

EXPERIMENTAL STUDY OF THE SERPENTINIZATION OF Mg-Fe-Ni OLIVINE IN THE PRESENCE OF SULFUR

ANESTIS FILIPPIDIS

Department of Mineralogy and Petrology, Institute of Geology,
University of Uppsala, Box 555, S-75122 Uppsala, Sweden

ABSTRACT

The serpentinization of Mg-Fe-Ni olivine in the presence of sulfur has been experimentally investigated below the stability limit of the assemblage olivine + water, at $350 \pm 5^\circ\text{C}$ and 2000 ± 50 bars. Serpentinization at low sulfur fugacity produces heazlewoodite + Ni-rich magnetite and, at high sulfur fugacity, an assemblage of millerite \pm pyrite + Ni-poor magnetite. The serpentinization products have been dehydrated within the stability field of olivine + H_2O ($500 \pm 5^\circ\text{C}$ and 2000 ± 50 bars). The olivine formed under the dehydration process (*i.e.* metamorphic olivine) is richer in Mg than the starting material (*i.e.*, primary magmatic olivine).

Keywords: serpentinization, metamorphic olivine, sulfur fugacity, experimental study.

SOMMAIRE

On a étudié la serpentinisation de l'olivine Mg-Fe-Ni en présence de soufre en dessous du champ de stabilité de l'assemblage olivine + H_2O à $350 \pm 5^\circ\text{C}$, 2000 ± 50 bars. A faible fugacité de soufre, la réaction produit l'association heazlewoodite + magnétite enrichie en Ni; à forte fugacité de soufre, elle donne l'association millérite \pm pyrite + magnétite appauvrie en Ni. Ces produits de serpentinisation ont ensuite été déshydratés dans le champ de stabilité de l'olivine (+ H_2O), à $500 \pm 5^\circ\text{C}$, 2000 ± 50 bars. L'olivine néoformée, tout comme l'olivine métamorphique, est plus riche en Mg que le matériau de départ, qui représente l'olivine primaire (magmatique).

(Traduit par la Rédaction)

Mots-clés: serpentinisation, olivine métamorphique, fugacité de soufre, étude expérimentale.

INTRODUCTION

Numerous studies of ultramafic rocks have shown that nickel is mainly found in olivine. When serpentinized in the presence of water and sulfur, the assemblage serpentine + brucite + oxide + sulfide becomes stable. Filippidis & Annersten (1980, 1981) suggested that the serpentinization of Ni-bearing olivine resulted in the

formation of Ni-sulfides and Ni-bearing magnetite. Various nickel-rich minerals have been reported from serpentinized ultramafic rocks (*e.g.*, du Rietz 1956, Chamberlain 1966, Ramdohr 1967, Groves *et al.* 1974, Eckstrand 1975, Groves & Keays 1979).

The reaction $2\text{Mg}_2\text{SiO}_4 + 3\text{H}_2\text{O} = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg}(\text{OH})_2$ studied experimentally by Johannes (1968) and Martin & Fyfe (1970) defines the lower stability of olivine in the presence of water and is one of the hydration reactions of dunite. Their studies indicate the field of stability of serpentine + brucite to be below 400°C . Scarfe & Wyllie (1967) and Evans *et al.* (1976) demonstrated experimentally that the reaction $6\text{Mg}_2\text{SiO}_4 + \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 9\text{H}_2\text{O} = 5\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ represents a higher P, T condition than the above serpentinization reaction. Experimental work by Moody (1976) in the iron-containing system $10(\text{Mg}_{1.86}\text{Fe}_{0.14})\text{SiO}_4 + 14.2\text{H}_2\text{O} = 5\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3.8(\text{Mg}_{0.95}\text{Fe}_{0.05})(\text{OH})_2 + 0.4\text{Fe}_3\text{O}_4 + 0.4\text{H}_2$ indicates that the addition of iron to the system slightly decreases the upper thermal stability of serpentine + brucite. On the other hand, the investigations of Caruso & Chernosky (1979) on the hydration reaction $12\text{Mg}_2\text{SiO}_4 + 2\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 5\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 18\text{H}_2\text{O} = 10\text{Mg}_{5.5}\text{Al}_{1.0}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_8$ indicates that the thermal stability of lizardite increases with increasing aluminum content.

