Phase relations in $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ and formation of majoritic knorringite garnet at high pressure and high temperature

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High-pressure and high-temperature phase relations for $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ have been studied at pressures from 8 to 16 GPa and temperatures of 1200–1800 °C using a Kawai-type multianvil apparatus. The low-pressure phase assemblage of MgSiO_3 pyroxene + Cr_2O_3 eskolaite was found to transform into a high-pressure phase assemblage of majoritic knorringite + eskolaite with a negative phase boundary of $dP/dT = -0.010$ GPa/°C. No pure $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ knorringite garnet was observed over the entire range of the P - T conditions in the present study, suggesting that pure knorringite garnet may not be a stable phase under these pressure and temperature conditions. This result is inconsistent with earlier studies, where knorringite was reported to be stable at pressures higher than ~ 10 GPa. On the other hand, the present result agrees well with recent results for the synthesis of majoritic knorringite at pressures of 11 and 14 GPa and at temperatures of 1500–1600 °C. Majoritic knorringite becomes more Cr-deficient with increasing pressure, which is similar to the Al-deficient nature of majoritic garnet in the MgSiO_3 - Al_2O_3 system.

Keywords: Stability field, Knorringite-rich garnet, Majorite garnet, High pressure and high temperature, Diamond inclusions

INTRODUCTION

Knorringite ($\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$) is an important component of garnet solid solutions in the deeper parts of the upper mantle. This mineral is often found in ultramafic xenoliths and natural diamonds from kimberlite (Nixon and Hornung, 1968; Sobolev, 1974; Tsai et al., 1979). Stachel and Harris (1997) reported that the highest content of knorringite within natural garnet inclusions in kimberlitic diamonds is about 66 mol%. Thus, the stability of knorringite at high pressure and high temperature is an important subject in mineralogical studies of the deep mantle.

The high-pressure phase relations and stability of knorringite are controversial. The successful synthesis of knorringite garnet was first reported by Coes (1955) in a brief communication, in which neither the synthetic method nor the physical properties of this novel garnet was specified. Since then, many scientists have shown great interest in experimental studies of the phase stability and synthesis of knorringite-rich garnet (e.g., Bykova and Genshaft, 1972; Ringwood, 1977; Irifune et al., 1982;

Turkin et al., 1983; Taran et al., 2004; Juhin et al., 2010).

Ringwood (1977) reported the synthesis of knorringite garnet at pressures from 8 GPa to 16 GPa and temperatures of 1400–1500 °C. However, this work only provided results corresponding to a single P - T condition of 7 GPa and 1400 °C obtained from one experiment rather than the full stability range of knorringite. The first detailed experimental study on the stability of knorringite was carried out by Irifune et al. (1982), who demonstrated that knorringite garnet was stable at pressures above 11.5 GPa at 1200 °C and 11.8 GPa at 1400 °C. In contrast, Turkin et al. (1983) reported a phase boundary located at significantly lower pressures of 8–9.5 GPa at 1200–1800 °C with a negative Clapeyron slope. Recently, Klemme (2004) reported that knorringite was synthesized at 16 GPa and 1600 °C, but the resultant knorringite coexisted with a small amount of eskolaite. Moreover, the univariant reaction $\text{MgCr}_2\text{O}_4 + 2\text{Mg}_2\text{Si}_2\text{O}_6 = \text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12} + \text{Mg}_2\text{SiO}_4$, has a negative slope in the P - T space between 1200 °C and 1600 °C. Similarly, Taran et al. (2004) confirmed the coexistence of $\sim 3\%$ eskolaite in the knorringite sample synthesized under similar pressure and temperature conditions except for one run at 11 GPa and 1400 °C, where the synthesis of pure knorringite was reported.

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However, a recent study by Juhin et al. (2010) demonstrated that the chemical composition of knorringite synthesized at 16 GPa and 1500 °C was deficient in Cr (i.e., majoritic) relative to that of stoichiometric garnet, possessing a composition close to $\text{Mg}_{3.2}\text{Cr}_{1.6}\text{Si}_{3.2}\text{O}_{12}$ with a minor amount of eskolaite.

