

## Experimental melting of magnesite-bearing peridotite with H<sub>2</sub>O and F at 6-10 GPa, and implications for the genesis of kimberlites

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Minor amounts of C may have a profound effect on the melting of mantle peridotites. Previous experimental studies in simple and complex systems showed that the presence of carbonate phases strongly depresses the solidus of mantle peridotite at pressures >3 GPa (e.g. Wyllie & Huang, 1976; Dasgupta & Hirschmann, 2006). The composition of low-degree melts changes from dolomitic to kimberlite-like with increasing temperature (e.g. Wallace & Green, 1988; Dalton & Presnall, 1998). Therefore, experimental studies of CO<sub>2</sub>-bearing mantle systems may have intriguing applications for mantle metasomatism and origin of primary carbonatite and kimberlite melts. In addition to CO<sub>2</sub>, the low-degree melts in the upper mantle probably contain considerable amounts of other volatile and incompatible elements. This study focuses on the influence of water and fluorine on the melting of magnesite-bearing mantle peridotite and is an extension of our previous experiments in the peridotite-CO<sub>2</sub> system (Brey et al., 2008, hereafter B08).

### Methods

Experiments were carried out at 6 and 10 GPa, 1100-1600°C in a Walker-type multianvil apparatus. Starting materials were mixtures of natural peridotite minerals with 10-20% of magnesite and either natural fluorite or hydrous Mg-carbonate. The starting material was loaded into a container machined from monocrystalline San Carlos olivine and sealed in a Pt capsule. During the experiment a carbonate-rich melt is formed within the central peridotite zone and migrates outside the olivine container to collect near the wall of the Pt capsule (Fig. 1).

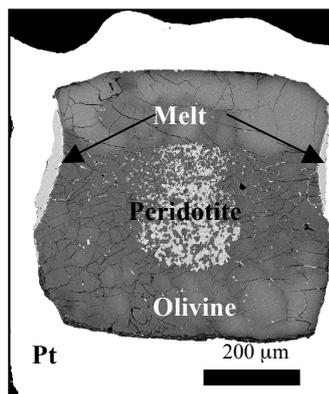


Fig. 1: BSE image of a 10 GPa/1500°C run. The melt is collected between olivine and Pt. Variations in the composition of the olivine container are related to variable degrees of Fe loss to Pt (light areas correspond to olivine unaffected by Fe loss).

The quenched melt pool is isolated from the peridotite matrix and can be readily analyzed with a defocused beam by electron microprobe. The experimental approach is discussed in detail in B08. In particular, equilibrium between melt and peridotite material was confirmed by (i) time series experiments and (ii) identity of mineral compositions in the peridotite and those occasionally grown in the melt pool. In the present experiments, interstitial melt was sometimes preserved in the peridotite material and in the olivine container (Fig. 2), and electron microprobe analysis revealed convergence of melt compositions within and outside the olivine container. This provides additional support to fast mass transfer in a peridotite matrix with carbonate melt films.

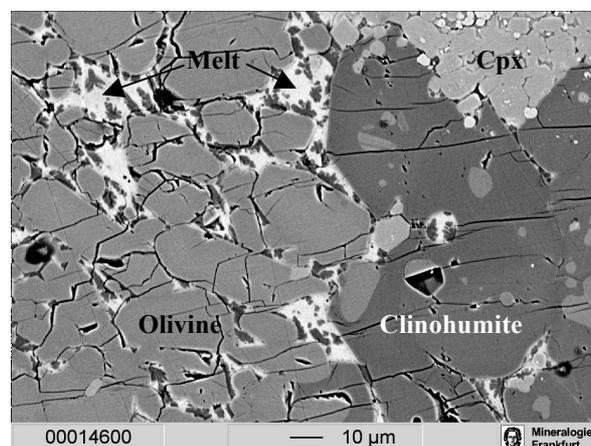


Fig. 2. BSE image of interstitial quenched melt in the olivine capsule and near peridotite material in an experiment in the peridotite-carbonate-fluoride system at 6 GPa, 1200°C.

### Results

The addition of both H<sub>2</sub>O and F strongly depresses the solidus of magnesite-bearing peridotite (Fig. 3) by more than 100 °C at 6 GPa and more than 300 °C at 10 GPa. The near-solidus phase assemblages include olivine+high-Ca-pyroxene+low-Ca-pyroxene+garnet+magnesite. No hydrous phases were observed in the experimental products even at 1100 °C, 6 GPa, when only traces of melt occurred near the wall of the Pt capsule. F-clinohumite [4(Mg,Fe)<sub>2</sub>SiO<sub>4</sub> MgF<sub>2</sub>] was

formed near the solidus of F-bearing peridotite at both 6 and 10 GPa. It occurred as rather large euhedral to subhedral crystals in peridotite and partly replaced the olivine of the container (Fig. 2). The temperature of F-clinohumite crystallization decreases from 1300 °C at 6 GPa to 1200 °C at 10 GPa. In contrast, the magnesite stability field expands with increasing pressure, especially in the hydrous system.

