

Note on rock-forming minerals in the Joetsu district, Niigata Prefecture, Japan.

(8) Chromite in serpentinite from the Kotaki-Omi district.

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ABSTRACT

The serpentinite melange including crystalline schist is distributed in the Omi-Kotaki district, Niigata Prefecture. Chromite and chromian spinel occur in the serpentinite. Three generations of chromite and chromian spinel were distinguished petrographically and chemically. Type I chromian spinel appears as xenolith, Type II chromite with low Al content occurs as a fine grained rectangle and square crystal in the serpentinite. Type III chromite and magnetite are as aggregates and a fine grained crystal.

The Type I chromian spinel of the xenolith (CX-1) has the formula $(\text{Mg}_{0.75}\text{Fe}^{2+}_{0.25}\text{Mn}_{0.01})_{1.01}(\text{Ti}_{0.01}\text{Al}_{0.96}\text{Cr}_{0.94}\text{Fe}^{3+}_{0.08})_{1.99}\text{O}_4$, and unit cell parameter $a = 8.240$ (1) Å. The structure of the fine grained chromite (OM-01) in serpentinite is $(\text{Mg}_{0.19}\text{Fe}^{2+}_{0.80}\text{Mn}_{0.03})_{1.02}(\text{Ti}_{0.02}\text{Al}_{0.25}\text{Cr}_{1.51}\text{Fe}^{3+}_{0.20})_{1.98}\text{O}_4$ with $a = 8.379$ (2) Å.

KEY WORDS

Chromite, Chromian Spinel, Magnetite, Spinel, Serpentinite

Introduction

Chromite is a typical mineral in alpine-type peridotite and serpentinite. The origin and nature of chromite and chromian spinel in layered ultrabasic and basic igneous rocks were studied by many workers (Henderson and Suddaby 1971, Campbell and Murck, 1993). Recently, chromian spinel is an important indicator for classifying mantle-derived peridotites (Dick and Bullen 1984) and for determining the chemical character of the mother magma such as mid-oceanic ridge basalts, arc basalts and intraplate basalts (Irvine 1965, Arai 1992). Arai (1987) and Ozawa (1994) reported that the changes of Mg/Fe and NiO in olivine and $\text{Cr}/(\text{Cr} + \text{Al} + \text{Fe}^{3+})$ in chromite show the trend of the melt segregation and the process of partial melting in the upper mantle. High NiO content of olivine in upper mantle is known. Relict crystal of olivine or pyroxene in serpentinite melange from the

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Kotaki-Omi district are not observed. Therefore, on the basis of only chemical composition of chromite, we attempt to determine the chemical character of the original rocks before serpentinization.

In this report, we will give description on the occurrence, chemical composition and physical properties of chromite and chromian spinel.

Occurrence

Serpentinite invaded along faults between the schists, Paleozoic and Metamorphic sediments (Fig. 1). The ultramafic rocks are almost completely serpenitimized. Relic

