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Experimental study of the system MgO–SiO_2–Cr_2O_3 at 7–16 GPa and 1200–1800°C

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The first results of experimental investigation of phase relations in the system MgO–SiO_2–Cr_2O_3 at 7–16 GPa are summarized. Samples synthesized at 7 GPa from different starting compositions contain chromium-bearing enstatite and eskolaite (Cr_2O_3). Increase of pressure (12–16 GPa) results in replacement of pyroxene by garnet of the majorite–knorringite series. The cubic symmetry with a space group *Ia*-3*d* and cell parameters a = 11.5718(1) Å, V= 1549.54(2) Å^3 was established for the most knorringite-rich garnet by single-crystal X-ray diffraction.

Key words: experiment at high temperatures and pressures, knoringite, majorite

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Numerous results of investigations of crystalline inclusions in diamonds provide evidence for the formation of most of them within the pressure range of 4–7 GPa, which corresponds to depths of 150–250 km [*Taylor, Anand, 2004 and others*]. Garnets are widely abundant as inclusions in diamonds and those of the ultrabasic paragenesis are characterized by significant chromium admixture in the composition of knorringite ($Mg_3Cr_2Si_3O_{12}$, *Knr*) end-member. It was established that incorporation of knorringite in garnet occurred from 3 GPa (beyond the diamond depth facies), and the concentration of chromium reached significant values (5–10 wt % Cr_2O_3 and more) in the pressure range of stability of most of natural diamonds (4–7 GPa) [*Malinovskii et al., 1975*], which is an indicative feature of diamondiferous dunite–harzburgite paragenesis of the lithospheric mantle.

Incorporation of majoritic component is another important peculiarity of mantle garnets. The concentration of aluminum and chromium in garnets decreases with pressure [*Akaogi, Akimoto, 1977; Irifune, 1987*], whereas the content of silicon in the octahedral site, as well as the concentration of divalent cations (Ca, Mg, Fe) and sodium regularly increase [*Ono, Yasuda, 1996*], which this results in the formation of garnet with the silicon content of >3 p.f.u. This is controlled by the beginning of dissolution of pyroxene (mainly (Mg,Fe)SiO_3) components in garnet already from 5 GPa [*Akaogi, Akimoto, 1979*]. The solubility of pyroxene in garnet increases with pressure reaching significant values at 10–15 GPa, which corresponds to the lowermost upper mantle and transition zone.

The relationship of majorite and knorringite with pressure providing evidence for similarity in their behavior, but, at the same time, for possible concurring reaction on pressure increase arose our interest to the experimental investigation of the knorringite–majorite (in chemical expression, MgO–SiO_2-Cr_2O_3) system in a wide range of *PT*-parameters. Here we report the first results of performed experiments.

Experiments on investigation of the system MgO–SiO_2–Cr_2O_3 were performed on high-pressure toroidal “anvil-with-hole” apparatus NL-13T in the Institute of Experimental Mineralogy, Russian Academy of Sciences, and multi-anvil apparatus in the Bayerisches Geoinstitut, Bayreuth, Germany.

At 7 GPa and 1200–1900°C (in the field of the enststite ($MgSiO_3$, *En*) stability) the starting compositions of $Knr_{50}En_{50}$, $Knr_{70}En_{30}$, $Knr_{30}En_{70}$ и $Knr_{100}En_{0}$ (mol %) were studied. The phase associations in all runs included enstatite (up to 3.2 wt % Cr_2O_3) and eskolaite (Cr_2O_3, *Esk*). Fig. 1*a* demonstrates the typical texture of obtained samples with relatively large enstatite crystals and small, often interstitial eskolaite segregations. Increase of chromium content in enstatite with temperature was observed (Table 1).

As is evident from Table 1, all orthopyroxenes are characterized by some depletion in magnesium (in relation to 1 p.f.u.), and it is this fact that illustrates chromium incorporation in the mineral structure. We should unlikely consider the scheme of heterovalent isomorphism like $Mg^{2+}+Si^{4+}\rightarrow 2Cr^{3+}$ in this case, when chromium enters both octahedral (replacing Mg) and tetrahedral (replacing Si) sites, by the analogy with orthorhombic corundum ($AlAlO_3$) component of orthopyroxene [*Berman, Aranovich, 1996*]. Based on the single-crystal X-ray diffraction study of chromium-bearing enstatite (Luca Bindi, personal communication), we suggest the structural formula $Mg_xCr_{1-x}Si_{(3-x)/4}\square_{(1-x)/4}O_3$, according to which chromium replaces magnesium in octahedrons being accompanied by appearance of vacancies instead of silicon atoms in tetrahedrons.

