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Chemistry of chromian spinel in picrite sill from Ogi, Sado island, Niigata Prefecture, Japan.

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Abstract

Chromian spinels occur in two textural forms in picrite sill intruded in Neogene volcanic rocks, from Ogi at the southwestern end of the Sado island, Niigata Prefecture. Small ($<40\mu m$) euhedral chromian spinels occur as inclusions in altered and fresh olivines throughout the sill. Some chromian spinels and magnetites occur as small phenocrysts and separate grains. There is no difference in composition between chromian spinels occurring as inclusion and phenocryst. Cr/(Al +Cr) ratio is from 0.38 to 0.57. $Fe^{3+}/(Cr+Al+Fe^{3+})$ atomic ratio of chromian spinel is lower than 0.2. The molecule proportion of spinel is more than about 40 %. The sum of the molecule proportions of spinel, chromite and magnesio-chromite is beyond 90 %.

The formula of the common chromian spinel was given as $(Mg_{0.65}Fe^{2+}{}_{0.37}Mn_{0.01})_{1.03}$ $(Ti_{0.03}Al_{1.08}Cr_{0.70}Fe^{3+}{}_{0.16})_{1.97}O_4$.

KEY WORDS

Chromian spinel, Mantle array, Ogi, Olivine, Picrite, Sado, Sill

Introduction

Chromian spinel is a typical mineral in ultramafic rocks derived by mantle. 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, Arai 1987, Henderson and Gibbs 1987, Campbell and Murck, 1993) . Although Yamakawa and Chihara (1968) reported the bulk compositions of the Ogi picritic basalt plotted on the alkali basalt, the present data are plotted on the field of tholeiite. SiO_2 wt % is from 45 to 48.

Yokoyama et al. (1992) discussed the origin of the picrite by using modal proportion and compositional profiles of olivine phenocrysts. They concluded that the variation of core compositions and reverse zonings may be attributed to heterogeneity of magma composition due to crystallization in a magma chamber with temperature gradient, rather than contamination of peridotite and wall rocks or multiple injection of various-type

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olivine basalts. Arai (1987) infered the origin of ultrabasic rocks by using the reletionship of Cr/(Cr+Al) of spinel and Fo content of olivine. However, Yokoyama et al. (1992) did not pay attention to chromian spinel. Therefore, on the basis of chemical composition of chromian spinel including olivine, we attempt to determine the chemical character of the original rocks. In this report, we will give description on the occurrence, chemical composition and physical properties of chromian spinel. A part of this study is Okada's graduation thesis (one of authors) at Joetsu University of Education.

Occurrence

The Ogi picritic sill intruded in Neogene volcanic rocks. Shinmura et al. (1995) reported that the K-Ar ages of picrite intrusive rock and the Ogi basalt formation are 15.5±2.2 Ma and 10.70±0.43~14.0±1.5 Ma, respectively. The volcanic activity of both igneous rocks is the same stage.

There are two outcrops of the sill in the Ogi district. Yokoyama et al. (1992) studied one of two outcropes of picrite sill. We investigated the other. Well-developed layering in the Ogi picritic sill is observed. The height of sills is about 30m (Figs. 1a and 1b). However the lower and upper boundaries between the sill and country rocks were not recognized. Weak layering is recognized in a weathered surface of the sill. We counted 84 units. We divided one unit of the apparent layering into three parts; lower part (convex), mediate part (halfpoint between convex and concave) and upper part (concave), as shown Fig. 1c. The thickness of one unit is about 30~40 cm. The samples were collected at every unit from the base of the outcrop of the picrite sill. The sampling at convex part is easy, but it is difficult to collect from the concave part. Therefore, the numbers of the samples at the concave part are less than those at the convex part. Yokoyama et al. (1992) described the variation of modal proportion of olivine from 40~60 % at the lower part of the sill to about 20 % at the upper parts. The grain size of olivine is variable in the lower part of the sill, on the other hand it is small in the upper part. However, the gain size between the convex and concave is almost similar.

