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Hydrogen isotope fractionation in the system brucite-water ± NaCl to elevated temperatures and pressures: Implications for the isotopic property of NaCl fluids under geologic conditions

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Abstract

A series of hydrothermal experiments have been conducted to determine equilibrium D/H fractionations between brucite and water as a function of temperature (200–600 °C), pressure (2.1–800 MPa), and dissolved NaCl (0–5 molal or 0–22.6 wt %). Along with our previous study, a total of 39 data points show that pressure and dissolved NaCl both increase the D/H fractionation factor at a given temperature. Theoretical treatment allowed a first direct comparison of experimental and theoretical results of brucite-water D/H fractionation at a zero pressure limit. After correcting the pressure effects on brucite D/H partition function ratios (β-factor), the isotope effects of pressure and dissolved NaCl on the D/H β-factor of water were for the first time rigorously evaluated. There is a good linear relationship between the D/H β-factor of the aqueous NaCl solutions and their densities of at a given temperature. A good, pseudo-linear relationship observed between the density of aqueous NaCl solutions and the maximum intensity of the asymmetric O—H vibrational frequency of water in turn suggests that this frequency is a fundamental property that determines the β-factor of water at elevated temperatures and pressures. Our study suggests that the density of aqueous solutions ($\rho_{aq-soln}$) could be used as a primary parameter to predict the effects of pressure and NaCl compositions on the β-factor of water under geologic conditions encountered in the crust and upper mantle: $\Delta 10^3 \ln \beta_{wat}/\Delta \rho_{aq-soln} = -0.0111\ (\pm 0.0012)$, where Δ is a difference in the value of $10^3 \ln \beta_{wat}$ or$\rho_{aq-soln}$, and $\rho_{aq-soln}$ in kg m^{-3}.

Keywords: Hydrogen isotopes; water; brucite

1. INTRODUCTION

Temperature and pressure are the two most important variables that determine the thermodynamics of earth materials and equilibrium distributions of chemical elements and their stable isotopes among them. During fluid-rock interaction, fluid compositions are another key factor controlling chemical reactions. However, unlike for chemical reactions, it has been commonly assumed in stable isotope geochemistry that equilibrium fractionation of the isotopes of light elements (hydrogen, oxygen, carbon, sulfur, *etc.*) among different phases and chemical species (minerals, waters, gases, dissolved species, *etc.*) depends largely on temperature, but little on pressure or the solute compositions of fluids. This assumption has been challenged in the past decades theoretically and experimentally (Polyakov and Kharlashina, 1994; Horita, 2005), especially for systems involving aqueous fluids (Horita et al., 1999; Horita et al., 2002). In addition,

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petrologic evidence clearly demonstrates that hot, saline waters have been responsible for large-scale fluid transport, water-rock interactions, and ore deposition in diagenetic, metamorphic, and magmatic processes throughout Earth history. Our understanding of the effect of aqueous fluid compositions on the isotope fractionation behavior of fluids remains incomplete despite some progress in the past decades (Horita, 2005). Trace amounts of water have been reported for various nominally anhydrous minerals from the mantle (Williams and Hemley, 2001; Pearson et al., 2014), suggesting that water may be more abundant within the crust and deep Earth than previously thought, especially in subduction zones. Thus, a quantitative understanding of the isotopic properties of aqueous fluids over a wide range of temperature, pressure, and fluid compositions are of great importance to the interpretation and modeling of isotope fractionation from near surface to deep-Earth conditions.

The fundamental property of substances that controls their equilibrium isotope fractionation is the reduced isotope partition function ratios (RIPFR, also known as the β-factor). Since the pioneering works in the 1940s (Bigeleisen and Mayer, 1947; Urey, 1947), many investigators have conducted statistical– mechanical calculations of the RIPFR for water and many other simple molecules. However, their results provide information only on isolated, 'ideal-gas' molecules at zero pressure. The study by Richet et al. (1977) is among the most accurate and updated calculations for water, including anharmonic, rotational and rotational-vibration corrections. Although small errors and uncertainties exist regarding the anharmonic corrections, the β-factor of 'ideal-gas' water is considered well determined. Conversely, the calculation of the β-factor for condensed phases of aqueous solutions (liquids and supercritical, dense aqueous fluids at elevated pressures) has met only limited success, because for aperiodic and dynamic systems such as liquids or supercritical fluids, detailed and accurate information on inter-molecular forces is required.

