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BEHAVIOR OF IRON, NICKEL, COBALT AND SULFUR DURING SERPENTINIZATION, WITH REFERENCE TO THE HAYACHINE ULTRAMAFIC ROCKS OF THE KAMAISHI MINING DISTRICT, NORTHEASTERN JAPAN

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ABSTRACT

A variety of Fe–Ni–Co sulfides occur in weakly to completely serpentinized dunite and wehrlite of the Hayachine (Hayachine–Goyozan) tectonic belt, northeastern Japan. The sulfide assemblages vary sympathetically with the degree of serpentinization, from pyrrhotite–pentlandite assemblage to pentlandite–heazlewoodite–godlevskite assemblage and, further, to pentlandite–violarite, pentlandite–violarite–millerite and violarite–millerite assemblage. Bulk compositions of the sulfide aggregates, estimated from modal abundances and electron-microprobe data, illustrate that Fe contents decrease and Ni and Co contents increase with serpentinization. Sulfur contents are characterized by gradual reduction with initial serpentinization, and by an increase in completely serpentinized rocks. The sequences of mineralogical and compositional modifications of aggregates of secondary sulfide are accounted for in terms of both the uptake of cations expelled from olivine and the removal of iron from precursor (probably magmatic) pyrrhotite–pentlandite aggregates. With the possible exception of sulfur, serpentinization was approximately isochemical with respect to Fe, Ni and Co. However, these elements became mobile with progressive serpentinization and moved up to about 10 cm at the most active stage of serpentinization.

Keywords: serpentinization, Fe–Ni–Co sulfides, mineralogical variation, Hayachine tectonic belt, Japan.

SOMMAIRE

On trouve une variété de sulfures de Fe–Ni–Co dans dunites et wehrlites faiblement à complètement serpentinisées de la ceinture tectonique de Hayachine (Hayachine–Goyozan), dans le secteur nord-est du Japon. L'assemblage de sulfures varie avec le degré de serpentinisation, de pyrrhotine - pentlandite à pentlandite - heazlewoodite - godlevskite et, aux stades plus avancés, pentlandite - violarite, pentlandite - violarite - millerite et violarite - millerite. Les compositions globales des agrégats de sulfures, évaluées à partir des proportions modales et des données obtenues à la microsonde électronique, montrent que la teneur en Fe diminue et les concentrations de Ni et de Co augmentent avec le degré de serpentinisation. La teneur en soufre diminue graduellement au début de la serpentinisation, mais augmente ensuite dans les roches complètement serpentinisées. Les séquences de modifications minéralogiques et chimiques dans les agrégats de sulfures secondaires reflètent à la fois l'incorporation des cations rejetés par l'olivine et la perte du fer du précurseur, qui sont les agrégats de pyrrhotine - pentlandite (qui seraient magmatiques). Sauf peut-être pour le soufre, la serpentinisation a été à peu près isochimique par rapport au Fe, Ni et Co. Toutefois, ces éléments ont été mobilisés au cours de la serpentinisation, à des distances atteignant 10 cm aux stades les plus intenses de la réaction.

(Traduit par la Rédaction)

Mots-clés: serpentinisation, sulfures de Fe–Ni–Co, variation minéralogique, ceinture tectonique de Hayachine, Japon.

INTRODUCTION

Unaltered ultramafic rocks generally contain a limited variety of sulfides, typically pyrrhotite, pentlandite and chalcopyrite. In the serpentinized and talc–carbonated equivalents, however, a variety of Fe–Ni–Co–S minerals, including native metals, are common, as described by previous investigators (Nickel 1959, Chamberlain *et al.* 1965, Papunen 1971, Kanehira *et al.* 1975, Hudson & Travis 1981, Onuki *et al.* 1981, Sakai & Kuroda 1983). The difference in mineralogy between unaltered and altered ultramafic rocks suggests that alteration reactions control the Fe–Ni–Co–S mineralogy.

Mineralogical observations on variably serpentinized ultramafic rocks from the Hayachine (Hayachine–Goyozan) tectonic belt in the Kamaishi mining district, northeastern Japan, reveal that assemblages of Fe–Ni–Co–S minerals have changed sympathetically with progressing serpentinization, from a pyrrhotite–pentlandite assemblage to a pentlandite–heazlewoodite–godlevskite assemblage and, further, to pentlandite–violarite, pentlandite–violarite–millerite and violarite–millerite assemblages. The present study attempts to define the behavior of iron, nickel, cobalt and sulfur, the elements predominantly responsible for the mineralogical variation, during serpentinization.

GEOLOGICAL SETTING

The Hayachine tectonic belt extends more than 100 km across the centre of the Kitakami massif, northeastern Japan (Fig. 1). The Kamaishi mining district is located at the southern extremity of the belt. It comprises mainly sediments (slate and tuff) of Carboniferous to Permian age, intrusive bodies

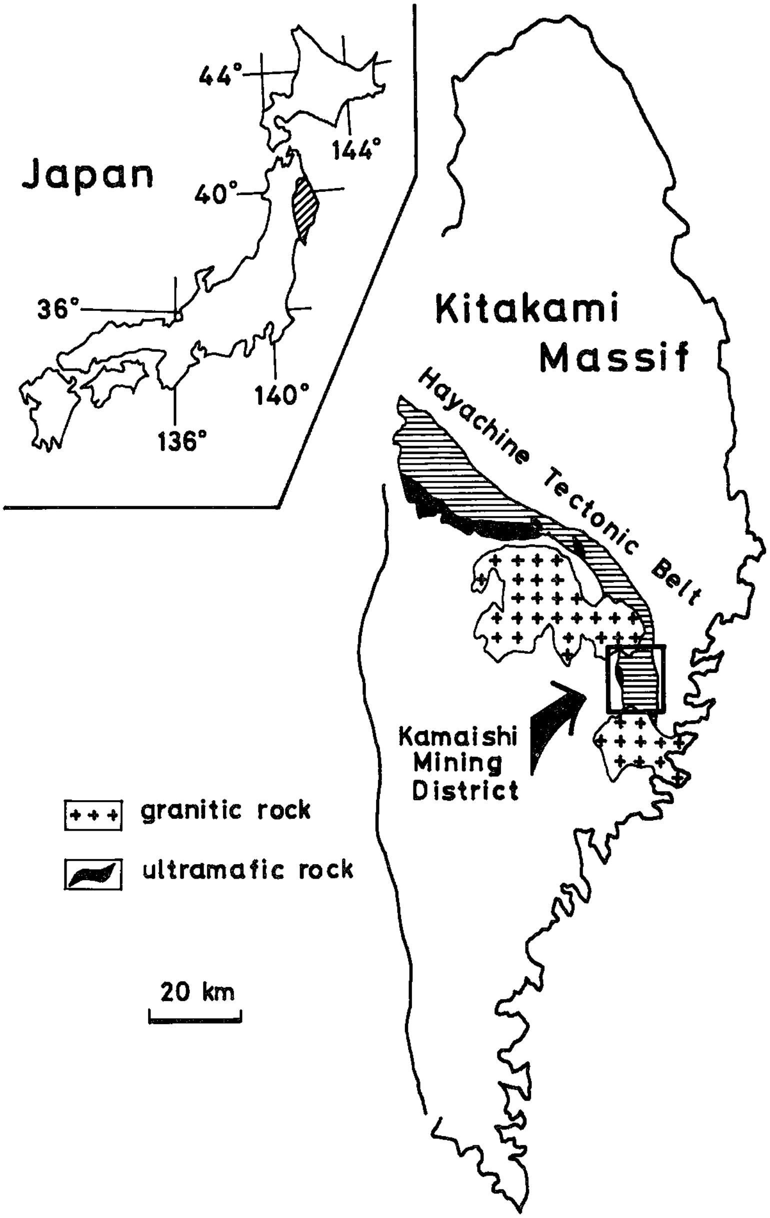

FIG. 1. Map showing location of the Hayachine tectonic belt and the Kamaishi mining district, northeastern Japan.

