

Iron-nickel partition in metamorphosed olivine–sulfide assemblages from Perseverance, Western Australia

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Abstract

A comparatively regular partition of Fe and Ni exists between forsteritic olivine and the bulk sulfide fraction in specimens from an ultramafic body metamorphosed under amphibolite facies conditions, estimated at $600 \pm 50^\circ\text{C}$ and 3 to 5 kbar. The distribution coefficient, $K_D = (\text{Fe}/\text{Ni})_{\text{olivine}} \times (\text{Ni}/\text{Fe})_{\text{sulfide}}$, is 23.9 ± 1.0 for three samples whose bulk sulfide fractions fall within the compositional field of monosulfide solid solution at 600°C , and 23 ± 4 for all samples. Available experimental and natural data indicate a pronounced temperature dependence in the partition relationship, which thus has potentially important applications in genetic studies of Fe–Ni sulfide ores in ultramafic rocks.

Introduction

Due to rapid reequilibration at low temperatures, geothermometric assessments of sulfide constituents usually have limited relevance to the conditions under which base metal deposits formed within their varied host rocks. However, this difficulty is alleviated in iron–nickel sulfide ores from mafic and ultramafic rocks, first because the two metals concerned show both chalcophile and lithophile affinities, and secondly since a monosulfide solid solution (M_{ss} ; $\text{Fe}_{1-x}\text{S}-\text{Ni}_{1-x}\text{S}$) dominates most observed ore compositions over a wide temperature range, as indicated by the experimental work of Kullerud (1963) and others. Clark and Naldrett (1972) found a systematic partition of iron and nickel between synthetic Fe–Ni olivine and M_{ss} at 900°C , and deduced a pronounced temperature variation in the distribution coefficient from thermodynamic data. Similar experimental results were obtained by Rajamani (1974) for orthopyroxene– M_{ss} at 900°C . Earlier, Häkli (1963) demonstrated a linear relationship between nickel contents of bulk sulfide fractions and of ferromagnesian silicates in a number of peridotite and norite intrusions from Finland. These observations suggest a powerful tool in genetic studies of such ores, for which data from well-understood igneous and metamorphic environments constitute an important test.

The recently-discovered nickel sulfide deposits in

Archean ultramafic rocks from the Yilgarn Block of Western Australia are metamorphosed and occur mainly in highly-deformed amphibolite facies terrains (Binns *et al.*, 1976). Material especially suitable for an evaluation of olivine–sulfide partition relationships at moderate temperatures occurs in the Perseverance deposit, 330 km north of Kalgoorlie, described by Martin and Allchurch (1976). This deposit lies in a steeply dipping ultramafic body up to 700 m wide, wherein a small core of comparatively unrecrystallized dunite with relic cumulate texture passes outwards into fine- or medium-grained (0.1–2 mm) tectonites, annealed mylonites, and granofelses showing equilibrium textural intergrowths between dominant metamorphic olivine, rarer talc and magnetite (some with chromite cores), and scarce tremolite, chlorite, and magnesite. Bladed olivine–talc rocks comparable with those described by Evans and Trommsdorff (1974) are developed locally, but the intrusion was evidently not entirely serpentinized prior to the high-grade metamorphic and deformational episode. Retrogressive serpentinization of metamorphic olivines, a common feature of many other Western Australian nickel deposits, is lacking in a large portion of the body. A wide compositional spectrum with respect to Fe–Ni ratio is represented in Perseverance ores and protores (Fig. 1). Sulfide aggregates, consisting largely of varying proportions of pyrrhotite, pentlandite, and pyrite (Table 1) but with minor chalcopyrite and valleriite, display smoothly

