# CONDITIONS OF METAMORPHISM OF THE OUTOKUMPU CU - CO - ZN DEPOSIT FROM SPHALERITE GEOBAROMETRY

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Electron microprobe analysis was used to determine Zn and Fe in homogeneous samples of sphalerite in mutual contact with pyrrhotite and pyrite from the disseminated ore layer stratigraphically high in the Keretti orebody at Outokumpu, Finland. On the bases that the composition of sphalerite (1) becomes less Fe-rich with increasing pressure in a system in which aFeS is buffered by pyrrhotite and pyrite and (2) is independent of temperature in much of the geologically important temperature range (c. 300°-650°C), a mean pressure of  $3.4 \pm 0.3$ kb (with a pressure range of 2.8–4.3 kb) has been calculated. This corresponds to the previous estimates of peak metamorphic conditions of 4 kb (at 500°C) and 3.5  $\pm$  1kb (at 600°  $\pm$ 50°C) based on silicate mineral assemblages. Zn and Fe determinations for sphalerite associated with an inequilibrium mineral assemblage such as remobilized pyrrhotite and chalcopyrite in which visible exsolution lamellae are present, give improbably high estimates of pressure. Determinations for sphalerite in contact with only one additional phase (pyrrhotite or pyrite) also give higher estimates than when buffered by the divariant assemblage pyrrhotite + pyrite. Previously published estimates correspond with those obtained for sphalerite in contact with pyrrhotite only, estimates that are discarded on account of the absence of a requisite buffer assemblage.

*Key words:* sphalerite, electron probe data, zinc, iron, geologic barometry, metal ores, metamorphism, Proterozoic, Keretti, Outokumpu, Finland.

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## INTRODUCTION

Pressure and temperature conditions during regional metamorphism of the Outokumpu orebodies of North Karelia, eastern Finland, have been estimated mainly from analysis of mineral assemblages in the country rocks. Evidence presented in Gaál et al. (1975) and Koistinen (1981) indicates greenschist facies (biotite grade) metamorphism during the  $D_1$  fabric-forming deformational phase: the metamorphic conditions during the earlier development of blind quartz veins before the initiation of F<sub>1</sub> folds were not established by these authors. On the basis particularly of staurolite - mica fabric relations, the peak of metamorphism (at middle amphibolite facies) has been established to have taken place between the  $D_{2c}$  and  $D_4$  defomational phases that are expressed both in the vicinity of the orebodies and in the surrounding region (Koistinen 1981, Table 1; Bowes et al. 1984, Table 2). With porphyroblasts of andalusite appearing to post-date most of the staurolite, and idioblastic kyanite and sillimanite being of sporadic occurrence, Koistinen (1981) proposed conditions of c. 500°C and 4 kb during the metamorphic peak. Based on element partitioning in co-existing phases in cordierite - anthophyllite (± cummingtonite) - almandine - staurolite rocks that are interpreted as the metamorphic products of a leached stockwork zone affected by pre-metamorphic fluid movements, Treloar et al. (1981) determined a metamorphic peak at  $600^{\circ} \pm 50^{\circ}$ C and  $3.5 \pm 1$  kb, relating to a static phase of mineral growth between  $D_2$  and  $D_3$ .

The only evidence for metamorphic conditions previously obtained from the Outokumpu orebodies themselves used sphalerite geobarometry. Based on limited sampling from the Keretti orebody as part of a regional study of metamorphosed Proterozoic ores in Finland, Törnroos (1982) obtained a range of model pressures from 4.3 to 6.0 kb, ie. higher than the estimates of pressures from the host mineral assemblages. In order to assess the integrity of the geobarometric estimates from the relatively small sample of sphalerites used by Törnroos, the sphalerite geobarometer has been applied to a larger sample range with sample selection taking into account the documented constraints on the application of the method.

# PRINCIPLES OF SPHALERITE GEOBAROMETRY

Because sphalerite is one of the more refractory

sulphides and displays a wide range of Fe concentrations as a function of the conditions of formation, it can be a useful tool in deciphering environments of sulphide deposition and metamorphism. The Fe content of sphalerite is related to three components, viz. pressure (P), FeS activity (aFeS), and temperature (T) (cf. Scott 1976).

