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Carbon speciation in silicate-C-O-H melt and fluid as a function of redox conditions: An experimental study, in situ to 1.7 GPa and 900 °C

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Abstract

Carbon speciation in and partitioning among silicate-saturated C-O-H fluids and (C-O-H)-saturated melts have been determined ~1.7 GPa and 900 °C under reducing and oxidizing conditions. The measurements were conducted in situ while the samples were at the conditions of interest. The solution equilibria were (1) $2CH_4 + Q^n = 2CH_3^- + H_2O + Q^{n+1}$ and (2) $2CO_3^{2-} + H_2O + 2Q^{n+1} = HCO_3^- + 2Q^n$, under reducing and oxidizing conditions, and where the superscript, *n*, in the Q^n-species denotes number of bridging oxygen in the silicate species (Q-species). The abundance ratios, CH_3/CH_4 and HCO_3^-/CO_3^{2-}, increase with temperature. The enthalpy change associated with the species transformation differs for fluids and melts and also for oxidized and reduced carbon [Reducing: $\Delta H_{(1)}^{\text{fluid}} = 16 \pm 5$ kJ/mol, $\Delta H_{(1)}^{\text{melt}} = 50 \pm 5$ kJ/mol; oxidizing $\Delta H_{(2)}^{\text{fluid}} = 81 \pm 14$ kJ/mol]. For the exchange equilibrium of CH_4 and CH_3 species between fluid and melt, the temperature-dependent equilibrium constant, $(X_{CH_4}/X_{CH_3})^{\text{fluid}}/(X_{CH_4}/X_{CH_3})^{\text{melt}}$, yields $\Delta H = 34 \pm 3$ kJ/mol.

Increased abundance ratios, CH_4/CH_3 and HCO_3^-/CO_3^{2-}, lead to increased polymerization of silicate+(C-O-H) melt. Because of such relations, melt transport properties (e.g., viscosity) and element partition coefficients between magmatic liquids, C-O-H fluids, and crystalline phases can vary by more than 100% with speciation changes of C-bearing volatiles upper mantle. These structure effects are more pronounced the higher the pressure and the more mafic the magma.

Keywords: Redox, COH volatiles, melt structure, melt properties, fluid structure