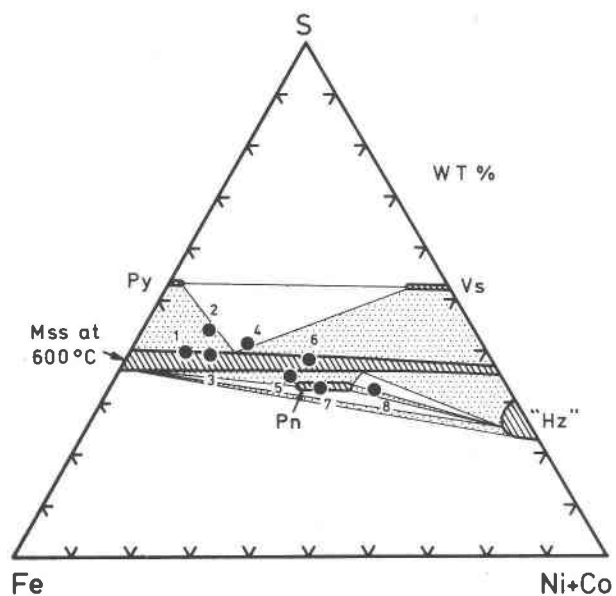


FIG. 1. Bulk composition of sulfide fractions in Perseverance ultramafic rocks (numbered as in Table 1), compared with phase relationships in the central portion of the system Fe-Ni-S in equilibrium with vapor at 600°C (after Naldrett *et al.*, 1967; Shewman and Clark, 1970). Hatching denotes solid solutions, and divariant fields are stippled.

curved boundaries against the metamorphic silicates to which they are largely interstitial. In places, sulfide particles are enclosed by olivine.

The immediate country rocks of the Perseverance

ultramafic body consist mainly of felsic schists (plagioclase-quartz-orthoclase-biotite-muscovite \pm almandine) and amphibolites (green hornblende-plagioclase \pm quartz \pm almandine \pm biotite), with some ferruginous metasediments (quartz-hornblende-cummingtonite-biotite \pm plagioclase \pm almandine) and smaller ultramafic horizons (olivine-talc \pm tremolite \pm chlorite, commonly retrogressively altered). The nature of hornblendes in metabasic and ferruginous rocks suggests mid-amphibolite facies metamorphism, while the occurrences of almandine indicate moderate pressures (probably exceeding 3 kbar; compare Winkler, 1974, pp. 208-211). In the ultramafic rocks, the stability of forsterite plus talc and the absence of anthophyllite or enstatite (known in comparable material from higher-grade portions of the Yilgarn Block; Binns *et al.*, 1976) constrain peak temperatures to the 500-680°C range (Bowen and Tuttle, 1949; Yoder, 1966; Greenwood, 1963), the assumption of water pressures equal to lithostatic pressure being geologically reasonable here for unmineralized rocks. As indicated by Trommsdorff and Evans (1972) the influence of Fe substitution can be ignored, and the low limit should perhaps be raised since antigorite rather than lizardite or chrysotile is the stable serpentine species in lower-grade environments north of Perseverance. The persistence of muscovite and the lack of anatexis phenomena in felsic schists impose comparable limits on maximum

TABLE 1. Analytical data for Perseverance samples

		1	2	3	4	5	6	7	8
OLIVINE wt. %	FeO	8.35	10.16	7.73	7.42	7.28	7.18	7.25	6.55
	NiO	0.068	0.125	0.100	0.22	0.33	0.29	0.33	0.34
Atom ratio	Fe/Ni	128	85	80	35	22.9	25.8	23.0	20.0
Mole %	Fo	91	89	92	92	92	92	92	93
BULK SULFIDE wt. %	Fe	9.77	16.59	6.99	2.54	0.33	0.93		0.14
	Co	0.039	0.094	0.041	0.028	0.011	0.002		0.007
	Ni	1.89	4.37	2.09	1.21	0.27	0.97		0.27
	Cu	0.036	0.190	0.105	0.017	0.003	0.002		0.004
	S	7.80	16.60	5.94	2.70	0.33	1.18		0.20
Total sulfide		19.5	37.8	15.2	6.5	0.9	3.1	Tr.	0.6
Atom ratio	Fe/Ni	5.43	3.99	3.52	2.21	1.28	1.01	0.93**	0.55
Mineralogy*		Po-Pn	Po-Pn-Py	Po-Pn-Py	Pn-Po	Pn-Po-Py	Pn-Py	Pn	Pn-Ml-Py
U.W.A. Museum No.		77902	77882	77883	77905	77884	77886	77887	77889

* Listed in order of decreasing abundance. Po, pyrrhotite; Pn, pentlandite; Py, pyrite; Ml, millerite. Traces of chalcopyrite and vallerite also present.

** From electron microprobe analysis of trace pentlandite: Fe=31.3; Ni=35.3; S=33.3 wt%. Olivine analyses by R.A. Binns, sulfide fractions by S.S. Michael.

temperature and minimum pressure (Althaus *et al.*, 1970; Day, 1973). Although aluminum silicates are unknown at Perseverance, andalusite is typical of similar environments elsewhere in the Yilgarn Block.