#### **Pressure** (P)

The potential use of sphalerite composition as a geobarometer was originally discussed by Barton and Toulmin (1966) who devised a deterministic curve for the iron content that showed the partial molar volume of FeS in sphalerite to be large compared with that of ZnS as evidenced by the substantial increase in the cell edge of sphalerite with increasing iron content. As a consequence it was proposed that in a system in which aFeS is buffered by pyrite + pyrrhotite, sphalerite should become less Fe-rich with increasing pressure. Scott and Barnes (1971) calculated this change in sphalerite composition with pressure and showed that within certain constraints it could be used as a geobarometer.

# FeS activity (aFeS)

The aFeS is a measure of the chemical potential of FeS in solution in the Fe - Zn - S system at the prevailing conditions, compared with its chemical potential at a specified standard state. The activity is expressed as the effective concentration of FeS relative to the true concentration at its standard state (both having the same chemical potential). Activity is defined only in so far as the standard state to which it refers is also defined.

The key point about the aFeS component is that variations in aFeS in the Fe - Zn - S system also change the FeS content of sphalerite in a way which is not neccessarily systematically related to pressure (or temperature). In order to be useful for geobarometry the sphalerite grain must be buffered by one or more iron sulphide phases. This means that sphalerite must be in equilibrium with at least one Fe sulphide phase during metamorphism. The function of the buffer is to provide or consume FeS at a constant temperature in order to maintain a constant value for aFeS in the system. Thus the influence of the buffer on sphalerite composition is in the removal of variations in the FeS content of sphalerite which would have otherwise been caused by changes in aFeS.

Scott (1974) demonstrated theoretically that hexagonal (ie. high temperature) pyrrhotite alone can act as a buffer because the relationships between aFeS, pyrrhotite composition and T are known and are independent of P. However coexisting pyrrhotite can undergo changes on cooling which may reduce its reliability as a single phase buffer (cf. Genkin 1971). Addition of pyrite to the assemblage buffers aFeS and overcomes the problem of having to preserve pyrrhotite compositions from high temperatures in order to use sphalerite as a geochemical tool (Scott 1974). For this reason, and because coexisting sphalerite + hexagonal pyrrhotite + pyrite are common in nature, the three-phase assemblage forms the basis for reliable use of the sphalerite geobarometer.

#### **Temperature** (T)

The effects of temperature on the composition of sphalerite buffered by pyrrhotite and pyrite were originally examined by Scott (1973) who measured sphalerite composition on the hexagonal pyrrhotite + pyrite solvus by hydrothermal recrystallization experiments over a wide range of pressures and temperatures. These data, subsequently refined and extended experimentally (e.g. Scott et al. 1977, Lusk & Ford 1978, Hutchison & Scott 1981), show that the slope of the sphalerite + pyrite + hexagonal pyrrhotite solvus isobars between 2.5 and 10.0 kb is essentially vertical, and consequently sphalerite composition is independent of temperature below approximately 650° C. The lower limit of the temperature-independent range occurs where the vertical isobars encounter the slope reversal of the pyrite + pyrrhotite solvus (265° C at 1 bar) or the stability field of monoclinic pyrrhotite, neither of which are known to occur at high pressures but are probably well below 300° C at 5 kb (cf. Scott & Kissen 1973).

#### Assessment

With the composition of sphalerite being *independent* of temperature but dependent on pressure within much of the geologically important temperature and pressure ranges, the mole % FeS can be used as an indicator of the pressure of metamorphism of ores. Hutchison and Scott (1981) describe this pressure dependence of sphalerite in equilibrium with pyrite and pyrrhotite by the equation  $P = 42.30-32.10 \log$  mole % FeS, where P is in kb and the standard error is  $\pm 0.30$  kb.

The presence of other elements in the system besides Zn, Fe and S has been shown to have a negligible effect on the geobarometer except where they occur in sphalerite or in pyrrhotite in large enough amounts either to change the partial molar volume of FeS in sphalerite or to change the aFeS of the system. Only rarely, for example, will Co and Ni reach high enough concentrations in the Fe sulphides to cause a significant decrease in FeS (Barton & Toulmin 1966). In the cases of Cd and Mn which are common impurities in sphalerite, even concentrations up to several wt % higher than normally found in natural sphalerites do not alter the location of the isobars (Craig & Scott 1974).