With rapidly expanding computational capabilities, classical- and quantum-mechanical molecular modeling of liquids and supercritical fluids has become a powerful tool. In classical-mechanical molecular dynamics simulations of liquid water, isotope fractionation of quantum-mechanical origins has been determined by quantum corrections with a perturbation method (Chialvo and Horita, 2009) or by quantum kinetic energy with a path-integral molecular simulations (PIMD) (Pinilla et al., 2014). In quantum-mechanical modeling (Hartree-Fock, DFT, Molecular-Orbital) of pure water and electrolyte solutions, liquids and solvated species have been treated with either cluster approximation or periodic boundary conditions (Driesner et al., 2000; Oi and Otsubo, 2010; Oi et al., 2013). These molecular modeling approaches have shown some promises, but still failed to reproduce accurately the experimental results of liquid-vapor isotope fractionation. On the other hand, thermodynamic modeling produced much better agreements, using a solute (minor isotopologue) dissolution model (Japas et al., 1995) or a corresponding-states principle (Polyakov et al., 2007).

The pressure effect on the β-factor of supercritical water has been estimated with some success, assuming that only the internal, symmetric O—H stretching frequency of water molecules red-shits with increasing pressure (Driesner, 1997), based on experimental high-pressure IR data (Frantz et al., 1993). Polyakov et al. (2006) developed a new, accurate method for calculating the β-factor of water on the basis of equations of states (EOS) of normal and isotope-substituted waters. This approach requires accurate equations of state for pure isotopologues of molecular fluids to elevated temperatures and pressures, which are often not available. In the case of water these exist only for H_2O and D_2O, the latter being limited to 800 K and 100 MPa, whereas no respective equation of state is available for $H_2^{18}O$.

In this study, we have conducted a systematic and detailed experimental study of D/H isotope fractionation in a brucite-water system over a wide range of temperature, pressure and NaCl concentrations. The purposes of the study are to: (1) delineate general patterns of the effects of three variables (temperature, pressure and NaCl concentrations) on the D/H isotope fractionation, (2) test the accuracy of theoretically calculated D/H fractionation of brucite-water after applying the corrections of pressures (density), and (3) develop a first-order understanding of underlying physicochemical properties that determine the effect of pressure and NaCl concentrations on the β-factor of water. Such understanding is expected to lead to the development of a general model of the β-factor of aqueous fluids over a wide range of geologic conditions to elevated pressures and temperatures in the Earth's crust and upper mantle.

2. EXPERIMENTAL

The brucite [$Mg(OH)_2$] – water system was selected to investigate the effects of pressure and fluid compositions on the equilibrium hydrogen isotope fractionation factor (α):

$$\frac{1}{2}Mg(OH)_2 + \frac{1}{2}D_2O \leftrightarrow \frac{1}{2}Mg(OD)_2 + \frac{1}{2}H_2O \tag{1}$$

and

$$\alpha_{bruc-wat} = \frac{\beta_{bruc}}{\beta_{wat}} = \frac{(D/H)_{bruc}}{(D/H)_{wat}} \tag{2}$$

The β stands for the reduced isotope partition function ratio (RIPFR, β-factor) and the (D/H) represent an atomic ratio. Brucite is a chemically and structurally simple mineral, which is stable over a wide pressure-temperature range. Its solubility in water is low (Walther, 1986) and water content is high (stoichiometric value, 30.9 wt%). In addition, several investigators reported thermodynamic and spectroscopic properties of brucite at very high temperatures and pressures (Gillet et al., 1996; Bai and Koster van Groos, 1998). Brucite-type minerals serve as a simple, yet useful analog for more complex, hydrogen-bearing oxide and silicate minerals in the deep-earth. These properties make brucite well suited for the investigation of the isotope pressure effects, both experimental and theoretical.