

Occurrence and chemical composition of amphiboles and related minerals in corundum-bearing mafic rock from the Horoman Peridotite Complex, Japan

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Abstract

A corundum-bearing mafic rock in the Horoman Peridotite Complex, Japan, was derived from upper mantle conditions to lower crustal conditions with surrounding peridotites. The amphiboles found in the rock are classified into 3 types: (1) as interstitial and/or poikilitic grains (Green amphibole), (2) as a constituent mineral of symplectitic mineral aggregates with aluminous spinel at grain boundary between olivine and plagioclase (Symplectite amphibole) and (3) as film-shaped thin grains, usually less than 10 μm in width, at grain boundary between olivine and clinopyroxene (Film-shaped amphibole). The Film-shaped amphibole is rarely associated with orthopyroxene extremely low in Al_2O_3 , Cr_2O_3 and CaO (Low-Al OPX). These minerals were formed by infiltration of SiO_2 - and volatile-rich fluids along grain boundaries after the rock was recrystallized at olivine-plagioclase stability conditions, i.e. the late stage of the exhumation of the Horoman Complex.

Chondrite-normalized rare earth element patterns and primitive mantle-normalized trace-element patterns of the Green amphibole and clinopyroxene are characterized by LREE-depleted patterns with Eu positive and negative anomalies of Zr and Hf. These geochemical characteristics of the constituent minerals were inherited from original whole-rock compositions through a reaction involving both pre-existing clinopyroxene and plagioclase. We propose that the fluids were originally rich in a SiO_2 component but depleted in trace-elements. Dehydration of the surrounding metamorphic rocks in the Hidaka metamorphic belt, probably related to intrusion of hot peridotite body into the Hidaka crust, is a plausible origin for the fluids.

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1. Introduction

Aqueous fluids exist in diverse tectonic settings and in a wide range of pressure–temperature (P – T) conditions. The migration of these fluids causes modal and/or geochemical modifications in the wall-rocks, for example,

hydrated eclogite veins in granulite rocks in the Bergen Arcs, Norway (Austrheim, 1987), mantle metasomatism in sub-arc peridotites (e.g., Blatter and Carmichael, 1998; Zanetti et al., 1999; McInnes et al., 2001), and amphibolitization of high-grade rocks/eclogites (e.g., Goto and Banno, 1990; Zhang et al., 2003). The origin and evolution of the fluids as a function of changing P – T conditions, and differences in the composition of both source rocks and wall rocks, are, therefore, important for

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understanding the elemental recycling related to fluid migrations in the Earth. Regardless of its importance, the general geochemical characteristics of fluids in response to the differences in the P – T condition and their sources are still unclear making it viable for future studies.

The Horoman Peridotite Complex, Samani, Japan, was derived from garnet-lherzolite stability field to plagioclase-lherzolite stability field conditions without significant effect of serpentinization (Ozawa and Takahashi, 1995; Takazawa et al., 1996; Ozawa, 2004). Both modal and cryptic metasomatisms were recorded in the Horoman peridotites (Hirai and Arai, 1987; Arai and Takahashi, 1989; Takahashi et al., 1989; Frey et al., 1991; Takazawa et al., 1992, 1996; Yoshikawa and Nakamura, 2000; Matsumoto et al., 2001; Morishita et al., 2003a). The Horoman Complex is, therefore, a good subject to examine origin and evolution of metasomatising agents in a wide range of P – T conditions from upper mantle to lower crustal conditions. Origins of metasomatism agents in the Horoman Complex are still being debated. This is partly because the Horoman Complex has undergone multiple metasomatic events and the P – T conditions for the different metasomatisms are not well constrained.

Several types of mafic rock also exist in the Horoman Complex, (Niida, 1984; Shiotani and Niida, 1997; Takazawa et al., 1999), one of which is the corundum-bearing mafic rock (Morishita and Kodera, 1998) which is interpreted to be derived from upper mantle conditions with surrounding peridotites (Morishita and Arai, 2001b; Morishita et al., 2004). Amphiboles are found in the corundum-bearing rock, locally in association with extremely Al-poor orthopyroxene (Low-Al OPX). In this paper, petrological and geochemical studies revealed that amphiboles and Low-Al OPX in the studied samples were formed by infiltration of aqueous fluids in the late stage of exhumation of the Horoman Complex. This paper focuses on the occurrence and geochemical (major- and trace-elements) characteristics of minerals in the corundum-bearing mafic rock so as to reveal geochemical characteristics of the infiltrated fluids in the late stage of the exhumation of the Horoman Complex. Based on these data combined with previous works, we aim to discuss the source of the fluids in the studied rocks.

2. Geological background

2.1. Regional geology and general features of the Horoman Complex

Mantle peridotite bodies are locally discontinuously distributed in the basal part of the Main Zone of the

Hidaka metamorphic belt (Niida and Katoh, 1978; Komatsu et al., 1982), which represents an island arc crustal sequence (Komatsu et al., 1983, 1989). The Horoman Complex is located at the southern end of the Main Zone, and is the largest of these bodies, 8 km × 10 km in area and more than 3 km in thickness (e.g., Igi, 1953; Komatsu and Nochi, 1966; Niida, 1984; Sawaguchi, 2004) with a fault zone serving as direct contact with the metamorphic rocks including intrusive rocks. The southern part of the Hidaka Main Zone around the Horoman Peridotite Complex was described by previous workers (Arita et al., 1978; Shiba, 1988; Owada, 1989; Tagiri et al., 1989; Arita et al., 1993; Saeki et al., 1995; Shiba and Soeta, 1996). The metamorphic rocks in the southern part are divided into six metamorphic zones from greenschist facies to granulite facies (Zone A to F) based on the mineral assemblages in pelitic rocks (Shiba, 1988; Shiba et al., 1992; Shiba and Soeta, 1996). Granulite facies rocks are only distributed to the east and south of the Horoman Peridotite Complex (Shiba, 1988; Shiba et al., 1992; Shiba and Soeta, 1996). Arita et al. (1993) and Saeki et al. (1995) reported K–Ar ages of biotite and hornblende in metamorphic and igneous rocks in the middle to southern area (19–16 Ma) and in the southern area (36–17 Ma) of the Main Zone, respectively. They interpreted these ages as cooling age of the rocks during the stage of uplifting.

The Horoman Peridotite complex consists of various kind of layered peridotite with small amount of mafic rocks (e.g., Komatsu and Nochi, 1966; Niida, 1984; Takahashi, 1991, 1992). Komatsu and Nochi (1966) and Niida (1984) divided the complex into two zones, the Upper and Lower Zones. The former is characterized by an abundance of mafic layers and by sharp lithological boundaries and the latter is characterized by gradational lithological boundaries. Ozawa and Takahashi (1995), Takazawa et al. (1996), and Ozawa (2004) examined compositional zoning of pyroxenes (and plagioclase) in peridotite and interpreted that a decompression P – T path from the garnet lherzolite stability field to plagioclase lherzolite stability field (Fig. 1).

