

## Application of the sphalerite geobarometer to regionally metamorphosed terrains

S. D. SCOTT

Department of Geology, University of Toronto  
Toronto, Ontario M5S 1A1 Canada

### Abstract

Sphalerite is the most thoroughly investigated of the refractory sulfides and has proven to be a useful geobarometer, particularly in regionally metamorphosed terrains. The concept of the sphalerite geobarometer derives from the variation of the FeS content of sphalerite as a function of pressure, when the FeS activity is buffered by pyrite + hexagonal pyrrhotite and is not affected by additional Mn or Cd in the sphalerite. Application of the sphalerite geobarometer to the regionally metamorphosed sulfides of the Nairne Pyritic Formation (4.4 kbar), the Moke Creek area of the Otago Schist (5.7 kbar), and Balmat, New York (5.5 kbar) gives values which are in agreement with other, less precise, geological estimates. Sphalerite compositions from metamorphosed Aphebian massive sulfide ores near Snow Lake, Manitoba, coupled with isograds mapped in the surrounding greenschist and amphibolite facies rocks by Froese and Gasparrini (1975) are compatible with a geologically realistic geotherm of 27°C/km for that region.

### Introduction

Sulfide minerals occur widely in metamorphic rocks in concentrations ranging from minute dispersed grains to multi-million ton orebodies, yet they are seldom considered by petrologists as more than mineralogical curiosities in their studies of regionally metamorphosed terrains. This lack of attention to sulfides is in most cases well-founded, because the vast majority do not preserve their equilibrium compositions and assemblages attained during metamorphism. Instead, they readily reequilibrate during retrograde cooling, so are of little or no use as geothermometers and geobarometers (Barton, 1970). Of the commonly occurring sulfides, only molybdenite, pyrite, arsenopyrite, and sphalerite are sufficiently refractory to be considered as mineralogical tools. Sphalerite is the best understood of these and shows considerable promise as a geobarometer (Scott and Barnes, 1971; Scott, 1973; Scott, 1974; Essene, 1974). This paper examines some applications of the sphalerite geobarometer to metamorphism.

### The sphalerite geobarometer

The theory behind the sphalerite geobarometer was first evolved by Barton and Toulmin (1966) and extended by Scott and Barnes (1971) and Scott (1973). In brief, the FeS content of sphalerite is a function of temperature ( $T$ ), pressure ( $P$ ) and FeS activity ( $a_{\text{FeS}}$ ).

The  $a_{\text{FeS}}$  is not necessarily dependent on  $P$  and  $T$ , and for geobarometry must be buffered by one or more iron sulfide phases. Theoretically, hexagonal pyrrhotite alone can act as a buffer because the relationships among  $a_{\text{FeS}}$ , pyrrhotite composition ( $X_{\text{FeS}}^{\text{po}}$ ), and  $T$  are known and are independent of  $P$  (Toulmin and Barton, 1964). In practice, pyrrhotites can suffer compositional changes on cooling (Genkin, 1971; Kissin and Scott, in preparation) which, together with the large  $T$  coefficient of the  $a_{\text{FeS}} - X_{\text{FeS}}^{\text{po}}$  relationship, usually makes such a geobarometer of little use. However, when  $a_{\text{FeS}}$  is buffered by divariant assemblages in the Fe–S system such as troilite + iron or pyrite + pyrrhotite, retrograde variation in pyrrhotite composition is not important. The sphalerite + troilite + iron (or kamacite and taenite) assemblage is applicable only to meteorites, and its utility in estimating their pressures of formation is discussed by Schwarcz *et al.* (1975).

Figure 1 shows isobars of sphalerite composition along the pyrite + hexagonal pyrrhotite buffer, modified slightly from Scott (1973). Originally, I had drawn the 7.5 kbar isobar with considerable curvature to be consistent with the single experimental point at 411°C, but in retrospect, there are several good reasons for disregarding this point:<sup>1</sup> (1) no phase change is known in the Fe–Zn–S system to

<sup>1</sup>See also Lusk *et al.* (1975, p. 1079).

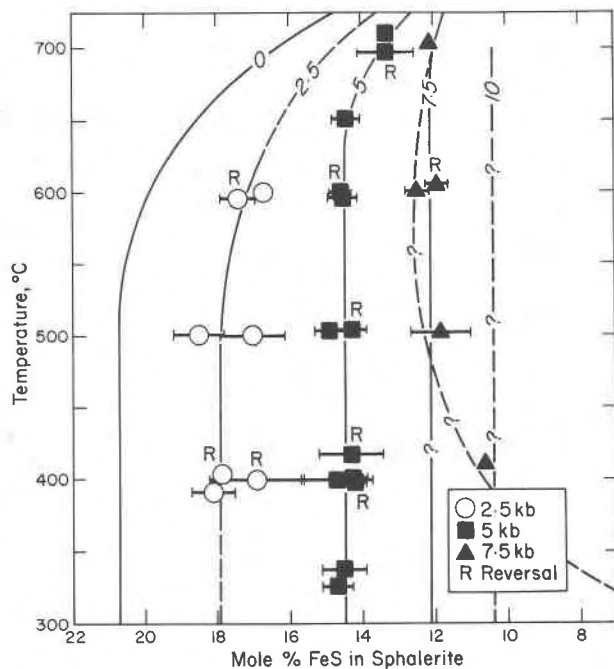


FIG. 1.  $T$ - $X$  projection onto the FeS-Zns join of sphalerite + pyrite + hexagonal pyrrhotite isobars (in kbar), modified from Scott (1973). The vertical 7.5 kbar isobar is preferred (see text). Sphalerite + pyrrhotite and sphalerite + pyrite coexist to the left and right, respectively, of each isobar.

account for such an abrupt departure from the shape of the more precisely fixed 0, 2.5, and 5 kbar isobars; (2) the point has not been reversed; and (3) re-examination of the run products shows the sphalerite to be unusually fine-grained, suggesting that it did not recrystallize sufficiently to achieve FeS saturation. Experiments presently in progress will ultimately resolve this question but, in the meantime, I prefer the vertical 7.5 kbar isobar in Figure 1. None of the conclusions drawn in this paper are contingent on the shape of this isobar below 500°C.