such as granodiorite (Cretaceous) and ultramafic and gabbroic rocks (Fig. 2). The ultramafic and gabbroic rocks are considered to have been emplaced in the solid state because there is no clear evidence of contact metamorphism in the surrounding sediments (MMEAJ 1970–1973). The age of emplacement is not clear. The probable source of the ultramafic rocks is a residual mantle material (Fujimaki & Yomogida 1986). Based upon previous investigations of this area (*e.g.*, Kawano & Ueda 1965, Onuki 1969, MMEAJ 1970–1973, Hamabe & Yano 1976), the geological history may be summarized as follows: 1) formation of the Hayachine tectonic belt, 2) emplacement of ultramafic and gabbroic rocks into the belt, and 3) intrusion of granitic magma and formation of ore deposits (*e.g.*, Kamaishi pyrometasomatic Cu–Fe deposit).

The slate of this area is changed to hornfels near the granitic plutons. The ultramafic rocks of the Arakawa and Iwakura-yama North bodies (Fig. 2) also underwent contact metamorphism due to the intrusion of granitic magma. Three ultramafic masses, Arakawa, Iwakura-yama North and Iwakura-yama Main bodies are dealt with in the present study.

SERPENTINIZATION AND THE OPAQUE MINERALS

Arakawa body

Ultramafic rocks from this body are composed of up to 10% olivine, 20 to 70% clinopyroxene, 25 to 35% serpentine and 5 to 35% chlorite, carbonate, tremolite and opaque minerals (Table 1). Serpentine, identified as antigorite by X-ray powder diffraction, develops as an aggregate of extremely fine scales along grain boundaries between olivine and clinopyroxene and their cracks and cleavages, and is generally accompanied by a small amount of chlorite. A common species of carbonate is dolomite, as determined from X-ray powder diffraction and electron-microprobe data. The mineral is an accessory phase that occurs generally in small veins, filling fractures of the rocks and cleavages of clinopyroxene. Tremolite develops as fine laths and needles in serpentine, and is especially abundant near clinopyroxene. The mineral is fresh in appearance, without indication of alteration. Such opaque minerals as magnetite, hexagonal pyrrhotite, pentlandite, mackinawite, ilmenite and chalcopyrite, in order of decreasing abundance, have been found in the specimens (Table 2). The opaque minerals were identified mainly using electron-microprobe data.

Magnetite occurs as irregularly shaped aggregates (Fig. 3A), threads, stringers and veinlets in serpentine; it is rarely in association with ilmenite, and commonly develops also as a narrow rim around hexagonal pyrrhotite (Fig. 3B). In the serpentine matrix, minute, euhedral to subhedral grains of pentlandite, ranging from 5 to 15 μm in diameter, are sparsely disseminated, without apparent association with other opaque minerals (Fig. 3A).

Aggregates of hexagonal pyrrhotite and pentlandite, commonly with minor mackinawite and magnetite and less commonly with chalcopyrite, occur interstitially to olivine and clinopyroxene grains (Fig. 3B), which are now partly altered to serpentine and chlorite. Mackinawite in the aggregates occurs along cleavages of pentlandite and boundaries between pentlandite and hexagonal pyrrhotite (Fig. 3B). The interstitial occurrence of the aggregates suggests that, except for mackinawite, the sulfides are essentially magmatic in origin, although there may have been a minor compositional readjustment among sulfides and magnetite during serpentinization (see below).

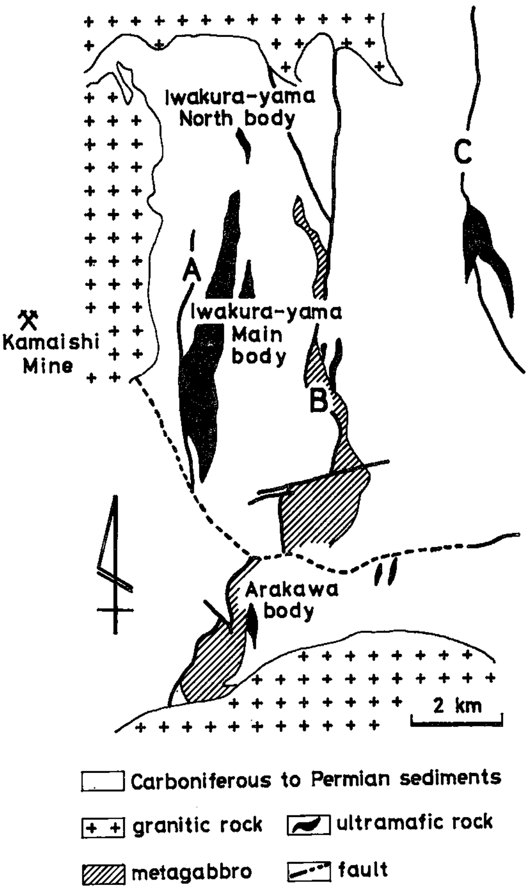

FIG. 2. Distribution of ultramafic rocks in the Kamaishi mining district, northeastern Japan. A: the Iwakura-yama tectonic line, B: the Ninokura-yama tectonic line, C: the Kogawa tectonic line.

TABLE 1. MODAL COMPOSITION OF THE HAYACHINE ULTRAMAFIC ROCKS OF THE KAMAISHI MINING DISTRICT, NORTHEASTERN JAPAN

Locality	Specimen No.	ol (volume %)	cpx	srp	others *
Arakawa body	A760510	minor	70	25	5
	A760504	10	20	35	35
	A760507	10	45	35	10
Iwakura-yama North body	I760824	25	5	50	20
	I760835	–	20	60	20
	I760828	20	–	70	10
	I760831	10	–	80	10

Estimated by point-counting method. ol:olivine, cpx:clinopyroxene, srp:serpentine. *others include chlorite, carbonate, tremolite and opaque minerals. -:nil.

Iwakura-yama North body

Specimens from this body are composed of up to 25% olivine, less than 20% clinopyroxene, 50 to 80% serpentine and 10 to 20% chlorite, carbonate, tremolite and opaque minerals (Table 1). Serpentine, identified as antigorite, shows mesh, band and lattice

TABLE 2. ASSEMBLAGE OF OPAQUE MINERALS IN THE HAYACHINE ULTRAMAFIC ROCKS OF THE KAMAISHI MINING DISTRICT, NORTHEASTERN JAPAN

Locality	Specimen No.	Opaque Minerals
Arakawa body	A760510	hpo,pn,mk,mag
	A760504	hpo,pn,mk,ccp,mag,ilm
	A760507	hpo,pn,mk,mag,ilm
Iwakura-yama North body	I760823-24	mpo,pn,ccp,mag,ilm,chr
	I760836-37	mpo,pn,cbt,ccp,mag,chr
	I760834-35	mpo,pn,cbt,ccp,mag,chr
	I760827-29	mpo,pn,ccp,ncl,mag,ilm,chr
	I760830-31	pn,hz,gd,mag,chr
Iwakura-yama Main body	I760516-22	pn,hz,gd,mag,chr
	I760512-14	pn,vl,py,cbt,ccp,mag,chr
	I760844-45	pn,vl,ccp,ilm
	I760838	pn,vl,ccp
	I760510-11	pn,vl,mag,chr
	I760841	pn,vl,ml,ccp,mag,chr
	I760843	pn,vl,ml,ccp,mag
	I760506-07	vl,ml,ccp,mag,chr
	I760508-09	vl,ml,ccp,mag,chr

hpo:hexagonal pyrrhotite, pn:pentlandite, mk:mackinawite, mag:magnetite, ccp:chalcopyrite, ilm:ilmenite, mpo :monoclinic pyrrhotite, chr:chromite, cbt:cobaltite, ncl:niccolite, hz:heazlewoodite, gd:godlevskite, vl: violarite, py:pyrite, ml:millerite.
For niccolite, read nickeline (ed.).