The olivine in noncumulus ultramafic rocks is very magnesian and usually contains up to 0.5 wt. % NiO. The presence of hydrous silicates and sulfides in many serpentinized ultramafic rocks is indicative of the presence of a fluid phase and sulfur. The aim of the present study is to investigate experimentally the serpentinization of Ni-bearing olivine in the presence of water and sulfur below the lower limit of stability of olivine + H_2O at $350 \pm 5^\circ\text{C}$ and 2000 ± 50 bars. High-temperature experiments also were performed in order to investigate the dehydration of the serpentinization products within the stability field of olivine at $500 \pm 5^\circ\text{C}$ and 2000 ± 50 bars.

EXPERIMENTAL METHODS

All experiments were conducted in vertically mounted cold-seal hydrothermal vessels at 2000 \pm 50 bars. The starting materials of the experiments were synthetic olivine (Table 1), sulfur and a fluid phase (water or NaCl solution), except for experiment 11, where, an excess of MgO also was added (Table 2). The NaCl solution was used to remove excess quartz through the formation of sodium metasilicate $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in solution, to prevent the alteration of serpentine and brucite to talc.

The samples of synthetic olivine were prepared from stoichiometric oxide mixtures in an arc furnace using an argon atmosphere; they were examined for purity and homogeneity by X-ray powder-diffraction analyses, microprobe and Mössbauer techniques (Annersten *et al.* 1982, Nord *et al.* 1982). Chemical composition and unit-cell parameters of the olivine starting material are given in Table 1.

Each charge was loaded in a Au capsule,

TABLE 1. COMPOSITION AND CELL PARAMETERS OF OLIVINE STARTING MATERIAL

Olivine no.	7	4	1	02	01	03
SiO_2 wt. %	32.4	34.8	39.5	42.1	42.4	41.0
FeO	2.0	3.3	2.4	4.2	3.5	5.8
MgO	13.1	24.0	42.3	52.7	53.7	52.1
NiO	53.6	39.4	15.0	1.6	1.7	1.6
Total	101.1	101.5	99.2	100.6	101.3	100.5
Numbers of ions on the basis of 4 oxygen atoms						
Si	1.00	1.00	1.01	1.01	1.00	0.99
Fe	0.05	0.08	0.05	0.08	0.07	0.12
Mg	0.60	1.02	1.62	1.88	1.89	1.87
Ni	1.34	0.91	0.31	0.03	0.03	0.03
Mg/(Mg+Fe+Ni)	0.30	0.51	0.82	0.94	0.95	0.93
Cell parameters						
<i>a</i> (Å)	4.737(2)	4.747(1)	4.749(2)	4.761(1)	4.760(1)	4.756(1)
<i>b</i> (Å)	10.164(2)	10.193(2)	10.201(2)	10.214(1)	10.213(2)	10.209(1)
<i>c</i> (Å)	5.935(2)	5.951(3)	5.970(1)	5.987(1)	5.986(1)	5.987(1)
<i>V</i> (Å ³)	285.782	287.937	289.267	291.154	291.033	290.667

Figures in parentheses represent the estimated standard deviation; thus 4.737(2) indicates estimated standard deviation of 0.002.

welded shut and subjected to a temperature of $350 \pm 5^\circ\text{C}$ for 720 to 4128 hours. Experiment 033 was quenched, whereas experiments 031 and 032 were further heated at $500 \pm 5^\circ\text{C}$ for an additional 408 and 624 hours, respectively. All capsules were checked for leaks before and after the hydrothermal treatment by determining loss of weight. Those that had lost weight were discarded. Experimental products were examined with a petrographic microscope. One polished section and one thin section of each product were examined in reflected and transmitted light. X-ray powder-diffraction analysis was utilized for further identification of the phases, for estimating the degree of conversion and for determining the unit-cell parameters of olivine. A combination of point counting and X-ray powder-diffraction analysis was used to estimate the proportions of the phases present and to judge how far a reaction had proceeded. Results of microprobe analyses, which are given in Tables 3, 4 and 5, were performed at 15 kV on a Cambridge Geoscan microprobe. Each value represents the average of at least three grains in each experimental product and is corrected for background, dead time, absorption, fluorescence and atomic number effect. Relative errors for major elements are ± 0.8 to 1.5% and for minor elements ± 5 to 6%.

