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Sphalerite geobarometry in the Balmat-Edwards district, New York[1]

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Abstract

Sphalerite–pyrite–pyrrhotite barometry was undertaken in the Balmat-Edwards district in the NW Adirondacks to determine the pressures in the metamorphosed ore body. Metamorphic temperatures were estimated at 625 ± 25°C using calcite–dolomite thermometry. Sphalerites with extensive exsolution of chalcopyrite are very inhomogeneous, even within ten microns of the po + py + sp triple point, and have iron contents of 16–12 mole percent FeS, corresponding to 3–7 kbar (Scott, 1973). This local variation in pressure is unreasonable; either the system did not equilibrate during metamorphism, erratically reequilibrated afterwards, or exsolved chalcopyrite has variably affected the barometer. A few sphalerites without microscopic chalcopyrite blebs yielded consistent FeS contents of 13–12 mole percent where touching pyrrhotite–pyrite and correspond to pressures of 6.5–7.5 kbar. These data and the presence of sillimanite, indicative of pressures less than 6–6.5 kbar at 600–650°C, in the adjacent paragneisses suggest that the Balmat district was subject to a regional metamorphism of 6.5 ± 0.5 kbar. Incautious application of the sphalerite barometer based on a few samples or on heterogeneous materials can lead to large errors in estimated pressures.

Introduction

Since Kullerud's (1953) study of the system ZnS–FeS, many workers have applied the sphalerite "geothermometer" to diverse types of ore deposits. The geothermometer was based upon an inferred dependence of the iron content of sphalerite on the temperature of formation. Barton and Toulmin (1966) demonstrated that the original "solvus" was incorrect and that the FeS in sphalerite is buffered by the composition of the pyrrhotite with which it is in equilibrium. Scott and Barnes (1971) concluded that the iron content of sphalerite in equilibrium with pyrite and pyrrhotite was essentially temperature insensitive in the range 300–600°C but that the pressure effect was sufficiently large to allow the iron content of sphalerite to be a useful geobarometer. Scott reported further experiments in 1973 involving reversals which established the experimental basis for the sphalerite barometer.

Early estimates of the pressure in the Balmat-Edwards ore district on the NW flank of the Adirondacks, as summarized by Lea and Dill (1968), were 3–4 kbar. The presence of sillimanite in adjacent paragneisses restricts pressures to less than 6 kbar at 600°C, using Holdaway's (1971) Al_2SiO_5 diagram. Scott and Barnes (1971) offered Balmat as one of their test cases, using Doe's (1962) sphalerite data, and reported a pressure of 4.5 ± 1.0 kbar; when revised according to Scott's (1973) experiments, Doe's data yield 5.5 kbar. DeWitt (1976), in a regional study of sphalerite barometry across the Grenville province, reports a pressure of 6.5 kbar for Balmat. Scott (1976) reports new microprobe analyses for Balmat sphalerites, inferring pressures of 5.0 kbar from these data. The discrepancies are curious in that both Scott and DeWitt used the sphalerite barometer and the same microprobe reduction program (EMPADR VII) to generate their data. The present study was initiated to try to sort out the conflicting conclusions, and hopefully will provide a more accurate evaluation of pressure at Balmat to understand the metamorphism of the ore bodies in relation to the country rocks. Calcite–dolomite thermometry of marbles was undertaken to ensure that metamorphic temperatures in the Balmat-Edwards district were in the appropriate range (300–600°C) for application of the sphalerite geobarometer.

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Methods

Sphalerite and calcite compositions were determined by electron microprobe analysis, using an ARL-EMX electron microprobe analyzer with wavelength-dispersive PET, LiF, and TAP crystal spectrometers. A Kevex energy-dispersive detector and a Northern multi-channel analyzer were used for semiquantitative analyses and rapid identification of unknowns. An Ortex current digitizer was used to stabilize beam current, allowing the samples to be bombarded by a fixed number of electrons instead of collecting data for a fixed length of time. The accelerating voltages and sample currents employed for analyses were 15 kV and 0.01 microamps for the sphalerites and 10 kV and 0.005 microamps for the carbonates. Data reduction was made using EMPADR VII, developed by Rucklidge and Gasparrini (1969).

