

## Na-rich majoritic garnets: high-pressure experiments and application for UHP diamond genesis

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### Introduction

Data on the composition of deep-seated rocks and minerals are commonly used to justify the models of chemical composition and structure of deep zones of the Earth. Of particular interest are mineral assemblages with majoritic garnet, for which ultrahigh-pressure crystallization in deep upper mantle and transition zone is supposed and approaches for P and T estimation with account for garnet composition are developed (Akaogi, Akimoto, 1977; Irifune, 1987). Garnets included in diamonds are characterized by a stable sodium admixture (0.09–0.22 wt.% Na<sub>2</sub>O) providing evidence for a link between high concentration of this element and pressure. This is proved by finds of majoritic garnets containing >1 wt.% Na<sub>2</sub>O (Stachel, 2001). Garnet inclusions with extreme majoritic content were described in diamond from Helam Mine (South Africa). The concentration of Si in these garnets is high and reaches 3.5 f.u.; Na content gains 1.08 wt.%. Another E-type Na-bearing majoritic garnet was found in Monastery kimberlite; it contained 3.429 f.u. Si at a very low Al concentration (1.3–1.6 f.u.) (Moore, Gurney, 1985). Of special interest is the find of diamond in Guinea, in which along with garnet inclusion containing 1.37 wt.% Na<sub>2</sub>O K-rich clinopyroxene (1.44 wt.% K<sub>2</sub>O) was observed; that is an indicator of pressure above 6 GPa. These data specify high alkalinity of melts from which diamonds with such inclusions may crystallize; that is proved by finds of diamond crystals with syngenetic fluid inclusions having a wide range of compositions from water-silicate to alkaline-carbonate and chloride (Klein-BenDavid et al., 2007).

The present work summarizes the results of experimental study of two systems: pyrope Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> (Prp)–Na<sub>2</sub>MgSi<sub>5</sub>O<sub>12</sub> (NaGrt) modeling the sodium-bearing garnet solid solutions and pyrope–jadeite NaAlSi<sub>2</sub>O<sub>6</sub> (Jd), that is a simplified model of eclogite composition. Both systems are characterized by a high alkalinity with up to 13.5 mol.% of modal nepheline. Our experiments were aimed on the reconstruction of mechanism of high-pressure Na incorporation in garnets and PT-conditions of their formation.

Experiments were carried out at P = 7.0 and 8.5 GPa and T = 1300–1800°C using toroidal “anvil-with-hole” apparatus in the Institute of Experimental Mineralogy, Russian Academy of Sciences. Stoichiometric gels of pyrope, jadeite, and Na<sub>2</sub>MgSi<sub>5</sub>O<sub>12</sub> compositions mixed in desired mole proportions were used as starting materials.

### Pyrope–NaGrt system

The pseudo-binary system Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>–Na<sub>2</sub>MgSi<sub>5</sub>O<sub>12</sub> has been studied at 7 and 8.5 GPa and 1500–1950°C. The Na-bearing garnet is a liquidus phase of the system up to 60 mol% Na<sub>2</sub>MgSi<sub>5</sub>O<sub>12</sub> (NaGrt) (Fig. 1). At higher content of NaGrt in the system (>80 mol.%), enstatite (En) and coesite (Cs) are observed as liquidus phases (Fig. 2). Our experiments provided evidence for a stable sodium incorporation in Grt (0.3–0.6 wt% Na<sub>2</sub>O) and its control by temperature and pressure. The highest sodium contents were obtained in experiments at P = 8.5 GPa. Near the liquidus (T = 1840°C), the equilibrium concentration of Na-component in Grt is 5 mol% Na<sub>2</sub>MgSi<sub>5</sub>O<sub>12</sub>. With the temperature decrease, Na concentration in Grt increases, and the maximal Na<sub>2</sub>MgSi<sub>5</sub>O<sub>12</sub> content of 12 mol% (1.52 wt% Na<sub>2</sub>O) is gained at the solidus of the system (T = 1760°C).

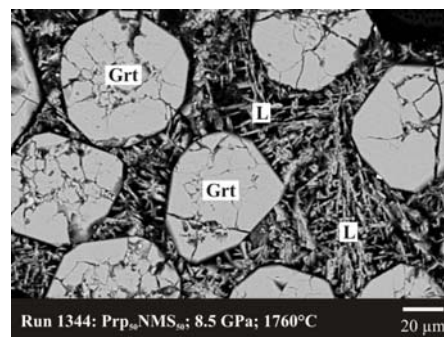


Fig. 1 BEI of porphyritic Na-rich garnet crystals in quenched groundmass synthesized in pyrope–NaGrt system at P=8.5 GPa and T=1760°C.