EXPERIMENTAL RESULTS

The hydration reaction in the experiments did not proceed to the complete decomposition of the olivine. Experiments performed for up to six months still show approximately 20% olivine left in the experimental products. The observed phases in the experimental products are shown in Table 2. The olivine appears as anhedral, massive grains, up to about 50 μm in size. Texturally, there is an alteration zone around each olivine grain, with the opaque phases occurring either between the reaction products and the

TABLE 2. RESULTS OF HYDROTHERMAL EXPERIMENTS AT 2000 BARS

Exp. no.	Starting materials	S		Fluid	T ($^\circ\text{C}$)	Duration (hours)	Products
		Fe	Ni				
71	0(7)+sulfur	1.65		water	350	720	0=9%, T=81%, Q=1.5%, E=1%, Mt=0.5%, Ml=7%
41	0(4)+NaCl+sulfur	1.24		water	350	1464	0=41.5%, T=45%, S=10%, Mt=1%, Ml=2.5%
11	0(1)+MgO+sulfur	1.41		water	350	720	0=94%, S=5%, Mt=0.5%, Bv=0.5%
12	0(1)+sulfur	1.12	5.4M	NaCl	350	720	0=41%, S=57.5%, Mt=0.5%, Ml+Bv+Py=1%
13	0(1)+sulfur	1.24	5.1M	NaCl	350	1464	0=79%, S=18.5%, Mt=0.5%, Ml+Py=2%
021	0(02)+sulfur	0.39	2.6M	NaCl	350	4080	0=18%, S=45.5%, B=28%, Mt=8%, Hz=0.5%
011	0(01)+sulfur	0.69	2.6M	NaCl	350	4128	0=34%, S=54%, B=9.5%, Mt=2%, Pn=0.5%
033	0(03)+sulfur	0.46	3.9M	NaCl	350	1104	0=39%, S=52%, B=2%, Mt=4.5%, Pn=2.5%
031	products of exp. 033	0.46	3.9M	NaCl	500	408	0=82%, S=11%, Mt=4.5%, Pn=2.5%
032	products of exp. 033	0.46	3.9M	NaCl	500	624	0=86%, S=7%, Mt=4.5%, Pn=2.5%

Abbreviations used: 0(7) olivine no. 7, cf. Table 1, O olivine, S serpentine, B brucite, T talc, E enstatite, Q SiO_2 , Mt magnetite, Ml millerite, Hz heazlewoodite, Bv bravoite, Pn pentlandite, Py pyrite

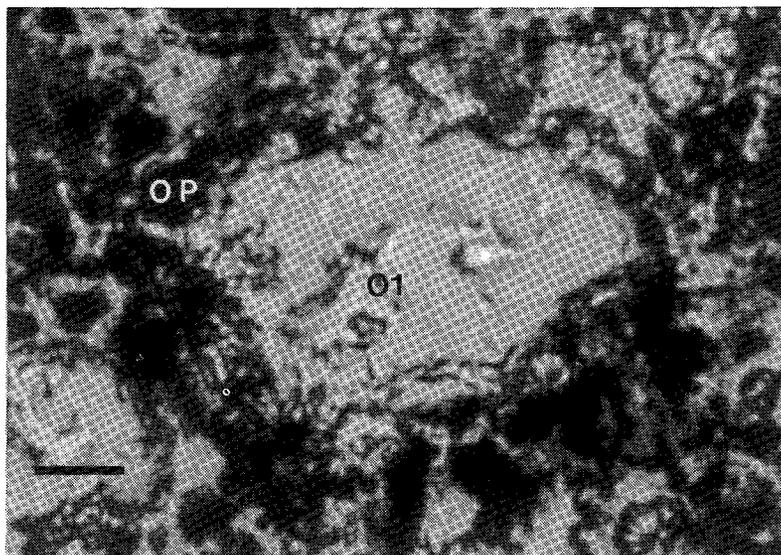


FIG. 1. Photomicrograph (transmitted light) of the products of hydration experiment 71. O1 olivine starting material, OP opaque phase. Bar scale 0.01 mm.