The mafic rocks in the Horoman Complex have been divided into a variety of sub-type (up to five types) (Niida, 1984; Shiotani and Niida, 1997; Takazawa et al., 1999). In this paper, we follow the nomenclature of Takazawa et al. (1999). The studied sample is a corundum-bearing mafic rock collected as a boulder and belongs to the Type II mafic rocks of Takazawa et al. (1999) (Morishita and Kodera, 1998). Type II mafic rock is the second most abundant mafic rock type in the complex and is more common in the

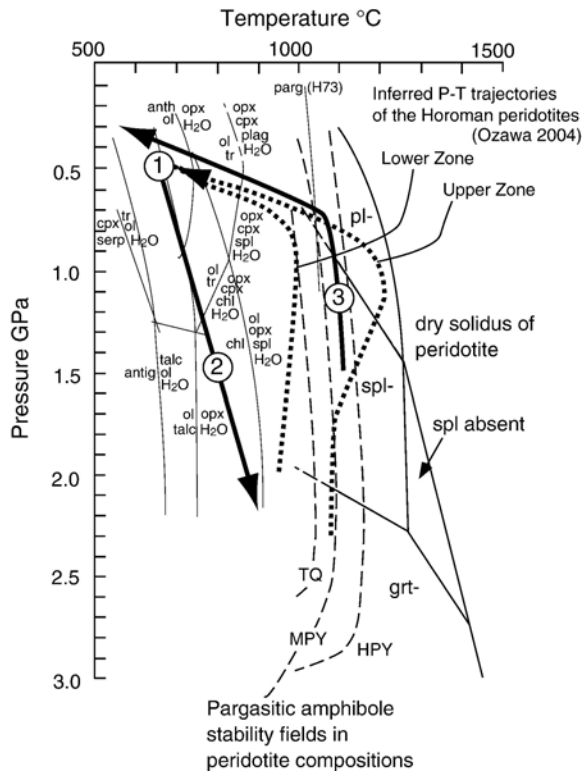


Fig. 1. *P*–*T* trajectory of the corundum-bearing mafic rock in the Horoman Peridotite Complex (thick arrow) (Morishita and Arai, 2001b; Morishita et al., 2004). *P*–*T* trajectories of plagioclase peridotites from the lower and upper parts of the Horoman Complex (Ozawa, 2004) were also shown with broken arrows. The protolith of the corundum-bearing mafic rock formed as cumulates at low pressures (1). The corundum-bearing mafic rock experienced higher-pressure metamorphism (2), although the maximum pressure conditions is not known. Finally the corundum-bearing mafic rock ascended from the garnet lherzolite stability field to the plagioclase lherzolite stability field with the surrounding peridotites (3). The metasomatic minerals in this study formed the last stage of (3). See text for details. Dry solidus and phase boundary (grt– = garnet–peridotite, spl– = spinel–peridotite, pl– = plagioclase–peridotite) for Hawaiian pyrolite are from Green and Falloon (1998). Pargasite stability field (parg H73) is from Holloway (1973). Pargasitic amphibole stability field in Tinaquillo lherzolite (TQ; Wallace and Green, 1991), MORB pyrolite (MPY; Niida and Green, 1999) and Hawaiian pyrolite (HPY; Green, 1973) are also shown. Phase relations related to hydrous minerals in the system CaO–MgO–Al₂O₃–SiO₂–H₂O are from Jenkins (1981, 1983). ol=olivine, pl=plagioclase, tr=tremolite, anth=anthophyllite, chl=chlorite, sp=spinel, antig=antigorite, parg=pargasite.

Upper zone than the Lower Zone. It occurs as thin layers (1–200 cm in thickness) restricted in cumulus peridotite (the SDW suite of Takahashi (1991, 1992). Constituent minerals in the Type II mafic rock are characterized by low TiO₂ contents compared with other types of mafic rocks in the Horoman Complex (Shiotani and Niida, 1997).

2.2. Previous work on metasomatism in the Horoman Complex

The enrichment of highly incompatible elements in whole-rock compositions and clinopyroxene porphyroclasts has been commonly found in the Horoman peridotites as evidence for cryptic metasomatism (Frey et al., 1991; Takazawa et al., 1992, 1996; Yoshikawa and Nakamura, 2000). On the other hand, there are several lines of petrographical evidence for modal mantle metasomatism in the Horoman peridotites, such as the local occurrence of phlogopite and pargasitic amphibole (Niida, 1975; Arai and Takahashi, 1989; Takahashi et al., 1989) and the presence of fluid inclusion relics, now replaced by hydrous minerals ($\pm$ carbonate minerals), in olivine grains (Hirai and Arai, 1987). Isotopic ages of approximately 20 Ma were reported for the formation of phlogopite veins (23 Ma: Rb–Sr method of Yoshikawa et al., 1993; 21 Ma: Ar–Ar method of Kaneoka et al., 2001). Saeki et al. (1995) suggested that the 20 Ma phlogopite age dates represents cooling of the Horoman Complex with surrounding metamorphic rocks because K–Ar ages of 35–17 Ma were reported from the metamorphic rocks. Unusually Al₂O₃-poor orthopyroxene was found in a spinel peridotite, and was interpreted to be formed through a very local reaction between peridotite and invasive fluid (Morishita et al., 2003a).

Yoshikawa and Nakamura (2000) reported positive anomalies of Sr and Pb for whole-rock compositions in some Horoman peridotites and suggested that these geochemical characteristics were caused by mantle metasomatism involving aqueous fluids derived from subducted crust. Metasomatism by a slab-derived metasomatising agent in the Horoman peridotites is supported by the noble gas data of Matsumoto et al. (2001).

3. Sample descriptions

3.1. Previous works on the corundum-bearing mafic rock

We have already reported petrography, mineral chemistry for constituent minerals except for Low-Al OPX and tremolitic hornblende, and whole-rock chemistry in both major- and trace-elements of the studied sample in separate papers (Morishita and Arai, 2001b; Morishita et al., 2004). The corundum-bearing Type II mafic rock shows a layered structure consisting of olivine-rich and clinopyroxene-rich sublayers, a few millimeter to a few centimeter in width, with the corundum concentrated in a lenticular portion of the

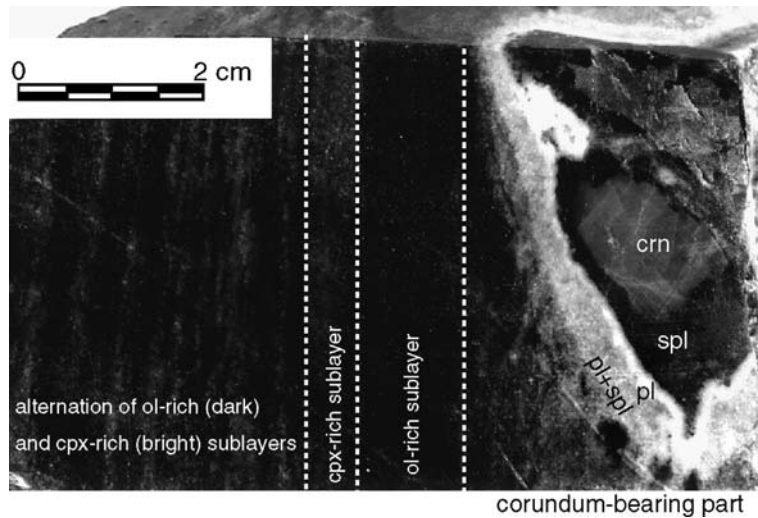


Fig. 2. Sawn surface of corundum-bearing mafic rock, which is parallel to lineation and perpendicular to foliation. Note the alternation between olivine (ol)-rich and clinopyroxene (cpx)-rich sublayers. Corundum occurs in a clinopyroxene-rich sublayer. crn=corundum, pl=plagioclase, spl=spinel.