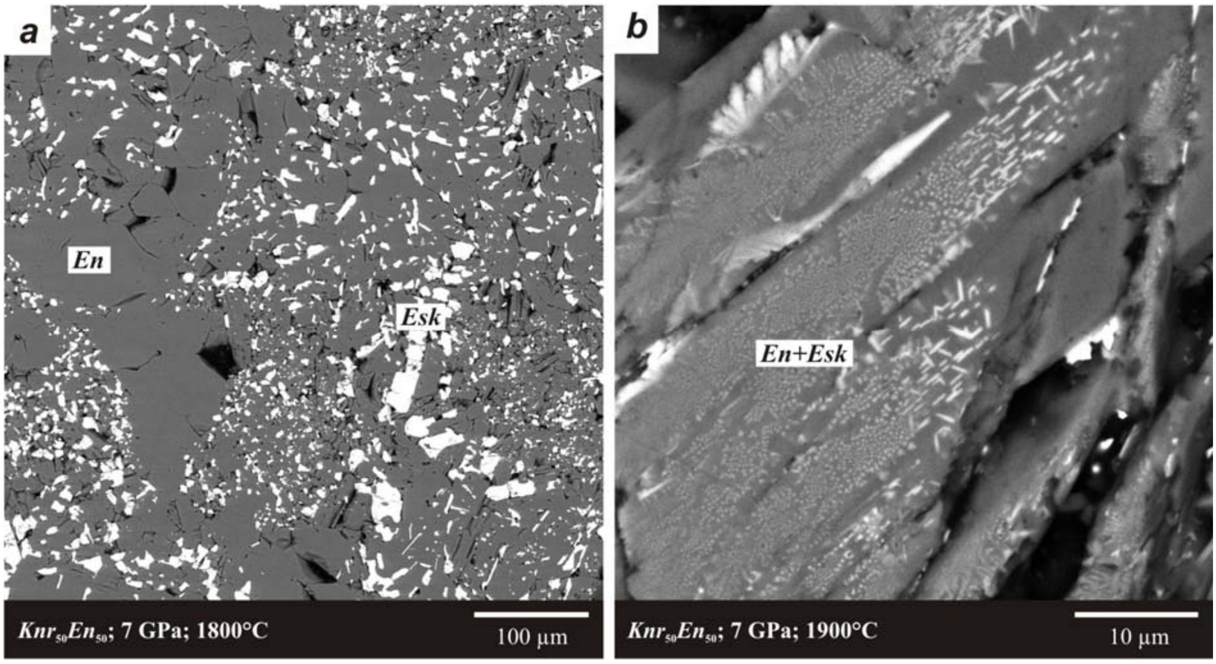

Fig. 1. Back-scattered electron images of textural peculiarities of experimental samples obtained in the system $MgO–SiO_2–Cr_2O_3$ at 7 GPa. (*a*) Relatively large grains of chromium-bearing enstatite and small grains of eskolaite in the groudmass ($Knr_{50}En_{50}$, T = 1800°C); (*b*) small oriented eskolaite intergrowths in enstatite.

Table 1. Composition of enstatite in the samples obtained at 7 GPa (starting composition $Knr_{50}En_{50}$)

Analysis	T, °C	MgO	SiO_2	Cr_2O_3	Total	Mg	Si	Cr	Total
12-02	1200	39.26	62.41	1.16	102.83	0.960	1.013	0.016	1.989
13-01	1500	37.44	59.07	1.44	97.95	0.955	1.009	0.020	1.984
04-01	1500	38.11	58.88	1.38	98.37	0.967	1.003	0.019	1.988
05-02	1600	37.40	59.62	1.57	98.59	0.945	1.012	0.021	1.978
08-01	1800	35.60	59.20	3.21	98.01	0.907	1.012	0.043	1.963

We should emphasize that liquidus enstatite obtained at a temperature >1800°C contains small (sometimes hardly visible even at the highest magnification) oriented eskolaite inclusions. Their shape and regular orientation allow us to interpret them as the texture of eutectic crystallization (Fig. 1*b*). The bulk analysis of such grains provided extremely high chromium concentrations in intergrowths reaching 7.23 wt % Cr_2O_3. The correlation between the concentrations of Mg, Cr, and Si in synthetic pyroxenes confirms their aggregate nature and provides evidence for existence of the concentration barrier (between 3.2 and 5.7 wt %) of Cr_2O_3 incorporation in orthopyroxene.