olivine (Fig. 1) or as inclusions in the olivine. The alteration of olivine is clearly dependent on the starting composition of olivine and the type of fluid phase in the experiment (Table 2). The alteration reaction was very sluggish in water + MgO (experiment 11), but rapid in water (experiment 71). In the hydration experiments, relict olivine shows almost no change in composition compared to the olivine starting material (Tables 1, 3). The microprobe analyses on the serpentine polymorphs (lizardite, chrysotile and

antigorite) were difficult to perform as the minerals got burnt during the analyses, but partial microprobe analyses of one grain from experiments 12 and 13, respectively, indicate FeO values of 3.7 and 1.3 wt. %, and NiO values of 9.3 and 1.2 wt. %, respectively. Talc was only found in experiments without NaCl solution and with an excess of SiO₂ (experiments 71 and 41), which was formed by decomposition of olivine, and which reacts with serpentine according to the reaction: serpentine + SiO₂ =

TABLE 3. RESULTS OF MICROPROBE ANALYSES OF OLIVINE FROM THE PRODUCTS OF THE EXPERIMENTS

Experiment no.	71	41	11	12	13	021	011	033	031	032		
Analysis no.	1	2	3	4	5	6	7	8	9	10 ^x	11	12 ^x
SiO ₂ wt. %	32.6	35.2	39.4	38.2	39.2	42.3	41.8	41.1	41.5	42.9	40.9	41.8
FeO	1.6	2.4	1.9	3.5	3.8	2.8	5.5	5.2	5.8	3.1	6.4	3.2
MgO	13.2	23.5	43.7	44.9	41.7	53.5	51.4	51.2	51.2	52.3	50.8	53.4
NiO	52.5	38.6	14.3	13.5	14.6	1.3	1.2	1.5	1.5	1.3	1.4	1.3
Total	99.9	99.7	99.3	100.1	99.3	99.9	99.9	99.0	100.0	99.6	99.5	99.7
Numbers of ions on the basis of 4 oxygen atoms												
Si	1.02	1.02	1.00	0.98	1.01	1.01	1.01	1.00	1.00	1.02	1.00	1.00
Fe	0.04	0.06	0.04	0.07	0.08	0.06	0.11	0.11	0.12	0.06	0.13	0.06
Mg	0.61	1.01	1.66	1.68	1.60	1.90	1.85	1.86	1.85	1.88	1.85	1.91
Ni	1.31	0.90	0.30	0.28	0.30	0.03	0.02	0.03	0.03	0.02	0.03	0.03
Mg(Mg+Fe+Ni)	0.31	0.51	0.83	0.83	0.81	0.95	0.93	0.93	0.93	0.96	0.92	0.96

x) newly formed olivine

TABLE 4. RESULTS OF MICROPROBE ANALYSES OF SULFIDE MINERALS FROM THE PRODUCTS OF THE EXPERIMENTS

Experiment no.	71	41	11	12	13	021	011	033	031	032		
Analysis no.	19	20	21	22	23	24	25	26	27	28	29	30
Ni	62.9	61.2	33.6	36.5	61.5	59.8	0.4	74.1	35.5	21.0	27.2	32.1
Fe	0.6	3.5	15.0	15.3	4.4	3.4	50.3	1.6	30.4	44.8	39.1	33.5
S	36.5	35.2	51.3	48.3	34.2	36.8	49.3	24.3	34.2	34.3	33.7	34.4
Total	100.0	99.9	99.9	100.1	100.1	100.0	100.0	100.0	100.1	100.1	100.0	100.0
Ni	0.48	0.47	0.23	0.26	0.48	0.46	-	0.62	0.27	0.16	0.21	0.25
Fe	0.01	0.03	0.11	0.11	0.03	0.03	0.37	0.01	0.25	0.36	0.32	0.27
S	0.51	0.50	0.66	0.63	0.49	0.51	0.63	0.37	0.48	0.48	0.47	0.48
Σ	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