sample (Fig. 2). Except for corundum-bearing part, the rock shows fine-grained equigranular metamorphic textures consisting of plagioclase (An 86–90), clinopyroxene ($\text{TiO}_2 < 0.2$ wt.%, $\text{Cr}_2\text{O}_3 < 0.6$ wt.%) and olivine (Fo=86, $\text{NiO} < 0.2$ wt.%) with small amount of amphibole, green spinel ($\text{Cr\#} = (\text{Cr}/(\text{Cr} + \text{Al}))$ atomic

ratio) < 0.01) and brown spinel ($\text{Cr\#} = 0.5$). Margarite locally occurs between corundum and plagioclase.

A zonal arrangement of inner green spinel and outer plagioclase around corundum indicates that the corundum was not stable in the Type II mafic rocks during the late P – T conditions of the complex (Morishita and Arai,

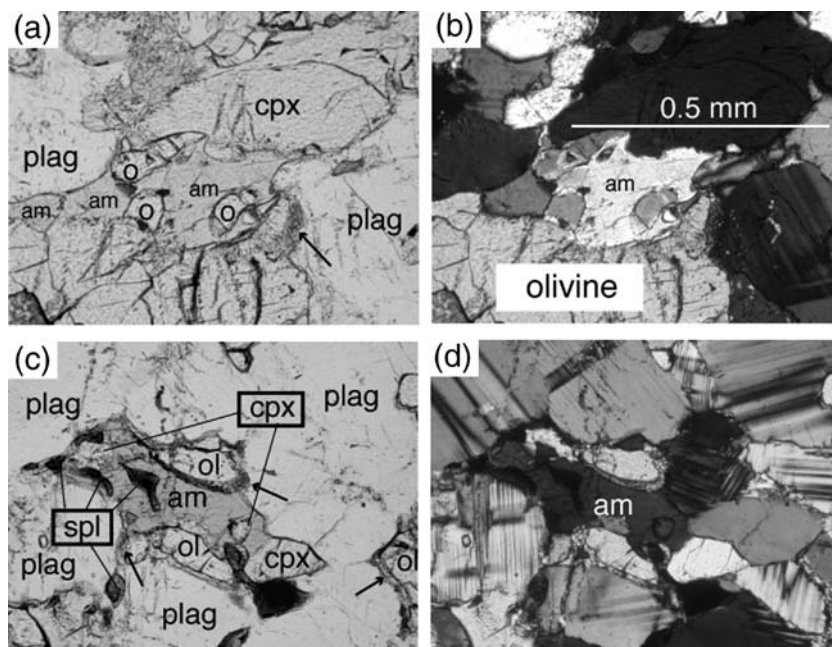


Fig. 3. Photomicrographs showing the occurrences of the Green amphibole and the Symplectite amphibole in the corundum-bearing mafic rock. (a) Interstitial to poikilitic grains of the Green amphibole. Note that one grain includes several olivine grains. Arrow indicates symplectitic mineral aggregate of spinel and amphibole (Symplectite amphibole). Plane-polarized light. (b) Crossed-polarized light of (a). (c) Interstitial to poikilitic grains of the Green amphibole including green spinel. Arrows indicate symplectitic mineral aggregate of spinel and amphibole. (d) Crossed-polarized light of (c). am=amphibole, cpx=clinopyroxene, ol=olivine, Plag=plagioclase, spl=spinel.

2001b). Morishita et al. (2004) experimentally examined corundum-stability conditions in aluminous mafic compositions and suggested that corundum-bearing mineral assemblages were stable at pressure of 2–3 GPa under dry conditions. On the other hand, whole-rock trace-element compositions of the Type II mafic rocks including the studied corundum-bearing mafic rock indicate that they formed as gabbroic rocks at low-pressure conditions and that the corundum-bearing mafic rock was derived from a plagioclase-rich portion of these gabbroic rocks (Morishita et al., 2004). Thus, a complex P – T trajectory, involving metamorphism of the plagioclase-rich protolith at a pressure higher than that at which it was formed, is

suggested as the origin of the corundum-bearing mafic rocks (Fig. 1). Finally the corundum-bearing mafic rock ascended from the upper mantle conditions with surrounding peridotites following the decompression P – T path as suggested by Ozawa and Takahashi (1995), Takazawa et al. (1996) and Ozawa (2004) (Fig. 1).

3.2. Amphiboles and related minerals in the corundum-bearing mafic rock

Amphiboles in the studied rock can be classified into three types based on their occurrences and are named as (1) Green amphibole, (2) Symplectite amphibole and