The sphalerites were analyzed for Fe, Zn, Cu, Mn, and Cd. Sulfur was not determined directly, but was inferred by a fixed stoichiometry function in the data reduction program. The calcites were analyzed for Ca, Mg, and Fe; carbon and oxygen were inferred from fixed stoichiometry. In order to minimize the correction functions outlined above, standards were employed which are as close in composition to the unknowns as possible. A synthetic troilite, prepared with excess iron, was used for the iron standard. The zinc standard was prepared from commercially available zinc sulfide. Synthetic cadmium sulfide and manganese sulfide standards were provided by Dr. Steven D. Scott of the University of Toronto. The total copper content of the Balmat sphalerites is low, and hence the loss of accuracy in using copper metal as the copper standard is negligible. The carbonate standards were natural calcites and dolomites that have been well analyzed by atomic absorption spectrophotometry.

Calcite–dolomite thermometry

Goldsmith and Heard (1961) and Goldsmith and Newton (1969) showed that the magnesium content of calcite in equilibrium with dolomite is temperature-dependent and hence a useful geothermometer. The phase relations in the system $CaCO_3$–$MgCO_3$ are nearly independent of pressure with an experimentally determined pressure dependence of only 0.003°C/bar (Goldsmith and Newton, 1969) up to 10 kbar. Therefore, knowing that the Balmat-Edwards district was metamorphosed at roughly 5 kbar is sufficient to choose a solvus. Goldsmith and Graf (1960) and Goldsmith *et al.* (1962) demonstrated that iron and manganese slightly alter the solvus, however, no corrections of this nature were involved in this study because the calcites of interest contain impurities in negligible amounts—analyses for iron typically gave results between 0.00 and 2.00 mole percent $FeCO_3$.

Because the carbonates are highly reactive, there is great potential for reequilibration of calcite by exsolution of dolomite or exchange of magnesium upon cooling. Therefore careful textural observation is required to interpret the resultant temperature data. The calcite and dolomite were easily distinguished by staining polished thin sections with a mixture of dilute HCl and Alizarin Red which selectively stains the calcite red. This technique allowed grains with microscopically visible exsolution to be identified optically and avoided.

In most Balmat samples the calcite and dolomite grains are relatively large, interlocking, and unaltered—increasing the likelihood that they were both present at the peak of metamorphism. Exsolution of dolomite from calcite usually takes one of three different forms: lamellar, patchy, or granular. Lamellar exsolution is the most readily recognized and the most rarely observed in the Balmat calcites. The second type, patchy exsolution, is somewhat more common, and generally appears as an irregular change from magnesian calcite to dolomite within a single grain. Granular exsolution involves complete migration of the exsolving dolomite to the grain boundaries where it forms an optically continuous grain. This type is difficult to detect, since the exsolved dolomite may be hard to distinguish from primary dolomite. Granular exsolution may not be recognized until microprobe results are obtained which show either compositional gradients across the calcite or anomalously low magnesium contents compared to other samples. The exsolution of dolomite lowers the magnesium content and therefore reduces the inferred temperature.

Results derived from apparently unexsolved calcites generally showed a sharp upper cut-off of magnesium values (and therefore of temperature) with some scatter to the low-magnesium side (Fig. 1). This is consistent with calcites partially reequilibrated by one or more of the exsolution processes described above. The inferred temperatures are in the range 530–620°C, but must be regarded as minima due to the uncertainty in evaluating the exsolution effects. Temperatures of 600–650°C are quite reasonable for the upper amphibolite facies metamorphism in the area and agree well with Bohlen and Essene's (1977) regional thermometry in the Adirondacks. On the basis of the present data, it is not possible to deter-