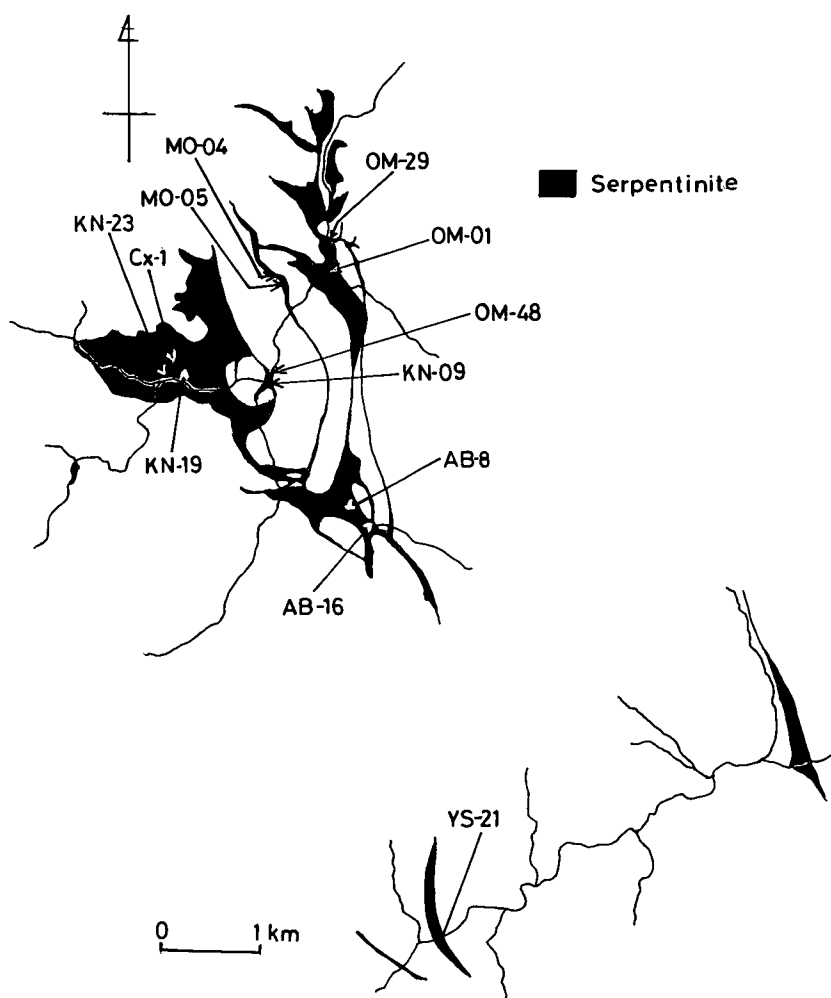


Figure 1. Geological map of the Kotaki-Omi district (after Kanayama 1991). Numbers indicate the collected points of the samples.

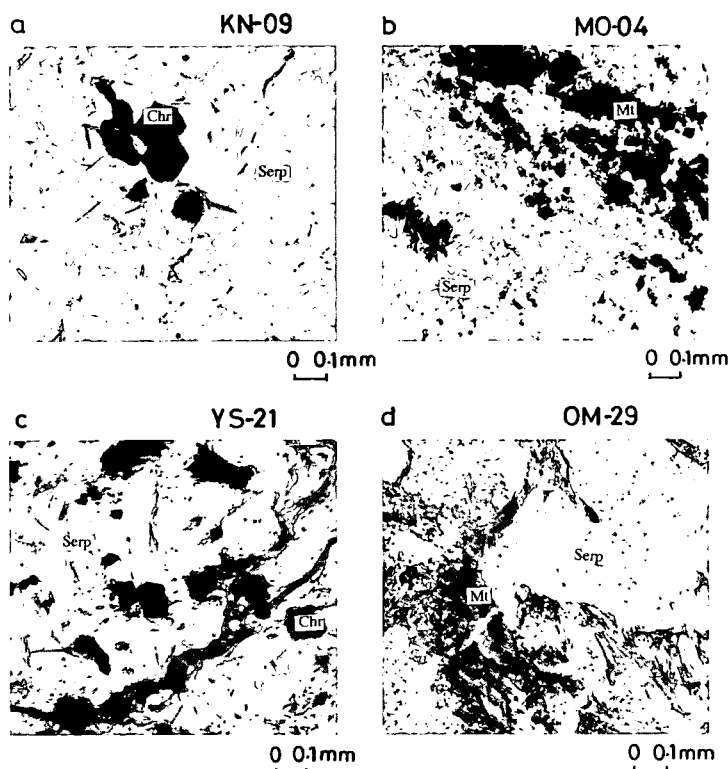


Figure 2. Photomicrographs of the chromite, chromian spinel and magnetite in the serpentinite from the Omi-Kotaki district. a: Chromite occurs as rectangular crystal in the KN-09 serpentinite. b: Aggregate magneite, together with Ni oxide and graphite (MO-04). c: Chromite shows rectangular form with notched rim in the YS-21 serpentinite. d: Magnetite occurs in the boundary of crystals and vein (OM-29). Chr: chromite, Serp: serpentine, Mt: magnetite.

crystals of olivine and pyroxene can hardly be observed in thin section. A xenolithic round of Type I chromian spinel (CX-1), 20 cm in size, is found in serpentinite at the Kinzan valley. The color of the chromian spinel at thin edge is brown under microscope and is dull grey in reflected light. Type II chromite from the serpentinites (AB-8, KN-09, KN-23, YS-21) shows rectangle and square forms (Figs. 2a and 3a). Chromite from Ys-21 serpentinite is rectangle crystal with notched rim (Figs. 2c and 3c). Type III magnetite in the serpentinites (AB-16, MO-05, KN-19, OM-29) occurs as aggregates together with nickel oxide and graphite (Figs. 2d and 3d) in grain boundary and serpentine vein, and chromite from the serpentinites (MO-04, OM-01, OM-48) occurs as anhedral grains and a cluster of aggregates (Fig. 2b). This aggregate is the result of breakdown of olivine and pyroxene.