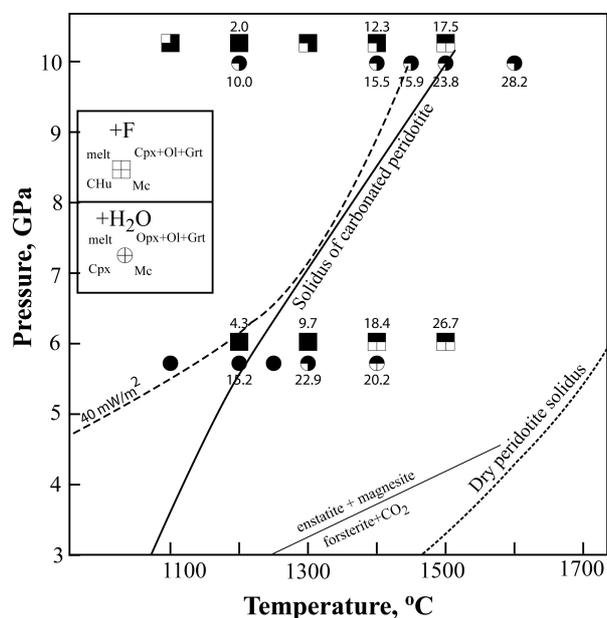


Fig. 3. P-T conditions and phase assemblages of experiments in the peridotite-carbonate system with the addition of F or H<sub>2</sub>O. Numbers near experimental points are SiO<sub>2</sub> contents of liquids calculated on a volatile-free basis. The solidus of carbonated peridotite is after Dasgupta and Hirschmann (2006), the forsterite carbonation line after Newton & Sharp (1975) and the 44 mW/m<sup>2</sup> geotherm, after Pollack and Chapman (1977).

Experimental melts vary from strongly carbonate-dominated liquids near the solidus (SiO<sub>2</sub> < 3 wt %) to kimberlite-like, carbonated silicate compositions (20-30 wt % SiO<sub>2</sub>) at higher temperatures. Melt in equilibrium with F-clinohumite contains 15-16 wt % F at 1200-1300 °C. With increasing temperature, the F content of melt decreases but remains >10 wt %. Carbonate species are major components in all melts as apparent from the high abundance of quench dolomite in the experimental products. The general compositional trends are the same as in anhydrous and F-free systems (e.g. B08; Fig. 4). There are, however, some important differences: (1) Melts from the H<sub>2</sub>O-bearing experiments show significantly higher Al contents compared with both B08 and F-bearing experiments. (2) The melt SiO<sub>2</sub> content in F-bearing experiments is slightly lower than in other systems at the same P-T conditions. (3) The contents of Fe, Mn, and Ni in the F-bearing, carbonated melts are significantly lower than in other systems. This is reflected in relatively high Fe-Mg olivine-melt distribution coefficients (0.5-0.6 in the F-bearing system versus 0.2-0.4 in both hydrous and anhydrous carbonate-peridotite systems) and in high olivine-melt and garnet-melt partition coefficients of Ni and Mn.

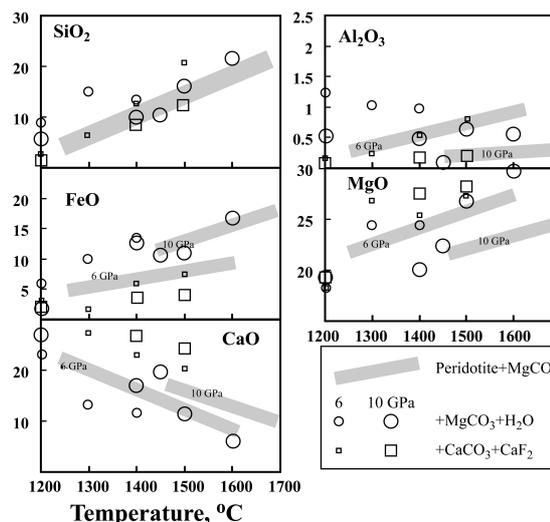


Fig. 4. Contents of selected components in experimental melts. The results for the peridotite+MgCO<sub>3</sub> system for 6 and 10 GPa are from B08.

