

**CaMgSi₂O₆–CaFeSi₂O₆–NaAlSi₂O₆ join at 7–24 GPa and 1600–2250°C:
Modeling of mineral assemblages of the upper mantle and transition zone**
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The diopside–hedenbergite–jadeite join traditionally arises interest of petrologists because omphacite is the main component of eclogites, the high-pressure metamorphic products of basalts. Eclogite minerals are also widely abundant among inclusions in natural diamonds from kimberlites and lamproites. Mineral inclusions in diamond are generally interpreted to yield a record of phase relations at depths of 150 to 200 km, equivalent to pressures of ~5.5 to 7 GPa. Over the last two decades, rare diamonds derived from even greater depths—the deep upper mantle, the transition zone (410–660 km), and the lower mantle—have been recognized [1]. These diamonds contain ultrahigh-pressure mineral assemblages of majorite, CaSiO₃ and MgSiO₃ perovskite, ferropericlase, and magnesio-wustite. From the Na–Si-rich majorite garnet record, the deeper upper mantle and transition zone should contain a layer with eclogitic composition that is inconsistent with the model of homogeneous, highly dynamic Earth made of pyrolite [2]. To study the precise boundary of the pyroxene–garnet transition versus the pyroxene composition and estimate the role of CaFeSi₂O₆ hedenbergite for high-pressure phase relations in the eclogite systems, new experiments were carried out on the CaMgSi₂O₆–CaFeSi₂O₆–NaAlSi₂O₆ join at 7–24 and 1600–2250°C.

Phase relations on the diopside (Di) – hedenbergite (Hd) – jadeite (Jd) system modeling mineral associations of natural eclogites were studied for the compositions (mol.%) Di₇₀Jd₃₀, Di₅₀Jd₅₀, Di₃₀Jd₇₀, Di₂₀Hd₂₀ и Di₄₀Hd₁₀Jd₅₀ in the Institute of Experimental Mineralogy using anvil-with-hole Bridgman-type apparatus (7 GPa) and in the Gakushuin University with split-cylinder type 8 multi-anvil high-pressure apparatus (12–24 GPa).

The phase diagram for the diopside–jadeite join at 7 GPa is shown in Fig. 1 and based primarily on the melting temperatures of end members determined in this study. At 1980°C (run 1058) we observed aggregate of acicular diopside crystals, which were interpreted as products of melt quenching. Homogeneous transparent jadeite glass was obtained at 1870°C (run 1073), indicating that complete melting above the liquidus had been attained. In all samples of intermediate compositions at high temperatures we observed dendritic clinopyroxene crystals providing evidence for complete melting (runs 1125, 1126, 1037, 1091, and 1079). The mentioned experiments allowed us to plot the liquidus line, below which we obtained clinopyroxene porphyric grains with a size of 20–50 μm in Si-rich glass or aggregate of skeleton quenched crystals. Clinopyroxene porphyric crystals are enriched in diopside component and show a notable excess of CaAl₂SiO₆ Ca-Tschermack pyroxene and Mg₂Si₂O₆ clinoenstatite relatively to starting pyroxene compositions Di₇₀Jd₃₀ (run 1093), Di₅₀Jd₅₀ (run 1042), and Di₃₀Jd₇₀ (run 1077). The analyzed interstitial glasses are Si-rich and also have a small excess of Na, so that the studied Di–Jd system may be considered as pseudobinary.

Thus, melting relations on the Di–Jd join at 7 GPa are characterized by complete series of solid and solutions. Preliminary experiments on the iron-containing clinopyroxene systems Di₈₀Hd₂₀ and Di₄₀Hd₁₀Jd₅₀ demonstrate that the addition of CaFeSi₂O₆ hedenbergite does not change complete solubility of pyroxene components at 7 GPa, but decreases the temperature of pyroxene melting down to 1790°C for Di₈₀Hd₂₀ and 1820°C for Di₄₀Hd₁₀Jd₅₀ solid solutions.

Phase relations for CaMgSi₂O₆–NaAlSi₂O₆ join at 1600°C and 12–24 GPa are illustrated in Fig. 2. Only clinopyroxene CaMgSi₂O₆–NaAlSi₂O₆ (Cpx_{ss}) is stable at pressure below 13 GPa, at which it dissociates into an assemblage of garnet (Grt) and stishovite (St). The appearance of garnet (majorite) is dependent on initial clinopyroxene composition: first garnet crystals are observed at 13.5 GPa in jadeite-rich part of the system (Di₃₀Jd₇₀), 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. The appearance of garnet is always accompanied by stishovite. Diopside-rich systems (Di₇₀Jd₃₀, Di₅₀Jd₅₀) above 18.5 GPa always contain CaSiO₃ (non-quenchable phase of presumably perovskite structure, Ca-Pv) associating with Grt and St, which are the products of pyroxene dissociation at ~18 GPa. At 24 GPa in the Di₇₀Jd₃₀ sample we obtained Grt, Ca-Pv, St, and MgSiO₃ ilmenite (Mg-Il) that is a product of further Grt dissociation.