Picrite is consisted of a lot of amounts of olivine and small amounts of chromian spinel as phenocryst (Figs. 2a and 2b). The groundmass minerals are plagioclase, clinopyroxene and Ti-magnetite with ophitic texture. Interstitial glass among the above described minerals is highly attacted by clay minerals (saponite etc.). Olivine is also altered by clay and carbonate along cracks. Figs 2c and 2d show the reflected light photomicrographs of the chromian spinel in olivine and separate chromian spinel. Most of chromian spinels occur as inclusions in altered and fresh olivines throughout the sill.

Mineralogical data and discussion

Electron microprobe analyses of chromian spinel and olivine were performed using

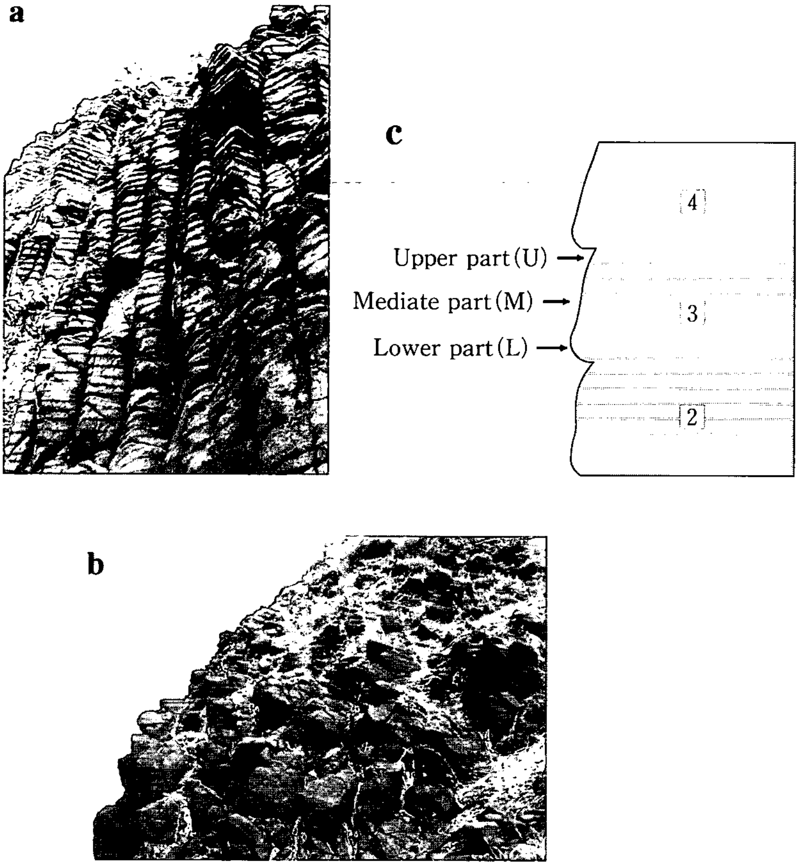

Figure 1. a: Outcrop of the picrite sill in the direction of west. b: Outcrop of the picrite sill in the direction of south. c: the shape of layering.

JEOL 733 superprob at the National Institute of Polar Research. They are given in Table 1 together with their structural formulae. Fe^{3+} contents of chromian spinel were calculated by assuming spinel stoichiometry on the basis of 4 oxygen atoms and 3 cations. The site occupancies of cations and the molecular proportions of end-members were calculated on the following order: Ulvospinel ($TiFe^{2+}{}_2O_4$), Jacobsite ($Mn^{2+}Fe^{3+}{}_2O_4$), Magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$), Chromite ($Fe^{2+}Cr_2O_4$), Magnesiochromite ($MgCr_2O_4$), Hercynite ($Fe^{2+}Al_2O_4$), Spinel ($MgAl_2O_4$). The molecule proportion of spinel is more than about 40 %. The sum of the molecule proportions of spinel, chromite and magnesiochromite is beyond 90 %. $Fe^{3+}/(Cr+Al+Fe^{3+})$ atomic ratio of chromian spinel is lower than 0.2. When plotted in the Al-Cr-Fe^{3+} diagram (Fig. 3), most spinels fall in the field of chromian spinel. It is also plotted on the A field of chromian spinel in dunite, harzburgite, wehrlite and lherzolite derived from mantle (Roeder and Campbell 1985, Ozawa 1994).