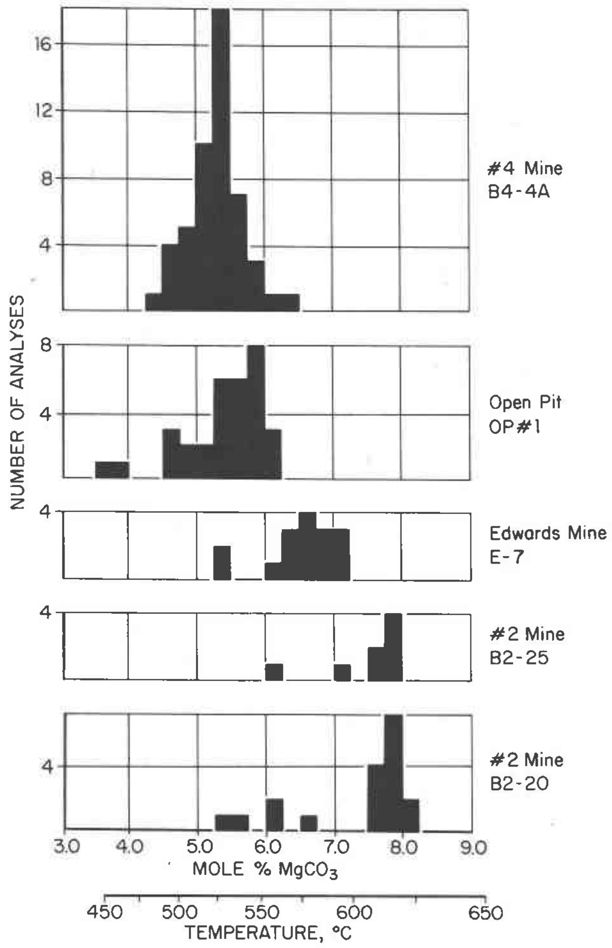


Fig. 1. Calcite-dolomite analyses. Temperature calibration from Goldsmith and Newton (1969).

mine whether the apparent temperature differences between the mines is real or due to reequilibration. If real, there must have been some local source of synmetamorphic heat to generate temperature differences of 90°C over such short distances. A much more extensive study of calcite-dolomite pairs and other independent geothermometers from the district would be necessary to clear up these uncertainties. We conclude that the Balmat-Edwards district was heated to 625 ± 25°C during Grenville metamorphism.

Sphalerite geobarometry

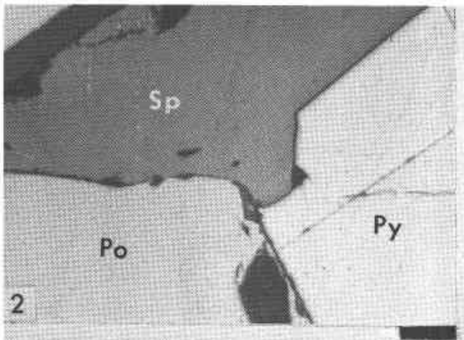
Numerous samples from all three Balmat mines as well as the mine at Edwards were collected both underground and from drill core in an attempt to obtain suitable samples for application of the geobarometer. To accurately apply this system, the activity of FeS in sphalerite must have been buffered at the time of metamorphism by the pair hexagonal pyrrhotite-pyrite. However, useful maximum and minimum pressure estimates respectively can be obtained from sphalerite which equilibrated with only pyrite or only pyrrhotite. A reconnaissance study of the samples supported previous observations (D. B. Dill, personal communication) that significant quantities of pyrrhotite can only be found in the Balmat #2 mine. Even there pyrrhotite is relatively rare and few of the polished sections had all three phases.