The distribution of melt in the samples also depends on the bulk composition of the system. In the B08 experiments carbonate and carbonated silicate melts escaped from the peridotite matrix and collected outside the olivine container near Pt already within the first hour. The rapid melt migration was explained by the pressure gradient created by the Fe loss to the Pt capsule. The same pressure gradient drives H<sub>2</sub>O- and F-bearing carbonated melts less efficiently, although the tendency of melt migration outside the olivine container was always obvious. Interstitial melt remained sometimes in the peridotite matrix, and pockets of quenched melts were often observed in the olivine container (Fig. 2). This implies an increase in either melt viscosity or wetting angle as either F or H<sub>2</sub>O substitutes for CO<sub>2</sub>.

## Discussion

### Fluorine-rich phases in the mantle

Phlogopite and apatite are often considered as F hosts in the upper mantle. However, the existence of magmas with high F/K and F/P ratios (e.g. Oldoinyo Lengai sodium carbonatites; Keller & Krafft, 1990) indicates that other F-rich phases may be stable in the mantle. The results of our experiments suggest that F-clinohumite is a viable candidate. It is stable along a normal continental geotherm at least up to 10 GPa (Fig. 3) and can be formed, if the amount of F is higher than can be accommodated in other mantle silicates and if potassium activity is insufficient for phlogopite crystallization. The clinohumite-melt partition coefficient of F is ~0.3, and F content in carbonated melt in equilibrium with this phase is higher than 10 wt %. Therefore, F-clinohumite must dissolve completely at a melt fraction of less than 0.1 wt % even in a mantle reservoir with 150 ppm F (cf. 25 ppm F in the primitive mantle, Palme & O'Neill, 2003). Further melting will rapidly decrease the content of F in the melt. The lower mobility of carbonate-fluoride melt compared with carbonate melt can explain the scarcity of fluoride

melts (Klemme, 2004) and geochemical indications for their migration in the mantle.

#### *Origin of kimberlite magmas*

B08 compared the composition of melts from peridotite-CO<sub>2</sub> experiments at 6-10 GPa with the composition of primary kimberlite liquids and concluded that direct melting of a carbonated peridotite source cannot produce kimberlite magmas. Melts formed at 6 GPa in equilibrium with a magnesite-bearing residue are too rich in MgO and (or) too poor in SiO<sub>2</sub>, whereas melting at 10 GPa produces kimberlite-like liquids with very low Al<sub>2</sub>O<sub>3</sub> (<0.5 wt %). The new results corroborate our previous conclusion and show that the addition of H<sub>2</sub>O and F does not significantly shift the composition of partial melts toward the kimberlite field. This inference is supported by trace element partitioning between garnet and carbonated silicate melt (B08). The abundances of strongly incompatible trace elements in kimberlite magmas are too high to be obtained by a single-stage melting of primitive or slightly depleted mantle reservoirs.

Our experiments provide the following constraints on the origin of primary kimberlite melts: (1) It can be seen from Fig. 3 that small amounts of hydrous carbonate-dominated melts may be common in the sublithospheric mantle even under normal thermal conditions (e.g. 40 mW/m<sup>2</sup> geotherm). The fraction of such melts decreases at pressures below 6 GPa. (2) The generation of kimberlite magmas with 30-35 wt % SiO<sub>2</sub> (anhydrous) requires very high temperatures, irrespective of the possible presence of water and F (1700 C at 10 GPa and 1600 C at 6 GPa). (3) Even at such high temperatures, the content of Al in 10 GPa melts is much lower than in Al-poor kimberlites. (4) The possible region of kimberlite-like magma formation approaches the line of olivine carbonation reaction at 6 GPa (Fig. 3). The convergence will increase, if the complex composition of the fluid phase is accounted for.

Given these constraints, we propose the following scenario for kimberlite magma genesis: melting begins in the sublithospheric mantle and produces volatile-rich liquids with geochemical and isotopic signatures of the primitive mantle. Under normal continental thermal regimes such melts are volatile-undersaturated and will be retained at the base of the lithosphere (~6 GPa) to form refertilized domains. A thermal event increasing the temperature at the base of the lithosphere by several hundred degrees is needed to produce primary

kimberlite melts. An important factor is the bulk composition of the mantle domain. Melting of magnesite-bearing harzburgitic (clinopyroxene-free) materials at ~6 GPa can lead to the appearance of a CO<sub>2</sub>-rich fluid phase, which could trigger eruptions and facilitate magma ascent. In the case of clinopyroxene-bearing materials, the stability of a fluid phase is constrained to pressures <3 GPa by the reaction of clinopyroxene carbonation. The loss of CO<sub>2</sub> during kimberlite magma ascent increases MgO activity in the melt, which becomes orthopyroxene-undersaturated. Therefore, kimberlite - wall rock interaction decreases MgO content in the melt at the expense of orthopyroxene dissolution and olivine crystallization in the wall rocks. Note that this model is appropriate for low-K kimberlites (group I) only. High K contents in the source region of group II kimberlites may change phase relations and mechanisms of magma generation.

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