INFLUENCE OF WATER AND FLUORINE ON MELTING OF CARBONATED PERIDOTITE AT 6 AND 10 GPa

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Experiments on partial melting of the garnet lherzolites-CO_2-H_2O and garnet wherlite-CO_2-F systems were performed at 6 and 10 GPa and 1100-1600°C using a multianvil apparatus. Details and calibration procedures are described in Brey et al. The starting peridotite mixture was the same as in our previous experiments [1]. The mineral powders with grain sizes of <10 μm were mixed with about 10 wt % of natural calcite and fluorite or the chemical reagent $4MgCO_3$ $Mg(OH)_2$ $5H_2O$ (Aldrich, 99%). The addition of volatile-bearing components changed the bulk compositions of the initial peridotite material and affected the modal composition of experimental samples, especially in the F-bearing system. As F was added as CaF_2, the amount of CaO became very high to the extent that orthopyroxene was eliminated. Therefore, the experimental systems are referred to as lherzolites-CO_2-H_2O and wehrlite-CO_2-F. We considered them as proxies for natural peridotites, which are useful for understanding general relationships during melting of volatile-bearing mantle.

In this study we employed the method of pressure gradient-driven melt segregation developed in our previous study on the partial melting of anhydrous carbonated perilotites [1]. The experimental sample (peridotite mixed with volatile-bearing phases) is loaded into an olivine container machined from natural olivine and sealed into a Pt capsule. During the experiment, partial melting of the starting material produces a small amount of liquid, which is initially distributed within the peridotite matrix. Simultaneously, the olivine container reacts with the Pt capsule to produce a Fe-Pt alloy and orthopyroxene. Owing to the negative volume effect of this reaction, a pressure gradient is created in the sample, which efficiently extracts the melt from the peridotite matrix. After the experiment, a quenched carbonate-silicate melt pool is found between the olivine container and the Pt wall. The melt pools are sufficiently large to be analyzed with an electron beam defocused to 10-30 μm in diameter.

After the experiment the capsule was mounted in epoxy, sectioned lengthwise and oil polished for analysis with a Jeol Superprobe 8900 electron microprobe equipped with five wavelength spectrometers and an EDS system. An accelerating voltage of 15 kV and a beam current of 20 nA were used; counting times on peak and background varied between 20 and 40 s. Minerals were analyzed with a focused beam, and quenched melts with a defocused beam from 10 to 30 µm in diameter. Standards were natural silicates, pure oxides, metals, natural fluorite and calcite. The ZAF algorithm was used for matrix correction.

The subsolidus experiment in lherzolites-CO_2-H_2O at 1100°C and 10 GPa produced olivine, orthopyroxene, clinopyroxene, garnet, magnesite and sparse grains of the humite-group mineral norbergite [$Mg_2SiO_4 \cdot Mg(OH)_2$]. The latter was found only as inclusions in garnet and was most likely formed during run-up conditions and is metastable under the experimental conditions. No other hydrous mineral phase was found in these experiments. This means that a hydrous fluid phase was probably present under near-solidus conditions. Experiments at low temperatures (1100-1200°C) yielded magnesite-bearing lherzolitic assemblages (olivine-orthopyroxene-clinopyroxene-garnet-magnesite+melt). With increasing temperature clinopyroxene disappeared first followed by magnesite, and the high-temperatures residual assemblage was garnet harzburgite (fig. 1).

In the F-bearing system, melt was absent at 1100°C and 10 GPa. In this experiment fluorite from the initial mixture reacted with olivine producing an alteration halo of clinopyroxene, ferropericlase and F-bearing magnesium silicates around the peridotite mixture. This zone disappeared above the solidus, and only a discontinuous clinohumite rim was observed between the olivine container and peridotite in some experiments. The addition of F stabilized humite-group minerals, which persisted for at least 100°C above the solidus (fig. 1). Various members of this group (humite, clinohumite, chondrodite) were found in the experimental products. Their proportions and the results of the higher temperature runs (1200–1300°C) suggest that F-clinohumite is probably the stable F-bearing silicate under near-solidus conditions, whereas humite and chondrodite are metastable phases. Clinohumite forms subhedral or euhedral grains in the peridotite material and in the olivine capsule near the peridotite mix. Clinohumite is stable to higher tempera-