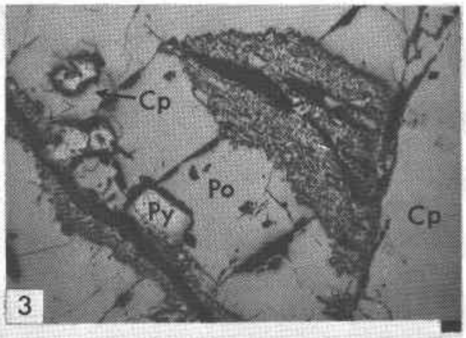
Textural relations

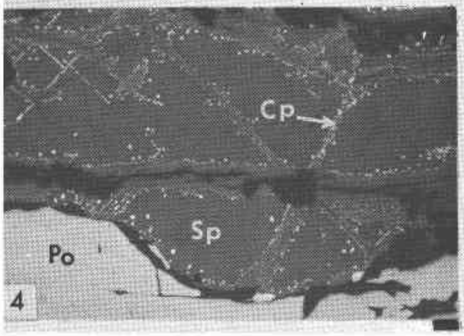
As a first attempt at finding appropriate assemblages, textural relations suggesting equilibrium between pyrite, pyrrhotite, and sphalerite were sought optically. Textural equilibrium of a monomineralic aggregate of grains tends toward development of 120° triple-junction points. Stanton (1964) demonstrated that in two- or three-phase aggregates the dihedral angles developed were usually between 105° and 135°. No experimental data are available on aggregates of pyrite plus sphalerite with minor pyrrhotite; therefore samples displaying geometries within the general range mentioned above were chosen for analysis (Fig. 2).

A detailed study of the sections bearing pyrrhotite showed that in some cases the pyrrhotite was cut by stringers of fine-grained pyrite and/or marcasite (Fig. 3). This secondary replacement product has developed along cracks in and contacts of the pyrrhotite, and must be distinguished from primary pyrite before applying the geobarometer to the three-phase assemblage.

Another striking feature of the Balmat sphalerites which may have a bearing on the application of the geobarometer is the presence of exsolved chalcopyrite. In the #3 and #4 mines, where pyrrhotite is rare, the sphalerite displays quite minor exsolution. Where present, the exsolved blebs are concentrated along contacts with pyrite grains. In the #2 mine there is usually more exsolution in sphalerites and it is most pronounced where pyrrhotite is present (Fig. 4). As above, the chalcopyrite is densest near the sphalerite–iron sulfide boundaries. Brown (1936) reports that pyrrhotite at Balmat is always associated with chalcopyrite inclusions in sphalerite. In several cases the grain size of the chalcopyrite seems to be a function of the distance from the iron sulfide or from cracks in the sphalerite. The exsolved blebs become finer and more numerous toward the contacts and cracks (Fig. 4). The possible ramifications of these observations will be discussed below.







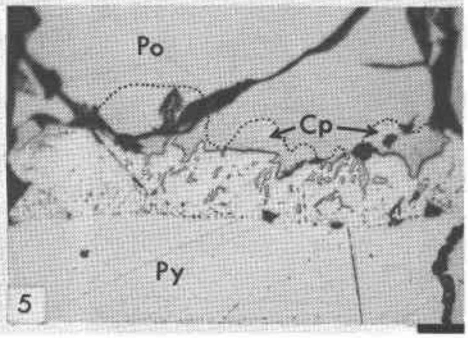


Fig. 2. Typical three-phase triple point showing minor chalcopyrite exsolution from sphalerite.
Fig. 3. Pyrite/marcasite replacing pyrrhotite along fractures. Note abundant chalcopyrite.
Fig. 4. Chalcopyrite exsolved from sphalerite. Note localization along twins (upper left) and along cracks and grain boundaries.
Fig. 5. Porous pyrite in reaction (?) rim along pyrite–pyrrhotite contact; voids infilled by chalcopyrite.
[All pictures in plane polarized reflected light; bar scale 50 μm.]