structures, and occurs also as aggregates of fine scales and fibers. In some specimens olivine and clinopyroxene were selectively altered to serpentine and chlorite, respectively, but clinopyroxene is rather well preserved. Carbonate, identified as magnesite, generally occupies the smooth fractures that develop characteristically in serpentine. The irregularly shaped grains of carbonate are rarely enclosed in serpentine and chlorite. Tremolite is very similar in mode of occurrence to that in the Arakawa body. Clinopyroxene is less abundant in this body than in the Arakawa body, indicating a dunite or wehrlite parent. The following opaque minerals have been found in minor to trace amounts: magnetite, pyrrhotite (mainly monoclinic), pentlandite, chromite, heazlewoodite, ilmenite, godlevskite, chalcopyrite, cobaltite and nickeline, in order of decreasing abundance (Table 2). Magnetite is abundant in chlorite as well as in serpentine, and some chromite grains in serpentine have a magnetite rim. Other chromite grains are in direct contact with olivine and clinopyroxene, but are rarely enclosed in those minerals.

Pyrrhotite–pentlandite–magnetite aggregates are commonly accompanied by minor chalcopyrite and, rarely, traces of cobaltite and nickeline. Magnetite in the aggregates is associated with pyrrhotite rather than pentlandite (Fig. 3C). In the most intensely serpentinized rocks, pentlandite–heazlewoodite aggregates are invariably associated with minor magnetite (Fig. 3D) and rarely, with a trace of godlevskite. Godlevskite is included in heazlewoodite grains.

The pyrrhotite–pentlandite–magnetite aggregates occupy interstices between olivine and clinopyroxene grains (now partly to completely altered). An interstitial texture is broadly preserved despite extensive retexturing by silicates (Fig. 3C). The textural and mineralogical features suggest that pre-existing aggregates of magmatic pyrrhotite and pentlandite were modified texturally and mineralogically during serpentinization.

Iwakura-yama Main body

Ultramafic rocks from this body are essentially serpentinites with carbonate and minor chlorite, without any relict olivine or clinopyroxene. Serpentine, identified as antigorite, occurs as an aggregate of fine scales and fibers. Carbonate, identified as dolomite, is found as a minor constituent in all specimens. The mineral generally occurs along fractures in the rocks. The rocks include many kinds of Fe–Ni–Co–S minerals, *i.e.*, pentlandite, violarite (or polydymite), millerite, heazlewoodite, pyrite and godlevskite, in order of decreasing abundance (Table 2). Two varieties of violarite are easily distinguishable microscopically by differences in appearance and occurrence: one, greyish in color, is usually found replacing pentlandite and is characterized by prominent cleavages; the other, pinkish or brownish in color, has a smooth surface without cleavage. The former is very similar in appearance and occurrence to supergene violarite described by many previous investigators (*e.g.*, Imai *et al.* 1978), and is considered to be a replacement product after pentlandite by supergene oxidation. The latter probably formed contemporaneously with the associated minerals. Supergene violarite is not discussed further.

Sulfide assemblages and their modes of occurrence are highly variable. The pentlandite–heazlewoodite–godlevskite assemblage generally occurs as irregularly shaped massive aggregates with a small amount of magnetite, whereas the pentlandite–violarite–pyrite, pentlandite–violarite, pentlandite–violarite–millerite and violarite–(or polydymite–) millerite assemblages occur as vein-like, oval and island-like aggregates with minor or no magnetite, filling cracks and fracture cleavages of serpentinite (Figs. 3E, F).

CHEMICAL ANALYSES

Silicate minerals

Chemical analyses of silicate minerals were obtained with an electron microprobe (Table 3). Values of the Mg/(Mg+Fe) ratio (total Fe as FeO) of relict olivine from wehrlite of the Arakawa body and dunite of the Iwakura-yama North body are 0.84 to 0.87 (Fo_{84} to Fo_{87}) and 0.82 to 0.91 (Fo_{82} to Fo_{91}), respectively. The Ni content of olivine is slightly higher in the dunite of the Iwakura-yama North body (0.12 to 0.30% NiO) than in the wehrlite of the Arakawa body (0.10 to 0.21% NiO). The Ni content of olivine is positively correlated with Mg content, and negatively correlated with Fe content.