19, 20, 23 and 24 millerite, 21 and 22 bravoite, 25 pyrite, 26 heazlewoodite, 27, 28, 29 and 30 pentlandite

talc + H₂O (Johannes 1969). Enstatite (experiment 71) may be obtained through the reaction: olivine + 2 talc + serpentine = 11 enstatite + 4H₂O (Martin & Fyfe 1970). A partial microprobe analysis of talc in experiment 71 shows a FeO content of 4.0 wt. % and a NiO content of 30.6 wt. %. Magnetite is more extensively formed in the alteration of Fe-rich olivine but some magnetite was identified in all experiments. It appears both as fine particles and as larger grains (5–20 μ m); all contain nickel (maximum amount: 2.0 wt. % in the magnetite from experiment 021). Sulfides, with a grain size of 6–60 μ m, were observed optically in all experimental

products. Identification of these phases was performed by means of microprobe analysis. The formation of sulfides is more extensive during the alteration of Ni-rich olivine than of Ni-poor olivine. The Fe content of millerite varies between 0.6 and 4.4 wt. % and increases with decreasing Ni content of the starting olivine. The Ni/Fe ratio varies between 0.4 and 1.1 in the pentlandite and between 2.1 and 2.3 in the bravoite, which is metastable in the temperature range of the present experiments (Springer *et al.* 1964, Shimazaki 1971). The Ni/Fe ratio of the sulfides is typically dependent on the starting composition of olivine.

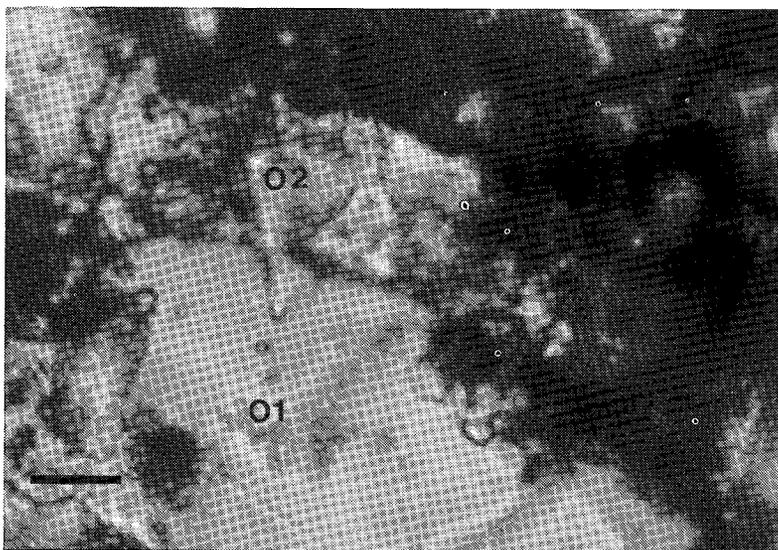


FIG. 2. Photomicrograph (transmitted light) of the products of dehydration experiment 032. O1 olivine starting material (primary olivine), O2 newly formed olivine (metamorphic olivine). Bar scale 0.01 mm.

In the high-temperature dehydration experiments (031 and 032) the reaction of serpentine into olivine was not complete. The experiment performed for up to 26 days still shows 7% serpentine (antigorite) left in the experimental products (Table 2). In these experiments, two chemically distinct types of olivine are distinguished. One is similar in composition to the starting olivine (primary olivine), and the other has a lower Fe content (newly formed olivine; Tables 1, 3). The NiO content of the newly formed olivine is slightly lower than in the primary olivine. Texturally, the fine-grained newly formed olivine occurs around the primary olivine as a foam-textured overgrowth (Fig. 2), similar to the olivine described by Stigh (1979) and recognized by him as being metamorphic in origin.