Sphalerite analyses

The sphalerites in the cogenetic three-phase assemblages were analyzed for Fe, Zn, Cu, and occasionally Mn and Cd. The range of concentrations of the minor cations are as follows: Cu, 0.0–2.0 mole %; Mn, 0.0–2.5 mole %; and Cd, 0.0–1.2 mole %. A few analyses with considerably more copper (2.5–6.5 mole %) are attributed to anomalous concentrations of microscopic or submicroscopic exsolved chalcopyrite. The blebs were in many cases resolved under the microscope but not by the poorer optical system on the microprobe. This led to uncertainty in avoiding the exsolved phase during analysis. The variability in iron content is displayed in the histogram in Figure 6D. Inhomogeneity in FeS content is apparent on all scales—from sample to sample as well as over short distances (1–200 microns) in single crystals (Fig. 7).

When the large inhomogeneity in the FeS content of sphalerite became apparent, the samples from Balmat used in DeWitt's (1976) study were reanalyzed. DeWitt obtained tight consistent results, giving a pressure of 7 kbar using Scott's isobars (Fig. 6C). DeWitt proposed that a correction factor of −0.5 kbar be applied to Scott's isobars, because of small systematic errors in the microprobe corrections of Scott. The samples were obtained from Dr. Bruce Doe, who completed a study on Balmat in 1962. The three-phase assemblages were collected from the Main ore zone on the 900, 1100GS, and 1500GS levels in the #2 mine. Texturally those samples were quite similar to the ones collected for this study except that they have very little exsolved chalcopyrite. Reanalysis confirmed the tight consistent results obtained by DeWitt (1976), with only minor scatter toward higher iron contents (Fig. 6B). The samples collected for this study containing the three-phase assemblages were from the #1 ore zone on the 500 and 700 levels and the Main and Footwall ore horizons on the 2300 sublevels.

Discussion

Sphalerite barometry yields different pressures for different samples at Balmat. Doe's and Scott's analyses give pressures of 5–5.5 kbar (Fig. 6), corresponding well to the maximum obtained in this study for inhomogeneous sphalerites with extensive chalcopyrite exsolution (Fig. 6D). These sphalerites yield apparent pressures from 3–7 kbar. Reanalysis of De-

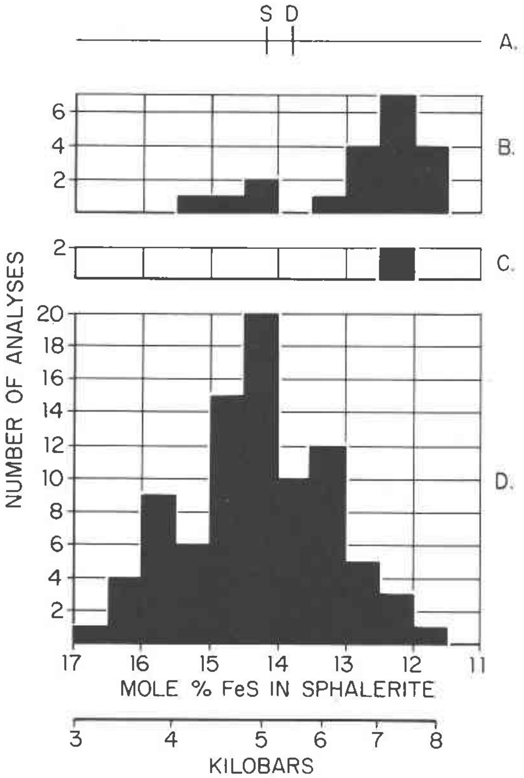


Fig. 6. Iron contents of sphalerite in three-phase assemblages. *A*, mean results obtained by Scott (1976) (S) and Doe (1962) (D); *B*, reanalysis of specimens from DeWitt; *C*, DeWitt (1976); *D*, present study.