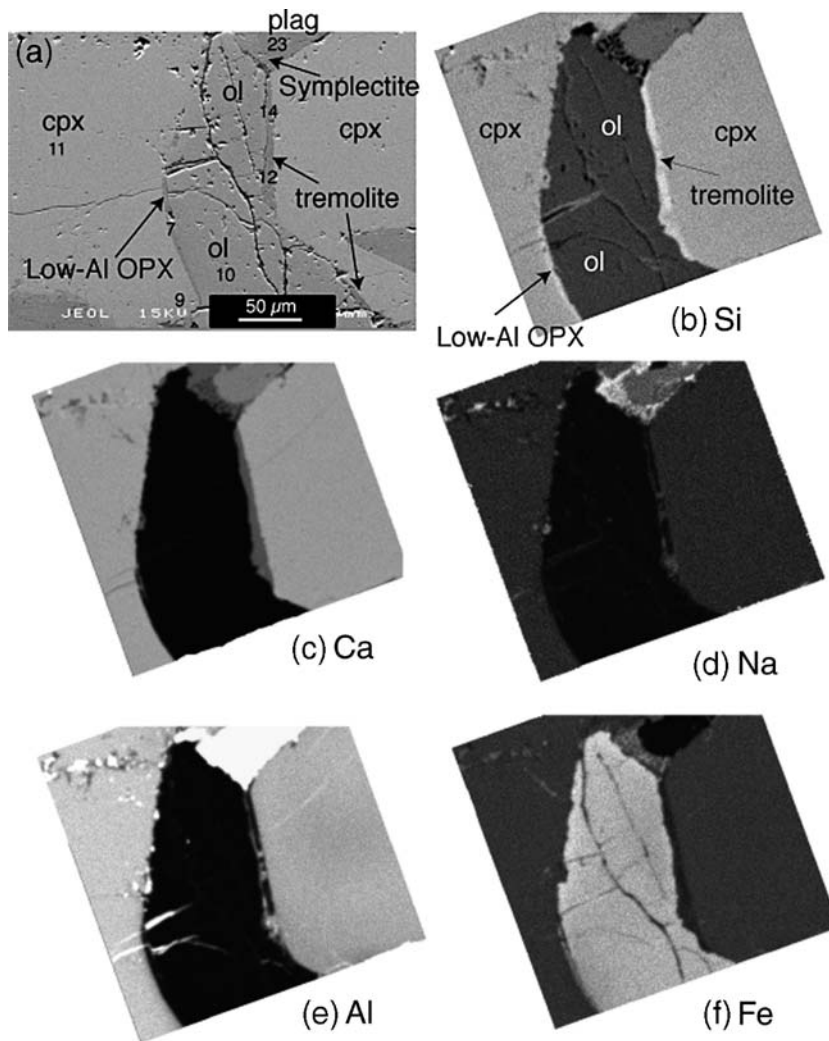


Fig. 4. Occurrence of the Film-shaped amphibole (tremolitic amphibole) and the Low-Al OPX. (a) Back scattered electron image with analytical points (numbers are analytical points which are the same as those in Tables 1 and 2), and X-ray intensity maps in (b) Si, (c) Ca, (d) Na, (e) Al and (f) Fe. The brighter area is higher in X-ray intensity of element than the darker area. Symplectitic aggregate (as indicated by Symplectite) of amphibole (Symplectite amphibole) and spinel is also observed at grain boundaries between plagioclase and olivine. Note that X-ray intensities of Na (d) and Al (e) for the Film-shaped amphibole are heterogeneous in a few μm scale. ol = olivine, plag = plagioclase, cpx = clinopyroxene.

(3) Film-shaped amphibole in this study. The Green amphibole occurs as irregular-shaped interstitial and/or poikilitic grains that usually developed around clinopyroxene or green spinel (Fig. 3). It should be noted that the Green amphibole is more abundant in olivine-rich sublayer than cpx-rich sublayer. Shiotani and Niida (1997) reported “green pargasite” as a minor phase of the Type II mafic rocks (GBII in their nomenclature). The Symplectite amphibole occurs as a constituent mineral of symplectitic mineral intergrowth with Al-spinel (spinel-amphibole symplectite) at grain boundaries between olivine and plagioclase (Morishita and Arai, 2001b) (Figs. 3 and 4). The spinel-amphibole symplectite is usually less than 50 μm in width and is different from pyroxene-spinel symplectite after garnet that commonly occurs in peridotites (Kushiro and Yoder, 1966; Takahashi and Arai, 1989; Ozawa and Takahashi, 1995; Takahashi, 2001; Morishita and Arai, 2003). The spinel-amphibole symplectite is found in the studied sample but it is scarce in the other Type II mafic rocks (Morishita, 1999; Morishita and Arai, 2001b). Similar spinel-amphibole symplectite is also widely found but is locally well developed in between olivine and plagioclase in plagioclase-bearing lherzolites through Horoman Complex (Morishita, 1999). It is emphasized that the distribution of the spinel-amphibole symplectite is heterogeneous within a thin section. Though both the Low-Al OPX and the Film-shaped amphibole are rare and occur as very thin grains (usually <10 μm in width) (Fig. 4). Low-Al OPX is less abundant than the Film-shaped amphiboles. Two-dimensional X-ray intensity images of the Film-shaped amphibole show local heterogeneity, particularly in Al and Na contents, on a few μm scale whereas the Low-Al OPX seem to show homogeneous distribution of these elements on the same scale (Fig. 4).

4. Chemical compositions of minerals

4.1. Analytical methods

We determined chemical compositions of minerals from three samples; (1) the olivine-rich sublayer-dominant part where the Green, Symplectite and Film-shaped amphiboles as well as the Low-Al OPX were found, (2) the cpx-rich sublayer-dominant part where the Green amphibole is absent or rare (if any) in a thin section scale, and (3) the corundum-bearing portion with the Green and Symplectite amphiboles. Major-element compositions of minerals were analyzed with a JEOL 6400 SEM fitted with Link Energy Dispersive Detector at the Electron Microscopy Unit of the Australian National

University (ANU), and a JEOL JXA-8800 Superprobe at the Center for Cooperative Research of Kanazawa University. The analyses were performed under an accelerating voltage of 15 kV and beam current of 1 nA, using a spot mode (2–3 μm diameter beam) for JEOL 6400 and were 15 kV, 20 nA and a 3 μm diameter beam for JEOL JXA-8800. Natural and synthetic mineral standards were employed for all minerals. The Low-Al OPX and Film-shaped amphiboles were analyzed by JEOL JXA-8800 and X-ray peaks of Ti, Al, Cr, Fe, Mn, Ca, Na and K were counted for 20 s, Ni for 50 s, and Si and Mg for 10 s. JEOL software using ZAF corrections was employed. Details of EPMA analysis were described in Morishita et al. (2003a, b). Representative major-element compositions of minerals are shown in Table 1.

Selected rare earth element (REE) (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu) and trace-element (Ti, V, Cr, Rb, Sr, Y, Zr, Nb, Ba, Hf, Pb, $\pm\text{Li}$, $\pm\text{Sc}$) compositions of minerals were determined by 193 nm ArF excimer laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Research School of Earth Sciences of the Australian National University (Agilent 7500S equipped with in-house laser system) and the Incubation Business Laboratory Center of Kanazawa University (Agilent 7500S equipped with MicroLas GeoLas Q-plus +, Ishida et al., 2004). Low-Al OPX, Symplectite amphibole and Film-shaped amphibole could not be analyzed by LA-ICP-MS due to its small size. Olivine and plagioclase in the olivine-rich sublayer-dominant sample were analyzed by abating 100 μm spot diameter, and 50–70 μm spot diameter for clinopyroxenes and amphiboles, at 5 Hz. The NIST SRM 612 glass was used as the primary calibration standard and was analyzed at the beginning of each batch of <8 unknowns, with a linear drift correction applied between each calibration. The element concentration of NIST SRM 612 for the calibration is selected from the preferred values of Pearce et al. (1997). Data reduction was facilitated using ^{29}Si and ^{42} or ^{43}Ca as internal standard elements for olivine and other minerals, respectively, based on their contents obtained by EPMA analysis, and followed a protocol essentially identical to that outlined by Longerich et al. (1996). Details of the analytical method and data quality were described in Eggins et al. (1998) and Morishita et al. (2005a, b). Representative analyses in trace-element compositions of minerals are shown in Table 2.