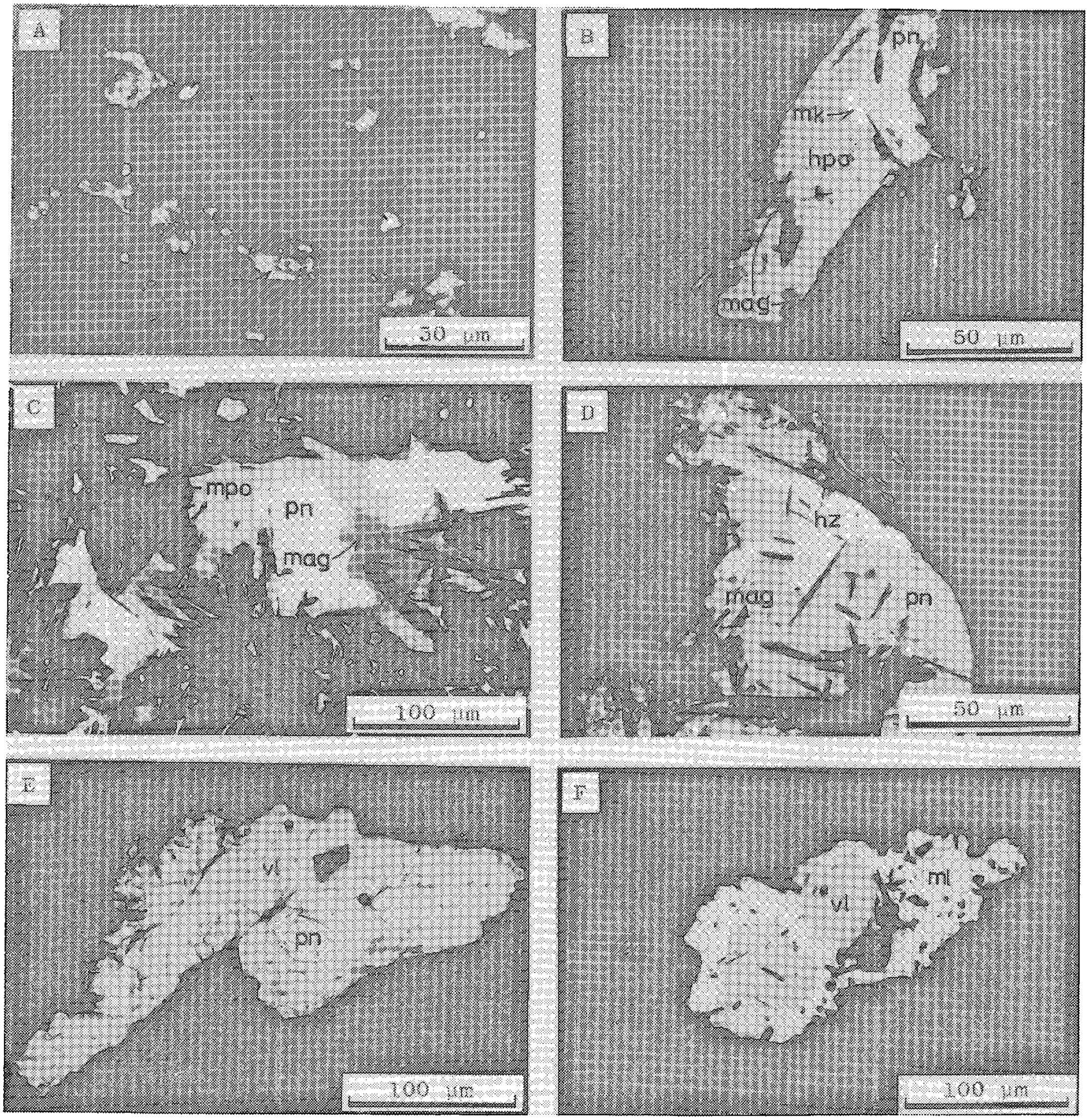

FIG. 3. Photomicrographs of polished surfaces, showing the mode of occurrence of opaque minerals in the Hayachine ultramafic rocks of the Kamaishi mining district, northeastern Japan. A: euhedral pentlandite (pn) and magnetite (mag) in weakly serpentinized rock of the Arakawa body (specimen A760504, single polar in air); B: hexagonal pyrrhotite (hpo) - pentlandite (pn) - mackinawite (mk) - magnetite (mag) aggregate in weakly serpentinized rock of the Arakawa body (specimen A760504, obliquely crossed polars in air); C: monoclinic pyrrhotite (mpo) - pentlandite (pn) - magnetite (mag) aggregate in strongly serpentinized rock of the Iwakura-yama North body (specimen I760823, single polar in air); D: pentlandite (pn) - heazlewoodite (hz) - magnetite (mag) aggregate in intensely serpentinized rock of the Iwakura-yama North body (specimen I760831, obliquely crossed polars in air); E: pentlandite (pn) - violarite (vl) aggregate in completely serpentinized rock of the Iwakura-yama Main body (specimen I760512, single polar in air); F: violarite (vl) - millerite (ml) aggregate in completely serpentinized rock of the Iwakura-yama Main body (specimen I760507, obliquely crossed polars in air).

Olivine contains negligible quantities of Al and Cr (less than 0.03% Al_2O_3 and 0.02% Cr_2O_3, respectively). Sparse data for clinopyroxene from the Iwakura-yama North body indicate contents of 0.03% NiO, 13.58 to 14.78% Al_2O_3 and 0.69 to 0.95% Cr_2O_3. The Ni and Fe contents of serpentine correlate fairly well with those of parental olivine. Levels of Al and Cr in serpentine are higher than

TABLE 3. CHEMICAL COMPOSITION OF OLIVINE-SERPENTINE PAIRS AND CLINOPYROXENE IN THE HAYACHINE ULTRAMAFIC ROCKS OF THE KAMAISHI MINING DISTRICT, NORTHEASTERN JAPAN

Locality	Specimen		SiO_2	Al_2O_3	Cr_2O_3	FeO	MgO	NiO	CaO	Total
Arakawa body	A760504-1	ol	40.18	0.01	0.02	14.67	44.13	0.16	-	99.17
		srp	41.68	1.23	0.02	4.04	38.16	0.09	-	85.22
	A760504-2	ol	39.92	-	0.01	12.67	47.61	0.13	-	100.34
		srp	43.54	1.29	0.01	4.23	37.19	0.04	-	86.30
	A760507-1	ol	41.03	-	0.01	12.27	46.82	0.10	-	100.23
		srp	42.72	1.52	0.48	4.17	37.21	0.09	-	86.19
	A760507-2	ol	40.26	0.01	0.01	12.71	47.30	0.21	-	100.50
		srp	43.70	1.93	0.33	4.46	39.01	0.13	-	89.56
Iwakura-yama North body	I760824	ol	40.16	0.03	-	16.34	42.04	0.14	0.01	98.72
		srp	43.41	1.28	0.33	5.26	36.93	0.02	0.01	87.24
	I760828	ol	40.84	0.02	0.01	14.37	44.75	0.22	0.02	100.23
		srp	43.38	1.20	0.31	4.73	37.39	0.09	0.02	87.12
	I760831	ol	41.20	0.01	-	8.71	50.34	0.30	0.01	100.57
		srp	43.51	0.97	0.07	2.88	38.39	0.16	0.01	85.99
	I760837	ol	39.37	0.01	-	13.33	47.27	0.12	0.01	100.11
		srp	40.89	1.87	0.01	4.60	38.26	0.06	-	85.69
	I760835	cpx	47.54	13.58	0.69	6.68	18.38	0.03	13.13	100.03
	I760837	cpx	45.92	14.78	0.95	6.24	18.99	0.03	13.11	100.02

ol:olivine, srp:serpentine, cpx:clinopyroxene. -:not detected. Compositions are reported in weight % and determined by electron microprobe, JEOL-50A. Accelerating voltage:15 kv, specimen current:1.5×10^{-8} A on MgO, size of beam spot:10 μmφ, manner of X-ray intensity measurement:fixed-time counting method for 10 sec, standard materials:synthetic $CaSiO_3$ and Fe_2O_3, respectively for Ca and Fe, synthetic simple oxides for Si, Al, Cr, Mg and Ni, correction for matrix effects:Bence-Albee method (Bence & Albee 1968).

those in olivine. The Co content of silicate minerals is below the detection limit of the electron microprobe.

Sulfide minerals

Microprobe data of sulfide minerals are given in Table 4. Pentlandite and violarite show systematic chemical variations dependent on the sulfide association. The discrete, euhedral to subhedral grains of pentlandite from the Arakawa body are characterized by high Co concentration in comparison with pentlandite coexisting with hexagonal pyrrhotite and mackinawite in the same specimens. With this exception, pentlandite becomes gradually enriched in Co with progressing serpentinization, from the hexagonal pyrrhotite–pentlandite–mackinawite association to the monoclinic pyrrhotite–pentlandite association and, finally, to the pentlandite–heazlewoodite–godlevskite association. The pentlandite associated with violarite has very low Co contents; in such associations, Co is strongly concentrated in violarite.

BULK COMPOSITION OF SULFIDE AGGREGATES

Modal analyses of sulfide aggregates were made in order to estimate their bulk compositions. As the sulfides are generally minute, analyses were performed on enlarged photomicrographs of five representative areas in each specimen, using graph paper to count over 2500 squares (each 1–2 × 1–2 μm) in each area. The bulk compositions (Table 6) were determined from the modal compositions in conjunction with structural formulae of phases (Table 4), Z-numbers and unit-cell volumes (Table 5). The change of unit-cell volume with composition was ignored here.

DISCUSSION

Behavior of metals and sulfur during serpentinization

The Hayachine ultramafic rocks underwent contact metamorphism after serpentinization, as indicated by the formation of tremolite in serpentine.