Garnets of the majorite–knorringite composition were synthesized in multi-anvil experiments performed at 12–16 GPa and 1400–1600°C.

The starting compositions of $Knr_{100}Maj_0$ and $Knr_{50}Maj_{50}$ (mol %) were studied in the system $MgO–SiO_2–Cr_2O_3$ at 16 GPa and 1600°C. The main phases obtained in experiments are garnet of the majorite–knorringite composition and eskolaite (Fig. 2*a*). The synthesized garnets contain from 15 to 25 mol % majoritic component (Table 2). It is typical that even for the starting composition of pure knorringite $Mg_3Cr_2Si_3O_{12}$, we obtained the garnet solid solution containing 15 mol % $Mg_4Si_4O_{12}$, which reflects the more significant influence of pressure on the formation of majorite in comparison with knorringite.

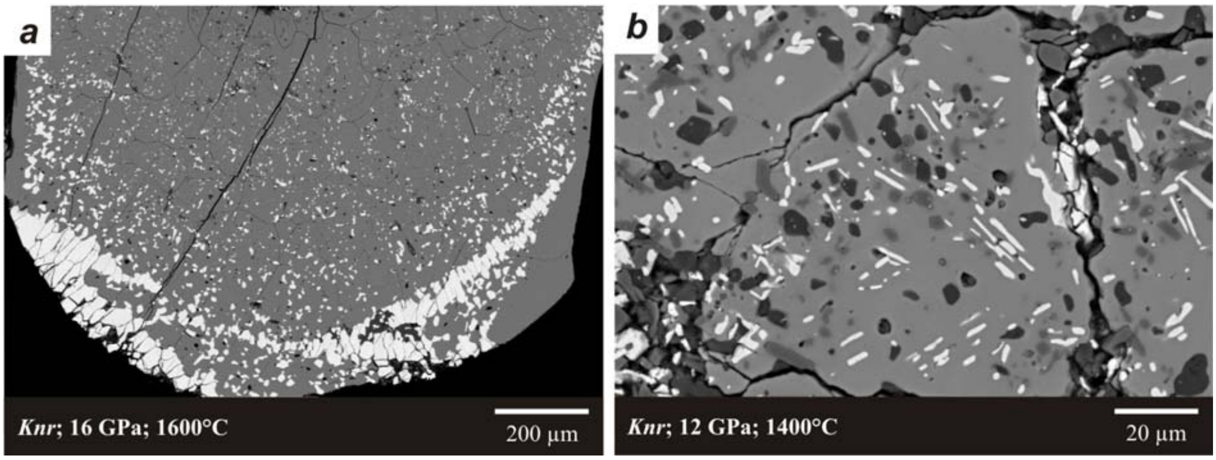

Fig. 2. Back-scattered images of textural features of experimental samples obtained in the system MgO–SiO$_2$–Cr$_2$O$_3$ at 16 GPa and 1600°C (*a*) and 12 GPa and 1400°C (*b*) for the starting composition $Mg_3Cr_2Si_3O_{12}$. (*a*) Relatively large knorringite grains (gray) and small grains of eskolaite (white) in the groundmass; (*b*) knorringite (gray) with small oriented intergrowths of eskolaite (white) in the central part of grain and with inclusions of stishovite (dark-gray) and periclase (black) in the marginal part of grain.

Table 2. Composition of garnet in samples obtained at 16 GPa

Composition	SiO$_2$	MgO	Cr$_2$O$_3$	Total	Si	Mg	Cr	Total
$Knr_{100}Maj_0$	42.73	27.66	28.64	98.33	3.15	3.09	1.71	7.95
$Knr_{50}Maj_{50}$	44.36	28.87	24.97	98.20	3.25	3.27	1.41	7.94

Fig. 3 demonstrates the Raman spectra of synthesized garnets in comparison with the data on pure pyrope and majorite. Since the data on Raman spectra are not available for pure knorringite, the morphology of spectra of garnets obtained from the starting compositions $Knr_{50}Maj_{50}$ (H3421) and $Knr_{100}Maj_0$ (H3420) may be analyzed by their mutual comparison, as well as by comparison with the spectra of pyrope and majorite. As garnet from Sample H3421 contains the higher portion of majoritic component (25 mol %) in comparison with garnet from Sample H3420 (15 mol %), we may suggest that the peaks at 625 cm^{-1} for H3421 and 624 cm^{-1} for H3420 correspond to the spectrum of majorite. The same is evident for the peaks in the range of 937–943 cm^{-1}. Garnets (H3420 and H3421) synthesized at 12–16 GPa are represented by the majorite–knorringite solid solution and consequently all other peaks correspond to knorringite.