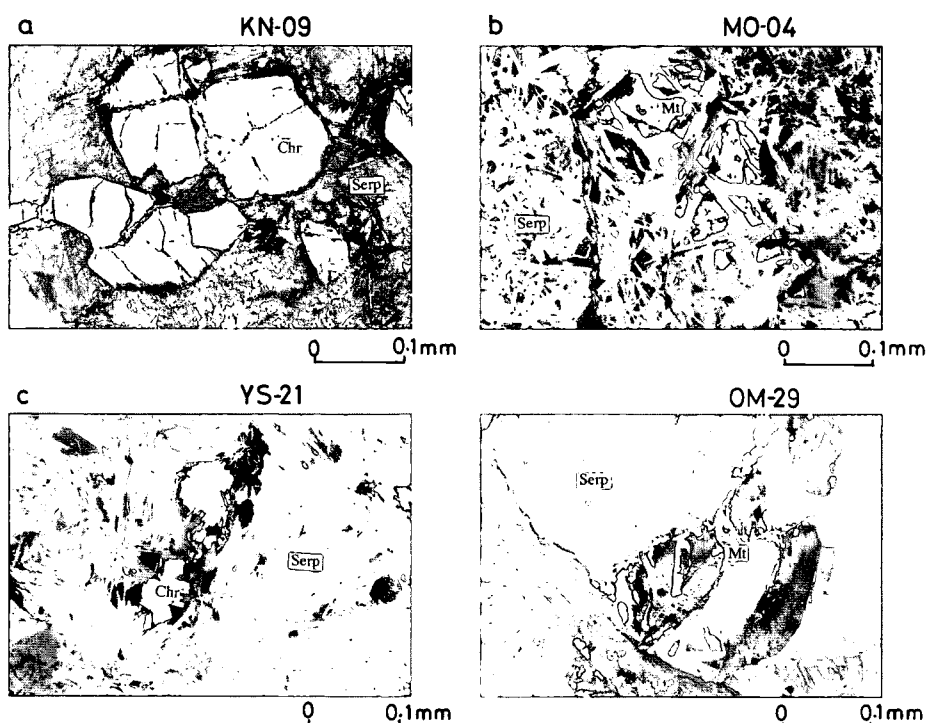


Figure 3. Reflected light photomicrographs of the chromite, chromian spinel and magnetite in the serpentinite from the Omi-Kotaki district. a: The rim of chromite is sharp (KN-09). b: Magnetite remained after serpentinization (MO-04). c: Chromite with notched rim (YS-21). d: fine grained magnetite at the boundary of crystals (OM-29). Chr: chromite, Serp: serpentine, Mt: magnetite.

Mineralogical data and Discussion

X-ray analysis: The X-ray powder data for spinel minerals, together with chromite reported by Hill et al.(1979), are given in Table 1. The unit-cell parameters were obtained from the sharp reflections with asterisk by using silicon as an external standard. Calculation was made on the computer program UNICS RSLC-3 (Sakurai 1968). The unit-cell parameters of a^* are calculated by using the molecular proportions of end-members and the unit-cell parameters reported by Hill et al.(1979). The observed values of a^* approximately agree with the calculated values of a^* . These facts supported that Fe^{3+} calculated by assuming spinel stoichiometry is close to real value.

Chemical composition: The chemical compositions of the spinel minerals were determined with a JEOL 8060 superprobe, using standard procedure at Niigata University. EPMA

Table 1. X-ray powder data of chromite and magnetite.