In the high-temperature dehydration experiments, the modal proportions of serpentine decrease with increasing time of the experiment. Brucite is not present, and magnetite shows lower Mg and Ni contents but a higher Fe content than the magnetite from the low-temperature experiments (Table 5). The Ni/Fe ratio of pentlandite from the high-temperature experiments varies between 0.7 and 0.9 and increases with increasing duration of the experiments (Table 4, # 29 and 30). The modal proportions of magnetite and pentlandite remain the same as those in the low-temperature experiment 033 (Table 2). In the present study, no buffers were used. The silicate-oxide-sulfide reactions in these experiments involve gas phases in the system H-O-S. It may well be that the oxygen fugacity is buffered by the observed mineral assemblage and the gas phase in the system H-O-S (Popp & Frantz 1977). The species HS and SO predominate in systems with low oxygen and sulfur fugacities, whereas SO₂, H₂S, S₂, H₂ and H₂O predominate in systems with high oxygen and sulfur fugacities (Eugster & Skippen 1967). Experiments in which the S/(Fe+Ni) ratio is high gave a typical smell of H₂S upon opening the capsules. The presence of these sulfide minerals is in good agreement with the S/(Fe+Ni) ratio of the starting materials in each experiment (Table 2).

DISCUSSION

It is important to remember that none of the experiments achieved complete conversion, owing to the slow kinetics; thus they do not represent equilibrium. The hydration experiments show that at low temperature, in the serpentine stability field, Mg-Fe-Ni olivine

TABLE 5. RESULTS OF MICROPROBE ANALYSES OF MAGNETITE FROM THE PRODUCTS OF THE EXPERIMENTS

Experiment no.	13	021	011	033	031	032
Analysis no.	13	14	15	16	17	18
SiO ₂ wt.%	1.5	1.8	1.5	1.6	0.6	0.6
FeO ^x	90.3	85.9	85.7	87.9	91.9	91.3
MgO	0.8	3.4	5.2	3.2	0.4	0.6
NiO	0.5	2.0	0.4	0.8	0.2	0.3
Total ^{xx}	99.8	99.5	99.2	100.0	99.9	99.6
Number of ions on the basis of 4 oxygen atoms						
Si	0.07	0.09	0.07	0.08	0.03	0.03
Fe ³⁺	1.93	1.91	1.93	1.92	1.97	1.97
Fe ²⁺	0.92	0.68	0.60	0.74	0.96	0.95
Mg	0.06	0.24	0.38	0.23	0.03	0.04
Ni	0.02	0.08	0.02	0.03	0.01	0.01

x) FeO as total iron, xx) total for oxides corrected assuming stoichiometry

breaks down in the presence of sulfur according to the following schematic reaction (serpentinization): (Mg,Fe,Ni) olivine + H₂O + S₂ = serpentine + brucite + Ni-magnetite + sulfides.

The opaque mineral assemblages of the experimental products consist of Ni-sulfides, (Ni, Fe)-sulfides, Fe-sulfide and magnetite (Fig. 3). No awaruite or hematite was observed. These mineral assemblages suggest an approximate log *f*(S₂) value greater than -17 and a log *f*(O₂) value greater than -38 (Holland 1959, Barton & Skinner 1967, Craig & Naldrett 1972, Popp & Frantz 1977). The sulfide minerals include heazlewoodite, pentlandite and the assemblage millerite ± bravoite ± pyrite in order of increasing initial S/(Fe+Ni) ratio from 0.39 up to 1.65. The sulfide minerals observed in this study correspond to those in naturally occurring assemblages documented by Graterol & Naldrett (1971), Harris & Nickel (1972), Eckstrand (1975) and Filippidis & Annersten (1981).

The Ni content of magnetite increases with decreasing fugacity of sulfur. The highest NiO content of magnetite is observed in experiment 021, the experiment with the lowest S/(Fe+Ni) ratio (0.39). The low sulfur fugacity favors the formation of heazlewoodite and Ni-rich magnetite. At high fugacity of sulfur, however, magnetite becomes poor in nickel by the reaction with sulfur: NiFe₂O₄ + S₂ → millerite + Fe₃O₄ + FeS₂, which explains the coexistence of pyrite and Ni-poor magnetite. Similar observations were noticed in natural parageneses in serpentinized ultramafic rocks from the Swedish Caledonides (Filippidis & Annersten 1981).