Of the remaining elements commonly found in sphalerite, only Cu presents a problem (cf. Craig & Scott 1974, Hutchison & Scott 1981). Natural sphalerites normally contain less than 0.5 % copper in solid solution (cf. Törnroos 1982), but the common occurrence of chalcopyrite exsolution blebs indicates that solid solution is much greater at high T and P. The question therefore is whether or not the additional Fe in the dissolved and exsolved chalcopyrite has affected the phase relations in the system, and thus the viability of the geobarometer. Phase data in the system Cu -Fe - Zn - S indicate that CuFeS<sub>2</sub> and FeS are separate components in sphalerite solid solutions and thus the Fe in the exsolved chalcopyrite or dissoved CuFeS<sub>2</sub> component should not be included in the estimation of pressure (Craig & Scott 1974). Any sphalerite which is heterogeneous in FeS and which contains chalcopyrite blebs in excess of the amount which can be accounted for by dissolution

and exsolution under equilibrium conditions should be avoided in the use of the geobarometer (Törnroos 1982). This constraint has been applied in the present study

#### Constraints

In order to adhere to the documented constraints on the application of the sphalerite geobarometer, and for valid comparison with measurements made in previous analyses of Outokumpu sphalerite compositions, the following factors were taken into account as had been done by Törnroos (1982).

- The temperature of metamorphism of the host rocks was established to be higher than the abrupt reversal of the pyrite + hexagonal pyrrhotite solvus (265° C at 1 bar) and lower than the upper limit of the temperature-independent region (c. 650° C).
- (2) The sphalerites analysed were in mutual contact with pyrrhotite and pyrite (ie. crystals that had equilibrated with high temperature hexagonal pyrrhotite and pyrite).
- (3) Compositionally heterogeneous grains and grains with chalcopyrite exsolutions were avoided.
- (4) Grains containing other elements in significant amounts were treated with caution.

# SAMPLE SELECTION, RESULTS AND DISCUSSION

Sample selection, using the above criteria, also took into account the fact that many of the contact relationships of sphalerite – pyrrhotite – pyrite in the orebodies relate not to their original dispositions but to their remobilization and the establishment of disequilibrium conditions during deformation. Accordingly, although remobilized ore was sampled for comparative purposes, care was taken in the sample selection of sphalerites for geobarometry to avoid those which exhibited obvious remobilization textures in case equilibrium had not been reached and aFeS had not been completely buffered. The sections used for analysis were from the disseminated ore layer stratigraphically high in the Keretti orebody, within carbonaceous quartz-rich rock (quartzite of Koistinen 1981, p. 120 and Treloar et al. 1981, fig. 2) and away from any recognisable  $F_1$  hinge or other high strain zone. Pyrite is the most common sulphide mineral in the quartz-rich layers at this level but is also found in association with pyrrhotite and sphalerite (± chalcopyrite) where the quartz-rich rock becomes enriched in carbon. Grain associations were selected where chalcopyrite was absent.

Average (of 3) microprobe analyses for thirteen selected sphalerite grains associated with pyrrhotite and pyrite are given in Table 1. In addition, microprobe analyses for sphalerites found in association with other sulphide assemblages are given for comparison.

The most consistent FeS contents in the sphalerites are from the thirteen sphalerite + pyrrhotite + pyrite assemblages examined; they cluster around 16.5 mole%, with a range of 15.3 to 17.5 mole%. The corresponding mean pressure is calculated using the equation of Hutchison and Scott (1981) to be 3.4 ( $\pm$  0.3) kb with a pressure range of 2.8 to 4.3 kb. This mean pressure, and the relatively narrow pressure range expressed by the sphalerite compositions, agrees with the pressure estimate of 3.5  $\pm$  1 kb (at 600° C) obtained by Treloar et al. (1981) using element partitioning, and is consistent with P–T conditions (4 kb at 500° C) deduced by Koistinen (1981).

The sensitivity of the sphalerite geobarometer to any suggested inequilibrium in the mineral assemblage with which it formed is illustrated by a number of the additional measurements that were made. Five samples of sphalerite grains in association with remobilized pyrrhotite and chalcopyrite, in which visible chalcopyrite exsolution lamellae are present, give pressures in the range of 7.4 to 10.4 kb. These improbably high estimates suggest that solid solution between sphalerite and chalcopyrite had caused re-equilibration of the sulphide system.