Collectively, the above criteria and the regional setting of Perseverance (Binns *et al.*, 1976, Fig. 3) indicate that this area suffered a metamorphism whose peak conditions are reasonably well established at $600 \pm 50^\circ\text{C}$ and 3 to 5 kbar. Using models based on the mathematics of Crank (1956) and extrapolating the distribution coefficient determined by Clark and Long (1970), it may be estimated that effective equilibration of nickel throughout 1 mm diameter olivine grains would require about 10 million years at 600°C , which seems acceptably close to reality. The compositional limits of M_{ss} at 600°C in the synthetic system Fe-Ni-S are indicated on Figure 1, after Naldrett *et al.* (1967). Although the possible occurrence of other phases will be discussed below, a monosulfide solid solution would evidently dominate the sulfide fraction of most Perseverance samples during their metamorphism.

Methods

Analyses of bulk sulfide fractions were obtained from finely-crushed slices of drill core, using the selective bromine leach and acid extraction procedure of Davis (1972). Iron, nickel, cobalt, and copper were determined by atomic absorption spectrophotometry, and sulfur was measured gravimetrically. Some attack of silicates occurred, for which corrections were applied to Fe values, based on the Mg contents of leach solutions and equivalent data for unmineralized dunites and serpentinites. The effect of these corrections on Fe/Ni ratios of bulk sulfide fractions is greatest in those samples with the least total sulfide, and estimates of likely errors are indicated by bars on Figure 2. Additional confidence for the figures cited in Table 1 arises from the close correspondence between the plotted positions on Figure 1 and the present modal mineralogy of the samples. The most discrepant sample in this connection is No. 4, but the correction necessary to make the analysis more consistent with the sulfide mode would not improve its plot on Figure 2. Non-representivity of the polished slice or of the analyzed sample is suspected. The bulk analysis of sample 8 is slightly sulfur-deficient relative to its mineralogy, but in this case the Mg content of the leached solution required a comparatively large though apparently well-established correction to the Fe content of the bulk sulfide fraction.

Olivine analyses were performed on a Geoscan

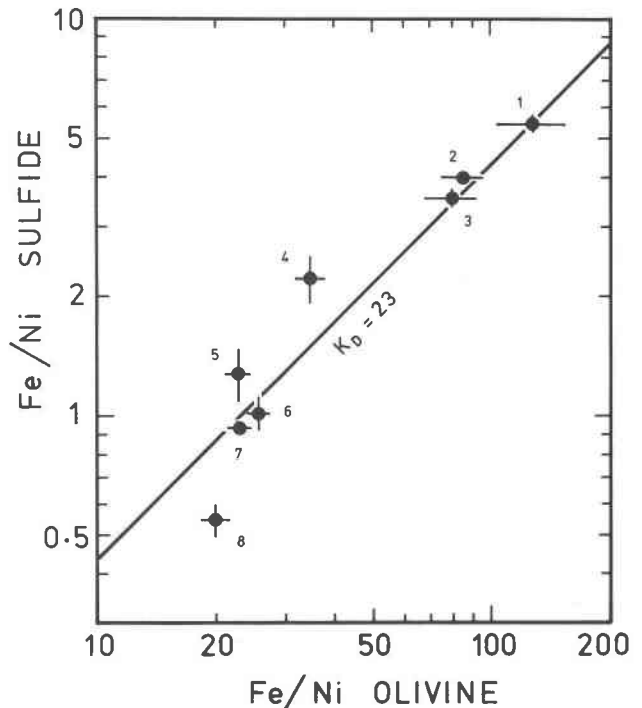


FIG. 2. Logarithmic plot of the atom ratio Fe/Ni in olivine against that of coexisting bulk sulfide fractions. Error bars are discussed in the text. Specimens are numbered as in Table 1.

electron microprobe in the Department of Mineralogy and Petrology, University of Cambridge, using pure metal standards and the procedures of Sweetman and Long (1969). No continuous fluorescence factor was applied. Particular care was taken in selecting equidistant high and low Ni background positions from peak profiles and to optimize pulse-height discrimination. For each sample, 20 separate olivine points were counted for between 30 and 50 seconds so as to accumulate between 25,000 and 40,000 counts for Ni radiation, and background values were determined over a comparable total time. Error bars representing two standard deviations from count statistics are shown on Figure 2. No statistically significant variations were observed between individual grains in a sample. Forsterite contents listed in Table 1 are based on less systematic microprobe analyses for Mg and Si. MnO contents averaged 0.12 weight percent, and Al, Cr, and Ca are negligible.