It should be noted that, in these earlier studies, only X-ray diffractometry was used to identify the existing phases, while later studies demonstrated the presence of large temperature gradients within samples in early stage multianvil experiments (e.g., Ito and Takahashi, 1987). Moreover, no electron microprobe analyses were made on the run products in these earlier studies from over 30 years ago (e.g., Irifune et al., 1982). Note also that knorringite garnet tends to nucleate very sluggishly in high-pressure experiments by Klemme (2004). Therefore, further extensive studies based on X-ray diffractometry combined with SEM observations are needed in order to clarify these discrepancies.

In this study, we have re-examined the phase relations of knorringite under pressures between 8 GPa and 16 GPa and at temperatures up to 1800 °C using a Kawai-type multianvil apparatus. Both a glass and an oxide mixture were used as starting materials in order to ensure chemical equilibrium of the resultant phases. Phase identification and lattice parameters/unit cell volume measurements were performed using a microfocus X-ray diffractometer (XRD), and chemical composition analyses were carried out using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX). The phase stability of knorringite garnet under these pressure and temperature conditions is discussed and the likely high-pressure phase relations in the $\text{MgSiO}_3\text{--Cr}_2\text{O}_3$ system are proposed on the basis of the experimental results.

EXPERIMENTAL PROCEDURES

High pressure and high temperature experiments were performed using a Kawai-type multianvil apparatus at the Geodynamics Research Center, Ehime University. Tungsten carbide cubic anvils with a 4.0 mm truncation edge length (TEL) were used as second-stage anvils of the high-pressure apparatus. The pressure medium was a semisintered (Mg, Co) O octahedron of 10.0 mm in edge length, in which a cylindrical LaCrO_3 heater was inserted. The cell assembly used in the present experiments is shown in Figure 1.

Two kinds of starting materials, a mixture of MgO , Cr_2O_3 , and SiO_2 in a molar ratio of 3 : 1 : 3 and a glass obtained from this oxide mixture were used for the high pressure and high temperature experiments. Very fine

Figure 1. A schematic illustration of a cross section of the cell assembly for high-pressure experiments. Cylindrical platinum foil was used as the capsule material.

powders (<100 nm) of these oxides (purities: 99.99%) were mechanically mixed in stoichiometric proportions using an agate mortar for 2 h to obtain the starting material. The prepared oxide mixture was then melted at 1700 °C under the atmospheric pressure and subsequently quenched in water. The resultant glass contained a small amount of magnesiochromite and cristobalite, and it was crushed and mixed in an agate mortar for 2 h. The two different starting materials were directly enclosed within Pt capsules of 1.3 mm in both diameter and length. The enclosed two starting materials were then surrounded by MgO sleeves and inserted into the same cell assembly, as shown in Figure 1.

Pressure was calibrated against the ram load using the pressure-fixed points of Bi, ZnS, and GaAs at room temperature (Irifune et al., 2004; Zou, 2009; Zou et al., 2010). The effect of temperature on pressure was further corrected using the α - β and β - γ phase transitions of olivine (Katsura and Ito, 1989; Yamada et al., 2004). Uncertainties in pressure are believed to be within ~ 0.5 GPa (Irifune et al., 1991). The temperature was measured using a $\text{W}_{97}\text{Re}_3\text{--W}_{75}\text{Re}_{25}$ thermocouple with a precision of ± 10 °C, which was located between the glass and oxide mixture starting materials, as shown in Figure 1. No correction was made for pressure effects on the emf of the thermocouple.

As there was some temperature gradient within the sample, only the high temperature portions near the thermocouple junction were examined in the following analyses. The samples were maintained at the desired P - T conditions for 2–10 h depending on the temperature, quenched by turning off the electric power supply, and recovered at ambient conditions after the release of pressure. The well-sintered samples were fixed in epoxy resin, polished, and

characterized by microfocus XRD analyses, optical microscope observations, and SEM-EDX measurements, respectively. In the microfocus XRD measurements, an X-ray beam 50 μm in diameter was adopted using a rotating Cu anode operated at 40 kV and 200 mA (MAC Science, M21X). Unconsolidated samples and/or starting materials were analyzed using a powder X-ray diffractometer with Cu radiation operated over the 2θ range from 10° to 100° with steps of $0.02^\circ/\text{min}$. Microstructure/morphology and chemical composition analyses were made by using an SEM-EDX (JEOL, JSR-1000). The lattice parameters and unit-cell volumes were calculated from the microfocus XRD data after correction of the 2θ data using pure polycrystalline pyrope as a reference material. More comprehensive studies on the pressure dependences of the phases present, chemical compositions of the coexisting phases, and their lattice parameters were made at various temperatures, particularly 1600°C .

