

## H/D isotope salt effects in electrolyte-bearing aqueous solutions: In situ experiments at supercritical conditions

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Equilibrium involving two-phase fluid flow (vapor and brine) describes the evolution of halogen-enriched magmatic systems and defines the relative distribution and chemical composition of the immiscible ionic vapor and brine endmembers. The stable hydrogen and oxygen isotope composition of these phases is often used to describe evolution pathways and to determine the source of hydrothermal crustal fluids and volatile emissions from arc volcanoes. For example, the exchange and fractionation of hydrogen isotopes between H-bearing volatiles (e.g. H<sub>2</sub>, CH<sub>4</sub>, hydrocarbons, H<sub>2</sub>O) in open-system Rayleigh distillation processes associated with magmatic degassing in subduction zones is critical to understanding the isotopic composition of evolved magmatic fluids, and the overall mantle-crust cycling of water and reduced C-O-H volatiles.

Experiments have shown that the presence of water affects the distribution of H- and D-bearing C-O-H species, inducing substantial changes in the isotope composition of C-O-H volatiles even at lower crust/mantle conditions (>600 °C) (1,2). Thus, isotope fractionation effects in magmatic fluids depart significantly from the traditional statistical mechanics models that calculate isotope fractionations assuming ideal-gas conditions. Such effects have also been shown to be prominent in the presence of dissolved ions that control the dielectric properties of the supercritical fluids and the structure of water (3,4). Key hypothesis is that the solvation mechanisms and the solubility of neutral species (e.g. H<sub>2</sub>, CH<sub>4</sub>) are greatly affected under conditions of elevated ionic strength in electrolyte-concentrated aqueous solutions ('salting-out'). For the H<sub>2</sub>O-NaCl system, in particular, experimental studies have shown that low-salinity vapors are D-enriched relative to brines, with the extent of D/H fractionation being dependent of the density of the vapor phase (Fig. 1a) (review in (5)).

Here, we present a series of hydrothermal diamond anvil cell experiments that assess the partitioning of D and H between coexisting magmatic vapors and brine in-situ and in real-time by Raman vibrational spectroscopy (Fig. 1b). These HDAC experiments have been conducted in Na-bearing and Mg-bearing H<sub>2</sub>O and D<sub>2</sub>O solutions that reached the supercritical phase (homogeneous fluid) at temperatures and pressures exceeding 900 °C and 2 GPa, respectively. However, when lower temperatures were approached (e.g. 600-450 °C), phase separation effects were induced allowing for the formation of a volumetrically abundant vapor phase coexisting with a conjugated brine endmember. The effect of Na<sup>+</sup> on the speciation and structure of the H<sub>2</sub>O and D<sub>2</sub>O was monitored in-situ and in real time. Our data suggest for the dominant presence of NaOD<sub>(aq)</sub> (and MgOD<sub>2(aq)</sub>) neutral aqueous species in the vapor, consistent with the 'salting out' effects imposed by highly ionic brine (liquid) phase. Enhanced stability of Na-OD relative to Na-OH neutral species can explain the D/H enrichment of low-salinity vapors sampled from low-pressure hydrothermal experiments (Fig. 1a).

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