Mantle melting and volatiles: Redox-controlled solution behavior in silicate-COH magmatic systems

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The behavior of hydrogen-bearing fluids and magmatic liquids is at the core of understanding formation and evolution of the Earth, its oceans, and atmosphere. To advance this knowledge, infrared and Raman spectroscopy has been employed for melt structural characterization and for determination of hydrogen and carbon isotope partitioning within and between melts and fluids in alkali aluminosilicate–C-O-H systems contained in externally-heated diamond anvil cells. The measurements were carried out in-situ under equilibrium conditions while the samples were at the temperatures, pressures, and redox conditions corresponding to those of the Earth's upper mantle and deep crust.

Hydrogen as H_2O is the major component of the silicate Earth. Its solubility in magma can reach >30 wt% under crustal and upper mantle conditions. The CH_4 and H_2 solubility is in the 0.1-1 wt% range, and CO_2-solubility typically 1-5 wt%. These variations reflect bulk chemical and, therefore, structural control of solubility. Water dissolved in magmatic liquids to form predominantly Si-OH and Al-OH bonding together with molecular H_2O. The OH/H_2O ratio is positively correlated with SiO_2 and Al_2O_3 concentrations in melts. The carbon solution equilibria are, $2CH_4+Q^n=2CH_3+H_2O+Q^{n+1}$ and, $2CO_3+H_2O+2Q^{n+1}=HCO_3+2Q^n$, under reducing and oxidizing conditions, respectively. In the Q^n-notations, 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, increase with temperature.

The resulting structural changes result in hydrogen and carbon isotope fractionation factors between melt, fluid, and crystalline materials significantly different from 1 even at magmatic temperatures. The D/H and fractionation between aqueous fluid and magma are also temperature dependent with a small enthalpy change near -5 kJ/mol. In silicate-C-O-H systems, the enthalpy-values for $^{13}C/^{12}C$ fractionation factors are near -3.2 and 1 kJ/mol under oxidizing and reducing conditions, respectively. These differences reflect different energetics of O-D, O-H, O-^{13}C, and O-^{12}C bonding environments governed by different solution mechanisms in melts of the individual volatile components.

From experimentally-determined temperature- and pressure-dependent D/H fractionation between fluids and melts, it is suggested suggest that (C-O-H)-saturated partial melts in the upper mantle can have dD-values 100%, or more, lighter than coexisting silicate-saturated fluid. This effect is greater under oxidizing than under reducing conditions. Analogous relationships exist for $^{13}C/^{12}C$ with $\partial^{13}C$-differences between silicate melts and coexisting CO_2+H_2O (oxidizing) and $CH_4+H_2O+H_2$ (reducing) fluid and at magmatic temperatures in the Earth's upper mantle increases with temperature from about 40 to > 100‰ and 80 –120 ‰under oxidizing and reducing conditions, respectively. The use of hydrogen and carbon isotopes of mantle-derived magma to derive isotopic composition of upper mantle source regions, therefore, is discouraged as these are affected by temperature, bulk composition, and redox conditions during melting, crystallization, and degassing events.

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