The remaining analyses are for sphalerites in contact with only one additional phase (pyrrhotite or pyrite). In the case of two samples of sphaler-

Sample	% Fe	% Zn	Mole% FeS	P (kb)
sp+pyrr+py	8.7065	56.8432	15.32	4.30
sp+pyrr+py	9.6057	56.3741	17.04	3.05
sp+pyrr+py	9.4438	54.6970	17.27	2.90
sp+pyrr+py	9.2652	56.3605	16.44	3.45
sp+pyrr+py	9.5959	57.2812	16.75	3.25
sp+pyrr+py	9.1778	54.1948	16.93	3.15
sp+pyrr+py	9.5887	54.8788	17.47	2.80
sp+pyrr+py	8.8323	56.2536	15.70	3.95
sp+pyrr+py	9.0881	55.7431	16.30	3.55
sp+pyrr+py	9.3050	55.9697	16.63	3.30
sp+pyrr+py	9.0763	56.6065	16.03	3.70
sp+pyrr+py	9.6702	55.8316	17.32	2.85
sp+pyrr+py	9.0200	55.9292	16.13	3.70
sp+pyrr(+cpy)	6.2562	56.4210	11.09	8.40
sp+pyrr(+cpy)	6.2147	57.5411	10.80	8.95
sp+pyrr(+cpy)	6.4791	54.7464	11.83	7.40 -
sp+pyrr(+cpy)	5.9815	57.6424	10.38	9.80
sp+pyrr(+cpy)	5.8008	57.5145	10.08	10.40
sp+pyrr	7.2129	56.2254	12.83	6.38
sp+pyrr	7.1833	56.2249	12.78	6.25
sp+py(encl.)	9.1720	56.1512	16.33	3.50
sp+py	5.8437	59.0649	9.89	10.90
sp+py	5.7658	59.2843	9.73	11.10
sp+py	6.0754	58.0840	10.46	9.55

Table 1. Average (of 3) microprobe analyses of sphalerite samples from the Keretti orebody, Outokumpu and calculated estimates of pressure ( $\pm 0.30$  kb).

sp sphalerite; pyrr pyrrhotite; py pyrite; cpy chalcopyrite

ite in contact with pyrrhotite (with no visible chalcopyrite exsolutions and low wt % Cu), a pressure estimate of c. 6.3 kb was obtained. This is still considerably higher than the range established for sphalerites buffered by the divariant assemblage pyrrhotite + pyrite, and reflects the significance of having an aFeS buffer. The compositions and the pressure estimate are, however, close to those given in Törnroos (1982). Sphalerite grains in contact with pyrite (3 samples) give pressures as high as 11.1 kb. The only exception to this "high pressure" trend is a single sphalerite grain encapsulated within metablastic pyrite which yields a 3.5 kb pressure (ie. the same as the sphalerite + pyrrhotite + pyrite assemblages). Hutchison and Scott (1981) suggested that such sphalerites represent high P–T equilibrium assemblages and thus could be expected to have FeS contents very similar to sphalerites in mutual contact with pyrrhotite and pyrite. While a single analysis can neither prove nor refute this finding, its agreement with the main group of three phase measurements, and its significant departure from the measurements for non-enclosed sphalerite pyrite, is nevertheless consistent with the interpretation of Hutchison and Scott.

An FeS content in the range 13.5 to 15.3 mole% was obtained by Törnroos (1982) using samples from the Keretti orebody, corresponding to pressures of 4.3 to 6.0 kb. This range is significantly higher than the pressure estimates from the silicate mineral assemblages in the country rocks

given by Koistinen (1981) and Treloar et al. (1981).

Comparing the two sets of analyses, two observations can be made. Firstly, in evaluating his results, Törnroos discusses the fact that they suggest that the pressure of metamorphism in the ore at Outokumpu differs from that in the surrounding rocks: the present study suggests that this apparent difference is not real, and that both the orebodies and their host rocks were deformed under the same metamorphic conditions. Secondly, the role of remobilization of sulphides in preventing equilibration, and hence influencing the pressures determined by sphalerite geobarometry, is also acknowledged by Törnroos. Although no assessment of the ore association from which Törnroos's samples were taken can be made, it seems likely that the reason for the reported higher pressures was linked to ore remobilization with related sulphide re-equilibration having affected the measurements on which the estimates were based. In the present study the selection of mineral assemblages in structural positions least likely to be affected by mobilization means that confidence in the validity of the current pressure determinations is considered to be high.

# CONCLUSIONS

(1) The application of the sphalerite geobarometer to the Outokumpu ores yields a set of consistent pressure estimates in the range 2.8–4.3 kb (mean  $3.4 \pm 0.3$  kb).

(2) The new results are consistent with the estimates of conditions of metamorphism given by Koistinen (1981) and Treloar et al. (1981) based on mineral assemblages in host rocks of the orebodies.

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