10IKC-199

SODIUM MAJORITE AND ITS PYROPE SOLID SOLUTIONS: HIGH PRESSURE EXPERIMENT AND CRYSTAL-CHEMICAL IMPLICATIONS.

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Currently a number of ultrahigh pressure minerals are described as inclusions in diamonds (e.g. Stachel, 2001). The proof of their truly deep origin often appears problematic because of decompressional structural transformations. Experimental researches available for today, and also complex analysis of the Earth's mantle P−T conditions allow to establish the whole series of the phase transitions and chemical reactions in the conditions of the asthenosphere (> 200 km) and transition zone (410−660 km). Ultrahigh-pressure minerals, such as MgSiO with ilmenite and perovskite structures, $CaSiO_3$ with perovskite structure, magnesiowustite (ferropericlase), and majoritic garnet. One characteristic feature of the latter mineral is silicon excess (over 3 pfu) and an isomorphic sodium admixture that allows to attribute them to Na-bearing majoritic garnets.

Our experimental study was aimed on obtaining of the every possible data about garnet phase $Na_2MgSi_5O_{12}$ (NaMaj): an establishment of pyroxene/garnet phase transition boundaries in *P-T* coordinates, definition of structural features in the pure state and in solid solutions with a pyrope (Prp), and also study of solubility in the model system Prp-NaMaj. Experiments were performed in the Tohoku University (Sendai, Japan) at *P* =11-20 GPa and *T*= 1500-2100°C on a high -pressure Kawai-type apparatus, where cell assemblage with the sample was compressed by eight cubic anvils truncated with triangular faces. Single-crystal shooting of samples was spent with a Bruker-Enraf MACH3 diffractometer using graphite-monochromatized Mo*K*α radiation. The small crystals were additionally studied on an Oxford Diffraction Xcalibur 3 diffractometer equipped with a Sapphire 2 CCD detector.

Crystals of a Na-pyroxene and Na-majorite and synthesized and the fields of their stability were obtained in experiments at 13-19 GPa (Dymshits et al., 2010). The largest Na-majorite (up to 100 µm) crystals were obtained in the long -time run (ES-238, 1440 min). Their compositions (wt %, SiO_2 75.32; MgO 10.11; Na_2O 15.08; total 100.51; formula $Na_{1.944}Mg_{1.003}Si_{5.013}O_{12.000}$) are quite close to the ideal stoichiometric composition. In some runs (1810 and 1811) incorporation of a small admixture of majoritic component ($Mg_4Si_4O_{12}$) is assumed judging from the higher magnesium concentration in some grains (up to 1.273 f. u. Mg) and lower content of Si (up to 4.911 f. u.) relatively to 5.000 per formula unit. The phase boundary is described by the equation P (GPa) = 0.0050(2)·T + 7.5(4) and has quite steep slope, because the first appearance of garnet is observed at a pressure of 16 GPa and a temperature of 1500°C; garnet is formed at 1900°C GPa with increase of pressure up to 17.5 (fig. 1). Detailed studying of Na-majorite by single-crystal X-ray diffraction has allowed to establish that Na-majorite is tetragonal, space group $I4_1/acd$, with lattice parameters a = 11.3966(6), c = 11.3369(5) Å, V = 1472.5(1) Å^3 (Bindi et al., 2011).
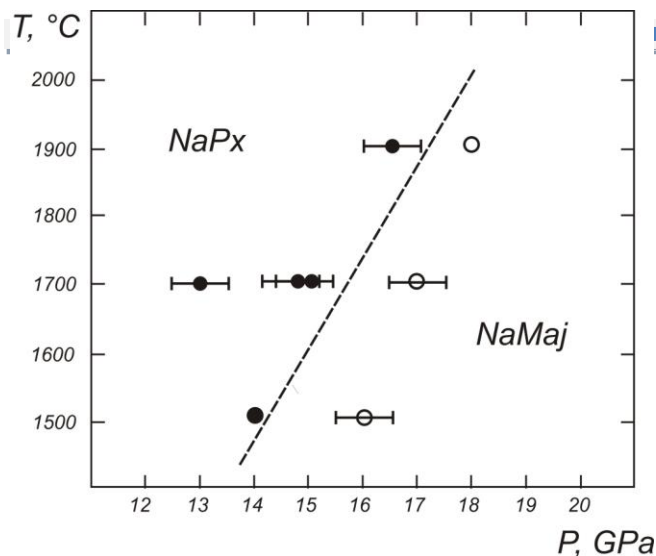
Fig.1 Phase diagram demonstrating stability of Na-pyroxene (full circles) and Na-garnet (empty circles) in the *P–T* coordinates. An accuracy of pressure measurement is indicated by horizontal bars. Dashed line illustrates the assumed phase boundary.