TABLE 4. CHEMICAL COMPOSITION OF SULFIDE MINERALS IN THE HAYACHINE ULTRAMAFIC ROCKS OF THE KAMAISHI MINING DISTRICT, NORTHEASTERN JAPAN

Locality	Specimen No.	Assemblage	Phase	Fe	Ni	Co	S	Total	Structural Formula
Arakawa body	A760504	pn*	pn	29.75	29.45	6.48	33.72	99.40	$Fe_{4.052}Ni_{3.816}Co_{0.836}S_8$
		hpo-pn-mk	hpo	61.25	0.02	0.06	38.55	99.88	$Fe_{0.912}Ni_{0.000}Co_{0.001}S$
		hpo-pn-mk	pn	36.17	28.45	2.54	33.58	100.74	$Fe_{4.949}Ni_{3.706}Co_{0.324}S_8$
	A760507	pn*	pn	30.99	28.82	6.34	32.61	98.76	$Fe_{4.364}Ni_{3.862}Co_{0.845}S_8$
		hpo-pn-mk	hpo	60.98	0.01	0.08	38.89	99.96	$Fe_{0.900}Ni_{0.000}Co_{0.001}S$
		hpo-pn-mk	pn	31.07	33.74	2.28	32.59	99.68	$Fe_{4.382}Ni_{4.516}Co_{0.306}S_8$
Iwakura-yama North body	I760824	mpo-pn	mpo	59.31	0.30	0.06	39.65	99.32	$Fe_{0.859}Ni_{0.004}Co_{0.001}S$
		mpo-pn	pn	30.26	33.37	3.57	33.80	101.00	$Fe_{4.118}Ni_{4.318}Co_{0.463}S_8$
	I760835	mpo-pn	mpo	59.68	0.39	0.07	39.52	99.66	$Fe_{0.867}Ni_{0.005}Co_{0.001}S$
		mpo-pn	pn	30.81	34.06	2.28	33.47	100.62	$Fe_{4.223}Ni_{4.447}Co_{0.299}S_8$
	I760828	mpo-pn	mpo	60.21	0.34	0.05	39.21	99.81	$Fe_{0.882}Ni_{0.005}Co_{0.001}S$
		mpo-pn	pn	31.91	32.95	2.28	33.43	100.57	$Fe_{4.387}Ni_{4.317}Co_{0.299}S_8$
	I760831	pn-hz-gd	pn	27.66	35.81	3.72	33.56	100.75	$Fe_{3.787}Ni_{4.655}Co_{0.479}S_8$
		pn-hz-gd	hz	1.00	72.76	-	26.30	100.06	$Fe_{0.044}Ni_{3.024}S_2$
Iwakura-yama Main body	I760522	pn-hz-gd	pn	24.33	37.34	5.54	33.28	100.49	$Fe_{3.352}Ni_{4.894}Co_{0.719}S_8$
		pn-hz-gd	hz	-	73.33	-	26.33	99.66	$Ni_{3.044}S_2$
		pn-hz-gd	gd	0.07	66.95	-	31.29	98.31	$Fe_{0.008}Ni_{7.010}S_6$
	I760512	pn-vl-py	pn	27.68	39.27	0.12	33.73	100.80	$Fe_{3.775}Ni_{5.096}Co_{0.014}S_8$
		pn-vl-py	vl	21.50	32.80	3.60	42.20	100.10	$Fe_{1.170}Ni_{1.698}Co_{0.186}S_4$
		pn-vl-py	py	44.50	0.80	1.60	53.03	99.93	$Fe_{0.964}Ni_{0.017}Co_{0.033}S_2$
	I760838	pn-vl	pn	25.92	40.30	0.15	34.46	100.83	$Fe_{3.454}Ni_{5.110}Co_{0.018}S_8$
		pn-vl	vl	20.51	33.91	3.32	43.22	100.96	$Fe_{1.090}Ni_{1.714}Co_{0.167}S_4$
	I760511	pn-vl	pn	26.83	39.89	0.33	33.46	100.51	$Fe_{3.674}Ni_{5.204}Co_{0.039}S_8$
		pn-vl	vl	18.32	32.34	7.09	41.98	99.73	$Fe_{1.001}Ni_{1.680}Co_{0.368}S_4$
	I760841	pn-vl-ml	pn	25.96	41.07	0.20	33.75	100.98	$Fe_{3.532}Ni_{5.315}Co_{0.025}S_8$
		pn-vl-ml	vl	16.62	37.83	4.63	42.42	101.50	$Fe_{0.900}Ni_{1.949}Co_{0.237}S_4$
		pn-vl-ml	ml	1.95	60.16	0.13	36.37	98.61	$Fe_{0.031}Ni_{0.903}Co_{0.002}S$
	I760506	vl-ml	vl	8.93	37.75	11.08	42.34	100.10	$Fe_{0.483}Ni_{1.952}Co_{0.571}S_4$
		vl-ml	ml	0.92	63.14	0.28	35.29	99.63	$Fe_{0.015}Ni_{0.976}Co_{0.005}S$
	I760509	vl-ml	vl	8.92	37.14	11.54	42.26	99.86	$Fe_{0.483}Ni_{1.916}Co_{0.591}S_4$
		vl-ml	ml	1.00	63.64	0.34	35.44	100.42	$Fe_{0.016}Ni_{0.981}Co_{0.005}S$

Abbreviations of mineral names are the same as in TABLE 2. *discrete, euhedral to subhedral pentlandite. Compositions, in weight %, are determined by electron microprobe, JEOL-50A. Accelerating voltage:20 kv, specimen current:$1.4\text{x}10^{-8}$ A on MgO, size of beam spot:2 μmϕ, manner of X-ray intensity measurement:fixed-time counting method for 10 sec, standard materials:synthetic troilite for Fe, synthetic millerite for Ni, pure metallic cobalt for Co, and troilite and millerite for S, correction for matrix effects:Sweatman-Long method (Sweatman & Long 1969).

As described before, however, the rocks have smooth fracture-cleavages peculiar to serpentinite or serpentinized rock, and the textural relations among serpentine, olivine and clinopyroxene prior to metamorphism are well preserved. These features of the rocks are consistent with a moderate effect of metamorphism.

The development of magnetite and finely disseminated pentlandite in serpentine in the Arakawa body (Fig. 3A) suggests the following equation for the hydration of olivine to serpentine:

$$\underset{\text{ol}}{3.090\mathrm{Mg}_{1.720}\mathrm{Fe}_{0.272}\mathrm{Ni}_{0.003}\mathrm{SiO}_4} + 0.910\mathrm{SiO}_2 + (3.820+4x)\mathrm{H}_2\mathrm{O} = \underset{\text{srp}}{\mathrm{Mg}_{5.314}\mathrm{Fe}_{0.333}\mathrm{Ni}_{0.007}\mathrm{Si}_4\mathrm{O}_{10}(\mathrm{OH})_8} + \underset{\text{mag}}{x\mathrm{Fe}_3\mathrm{O}_4} + \underset{\text{in pn}}{\underline{(0.507-3x)\mathrm{Fe}^{2+} + 0.002\mathrm{Ni}^{2+}}} + (4x-0.180)\mathrm{H}_2 + (1.018-6x)e^- \qquad (1)$$

The formulae of olivine and serpentine in this equation reflect the average chemical compositions (Table 3). The small amounts of Al and Cr are neglected.