Recently, chromian spinel is an important indicator for classifying mantle-derived peridotites (Dick and Bullen 1984, Arai 1987) and for determining the chemical character

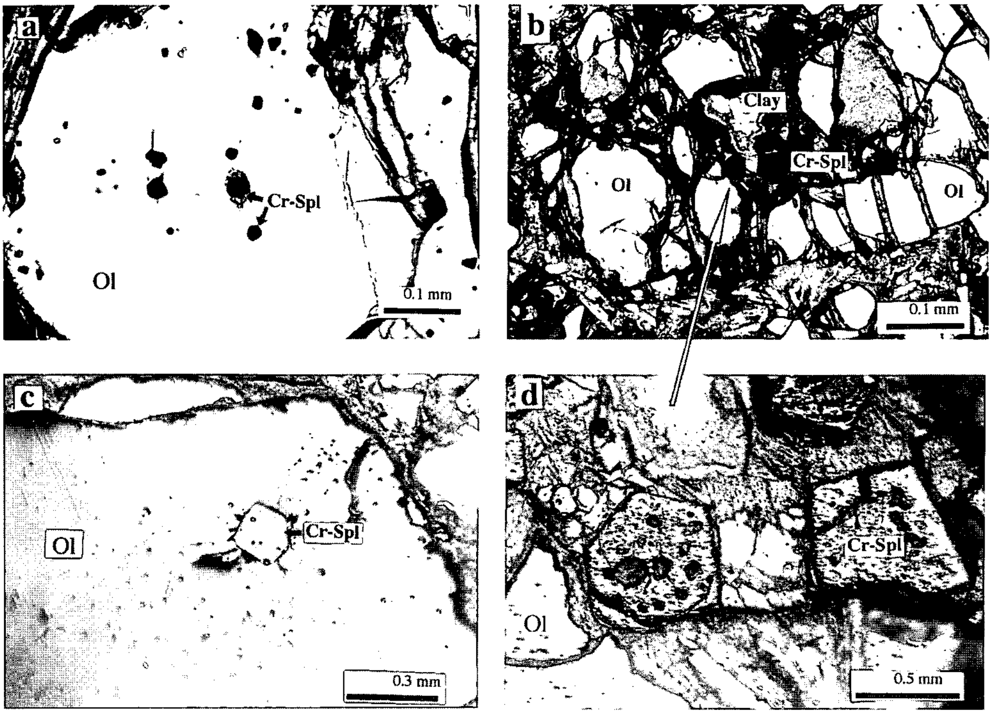

Figure 2. Photomicrographs and reflected light photomicrographs of chromian spinels in the Ogi picrite. a: Chromian spinel occurs as inclusion in the 15L.
b: Some chromian spinels in 76L occur as small phenocrysts and separate grains.
c: Reflected light photomicrograph of chromian spinel as inclusion in 31L.
d: Reflected light photomicrograph shows chromian spinel in the same thin section of 76L.
Clay: clay mineral, Cr-Spl: Chromian spinel, Ol: olivine

of the mother magma such as mid-oceanic ridge basalts, arc basalts and intraplate basalts (Irvine 1965, Arai 1992). The chromian spinels from the Ogi picrite are plotted in Fig. 4. Plots of the Cr/(Cr+Al) ratio of chromian spinel against Fo of coexisting olivine are near the boundary of olivine-spinel mantle array of Arai (1987). This area of plots overlaps midocean ridge basalt (MORB), intraplate basalts and Quaternary basalts, NE Japan arc reported by Arai (1992). The relationship between the chromian spinel and coexisting olivine is not enough to explain the parent magma origin of the Ogi picrite. Ozawa (1994) reported that the changes of Mg/Fe and NiO in olivine and Cr/(Cr+Al+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. NiO content of olivine in the Ogi picrite is below 0.32 wt %. The value is close to that reported by Ozawa (1994).

Table 1. Chemical compositions and formulae of chromian spinel and olivine.

