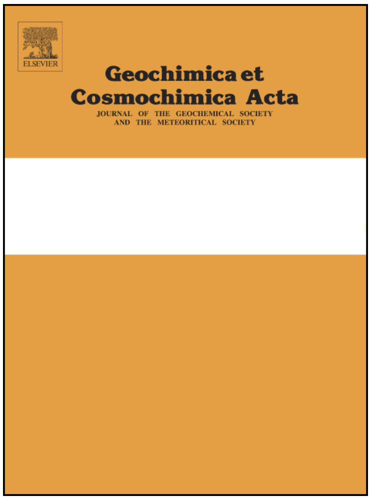

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Kinetics of D/H isotope fractionation between molecular hydrogen and water

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ABSTRACT

At equilibrium, the D/H isotope fractionation factor between H_2 and H_2O ($\alpha_{H2O\text{-}H2(eq)}$) is a sensitive indicator of temperature, and has been used as a geothermometer for natural springs and gas discharges. However, δD_{H2} measured in spring waters may underestimate subsurface temperatures of origin due to partial isotopic re-equilibration during ascent and cooling. We present new experimental data on the kinetics of D–H exchange for H_2 dissolved in liquid water at temperatures below 100 °C. Comparing these results with published exchange rates obtained from gas phase experiments (100–400 °C), we derive a consistent activation energy of 52 kJ/mol, and the following rate expressions;

$$\ln k = 9.186 - 6298/T \quad \text{and} \quad k_1 = 9764.61[\mathrm{H_2O}]\mathrm{e}^{-6298/T}$$

where T is absolute temperature (K), k is the universal rate constant ([L/mol] / hr), and k_1 is a pseudo-first-order constant (hr^{-1}) applicable to water-dominated terrestrial systems by constraining [H_2O] as the density of H_2O (in mol/L) at the P-T of interest. The density-dependent rate constant accounts for the kinetic disparity of D–H exchange with H_2 when dissolved in liquid H_2O relative to a gas/steam phase, exemplifed by $1/k_1$ at 100 °C of ~2 days in liquid, versus ~7 yrs in saturated steam. This difference may explain the high variability of δD_{H2} observed in fumarolic gases. Fluids convecting in the crust frequently reach $T > 225$ °C, where isotopic equilibrium is rapidly attained (< 1 hr). We compare fractionation factors measured in natural fluids (α_{OBS}) with values expected for equilibrium at the T of acquisition. Where these values differ, we use kinetic models to estimate cooling rates during upward advection that account for the observed disequilibrium. Models fit to fluids from Yellowstone Park and the Lost City (deep-sea) vent field, both recovered at ~90 °C, require respective transit times of ~7 hrs and ~11 days between higher temperature reaction zones and the surface. Using estimates of subsurface depths of origin, however, suggests similar mean fluid flow rates (10s of meters / hr). Additional complications