Scott and Barnes (1971) and Scott (1973) have demonstrated that, of the common minor elements in sphalerite, Cd and Mn have no effect on Figure 1. Only Cu is potentially effective in modifying the isobars (Wiggins and Craig, 1975). Most sphalerites contain much less than 1 weight percent Cu in solid solution, but in Cu-rich ores they often host exsolved chalcopyrite blebs, indicating a higher solubility of Cu in sphalerite at high  $P$  and  $T$ . However, Toulmin (1960) found very low solubility of Cu in sphalerite and no effect of Cu-substitution on sphalerite + pyrite + pyrrhotite phase relations at 666°C and the vapor pressure of the system. Further experiments

are in progress to resolve this question. With the possible exception of interference by Cu, the FeS contents of natural sphalerites buffered by pyrite + hexagonal pyrrhotite must correspond to the isobars in Figure 1 and are independent of  $T$  to at least 5 kbar over a very wide range of temperatures encompassing the greenschist to upper amphibolite facies of regional metamorphism. These observations, together with the ubiquity of this assemblage, the refractory behavior of sphalerite, and scarcity of mineralogical geobarometers, combine to make the sphalerite geobarometer an attractive tool for metamorphic petrologists.

Application of the sphalerite geobarometer requires the fulfillment of three criteria:

(1) Sphalerite must have equilibrated with pyrite and hexagonal pyrrhotite. The fact that the three phases were annealed throughout the duration of a regional metamorphic event probably assures at least an approach to equilibrium. However, both iron sulfides must be present and preferably in mutual contact with sphalerite, particularly at lower metamorphic grades, as is demonstrated below. Sphalerite in contact only with pyrite typically contains very low FeS contents to the right of its respective isobar in Figure 1, even when pyrrhotite may have been but a few meters or even centimeters away. Similarly, sphalerite in contact with pyrrhotite only, as at Broken Hill, N.S.W. (Scott, Both and Kissin, in preparation), is much more FeS-rich than its respective isobar, consistent with Fe-Zn-S phase relations.

Reequilibration of sphalerite with pyrite and pyrrhotite during declining pressure is unlikely because, as shown by Figure 1, it requires *dissolution* of FeS, which process is kinetically unfavorable for coarse grain-sizes compared with exsolution. Such a retrograde compositional change would produce FeS-rich rims in sphalerite, a feature that I have looked for in metamorphosed massive Cu-Zn sulfide ores but not found. However, Groves *et al.* (1975) have described such a retrograde reequilibration in metamorphosed nickel ores as discussed further, below.

(2) Although temperature is not an important variable over most of Figure 1, it must be greater than that of the abrupt reversal in slope of the pyrite + hexagonal pyrrhotite solvus (265°C at 1 bar but not located at higher pressure; Kissin and Scott, 1972; Scott and Kissin, 1973), and less than the upper stability of pyrite (743°C at 1 bar and increasing by 14°C/kbar; Kullerud and Yoder, 1959). In practice, curvature of the isobars above 600°–700°C requires

too accurate an estimate of metamorphic temperature to give reliable pressures.

(3) Precise microprobe analyses of sphalerite are required, as  $\pm 0.5$  mole percent uncertainty corresponds to  $\pm 400$ –500 bars. At the University of Toronto, we use synthetic  $\text{FeS}_2$  or  $\text{FeS}$  as microprobe standards for Fe and S, and zinc metal or synthetic  $\text{ZnS}$  for Zn. Data reduction is by the EMPADR VII program of Rucklidge and Gasparrini (1969). DeWitt and Essene (1974) claim that small systematic errors in EMPADR require an adjustment of the isobars in Figure 1 by  $-0.7$  mole percent  $\text{FeS}$ . I have tested the EMPADR program extensively and find no basis for DeWitt and Essene's argument. In one test a 2 mm homogeneous synthetic Fe-sphalerite crystal was probed four times over the period of a year at The Pennsylvania State University using synthetic Fe-sphalerites prepared by P. B. Barton, Jr. as standards for a calibration curve (Scott and Barnes, 1971, p. 655). This sample has also been probed 18 times over a period of several years at Toronto using the procedures described above. The Penn State results gave a mean of 26.3 mole percent  $\text{FeS}$  and standard error of the mean of 0.2 mole percent  $\text{FeS}$ . The Toronto results gave, respectively, 26.5 and 0.1 mole percent  $\text{FeS}$ . In another test five synthetic sphalerites containing 5.0 to 25.0 mole percent  $\text{FeS}$  were analyzed at Toronto, and their compositions were reproduced within 0.2 mole percent  $\text{FeS}$  in the worst case. This latter test did show, however, that zinc metal is not as good a microprobe standard as  $\text{ZnS}$ . Fortunately, the data points in Figure 1 are not dependent on choice of zinc standard because mole percent  $\text{FeS}$  was calculated directly from the iron analyses for analyses totalling within 0.5 weight percent of 100 percent (Scott, 1973).

#### Application of the sphalerite geobarometer

Table 1 summarizes sphalerite compositions believed to be buffered by pyrite + hexagonal pyrrhotite and estimated pressures from a variety of metamorphic terrains. A range of metamorphic conditions is represented, including some thoroughly examined metamorphic belts for which there may or may not be independent estimates of pressure, sphalerite from large metamorphosed massive sulfide orebodies and from uneconomic sulfide disseminations in metamorphic rocks, and a special case of pressure variation in a boudinage. Unless indicated otherwise, I have estimated temperatures rather crudely from metamorphic grade or silicate assemblages using Winkler (1974) and Turner (1968) as guides.

Massive sulfide ores are obviously the best source of sphalerite, so there is a preponderance of data from these. Although the debate still continues on the epigenetic versus syngenetic origin of these deposits, Sangster and Scott (1976) give evidence for believing that those in Table 1, with the possible exception of Balmat, formed on or close to the sea floor and were subsequently buried and metamorphosed with their enclosing rocks.

A few highlights of the sphalerite data follow.

