix sphalerite of similar composition to sphalerite grains encapsulated in pyrite.

These criteria are most frequently satisfied in baryte rocks containing disseminated sulphides. However, primary sphalerites have been recognized in other mineralized lithologies such as quartz celts cherts (e.g. samples 80-30A and 429-8) and also in some metasediments, notably thick (> 1 m) beds of graphitic dolomite rock containing sphalerite laminae.

Primary sphalerites and ore formation. Within many samples, a bimodal distribution of sphalerite compositions is observed, the Fe-poor fraction usually predominating (fig. 5). Primary Fe-rich sphalerites are commonly finer-grained, more equant in shape and more often encapsulated in pyrite than the Fe-poor sphalerite in the same rock. The sum of these textural features suggest that the Fe-rich sphalerite may have been precipitated earlier than both the Fe-poor sphalerite and much of the pyrite.

To account for the origin of a range of primary sphalerite compositions within the same rock, it is necessary to speculate on the mechanisms of ore

formation. Many authors have sought to define the nature of ore-forming fluids and the physico-chemical environment of deposition of submarine-exhalative deposits (e.g. Finlow-Bates, 1980; Large, 1981; Russell *et al.*, 1981b). The chloride-complex models of Sato (1972, 1973) and Large (1977) for ore solutions forming massive sulphide deposits in volcanic terrains, are generally accepted as broadly applicable to sedimentary-exhalative deposits.

The progressive change in temperature, total sulphur concentration, and oxygen fugacity in the brines which formed the Kuroko deposits has been described by Sato (1977). Decrease in the Fe content of sphalerite with stratigraphic height in the Kuroko deposits (Urabe, 1974) is ascribed largely to a decline in temperature (typically by 50 °C from the stockwork to the top of the stratiform ore). However, this trend may also be related to an increase in total sulphur concentration and oxygen fugacity in the brines (Finlow-Bates, 1980), which also favours the formation of baryte.

The following scenario is envisaged during formation of the ore-bearing stratiform lenses of the Foss deposit. During the expulsion of relatively hot (> 200 °C?), saline, weakly acidic, and sulphur-poor metalliferous brines at exhalative vents, fine-grained and Fe-rich sphalerite (or wurtzite; cf. Styrst *et al.*, 1981; Scott, 1983) was precipitated and carried upwards in the buoyant brine plume together with sulphides of iron and lead (Solomon and Walshe, 1979). The brine then spread laterally as it entrained sea-water (Turner and Gustafson, 1978) and became cooler, less saline, more oxidized and enriched in sulphur (derived by bacteriogenic reduction from sea-water sulphate; Willan and Coleman, 1981). Sphalerite with a lower Fe content precipitated from the bottom-hugging or buoyant brine layer, together with baryte, pyrite, and (with increasing f_{O_2}) magnetite. Alternatively, Fe-poor sphalerite may have crystallized within the unconsolidated ore as reduced sulphur became available (cf. McArthur River ore: Croxford, 1968).

In this model, the Fe-rich sphalerite fraction is regarded as allochthonous whereas the Fe-poor sphalerite crystallized *in situ*. If this is the case, one might expect to find a lateral variation in the Fe content of the Fe-poor sphalerite fraction with increasing distance from the exhalative centre, but less variation in the Fe-rich fraction. However, a simple pattern in the distribution of primary sphalerite compositions has not emerged from a study of the lower mineralized horizon in Foss East (fig. 2) using over 50 samples. Variation in primary sphalerite compositions is greater between samples taken through drill hole intersections of this horizon, than from east to west in the area.

Stratigraphic variation in sphalerite compositions

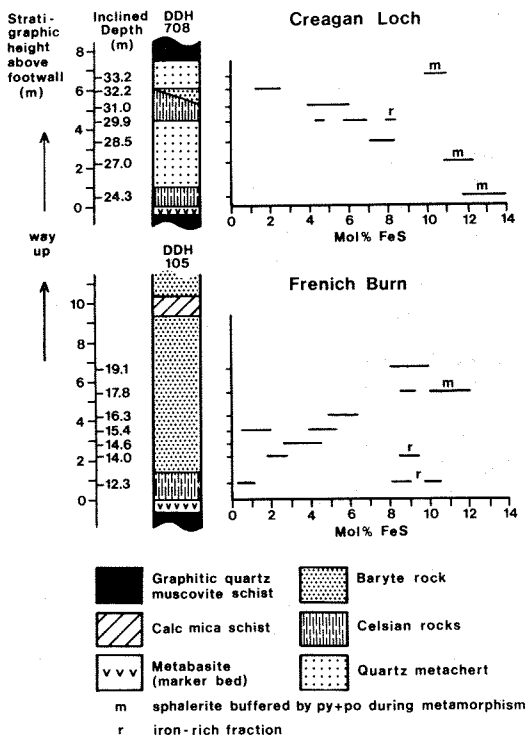


FIG. 11. Primary sphalerite compositions in samples from two drillhole intersections of the lower mineralised horizon (M3) in Foss East, located near IGS boreholes 1 and 3 (see fig. 2).

can be discerned locally (fig. 11). Sphalerite becomes progressively Fe-poor towards the hanging wall near the eastern limit of the deposit in Foss East (near IGS borehole 3), where a lense of baryte overlies thick sulphidic cherts deposited on the downthrown side of a probable syndimentary fault (Laux *et al.*, in prep.). This stratigraphic trend, which is similar to that observed in the Kuroko deposits, may be due to an increase in f_{O_2} and decrease in temperature and salinity as the ponded brine mixed with the overlying sea-water. This hypothesis is supported by sulphur isotope studies which show a marked decrease in $\delta^{34}S$ of baryte and pyrite near the stratigraphic hanging wall (Willan and Coleman, 1981; Moles, in prep.).

