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Solution mechanisms of COHN fluids in melts to upper mantle temperature, pressure, and redox conditions

Bjorn Mysen[1,*]

[1]Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20015, U.S.A.

Abstract

We wished to advance the knowledge of speciation among volatiles during melting and crystallization in the Earth's interior; therefore, we explored the nature of carbon-, nitrogen-, and hydrogen-bearing species as determined in COHN fluids and dissolved in coexisting aluminosilicate melts. Micro-Raman characterization of fluids and melts were conducted in situ while samples were at a temperature up to 825 °C and pressure up to ~1400 MPa under redox conditions controlled with the Ti-TiO_2-H_2O hydrogen fugacity buffer. The fluid species are H_2O, H_2, NH_3, and CH_4. In contrast, under oxidizing conditions, the species are H_2O, N_2, and CO_2.

The equilibria among silicate structures (Q-species) and reduced carbon and nitrogen species are, $2NH_3 + 4Q^n \leftrightharpoons 2Q^{n-1}(NH_2) + 2Q^{n-1}(OH)$, and $2CH_4 + 4Q^n \leftrightharpoons 2Q^{n-1}(CH_3) + 2Q^{n-1}(OH)$. The Q^n and Q^{n-1} denote silicate species with, respectively, n and n–1 bridging O atoms. The formulation in parentheses, (NH_2), (CH_3), and (OH), is meant to indicate that those functional groups replace one or more oxygen in the silicate tetrahedra. There is no evidence for O-NH_2 or O-CH_3 bonding. Therefore, a solution of reduced C- and N-species species in the COHN system results in depolymerization of silicate melts. The ΔH values derived from the X_{NH_2}/X_{NH_3} and X_{CH_3}/X_{CH_4} evolution with temperature, respectively, were 8.1 ± 2.3 kJ/mol and between –4.9 ± 1.0 and –6.2 ± 2.2 kJ/mol.

The fluid/melt partition coefficients, $K^{\text{fluid/melt}}$, of the reduced species, H_2O, H_2, NH_3, and CH_4, remain above unity at all temperatures. For example, for carbon it is in the 6–15 range with a $\Delta H = -13.4 \pm 2.4$ KJ/mol. These values compare with a 0.8–3 range with $\Delta H = -19 \pm 2.4$ kJ/mol in N-free silicate-COH systems. The $K^{\text{fluid/melt}}$ values for reduced nitrogen and molecular hydrogen are in the 6–10 and 6–12 range with ΔH values of –5.9 ± 0.9 and = 8 ± 6 kJ/mol, respectively.

A change in redox conditions during melting and crystallization in the Earth sufficient to alter oxidized to reduced carbon- and nitrogen-bearing species will affect all melt properties that depend on melt polymerization. This suggestion implies that changing redox conditions during melting of a COHN-bearing mantle can have a profound effect on physical and chemical properties of melts and on melting and melt aggregation processes.

Keywords: Volatiles, COHN, Redox, pressure, structure, mantle