#### *Influence of the pyrite + pyrrhotite buffer*

The necessity of buffering the sphalerite by direct mutual contact with both pyrite and pyrrhotite is illustrated in Figures 2–5. Figure 2 demonstrates that consistent results can be obtained from a highly-metamorphosed massive sulfide orebody where the buffering criterion is met. DeWitt and Essene (1974) found a similar close grouping of sphalerite analyses from triple junctions in metamorphosed disseminated sulfides within Grenville marbles of eastern Ontario. At both the Anvil mine (greenschist facies) and Balmat No. 2 mine (amphibolite facies) sphalerite + pyrite is found with and without pyrrhotite (Figs. 3 and 4). Taken as a whole, both orebodies contain all three of the sulfides, but those sphalerite samples which are not in contact with pyrrhotite, or do not even have pyrrhotite in the same polished section, are usually considerably less  $\text{FeS}$ -rich than those with both pyrite and pyrrhotite present. The poorer segregation of analyses by assemblages and wider range of analyses for sphalerite + pyrite + pyrrhotite at Anvil compared with Balmat is probably a reflection of their respective metamorphic grades. Variation in sphalerite composition by assemblage in a massive sulfide deposit is further illustrated in Figure 5. The three samples along the traverse which contain both pyrite and pyrrhotite have very similar sphalerite compositions and are consistent with those from other parts of the orebody. Sphalerite coexisting with pyrite only contains much less  $\text{FeS}$ , and that coexisting with pyrrhotite only contains much more  $\text{FeS}$  as expected from Figure 1.

#### *Nairne Pyritic Formation, South Australia*

Skinner (1958) described coexisting kyanite + andalusite at the Shephard Hill Quarry which he felt were in equilibrium. About a km away, Fleming (1971) has found coexisting andalusite + sillimanite, and at the Williamstown-Warren Reservoir, 35 km to the north, there are occurrences of sillimanite + kyanite, so it would appear that metamorphic conditions

TABLE 1. Applications to metamorphism of the sphalerite geobarometer in the assemblage sphalerite+pyrite+pyrrhotite

Location	Est. T, °C	Sphalerite Data				Comments
		Mole % FeS (s.d.)*	N**	Source	P (s.d.)*, kb	
Rogers Pass, B.C.	365 {1}***	14	1	{1}***	5.4	Garnet isograd; P calc. 3.9 kb from silicates {1}***
Moke Creek, (Otago Schist, N.Z.)	440 - 550 {2}	13.6(8)	76	{3}	5.8(7)	Chlorite Zone: high P green-schist; 20°/km geotherm {2} gives 5.8-6.8 kb
Anvil mine, Yukon	400 - 500? {4}	17.3(10)	34	{5}	2.9(8)	Min. P = 1.7 kb {5} Max. P ~ 3.2 kb {21}
No. 2 mine, Balmat, N.Y.	525 - 625 {6}	(a) 13.7(4) (b) 14.2(7) (c) 13.9(5)	20 14 34	{7} {8} {9}	5.5(5)	P = 2.5-4.5 ? kb {10}; see {6} for other estimates of P in the Grenville
Nairne Pyritic Fm., South Australia	500 - 600? {11}	15.2(1)	2	{12}	4.4(1)	Close to Al <sub>2</sub> SiO <sub>5</sub> triple point {11}
Geco mine, Manitowadge, Ontario	~600? {4}	(a) 12.25(30) (b) 11.94(41) (c) 12.19(49)	8 3 86	{13} {14} {15}	7.3(6)	Amphibolite facies; abundant granitic pegmatite and migmatite; granodiorite stock nearby
Snow Lake area Manitoba						
1. Chisel L. mine	~600 {4}	13.4(6)	33	{8,16}	5.9(5)	Relation to isograds of {18} discussed in text.
2. Stall L. mine	~640 {4}	12.5(8)	9	{16}	7.0(9)	
3. Anderson L. mine	~640 {4}	12.5(7)	3	{17}	7.0(8)	
4. Osborne L. mine	>700 {4}	10.4(9)	15	{16}	<10	
Fox L. mine, Manitoba	550 - 600 {4}	13.3(9)	47	{8}	6.0(9)	
Ruttan L. mine, Manitoba	500 - 600 {4}	(a) 13.9(2) (b) 13.5(5) (c) 13.8(3)	12 4 16	{17} {8} {9}	5.6(3)	
Boudinage, Udden mine, Skellefte, Sweden	<400? {4}					Metamorphic grade discussed by {20}; ΔP = 1.20(45) Kb, see text for discussion
1. pressure shadow		15.74(29)	7	{19}	4.1(2)	
2. corners		14.10(44)	3	{19}	5.3(4)	

\* Standard deviation of the data in terms of least units cited for the value to their immediate left, i.e. 13.6(8) represents a standard deviation of 0.8.

\*\* Number of analyses.

\*\*\* Numbers in brackets { } are references:

- |  |                                 |  |
|--|---------------------------------|--|
| {1} Jones (1972); E.D. Ghent (Univ. of Calgary, personal communication, 1975) finds 5.4 kb not unreasonable based on his work in the Esplanade Range | {5} Campbell & Ethier (1974)    | {18} Froese & Gasparrini (1975)  |
| {2} Henley (1975); Landis and Coombs (1967) give 350-400°C   | {6} DeWitt & Essene (1974)      | {19} Berglund & Ekström (1974)   |
| {3} Combined data of Wright & Lovering (1967) & Henley (1975)  | {7} Doe (1962)                  | {20} Rickard & Zweifel (1975)  |
| {4} Temperatures estimated from metamorphic assemblages & Winkler (1974) or Turner (1968)  | {8} This study                  | {21} Andalusite + staurolite in contact facies of metamorphism (Campbell & Ethier, 1974); data from Holdaway (1971) and Winkler (1974) |
|  | {9} Combined data               |  |
|  | {10} Engel & Engel (1958)       |  |
|  | {11} Fleming (1971)             |  |
|  | {12} Skinner (1958)             |  |
|  | {13} Massive ore; this study    |  |
|  | {14} Pinch zone; this study     |  |
|  | {15} Entire orebody; this study |  |
|  | {16} Bristol (1974)             |  |
|  | {17} Sangameshwar (1972)        |  |

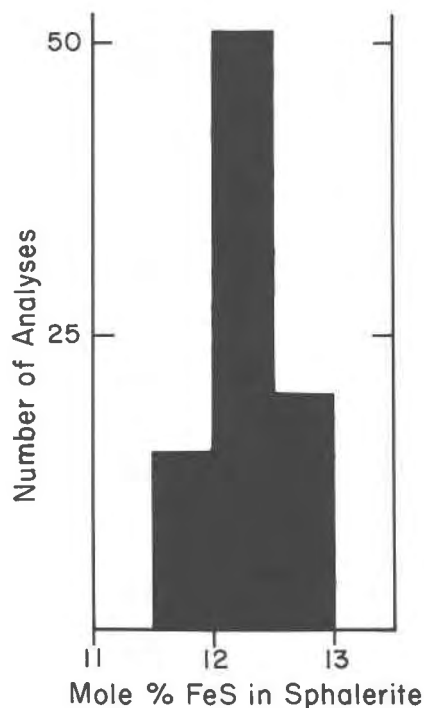


FIG. 2. Histogram of analyses of sphalerite buffered by pyrite + pyrrhotite (+ chalcopyrite) from the Geco massive sulfide orebody, Manitouwadge, Ontario. The 86 analyses from 18 polished sections give a mean of 12.19 mole percent FeS and a sample standard deviation of 0.49 mole percent FeS.