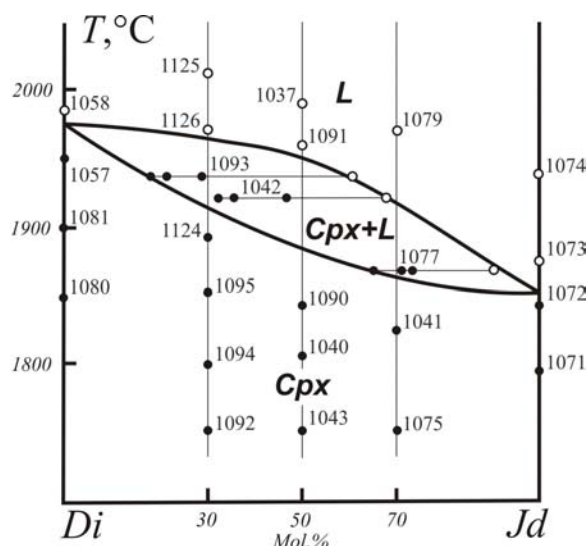


Fig.1. T - X phase diagram for the system $\text{CaMgSi}_2\text{O}_6$ — $\text{NaAlSi}_2\text{O}_6$ at 7 GPa. Full circles denote experimentally established clinopyroxene compositions; empty circles indicate melt compositions; co-existing clinopyroxenes and melts are connected by connodes.

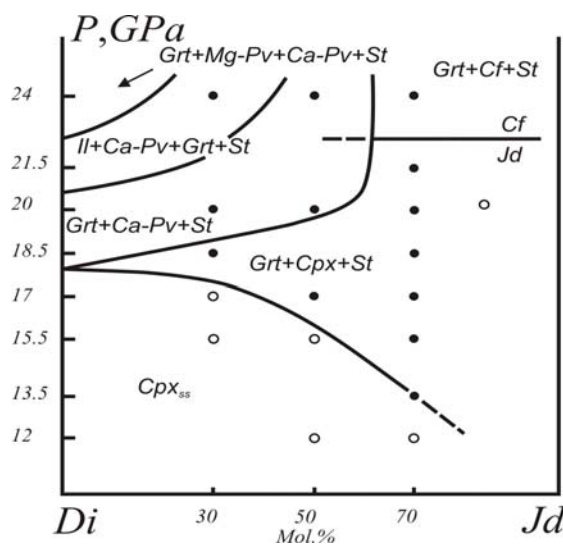


Fig.2. Schematic P - X phase diagram for the system $\text{CaMgSi}_2\text{O}_6$ — $\text{NaAlSi}_2\text{O}_6$ at 1600°C. Full circles indicate garnet-containing mineral assemblages; empty circles indicate garnet-free associations.

The composition of coexisting clinopyroxene and garnet at 13.5—21.5 GPa and 1600°C are strongly dependent on pressure. The Jd content of pyroxene grows with increasing pressure, reaching the maximum of 95 mol.% $\text{NaAlSi}_2\text{O}_6$ at 21.5 GPa for the $\text{Di}_{30}\text{Jd}_{70}$ starting material. Jadeitic omphacite is stable to greater pressures than Di-rich mineral and transforms to NaAlSiO_4 + St at ~22 GPa. NaAlSiO_4 has calcium ferrite structure (Cf) and contains up to 20 mol. % MgAl_2O_4 component. Several experiments were performed to evaluate the effect of pressure on the majorite composition. With increasing pressure, garnet with ~3 Si^{4+} atoms pfu becomes progressively depleted in Al and enriched in Si (up to 3.619 Si^{4+} pfu) and Na (up to 0.735 Na^+ pfu), so that the contents of enstatite and Na pyroxene increase.

Experiments with Fe-containing starting materials ($\text{Di}_{80}\text{Hd}_{20}$ and $\text{Di}_{40}\text{Hd}_{10}\text{Jd}_{50}$) demonstrate that Grt is stable at 15.5 GPa in Jd-rich system associating with St and Cpx. At a higher pressure of 20 GPa, Cpx is absent and Grt exsolves Ca-Pv. Jd-free starting composition ($\text{Di}_{80}\text{Hd}_{20}$) produces Cpx in association with Grt, Ca-Pv, and St, that provides evidence for stabilizing influence of $\text{CaFeSi}_2\text{O}_6$ (as well as Jd) on pyroxene structure. At 24 GPa Grt partly dissociates into Ca-Pv and Mg-Il.

Results of our experiments are applicable to transitional zone of the Earth (410—660 km) demonstrating a wide range of transition from eclogite to garnetite. In addition, mineral associations obtained model paragenesis of inclusions in diamonds formed under the conditions of transitional zone and lower mantle.

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