In contrast to the trend described above, the Fe content of primary sphalerite increases stratigraphically upwards through the footwall chert and the overlying baryte in the vicinity of the Frenich Burn headwater (figs. 2 and 11). Sphalerite is absent from the upper part of the relatively thick baryte unit in this area (Coats *et al.*, 1981; IGS borehole 1), which formed by the stacking of five

mineralized horizons and wedging out of the intervening metasediments (Laux *et al.*, in prep.). This trend in sphalerite compositions may reflect a decrease in sulphur concentration due to the restriction of bacterial activity in a relatively shallow, oxidizing environment during deposition of the baryte. Oxidizing conditions are also suggested by the absence of carbonaceous matter in the intervening and overlying metasediments in this area.

Primary sphalerites have been described from several other stratabound base-metal deposits, but analytical data from unmetamorphosed deposits is scarce. Croxford (1968), Croxford and Jephcott (1972), and Oehler and Logan (1977) describe bedded, disseminated and colloform sphalerites in black shales from the McArthur River deposit, Northern Territory, Australia. The sphalerite varies from colourless to red-brown in appearance, corresponding to a range in iron content from 1.4 to 11.2 mol. % FeS. Fe-rich compositions occur late in the paragenesis in concentrically zoned colloform and vein sphalerite. A similar increase in sp_{FeS} with paragenetic sequence has been observed by Schroll *et al.* (1983) in zoned colloform sphalerite at Bleiberg, Austria.

Pyrrhotine is absent from the McArthur River deposit, but is a major constituent of the low-grade metamorphosed deposit of Hilton, Queensland. At Hilton, pyrrhotine and chalcopyrite are associated with Fe-rich sphalerite in the upper part of the ore horizon (Mathias *et al.*, 1973). Elsewhere in the deposit, sphalerite ranging in colour from pale yellow to dark brown occurs as disseminations and late-stage veinlets. The association of Fe-rich sphalerite with pyrrhotine in metamorphosed sulphide deposits containing a wide range of sphalerite compositions, has also been observed at Gamsberg, South West Africa (Rozendaal, 1978, and Stumpf, 1979) and at Balmat, New York (Doe, 1962, and Scott, 1976). The preservation of primary sphalerite compositions in some rocks, while in others sphalerite has been buffered by coexisting pyrite + pyrrhotine, is one feature which these deposits have in common with Foss.

Conclusions

Disillusionment with the sphalerite-pyrite-pyrrhotine barometer has been expressed by several authors in recent years (e.g. Stumpf, 1979; Plimer, 1980) and, indeed, 'sphalerite geobarometry does not appear to provide a panacea for estimating pressures in metamorphic rocks' (Brown *et al.*, 1978). This is due to the extensive resetting of sulphide compositions at lower pressures in many metamorphosed orebodies. The present study

amplifies the need for detailed textural studies before applying the geobarometer, but also illustrates the variety of other geological information, pertaining to metamorphism and to the environment of deposition, which can be derived from sphalerite studies.

In many granoblastic baryte, quartz and feldspar rocks in the Foss deposit, the variable FeS and MnS contents of disseminated sphalerite grains appear to have remained essentially unaltered through metamorphism to garnet-grade conditions. Very localized buffering of sphalerite adjoining pyrrhotine grains is evidence of small (1 cm–1 mm) equilibrium domains in these lithologies. In contrast, sphalerite in the enclosing mica schists has undergone widespread buffering by fluids in equilibrium with pyrite + pyrrhotine, which suggests that large equilibrium domains are associated with penetrative deformation. In rocks which lack evidence of retrograde alteration, the occurrence of buffered sphalerites containing 10.4–12.7 mol. % FeS indicates that peak metamorphic pressures of 7–10 kbar were attained in the Aberfeldy area. Similar pressures are also indicated by silicate geobarometers including the cymrite–celsian reaction (Moles, 1983). Continued buffering of sphalerite coexisting with pyrrhotine (+pyrite) to low pressures may be used in charting the *P–T* path in the Aberfeldy area during cooling and uplift.

Depositional growth zoning, if originally present in sphalerite of the Foss deposit, has been erased by intracrystalline diffusion during metamorphism. Partitioning of Fe and Mn between sphalerite and enclosing phases has produced diffuse zonation in sphalerite in recrystallized carbonate rocks.

Primary sphalerite compositions vary in vertical transects through mineralized horizons, which suggests that mineral chemistry relates to depositional processes. Bimodal sphalerite compositions occur in many mineralized rocks: the Fe-rich sphalerites are usually subordinate in quantity and grain size to the Fe-poor sphalerite, and are often encapsulated by pyrite. The Fe-rich fraction is thought to have precipitated from the metalliferous brines during their expulsion from hydrothermal vents, and to have been carried in suspension in the laterally spreading brines. The Fe-poor sphalerite subsequently precipitated from cooler, bottom-hugging brine layers, or within the ore sediment as reduced sulphur became available.

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