in the area were close to the  $\text{Al}_2\text{SiO}_5$  triple point. In Figure 6 sphalerite isobars from Figure 1 are superimposed on the triple-point diagrams of Holdaway (1971) and Richardson *et al.* (1969). Shephard Hill sphalerites analysed by Skinner (1958) contain 15.2 mole percent FeS and were thought by him to be in equilibrium with both pyrite and pyrrhotite. Skinner's analyses indicate a pressure of 4.4 kbar which is about midway between the two triple points. Although the sphalerite data are slightly closer to Holdaway's triple point, absence of a kyanite + sillimanite assemblage in the immediate Shephard Hill area might be taken as evidence for a pressure lower than the triple point, favoring Richardson *et al.*, provided the pyrite, which is a minor phase, was truly in equilibrium with the other sulfides.

#### Snow Lake area, Manitoba

The Snow Lake area, 115 km east of Flin Flon, Manitoba, contains a number of volcanogenic massive sulfide deposits in metamorphosed volcanic and sedimentary rocks of Apebian (Lower Proterozoic) age. There is a well-defined progressive regional metamorphism increasing from greenschist facies in

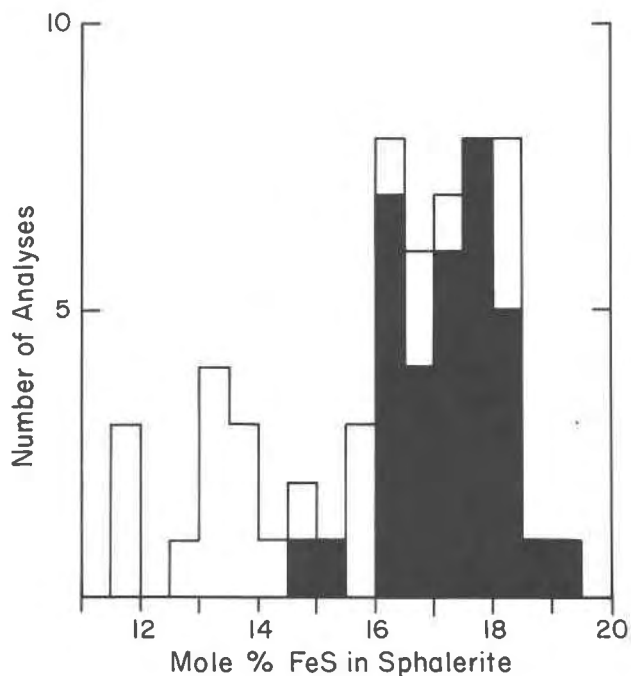


FIG. 3. Histogram of sphalerite analyses from two assemblages, Anvil mine, Yukon. Filled boxes represent 34 analyses for sphalerite coexisting with pyrite + pyrrhotite giving a mean of 17.3 mole percent FeS and sample standard deviation of 1.0 mole percent FeS. Empty boxes represent 23 analyses for sphalerite coexisting with pyrite only giving a mean of 14.9 mole percent FeS and sample standard deviation of 2.1 mole percent FeS. Data are from Campbell and Ethier (1974).

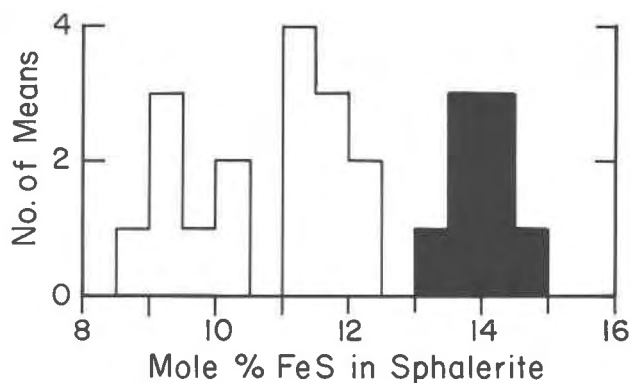


FIG. 4. Histograms of sphalerite analyses from two assemblages, Balmat No. 2 mine, New York. Filled boxes represent 14 means from a population of 34 analyses of sphalerite coexisting with pyrite + pyrrhotite. These give a mean of means of 13.9 mole percent FeS and a standard error of the mean of 0.5 mole percent FeS. Empty boxes represent 17 means from a population of 188 analyses of sphalerite coexisting with pyrite only. These give a mean of means of 10.8 mole percent FeS and a standard error of the mean of 1.0 mole percent FeS. Data are from Doe (1962) and this study.