4.2. Results

Differences in major-element compositions were not found between Green amphiboles and Symplectite

Table 2
Trace-element compositions (ppm) of minerals

Sample	Olivine-rich sublayer										cpx-rich sublayer										cm-bearing portion				
	Anal. no.	Phase	Olivine	STD 9	Plag	STD 8	cpx core	#11	#9	#39	#16	#24	Green-am	Green-am	#25	#34	#C1-1	#C2-1	#921	#Cm3-1	#Cm4-1	#Cm-5			
Li		0.7	0.3	0.9*	0.4*		0.42	0.44	0.44	0.43	0.51	0.47	0.71	0.44	2.2	0.44	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			
Sc		3.2	0.9	0.47	0.07		75	70	50	102	134	134	133	176	133	176	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			
Ti		6	1	11	4		967	974	817	901	3253	3170	2811	331	356	2811	1141	1105	11	1251	925	4176			
V		0.4	0.2	0.19	0.05		169	168	149	168	364	364	356	331	356	331	165	167	0	182	157	470			
Cr		3	2	<2			1774	1454	1405	1514	2516	2516	2502	2425	2502	2425	810	939	<5	1325	2407	2413			
Rb		<0.07		0.14	0.07		<0.05	<0.06	<0.06	<0.06	0.097	3.6	2.2	2.2	2.2	2.2	<0.15	<0.15	<0.1	<0.15	<0.15	3.5			
Sr		<0.01		58	6		2.7	2.5	2.8	2.8	2.9	9.4	7.5	7.9	7.5	7.9	1.9	2.6	68	2.9	3.3	8.1			
Y		<0.01		0.04	0.02		6.5	7.5	5.9	6.3	6.3	13	14	14	14	14	5.2	6.2	<0.02	5.4	3.9	15			
Zr		<0.01		<0.01			0.98	1.16	0.87	1.03	1.03	1.5	1.6	1.7	1.6	1.7	1.0	1.1	<0.02	1.1	0.74	2.2			
Nb		<0.01		<0.01			0.02	<0.01	0.02	0.02	0.03	0.62	0.39	0.33	0.44	0.33	0.02	0.02	<0.02	<0.02	<0.02	0.33			
Ba		<0.01		2.1	0.4		0.02	0.02	<0.01	<0.01	0.65	4.7	4.4	4.1	4.4	4.1	0.12	<0.08	3.0	<0.08	<0.08	6.4			
La		<0.01		0.04	0.01		0.04	0.04	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.06	0.05	0.04	0.04	0.03	0.04	0.07			
Ce		<0.01		0.08	0.01		0.22	0.21	0.22	0.24	0.28	0.28	0.33	0.31	0.33	0.31	0.22	0.17	0.09	0.22	0.19	0.35			
Nd		<0.03		0.05	0.02		0.44	0.44	0.40	0.40	0.38	0.56	0.69	0.66	0.56	0.66	0.39	0.37	0.05	0.48	0.44	0.82			
Sm		<0.03		<0.03			0.34	0.38	0.33	0.30	0.30	0.55	0.56	0.60	0.56	0.60	0.32	0.25	<0.03	0.35	0.23	0.66			
Eu		<0.01		0.06	0.01		0.28	0.34	0.30	0.28	0.28	0.46	0.51	0.48	0.51	0.48	0.24	0.27	0.07	0.25	0.22	0.48			
Gd		<0.02		<0.02			0.70	0.80	0.67	0.66	0.66	1.3	1.4	1.4	1.4	1.4	0.65	0.69	0.04	0.69	0.57	1.6			
Dy		<0.03		<0.03			1.1	1.3	1.1	1.1	1.1	2.1	2.4	2.3	2.4	2.3	0.87	1.13	<0.03	1.02	0.69	2.6			
Er		<0.02		<0.03			0.74	0.92	0.71	0.78	0.78	1.6	1.6	1.6	1.6	1.6	0.45	0.73	<0.03	0.62	0.42	1.8			
Yb		<0.03		<0.04			0.82	0.96	0.76	0.78	0.78	1.6	1.7	1.8	1.7	1.8	0.59	0.69	<0.02	0.66	0.40	1.8			
Lu		<0.01		<0.01			0.12	0.14	0.11	0.11	0.11	0.23	0.25	0.24	0.25	0.24	0.06	0.11	<0.02	0.09	0.06	0.27			
Hf		<0.03		<0.03			0.05	0.06	0.03	0.06	0.06	0.07	0.07	0.10	0.07	0.10	<0.07	0.08	<0.07	<0.07	<0.07	0.12			
Pb		<0.1		<0.2			<0.03	0.10	<0.03	<0.03	<0.03	0.06	<0.03	0.11	<0.03	0.11	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2			

Detection limit was calculated for each analysis. Anal. no. = name of analyzed point.

Detection limit was calculated for each analysis. cpx = clinopyroxene, Green-am = Green amphibole, n.a. = not analyzed, STD = standard deviation of analysis. Numbers next to STD are numbers of analysis. Li content and standard deviation of plagioclase (number with *) are average of 6 analyses.

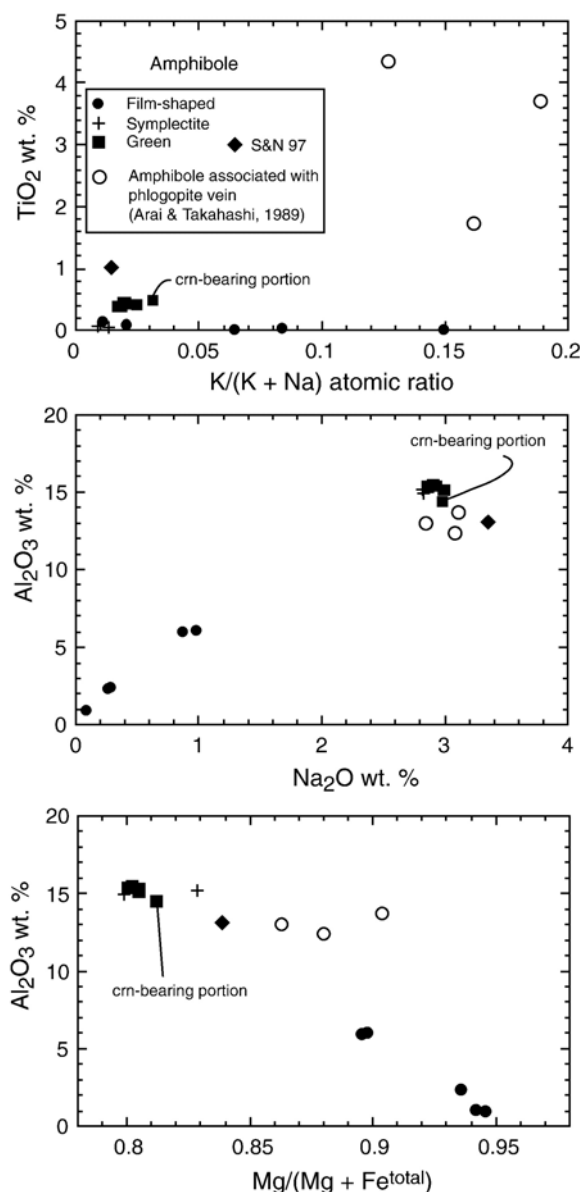


Fig. 5. Compositional variations of amphiboles. (a) $K/(K+Na)$ atomic ratio vs TiO_2 wt.%, (b) Na_2O vs Al_2O_3 wt.% and (c) $Mg/(Mg+Fe^{total})$ atomic ratio vs Al_2O_3 wt.%. It is noted that the TiO_2 content of amphiboles in the studied sample is apparently lower than that associated with phlogopite-vein in Horoman peridotites (Arai and Takahashi, 1989). S and N 97 = green pargasite in Type II mafic rock reported in Shiotani and Niida (1997).

amphiboles except for TiO_2 content (Table 1, Fig. 5). The Green and Symplectite amphiboles, pargasite in the nomenclature of Leake et al. (1997), have low Na_2O (<3 wt.%) and K_2O (<0.1 wt.%) contents and low $K/(K+Na)$ atomic ratio (<0.2) (Fig. 5). These contents tend to be slightly lower in the Symplectite amphibole than in the Green amphibole (Fig. 5). The Al_2O_3 and Cr_2O_3 contents

of the Green amphibole and Symplectite amphibole are c.a. 15 wt.% and <0.04–0.6 wt.%, respectively. The TiO_2 content is higher in the Green amphibole (0.4–0.6 wt.%) than in the Symplectite amphibole (<0.1 wt.%) (Fig. 5). The compositions of the “green pargasite” in Type II rocks reported by Shiotani and Niida (1997) are higher in TiO_2 (<1.44 wt.%) and Cr_2O_3 (0.74–1.43 wt.%) contents than the Green and Symplectite amphiboles in the studied corundum-bearing Type II mafic rock.