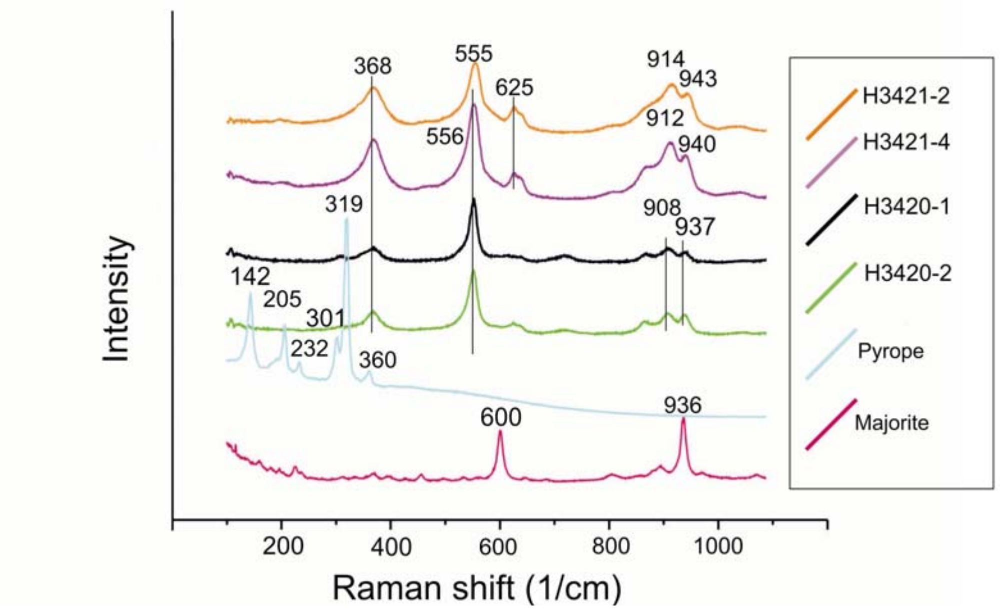

Fig. 3. Raman spectra of garnets of the majorite–knorringite composition synthesized at 12–16 GPa in comparison with the spectra of pyrope and majorite.

It should be noted that garnet monocrystals with such a high portion of knorringite component were not previously synthesized in experiments, which did not allow to obtain reliable crystallochemical characteristics of knorringite. [*Juhin et al., 2010*] determined the structural peculiarities of garnet of the similar composition by powder X-ray diffraction. In our study synthesized knorringite-rich garnet was studied by single-crystal X-ray diffraction for the first time. We established its cubic symmetry with a space group *Ia*-3*d* and cell parameters a = 11.5718(1) Å, V= 1549.54(2) Å^3.

To obtain garnet with the higher content of knorringite end-member, we studied the starting composition $Knr_{100}Maj_0$ at the lower *PT*-parameters (12 GPa and 1400^{o}C). The phase associations also included garnet of the majorite–knorringite composition and eskolaite (Fig. 2*b*); inclusions of periclase (MgO) and stishovite (SiO$_2$) were registered in the marginal parts of garnet grains. According to the tabular shape and mutual orientation of eskolaite inclusions, we may suggest that they were formed as a result of decomposition of chromium-rich garnet. The bulk analysis of garnet demonstrated that before decomposition this was pure knorringite.

Thus stable incorporation of majoritic component in knorringite garnets synthesized at high pressures (12–16 GPa) illustrates the concurring behavior of majorite and knorringite under the conditions of pressure increase. Being applied to natural garnets, this observation provides evidence for the fact that relative enrichment of garnet in knorringite may occure in the lithospheric mantle, whereas significant concentrations of majoritic component (>5–10 mol %) may be gained only in the lowermost upper mantle and transition zone. The results of our experiments demonstrate that pure knorringite is unstable under the atmospheric conditions and should be studied *in situ* in experiments at high temperatures and pressures.

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