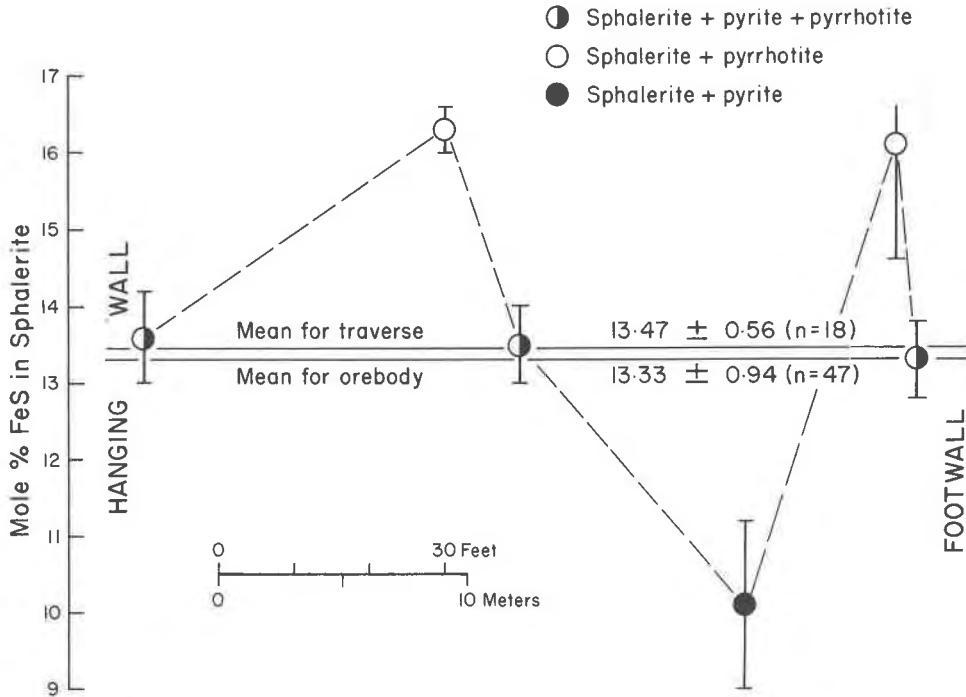


FIG. 5. Sphalerite analyses from three assemblages in a traverse through massive sulfide ore of the Fox Lake mine, northern Manitoba. Data are from this study. Vertical bars represent one standard deviation in mole percent FeS of 2 to 10 analyses at each sampling point. Means for the traverse and the orebody as a whole refer to mole percent FeS in sphalerite buffered by pyrite + pyrrhotite and exclude the other two assemblages. For both means, the standard deviation refers to a population of  $n$  analyses.

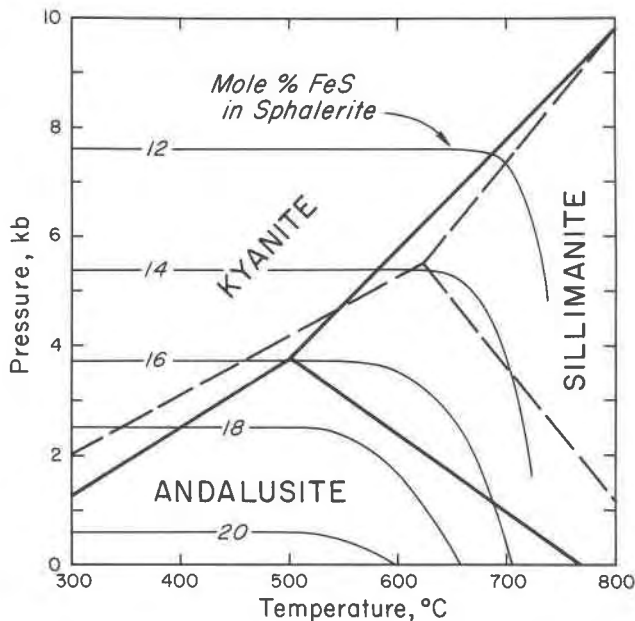


FIG. 6.  $P$ - $T$  projection of sphalerite isopleths from FIG. 1 superimposed on the  $Al_2SiO_5$  diagrams of Holdaway (1971, solid lines) and Richardson *et al.* (1969, dashed lines).

the south to amphibolite in the north and culminating in the metasedimentary Kiseynew gneisses. Figure 7 shows isograds mapped in pelitic metasedimentary rocks by Froese and Gasparrini (1975) superimposed on a simplified version of Bailes' (1971) geology, together with estimated pressures from Table 1 for four ore deposits. Temperatures on Froese's isograds are estimated from experimental data of Bird and Fawcett (1973), Winkler's (1974) summary, and Holdaway's (1971)  $Al_2SiO_5$  diagram, and are somewhat different (up to 35°C higher) from those given by Froese and Gasparrini (1975), who assumed a fixed pressure of 5.5 kbar and derived their own version of  $Al_2SiO_5$  phase relations. The pressures determined from sphalerite compositions are consistent with the increase in metamorphic grade from south to north.

Particularly interesting are the Anderson Lake and Stall Lake mines which are close together on either side of the sillimanite-biotite isograd and which give the same pressure of  $7 \pm 0.8$  or  $0.9$  kbar. By comparison, Bird and Fawcett (1973) determined an invariant point involving Mg-chlorite + muscovite +

