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MINERALOGICAL NOTES

ELECTRON PROBE MICROANALYSIS AND GEOTHERMOMETRY OF SPHALERITE IN THE MOKE CREEK SULPHIDE LODE, WAKATIPU, QUEENSTOWN

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Introduction

A recent paper (Wright, 1967) describes the petrography and paragenesis of the Moke Creek sulphides which occur as narrow concordant bands in a chloritic greenschist of the Otago schists, and are probably of syngenetic origin. X-ray and thermomagnetic investigation of pyrrhotites showed that both monoclinic and hexagonal modifications are present, as well as intimate mixtures of the two.

Hexagonal pyrrhotite occurs with pyrite as small irregular lenses in chalcopyrite-rich facies of the lode, while parts rich in pyrite or pyrrhotite contain monoclinic pyrrhotite or mixtures of monoclinic and hexagonal phases. The pyrrhotite falls into two compositional groups: 47.2 ± 0.1 atomic %Fe (hexagonal modifications) and 46.5 ± 0.1 atomic %Fe (monoclinic modifications) which plot on Arnold's (1962) solvus at about 350°C and 500°C, respectively. Results of recent investigations (*e.g.* Desborough and Carpenter, 1965; Clark, 1966) strongly suggest that neither monoclinic nor hexagonal pyrrhotite is a reliable geothermometer.

Small sphalerite grains occur scattered through the lode and these were analysed with the electron probe X-ray microanalyser, in hopes that the sphalerite geothermometer (Kullerud, 1953) could be used to supplement the pyrrhotite data. Recent work by Barton and Toulmin (1963 and written communication) has shown, however, that this solvus does not have the form determined by Kullerud and is also of doubtful value as a geothermometer. On the other hand it is of some importance to the eventual delineation of the Fe-Zn-S system to know the composition of sphalerites in well-defined natural assemblages such as the Moke Creek sulphide lode.

Analytical Method

Analyses of sphalerites and other sulphides were carried out using the Applied Research Laboratories' electron probe X-ray microanalyser at the Australian National University. An accelerating potential of 20Kv on the primary electron beam (approximately 1–2 microns wide), was employed, and iron and manganese concentrations were measured using pure

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metals as standards. All X-ray intensity readings were corrected for beam current drift, detector dead time and background. A procedure for the remaining absorption, fluorescence and matrix corrections, developed by K. L. Williams (1965; 1967), was used to arrive at the final values. Iron contents of standard troilite and of pyrite and pyrrhotite in the samples were also measured as a check on the method.

Step traverses of 5- or 10-micron interval were made across each analyzed grain to test for compositional zoning. No positive evidence of zoning was found, even in the largest grains (1 mm) where over 20 analysis points were made.

TABLE 1. ELECTRON PROBE ANALYSES OF MOKE CREEK SPHALERITES AND CO-EXISTING PYRRHOTITE DATA (FROM WRIGHT, 1967)

Specimen Number[1]	Paragenesis		Sphalerite		Pyrrhotite	
	Dominant Phase	Phases in contact with sphalerite	FeS (wt. %)	MnS (wt. %)	Fe (wt. %)	Original symmetry state
P.26121	chalcopyrite	pyrrhotite	13.2±0.4(13)[2] 13.3±0.3(3)	1.2±0.2 1.0±0.2	47.3±0.1	hexagonal
		chalcopyrite	13.5±0.2(24)	0.8±0.2		
OU 19006	chalcopyrite	pyrrhotite	12.9±0.3(5) 12.4±0.4(3)	0.8±0.2 0.8±0.2	47.2±0.1	hexagonal
		chalcopyrite	13.0±0.3(3)	0.8±0.2		
P.26119	pyrite	pyrite-chalcopyrite	12.8±0.4(4) 12.4±0.4(6)	0.3±0.1 0.2±0.1	46.5±0.1 (after annealing)	monoclinic
P.26117	pyrrhotite	pyrrhotite	11.4±0.3(3) 11.4±0.5(4) 11.5±0.3(3)	0.3±0.1 0.3±0.1 0.3±0.1	46.6±0.1 (afrer annealing)	monoclinic and hexagonal (intergrown)

[1] Numbers prefixed P refer to New Zeal. Geol. Surv. specimens, that with OU prefix to an Otago Univ. specimen.

[2] Number of analyses.

N.B. Sphalerites have <0.01% Cu.

Pyrite and pyrrhotite (both hexagonal and monoclinic modifications) have <0.1% Mn and <0.1% Cu.

The results are presented in Table 1, together with some additional information about associated pyrrhotite in the samples, taken from Wright (at the press).