RESULTS AND DISCUSSION

Phase relations in $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$

High pressure and high temperature experiments were performed using both the glass (plus minor subsolidus phases; referred to as 'glass') and oxide mixtures as starting materials. Experimental conditions and results, as well as the microstructure and composition analyses of some representative samples, are shown in Tables 1 and 2, respectively.

The phases observed in Table 1 were identified using a microfocus or powder XRD combined with electron microprobe analyses. It was found that no single phase of garnet was observed over the entire range of the present P - T conditions up to 16 GPa and 1800°C , in contrast to earlier studies by Ringwood (1977), Irifune et al. (1982), Taran et al. (2004), and Klemme (2004), where the formation of pure knorringite was reported at pressures higher than 8–12 GPa. In the present study, knorringite is subjected to majorite substitution at pressures above ~ 8 GPa, which exhibits a behavior similar to that observed in pyrope at lower pressures (Ringwood, 1967; Ringwood and Major, 1971; Liu, 1977; Ito and Takahashi, 1987). However, the substitution behavior in knorringite found in the present study differs from that reported by Ringwood (1977), Irifune et al. (1982), Taran et al. (2004), and Klemme (2004), where no majorite component was found in knorringite. In addition, we also found that the chromium content in garnet and eskolaite decreased significantly with increasing pressures from 8 GPa to 16 GPa at 1600°C . The Cr-deficient garnet phase synthesized in the present study was always accompanied by a small amount of

Table 1. Experimental conditions and results

Run No.	Sample	P (GPa)	Time (hours)	* Phases present
$T = 1200^\circ\text{C}$				
OS2122	Mix	11	10	En+Es
	Gl			En+Es
OS2026	Mix	12	10	En+Es
	Gl			En+Es
OS2116	Mix	13	10	Mj-kn+Es
	Gl			Mj-kn+Es
$T = 1300^\circ\text{C}$				
OD825	Mix	10	6	Es+ En+ (Trace, St)
	Gl			Es+ En+ (Trace, St)
OS2120	Mix	11	5	Mj-kn+Es
	Gl			Mj-kn+Es
OS2114	Mix	12	10	Mj-kn+Es
	Gl			Mj-kn+Es
$T = 1350^\circ\text{C}$				
OD830	Mix	12	10	Mj-kn+Es
	Gl			Mj-kn+Es
$T = 1400^\circ\text{C}$				
OS2068	Mix	8	10	Es+En
	Gl			Es+En
OS2107	Mix	10	10	Mj-kn+Es
	Gl			Mj-kn+Es
OS2105	Mix	11	10	Mj-kn+Es
	Gl			Mj-kn+Es
OS1979	Mix	16	1	Mj-kn+Es+(Trace, St+Wad)
	Gl			Mj-kn+Es+(Trace, St+Wad)
$T = 1500^\circ\text{C}$				
OS2108	Mix	8	5	Es+En
	Gl			Es+En
OD810	Mix	10	10	Mj-kn+Es
	Gl			Mj-kn+Es
$T = 1600^\circ\text{C}$				
OS2013	Mix	8	5	Mj-kn+Es
	Gl			Mj-kn+Es+ (Minor, En)
	Mix	10	5	Mj-kn+Es
	Gl			Mj-kn+Es
OD819	Mix	11	10	Mj-kn+Es
	Gl			Mj-kn+Es
OS2009	Mix	12	5	Mj-kn+Es
	Gl			Mj-kn+Es
OS2007	Mix	14	5	Mj-kn+Es
	Gl			Mj-kn+Es+(Trace, St)
OS1985	Mix	16	3	Mj-kn+Es+(Trace, St)
	Gl			Mj-kn+Es
OS2003	Mix	16	5	Mj-kn+Es
	Gl			Mj-kn+Es
$T = 1800^\circ\text{C}$				
OS2010	Mix	10	2	Mj-kn + Es
	Gl			Mj-kn+Es
OS2038	Mix	12	2	Mj-kn + Es
	Gl			Mj-kn+Es
OS2033	Mix	14	2	Mj-kn+Es
	Gl			Mj-kn+Es
OS2030	Mix	16	2	Mj-kn +Es
	Gl			Mj-kn+Es

* Phase identification was carried out on the high temperature (High- T) side of the run product.