Structural patterns of garnets with the compositions between Na-majorite and pyrope (NaMaj$_{20}$, NaMaj$_{40}$, NaMaj$_{50}$, NaMaj$_{60}$ и NaMaj$_{80}$) were also studied using a Bruker-Enraf MACH3 single-crystal diffractometer. The results show that increase of NaMaj in starting material leads to gradual decrease of lattice parameter and, finally, change from cubic to tetragonal symmetry at NaMaj content of >80 %. It is important to note that the similar transformation was observed for pyrope-majorite join, which is evident from Fig. 2.
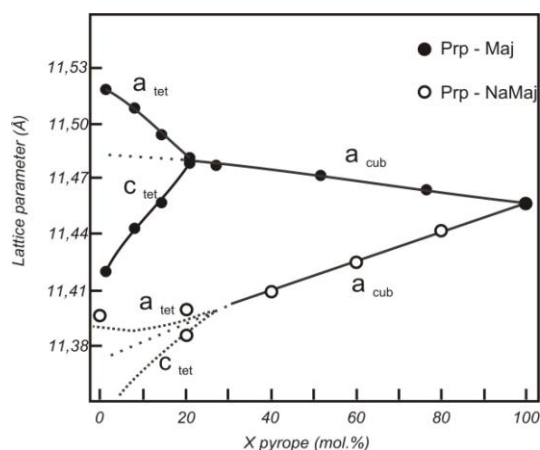

Fig. 2. Lattice parameters depending on the composition of synthetic garnets. Data for the pyrope-majorite system is taken from (Parise et al., 1996).

Experimental study at 11-20 GPa of the starting composition 50 mol.% NaMaj was aimed on investigation of a further tendency of sodium content increase in garnet with pressure. As a result of experiments, the following phase fields on the PT-diagram were obtained: the three-phase field of garnet plus two pyroxenes; the three-phase field of pyroxene plus garnet and stishovite; two-phase field of garnet solid solutions and stishovite. Field of a possible sodium-rich solid solution plus garnet may also occur at a pressure of >18 GPa Pyroxene of enstitite-jadeite composition was also registered among the run products together with garnet and stishovite at a pressure of 11-15 GPa. At a pressure of >16 GPa, pyroxene was not established in run products, and the portion of stishovite was the lowest (<5-7%) as well. The main phases synthesized in the experiments were garnet, clinopyroxene and stishovite (or coesite). Sodium rich phase were detected in the two experiments but because of the small fine grain size (5-10 µm) it was not possible to obtain good analyses. Melt was also detected in a few experiments by small La concentration in it (Fig. 3). With increasing pressure, the relative proportions of garnet solid solutions to pyroxene increased, which was also impacted in phase compositions. This also indicates the presence of the boundary between Grt plus Px field and Grt region. Representative analyses of observed phases are listed Table 1.

Garnets with the maximal Na$_2$O content (>5 wt.%) forming subidiomorphic crystals in a small amount of quenched melt (<5%) (Fig. 3) were registered at the assumed solidus of the system. Small phenocrysts (5-10 µm) of sodium-rich phase Na(Mg$_x$Si$_x$Al$_{1-2x}$)SiO$_4$ (0<x<0.5, MgO <3.8 wt %) along with Grt are observed in run products with decrease of temperature. This phase, apparently, corresponds to NaAlSiO$_4$ (with calcium ferrite structure) with a various content of MgAl$_2$O$_4$ component.
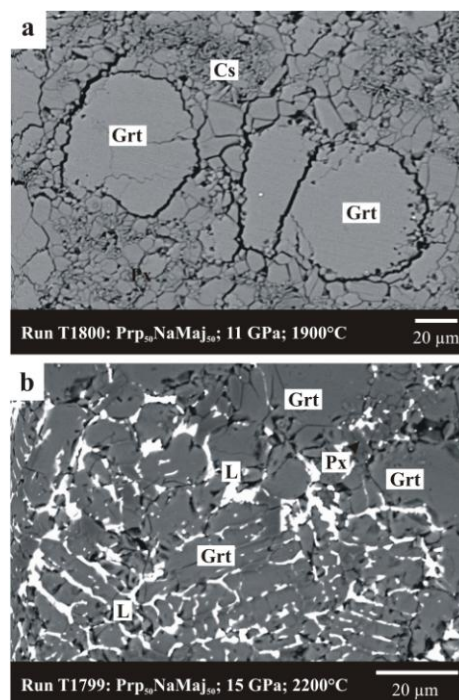

Fig. 3. BSE images of the samples obtained in experiments on the Prp$_{50}$– Na-majorite$_{50}$.