	8L		20U			42L			56L		82U	
	Cr-Sp	Ol	Cr-Sp	Mt	Ol	Cr-Sp	Mt	Ol	Cr-Sp	Ol	Cr-Sp	Ol
SiO_2	0.08	40.75	0.11	0.09	40.71	0.13	0.15	40.27	0.06	39.95	0.11	41.36
TiO_2	1.24	0	0.66	16.13	0	0.58	17.32	0.03	0.65	0	0.49	0
Al_2O_3	30.37	0.03	28.09	1.98	0.05	26.53	2.48	0.05	24.77	0.03	29.75	0.05
Cr_2O_3	29.51	0.21	35.75	0.05	0.16	38.21	0.06	0.33	36.47	0.07	32.53	0.14
FeO	21.07	10.75	17.67	73.96	10.52	20.50	74.18	11.48	24.90	12.21	18.07	10.98
MnO	0.36	0.27	0.23	0.64	0.19	0.28	0.54	0.19	0.38	0.13	0.23	0.20
MgO	14.48	47.12	14.63	1.16	48.70	14.11	1.22	46.79	11.87	48.09	15.58	49.73
CaO	0.02	0.22	0.02	0	0.26	0.05	0.13	0.27	0	0.26	0.01	0.26
Total	97.13	99.35	97.16	94.01	100.59	100.39	96.08	99.41	99.10	100.74	96.77	102.72
	Atomic formulae on the basis of 4 oxygen atoms											
Si	0.002	1.009	0.003	0.003	0.996	0.004	0.006	1.000	0.002	0.984	0.003	0.991
Ti	0.028	0	0.015	0.462	0	0.013	0.485	0.001	0.015	0	0.011	0
Al	1.077	0.001	1.005	0.089	0.001	0.936	0.109	0.001	0.899	0.001	1.054	0.001
Cr	0.702	0.004	0.858	0.002	0.003	0.904	0.002	0.006	0.888	0.001	0.773	0.003
Mg	0.650	1.739	0.662	0.066	1.776	0.629	0.068	1.732	0.545	1.767	0.698	1.777
Fe^{3+}	0.159		0.099	0.978		0.127	0.909		0.179		0.144	
Fe^{2+}	0.371	0.223	0.349	1.379	0.215	0.379	1.400	0.238	0.462	0.252	0.310	0.220
Mn	0.009	0.006	0.006	0.021	0.004	0.007	0.017	0.004	0.010	0.003	0.006	0.004
Ca	0.001	0.006	0.001	0	0.007	0.002	0.005	0.007	0	0	0	0.007
Total	2.999	2.988	2.998	3.000	3.002	3.001	3.001	2.989	3.000	3.008	2.999	3.003
Ups	2.8		1.5	46.2		1.3	48.7		1.5		1.1	
Jac	0.9		0.6	2.1		0.7	1.7		1.0		0.6	
Mt	7.1		4.4	45.5		5.7	43.1		8.0		6.6	
Chr	24.4		27.6			29.6			35.3		22.2	
Mg-Chr	10.7		15.4	0.1		15.6	0.1		9.2		16.5	
Spl	54.1		50.5	6.0		47.0	6.4		45.0		53.0	
$Mg/Mg+Fe^{2+}$	0.637	0.887	0.655	0.046	0.892	0.624	0.046	0.879	0.541	0.875	0.692	0.890

Chr: Chromite($Fe^{2+}Cr_2O_4$), Hc: Hercynite($Fe^{2+}Al_2O_4$), Jac: Jacobsite($Mn^{2+}Fe^{3+}{}_2O_4$), Mg-Chr: Magnesiochromite($MgCr_2O_4$), Mt: Magnetite($Fe^{2+}Fe^{3+}{}_2O_4$), Spl: Spinel($MgAl_2O_4$), Usp: Ulvospinel($TiFe^{2+}{}_2O_4$).