Most analyzed samples conform to the generalized description given above. However, specimens 6 and 8 contain substantial quantities of relic igneous olivine, recognizable by its habit and brownish color (Martin and Allchurch, 1976; Binns *et al.*, 1976). Although differences between the two types are barely significant, only data for colorless metamorphic olivine

granules between the larger relics were used. In specimen 1 about 90 percent of the olivine is retrogressively altered to serpentine. From experience with other Western Australian localities, this falls in the danger range where redistribution of Fe and Ni might occur in olivine remnants (*cf.* Rucklidge, 1972), and sulfides could suffer some oxidation. However, microprobe analyses taken at the centers of the largest olivine remnants showed no significant variations, and the sample plots satisfactorily on Figure 2. About 10 percent of the olivine in specimen 4 is replaced by veins of serpentine. The other specimens show no such alteration. Specimen 7 contains too little sulfide for bulk analysis by the method above, and an averaged microprobe analysis of the trace pentlandite has been used in Figure 2.

Discussion

A comparatively regular partition relationship is shown by the logarithmic plot of atom ratios in Figure 2. Before discussing this further, the possible influence of other sulfide phases coexisting with or occurring in place of *Mss* at peak metamorphic temperatures will be examined. Allowing no tolerance in the analyses of bulk sulfide fractions, those of specimens 2 and 4 lie to the sulfur-rich side of the 600°C *Mss* limits (Fig. 1). From the location of the *Mss*-pyrite-vaesite univariant field determined by Naldrett *et al.* (1967), dominant *Mss* would have been accompanied during metamorphism by some pyrite in specimen 2, and by a little vaesite and minor pyrite in specimen 4 (Fig. 1). However, tie-line orientations are such that the Fe/Ni ratio of peak metamorphic *Mss* in both samples would resemble that of the respective bulk sulfide fractions (see also Kullerud, 1963, Fig. 70; Shewman and Clark, 1970, Fig. 1). Specimen 5 lies so close to the *Mss* field in Figure 1 that the effect of other phases is negligible. Relationships in metal-rich specimens 7 and 8 depend on whether the stability of pentlandite (610°C at low pressure) was exceeded during metamorphism. If it was, an almost equal volume of the (Ni, Fe)_{3±x}S₂ phase ("Hz", Fig. 1) would have accompanied *Mss*, and the Fe/Ni ratios of *Mss* would be drastically altered to about 6 and 1.5, respectively, according to the qualitative tie-lines of Kullerud (1963, Fig. 69). This would certainly not improve the expected plotting of these samples on Figure 2. On the other hand, had pentlandite remained stable during metamorphism (see Fig. 1), tie lines in experimental 600° isothermal sections for the system Fe-Ni-S (Shewman and Clark, 1970, Fig. 1) suggest a small *Mss* component

with a fortuitously similar Fe/Ni ratio to the bulk sulfide fraction for specimen 8, whereas Fe and Ni activities in the pentlandite persisting in specimen 7 would be in the same proportion as in an *Mss* with similar Fe/Ni ratio, resulting in an almost coincidental conformity of these two specimens to the olivine-sulfide relationship defined by problem-free specimens 1, 3, and 6.

However, the imprecision of analytical data and of the metamorphic temperature estimate, plus uncertain pressure effects, do not justify rigorous application of such arguments to the Perseverance samples at this stage. An alternative, but unsubstantiated, interpretation of Figure 2 is that *Mss* (with which the olivines equilibrated) was indeed the sole sulfide phase during metamorphism, and that adjustments took place in the metal-sulfur ratio during subsequent cooling, with olivine and magnetite acting as a buffer. The original magmatic sulfides were probably also altered in composition during serpentinization prior to the olivine-producing metamorphism (Groves *et al.*, 1974), but so far as the higher temperature reequilibration was concerned, diffusion calculations similar to those mentioned previously suggest that after a temperature fall of not much more than 100°C the silicates and sulfides effectively become separate systems. Although it is difficult to assess the consequential changes in nickel contents of silicates during this cooling interval, there need be little modification of olivine Fe/Ni ratios, since *Mss* would remain an important phase and the olivine-*Mss* Fe-Ni partition coefficient is unlikely to alter greatly before olivine ceased to participate in the reequilibration. A more careful appraisal of compositional zoning in olivines might resolve this point.

