

# MELTING EXPERIMENTS ON THE JOIN DIOPSIDE-MAGNESITE AT 7 GPa AND THEIR BEARING ON THE GENESIS OF KIMBERLITE MAGMAS

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The presence of volatile components such as H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> play a major role in petrogenetic processes in the Earth's mantle. The transport of volatile components in the mantle is dominated by the migration of "fluid" (volatile-rich melts or low-density supercritical fluids) thought to be highly enriched in K, Rb, and other elements incompatible with mantle peridotites and eclogites. It is widely accepted that mantle metasomatism and diamond genesis have been associated with the presence of carbon-rich kimberlitic melts. Melting relationships in the quaternary system forsterite-diopside-enstatite-magnesite, closely approximate those of a carbonated mantle, and are important to an understanding of the generation of kimberlitic and carbonatitic magmas. Experimental data for a carbonated mantle at pressure greater than 5 GPa is limited. In the system enstatite-magnesite at 8 GPa, Katsura and Ito (1990) found that the liquidus boundary between the enstatite and magnesite fields occurs at 59 wt.% magnesite. In the system forsterite-enstatite-magnesite at 9 GPa, Hirayama and Fujii (1995) found that the melt composition in equilibrium with forsterite, enstatite and magnesite contains 45 wt.% CO<sub>2</sub> and 20 wt.% SiO<sub>2</sub>. Melting experiments in simplified peridotite + CO<sub>2</sub> system by Canil and Scarfe (1990) indicate that kimberlite magmas could be derived by partial melting of carbonated peridotite at 5 to 7 GPa, but melt compositions above 7 GPa are more Mg-rich than any kimberlite compositions.

In order to extend these data and more toward a better understanding of phase relationships in the quaternary system CaO-MgO-SiO<sub>2</sub>-CO<sub>2</sub>, we have studied melting relationships on the join diopside-magnesite at 7 GPa using a multianvil apparatus at the University of Texas at Dallas. The octahedrons used were made of 95% MgO and 5% Cr<sub>2</sub>O<sub>3</sub>. All experiments were carried out with an octahedron of 18 mm edge length, WC cubes with 11 mm truncation, a W3Re/W26Re thermocouple positioned axially and directly above the capsule, a stepped graphite heater, and a welded Pt sample capsule. Temperatures were not corrected for the effect of pressure on thermocouple emf. To remove water, the octahedron assembly, except for the sample capsule, was preheated for 1 hour at 1000°C. The sample capsule was heated for 24 hours at 180°C immediately prior to sealing by welding. The sealed sample capsule was then loaded into the octahedron assembly and the entire assembly heated again at 180°C for 24 hours. The pressure calibration at high temperature is based on the melting point of CaMgSi<sub>2</sub>O<sub>6</sub> at 2.5 and 5.0 GPa (Boyd and England, 1963), the quartz/coesite transition at 3.0 GPa (Bohlen and Boettcher, 1982), and the garnet/perovskite transition of CaGeO<sub>3</sub> at 6.0 GPa (Susaki et al., 1985). The starting materials were prepared from gem quality natural magnesite (Young, NSW, Australia) and synthetic crystalline diopside. The capsule was

subhorizontally placed to minimize gravitational settling of crystalline phases. Melting experiments of synthetic diopside at various temperatures indicate a temperature variation within the sample capsule of about 20-30°C.

The liquid portions of the run-products were composed of fine-grained dendritic quench-crystal aggregates. The quench phases were dolomitic carbonate and diopsidic pyroxene showing a feathery texture readily distinguished from the euhedral primary phases. The liquid compositions were determined by electron microprobe analyses on the quench-crystal aggregates using a defocused beam. The primary clinopyroxene at a given starting composition exhibits a systematic increase of the Mg/(Mg+Ca) ratio with increasing temperature, which suggests that the primary clinopyroxenes reached equilibrium. The primary enstatite and magnesite also exhibit a narrow but systematic compositional variation with temperature.

The liquidus temperature for magnesite and the solidus temperature for magnesite + enstatite assemblage were determined at 2000°C and 1680°C respectively (Fig. 1), values that are consistent with the results on the enstatite-magnesite join by Katsura and Ito (1990). The enstatite and forsterite liquidus fields cross the join diopside-magnesite and create a boundary between the diopside and enstatite fields at roughly 41 wt.% magnesite, a boundary between the enstatite and forsterite fields at roughly 71 wt.% magnesite, and a boundary between forsterite and magnesite fields at roughly 82 wt.% magnesite (Fig. 1).