DISCUSSION

It will be seen that manganese is low in all the sphalerites, especially in those accompanying the more iron-deficient monoclinic pyrrhotite. Sympathetic variation of iron and manganese in pyrite-sphalerite assemblages has been noted by Sims and Barton (1961).

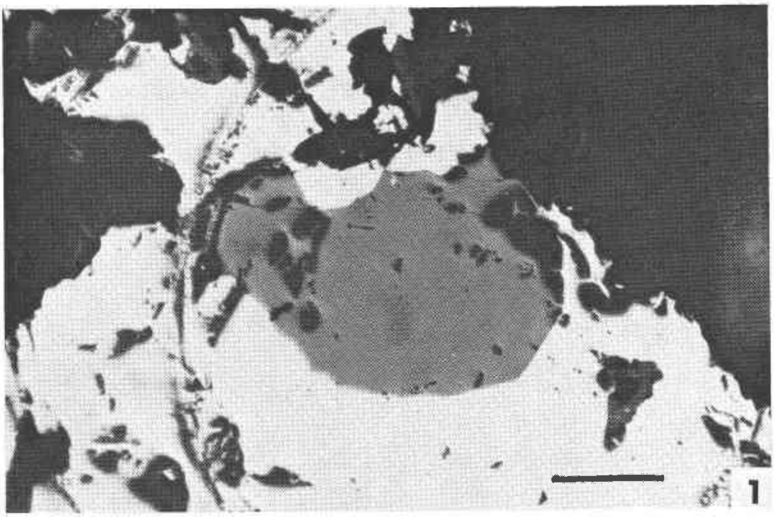

FIG. 1. Subhedral sphalerite grain (grey) in chalcopyrite. Scale bar 0.1 mm. Specimen P. 26121

It seems clear that grain size and immediate mineralogical environment (Figs. 1–4) of the sphalerite in a given specimen does not significantly affect the iron content, but there is a slight tendency for sphalerite in iron sulphide-rich samples to contain less FeS—particularly in P26117, which is mainly composed of monoclinic pyrrhotite.

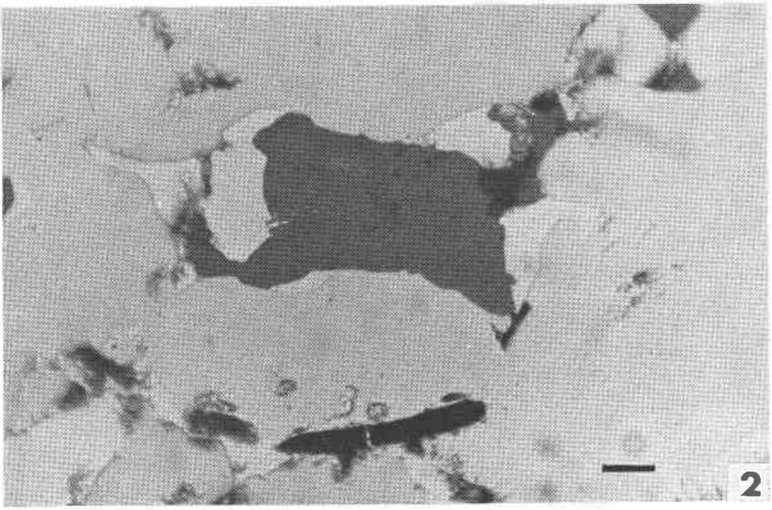

FIG. 2. Small anhedral sphalerite grain in pyrrhotite, with discontinuous border of chalcopyrite (palest grey). Scale bar 0.01 mm. Specimen P. 19006.

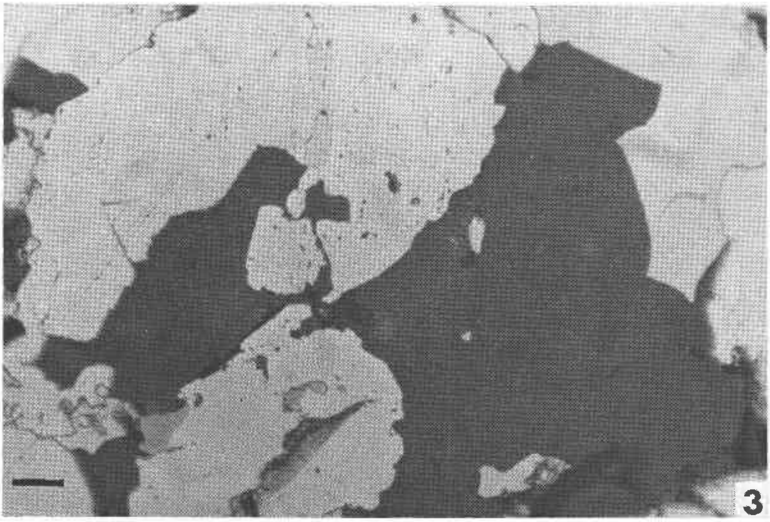

FIG. 3. Anhedral sphalerite in pyrite aggregate, with some chalcopyrite, esp. in upper right of picture, and rare pyrrhotite. Scale bar 0.01 mm. Specimen P. 26119.