For samples 1, 3, and 6—whose bulk sulfide fractions fall within the *Mss* field at 600°C—the indicated distribution coefficient, $K_D = (\text{Fe}/\text{Ni})_{\text{olivine}} \times (\text{Ni}/\text{Fe})_{\text{sulfide}}$, is 23.9 ± 1.0 (mean deviation). The equivalent coefficient for all eight samples is 23 ± 4 , or 22 ± 3 for all except the most seriously discrepant specimen 8. These values differ significantly from the 900°C experimental figure of 33.2 ± 3.4 obtained by Clark and Naldrett (1972) using synthetic Fe-Ni olivines, and are much too low relative to their calculated temperature dependence. In comparing their experiments with measurements on ores from high-temperature igneous environments, Clark and Naldrett (1972) recorded a coefficient of 10.8 for the Giant Nickel Deposit of British Columbia, and K_D ranging from 2 to 36 (average 17.0) in basal units of the Duluth gabbro complex. Unfortunately Häkli

(1963) did not determine iron in the olivines used for his study of nickel partition in Finnish peridotites and norites, but from his cited Ni/Mg ratios it is possible to estimate an average Fe-Ni distribution coefficient, also with a low value of 8.5.

The limited natural data thus indicate a substantial variation in the olivine-sulfide partition of Fe and Ni between the igneous and metamorphic environments. Absolute differences between the natural and experimental distribution coefficients possibly arise from cation ordering effects in olivine (Finger and Virgo, 1971; Rajamani *et al.*, 1975), the distinct preference of Ni for the M1 site preventing direct extrapolation from synthetic Fe-Ni olivines to their magnesian equivalents in igneous and metamorphic rocks. The apparent temperature dependence of the distribution coefficient exceeds that which is normal for coexisting silicates, so further experimental work and data collection from definitive natural environments are clearly warranted. The aberrant plotting on Figure 2 of specimens 4 and 8 from Perseverance, however, provide a warning that numerous measurements may be necessary to interpret particular localities. Factors such as cation order in olivine and non-ideality in monosulfide solid solutions, and the influence of varying metal-sulfur ratios in the sulfide fractions, will no doubt need further investigation before quantitative applications to natural situations become possible.

However, the potential of the method in resolving important problems of ore genesis is clear. For example, olivines close to Fo₉₀ with NiO about 0.5 weight percent are characteristic in ultramafic rocks of komatiitic affinity (*cf.* Green *et al.*, 1975), with which Archean nickel sulfide deposits are typically associated. Knowledge of partition relationships at temperatures near the crystallization point of *Mss* from sulfide or sulfide-oxide melts (*ca.* 1000–1200°C; Kullerud, 1963) would place constraints on possible compositions of unmetamorphosed magmatic sulfides that had opportunity for subsolidus equilibration with such olivines. Basal nickel ores at Kambalda, Western Australia, which are thought to have accumulated from disseminated globules of immiscible sulphide liquids before consolidation of their ultramafic host rocks (Ewers and Hudson, 1972; Naldrett, 1973), possess very high Fe/Ni ratios (average 5.4; Ewers and Hudson, 1972). For these to have equilibrated with typical komatiitic olivines (Fe/Ni \approx 20) a very low distribution coefficient ($K_D \approx$ 4) would be necessary. Perhaps this is a guide to partition relationships between sulphide and silicate melts

near the liquidus temperatures of the latter, or alternatively the ore compositions have been seriously modified during serpentinization.

Note added in proof

Porphyroblasts of anthophyllite, 100Mg/(Mg + Fe) = 90.3, have now been discovered in an unmineralized sample (77906) of the Perseverance ultramafic, associated with metamorphic olivine (Fo 92.5), minor chlorite, and chromite. The lack of carbonates and sulfides suggests these cannot be attributed to dilution of water vapor by other volatiles. Although forsterite-talc assemblages are the more general rule at Perseverance, this occurrence of anthophyllite indicates metamorphic temperatures may have locally fluctuated up to or slightly in excess of 680°C.

