



An experimental study on isotope fractionation in a mesoporous silica-water system with implications for vadose-zone hydrology

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Abstract

Soil water dynamics within a thick vadose (unsaturated) zone is a key component in the hydrologic cycle in arid regions. In isotopic studies of soil water, the isotopic composition of adsorbed/pore-condensed water within soils has been assumed to be identical to that of bulk liquid water. To test this critical assumption, we have conducted laboratory experiments on equilibrium isotope fractionation between adsorbed/condensed water in mesoporous silica (average pore diameter 15 nm) and the vapor at relative pressures $p/p_o = 0.3$ –1.0 along the adsorption–desorption isotherm at 30 °C. The isotope fractionation factors between condensed water in the silica pores and the vapor, $\alpha(^2\text{H})$ and $\alpha(^{18}\text{O})$, are smaller than those between liquid and vapor of bulk water (1.074 and 1.0088, respectively, at 30 °C). The $\alpha(^2\text{H})$ and $\alpha(^{18}\text{O})$ values progressively decrease from 1.064 and 1.0083 at $p/p_o = 1$ to 1.024 and 1.0044 at $p/p_o = 0.27$ for hydrogen and oxygen isotopes, respectively, establishing trends very similar to the isotherm curves. Empirical formulas relating $\alpha(^2\text{H})$ and $\alpha(^{18}\text{O})$ to the proportions of filled pores (f) are developed. Our experimental results challenge the long-held assumption that the equilibrium isotope fractionation factors for the soil water–vapor are identical to those of liquid water–vapor system with potential implications for arid-zone and global water cycles, including paleoclimate proxies in arid regions.

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1. INTRODUCTION

Arid regions, generally classified based on mean annual precipitation (hyperarid, 0–50 mm; arid, 50–200 mm; and semiarid, 200–500 mm), constitute much of the Earth's land between latitudes 18° and 40° north and south of the

equator, where the patterns of atmospheric circulation diverge or the lee sides of mountain chains create “rain shadows”. These arid regions currently cover approximately 30% of the terrestrial land surface and account for a significant fraction of global net primary productivity (Grace et al., 2006). Under increasing human activities and the prospect of climate change, including reoccurring severe droughts in many parts of the globe, arid zones are ever expanding and becoming drier (e.g., Feng and Fu, 2013).

The land surface system in arid regions of terrestrial environments is located at a very critical interface within land–atmosphere–vegetation continuum of the energy–water

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balance and ecological systems (Gat, 2010). The partitioning of precipitation and soil water into fluxes of percolation to the subsurface, surface runoff and evapotranspiration at the land–atmosphere–vegetation interface is accompanied by large changes in the stable isotopic ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) values, due to temporal and spatial variations in the isotopic compositions of precipitation events and the isotopic fractionation associated with the evaporation of water, both from open surface water and subsurface soil water (Gat, 2010). The two evaporation fluxes have distinct isotopic compositions and the latter becomes an increasingly dominant flux in arid regions (Good et al., 2015). On the other hand, the isotopic composition of the transpiration flux is very similar to that of soil water since the uptake by plant roots is usually not associated with isotope fractionation (Flanagan and Ehleringer, 1991). Thus, the isotopic compositions of soil water and evaporation flux are the key parameters for our understanding of the land–atmosphere–vegetation interface in arid regions.

Soil pore space, which is the void within and between soil particles, is a continuum of pores whose sizes and shapes vary extremely. Recent studies revealed (Hajnos et al., 2006; Ferreira et al., 2010; Lu et al., 2014) that soil pore sizes range from smaller than nanometers within soil particles to the order of centimeters in shrinkage cracks. Clay minerals also constitute a large fraction of matured soils with interlayers in the range of 1–2 nm. In arid regions strong evaporation from the surface dramatically decreases the water content of soil much below the saturation value. Many observations in desert vadose zones in the U.S. Southwest and elsewhere (Scanlon et al., 1997; Scanlon, 2000; Flint et al., 2002; Duniway et al., 2007) show extremely negative matric potentials of water (–10 to –100 MPa) near the surface due to strong evaporation from the soil surface. Under such dry conditions, large interparticle pores are quickly drained and other mechanisms of water adsorption in soils become dominant, including mono-/multi-layer films on grain surfaces, narrow pore throats, intraparticle pores, and clay interlayer pores. The total reservoir capacity of the “tight” water is probably limited, but large and varying fluxes of water vapor within thick vadose zones make “tight” water an active and crucial component of the water cycle in arid regions.