MO-04			KN-23			OM-01		CX-1		Hill et al. (1979)
HKL	d (Å)	I/Io	d (Å)	I/Io	d (Å)	I/Io	d (Å)	I/Io	d (Å) (calc)	
1 1 1	4.840*	6	4.822*	37			4.761*	25	4.845	
0 2 2	2.965*	25	2.957*	32	2.961*	30	2.915*	30	2.915	
1 1 3	2.529*	100	2.523*	100	2.527*	100	2.485*	100	2.530	
2 2 2							2.379*	7	2.422	
0 0 4	2.098*	13	2.092	26	2.095*	20	2.060*	55	2.098	
2 2 4	1.713*	8					1.682*	10	1.713	
1 1 5	1.615*	22	1.611*	32	1.612*	35	1.586*	55	1.615	
0 4 4	1.484*	22	1.480*	32	1.482*	40	1.457*	60	1.483	
a Å	8.391(1)		8.369(2)		8.373(2)		8.240(1)		8.393	
a* Å	8.399		8.377		8.364		8.228			
a-a*	0.008		0.008		0.009		0.012			

Chromite: 8.393 Å, Hercynite: 8.1490 Å, Jacobsite: 8.511 Å, Magnesiochromite: 8.333 Å, Magnetite: 8.3958 Å, Spinel: 8.0834 Å, Ulvospinel: 8.536 Å (Hill et al. 1979)

a*: recalculated by using the molecular proportions of end-members in Table 2 and unit cell parameters (Hill et al. 1979).

analyses of the spinel minerals are given Table 2 together with their structural formulae on the basis of 4 oxygen atoms. Fe^{3+} contents of chromite were calculated by assuming spinel stoichiometry. The site occupancies of cations and the molecular proportions of end-members were calculated on the following order: Ulvospinel ($\text{TiFe}^{2+}_2\text{O}_4$), Jacobsite ($\text{Mn}^{2+}\text{Fe}^{3+}_2\text{O}_4$), Magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$), Chromite ($\text{Fe}^{2+}\text{Cr}_2\text{O}_4$), Hercynite ($\text{Fe}^{2+}\text{Al}_2\text{O}_4$), Magnesiochromite (MgCr_2O_4), Spinel (MgAl_2O_4). All Ti was combined with Fe^{2+} as the ulvospinel component ($\text{TiFe}^{2+}_2\text{O}_4$).

When plotted in the Al-Cr- Fe^{3+} diagram (Fig. 4), CX-1 chromite falls in the field of chromian spinel. It is also plotted on the field of chromite from harzburgite in the Miyamori complex (Ozawa 1994). The chromite in the KN-09 serpentinite is variable in Al content. These chromites fall in the fields of chromian spinel in cumulates from the Jimberlana intrusion (Roeder and Campbell 1985) and the chromite-bearing wehrlite of the Miyamori ophiolite complex (Ozawa 1994). Al content in chromite is different at every grains. The texture of relict magnetite in MO-04 serpentine crystallized before serpentinization, as shown in Fig. 3b. Compared with aggregate magnetite, these magnetites have high Al content. Opaque minerals in the other serpentinites are plotted on the chromite-magnetite join.

Fisk and Bence (1980) reported on the basis of melting experiments for basalt at 1175-1270°C that Cr(Cr+Al+ Fe^{3+}) of chromite decreases with decreasing temperature, on the other hand Fe_2O_3 wt % increases with increasing oxygen fugacity. Ozawa (1994)

Table 2. Chemical compositions and formulae of chromite and magnetite.