GEOTHERMOMETRY, AND THE FE-ZN-S SYSTEM

From a study of aegirine-riebeckite-bearing intercalations in garnet-oligoclase zone schists of the Haast Schist group in South Westland, White (1962) has inferred a possible maximum recrystallisation tempera-

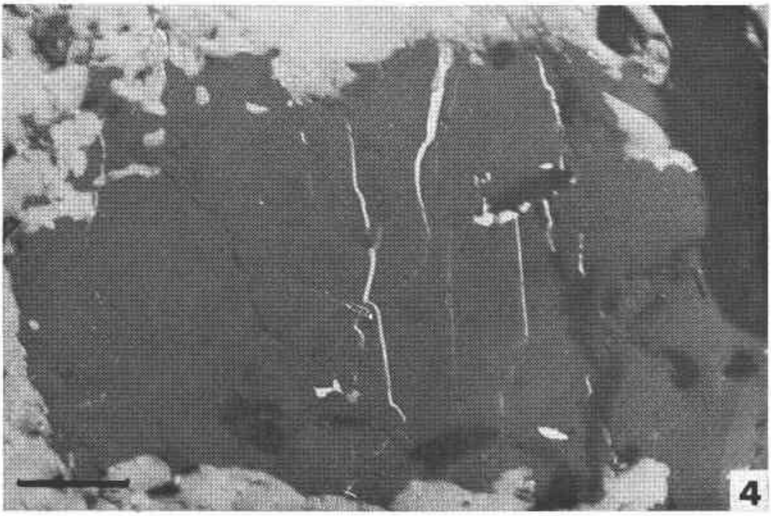

FIG. 4. Large sphalerite thinly veined by chalcopyrite and surrounded by pyrrhotite. Scale bar 0.1 mm. Specimen P. 26117.

ture of 520°C. Metamorphic temperatures of chlorite-zone rocks would be considerably lower, and Mason (1962) records a figure of 390°C, deduced from the soda content of muscovite in the Chl 4 zone of Turner and Hutton—although with some reservations as to its reliability. His figure approaches that originally deduced from primary hexagonal pyrrhotites at Moke Creek, (*i.e.* 350°C) which are also in Chl 4 rocks. If the sphalerites in the Moke Creek assemblages formed around 350–400°C (*i.e.* well below 580°C) then their relatively low iron contents are consistent with the suggestion by Barton nd Toulmin (1963 and written communication), that the boundary between the pyrite+sphalerite and sphalerite+pyrrhotite fields in their plot of the FeS-ZnS-S system (projected on the FeS-ZnS binary), at temperatures below 580°C, has a positive slope (*i.e.* increasing %FeS with increasing temperatures).

There is some evidence that iron-deficient monoclinic pyrrhotites can crystallise as primary phase at relatively low temperatures (Carpenter and Desborough, 1964; Sawkins *et al.*, 1964; Clark, 1966) and monoclinic pyrrhotite at Moke Creek may have crystallized as a primary phase at a lower temperature than the hexagonal modification. The slightly lower iron content of sphalerite in association with monoclinic pyrrhotite is consistent with such a possibility.

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THE EFFECT OF SYNNEUSIS ON PHENOCRYST DISTRIBUTION PATTERNS IN SOME PORPHYRITIC IGNEOUS ROCKS

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INTRODUCTION

Segregation of early crystals into clusters exhibiting glomero-porphyritic or synneusis structure characterizes many igneous rocks and is especially striking in porphyries. These widespread, but largely neglected, structures are of general petrologic interest for several reasons. First, their formation implies a drifting together and attachment of crystals freely suspended in a fluid medium (synneusis: Vogt, 1921). Such structures, accordingly, provide clear petrographic evidence of igneous origin. Moreover, this process of attachment controls several basic elements of the magmatic fabric, notably: (1) the mutual orientation of adjacent crystals in synneusis relation; (2) the nature of their common boundary; and, (3) the small-scale segregation of minerals within the fabric as a whole. A more general survey of the problem of synneusis will be given in a subsequent paper. The present note is concerned only with the last of these textural features.

It is a common observation that grouping of like crystals into glomeroporphyritic structures is more frequent than that of unlike minerals. If this relation is a general one, then synneusis is a selective process exerting a definite control on the distribution pattern of the minerals in the overall fabric. This study is an attempt to test this generalization and to quantitatively define the preferential character of synneusis for several common individual minerals and mineral pairs.