

Effects of fluid and melt density and structure on high-pressure and high-temperature experimental studies of hydrogen isotope partitioning between coexisting melt and aqueous fluid

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ABSTRACT

Hydrogen isotope partitioning (as H₂O and D₂O) between silicate-saturated aqueous fluid and water-saturated aluminosilicate melt has been determined with vibrational spectroscopy (Raman and infrared) in situ with the samples at high temperature and pressure by using a hydrothermal diamond-anvil cell (HDAC) for sample containment. To assess the effects of pressure and, therefore, different silicate speciation in fluids and melts, on the D/H partitioning behavior, two pressure/temperature experimental trajectories (450–800 °C/155–754 MPa, and 450–800 °C/562–1271 MPa) were used. In these temperature and pressure ranges, the fluid/melt partition coefficients are temperature (and pressure) dependent with the average enthalpy change, $\Delta H = -6.6 \pm 1.5$ kJ/mol and -10.3 ± 1.1 kJ/mol for H₂O and D₂O, respectively. The ΔH -values for the lower-pressure trajectory (and, therefore, lower fluid density) were 15–20% higher than for the higher-pressure (and higher fluid density) trajectory. The (D/H) ratios of fluids and melts, (D/H)^{fluid} and (D/H)^{melt}, are also temperature dependent with a small negative ΔH for (D/H)^{fluid} (average: -2.4 ± 0.8 kJ/mol) and a positive ΔH -value for (D/H)^{melt} (2.3 ± 1.4 kJ/mol). The (D,H) exchange equilibrium between fluid and melt is also temperature (and pressure) dependent so that for the low-density *P/T* trajectory, the $\Delta H = -4.2 \pm 0.6$ kJ/mol, whereas for the higher-density trajectory, $\Delta H = -5.4 \pm 0.7$ kJ/mol. The difference between the H₂O and D₂O fluid/melt partition coefficients and the temperature- and pressure-dependent D/H fractionation behavior in and between hydrous silicate melts and silicate-saturated aqueous fluid in part is because pressure increases with increasing temperature in the HDAC experiments and the volume difference between fluid and melt differ for H₂O and D₂O. In addition, the silicate speciation in fluids and melts are temperature and pressure dependent, which also leads to significantly temperature- and pressure-dependent D/H fractionation within and between silicate melts and fluids at high temperature and pressure. In the Earth's deep crust and upper mantle, hydrogen isotope partitioning between condensed phases and aqueous fluid can differ substantially from that between condensed phases and pure H₂O because the aqueous fluid in the Earth's interior is a concentrated silicate solution wherein the silicate speciation affects the isotope partitioning.

Keywords: Hydrogen isotopes, vibrational spectroscopy, aqueous fluid, hydrous melt, structure, pressure, temperature