Here, since the composition of the discrete pentlandite approximates $\mathrm{Fe}_{4.208}\mathrm{Ni}_{3.839}\mathrm{Co}_{0.841}\mathrm{S}_8$ (average of the two structural formulae presented in Table 4), the value of x is arithmetically estimated as:

$$(0.507-3x) : 0.002 = 4.208 : 3.839$$
$$x = 0.168$$

TABLE 5. Z-NUMBERS, UNIT-CELL DIMENSIONS AND UNIT-CELL VOLUMES FOR SOME PHASES IN THE SYSTEM Fe-Ni-Co-S

Phase	Z-number	Unit-cell Dimension (Å, °)	Unit-cell Volume (Å^3)	Source
hexagonal pyrrhotite	2	a 3.4452 c 5.7352	58.953	Morimoto *et al.* (1975)
monoclinic pyrrhotite	64	a 11.885 b 6.870 c 22.796 β 90.469°	1861.2	Morimoto *et al.* (1975)
pentlandite-cobalt pentlandite	4	a 10.067 -9.937	1020.2 -981.2	Kouvo *et al.* (1959) Petruk *et al.* (1969) Imai *et al.* (1980)
heazlewoodite	1	a 4.080 α 89°26'	67.91	Peacock (1947)
violarite-polydymite	8	a 9.465- 9.489	847.9- 854.4	Craig (1971)
millerite	9	a 9.62 c 3.15	252.5	Shiga (1975)

Equation (1), hence, may be recast as follows:

$$\underset{\text{ol}}{3.090\mathrm{Mg}_{1.720}\mathrm{Fe}_{0.272}\mathrm{Ni}_{0.003}\mathrm{SiO}_4} + 0.910\mathrm{SiO}_2 + 4.492\mathrm{H}_2\mathrm{O} = \underset{\text{srp}}{\mathrm{Mg}_{5.314}\mathrm{Fe}_{0.333}\mathrm{Ni}_{0.007}\mathrm{Si}_4\mathrm{O}_{10}(\mathrm{OH})_8} + \underset{\text{mag}}{0.168\mathrm{Fe}_3\mathrm{O}_4} + \underset{\text{in pn}}{\underline{0.003\mathrm{Fe}^{2+} + 0.002\mathrm{Ni}^{2+}}} + 0.492\mathrm{H}_2 + 0.010e^- \qquad (2)$$

Chlorite in the rocks likely formed from break-

TABLE 6. MODAL COMPOSITION AND BULK CHEMICAL COMPOSITION FOR SULFIDE AGGREGATES IN THE HAYACHINE ULTRAMAFIC ROCKS OF THE KAMAISHI MINING DISTRICT, NORTHEASTERN JAPAN

Locality and Specimen No.	Volume Percent of Serpentine	Modal Composition of Sulfide Aggregate (volume %)	Bulk Composition of Aggregate (atomic %)			
			Fe	Ni	Co	S
Arakawa body						
(1) A760504	35	hpo(66)-pn(34)-mk(-*)	41.26	7.55	0.69	50.50
(2) A760507	35	hpo(68)-pn(32)-mk(-)	40.11	8.68	0.63	50.58
Iwakura-yama North body						
(3) I760824	50	mpo(69)-pn(31)	39.19	8.27	0.89	51.65
(4) I760835	60	mpo(37)-pn(63)	32.63	16.82	1.14	49.41
(5) I760828	70	mpo(29)-pn(71)	31.74	18.26	1.27	48.73
(6) I760831	80	pn(94)-hz(6)-gd(-)	20.94	29.66	2.64	46.76
Iwakura-yama Main body						
(7) I760522	**	pn(70)-hz(30)-gd(-)	13.38	39.02	2.87	44.74
(8) I760512	**	pn(19)-vl(81)-py(-)	17.68	25.23	2.15	54.94
(9) I760838	**	pn(80)-vl(20)	19.79	29.56	0.57	50.08
(10) I760511	**	pn(69)-vl(31)	19.39	28.61	1.78	50.23
(11) I760841	**	pn(19)-vl(80)-ml(1)	14.14	28.45	2.71	54.70
(12) I760506	**	vl(45)-ml(55)	3.39	39.85	3.63	53.13
(13) I760509	**	vl(37)-ml(63)	2.96	41.43	3.12	52.50

Abbreviations of mineral names are the same as in TABLE 2. *negligible.
**Rock is essentially serpentinite.

down of clinopyroxene rather than olivine, and carbonate formed after serpentinization. Therefore, these minor phases are neglected in the equation. Serpentinization of olivine yields an excess of magnesium and iron, which are normally accommodated in brucite and magnetite, respectively. Brucite was not detected in the present rocks, either under the microscope or by the X-ray-diffraction method. It is necessary to introduce silica as a reactant from an unspecified source (*e.g.*, coexisting clinopyroxene) to balance the excess magnesium, although a part of the magnesium may have been accommodated in carbonate. Then, picking up Fe and Ni from equation (2) in order to define their partition into the relevant minerals,

$$280\mathrm{Fe}^{\mathrm{ol}} = 111\mathrm{Fe}^{\mathrm{srp}} + 168\mathrm{Fe}^{\mathrm{mag}} + \mathrm{Fe}^{\mathrm{pn}} \quad (3)$$

$$9\mathrm{Ni}^{\mathrm{ol}} = 7\mathrm{Ni}^{\mathrm{srp}} + 2\mathrm{Ni}^{\mathrm{pn}} \quad (4)$$

Here $\mathrm{Fe}^{\mathrm{ol}}$ indicates the iron in the olivine structure, *etc.*

In some Archean dunites in Western Australia, approximately 30% of the nickel in the original silicate was redistributed to newly formed sulfide minerals during initial serpentinization, and at a higher temperature up to 60% of bulk-rock nickel was incorporated in sulfide form (Donaldson 1981). In the Arakawa body, metal loss from the serpentinized olivine was probably balanced by the generation of magnetite and discrete pentlandite. Based on equation (3), most of the iron in olivine was incorporated in both serpentine (39.6 atomic %) and magnetite (60.0 atomic %), and the extra 0.4 atomic % was redistributed to the discrete pentlandite. From equation (4), 77.8 atomic % of the nickel composing olivine entered serpentine, and the remainder (22.2 atomic %) entered the discrete pentlandite, together with the liberated iron. A possible source for cobalt in the discrete pentlandite is olivine, which may contain a trace of cobalt, although below the detection limits of the microprobe. Based on both equation (2) and the average structural formula of the discrete pentlandite, an atomic proportion of iron, nickel and cobalt expelled from olivine to form opaque minerals (magnetite and pentlandite) is roughly estimated as follows:

$$\mathrm{Fe} : \mathrm{Ni} : \mathrm{Co} = 1200 : 5 : 1$$

Many investigators reported the formation of sulfide–magnetite aggregates during serpentinization from sulfides originally disseminated in dunite (*e.g.*, Ramdohr 1967, Papunen 1971, Groves *et al.* 1974, Eckstrand 1975, Groves & Keays 1979). In the Mt. Keith - Betheno area, Western Australia, magmatic pentlandite was progressively replaced by heazlewooddite and magnetite with increasing degree of serpentinization (Groves & Keays 1979). The textural relations between hexagonal pyrrhotite and magnetite in the Arakawa body suggest that they both may be pseudomorphous breakdown-products after magmatic pyrrhotite (Fig. 3B). Although the chemical composition of the original pyrrhotite is uncertain, the breakdown equation may be approximated as:

$$\underset{\text{magmatic po}}{9x\mathrm{Fe_7S_8}(?)} + 18\mathrm{O_2} = \underset{\text{hpo}}{(7x{-}3)\mathrm{Fe_9S_{10}}} + \underset{\text{mag}}{9\mathrm{Fe_3O_4}} + (x+15)\mathrm{S_2} \quad (5)$$

Although its coefficients cannot be defined, this oxidation reaction is considered to have taken place contemporaneously with the hydration reaction (2).