	1	2	3	4	5	6
	AB-8	AB-16	KN-09	KN-19	KN-23	MO-04
SiO ₂	0.08	0	0.04	0.08	0.06	0.77
TiO ₂	0.74	1.88	0.40	0.72	0.34	0.32
Al ₂ O ₃	0.97	0.15	13.84	0.11	2.55	0.18
Cr ₂ O ₃	47.53	19.49	39.76	6.17	40.08	20.92
Fe ₂ O ₃	13.58	45.70	13.06	61.48	24.81	44.78
FeO	28.90	30.01	26.97	31.19	28.19	28.12
MnO	0.68	0.61	0.91	0.37	0.75	1.50
MgO	1.91	1.47	4.12	0.24	2.05	1.60
CaO	0.05	0	0	0.11	0.04	0.06
Total	99.26	99.31	99.10	100.47	98.87	98.26
Atomic formulae on the basis of 4 oxygen atoms						
Si	0.003	0	0.001	0.003	0.002	0.029
Ti	0.021	0.054	0.010	0.021	0.009	0.009
Al	0.042	0.007	0.560	0.005	0.111	0.008
Cr	1.532	0.584	1.079	0.186	1.174	0.630
Mg	0.105	0.084	0.211	0.014	0.113	0.091
Fe ³⁺	0.378	1.303	0.337	1.762	0.692	1.285
Fe ²⁺	0.895	0.951	0.774	0.993	0.873	0.897
Mn	0.021	0.020	0.026	0.012	0.024	0.048
Ca	0.002	0	0	0.004	0.002	0.002
Total	3.001	3.003	2.998	3.000	3.000	2.999
Usp	2.1	5.4	1.0	2.1	0.9	0.9
Jac	2.1	2.0	2.6	1.2	2.4	4.9
Mt	16.8	63.1	14.3	87.1	32.2	61.3
Chr	68.6	21.1	54.0	8.2	53.4	29.3
Mg-Chr	8.1	8.1	0	1.1	5.4	3.2
Hc	0	0	7.1	0	0	0
Spl	2.2	0.3	21.0	0.3	5.7	0.4
Cr	78.5	30.8	54.6	9.5	59.4	32.8
Al	2.2	0.4	28.3	0.3	5.6	0.4
Fe ³⁺	19.4	68.8	17.1	90.2	35.0	66.8
Cr	97.3	98.8	65.8	97.4	91.4	98.7
Al	2.7	1.2	34.2	2.6	8.6	1.3
Mg/Mg+Fe ²⁺	0.11	0.08	0.21	0.01	0.11	0.09

Table 2 (Continued).

	7	8	9	10	11	12
	MO-05	OM-01	OM-29	OM-48	YS-21	CX-1
SiO ₂	0.46	0.03	0.11	0.16	0.06	0.03
TiO ₂	0.52	0.69	0.19	0.10	0.76	0.38
Al ₂ O ₃	0.11	6.04	0.05	0.97	0.22	27.94
Cr ₂ O ₃	37.76	53.74	0.03	27.43	43.13	41.04
Fe ₂ O ₃	30.09	7.37	68.73	42.42	24.32	3.64
FeO	27.54	26.95	30.84	19.61	27.78	10.32
MnO	1.96	0.86	0.07	3.77	3.02	0.22
MgO	2.23	3.60	0.33	5.53	1.20	17.34
CaO	0	0.04	0.05	0	0	0.02
Total	100.67	99.32	100.39	99.99	100.50	100.93
Atomic formulae on the basis of 4 oxygen atoms						
Si	0.017	0.001	0.004	0.006	0.002	0.001
Ti	0.014	0.018	0.005	0.003	0.021	0.008
Al	0.005	0.253	0.002	0.041	0.010	0.958
Cr	1.099	1.511	0.001	0.786	1.265	0.944
Mg	0.122	0.191	0.019	0.299	0.095	0.752
Fe ³⁺	0.834	0.197	1.978	1.156	0.679	0.080
Fe ²⁺	0.848	0.801	0.986	0.594	0.862	0.251
Mn	0.061	0.026	0.002	0.116	0.095	0.005
Ca	0	0.002	0.002	0	0	0.001
Total	3.000	3.000	2.999	3.003	3.000	3.000
Usp	1.4	1.8	0.5	0.3	2.1	0.8
Jac	6.2	2.6	0.2	11.6	9.5	0.5
Mt	36.2	7.3	97.8	46.2	24.5	3.5
Chr	47.1	69.3	0	12.8	57.5	20.0
Mg-Chr	8.7	6.4	0.1	26.5	5.8	27.2
Hc	0	0	0	0	0	0
Spl	0.3	12.7	0.1	2.1	0.5	48.0
Cr	56.7	77.1	0.1	39.6	64.7	47.6
Al	0.3	12.9	0.1	2.1	0.5	48.3
Fe ³⁺	43.0	10.0	99.8	58.3	34.7	4.0
Cr	99.5	85.7	—	95.0	99.2	49.6
Al	0.5	14.3	—	5.0	0.8	50.4
Mg/Mg+Fe ²⁺	0.13	0.19	0.02	0.33	0.07	0.75