Witt's homogeneous sphalerites lacking blebby chalcopyrite exsolution gives pressures of 6.5–7.5 kbar, confirming DeWitt's data. Pressures are limited by the presence of sillimanite to less than 6 kbar at 600°C and less than 6.5 kbar at 650°C. Presumably the homogeneous unexsolved sphalerites have preserved the maximal pressures. The accuracy of the location of univariant boundaries in the sphalerite and sillimanite experiments is probably no better than ±0.5 kbar at these P–T conditions, and 6.5 kbar fits both sets of data. Perkins and Essene (1977) applied garnet–plagioclase–sillimanite–quartz barometry to rocks at Benson Mines, about 20 miles east of Balmat, and obtained 6.5 kbar, in good agreement with pressures inferred at Balmat. Combining this with the temperature data allows an estimate of 6.5 ± 0.6 kbar at 625 ± 25°C.

The textural relations as well as the chemical analyses in this study point out several problems with "grab sample" application of the sphalerite geobarometer. A few determinations of FeS in sphalerite coexisting with pyrite–hexagonal pyrrhotite clearly may not give dependable pressures. The system also may not be fully characterized as to the effects of other cations on the pressure–temperature equilibria.

At the temperatures estimated for the metamorphic event (625 ± 25°C) the hexagonal form of pyrrhotite (1C) would have been stable and have had a composition approaching Fe_8S_9 (Kissin, 1974). The Balmat pyrrhotite is strongly magnetic, suggesting a dominance of the monoclinic form, (4C), Fe_7S_8. Splitting of the d_{102} reflection on the X-ray diffractometer tracings indicates a mixture of the monoclinic and hexagonal types, but as pointed out by Kissin (1974), it is not possible to determine the percentages of the two from such data. The change from the high-temperature hexagonal (1C) to the low-temperature monoclinic (4C) form must be accompanied by either the release of iron or the addition of sulfur. The lack of secondary porosity in the pyrrhotites and the lack of low-temperature iron hydroxides or carbonates suggest that the latter process was dominant. Earlier workers (Brown, 1936) have called upon retrograde fluids as the source for water to form the extensive

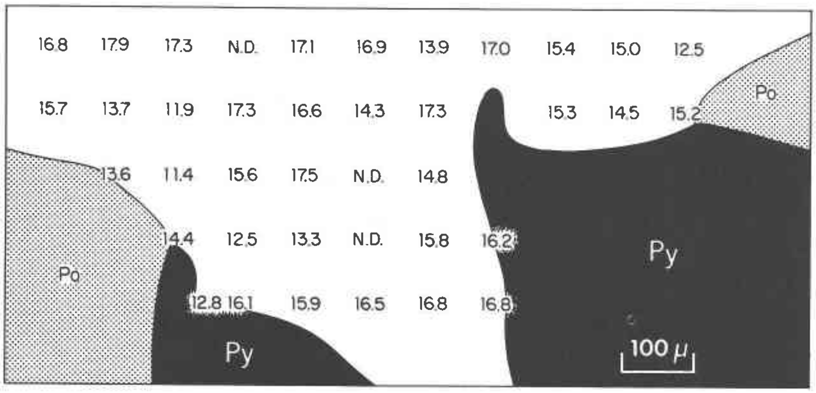
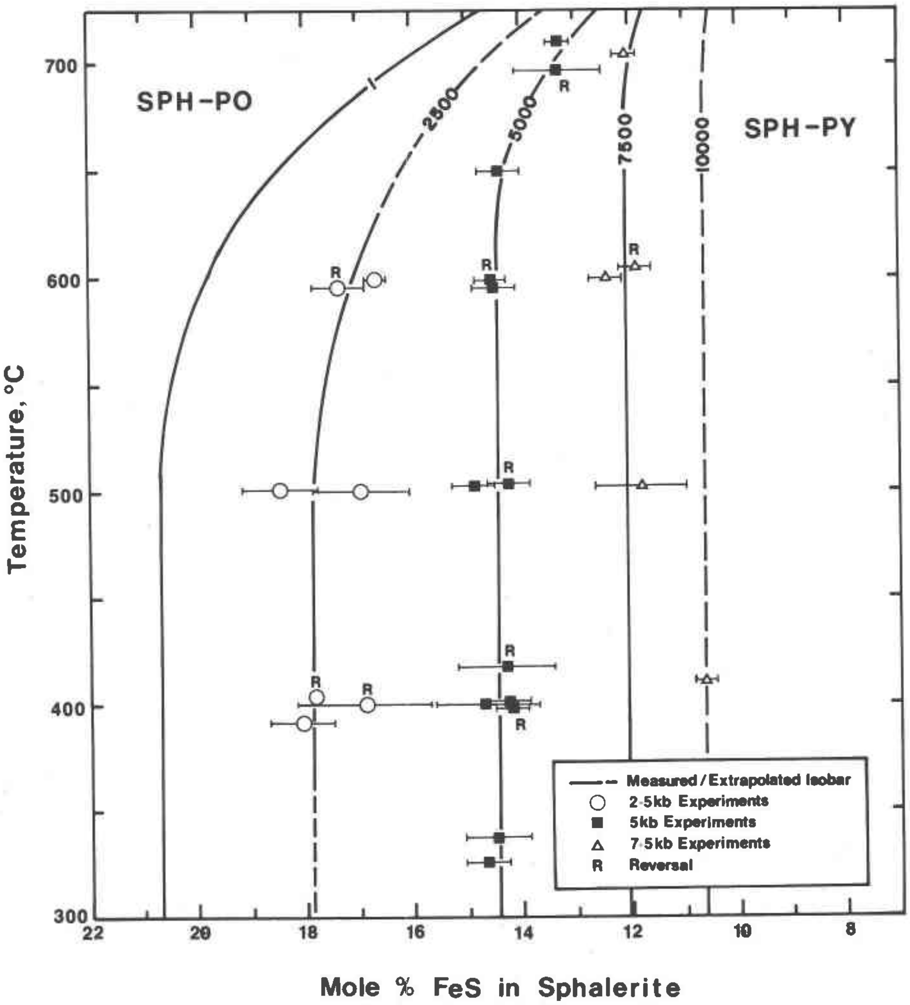