The Film-shaped amphibole is magnesiohornblende to tremolite, i.e., Na- and Al-poor amphibole with Na_2O and Al_2O_3 contents ranging from 0.1 to 0.9 wt.%, and from 0.8 to 6 wt.%, respectively (Fig. 5). The TiO_2 and K_2O contents of the Film-shaped amphibole are usually low, <0.04 wt.% and <0.03 wt.%, respectively. Amphiboles associated with phlogopite in the Horoman peridotites are distinctively higher in TiO_2 and K_2O contents than the studied amphiboles (Fig. 5). The $Mg\#$ ($= Mg/(Mg+Fe^{total})$ atomic ratio) increases from the Green and Symplectite amphiboles to the Film-shaped amphibole (Fig. 5).

Only one analytical point was successfully obtained for major-element compositions of the Low-Al OPX because of its tiny size that the Low-Al OPX is low in the Al_2O_3 , Cr_2O_3 and CaO contents, 0.1, <0.02 and 0.3 wt.%, respectively (Table 1), and is $Ca_{0.5}Mg_{83.3}Fe_{12.2}$.

Clinopyroxenes in all samples are slightly chemically zoned from core to rim (Table 1). The Al_2O_3 content of the clinopyroxene directly in contact with the Low-Al OPX is 5.5 wt.%. The TiO_2 and Cr_2O_3 contents of clinopyroxenes tend to be lower in the studied corundum-bearing Type II mafic rock (<0.25 wt.% and <0.3 wt.%, respectively) than in other Type II mafic rocks reported by Shiotani and Niida (1997) (<0.35 wt.% and 0.15–1.23 wt.%, respectively).

Fig. 6 shows chondrite-normalized REE (CH-normalized REE) and primitive mantle-normalized trace-element (PM-normalized TE) patterns for clinopyroxenes and the Green amphiboles. Since no significant differences in trace-element compositions are found between core and rim of clinopyroxenes at the studied spatial resolution (c.a. 50–70 μm) (Table 2), only core compositions were discussed hereafter. Also, except for one analysis there are no significant differences in both CH-normalized REE and PM-normalized TE patterns of clinopyroxene among the samples irrespective of the presence or absence of the Green amphibole. The CH-normalized REE patterns of all clinopyroxene in the samples show depletion of light REE (LREE) with slight positive Eu anomaly. The PM-normalized TE patterns of clinopyroxenes show negative anomalies of Hf and Zr. Although one

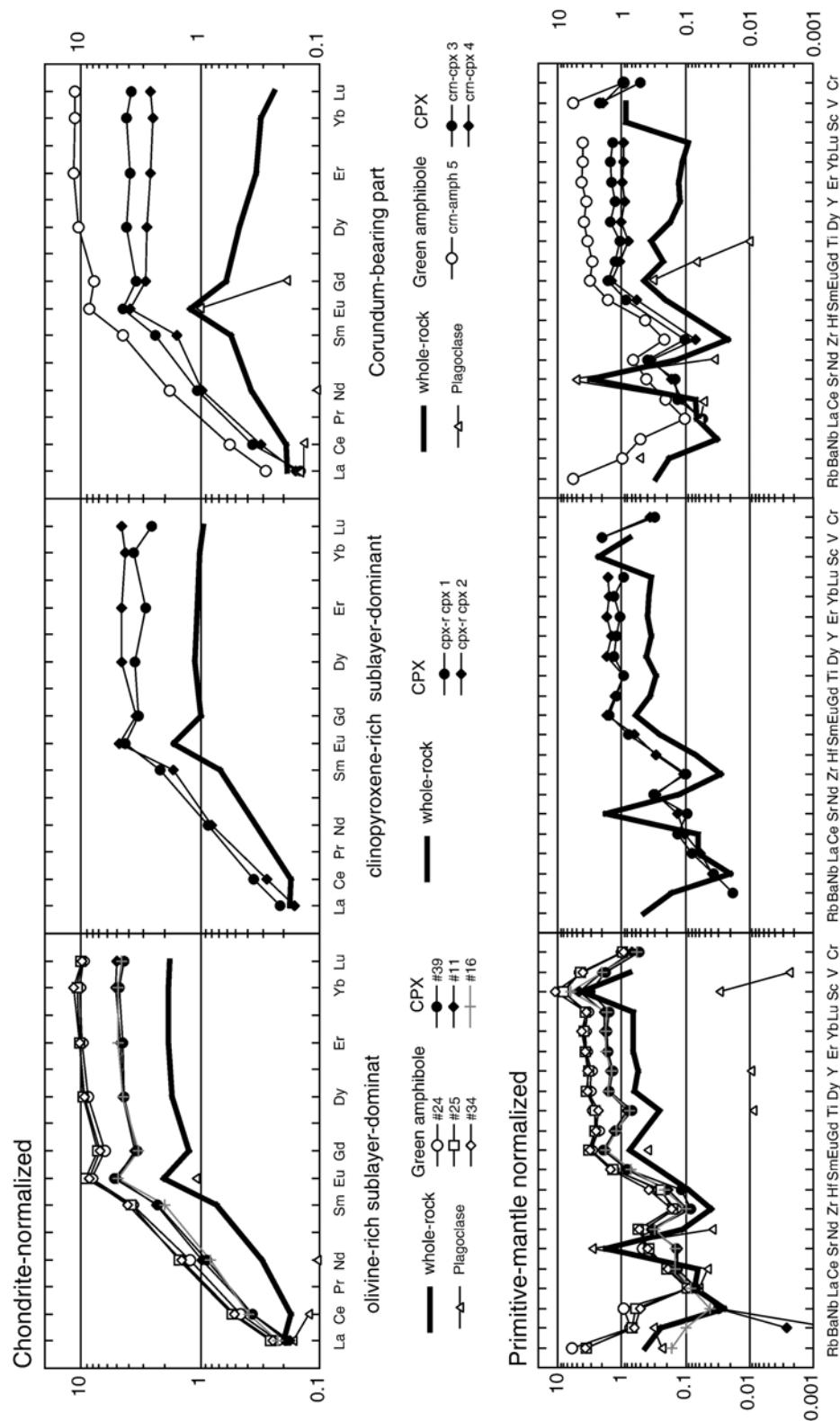


Fig. 6. Chondrite-normalized REE patterns and primitive mantle-normalized trace-element patterns for clinopyroxene and the Green amphibole ($\pm$ olivine and plagioclase). The analytical numbers are the same as those in Table 2. The chondrite and the primitive mantle values are from McDonough and Sun (1995). Data of whole-rock trace-element compositions are from Morishita et al. (2004).

clinopyroxene associated with the Film-shaped amphibole is rich in Rb and Ba, these elements in other clinopyroxenes are usually very low or lower than the detection limit of the LA-ICP-MS analysis. The reasons for high-Rb–Ba contents in one clinopyroxene are not clear yet.