The structural layers of clay minerals have permanent negative charges, counter-charged by exchangeable cations. These cations adsorbed to clay particles interact with surrounding water and change their properties, including isotope ratios. Stewart (1972) performed experiments on $^2\text{H}/^1\text{H}$ isotopic fractionation between adsorbed water in clays and water vapor. He determined the equilibrium fractionation factors $\alpha = (^2\text{H}/^1\text{H})_{\text{adsorbed water}} / (^2\text{H}/^1\text{H})_{\text{vapor}}$ to be 0.93–1.06 with a median of 1.04, which are significantly lower than that for bulk liquid water–vapor system with $\alpha_{\text{L-V}} = 1.079$ at 25 °C (Horita and Wesolowski, 1994). Oxygen isotope fractionation effects in the homoionic smectite-water mixture were found to be positive for Mg^{2+} and Ca^{2+} exchanged smectites and negative for K^+ exchanged smectite relative to the added water and these isotope effects increase with decreasing water contents (Oerter et al., 2014). Coplen and Hanshaw (1973) found that hydrogen and

oxygen isotopes fractionated in the ultrafiltration experiments through a compacted clay membrane.

Oxides such as silica and alumina are major chemical components of soil minerals. Richard et al. (2007) carried out an experimental study on adsorbed water inside porous silica tubes (10–16 nm pore diameter) at 20 °C and found significantly lower $^2\text{H}/^1\text{H}$ fractionation factors between adsorbed water and water vapor ($\alpha = 1.03$ and 1.065 at 10 and 85% relative humidity, respectively) relative to the bulk water ($\alpha_{\text{L-V}} = 1.084$ at 20 °C, Horita and Wesolowski, 1994). Channel water in various micropore (<2 nm) zeolite minerals (analcime, wairakite, chabazite, laumontite, and modernite) may serve as an analog to capillary condensed water in soil minerals. Limited and inconclusive experimental studies (Karlsson and Clayton, 1990; Feng and Savin, 1993; Noto and Kusakabe, 1997; Karlsson, 2001) suggest that channel water is depleted in both ^{18}O and ^2H relative to bulk water at near ambient temperature, except for modernite.

The objective of this study is to test the hypothesis that equilibrium isotope fractionation between adsorbed/pore-condensed water within soils and water vapor differs significantly from that of the bulk liquid water–water vapor system ($\alpha_{\text{L-V}}$) at the same temperature, due to complex hydrophilic interactions between the soil surface and water molecules. We conducted a series of laboratory experiments to systematically and accurately determine the associated $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ isotope fractionation factors between adsorbed/condensed water in a mesoporous silica sample and water vapor from very low vapor pressure to near the saturation pressure.

2. MATERIAL AND EXPERIMENTAL SETUP

2.1. Material

Soils are mixtures of various minerals of different compositions, sizes, and textures, including organic matter and bacteria. These natural soils are too complex to use in this experimental study. Quartz grains are often used in soil physics studies (e.g., Ottawa sand and Accusand), but they have low surface areas with very limited internal pores (<0.1 m²/g). Mesopores (2–50 nm, as defined by the International Union of Pure and Applied Chemistry, IUPAC) are our main interest as soil analog materials because of: (a) an increasing recognition of their occurrence in soils and various rock types (Gruszkiewicz et al., 2001; Hajnos et al., 2006; Chen et al., 2007; Nielsen and Fisk, 2010) and (b) their strong hysteresis in adsorption–desorption isotherm of water over a wide range of the water activity (p/p_o where p_o is the saturation pressure). Macropores (>50 nm) fill up only at near saturation and micropores (<2 nm) are not of relevance except at extremely dry conditions ($p/p_o < 0.2$).

We used a high-purity grade amorphous silica sample with an average pore diameter of 15 nm from Sigma–Aldrich (CAS No. 112926-00-8, Product No. 243981, Davisil Grade 62, 15 nm pore diameter, 75–250 μm particle size, pore volume 1.15 cm³/g, surface area 300 m²/g). The characteristics of simple chemical composition and variable,

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