From equation (2), it is likely that hydrogen released during serpentinization causes a locally reducing environment. According to Shiga (1983a), mackinawite associated with pentlandite and hexagonal pyrrhotite resulted from the desulfurization of aggregates of magmatic sulfides by such a release of hydrogen. A possible equation for the formation of mackinawite is:

$$\underset{\text{magmatic pn}}{35\mathrm{Fe_{4.6}(Ni,Co)_{4.4}S_8}} + \underset{\text{magmatic po}}{197\mathrm{Fe_7S_8}(?)} + 316\mathrm{H_2} = \underset{\text{mk}}{1540\mathrm{Fe(Ni,Co)_{0.1}S}} + 316\mathrm{H_2S} \quad (6)$$

Hence,

$$161\mathrm{Fe}^{\text{magmatic pn}} + 1379\mathrm{Fe}^{\text{magmatic po}} = 1540\mathrm{Fe}^{\mathrm{mk}} \quad (7)$$

$$\mathrm{(Ni,Co)}^{\text{magmatic pn}} = \mathrm{(Ni,Co)}^{\mathrm{mk}} \quad (8)$$

$$70\mathrm{S}^{\text{magmatic pn}} + 394\mathrm{S}^{\text{magmatic po}} = 385\mathrm{S}^{\mathrm{mk}} + 79\mathrm{S} \quad (9)$$

Here, the composition for magmatic pentlandite is considered to approximate that of the pentlandite in the aggregates of secondary sulfides, $\mathrm{Fe_{4.666}Ni_{4.111}Co_{0.315}S_8}$ (average of the two structural formulae presented in Table 4). Quantitative microanalyses of mackinawite were unsuccessful because of the minute grain-size, but minor Ni and trace Co (in addition to Fe and S) were detected. As naturally occurring mackinawite contains up to 11.8% Ni and up to 12.7% Co (Zōka *et al.* 1972), the mackinawite in equation (6) was assumed to contain several percent Ni + Co.

It is apparent from equations (5) and (7) that the iron in the magmatic pyrrhotite was consumed by the formation of hexagonal pyrrhotite, magnetite and mackinawite during initial serpentinization. As estimated from equation (7), the 89.5 atomic % of iron required for the formation of mackinawite was derived from magmatic pyrrhotite, and the

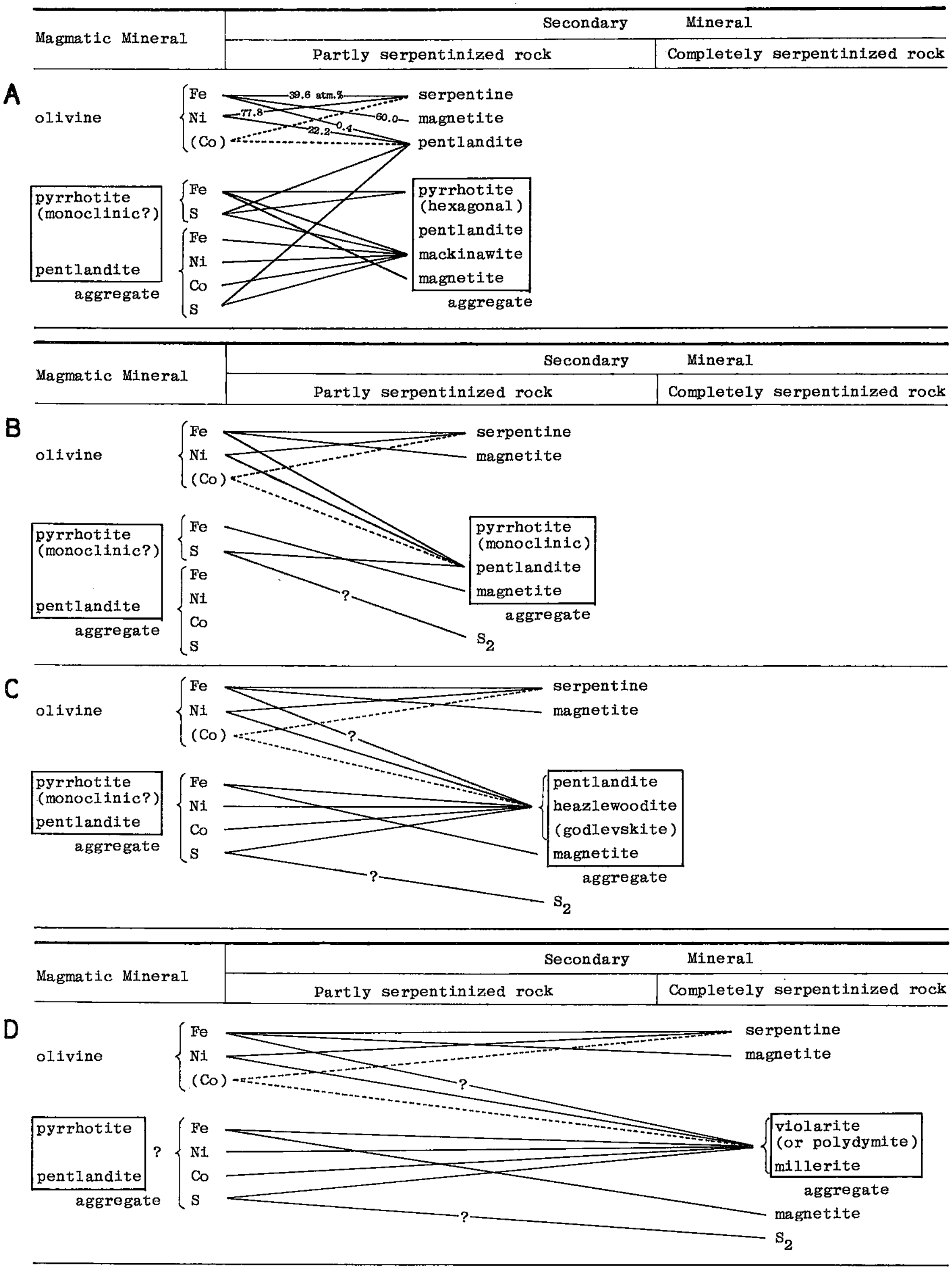

FIG. 4. Behavior of Fe, Ni, Co and S during serpentinization in the Hayachine ultramafic rocks of the Kamaishi mining district, northeastern Japan. A: Arakawa body, B and C: Iwakura-yama North body, D: Iwakura-yama Main body.

remainder (10.5 atomic %) from magmatic pentlandite. It is likely that the nickel and cobalt of mackinawite were mostly derived from magmatic pentlandite [equation (8)], as nickel (and cobalt) released from olivine were not necessarily related to mackinawite formation. Sulfur generated through reactions (5) and (6) contributed to the formation of the discrete pentlandite.

Reactions (2), (5) and (6) are considered all to have taken place almost *in situ*. The behavior of metals and sulfur at the incipient stage of serpentinization in the Arakawa body is shown schematically in Figure 4A.

Since, in the Iwakura-yama North body, there is no discrete sulfide like the pentlandite of the Arakawa body, it is not possible to suggest an equation for a suitable hydration reaction. As previously described, in the Iwakura-yama North body, magmatic pyrrhotite-pentlandite aggregates seem to have been modified almost *in situ*, taking up the liberated cations to form the present monoclinic pyrrhotite-pentlandite-magnetite aggregates. The gradual increase in proportion of pentlandite to monoclinic pyrrhotite with progressing serpentinization (Table 6) may be attributed both to the conversion of magmatic pyrrhotite to magnetite, and to the additional formation of pentlandite from the expelled cations (Fig. 4B). The equation for the conversion is represented as:

$$\underset{\text{magmatic po}}{3Fe_7S_8(?)} + 14O_2 = \underset{\text{mag}}{7Fe_3O_4} + 12S_2 \qquad (10)$$

Sulfur generated from this reaction enabled formation of new pentlandite in conjunction with the cations liberated. It is, however, not clear whether all the sulfur was consumed by pentlandite formation (Fig. 4B). The conversion may have gone on until magmatic pyrrhotite was totally consumed by the formation of magnetite and, finally, a pentlandite-magnetite assemblage was attained. Pentlandite had been nearly isochemical during this process (Table 4).