The CH-normalized REE and the PM-normalized TE patterns of the Green amphibole have similar patterns among samples where in LREE is depleted with positive Eu anomaly. The PM-normalized TE patterns show negative anomalies of Hf and Zr and positive anomalies of Nb, Ba and Rb.

Olivine and plagioclase in the Low-Al OPX-bearing sample are low in REE and trace-element except several elements in plagioclase. Plagioclase is an important host for Sr (58–68 ppm) and Ba (2–3 ppm) in the sample. Li contents in olivine grains and plagioclases grains are 0.7 ppm and 0.9 ppm, respectively, and are higher than those in clinopyroxene and the Green amphibole. This is consistent with the observation that Li is more preferentially partitioned into olivine than clinopyroxene (0.4–0.5 ppm) (Seitz and Woodland, 2000; Woodland et al., 2004).

The amphibole/clinopyroxene partition coefficients ($^{amph/cpx}D$) for REE (+Y, Zr, Sr) in the samples are 1–4.5. These values are generally consistent with those in metamorphosed gabbros (Tribuzio et al., 1995; Cortesogno et al., 2000) and mantle peridotites (e.g., Vannucci et al., 1995; Bodinier et al., 2004). The amphibole/plagioclase partition coefficients ($^{amph/plag}D$) for trace-element are 0.12–0.16 (Sr), 2–2.3 (Ba), 3.7–4.4 (Ce), and 12–16 (Nd). These values are also generally consistent with those in metamorphosed gabbros except for Ba (0.2–0.28 for Sr, 0.5–0.9 for Ba, 4–9 for Ce, and 11–36 for Nd) (Cortesogno et al., 2000). The $^{amph/plag}D$ for Ba between igneous amphibole and plagioclase rim in olivine gabbros from the Northern Apennine ophiolites (Italy) is, on the other hand, 0.7–2.2, usually >1 (Tribuzio et al., 1999). These data indicate inter-mineral chemical equilibrium of trace-element in the sample.

5. Discussions

5.1. Stage for the formation of amphiboles

Mazzucchelli et al. (1992) reported positive Eu and Sr anomalies in both whole rocks and clinopyroxenes (and also feldspars) in gabbros of the deep crustal mafic intrusion of the Ivrea Zone, Italy. The authors interpreted these geochemical characteristics as a result of mixing of a mantle component with crustal melts derived from partial melting of granulite facies metase-

diments. However, geochemical variations of the Type II mafic rocks including the studied corundum-bearing mafic rock cannot be explained by simple mixing of two end-members (Morishita et al., 2004). Instead, whole-rock geochemical variations of the Type II mafic rocks are similar to those in gabbroic rocks from ophiolite or oceanic lower crust and can be simply explained by accumulation of clinopyroxene and plagioclase with small amount of olivine (Morishita et al., 2004). Furthermore, depletion of Zr (and probably Hf) coupled with Eu positive anomaly of the PM-normalized TE pattern of clinopyroxenes is consistent with geochemical characteristics of igneous plagioclase in gabbroic rocks (Cortesogno et al., 2000). Trace-element compositions of minerals suggest that clinopyroxene in the studied rock was not an igneous mineral but a metamorphic mineral from plagioclase-rich protolith. This is consistent with the Type II mafic rocks in the Horoman Complex having been subjected to complex P – T trajectory, involving metamorphism of the plagioclase-rich protolith at a pressure higher than that at which it was originally formed (Takazawa et al., 1999; Morishita et al., 2004) (Fig. 1).

The textural relationships with the subsequent mineral assemblages support that the amphiboles and the Low-Al OPX were formed after the rock was crystallized at olivine-plagioclase stability conditions (<0.8 GPa), i.e. the latest P – T conditions recorded in the Horoman peridotites. Pargasite and olivine–tremolite stabilities require T conditions approximately <1000 °C and <800 °C at P = <1 GPa, respectively (e.g., Hollowy, 1973; Jenkins, 1981, 1983). However, exact P – T conditions for the formation of these amphiboles and the Low-Al OPX are not well constrained because their formation was controlled by local effective chemical compositions. Despite uncertainties, a wide range of amphibole compositions from pargasite to tremolite in the studied sample is consistent with the cooling in the later P – T trajectory estimated in the studied mafic rock as well as surrounding peridotites by previous workers (Ozawa and Takahashi, 1995; Takazawa et al., 1996; Morishita and Arai, 2001b; Ozawa, 2004; Sawaguchi, 2004).

5.2. Geochemical characteristics and origin of the fluids responsible for the formation of amphiboles

Reactions between host minerals and aqueous fluids can account for the occurrences of the amphiboles in the rock. Geochemical variations from pargasitic amphibole (the Green and Symplectite amphiboles) to tremolitic amphibole (the Film-shaped amphiboles) coupled with their low-Ti characteristics indicate that

the studied amphiboles were simultaneously formed by the fluids using the local effective chemical compositions in the late stage of the exhumation. The Low-Al OPX was locally formed with the Film-shaped amphibole on the basis of their occurrences and distributions in the sample. A reaction between olivine grains and a silica component can also form the Low-Al OPX. The silica component was locally supplied at grain boundary of olivines in the rock as (1) excess silica during the formation of spinel-amphibole symplectite by a reaction $\text{olivine} + \text{plagioclase} + \text{H}_2\text{O} \text{ in fluids} = \text{pargasite} + \text{spinel} + \text{SiO}_2$, and/or as (2) a major constituent in the volatile-rich fluids. Indirect field evidence and experimental works suggested that the fluids equilibrated with minerals in eclogite and/or peridotites at high P – T conditions are not pure H_2O but contain significant dissolved SiO_2 and Al_2O_3 (e.g., Nakamura and Kushiro, 1974; Schneider and Eggler, 1986; Manning, 1994; Brenan et al., 1995; Ayers et al., 1997; Becker et al., 1999). Orthopyroxene characterized by low Al_2O_3 contents was reported from metasomatised peridotites by slab-derived, SiO_2 -rich metasomatising agents (e.g., Blatter and Carmichael, 1998; Smith et al., 1999; Zanetti et al., 1999; Arai and Kida, 2000; McInnes et al., 2001; Franz et al., 2002; Morishita et al., 2003b). Orthopyroxene low in Al_2O_3 was found in a spinel lherzolite from the Horoman Complex (Morishita and Arai, 2001a; Morishita et al., 2003a). The occurrence and geochemical characteristics of Low-Al OPX in the Horoman peridotite are similar to those in the studied mafic rock. Although no hydrous minerals were found in the Low-Al OPX-bearing peridotite sample, the Low-Al OPX in peridotites was interpreted to be a consequence of reaction between olivine and SiO_2 -rich aqueous fluid (Morishita et al., 2003a). Therefore we favor that the metasomatising fluids responsible for the formation of the studied amphiboles contained SiO_2 as a major constituent.