Chromite (Fe²⁺Cr₂O₄) : Chr, Hercynite (Fe²⁺Al₂O₄) : Her, Jacobsite (Mn²⁺Fe³⁺₂O₄) : Jac, Magnesiochromite (MgCr₂O₄) : Mg-Chr, Magnetite (Fe²⁺Fe³⁺₂O₄) : Mt, Spinel (MgAl₂O₄) : Spl, Ulvospinel (TiFe²⁺₂O₄) : Usp.

described that the relationship between $\text{Cr}/(\text{Cr} + \text{Al} + \text{Fe}^{3+})$ and $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ is negative. Fig. 5 shows that $\text{Cr}/(\text{Cr} + \text{Al} + \text{Fe}^{3+})$ against $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ does not seem to be present in the present study. $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios of chromite in the CX-1 serpentinite are higher than those of chromites and magnetites in the other serpentinite (Fig. 5). $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios of chromites from the Otomo section are from 20 to 60 (Ozawa 1994). $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios of chromian spinels in abyssal and Alpine-type peridotites from Southern Samail and Twin Sisters are from 50 to 80 (Dick and Bullen 1984). $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios of chromites in CX-1 serpentinites are similar to those from the ultra mafic rocks. $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios of chromites from the KN-09 serpentinite are close to those of chromites in westerite and clinopyroxenite from the Otomo section (Ozawa 1994). The chemical compositions and the occurrences of chromites in the CX-1 serpentinite suggest that the mother rock might be harzburgite. The chemical composi-

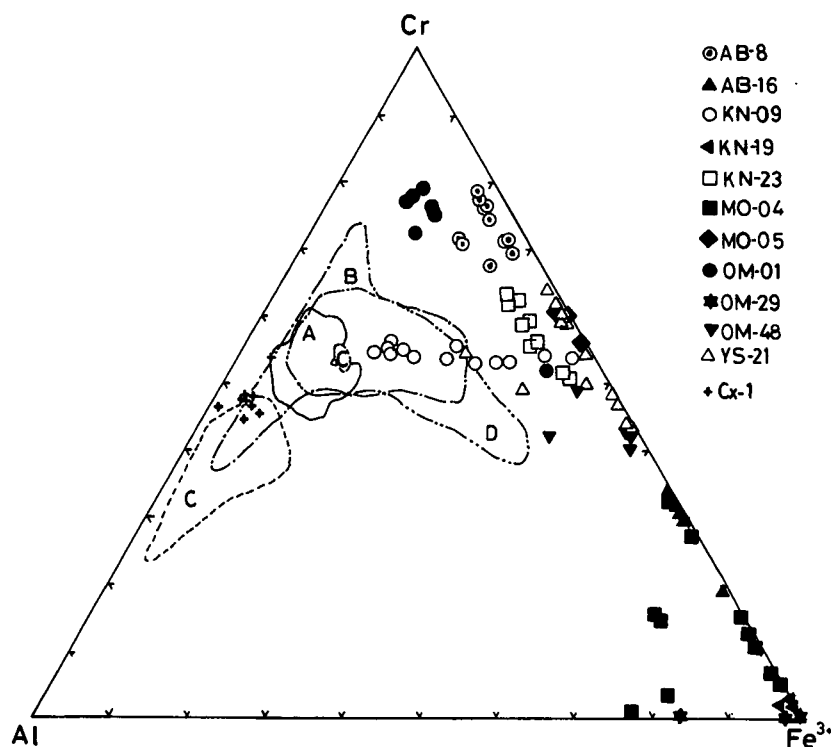


Figure 4. Proportions of Cr, Al and Fe^{3+} in chromite and magnetite from serpentinite, the Kotaki-Omi district. Circle A indicates chromite from ultramafic series of the Stillwater complex (Campbell and Murck 1993). Circle B shows chromite in peridotites of Ordovician Miyamori ophiolite. Circle C indicates chromite synthesized at 1175-1270°C under the f_{O_2} of 10^{-8} to 10^{-10} (Fisk and Bence 1980). Circle D is the chemical variation of chromites from the Jimberlana intrusion (Roeder and Campbell 1985).