presence of sulfur converts some of the iron and nickel into magnetite and sulfide minerals according to the reaction $(\text{Mg,Fe,Ni})\text{-olivine} + \text{H}_2\text{O} + \text{S}_2 \rightarrow \text{serpentine} + \text{brucite} + \text{magnetite} + \text{sulfides}$. The sulfide minerals of the experimental products include heazlewoodite, pentlandite and the assemblage, millerite \pm bravoite \pm pyrite, in the order of increasing sulfur fugacity. The values of oxygen fugacity in the experiments were low and within the magnetite stability field. Serpentinization at low sulfur fugacity gives rise to the formation of heazlewoodite and Ni-rich magnetite, whereas at high sulfur fugacity, the assemblage produced is millerite + pyrite + Ni-poor magnetite. In the dehydration experiments, the newly formed olivine (metamorphic olivine) has a higher Mg/(Mg+Fe+Ni) ratio than the olivine starting material (primary olivine). To a great extent, iron and nickel largely remained in magnetite and pentlandite during the dehydration of serpentine and brucite.

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REFERENCES

- ANNERSTEN, H., ERICSSON, T. & FILIPPIDIS, A. (1982): Cation ordering in Ni-Fe-olivines. *Amer. Mineral.* 67, (in press).
- ARAI, S. (1975): Contact metamorphosed dunite-harzburgite complex in the Chugoku district, western Japan. *Contr. Mineral. Petrology* 52, 1-16.
- BARTON, P.B., JR. & SKINNER, B.J. (1967): Sulfide mineral stabilities. In *Geochemistry of Hydrothermal Ore Deposits* (H.L. Barnes, ed.). Holt, Rinehart and Winston, New York.
- CARUSO, L.J. & CHERNOSKY, J.V., JR. (1979): The stability of lizardite. *Can. Mineral.* 17, 757-769.
- CHAMBERLAIN, J.A. (1966): Heazlewoodite and awaruite in serpentinites of the Eastern Townships, Quebec. *Can. Mineral.* 8, 519-522.
- CRAIG, J.R. & NALDRETT, A.J. (1972): Phase relations and PS_2 -T variations in the Fe-Ni-S system. *Can. Mineral.* 11, 571 (abstr.).
- DU RIETZ, T. (1956): The content of chromium and nickel in the Caledonian ultrabasic rocks of Sweden. *Geol. Fören. Stockholm Förh.* 78, 233-299.
- ECKSTRAND, O.R. (1975): The Dumont serpentinite: a model for control of nickeliferous opaque mineral assemblages by alteration reactions in ultramafic rocks. *Econ. Geol.* 70, 183-201.
- EUGSTER, H.P. & SKIPPEN, G.B. (1967): Igneous and metamorphic reactions involving gas equilibria. In *Researches in Geochemistry 2* (P.H. Abelson, ed.) John Wiley and Sons, New York.
- EVANS, B.W., JOHANNES, W., OTERDOOM, H. & TROMMSDORFF, V. (1976): Stability of chrysotile and antigorite in the serpentinite multisystem. *Schweiz. Mineral. Petrog. Mitt.* 56, 79-93.
- FILIPPIDIS, A. & ANNERSTEN, H. (1980): Mineral chemical investigation of an ultramafic nickel bearing body in the Swedish Caledonides. In *UNESCO - An International Symposium on Metallogeny of Mafic and Ultramafic Complexes: the Eastern Mediterranean-Western Asia Area, and its Comparison with Similar Metallogenic Environments in the World*, Proc. (S.S. Augustithis, ed.) 2, 115-130.
- & —— (1981): Nickel partitioning between silicates and ore minerals in serpentinized ultramafic rocks from the Swedish Caledonides. *Univ. Uppsala Dep. Mineral. Petrology (UUDMP) Res. Rep.* 24.
- GRATEROL, M. & NALDRETT, A.J. (1971): Mineralogy of the Marbridge no. 3 & no. 4 nickel-iron sulfide deposits, with some comments on low temperature equilibration in the Fe-Ni-S system. *Econ. Geol.* 66, 886-900.
- GROVES, D.I., HUDSON, D.R. & HACK, T.B.C. (1974): Modification of iron-nickel sulfides during serpentinization and talc-carbonate alteration at Black Swan, Western Australia. *Econ. Geol.* 69, 1265-1281.
- & KEAYS, R.R. (1979): Mobilization of ore-forming elements during alteration of dunites, Mt. Keith-Betheno, Western Australia. *Can. Mineral.* 17, 373-389.
- HARRIS, D.C. & NICKEL, E.H. (1972): Pentlandite compositions and associations in some mineral deposits. *Can. Mineral.* 11, 861-878.
- HIETANEN, A. (1977): Blades of olivine in ultramafic rock from northern Sierra Nevada, California. *J. Res. U.S. Geol. Surv.* 5, 217-219.
- HOLLAND, H.D. (1959): Some applications of thermochemical data to problems of ore deposits. I. Stability relations among the oxides, sulfides, sulfates and carbonates of ore and gangue metals. *Econ. Geol.* 54, 184-233.

