

AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY

Speciation of and D/H partitioning between fluids and melts in silicate-D-O-H-C-N systems determined in-situ at upper mantle temperatures, pressures, and redox conditions†

BJORN O. MYSEN^{1,*}, TOKIO TOMITA², EIJI OHTANI² AND AKIO SUZUKI²

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

²Department of Earth and Planetary Material Sciences, Graduate School of Science, Tohoku University, Japan

ABSTRACT

Speciation of D-O-H-C-N volatiles in alkali aluminosilicate melts and of silicate in D-O-H-C-N fluid has been determined in situ to 800 °C and >2 GPa under reducing and oxidizing conditions by using an externally heated hydrothermal diamond-anvil cell with Raman spectroscopy as the structural probe. Reducing conditions were near those of the IW oxygen buffer, whereas oxidizing conditions were obtained by conducting the experiments with oxidized components only and with Pt as a catalyst.

Raman bands assigned to C-H stretching in CH_xD_y isotopologues and CH₄ groups (including CH₃) were employed to determine the CH₄/CH_xD_y ratio in fluids and melts. This ratio decreases from 1.5–2 at 500 °C to between 1.2 and 1 with 800 °C with ΔH -values of 13.6 ± 2.1 and 5.5 ± 1.1 kJ/mol for melt and fluid, respectively. The CH₄/CH_xD_y fluid/melt partition coefficient ranges between ~16 and ~3 with $\Delta H = 33 \pm 6$ kJ/mol assuming no pressure effect. This behavior of deuterated and protonated complexes is ascribed to speciation of volatile and silicate components in fluids and melts in a manner that is conceptually similar to D/H partitioning among complexes and phases in brines and hydrous silicate systems.

Molecular N₂ is the N-bearing species in fluids and melts under oxidizing conditions. Under reducing conditions, the dominant species are molecular NH₃ and ammine groups, NH₂. The NH₃/NH₂ ratio varies between 0.15 and 0.75 in the 425–800 °C temperature range. The enthalpy change of the ammonia/ammine equilibrium, ΔH , derived from the temperature and assuming no pressure effect on the equilibrium, is 19 ± 8 and 61 ± 9 kJ/mol for melt and fluid, respectively. The fluid/melt partition coefficient, $(\text{NH}_3 + \text{NH}_2)^{\text{fluid}}/(\text{NH}_3 + \text{NH}_2)^{\text{melt}}$, ranges from 8 to 3 with $\Delta H = 45 \pm 12$ kJ/mol. For oxidized nitrogen, the fluid/melt partition coefficient is twice or more of those values for reduced nitrogen. Hydrogen bonding can be detected at 500 °C and below. This behavior resembles that of H₂O. Deuterium-containing analogues of the (N+H)-species could not be detected with precision because these were in the frequency-range of the second-order Raman shift of diamond in the diamond-anvil cell itself and could not be isolated from the strong background generated by the Raman intensity from the diamond. These results imply that, unlike noble gases, degassing of N-bearing species from the mantle is redox dependent, and is also more efficient at lower temperatures (shallow depths). Reduced and oxidized C-O-H-N species exist fluids and melts in the modern mantle, whereas reduced species dominated in the young Earth. The f_{H_2} -dependent speciation C-O-H-N volatile components result in f_{H_2} -dependent thermodynamic and transport properties of fluids and melts in the interior of the Earth and terrestrial planets. In fluids, the solubility of nominally incompatible trace elements can increase by orders of magnitude upon its saturation with silicate components. Trace element and stable isotope partitioning between fluids and melt can change by >100% for the same reason.

Keywords: Melt structure, volatiles, speciation, redox, isotope