Trace amounts of stishovite and/or wadsleyite are suggested by the XRD analyses, but may be metastable.

Mix, oxide mixture; Gl, glass; Mj-kn, majoritic knorringite; Es, eskolaite; En, enstatite; St, stishovite; Wad, wadsleyite.

eskolaite for both glass and oxide mixture starting materials. As shown in Table 1, the samples, synthesized at 16 GPa and 1400°C for a relatively short duration of 1 h

Table 2. Representative electron microscope analysis of the run products at 1600 °C

Run No	OS2013 (8 GPa)				OS2010 (10 GPa)			
	Oxide mixture		Glass*		Oxide mixture		Glass	
	Mj-kn	Es	Mj-kn	Es	Mj-kn	Es	Mj-kn	Es
MgO	28.58(25)	0.89(16)	28.48(15)	0.92(14)	27.35(18)	0.77(20)	27.57(18)	0.93(17)
SiO ₂	42.41(22)	1.24(14)	42.24(19)	1.14(13)	40.94(26)	1.51(34)	41.83(23)	0.96(35)
Cr ₂ O ₃	28.87(32)	97.86(22)	29.31(21)	97.86(7)	30.57(15)	96.72(33)	30.57(17)	99.67(31)
Total	99.86(38)	99.99(26)	100.03(34)	99.92(18)	98.85(30)	99.08(38)	99.97(31)	101.56(37)
No. of oxygens	12	3	12	3	12	3	12	3
Mg	3.161	0.032	3.151	0.033	3.078	0.029	3.062	0.034
Si	3.150	0.030	3.140	0.030	3.092	0.038	3.120	0.024
Cr	1.691	1.935	1.721	1.935	1.825	1.930	1.801	1.945
Sum	8.002	1.997	8.012	1.998	7.995	1.997	7.983	2.003

Run No	OD819 (11 GPa)				OS2009 (12 GPa)			
	Oxide mixture		Glass		Oxide mixture		Glass	
	Mj-kn	Es	Mj-kn	Es	Mj-kn	Es	Mj-kn	Es
MgO	28.04(42)	—	28.74(37)	—	28.38(12)	0.82(11)	28.33(13)	0.76(9)
SiO ₂	41.92(21)	—	42.70(24)	—	42.30(28)	1.20(20)	42.41(24)	1.05(17)
Cr ₂ O ₃	30.08(26)	—	31.24(32)	—	30.22(21)	99.37(32)	30.26(19)	99.72(34)
Total	100.04(49)	—	102.68(45)	—	100.90(26)	101.39(36)	100.99(27)	101.53(35)
No. of oxygens	12	—	12	—	12	3	12	3
Mg	3.115	—	3.109	—	3.119	0.030	3.110	0.028
Si	3.125	—	3.099	—	3.119	0.030	3.123	0.026
Cr	1.770	—	1.791	—	1.762	1.940	1.762	1.947
Sum	8.010	—	7.999	—	8.000	2.000	7.995	2.001

Run No	OS2007 (14 GPa)				OS2003 (16 GPa)			
	Oxide mixture		Glass		Oxide mixture		Glass	
	Mj-kn	Es	Mj-kn	Es	Mj-kn	Es	Mj-kn	Es
MgO	28.79(23)	1.18(36)	29.93(21)	1.87(41)	30.34(22)	2.75(24)	30.38(24)	2.51(22)
SiO ₂	43.00(29)	1.61(34)	44.23(26)	2.17(36)	44.44(37)	3.84(47)	44.77(32)	3.02(44)
Cr ₂ O ₃	26.96(24)	98.28(31)	27.45(23)	96.82(33)	24.73(31)	93.49(41)	24.66(22)	94.19(30)
Total	98.75(33)	101.07(46)	101.62(30)	100.86(48)	99.51(46)	100.08(55)	99.81(44)	99.72(49)
No. of oxygens	12	3	12	3	12	3	12	3
Mg	3.201	0.043	3.232	0.068	3.319	0.096	3.310	0.081
Si	3.207	0.040	3.204	0.053	3.263	0.092	3.270	0.081
Cr	1.590	1.918	1.573	1.883	1.436	1.810	1.430	1.831
Sum	7.998	2.001	8.009	2.004	8.017	1.998	8.011	1.993

