

Hydrogen isotope fractionation between coexisting hydrous melt and silicate-saturated aqueous fluid: An experimental study in situ at high pressure and temperature

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ABSTRACT

Hydrogen isotope fractionation between water-saturated silicate melt and silicate-saturated aqueous fluid has been determined experimentally by using vibrational spectroscopy as the analytical tool. The measurements were conducted in situ with samples at the high temperature and pressure of interest in an externally heated diamond cell in the 450–800 °C and 101–1567 MPa temperature and pressure range, respectively. The starting materials were glass of Na-silicate with Na/Si = 0.5 (NS4), an aluminosilicate composition with 10 mol% Al₂O₃ and Na/(Al+Si) = 0.5 (NA10), and a 50:50 (by volume) H₂O:D₂O fluid mixture. Platinum metal was used to enhance equilibration rate. Isotopic equilibrium was ascertained by using variable experimental duration at given temperature and pressure.

In the Al-free NS4 system, the enthalpy of the D/H equilibrium of fluid is 3.1 ± 0.7 kJ/mol, whereas that of coexisting melt equals 0 within error. For NA10 fluids the $\Delta H = 5.2 \pm 0.9$ kJ/mol, whereas for coexisting NA10 melt, ΔH is near 0 within error. For the exchange equilibrium between melt and coexisting fluid, H₂O(melt)+D₂O(fluid) = H₂O(fluid)+D₂O(melt) the $\Delta H = 4.6 \pm 0.7$ and 6.5 ± 0.7 kJ/mol for NS4 and NA10 compositions, respectively.

The D/H fractionation between melt and fluid is affected significantly by the positive temperature- and pressure-dependence of silicate solubility and silicate structure in silicate-saturated aqueous fluids. Water in melts is much less important than silicate in aqueous fluid because even at the lowest temperature and pressure conditions studied (450 °C/101 MPa), the water content in the melt is so high (>4 wt%) that further increase in total water by increasing temperature and pressure does not affect the silicate melt structure significantly. This is because most of the water in this concentration range is dissolved in molecular form.

Keywords: Fluid structure, melt structure, isotope fractionation, temperature, pressure, experimental petrology