tures at 6 GPa than at 10 GPa. But it is the first phase to disappear above the solidus (fig. 1). Magnesite disappears at about 1500°C at 10 GPa and between 1300 and 1400°C at 6 GPa. Melt pockets were often found in the peridotite zone and in the olivine capsule. This suggests that the addition of F increases the viscosity of carbonated silicate melt because in the experiments with carbonated peridotite only [1], melt was exclusively observed near the walls of Pt capsules.
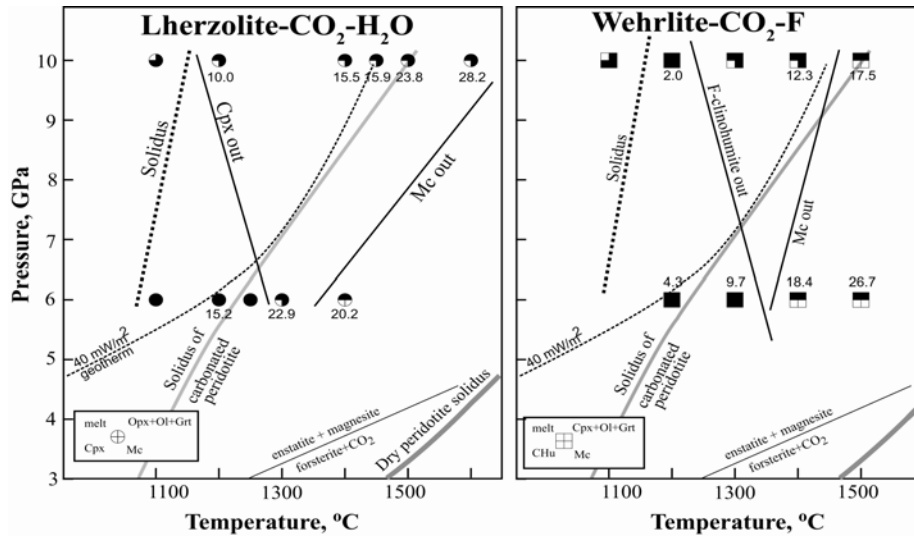

Fig.1. *P–T* diagram showing phase relations in experiments in the lherzolite–CO_2–H_2O and wehrlite–CO_2–F systems. Numbers near experimental points indicate SiO_2 melt contents in wt %. The solidus of carbonated peridotite is after Dasgupta and Hirschmann [2], the dry peridotite solidus is after Hirschmann [3], the reaction forsterite + CO_2 = enstatite + magnesite is after Newton and Sharp [4] and the 40 mW/m2 geotherm is after Pollack and Chapman [5]

The solidus temperature of anhydrous carbonated garnet lherzolite was experimentally constrained by Dasgupta and Hirschmann [2] at about 1200°C at 6 GPa and 1500°C at 10 GPa (shown in fig.1). The addition of both H_2O and F strongly depresses the solidus of carbonated peridotite by 300°C at 10 GPa and about 150°C at 6 GPa (if the wehrlite-CO_2 solidus is taken as a proxy for peridotite-CO_2). The similarity in the effects of H_2O and F on the solidus temperature of carbonated peridotite is in line with experimental data in CO_2-free silicate systems [6].

In the F-bearing system, the subsolidus phase assemblage includes humite-group minerals, whereas in the H_2O-bearing system, no hydrous phases were found in the lowest temperature experiments (1100°C). The run conditions may have been just above the upper stability limit of hydroxyl clinohumite [7] in the presence of a fluid phase. In the absence of a hydrous crystalline phase, an H_2O-bearing fluid had to be present near the solidus. Phase relations will depend on the critical relation between aqueous fluid and carbonate-dominated melt [8]. If the pressure is higher than the critical point, a gradual transition should be observed between melt and water-rich fluid, and if it was lower, a separate water-rich fluid phase will coexist with melt near the solidus. The sharp change in the texture of experimental samples between 1100 and 1200°C at 10 GPa argues for the second variant (i.e. the pressure of the critical end-point is higher than 10 GPa).

The compositions of melts from the lherzolites-CO_2-H_2O experiments are very similar to those reported for the peridotite-CO_2 system[1]. One notable exception is the relatively high Al_2O_3 content in the melts from the hydrous experiments. This effect is not related to different bulk compositions, since the activity of Al is buffered by the low-Ca pyroxene-garnet equilibrium.

The effect of F on the carbonate-peridotite (wehrlite) system is more significant in that it makes the melts somewhat SiO_2 poorer but significantly higher in MgO and CaO and lower in Al_2O_3.

Brey et al. [1] compared the compositions of experimental carbonated silicate melts with supposed primary kimberlite magmas and concluded that the latter cannot be produced by single-stage melting of primitive or slightly depleted mantle peridotites. The experimental melts obtained at moderate pressures

(6-7 GPa) appeared to be richer in MgO than the kimberlitic melts at identical SiO_2 contents, whereas the melts from 10 GPa experiments were too low in Al. The same holds true for the H_2O- and F-bearing carbonate–silicate melts reported here. The effects of H_2O and F in addition to CO_2 are too small to significantly shift the composition of melts toward the kimberlite field. Moreover, the addition of F reduces the SiO_2 content of partial melts and increases the divergence between kimberlite magmas and experimental melts. The increase of Al_2O_3 in hydrous melts is not sufficient to produce kimberlite-like melts at pressures higher than 6 GPa. Thus, the obtained data support our previous conclusions [1].

Nonetheless, our experiments have some implications for kimberlite magma genesis and mantle metasomatism: (1) Sublithospheric mantle domains enriched in CO_2 and water or fluorine must produce melts even under the normal undisturbed cratonic geotherm (fig.1). (2) Generation of kimberlite magmas with 30-35 wt % SiO2 (volatile-free composition) requires high temperatures in excess of 1600°C at 6 GPa and 1700°C at 10 GPa independent of the presence of H_2O and (or) F. The presence of H_2O strongly depresses the solidus but does not significantly affect the SiO_2 content of melt above the anhydrous solidus of carbonated peridotite. (3) The solidus of H_2O-bearing carbonated peridotite is intersected by the cratonic geotherm at pressures of about 6 GPa.

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