* We observed enstatite on the low temperature side with the following composition (in wt%): MgO, 40.14%; SiO₂, 58.92%; Cr₂O₃, 0.83%. Mj-kn, majoritic knorringite; Es, eskolaite.

from two different starting materials, yield the same phase assembly of majoritic knorringite + eskolaite together with an amount of stishovite + wadsleyite. It is known that the nucleation of knorringite is very sluggish at high pressure (Klemme, 2004). Therefore, we think that this short duration may be one of the possible reasons for the presence of a small amount of stishovite + wadsleyite. Moreover, the appearance of Si-poor knorringite is also another possible reason for the observed stishovite.

Figure 2 shows microfocus XRD patterns of the recovered samples prepared under different pressures at 1600 °C using the oxide mixture (a) and glass (b) as starting materials. Both of these two starting materials yielded identical phase assemblages of garnet + eskolaite at pres-

ures from 8 GPa to 16 GPa. Even at pressures as low as 8 GPa, we found that the knorringite-rich phase coexists with a small amount of Cr₂O₃. However, a small amount of enstatite was identified in the product from the glass sample by XRD measurements. The fact that the run products from both the oxide mixture and glass starting materials yielded virtually identical results in most of the present runs suggests that these high-pressure experiments have been conducted under equilibrium conditions.

Figure 3 shows the phase relations in Mg₃Cr₂Si₃O₁₂ based on the present high pressure and high temperature experiments, where the formation of an assemblage of majoritic knorringite (Mj-kn) + eskolaite (Es) was observed at pressures above ~ 8 GPa at 1600 °C with a neg-

Figure 2. Micro-focus X-ray diffraction patterns of quenched samples treated at different pressures using oxide mixture (a) and glass (b) as starting materials. All samples were kept at 1600 °C for several hours, and then quenched by turning off the electrical power. Kn, majoritic knorringite; Es, eskolaite, En, enstatite.

Figure 3. Phase relations in $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ based on the present high pressure and high temperature experiments. All the data were obtained from the runs using both oxide mixture and glass starting materials. Open circles: enstatite (En) + eskolaite (Es); Solid circles: majoritic knorringite (Mj-kn) + eskolaite (Es). For comparison, the phase boundaries between $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ knorringite and enstatite + eskolaite reported by Irifune et al. (1982) and Turkin et al. (1983), as well as the recent studies by Klemme et al. (2004), Taran et al. (2004) and Juhin et al. (2010), are also shown in this figure.

ative Clapeyron slope of $dP/dT = -0.010 \text{ GPa}/^\circ\text{C}$ (see Tables 1 and 2). For comparison, the previous results of Irifune et al. (1982), Turkin et al. (1983), Taran et al. (2004), Klemme (2004), and Juhin et al. (2010) are also shown in this phase diagram. Our results are quite different from the earlier studies by Irifune et al. (1982), Turkin et al. (1983) and Klemme (2004), where the synthesis of a single phase of pure knorringite was reported.

Irifune et al. (1982) reported that $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ knorringite garnet was stable at pressures above 11.5 GPa at

1200 °C and 11.8 GPa at 1400 °C, suggesting a positive Clapeyron slope for the phase boundary between knorringite and the low pressure phase assemblage of enstatite + eskolaite. In contrast, Turkin et al. (1983) reported a phase boundary located at significantly lower pressures from 8 GPa to 9.5 GPa at 1200–1800 °C with a slightly negative Clapeyron slope, but also reported the same phase transition from enstatite + eskolaite to pure knorringite at pressures below 8 GPa at 1600 °C. In an earlier study by Irifune et al. (1982), most of the runs were conducted at temperatures of 1200–1400 °C for heating durations of typically 60 min using only an oxide mixture of $3\text{MgO} + 3\text{SiO}_2 + \text{Cr}_2\text{O}_3$ as starting material; the phases present were identified only by XRD observations without electron microprobe analyses for the chemical compositions. In addition, it was reported that the synthesized knorringite was always accompanied by a small amount of eskolaite + enstatite.