The PM-normalized TE patterns of clinopyroxene and the Green amphibole in the studied mafic rock show no enrichment of LREE relative to HREE, with depletion of HFSEs (except Nb in the Green amphibole, and are basically low in LILE (except Rb and Ba) in the Green amphibole (Fig. 5). A reaction involving the surrounding plagioclase can account for the relatively high concentration of Rb and Ba, Eu positive anomaly and no apparent Sr negative anomaly in the Green amphibole. Cortesogno et al. (2004) reported trace-element characteristics of several types of amphiboles in metamorphosed oceanic gabbros where hornblendes formed through a reaction involving both pyroxene and the surrounding plagioclase and oxides showed similar

geochemical signatures to the Green amphibole. Thus trace-element characteristics of the Green amphibole were obtained by element partitioning that involved both pre-existing clinopyroxene and plagioclase rather than addition of elements from the fluids in the reaction. We propose that the aqueous fluids were depleted in trace-element components at onset of the formation of the Green amphiboles. It is however not apparent whether the composition of the fluid related to the formation of amphiboles was originally depleted in trace-element. The parent fluids might be highly modified during interactions with the host rocks (e.g., Vannucci et al., 1995).

The following hypotheses were first considered for the reason for the depletion of trace-element in fluids during hydration processes. Vannucci et al. (1995) reported LREE-depleted amphiboles in some mantle peridotites and suggest two possibilities for the formation LREE-depleted amphibole. One is subsolidus redistribution of elements in LREE-enriched amphiboles formed by interaction with LREE-enriched metasomatising agents to be equilibrium with LREE-depleted clinopyroxene. This is not the case for the studied sample because the PM-normalized TE patterns of clinopyroxene in the Green amphibole-free sample (clinopyroxene-rich sublayer-dominant sample) show almost the same characteristics as those in the Green amphibole-bearing samples (olivine-rich sublayer-dominant sample) (Fig. 5). Furthermore, no significant differences in trace-elements were found between core and rim of each clinopyroxene grain, although spatial resolution on trace-element analysis is low in this study (50 μm).

A chromatographic reaction model, which involves extensive reequilibration with ambient LREE-depleted peridotites, can cause progressive depletion of LREEs as the LREE-enriched metasomatising agent moves away from its source (Vannucci et al., 1995). Since the studied rock is a boulder, it is impossible to know how the fluids migrated to the studied rock through the Horoman Complex. However, several petrographic data allow us to estimate the fluid pathway. The corundum-bearing mafic rock belongs to the Type II mafic rock, which always appears as thin layer (usually < 1 m in thickness) in the cumulus peridotite (SDW suite) of the middle of the symmetrical layered structure. The harzburgite next to the SDW suite is generally characterized by enrichment in LREE ($\pm$ Sr), probably due to a metasomatism in the early stage of the Horoman Complex (Frey et al., 1991; Takazawa et al., 1992, 2000; Yoshikawa and Nakamura, 2000), rather than depletion of LREE. The local occurrence of amphiboles favors a local infiltration of fluids at a late stage of the development of whole Horoman Complex rather than a pervasive fluid flow

throughout the LREE-depleted host rocks. We propose that the aqueous fluids responsible for the formation of the amphiboles were originally depleted in trace-element components.

Several hypotheses can be discussed for the origin of the fluids. One possibility is redistribution of fluids derived from dehydration of pre-existing hydrous minerals in the Horoman Complex. Increasing of temperature was expected for the Upper part of the Horoman Complex during its exhumation (Ozawa, 2004) (Fig. 1). As suggested above, fluids responsible for the formation of spinel-amphibole symplectite were, however, also supplied to the low-temperature part of the complex (the Lower Zone) (Fig. 1). This model is probably not suitable for the origin of the fluids.

It is interesting to note that the peak metamorphic P – T conditions for the Hidaka metamorphic rocks (Osanai et al., 1991) are similar to the later P – T conditions of the Horoman Peridotite Complex as already pointed out by the previous work (e.g., Ozawa and Takahashi, 1995; Sawaguchi, 2004). Shiba and Soeta (1996) estimated the P – T conditions of granulite facies metamorphic rocks at the eastern side of the Horoman complex (0.4–0.6 GPa and 800 °C), which is different from those of other granulite facies rocks (0.3–0.4 GPa and 800 °C) in the southern part of the Hidaka metamorphic belt. These authors suggested that intrusion of hot mantle peridotite mass into the crust is considered to be one of the heat sources for the former granulite rocks, whereas the latter granulite rocks were formed by the Hidaka regional metamorphism. A plausible origin for the volatile-rich fluids infiltrated into the studied mafic rock is dehydration of the surrounding Hidaka crust by metamorphism due to the intrusion of hot mantle peridotites. Sawaguchi (2004) reported asymmetric reaction rims of tremolite sometimes containing chemically distinctive pargasite in peridotites within the cm-scale shear zone in the Internal Shear Zone and suggested that fluids for the formation of syn-kinematic amphibole in peridotites from the Internal Shear Zone were supplied from the dehydration of the surrounding Hidaka crustal rocks due to the Hidaka metamorphism.

Recent geochemical studies on metamorphic rocks and/or serpentinites metamorphosed with surrounding crust rocks indicate that dehydration of the oceanic crusts and/or sediments are not likely to produce the necessary LILEs observed in arc lava (Becker et al., 2000; Busingny et al., 2003; Chalot-Prat et al., 2003; Spandler et al., 2003, 2004), and suggest that dehydrated fluids from crustal rocks may not always have LILE-enriched signatures. Further comprehensive geochemical studies on compositional variations in trace-element coupled

with isotopic compositions of the metamorphic rocks around the Horoman Complex are needed to constrain the genetic relationships between the metasomatism in the late stage of the Horoman complex and the Hidaka metamorphism.

6. Conclusions

We present the occurrence and geochemistry of amphiboles and related minerals in corundum-bearing mafic rock in the Horoman Peridotite Complex. Amphiboles in the studied rock occur as three types, such as (1) interstitial to poikilitic grains, (2) a constituent mineral of symplectitic mineral aggregate with spinel between olivine and plagioclase, and (3) film-shaped thin grains at grain boundary between olivine and clinopyroxene. The former two amphiboles have pargasitic compositions whereas the latter has tremolitic compositions. Low- Al_2O_3 – Cr_2O_3 – CaO orthopyroxene occurs closely associated with the film-shaped amphibole. These minerals were formed by infiltration of SiO_2 -bearing aqueous fluids after the rock was equilibrated under olivine-plagioclase stability conditions, i.e., the late stage of the exhumation of the complex.

Chondrite-normalized rare earth element patterns and primitive mantle-normalized trace-element patterns of the interstitial to poikilitic amphibole and clinopyroxene show LREE-depleted patterns with Eu positive anomaly and negative anomalies of Zr and Hf. The fluids responsible for the formation of amphiboles was originally depleted in trace-element components. Dehydration of the surrounding metamorphic rocks in the Hidaka metamorphic belt is a plausible origin for the fluids.

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