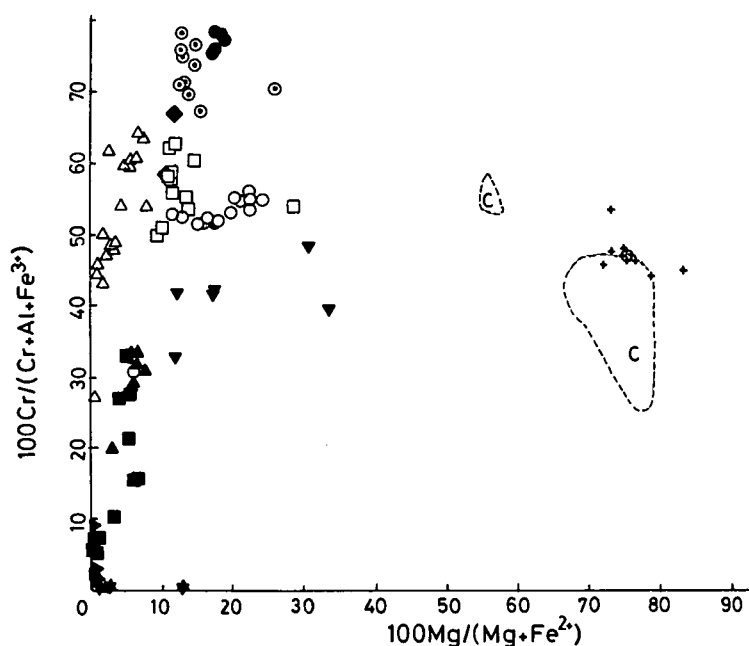


Figure 5. Chemical composition of chromites, magnetites and chromian spinels from serpentinites on plots of $100 \text{ Mg}/(\text{Mg} + \text{Fe}^{2+})$ vs. $100 \text{ Cr}/(\text{Cr} + \text{Al} + \text{Fe}^{3+})$. Symbols are the same as in Fig. 4.

tions and the occurrences of most chromites in other serpentinites excepted for CX-1 and KN-09 show that they crystallized during serpentinization.

Acknowledgements

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References

- Arai, S. 1987. An estimation of the least depleted spinel peridotite on the basis of olivine-spinel mantle array. *Neues Jahrb. Miner. Monatsh.*, 8, 347-354.
- Arai, S. 1992. Chemistry of chromian spinel in volcanic rocks as a potential guide to magma chemistry. *Mineral. Mag.*, 56, 173-184.
- Campbell, I. H. and Murck, B. W. 1993. Petrology of the G and H chromitite zones in the Mountain view area of the Stillwater complex, Montana. *Jour. Petrol.*, 34, 291-316.

- Dick, H. J. B. and Bullen, T. 1984. Chromian spinel as a petrogenetic indicator in abyssal and alpinotype peridotite and spatially associated lavas. *Contrib. Mineral. Petrol.*, 86, 54-76.
- Fisk, M. R. and Bence A. E. 1980. Experimental crystallization of chrome spinel in Famous basalt 527-1-1. *Earth Planet. Sci. Lett.*, 48, 111-123.
- Henderson, P. and Suddaby, P. 1971. The nature and origin of the chrome-spinel of the Rhum layered intrusion. *Contrib. Mineral. Petrol.*, 33, 21-31.
- Hill, R. J., Craig, J. R. and Gibbs, G. V. 1979. Systematics of the spinel structure type. *phys. Chem. Minerals*, 4, 317-339.
- Irvine, T. N. 1965. Chromian spinel as a petrogenetic indicator, Part I, Theory. *Canada J. Earth Sci.*, 2, 648-671.
- Kanayama, K. 1991. Geology and metamorphism in the Kotaki-Omi district, Niigata Prefecture. A graduation thesis, Joetsu Univ. Educ., 101 (manucripted in Japanese).
- Ozawa, K. 1994. Melting and melt segregation in the mantle wedge above a subduction zone: Evidence from the chromite-bearing peridotites of the Miyamori ophiolite complex, Northeastern Japan. *Jour. Petrol.*, 35, 647-678.
- Roeder, P. L. and Campbell, I. H. 1985. The effect of postcumulus reactions on the geochemistry of chromites from the Jimberlana intrusion. *Jour. Petrol.*, 26, 763-786.
- Sakurai, T. 1968. Universal crystallographic computation programm system (in Japanese). *Crystallogr. Soc. J. Publ.*