- JOHANNES, W. (1968): Experimental investigation of the reaction forsterite + H₂O \rightleftharpoons serpentine + brucite. *Contr. Mineral. Petrology* 19, 309-315.
- (1969): An experimental investigation of the system MgO-SiO₂-H₂O-CO₂. *Amer. J. Sci.* 267, 1083-1104.
- MARTIN, B. & FYFE, W.S. (1970): Some experimental and theoretical observations on the kinetics of hydration reactions with particular reference to serpentinization. *Chem. Geol.* 6, 185-202.
- MOODY, J.B. (1976): An experimental study on the serpentinization of iron-bearing olivines. *Can. Mineral.* 14, 462-478.
- MORGAN, B.A. (1978): Metamorphic forsterite and diopside from the ultramafic complex at the Tuolumne River, California. *J. Res. U.S. Geol. Surv.* 6, 73-80.
- NORD, A.G., ANNERSTEN, H. & FILIPPIDIS, A. (1982): The cation distribution in synthetic Mg-Fe-Ni olivines. *Amer. Mineral.* 67, (in press).
- OLIVER, R.L. & WARD, M. (1971): A petrological study of serpentinous rocks associated with nickel sulphide mineralization at Pioneer, Western Australia. *J. Geol. Soc. Aust. Spec. Publ.* 3, 311-319.
- PETERS, T. (1968): Distribution of Mg, Fe, Al, Ca and Na in coexisting olivine, orthopyroxene and clinopyroxene in the Totalp serpentinite (Davos, Switzerland) and in the alpine metamorphosed Malenco serpentinite (N. Italy). *Contr. Mineral. Petrology* 18, 65-75.
- POPP, R. K. & FRANTZ, J.D. (1977): Solubility of iron in Fe-O-H-S fluids. *Carnegie Inst. Wash. Year Book* 76, 601-603.
- RAMDOHR, P. (1967): A widespread mineral association, connected with serpentinization. *Neues Jahrb. Mineral. Abh.* 107, 241-265.
- SCARFE, C.M. & WYLLIE, P.J. (1967): Serpentine dehydration curves and their bearing on serpentinite deformation in orogenesis. *Nature* 215, 945-946.
- SHIMAZAKI, H. (1971): Thermochemical stability of bravoite. *Econ. Geol.* 66, 1080-1082.
- SPRINGER, G., SCHACHNER-KORN, D. & LONG, J.V.P. (1964): Metastable solid solution relations in the system FeS₂-CoS₂-NiS₂. *Econ. Geol.* 59, 475-491.
- STAMATELOPOULOU-SEYMOUR, K. & FRANCIS, D.M. (1980): Metamorphic olivine in peridotitic komatiite flows, Lac Guyer, Quebec. *Can. Mineral.* 18, 265-270.
- STIGH, J. (1979): *Ultramafites and Detrital Serpentinites in the Central and Southern Parts of the Caledonian Allochthon in Scandinavia*. Ph.D. thesis, Inst. of Geology, Chalmers University of Technology, Gothenburg, Sweden, Publ. A27.
- VANCE, J.A. & DUNGAN, M.A. (1977): Formation of peridotites by deserpentinization in the Darrington and Sultan areas, Cascade Mountains, Washington. *Geol. Soc. Amer. Bull.* 88, 1497-1508.

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