Fig. 7. Sample map showing variation in analyzed iron content of sphalerite in three-phase assemblage.



(after Scott, 1976)

Fig. 8. Experimentally determined isobars above 300°C in system pyrite–pyrrhotite–sphalerite (modified from Scott, 1976).

secondary talc and serpentine in the rocks of the district. These fluids, whether removing iron or adding sulfur, would facilitate the observed alteration of pyrrhotite to pyrite/marcasite along cracks and fractures (Fig. 3), as well as other alteration of the iron sulfides (Fig. 5). The same fluids may have enhanced the reequilibration of the sphalerite at pressures and temperatures much reduced from those at the peak of metamorphism. Any retrograde pressure–temperature path for an original equilibrium three-phase assemblage will result in reequilibration toward higher FeS contents at temperatures above 300°C (Fig. 8). Below 300°C, the sphalerite–pyrite–pyrrhotite isobars all swing to very low iron contents (Scott and Kissin, 1973), suggesting that if reequilibration occurs at these temperatures the resulting FeS contents will be low. Thus any retrograde path will increase FeS contents above 300°C and will decrease FeS contents below 300°C if equilibrium is maintained. The final result is then a complex function of the *P–T* conditions of peak metamorphism, the degree of reequilibration during the retrograde event, and the final *P–T* conditions where reequilibration stops and the final FeS content is frozen into the sphalerite.