As shown in Figure 3, our present results are more consistent with those of Turkin et al. (1983) in terms of the location of the phase boundary. However, Turkin et al. (1983) also reported the formation of pure knorringite at higher pressures. We believe that our results are more reliable as compared with those of the earlier studies because of the use of the high-pressure multianvil apparatus in conjunction with microanalyses. Moreover, we used two different starting materials, which yielded virtually identical results in most of the present runs and suggested that our results were in chemical equilibrium. Furthermore, recent results by Klemme (2004) and Juhin et al. (2010) demonstrated that the formation of knorringite plus eskolaite as the high pressure phases were 16 GPa at 1600 °C and 11 GPa at 1500 °C, respectively. Moreover, the latter study reported that the synthesized knorringite was

Figure 4. Comparison of representative back-scattered SEM images of the recovered samples synthesized at 12 GPa and 1600 °C using (a) oxide mixture and (b) glass as starting materials. Mj-kn, majoritic knorringite; Es, eskolaite.

of a majoritic composition. Thus, these studies also support the stability of majoritic knorringite + eskolaite as the high-pressure phase assemblage.

Microstructure and composition analyses

Figures 4a and 4b show typical back scattered SEM images of the recovered samples of knorringite-rich garnet + eskolaite using the oxide mixture and glass as starting materials, respectively. In these samples, knorringite-rich garnet is always accompanied by a small amount of eskolaite, which is consistent with the phase identification from microfocus X-ray diffraction (see in Fig. 2). SEM analyses show that these samples with different starting materials are homogeneous and have almost identical compositions within the uncertainties. These results further indicate that the present experiments have been done under equilibrium conditions.

Figure 5 shows an SEM image of the sample synthesized at 8 GPa and 1600 °C using the glass starting material. On the high temperature (High-*T*) side of the sample, where the thermocouple junction is located, knorringite-rich garnet is observed coexisting with eskolaite. However, on the low temperature (Low-*T*) side an assemblage of enstatite + eskolaite is observed instead of knorringite-rich garnet + eskolaite. This result clearly shows that majoritic knorringite garnet (+ eskolaite) is stable under this *P-T* condition, and that the phase boundary between this and the lower pressure phase assemblage of enstatite + eskolaite has a negative Clapeyron slope. These observations of SEM-EDX are consistent with the phase identification by microfocus X-ray diffraction (see Table 1 and Figure 2). The presence of a small amount of enstatite in the XRD profile of the sample may be attributed to the overlap of the X-ray beam with the lower temperature portions of the sample synthesized at 8 GPa and 1600 °C.

Figure 5. Back scattered SEM image of a sample synthesized at 8 GPa and 1600 °C with glass starting material. Mj-kn, majoritic knorringite; Es, eskolaite; En, enstatite.

Figure 6. Variations in atomic ratios of Mg, Si, and Cr to 12 oxygens in majoritic knorringite synthesized at various pressures at 1600 °C.

Figure 6 shows the changes in the atomic ratios of Mg, Si, and Cr to 12 oxygens in majoritic knorringite synthesized at various pressures at 1600 °C as a function of pressure. At pressures below ~ 11 GPa, the chemical composition is virtually constant. The Mg and Si content significantly increase with increasing pressures from 11 GPa to 16 GPa, while those of Cr decrease concomitantly. It is also observed that the knorringite-rich garnet becomes more majoritic (Cr-deficient) with increasing pressure, particularly at pressures above ~ 11 GPa. The pressure-induced variations of majorite composition in knorringite garnet are similar to those of the majorite component in pyrope (e.g., Irifune et al., 1996).