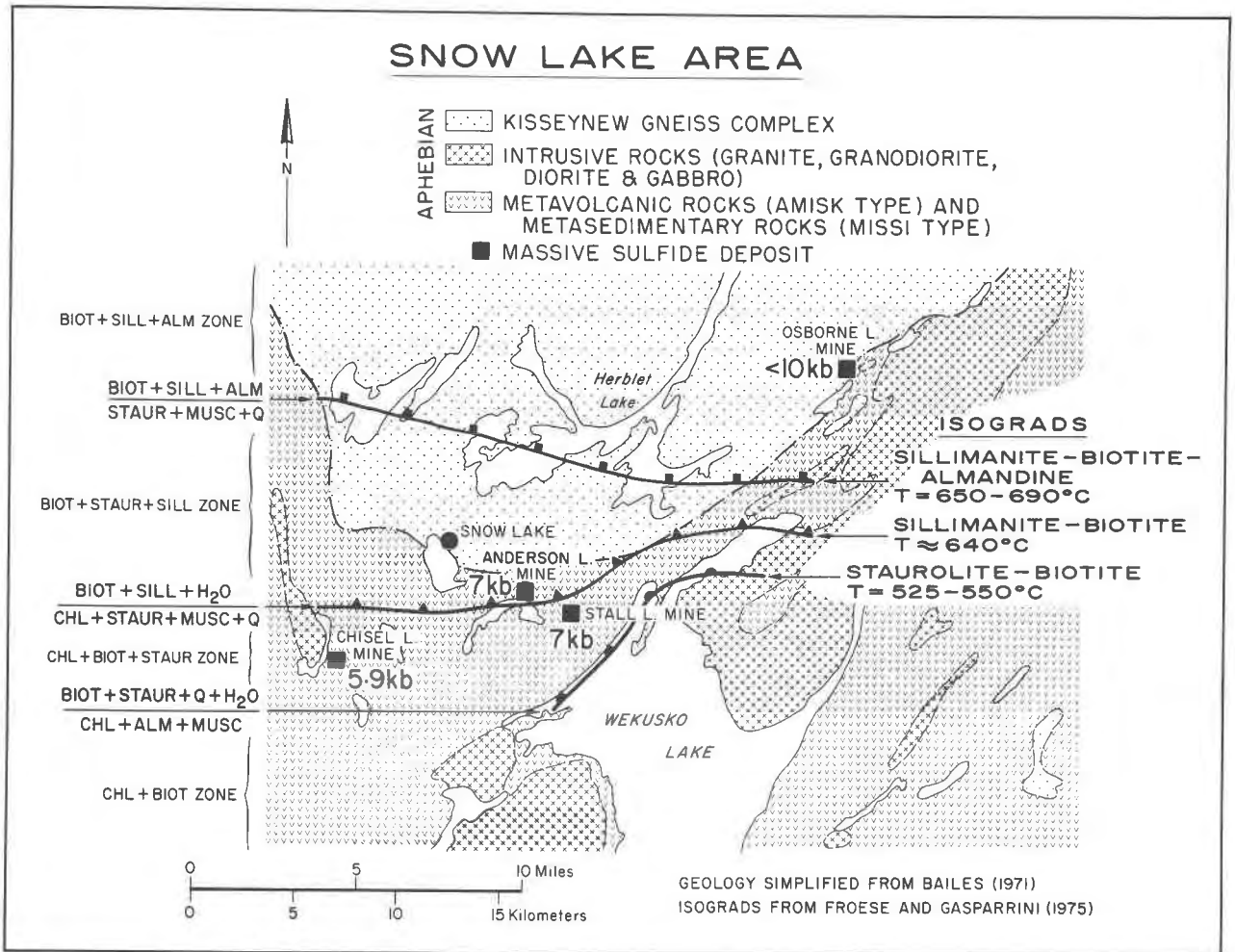


FIG. 7. Metamorphic geology of the Snow Lake area, Manitoba. Isograds mapped by Froese and Gasparrini (1975) are superimposed on a simplified version of Bailes' (1971) geological map. Isograd temperatures are estimated from Bird and Fawcett (1973), Winkler (1974) and Holdaway (1971). Pressures for four massive sulfide ore deposits are from Table 1.

quartz + aluminosilicate (+ phlogopite + cordierite +  $H_2O$ ) at 6.5 kbar which may be close to the value expected at the temperature of the sillimanite-biotite isograd. However, almandine and biotite are found in place of cordierite and phlogopite at Snow Lake, and the effect of iron on this invariant point is not known. Kyanite is abundant at the Anderson Lake mine, just north of the sillimanite-biotite isograd. At  $640^\circ C$ , the kyanite-sillimanite pair gives a pressure of 6.6 kbar on Holdaway's (1971) diagram or 5.9 kbar on Richardson *et al.*'s (1969) diagram (Fig. 6). All of these silicate and sulfide data are remarkably internally consistent and give a very reasonable geothermal gradient of  $27^\circ/km$  for the area. Because of curvature of the sphalerite isobars at high temperature in Figure 1, it is not possible to give a reliable pressure for

the Osborne Lake mine within the Kisseynew gneisses. However, if metamorphic temperatures here were not far above  $700^\circ C$ , the sphalerite compositions indicate a pressure of 8-9 kbar which, again, is consistent with a  $27^\circ/km$  geothermal gradient.

#### *Geco Mine, Manitowadge, Ontario*

The Geco deposit is a sheet-like pinching and swelling body of massive Cu-Zn sulfide ore reminiscent of a large boudinage (Sangster and Scott, 1976) contained within high-grade metamorphic rocks. As one test of the idea that the shape of the orebody was the result of differential stresses during tectonic deformation, sphalerite coexisting with pyrite + pyrrhotite was analyzed from the thick coarse-grained massive ore (the "boudin") and from a fine-

grained copper-rich pinch zone ("neck between boudins"). As shown in Table 1 there is a small difference between the two sets of data, but it is not significant at a 90 percent level of confidence. This result is in marked contrast with the Skellefte boudinage, discussed next, in which there is a well-developed pressure shadow between the boudins.

#### *Skellefte Boudinage, Sweden*

Berglund and Ekström (1974) have analyzed sphalerite in and around two small amphibolite boudins which are in a matrix of massive pyritic sulfide ore. They did not apply the sphalerite data because they doubted that  $a_{\text{FeS}}$  was properly buffered. However, this is not necessarily true for sphalerites in the pressure shadow (or gap) between the boudins and on the corners of the boudins, where pyrite and pyrrhotite are in close proximity to sphalerite. The data in Table 1 exclude two analyses from the pressure shadow and one analysis from the corners on the basis of the Dixon Criterion (Natrella, 1966) at a 90 percent confidence level. The indicated difference in stress between the pressure shadow and corners is  $1.20 \pm 0.45$  kbar which compares reasonably with a calculated value of about 0.85 kbar for a theoretical boudinage with a competency contrast of one order-of-magnitude in elastic moduli between the boudinage and matrix (Fig. 3 of Berglund and Ekström, 1974, taken from Stephansson and Berner, 1971). Increasing the competency contrast would result in a larger calculated difference in stress. Inclusion of the three outlying analyses scarcely alters the sphalerite data and gives a differential stress of  $1.3 \pm 0.7$  kbar.

#### Conclusions

The metamorphic assemblage sphalerite + pyrite + pyrrhotite is widespread in nature, and judging from the results presented here, represents the most sensitive geobarometer at the disposal of metamorphic petrologists, provided reasonable care is taken in the selection of samples and in their analysis. The two most serious limitations to the applicability of the sphalerite geobarometer appear to be (1) lack of complete equilibration among all of the coexisting sulfides in some (but certainly not all) cases of prograde metamorphism within the greenschist facies and, more disturbing, (2) at least one case of apparent retrograde recrystallization of low-temperature assemblages involving sphalerite (Groves *et al.*, 1975), perhaps aided and abetted by the presence of a chemically-active fluid phase. With regard to point (1), I have found that some massive Cu-Zn sulfide ores

from low-grade metamorphic terrains show abundant evidence of textural disequilibrium and, predictably, the sphalerites in these ores often exhibit a range of inter- and intragrain compositions which do not reflect their metamorphic environment. The retrograde reequilibration of sphalerite (point 2) found by Groves *et al.* (1975) was in metamorphosed nickel ores in ultramafic rocks of Western Australia and gave sphalerite compositions consistent with a *monoclinic* pyrrhotite + pyrite buffer below about 200°C (Scott and Kissin, 1973).

The observed variation in equilibrium sphalerite composition with iron sulfide assemblage over a few meters, or even cm, indicates that, in the absence of a fluid phase, the equilibrium domains of iron and sulfur are very small relative to the size of an orebody. If, for example, sulfur was mobile,  $a_{\text{S}_2}$  would be everywhere the same in an orebody, which at a given metamorphic  $T$  and  $P$  would fix  $a_{\text{FeS}}$  and hence sphalerite composition. The immobility of  $\text{S}_2$  is not surprising, however, in view of the like behavior of oxygen during metamorphism (*e.g.* Chinner, 1960; Mueller, 1967; Thompson, 1972; Greenwood, 1975), and the heterogeneity in sulfur isotopic ratios and fractionations encountered in some metamorphosed sulfide ores (*e.g.* Sangameshwar, 1972; Coomer and Schwarcz, 1974; Both and Smith, 1975).

