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H/D methane isotopologues dissolved in magmatic fluids: Stable hydrogen isotope fractionations in the Earth's interior

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Abstract

A series of hydrothermal diamond-anvil cell experiments have been conducted to evaluate the role of supercritical water on the isotopic equilibrium between H/D methane isotopologues at 600–800 °C and 409–1622 MPa. Raman spectroscopy was deployed to investigate the distribution of H/D isotopic molecules formed during hydrothermal decomposition of $Si_5C_{12}H_{36}$ in H_2O-D_2O aqueous solutions. To this end, the intensities of the fundamental vibrational C-H and C-D modes of deuteromethanes were employed to determine the thermodynamic properties of isotope exchange reactions between H/D isotopologues and to constrain the methane D/H molar ratios. By adjusting the initial volume ratios of silane/H_2O-D_2O, reactions in the CH_4-D_2O-H_2O system were monitored for gaseous and supercritical-water phases. Discreet differences between the equilibrium constants, describing the relationship between the CH_3D-CH_2D_2-CHD_3-CH_4 species dissolved in supercritical water or present as a homogeneous gas phase, are revealed. The bulk D/H methane composition in the liquid-system is also twice that of the D/H molar ratios recorded in the gas-bearing system. Accordingly, condensed-phase isotope effects are inferred to play a key role on the evolution of H/D isotopologues, likely induced by differences in the solubility of the isotopic molecules driven by the excess energy/entropy developed during mixing of non-polar species in the H_2O-D_2O structure. Our experiments show that isotope fractionation effects need to account for the presence of condensed matter (e.g., melts, magmatic fluids), even at conditions at which theoretical models suggest minimal (or nonexistent) isotope exchange, but comparable to those within the Earth's interior.

Keywords: Condensed-phase isotope effect, methane, H/D isotopologues, supercritical water, magmatic fluids, Raman vibrational spectroscopy