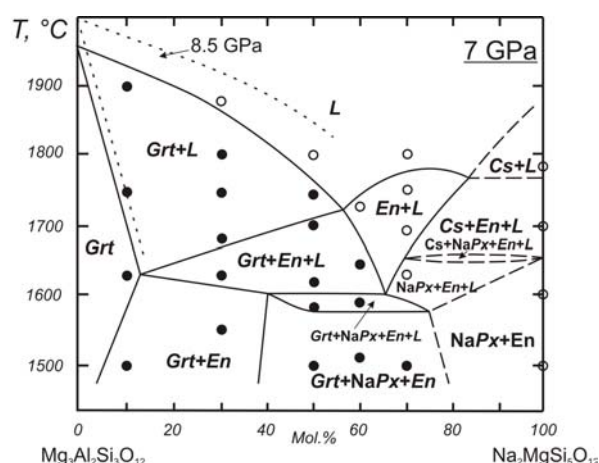


Fig. 2 Scheme of melting relations for the pseudo-binary system  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ – $\text{Na}_2\text{MgSi}_5\text{O}_{12}$  at 7 GPa. Dotted line indicates the position of subliquidus area Grt + L at 8.5 GPa. Full circles denote garnet-bearing mineral associations; empty circles denote garnet-free parageneses.

The unit-cell values for the NaGrt crystals investigated [ $a = 11.456$ ] are almost the same with respect to those observed for pure pyrope [ $a = 11.454$ , e.g., (Hazen and Finger 1978)]. The X site is always slightly larger (due to the entry of Na) and the Y site slightly smaller, because the effect of the substitution Si for Al is stronger in comparison to the Mg for Al substitution. These results verify the pressure dependent exchange reaction  $\text{Na}^+ + \text{Si}^{4+} = \text{M}^{2+} + \text{Al}^{3+}$  assumed in Na-bearing garnets on the base of the experiments (Bobrov et al., 2008).

### Pyrope–jadeite system

Experimental study of pyrope–jadeite system was carried out at  $P = 7.0$  and  $8.5$  GPa. Fig. 3 shows conditions of experiments and scheme of melting relations in the  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ – $\text{NaAlSi}_2\text{O}_6$  system at a pressure of 7 GPa within a temperature range of 1300–1800°C. The studied system should be considered as pseudo-binary, because Na is incorporated in garnet as  $\text{Na}_2\text{MgSi}_5\text{O}_{12}$  (Bobrov et al., 2008) and pyroxene forms jadeite–enstatite (En) solid solutions with Eskola (Esk)  $\text{Mg}_{0.5}\text{AlSi}_2\text{O}_6$  component. Main phases obtained in experiments were garnet, pyroxene, kyanite (sometimes corundum) and quenched melt. Complete melting of the system was observed at a temperature of  $>1900^\circ\text{C}$ . Glass was not observed in the system; the presence of melt was diagnosed by a fine-grained mass of skeletal pyroxene crystals. In pyrope-rich part of the system, we also observed garnet among products of quenching.

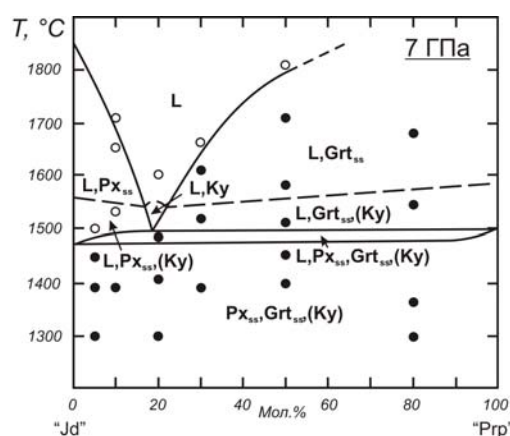


Fig. 3 Scheme of melting relations in the system pyrope  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ –jadeite  $\text{NaAlSi}_2\text{O}_6$  at 7.0 GPa. “Jd” is the solid solution of jadeite, enstatite, and Eskola molecule; “Prp” is the solid solution of pyrope, majorite, and  $\text{Na}_2\text{MgSi}_5\text{O}_{12}$ .