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References

- ALTHAUS, E., E. KAROTKE, K. N. NITSCH AND H. G. F. WINKLER (1970) An experimental reexamination of the upper stability limit of muscovite plus quartz. *Neues Jahrb. Mineral. Monatsh.*, 325–336.
- BINNS, R. A., R. J. GUNTHORPE AND D. I. GROVES (1976) Metamorphic patterns and development of greenstone belts in the eastern Yilgarn Block, Western Australia. In, B. F. Windley, Ed., *The Early History of the Earth*. John Wiley and Sons, London, in press.
- BOWEN, N. L. AND O. F. TUTTLE (1949) The system MgO-SiO₂-H₂O. *Geol. Soc. Am. Bull.* **60**, 439–460.
- CLARK, A. M. AND J. V. P. LONG (1970) The anisotropic diffusion of nickel in olivine. In, *Thomas Graham Memorial Symposium on Diffusion Processes*. Gordon and Breach, London, p. 511–521.
- CLARK, T. AND A. J. NALDRETT (1972) The distribution of Fe and Ni between synthetic olivine and sulfide at 900°C. *Econ. Geol.* **67**, 939–952.
- CRANK, J. (1956) *The Mathematics of Diffusion*. Oxford University Press, London, 347 p.
- DAVIS, C. E. S. (1972) Analytical methods used in the study of an ore intersection from Lunnon Shoot, Kambalda. *Econ. Geol.* **67**, 1091–1092.
- DAY, H. W. (1973) The high temperature stability of muscovite plus quartz. *Am. Mineral.* **58**, 255–262.
- EVANS, B. W. AND V. TROMMSDORFF (1974) On elongate olivine of metamorphic origin. *Geology*, **1**, 131–132.
- EWERS, W. E. AND D. R. HUDSON (1972) An interpretive study of a nickel-iron sulfide ore intersection, Lunnon Shoot, Kambalda, Western Australia. *Econ. Geol.* **67**, 1075–1091.
- FINGER, L. W. AND D. VIRGO (1971) Confirmation of Fe/Mg ordering in olivines. *Carnegie Inst. Wash. Year Book*, **70**, 221–225.
- GREEN, D. H., I. A. NICHOLLS, M. VILJOEN AND R. VILJOEN (1975)

- Experimental demonstration of the existence of peridotitic liquids in earliest Archean magmatism. *Geology*, **3**, 11-14.
- GREENWOOD, H. J. (1963) The synthesis and stability of anthophyllite. *J. Petrol.* **4**, 317-351.
- GROVES, D. I., D. R. HUDSON AND T. B. C. HACK (1974) Modification of iron-nickel sulfides during serpentinization and talc-carbonate alteration at Black Swan, Western Australia. *Econ. Geol.* **69**, 1265-1281.
- HÄKLI, A. (1963) Distribution of nickel between the silicate and sulfide phases in some basic intrusions in Finland. *Bull. Comm. Géol. Finlande*, **209**, 1-53.
- KULLERUD, G. (1963) The Fe-Ni-S system. *Carnegie Inst. Wash. Year Book*, **62**, 175-189.
- MARTIN, J. E. AND P. D. ALLCHURCH (1976) Perseverance nickel deposit. In, C. Knight, Ed., *Economic Geology of Australia and Papua-New Guinea*, Aust. Inst. Min. Metall., Melbourne, in press.
- NALDRETT, A. J. (1973) Nickel sulfide deposits—their classification and genesis, with special emphasis on deposits of volcanic association. *Trans. Can. Inst. Min. Metall.* **76**, 183-201.
- , J. R. CRAIG AND G. KULLERUD (1967) The central portion of the Fe-Ni-S system and its bearing on pentlandite exsolution in iron-nickel sulfide ores. *Econ. Geol.* **62**, 826-847.
- RAJAMANI, V. (1974) Distribution of nickel and cobalt between synthetic sulfide and orthopyroxene (abstr.). *Econ. Geol.* **69**, 1185-1186.
- , G. E. BROWN AND C. T. PREWITT (1975) Cation ordering in Ni-Mg olivine. *Am. Mineral.* **60**, 292-299.
- RUCKLIDGE, J. C. (1972) A study of the redistribution of nickel in the serpentinization of olivine. In, G. Shiroda, Ed., *Proceedings of the 6th International Conference on X-ray Optics and Microanalysis*, University of Tokyo Press. p. 743-747.
- SHEWMAN, R. W. AND L. A. CLARK (1970) Pentlandite phase relations in the Fe-Ni-S system and notes on the monosulfide solid solution. *Can. J. Earth Sci.* **7**, 67-85.
- SWEATMAN, T. R. AND J. V. P. LONG (1969) Quantitative electron-probe microanalysis of rock forming minerals. *J. Petrol.* **10**, 332-379.
- TROMMSDORFF, V. AND B. W. EVANS (1972) Progressive metamorphism of antigorite schist in the Bergell tonalite aureole (Italy). *Am. J. Sci.* **272**, 423-437.
- WINKLER, H. G. F. (1974) *Petrogenesis of Metamorphic Rocks*. 3rd Edition. Springer-Verlag, Berlin. 320 p.
- YODER, H. S. (1966) Spilites and serpentinites. *Carnegie Inst. Wash. Year Book*, **65**, 269-279.