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Formation of Na-bearing majoritic garnets in the Na₂O-MgO-CaO-Al₂O₃-SiO₂ system under extreme conditions of 7—24 GPa and 1500—2000[•]C

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High-sodium eclogitic garnets associated with diamonds were revealed by Sobolev and Lavrent'ev (1971). Therewith the garnets from both diamond-bearing eclogite xenoliths and primary inclusions in diamonds contain 0.09 - 0.22 wt.% Na₂O. Mc-Candless and Gurney (1989) proposed to use a threshold of 0.09 wt.% Na₂O in garnet as a criterion for chemical classification of the Group I eclogites to which most diamond-bearing eclogites were found to belong. Majoritic garnets occur in peridotitic and eclogitic suites; and the garnets with Si contents over 3.07 per formula units (pfu) are mostly eclogitic. The most majoritic garnet from eclogite suite (3.429 pfu Si) is described for the Monastery kimberlite pipe by Moore and Gurney (1985). High-sodium majoritic garnets were reported for many localities of South Africa, Guinea, Russia, and China, (Stachel et al., 2000; Stachel, 2001). The majoritic garnet with the highest Na content (1.37 wt. % Na₂O) is described in association with K-rich (1.44 wt.% K₂O) clinopyroxene for the Kankan region of Guinea, West Africa.

For the upper mantle and transition zone mineral assemblages, majorite garnet appears to be the only reliable pressure/depth indicator. With increasing pressure, garnet with $\sim 3\text{Si}^{4+}$ atoms pfu becomes progressively depleted in Al and enriched in Si, M^{2+} (Ca,Mg,Fe)²⁺ cations, and Na⁺. Most of the Na present in majoritic garnet is accommodated via the pressure dependent exchange reaction Na⁺+ Si⁴⁺ = M²⁺+ Al³⁺. Using the Si content of majorite, the pressures of majorite inclusions formation ranging from 7.5 to ~ 16 GPa was estimated (Stachel, 2001). Collerson et al. (2000) described garnetite and rare garnet peridotite xenoliths that contain majoritic and other

ultrahigh-pressure mantle assemblages in alnöite pipes on the island of Malaita, southwest Pacific, suggesting the pressure-depth interval for the rock formation from 9.5 GPa (260 km) to 22 GPa (570 km).

Our experiments were aimed on the study of the compositional range of pyropic and majoritic garnet and simulation of some mineral assemblages primarily included in diamonds under the conditions of deeper upper mantle and transitional zone.

Experiments at 7—8.5 GPa and 1500—2000°C on the Mg₃Al₂Si₃O₁₂ (Prp)— Na₂MgSi₅O₁₂ join were carried out in the Institute of Experimental Mineralogy, Russian Academy of Sciences, using the high-pressure toroidal anvil-with-hole apparatus and aimed on the evaluation of the lower pressure limit of Na-majorite formation. According to our experiments at 7 GPa, garnet is associated with Na-pyroxene of jadeite-clinoenstatite composition and replaced by MgSiO₃ enstatite + SiO₂ coesite + Na₂Si₄O₉ assemblage in the Na-rich part of the system (more than 30 mol.% Na₂MgSi₅O₁₂). Above 1700°C we obtained porphyric garnet crystals in Si- and Narich quenched aggregate. At 8.5 GPa the solidus temperature was estimated to be ~1800°C. Garnets at 7 GPa usually contain Na (up to 0.061 pfu) and extra Si (up to 3.102 Si pfu). The highest sodium and silicon contents were estimated in garnets synthesized at 8.5 GPa and 1840°C (3.235 Si pfu, 47.89 wt.% SiO₂; 0.142 Na pfu, 1.09 wt.% Na₂O). Such concentrations are similar to those estimated in natural majoritic garnets included in diamond crystals from kimberlites.

Experiments at 12–24 GPa and 1600°C were performed on the CaMgSi₂O₆(Di) -CaFeSi₂O₆(Hd) -NaAlSi₂O₆ (Jd) join by using a Kawai-type 6-8 multi-anvil high-pressure apparatus in Gakushuin University (Bobrov et al., 2007). Majoritic garnet first appears at 13.5 GPa in jadeite-rich part of the system ($Di_{30}Jd_{70}$), whereas diopside-rich starting material (Di₇₀Jd₃₀) produces garnet only above 17 GPa. The proportion of garnet increases rapidly above 18 GPa as pyroxene dissolves in the garnet structure and pyroxene-free garnetites are produced from diopside-rich starting materials. Garnet in all experiments is accompanied by stishovite (St); Di₇₀Jd₃₀ and $Di_{50}Jd_{50}$ starting materials also produce CaSiO₃ with perovskite structure (Ca-Pv). At a pressure above 18 GPa pyroxene is completely replaced by an assemblage of majorite (Maj) + St + Ca-Pv in Ca-rich systems, whereas Maj is associated with almost pure Jd up to a pressure of 21.5 GPa. Above \sim 22 GPa, Maj and St are associated with NaAlSiO₄ with calcium ferrite structure (Cf). In the Di₇₀Jd₃₀ system at 24 GPa an assemblage of Maj+Ca-Pv+MgSiO₃ with ilmenite structure (Mg-II) was obtained. The most majoritic garnet containing 3.619 Si pfu and 0.613 Na pfu was observed in association with Ca-Pv at 24 GPa and 1600°C. Our experiments suggest the correlation between Na, Si, Al contents and pressure. Incorporation of Na in majorite may be illustrated by the following reaction with shift to the right with pressure resulting in the appearance of Na-rich garnet and CaSiO₃ perovskite:

 $4CaMgSi_2O_6 \quad \cdot \ 2NaAlSi_2O_6 = 4CaSiO_3 + (Mg_3Al_2Si_3O_{12} + Na_2MgSi_5O_{12}).$

Cpx Ca-Pv Maj

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