

## The Structure of Water-Saturated Carbonate Melts The Structure of Water-Saturated Carbonate Melts

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The structure of water-saturated Ca- and Mg-bearing carbonate melts under reducing and oxidizing conditions was investigated in a series of hydrothermal anvil cell experiments conducted at 400 - 1100 °C and 442 - 2839 MPa. Equilibria were investigated in the calcite-H<sub>2</sub>O, calcite-CaO-H<sub>2</sub>O, magnesite-H<sub>2</sub>O and magnesite-MgO-H<sub>2</sub>O systems, with redox conditions controlled by Re/ReO<sub>2</sub> and Ti/TiO<sub>2</sub> assemblages. Melting relationships and the C-O-H speciation of the coexisting aqueous fluid and melt were assessed in-situ by Raman vibrational spectroscopy. Hydrous melting of MgCO<sub>3</sub>-MgO occurred at ~850 °C, 1.5 - 2 GPa. In the CaCO<sub>3</sub>-CaO-H<sub>2</sub>O system, melt was formed at 600 - 900 °C and pressures of 0.5 - 1.5 GPa because of melting-point depression imposed by the presence of CaO. The C-O-H speciation of the carbonate melts and coexisting supercritical aqueous solutions was mainly H<sub>2</sub>O and CO<sub>3</sub><sup>2-</sup>, with traces of CO<sub>2(aq)</sub> and CH<sub>4(aq)</sub> in the fluid phase. The melt-fluid H<sub>2</sub>O partition coefficients attained in the Mg-bearing melt (median 0.5) were higher than in the Ca-bearing melt (median 0.3). Under oxidizing redox conditions, dissolved ReO<sup>4-</sup> was present in all phases, underscoring the enhanced solubility of trace elements and metals in carbonate-bearing melts and carbonatites. In effect, the enhanced solubility of H<sub>2</sub>O along with the ionic nature of the carbonate melts may promote the solvation of ionic species in the melt structure.

From in-situ vibrational spectroscopy, the  $\nu_1$ -CO<sub>3</sub><sup>2-</sup> vibration recorded in the melt spectra suggests the presence of intermolecular interactions between the oxygen of the carbonate ion with water dissolved in the melt. The thermodynamic properties of this water appear to be similar to the supercritical aqueous phase. For example, the estimated enthalpy for the breakage of the hydrogen bonding between water molecules attained values of  $6.8 \pm 1.5$  kcal/mol and  $8.4 \pm 1.3$  kcal/mol in the melt and fluid phase, respectively. The calculated partial molar volume of H<sub>2</sub>O in the melt ( $\sim 48 \pm 6$  cm<sup>3</sup>/mol) is also comparable to the partial molar volume of supercritical water at similar conditions. Interestingly, this value is considerably greater than published partial molar volume values for H<sub>2</sub>O in silicate melts (10-12 cm<sup>3</sup>/mol).

The pressure-temperature melting relationships of the CaO-CO<sub>2</sub>-H<sub>2</sub>O and MgO-CO<sub>2</sub>-H<sub>2</sub>O systems highlight the important role of water and alkali earth oxides on the hydrous melting of the carbonate-bearing subducting oceanic crust. Carbonates present in marine sediments or serpentinized peridotites may melt before complete dehydration at the slab-mantle wedge transition zone, and thus, never reach sub-arc depths. To this end, melting of carbonate minerals at crustal temperatures and pressure can contribute to the volcanic CO<sub>2</sub> flux at the arc through melt/fluid interactions.

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