Table 3. Lattice parameters and unit-cell volumes of the run products at 1600 °C

Run No.	Sample	$a \pm \delta a$ (Å)	$V \pm \delta V$ (Å ³)
OS2013 (8 GPa)	Mix	11.596 ± 0.004	1559.23 ± 1.78
	Gl	11.603 ± 0.004	1562.20 ± 1.90
OS2010 (10 GPa)	Mix	11.610 ± 0.004	1564.76 ± 1.52
	Gl	11.612 ± 0.003	1565.71 ± 1.18
OD819 (11 GPa)	Mix	11.606 ± 0.004	1563.42 ± 1.39
	Gl	11.609 ± 0.003	1564.54 ± 1.78
OS2009 (12 GPa)	Mix	11.591 ± 0.003	1557.26 ± 1.17
	Gl	11.595 ± 0.003	1558.86 ± 1.28
OS2007 (14 GPa)	Mix	11.581 ± 0.001	1553.28 ± 0.24
	Gl	11.584 ± 0.004	1554.47 ± 1.43
OS2003 (16 GPa)	Mix	11.575 ± 0.003	1550.97 ± 1.15
	Gl	11.578 ± 0.003	1552.01 ± 1.18

Mix, oxide mixture; Gl, glass.

Figure 7. Variations of the lattice parameter (a) and the unit-cell volume (V) of majoritic knorringite synthesized at 1600 °C as a function of pressure. The heating temperature and duration for all the samples were 1600 °C and 5 h.

Lattice parameters of majoritic knorringite

Lattice parameters and unit-cell volumes of some representative samples prepared at 1600 °C are shown in Table 3. Figure 7 shows variations of the lattice parameter (a) and the unit-cell volume (V) of majoritic knorringite as a function of pressure at 1600 °C. Both the lattice parameters and unit-cell volumes of majoritic knorringite are nearly constant with increasing pressure up to 11 GPa, consistent with the variation in chemical composition, as shown in Figure 6. These values then start to decrease at pressures higher than 11 GPa owing to the substantial pressure-induced majorite substitution in knorringite.

The decreases in the lattice parameters and the unit-cell volumes are due to the average effects of the couple substitution of 2Cr^{3+} (ionic radius $r = 0.615$ Å for the octahedral site) by Mg^{2+} ($r = 1.03$ Å) and Si^{4+} ($r = 0.43$ Å), (Shannon and Prewitt, 1969), as well as another possible substitution of $\text{Al}^{3+} + \text{V}_0 \leftrightarrow 2\text{Si}^{4+} + \text{O}^{2-}$ upon the formation of majoritic knorringite garnet. The second substitution occurs where an oxygen vacancy (V_0), or ‘O-defect,’ is created in the structure in order to maintain charge balance. In this case, two Cr^{3+} cations substitute for two Si^{4+} cations in the 4-fold coordination, as shown in: $2\text{Cr}^{3+} + \text{V}_0 \leftrightarrow 2\text{Si}^{4+} + \text{O}^{2-}$. This substitution may occur at pressures of more than 16 GPa, in addition to the coupled substitution of: $2\text{Cr}^{3+} = \text{Mg}^{2+} + \text{Si}^{4+}$. This variation is opposite to that for pyrope majorite, where the couple substitution

Figure 8. Effect of majorite substitution on the lattice parameter of majoritic knorringite based on the present study. For comparison, previous studies are also shown with different symbols. The solid line indicates a linear fitting result based on the present data, yielding an extrapolated lattice parameter of pure knorringite of 11.633 Å, which is in good agreement with the theoretically estimated values of 11.64 Å (Novak and Gibbs, 1971) and 11.646 Å (Milman et al., 2001). The lattice parameters reported by earlier studies (Irifune et al., 1982; Taran et al., 2004) for pure knorringite should correspond to those with lower Cr_2O_3 contents, as suggested by the solid arrow.

$2\text{Al}^{3+} = \text{Mg}^{2+} + \text{Si}^{4+}$ (ionic radius of Al^{3+} : $r = 0.535 \text{ \AA}$, Shannon and Prewitt, 1969) and/or $2\text{Al}^{3+} + \text{V}_0 \leftrightarrow 2\text{Si}^{4+} + \text{O}^{2-}$ occur, resulting in an increasing lattice parameter and unit-cell volume. In other words, the trends of lattice parameter changes with increasing pressure are different for majoritic knorringite garnet and majorite-pyropite garnet. These changes are attributed to the difference in the ionic radii of Cr^{3+} , Al^{3+} , Mg^{2+} , and Si^{4+} .