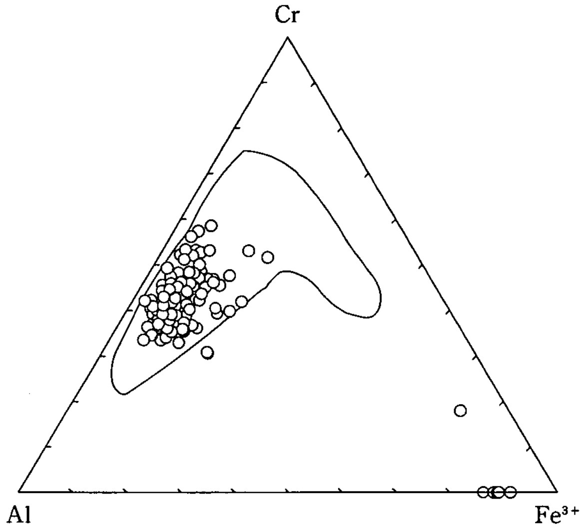

Figure 3. Propotions of Cr, Al and Fe^{3+} in chromian spinels from the Ogi picrite.
The dotted area indicates chromite from mantle derived ultramafic rocks (Arai 1987, Roeder and Campbell 1985, Campbell and Murck 1993, Ozawa 1994).

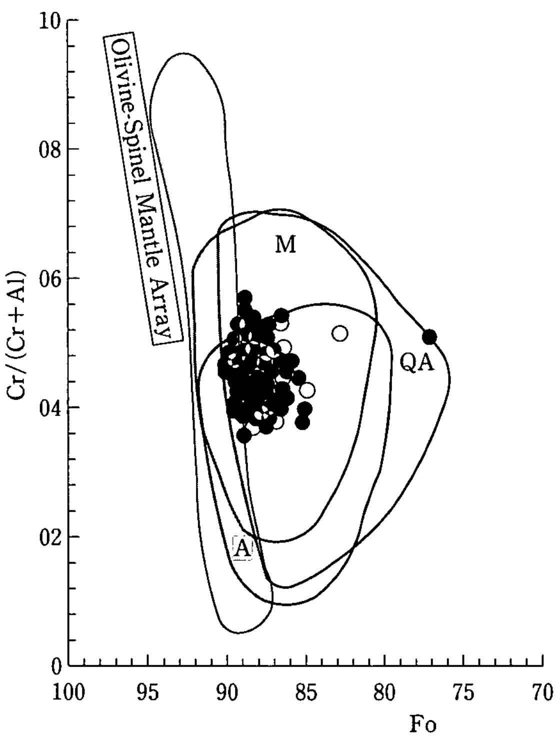

Figure 4. Relationships between Cr/(Cr+Al) of chromian spinel and Fo of coexisting olivine.
The dotted area is the range of mantle peridotites after Arai (1987).
A: Intraplate alkali basalts, QA: Quaternary basalts, NE Japan arc, M: Midocean ridge basalts,