Liquidus garnet appeared at a temperature  $<1800^\circ\text{C}$  in a wide range of starting compositions of the system (20–100 mol.% Prp) forming transparent colorless crystals with sizes of 10–150  $\mu\text{m}$  (Fig. 4). The decrease of temperature results in the regular decrease of crystal sizes and growth of the amount of crystallization centers up to the formation of massive aggregates on the solidus of the system. The decrease of temperature to  $\sim 1550^\circ\text{C}$  leads to the formation of kyanite in groundmass together with garnet. All synthesized garnets are characterized by a stable  $\text{Na}_2\text{O}$  admixture (up to 0.8 wt.% at 8.5 GPa and up to 0.6 wt.% at 7 GPa) and elevated Si concentration (up to 3.128 f.u.). At near-eutectic temperatures ( $\sim 1500^\circ\text{C}$ ) garnet becomes progressively enriched in  $\text{Na}_2\text{MgSi}_5\text{O}_{12}$  and majorite  $\text{Mg}_4\text{Si}_4\text{O}_{12}$ . Residual melt accumulates and Al that is confirmed by the data on partition coefficients of different elements between garnet and melt (Table). Garnets crystallizing from near-eutectic starting materials ( $\text{Prp}_{20}\text{Jd}_{80}$ ) are the most sodium-rich. This fact indicates the influence of melt alkalinity on the formation of Na-bearing majoritic garnets.

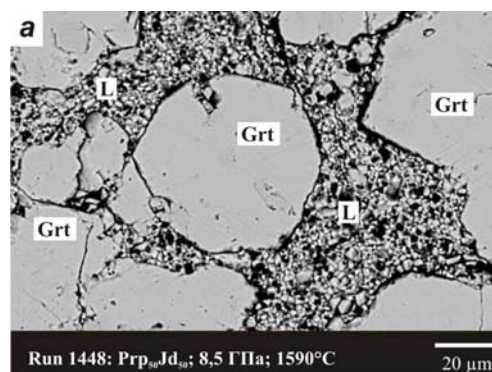


Fig. 4 BEI of porphyritic Na-rich garnet crystals in quenched groundmass synthesized in pyrope–jadeite system at  $P=8.5$  GPa and  $T=1590^\circ\text{C}$ .

Jadeite-rich starting materials (80–100 mol.% Jd) produce pyroxene (Jd–En–Esk) in equilibrium with

melt. Significant concentrations of Esk molecule (~ 20 mol.%) were observed only in jadeite-rich pyroxenes. Such pyroxenes were found in natural kyanite eclogites. In our experiments high-Al phases (kyanite and corundum) were obtained as accessory minerals with contents of <5%.

Table. Partition coefficients ( $K_p$ ) of Na, Si, and Al between garnet and melt in Prp–NaGrt and Prp–Jd at different temperatures

System	Temp., °C	$K_p(\text{Na})$	$K_p(\text{Si})$	$K_p(\text{Al})$
Prp–NaGrt	1840	0.057	0.631	12.993
	1800	0.068	0.640	11.814
	1760	0.111	0.648	8.127
Prp–Jd	1810	0.031	0.892	0.989
	1730	0.047	0.885	0.982
	1590	0.105	0.919	0.849

## Conclusions

The results obtained for both studied systems demonstrate impossibility of Na incorporation in garnet directly as jadeite component and show that Na is incorporated in garnet as  $\text{Na}_2\text{MgSi}_5\text{O}_{12}$  component independently on the starting composition of the system (Fig. 5). Thus, mechanism of the formation of Na-bearing majoritic garnets suggested by Sobolev and Lavrent'ev (Sobolev, Lavrent'ev, 1971) and experimentally simulated by Bobrov et al. (2008) was confirmed.

The crystallization of Na-bearing garnets is mainly controlled by temperature, pressure, and composition of the system. The increase of Na concentration in garnet at given PT-parameters may result only from the increase of melt alkalinity. The increase of pressure causes only the growth of melting temperature and regular increase of Na content in garnet.

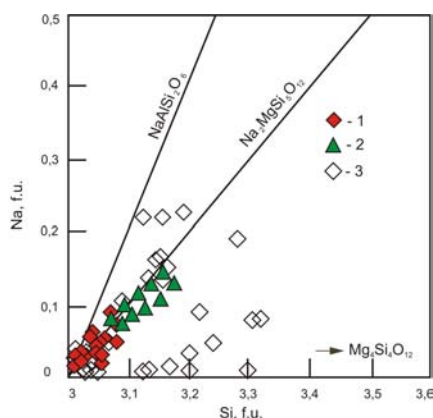


Fig. 5 Compositions of Na-bearing majoritic garnets. (1) Prp–Jd system; (2) Prp– $\text{Na}_2\text{MgSi}_5\text{O}_{12}$  system; (3) inclusions in natural diamonds worldwide.

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