The observed extensive exsolution of chalcopyrite from most of the Balmat three-phase assemblages presents an unsolved complication in applying the barometer. The exsolution origin for the chalcopyrite is supported by both the small grain size and the location of the blebs along annealing twins and grain boundaries. When analyzed using ZnS, FeS, and cop-

Table 1. Pressure determinations

Investigation	FeS Mole %	Standard Deviation	Inferred Pressure
Scott (1973) [data from Doe (1962)]	13.8	1.5	5.5 kbar
DeWitt (1976)	12.5	0.2	6.5 kbar
Scott (1976)	14.2	0.7	5.0 kbar
Present Paper-			
Cpy bearing and inhomogeneous	14.3	1.0	4.8 kbar
Homogeneous	12.8	1.0	6.5 kbar

per metal as standards, the blebs appear to be one-phase stoichiometric $CuFeS_2$. The exsolution may be an isochemical adjustment of the sphalerite upon cooling. Alternatively, if the cooling behavior of the quaternary system Zn–Fe–Cu–S is analogous to that of the ternary system Cu–Fe–S, exsolution of stoichiometric $CuFeS_2$ would not be possible without the addition of sulfur. This was demonstrated by Cabri (1973), who showed that the intermediate solid solution (ISS) in the Cu–Fe–S system is sulfur-deficient and does not include the composition $CuFeS_2$. A possible reaction would be:

$$[\mathrm{Zn},(\mathrm{Cu},\mathrm{Fe})_{\mathrm{rich}}]\mathrm{S}_{1-x} + (x/2)\mathrm{S}_2 = [\mathrm{Zn},(\mathrm{Cu},\mathrm{Fe})_{\mathrm{poor}}]\mathrm{S} + \mathrm{CuFeS}_2$$

Phase relations are not well enough known in the more complex system to decide which exsolution process is correct or to answer questions such as how the iron in the exsolved chalcopyrite should be treated, *i.e.*, should an amount of iron equal to the amount of analyzed copper be subtracted from the analyses before calculating Fe/(Fe + Zn)? An adjustment of this type was attempted, but did not significantly lessen the scatter in the inferred pressures. Exsolved chalcopyrite is possibly one indication of reequilibration of this system. Other textural indications of reequilibration may not be obvious, as the sphalerite barometer requires incorporation of additional FeS to reequilibrate with decreasing pressure above 300°C, and therefore no pyrrhotite exsolution lamellae would be seen. Below 300°C, however, sphalerite could reequilibrate by exsolving FeS as pyrrhotite + pyrite.

Despite our lack of understanding of the effect of copper on the sphalerite barometer, the presence of exsolved chalcopyrite corresponds to highly variable FeS content in sphalerite and hence highly variable pressure estimates. Nevertheless the maximum pressures and temperatures determined in this study are in good agreement with other data collected in the area. Bohlen and Essene (1977), working in the para- and orthogneisses a few miles south and east of Balmat, report two-feldspar temperatures of 640 ± 50°C and a Fe–Ti oxide temperature of 620 ± 50°C. Thus the three geothermometers give the same result, within their error limits of 625 ± 25°C. The presence of sillimanite in the paragneisses restricts pressures to a maximum of 6.5 ± 0.5 kbar at the temperatures found. Engel and Engel (1953) mapped two isograds in the NW Adirondacks—the first appearance of orthopyroxene in the gneisses and the breakdown of muscovite + quartz to give sanidine + sillimanite. Since these isograds involve a hydrous phase, P_f is as important as P_t in determining when these reactions will take place. Essene *et al.* (1977) have presented convincing evidence that for most of the non-carbonate rocks in the Adirondacks P_f is less than P_t and quite variable. Consequently, in order to interpret the significance of the two proposed isograds which are tentatively mapped near Balmat, both P_{total} and $P_{\mathrm{H_2O}}$ must be defined. Definition of regional $P_{\mathrm{H_2O}}$ variations and the remapping of Engel's isograds are currently in progress.

Conclusions

Pressures of metamorphism at Balmat are tentatively inferred to be 6.5 ± 0.5 kbar, using sphalerite barometry and limiting Al_2SiO_5 data. Inhomogeneous sphalerites with chalcopyrite exsolution yield a wide range of pressures from 3–7 kbar. These sphalerites have either partially reequilibrated upon decompression or have been variably affected by chalcopyrite solution. Sphalerite barometry does not appear to provide a panacea for estimating pressures in metamorphic rocks.

Acknowledgments

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