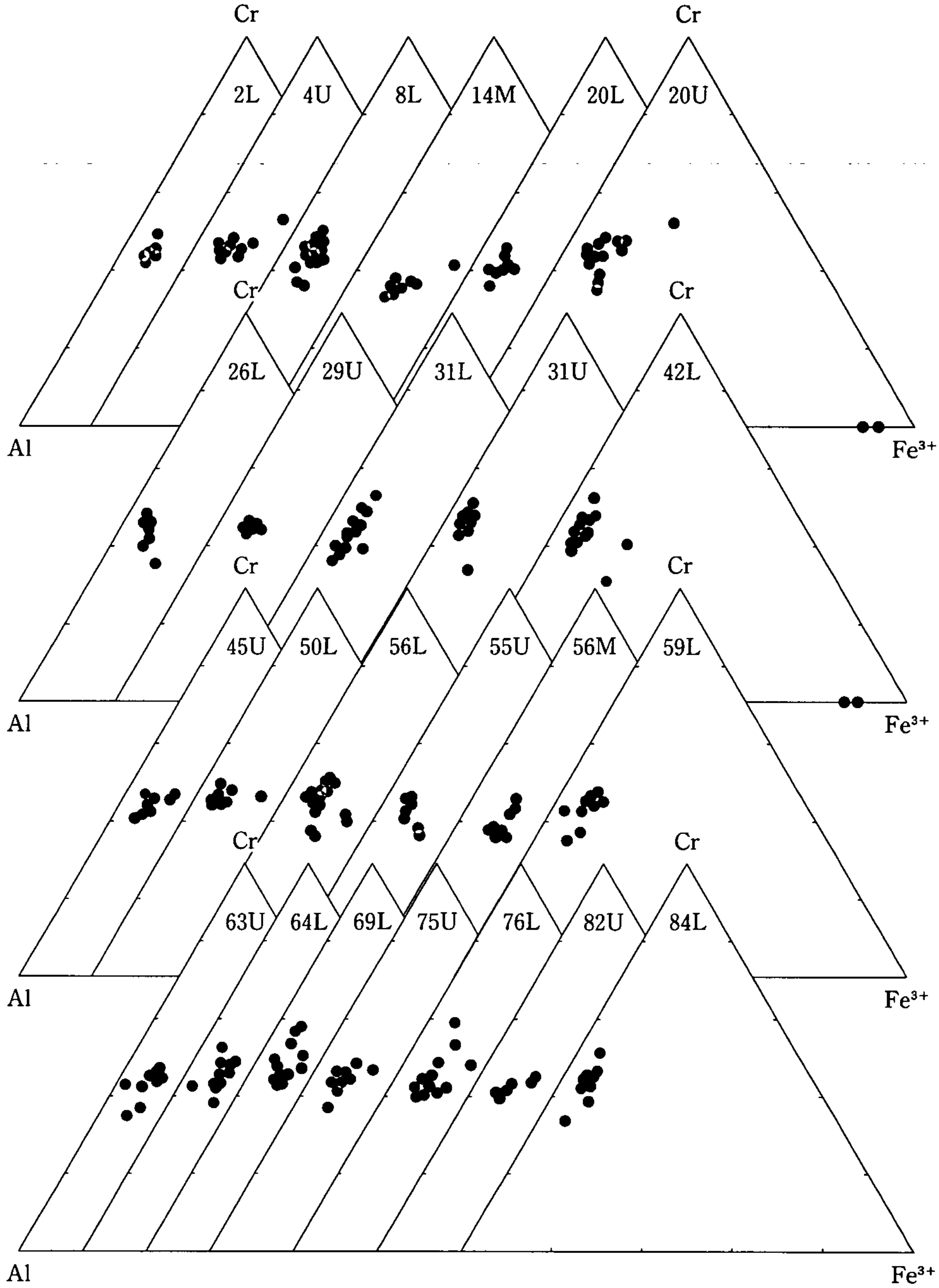

Figure 5. Propotions of Cr, Al and Fe^{3+} in chromian spinels from several units in the Ogi picrite.

The chemical composition of olivine in the Ogi picrite is rangging from Fo_{84} to Fo_{91}. Most olivines have normal zoning, some olivines have reverse zoning. The proportion of olivine with Fo_{84} content at the lower part of the sill is more than that at the upper parts. Fo content of olivine changes in zigzag from the bottom to the top. It is not enough to explain the layering of the Ogi picrite. Fo content at the convex part of the layer is not usually high (Okada 1997). The variation of olivine can not be simply explain the picrite derived from olivine-spinel mantle by partial melting.

Fisk and Bence (1980) reported on the basis of melting experiments for basalt at 1175-1270℃ 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. $Fe^{3+}/(Cr+Al+Fe^{3+})$ ratios of chromian spinel coexisted with Ti-magnetite in 20U and 42U are slightly higher than those in other samples. The chemical variations of chromian spinel of each unit are small, as shown in Fig. 5. $100Mg/(Mg+Fe^{2+})$ ratios of chromian spinel in the Ogi picrite are from 50 to 70. These ratios are similar to $100Mg/(Mg+Fe^{2+})$ ratios of chromian spinels in abyssal and Alpine-type peridotites from Southern Samail and Twin Sisters (Dick and Bullen 1984).

Although there is no sufficient evidence, the present study shows that the Ogi picrite may be derived from mantle.

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