In contrast, the more Ni-rich pentlandite-heazlewoodite (-godlevskite)-magnetite aggregates of the Iwakura-yama North body appear to have formed from metals and sulfur that originated from both dissolution of magmatic sulfides and hydration of olivine. The formation of sulfide-magnetite aggregates from a mixture of the elements different in origin is a feature of this stage of serpentinization (Fig. 4C).

The modes of occurrence of sulfide (-magnetite) aggregates from the Iwakura-yama Main body (Figs. 3E, F) suggest that metals and sulfur that originated from both olivine and probably pre-existing magmatic sulfides moved only a short distance and precipitated in the present sites contemporaneously with serpentinization or somewhat later (Fig. 4D). The movement of the elements before precipitation is one of the most pronounced characteristics of mineralization in the Iwakura-yama Main body. In the body, sulfide stringers and veinlets that formed at a later stage (*e.g.*, violarite-millerite aggregates) coexist with a smaller quantity of magnetite than sulfide masses that formed at an earlier stage (*e.g.*, pentlandite-heazlewoodite-godlevskite aggregates). This suggests that iron in the fluids may have been removed to form magnetite before precipitation of sulfides. Figure 4D is a diagram illustrating the formation of violarite-millerite aggregates, in which magnetite is generally absent.

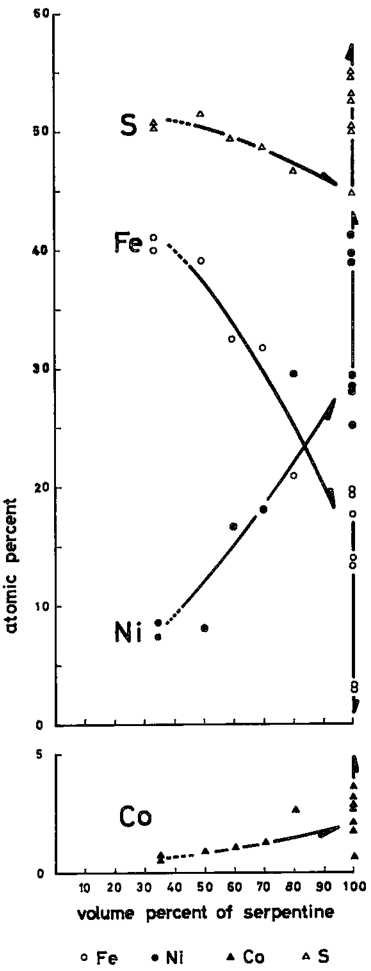

FIG. 5. Relationship between the degree of serpentinization and the bulk chemical compositions of sulfide aggregates in the Hayachine ultramafic rocks of the Kamaishi mining district, northeastern Japan.

Variation of bulk composition

Figure 5 illustrates the relationship between degree of serpentinization and bulk compositions of sulfide aggregates. Fe contents of the sulfide aggregates are reduced with progressing serpentinization. Nickel, in contrast, is strongly enriched with increasing serpentinization. Cobalt contents vary sympathetically with nickel. Sulfur contents are characterized by a gradual depletion with initial serpentinization and an increase in completely serpentinized rocks. The bulk-composition variations may be interpreted as follows.

The continuous removal of iron from aggregates of magmatic sulfides to form magnetite, as well as the uptake of nickel and cobalt from olivine, account for the progressive formation of relatively Ni- and Co-enriched sulfide aggregates. From equation (3), iron released from olivine was not so important in its effect on the Fe contents of secondary sulfides. As previously discussed, sulfur released through the decomposition of magmatic sulfides contributed to the formation of additional sulfides in conjunction with metals released from olivine, and the remainder, if present, may have formed S_2 or H_2S. The gradual depletion of secondary sulfides in sulfur during serpentinization is likely attributed to an increase in total metals, due to predominance of the incorporated nickel and cobalt over the removed iron, or to the generation of S_2 or H_2S.

Although the uptake of metals released from olivine ceases upon complete serpentinization of olivine, the removal of iron from magmatic sulfides to form magnetite may continue. If this is the case, there should be a gradual depletion in the Fe content of aggregates of secondary sulfides and a resultant relative increase in nickel, cobalt and sulfur. Moreover, all aggregates of secondary sulfides, regardless of the mineral assemblages present, should have identical Ni:Co:S proportions. The general trends of the bulk-composition variations in completely serpentinized rocks (Fig. 5) are consistent with the above suggestion, but in some other respects this is not necessarily so: the bulk compositions do not vary linearly, and the Ni:Co:S proportions are very variable (see the last column of Table 6). These discrepancies may provide evidence for movement of the relevant elements, as discussed farther below. It can be inferred that, where all iron has entered magnetite, Fe-free Ni- and Co-sulfides such as millerite, Fe-free polydymite and vaesite would form. Violarite coexisting with millerite in the Iwakura-yama Main body is essentially polydymite (Table 4).

Movement of metals and sulfur

In some ultramafic bodies, serpentinization occurred as an essentially isochemical process (Coleman & Keith 1971) without any apparent change of major components Si, Mg and Fe, nor of minor components Cr, Al and Ni (Donaldson 1981). It is reasonable to regard Al and Cr in serpentine of the Hayachine ultramafic rocks as derivatives from the surrounding clinopyroxene and chromite rather than as introduced from external sources with serpentinizing fluids. It is likely that characteristics of serpentine composition, especially its minor constituents, depend not only on parental olivine composition, but also significantly on mineralogy and modal composition of original rock.

According to Shiga (1983b), Ni and Co contents of partly serpentinized rocks of the Iwakura-yama North body range from 1580 to 2260 ppm and from 106 to 119 ppm, respectively, whereas those of completely serpentinized rocks of the Iwakura-yama Main body range from 1790 to 2180 ppm and from 76 to 113 ppm, respectively. There is no significant difference in Ni and Co contents between the partly and completely serpentinized rocks, suggesting that the serpentinization occurred isochemically on a hand-specimen scale with respect to Ni and Co. However, the modes of occurrence and the variable Ni:Co:S proportions of sulfide aggregates indicate that the relevant elements must have become gradually mobile with progressive serpentinization and have moved up to about 10 cm in the completely serpentinized rocks of the Iwakura-yama Main body.

Most investigators believe that serpentinizing fluids transport considerable amounts of sulfur, besides H_2O, CO_2 and Cl, from external sources into ultramafic masses (*e.g.*, Ashley 1973, Donnelly *et al.* 1978, Groves *et al.* 1979, Donaldson 1981, Seccombe *et al.* 1981). There are also reports on the migration of "internal" sulfur yielded by modification of magmatic sulfides toward the periphery of masses during serpentinization (Chamberlain 1967, Seccombe *et al.* 1981). But there is no apparent evidence for sulfur addition or removal in the Hayachine ultramafic bodies.

CONCLUSIONS

Mineralogical and compositional variations of sulfides in the Hayachine ultramafic rocks are accounted for in terms of both the hydration of olivine and the decomposition of precursor (probably magmatic) sulfides. The variations may be typical wherever abundant sulfides exist in rocks prior to serpentinization.

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