The solidus for diopside + magnesite is located at about 1425°C. Liquid in the run-products above 1600°C exhibit a systematic shift toward CO<sub>2</sub>-rich and SiO<sub>2</sub>-poor compositions as crystallization proceeds. An extremely small amount of quench crystal aggregate (after liquid) exists in runs at 1450 and 1500°C but its composition could not be directly determined by electron microprobe. Chemographic analysis, however, suggests that the minimum melt composition in equilibrium with forsterite, enstatite, diopside, and magnesite is characterized by moderate Mg/(Mg+Ca) ratio (0.55), very high CO<sub>2</sub> (> 50 wt.%) and low SiO<sub>2</sub> (<2 wt.%) as shown in Fig. 2. This melt composition lies outside the forsterite-enstatite-diopside-magnesite tetrahedron, which implies that a peridotitic mantle containing magnesite melts incongruently at 7 GPa to form a carbonatitic initial melt (Fig. 3).

Our results are consistent with the data on melting of natural group II kimberlite compositions (Yamashita et al., 1993, this volume) which show that phlogopite is no longer a stable phase above 6.5 GPa and extremely CO<sub>2</sub>- and K<sub>2</sub>O-enriched and SiO<sub>2</sub>-poor melts can be in equilibrium with garnet peridotite at pressure above 6.5 GPa. Navon et al., (1988) showed that melt (or fluid) inclusions in cubic diamonds are enriched in CO<sub>2</sub> and H<sub>2</sub>O, and contain appreciable amounts of K<sub>2</sub>O, SiO<sub>2</sub>, CaO and other oxides, compositions that are broadly similar to kimberlite and lamproite compositions. A genetic link between such carbon-rich kimberlitic melts and diamond was experimentally suggested by Arima et al., (1993, this volume), who demonstrated that diamonds crystallize and grow in carbon-rich kimberlite melts at 7-7.7 GPa and 1800-2200°C. Upward migration of such carbon-

rich kimberlitic melts might result in diamond formation and mantle metasomatism in the subcratonic lithosphere.

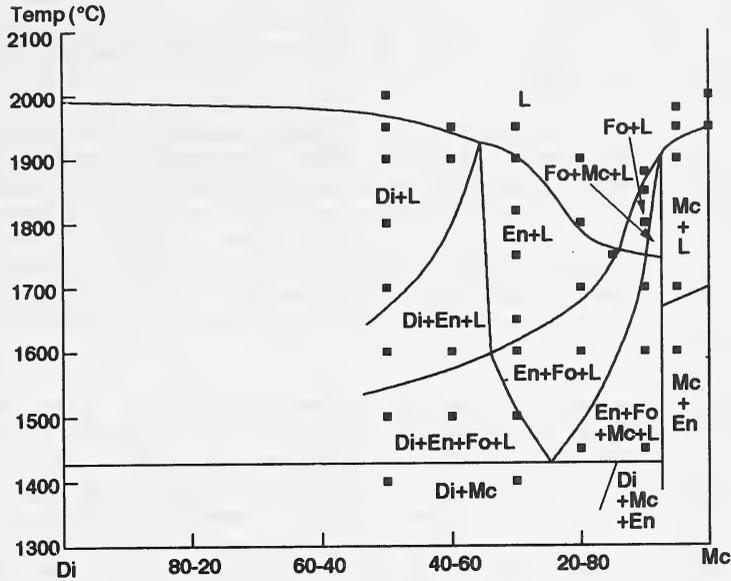


Fig. 1. Phase relationships for the join of diopside and magnesite at 7.0 GPa. The melting temperature of diopside at 7 GPa is estimated by the extrapolating the data of Boyd and England (1963) using the Simon equation given by them.

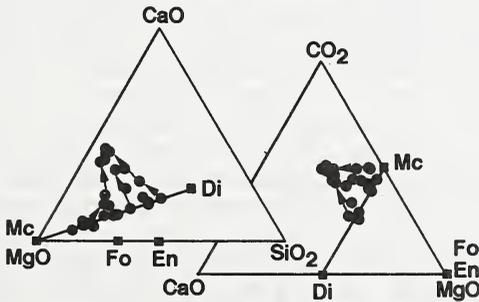


Fig. 2. Liquid compositions in runs above 1600°C plotted in terms of CaO-MgO-SiO<sub>2</sub> (left) and CO<sub>2</sub>-CaO-MgO (right).

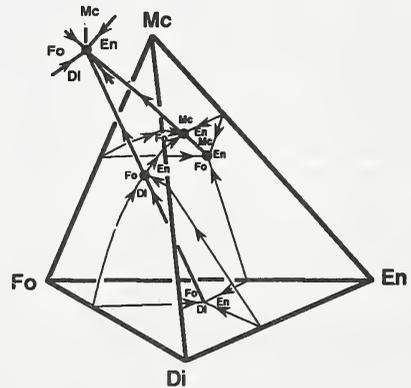


Fig. 3. Schematic diagram showing liquidus phase relationships in the system Fo-En-Di-Mc. The invariant point (I) where liquid coexists with Fo, En, Di and Mc lies outside of the tetrahedron.