

MIS002-08

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COH Solubility, solution behavior and $^{13}/^{12}\text{C}$ fractionation melt-fluid systems at mantle redox, P, and T conditions

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The solubility and solution mechanisms in melts and speciation in coexisting fluid of reduced and oxidized C-bearing volatiles in the system C-O-H have been determined as a function of melt composition (from haplobasalt to haploandesite) and redox conditions in the range from the MH to the IW buffer to upper mantle temperatures and pressures. Sample characterization was conducted with samples quenched from high temperature and pressure and with melt+fluid samples in-situ in hydrothermal diamond anvil cells. Raman, FTIR, and NMR spectroscopies were employed as structural tools for studies of glasses, melts, and fluids. Carbon solubility and carbon isotope fractionation between melt and fluid were determined mass-spectrometrically and interpreted with the aid of speciation of C-O-H in melt and in coexisting fluids (see also [1]).

Methane solubility increases from 0.2 wt percent to about 0.5 wt percent in the composition range between haploandesite and haplobasalt and increases by 150 percent between the IW and MH oxygen buffers at constant temperature and pressure. Carbon isotope fractionation between methane-saturated melts and (CH₄+H₂+H₂O)-fluid changes by 14 per mil with the melt compositions studied (haploandesite to haplobasalt). In the COH-silicate system at redox conditions of the NNO oxygen buffer and more oxidizing, carbon exists in melts as carbonate complexes and in the fluid as CO₂. Carbonate occurs in two forms, as CO₃-groups sharing one or more oxygen with the silicate melt network structure and as isolated CO₃-groups bonded to metal cations. Isolated CO₃-groups become more abundant the less polymerized the melt (more mafic melts). Reduced (C+H)-bearing species were detected in silicate melts at the redox conditions of the MW buffer and more reducing. From diamond cell (HDAC) experiments conducted in-situ from ambient temperature and pressure to 800 C and 1435 MPa under redox conditions near those of the IW buffer, the dominant fluid species in the fluid are CH₄, H₂, and H₂O. In coexisting melt, CH₃ - groups linked to the silicate melt structure via Si-CH₃ bonding occur together with molecular CH₄. There is no evidence of changes in hydrocarbon species or polymerization with temperature and pressure.

The melt composition-dependent solubility and change in carbon isotope fractionation is because of silicate composition-dependent changes of C-bearing species in the melt. The composition- and redox-dependent solution mechanisms of C-species in melts governs how melt properties can change with redox conditions. Redox melting in the interior of the Earth has been explained with the aid of the solution mechanisms of oxidized and reduced carbon in silicate melts. Further, effects of oxidized and reduced carbon on melt viscosity and on element partitioning between melts and minerals have been estimated from relationships between melt polymerization and dissolved carbon combined with existing experimental data that link melt properties and melt polymerization. With total carbon contents in the melts on the order of several mol percent, mineral-melt element partition coefficients and melt viscosity may change by several tens to several hundred percent as a function of redox conditions in the range of the deep crust and upper mantle of the Earth.

[1] Mysen, B. O., Cody, G. D., and Morrill, P. L. (2009) *Geochim. Cosmochim. Acta.* 73, 1699.

Keywords: carbon speciation, COH fluid, silicate melt, solubility, solution mechanism, isotope fractionation