Table 1. Composition of garnets in the system $Mg_3Al_2Si_3O_{12}$– $Na_2MgSi_5O_{12}$

Run	T1800	ES-243	T1796	T1804
P, GPa	11	15	18	20
SiO_2	49.33	54.86	54.72	56.66
Al_2O_3	19.31	15.67	17.03	14.57
MgO	28.57	27.07	24.83	23.52
Na_2O	1.8	3.72	4.60	5.71
Total	99.01	101.33	100.00	100.46
Formula units				
Si	3.343	3.630	3.628	3.785
Al	1.542	1.222	1.330	1.147
Mg	2.884	2.668	2.452	2.340
Na	0.236	0.477	0.591	0.739
Total	8.005	7.997	8.002	8.011

As a result of the experiments, Na-bearing majorite garnets were synthesized in a wide range of temperatures and pressures, increase of sodium, silicon and, consequently, concentration of sodium majorite in garnets with pressure was observed (Fig. 4).
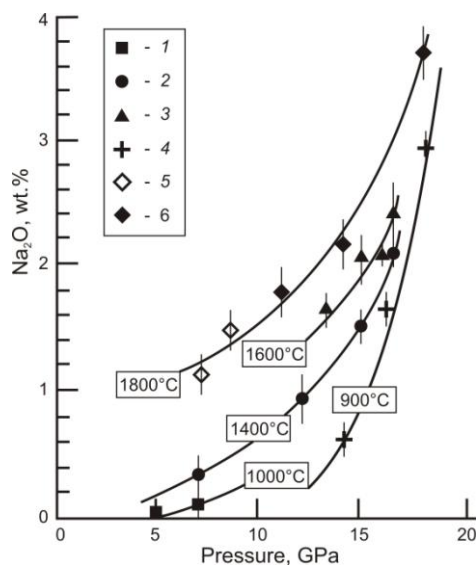

Fig. 4. Variation of Na_2O content in garnets, synthesized at different temperatures and pressures in eclogite system (Okamoto, Maruyama, 1998) (1), MORB (Ono, Yasuda, 1996) (2, 3), eclogite (Okamoto, Maruyama, 1998) (4), modeling system pyrope–$Na_2MgSi_5O_{12}$ (our data) at 7.0 and 8.5 GPa (Bobrov et al., 2008) (5) and 11−20 GPa (6). An accuracy of pressure measurement is indicated by vertical bars.

Presence of pyroxene (one more Na-bearing phase) at a number of experiments complicates the observed tendency in the garnet liquidus crystallization and leads to change of distribution coefficient of sodium between garnet and liquid. Nevertheless, as is evident from the results of our experiments, the solubility of Na-component in garnet in the studied system is observed at least up to 40 mol%, that
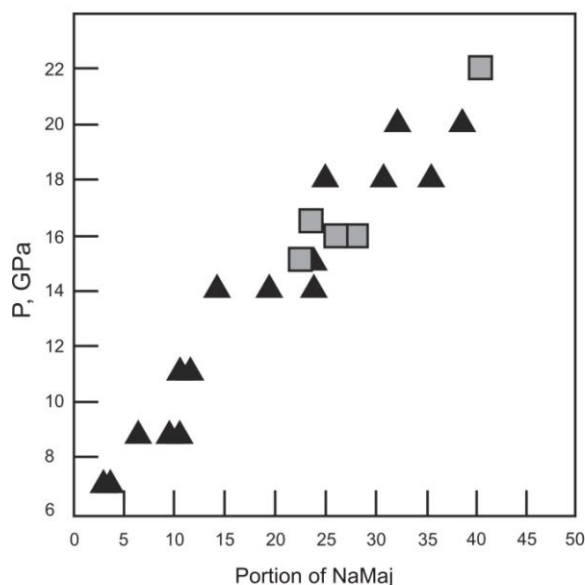
is in a good agreement with the forsterite-jadeite system (Table 1; Fig. 5) [Gasparik, Litvin, 1997].

Fig. 5. Solubility of $Na_2MgSi_5O_{12}$ in garnet with pressure in the system Prp_{50}–Na-majorite$_{50}$ (triangles) in comparison with the data (Gasparik, Litvin, 1997) (squares).

Significant solubility of Na-majorite in pyrope, as well as finds of natural garnets with the high concentration of Na (> 1 мас. % Na2O) allow us to consider that Na-bearing majoritic garnet can be an important potential sodium concentrator in the lower parts of the upper mantle and transition zone. The successful synthesis of the $Na_2MgSi_5O_{12}$ end-member and its structural characterization is of key importance, because the study of its thermodynamic constants combined with the data of computer modeling provide new constraints on thermobarometry of majorite garnet assemblages.

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