Despite the fact that in several cases sphalerite compositions in Table 1 are in agreement with other metamorphic indicators, some of the pressures do seem, at first glance, to be excessively high when it is considered that each kilobar of confining pressure is equated with some 3.3 km of burial. The Geco deposit at Manitouwadge in the western Superior Province of the Archean Precambrian Shield must have been exhumed from a depth of about 24 km, while 500 km away in the eastern Superior Province, prehnite pumpellyite facies of metamorphism in the Abitibi Belt (Jolly, 1974) indicate relatively little erosion since metamorphism. Not only are these erosional levels grossly dissimilar, but the very deep burial of Geco seems incompatible with views expressed by Goodwin (1968) and others that the crust was much thinner in the Archean than it is now. One possible explanation is that confining pressure on the system is not due entirely to the weight of an overlying column of rock but includes an additional component of "tectonic overpressure." However, Brace *et al.* (1970) have argued that most rocks, under high pore pressures expected during metamorphism, can withstand only a few hundred bars of overpressure, even at high confining pressure. That  $P_{\text{H}_2\text{O}}$  was high during meta-



morphism in the Manitowadge area appears certain, in view of the abundant pegmatite bodies, migmatites, and hydrous minerals. Therefore, it must be concluded on the basis of the sphalerite data that the Geco deposit was indeed subjected to very deep burial, and that the Archean crust in the Manitowadge area was sufficiently thick to permit a tectonic regime consistent with the relatively high-pressure metamorphism.

### Acknowledgments

Many people have provided me with samples, stimulating advice, and geological information pertaining to this study on the sphalerite geobarometer. These include: G. M. Anderson, J. J. Fawcett, and F. G. Smith of the University of Toronto; R. J. Hamann and P. D. Fleming, formerly of the University of Toronto; S. R. R. Sangameshwar, formerly of the University of Saskatchewan; A. H. Bailes, formerly of the Manitoba Mines Branch; R. Weeks, Chief Geologist, Geco Division of Noranda Mines; V. G. Milne, Chief Geologist, Ontario Division of Mines; Edgar Froese, Geological Survey of Canada; C. J. A. Coates, Falconbridge Nickel Mines; Julian Boldy, formerly of Freeport Exploration; R. W. Henley, University of Otago; J. V. Ross, University of British Columbia; E. D. Ghent, University of Calgary; and Sandor Berglund, Institute of Geology, Uppsala, Sweden.

The microprobe facility at the University of Toronto is supervised and maintained by J. C. Rucklidge whom I thank for his help these past several years. Microprobe analyses were done by Elvira Gasparrini, O. P. Malik, A. Farkas and Z. L. Mandziuk.

The manuscript has benefitted from incisive criticism by G. M. Anderson.

Figures were drafted by F. Jurgeneit.

My research on sulfides is supported by operating grant A7069 from the National Research Council of Canada.

### References

- BAILES, A. H. (1971) Preliminary compilation of the geology of the Snow Lake-Flin Flon-Sherridon area. *Man. Dept. Mines Nat. Resour., Geol. Pap.* 1-71.
- BARTON, P. B. JR. (1970) Sulfide petrology. *Mineral. Soc. Am. Spec. Pap.* 3, 187-198.
- AND P. TOULMIN III (1966) Phase relations involving sphalerite in the Fe-Zn-S system. *Econ. Geol.* 61, 815-849.
- BERGLUND, SANDOR AND T. K. EKSTRÖM (1974) Sphalerite composition in relation to the stress distribution of a boudinage. *Lithos*, 7, 1-6.
- BIRD, G. W. AND J. J. FAWCETT (1973) Stability relations of Mg-chlorite-muscovite and quartz between 5 and 10 kb water pressure. *J. Petrol.* 14, 415-428.
- BOTH, R. A. AND J. W. SMITH (1975) A sulfur isotope study of base-metal mineralization in the Willyama complex, western New South Wales, Australia. *Econ. Geol.* 70, 308-318.
- BRACE, W. F., W. G. ERNST AND R. W. KALLBERG (1970) An experimental study of tectonic overpressure in Franciscan rocks. *Geol. Soc. Am. Bull.* 81, 1325-1338.
- BRISTOL, C. C. (1974) Sphalerite geobarometry of some metamorphosed orebodies in the Flin Flon and Snow Lake districts, Manitoba. *Can. Mineral.* 12, 308-315.
- CAMPBELL, F. A. AND V. G. ETHIER (1974) Sulfur isotopes, iron content of sphalerites, and ore textures in the Anvil ore body, Canada. *Econ. Geol.* 69, 482-493.
- CHINNER, G. A. (1960) Pelitic gneisses with varying ferrous/ferric ratios from Glen Clova, Angus, Scotland. *J. Petrol.* 1, 178-217.
- COOMER, P. G. AND H. P. SCHWARZ (1974) Sulfur isotopic study of a massive, volcanogenic Archean sulfide ore deposit (abstr.). *Geol. Soc. Am. Abstr. Progr.* 6, 693-694 (also in *Econ. Geol.* 69, 1179).
- DEWITT, D. B. AND E. J. ESSENE (1974) Sphalerite geobarometry applied to Grenville marbles (abstr.). *Geol. Soc. Am. Abstr. Progr.* 6, 709-710.
- DOE, B. R. (1962) Distribution and composition of sulfide minerals at Balmat, New York. *Geol. Soc. Am. Bull.* 73, 833-854.
- ENGEL, A. E. J. AND C. G. ENGEL (1958) Progressive metamorphism and granitization of the major paragneiss, Northwest Adirondack Mountains, New York, Part I, Total rock. *Geol. Soc. Am. Bull.* 69, 1369-1414.
- ESSENE, E. J. (1974) Barometry in metamorphic rocks (abstr.). *Geol. Soc. Am. Abstr. Progr.* 6, 724-726.
- FLEMING, P. D. (1971) *Metamorphism and Folding in the Mt. Lofty Ranges, South Australia with Particular Reference to the Dawesley-Kanmantoo Area*. Ph.D. Thesis, University of Adelaide, Adelaide, South Australia.
- FROESE, E. AND E. GASPARRINI (1975) Metamorphic zones in the Snow Lake area, Manitoba. *Can. Mineral.* 13, 162-167.
- GENKIN, A. D. (1971) Some replacement phenomena in copper-nickel sulfide ores. *Mineral. Deposita*, 6, 348-355.
- GOODWIN, A. M. (1968) Archean protocontinental growth and early crustal history of the Canadian Shield. *23rd Int. Geol. Congr.*, Vol. 1, 69-89.
- GREENWOOD, H. J. (1975) Buffering of pore fluids by metamorphic reactions. *Am. J. Sci.* 275, 573-593.
- GROVES, D. I., R. A. BINNS, F. M. BARRETT AND K. G. MCQUEEN (1975) Sphalerite compositions from Western Australian nickel deposits, a guide to equilibria below 300°C. *Econ. Geol.* 70, 391-396.
- HENLEY, R. W. (1975) Metamorphism of the Moke Creek lode, Otago, New Zealand. *New Zealand J. Geol. Geophys.* 18, 229-237.
- HOLDAWAY, M. J. (1971) Stability of andalusite and the aluminum silicate phase diagram. *Am. J. Sci.* 271, 97-131.
- JOLLY, W. T. (1974) Regional metamorphic zonation as an aid in study of Archean terrains: Abitibi region, Ontario. *Can. Mineral.* 12, 499-508.
- JONES, J. W. (1972) An almandine garnet isograd in the Rogers Pass area, British Columbia: the nature of the reaction and an estimation of the physical conditions during its formation. *Contr. Mineral. Petrol.* 37, 291-306.
- KISSIN, S. A. AND S. D. SCOTT (1972) Phase relations of intermediate pyrrhotites (abstr.). *Geol. Soc. Am. Abstr. Progr.* 4, 562 (also in *Econ. Geol.* 67, 1007).
- KULLERUD, G. AND H. S. YODER (1959) Pyrite stability relations in the Fe-S system. *Econ. Geol.* 54, 533-572.
- LANDIS, C. A. AND D. S. COOMBS (1967) Metamorphic belts and orogenesis in southern New Zealand. *Tectonophysics*, 4, 501-518.
- LUSK, J., F. A. CAMPBELL AND H. R. KROUSE (1975) Application of sphalerite geobarometry and sulfur isotope geothermometry to ores of the Quémont mine, Noranda, Quebec. *Econ. Geol.* 70, 1070-1083.