Figure 8 shows the effect of majorite substitution on the lattice parameter of majoritic knorringite. It is shown that the lattice parameter decreases with increasing majorite substitution, as discussed above, which is best described by the equation $a = 11.428(2) + 0.008(1)X_{\text{Cr}_2\text{O}_3}$, as shown by the solid black line. The lattice parameter extrapolated to the composition of pure knorringite is $11.63(2) \text{ \AA}$, which is in good agreement with the theoretically estimated values of $11.64 \text{ \AA}$ (Novak and Gibbs, 1971) and $11.646 \text{ \AA}$ (Milman et al., 2001), as shown in Figure 8. Moreover, the observed variation in lattice parameter agrees well with that of the majoritic knorringite reported by Juhin et al. (2010), within the mutual uncertainties. In contrast, the lattice parameters of $11.596(1) \text{ \AA}$ and $11.5954(5) \text{ \AA}$ reported for “pure knorringite” by Irifune et al. (1982) and Taran et al. (2004) are substantially lower than the extrapolated value. This fact also suggests that the knorringite synthesized by these authors was instead Cr-deficient majoritic knorringite.

Figure 9 illustrates a plausible high-pressure phase relation in the system $\text{MgSiO}_3\text{--Cr}_2\text{O}_3$ at $1600 \text{ }^\circ\text{C}$ and at pressures up to $\sim 16 \text{ GPa}$, based on the present experi-

Figure 9. A plausible high-pressure phase relation in the system $\text{MgSiO}_3\text{--Cr}_2\text{O}_3$ at $1600 \text{ }^\circ\text{C}$ and at pressures up to $\sim 16 \text{ GPa}$, based on the present experimental results on the knorringite composition (i.e., for a Cr_2O_3 content of 25 mol%). Note that the black dash lines symbolize phase boundaries that have not been defined experimentally. Mj-kn, majoritic knorringite; Es, eskolaite; Px, pyroxene (enstatite).

mental results on the knorringite compositions (i.e., for a Cr_2O_3 content of 25 mol%). At pressures below about 8 GPa, a low-pressure phase assemblage of enstatite + eskolaite should be present, which transforms into that of majoritic knorringite + eskolaite at higher pressures for the composition range between $\sim 18\text{--}23$ and $\sim 90\text{--}98$ mol% of Cr_2O_3 , depending on the pressure. The region of enstatite may also be present for compositions with a Cr_2O_3 content less than ~ 20 mol%, as shown in Figure 8. Moreover, it is observed that the knorringite-rich garnet becomes more majoritic (Cr-deficient) with increasing pressure, particularly at pressures above $\sim 11 \text{ GPa}$.

Majorite garnets have been found in some natural diamonds originating from the upper mantle (Gasparik, 2002) or from the mantle transition region (Moore et al., 1991). However, all of these majorite garnets are of eclogitic compositions, with large proportions of grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) components, in addition to the pyrope component. On the other hand, it has been demonstrated that some natural diamonds contain knorringite-rich garnets with up to about 66 mol% (Stachel and Harris, 1997), as inclusions of refractory peridotitic suites. In fact, the knorringite-rich garnets contain only minor amounts of almandine and grossular components and are approximately expressed by the compositions in the pyrope-knorringite join. As the proportion of the majoritic component in majoritic knorringite significantly decreases with decreasing pressure, this could be an indicator of the pressures where peridotitic inclusions are formed. However, further studies on the phase relations in the pyrope-knorringite system are needed in order to apply this method to actual garnet inclusions. Although Irifune et al. (1982) reported that a single phase of stoichiometric garnet was synthesized with the composition of $\text{Mg}_3\text{AlCrSi}_3\text{O}_{12}$ under a pressure of 12 GPa and at temperatures of 1100 and 1200 $^\circ\text{C}$, this material could also have been metastable because of the relatively low temperatures in their study. In addition, no electron microprobe analyses were made on the run products in these earlier studies of over 30 years ago, and further detailed studies on the pyrope-knorringite join, as well as on enstatite-knorringite, should be carried out using the currently available advanced techniques of high-pressure experiments and microanalyses of the run products.

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