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

DIONYSIS I. FOUSTOUKOS* AND BJORN O. MYSEN

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, D.C. 20015, U.S.A.

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 SiC2H10 in H2O-D2O 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/H2O-D2O, reactions in the CH4-D2O-H2O system were monitored for gaseous and supercritical-water phases. Discreet differences between the equilibrium constants, describing the relationship between the CH3D-CH2D2-CHD3-CH4 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 H2O-D2O 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

INTRODUCTION

Theoretical studies on the distribution between isotopic molecules and their equilibrium relationships are commonly based on statistical mechanics models that calculate the partition functions (rotational, translational, vibrational) of the molecules by adopting a Wigner-Kirkwood free energy expansion (Kirkwood 1934; Wigner 1932) and by assuming simple harmonic oscillators (Bigeleisen and Mayer 1947; Bottinga 1969). These methods adopt ideal gas behavior between species with zero intermolecular forces, and, thus, do not account for the solubility, molar volume, and vapor pressure induced fractionations imposed by intermolecular interactions with condensed phases such as, for example, supercritical water (Bacsik et al. 2002; Chialvo and Horita 2003; Gomes and Grolier 2001; Jancso et al. 1993; Muccitelli and Wen 1978; Van Hook 2006). Condensed-phase isotope effects are attributed to the free energy differences between the condensed and gas phase (Van Hook 2006) as reflected, for example, in differences on the solution properties (e.g., Henry’s/ Raoult’s law) and/or the temperature and pressure dependence of isotopologues’s vapor pressure and partial molar volumes (Bigeleisen 2006; Herzfeld and Teller 1938).

Silicate melts and coexisting magmatic fluids represent the condensed phases present in the Earth’s interior. Determining the solubility and solution mechanisms of volatiles (e.g., H2O, H2, CO2, and CH4) in these phases is essential to constrain melting and crystallization processes. Advances in our current understanding of stable isotope fractionations (e.g., 18O/16O, 13C/12C, D/H, and 15N/14N) under temperature and pressure conditions corresponding to lower crust/upper mantle conditions, and how this behavior can be related to the structural roles of C-O-H-N-rich functional groups [a factor of 1/\sqrt{2} (reduced mass effect)]. Accordingly, by combining Raman vibrational spectroscopy with experimental designs that allow in situ monitoring of chemical processes at high temperatures and pressures (>600 °C, >300 MPa) (Bassett et al. 1996), D/H exchange between functional groups can be determined as a function of temperature and pressure. Thus, volume, enthalpy, and entropy effects on isotopic distribution can be examined while the samples are at the desired temperature and pressure. For example, recent studies have shed light on the role of hydrogen bonding on the distribution of...