- MUELLER, R. F. (1967) Mobility of the elements in metamorphism. *J. Geol.* **75**, 565-582.
- NATRELLA, M. G. (1966) *Experimental Statistics*. N.B.S. Handbook **91**.
- RICHARDSON, S. W., M. C. GILBERT AND P. M. BELL (1969) Experimental determination of kyanite-andalusite and andalusite-sillimanite equilibria; the aluminum silicate triple point. *Am. J. Sci.* **267**, 259-272.
- RICKARD, D. T. AND H. ZWEIFEL (1975) Genesis of Precambrian sulfide ores, Skellefte District, Sweden. *Econ. Geol.* **70**, 255-274.
- RUCKLIDGE, J. C. AND E. GASPARRINI (1969) *Specifications of a Computer Program for Processing Electron Microprobe Analytical Data: EMPADR VII*. Department of Geology, University of Toronto.
- SANGAMESHWAR, S. R. R. (1972) *Trace Element and Sulphur Isotope Geochemistry of Sulphide Deposits from the Flin Flon and Snow Lake Areas of Saskatchewan and Manitoba*. Ph.D. Thesis, University of Saskatchewan, Saskatoon, Canada.
- SANGSTER, D. F. AND S. D. SCOTT (1976) Precambrian, stratabound, massive, Cu-Zn-Pb sulfide ores of North America. In, K. H. Wolf, Ed., *Handbook of Stratabound and Stratiform Ore Deposits*, Vol. 6, Elsevier, Amsterdam, in press.
- SCHWARCZ, H. P., S. D. SCOTT AND S. A. KISSIN (1975) Pressures of formation of iron meteorites from sphalerite compositions. *Geochim. Cosmochim. Acta*, **39**, 1457-1466.
- SCOTT, S. D. (1973) Experimental calibration of the sphalerite geobarometer. *Econ. Geol.* **68**, 466-474.
- (1974) Sphalerite geobarometry of regionally metamorphosed terrains (abstr.). *Geol. Soc. Am. Abstr. Progr.* **6**, 946-947.
- AND H.L. BARNES (1971) Sphalerite geothermometry and geobarometry. *Econ. Geol.* **33**, 653-669.
- AND S.A. KISSIN (1973) Sphalerite composition in the Zn-Fe-S system below 300°C. *Econ. Geol.* **68**, 475-479.
- SKINNER, B.J. (1958) The geology and metamorphism of the Nairne Pyritic Formation, a sedimentary sulfide deposit in South Australia. *Econ. Geol.* **53**, 546-562.
- STEPHANSSON, O. AND H. BERNER (1971) The finite element method in tectonic processes. *Phys. Earth Planet. Inter.* **4**, 301-321.
- THOMPSON, J.B. JR. (1972) Oxides and sulfides in regional metamorphism of pelitic schists. *24th Int. Geol. Congr., Sect. 10, Geochem.* 27-35.
- TOULMIN, P. III (1960) Effect of Cu on sphalerite phase equilibria—a preliminary report (abstr.). *Geol. Soc. Am. Bull.* **71**, 1993.
- AND P.B. BARTON, JR. (1964) A thermodynamic study of pyrite and pyrrhotite. *Geochim. Cosmochim. Acta*, **28**, 641-671.
- TURNER, F.J. (1968) *Metamorphic Petrology*. McGraw-Hill, 403 p.
- WIGGINS, L.B. AND J.R. CRAIG (1975) A reconnaissance investigation of chalcopyrite-sphalerite relationships in the Cu-Fe-Zn-S system (abstr.). *Geol. Soc. Am. Abstr. Progr.* **7**, 1317.
- WINKLER, H.G.F. (1974) *Petrogenesis of Metamorphic Rocks*. Springer-Verlag, 3rd Ed., 320 p.
- WRIGHT, J.B. AND J.F. LOVERING (1967) Electron probe microanalysis and geothermometry of sphalerite in the Moke Creek sulphide lode, Wakapitu, Queenstown. *Am. Mineral.* **52**, 524-529.