



Oxygen isotope fractionation effects in soil water via interaction with cations (Mg, Ca, K, Na) adsorbed to phyllosilicate clay minerals



Erik Oerter^{a,*}, Kari Finstad^a, Justin Schaefer^b, Gregory R. Goldsmith^c, Todd Dawson^d, Ronald Amundson^a

^a Department of Environmental Science, Policy and Management, University of California, Berkeley, 145 Mulford Hall, CA 94720, United States

^b Department of Earth and Planetary Science, University of California, Berkeley, United States

^c Environmental Change Institute, Oxford University, Oxford, United Kingdom

^d Department of Integrative Biology, University of California, Berkeley, United States

ARTICLE INFO

Article history:

Received 5 February 2014

Received in revised form 5 April 2014

Accepted 11 April 2014

Available online 26 April 2014

This manuscript was handled by Corrado Corradini, Editor-in-Chief, with the assistance of Juan V. Giraldez, Associate Editor

Keywords:

Smectite

Isotope hydrology

Isotopic partitioning

Soil-atmosphere interaction

Pedogenic carbonate

Vertisols

SUMMARY

In isotope-enabled hydrology, soil and vadose zone sediments have been generally considered to be isotopically inert with respect to the water they host. This is inconsistent with knowledge that clay particles possessing an electronegative surface charge and resulting cation exchange capacity (CEC) interact with a wide range of solutes which, in the absence of clays, have been shown to exhibit $\delta^{18}\text{O}$ isotope effects that vary in relation to the ionic strength of the solutions. To investigate the isotope effects caused by high CEC clays in mineral–water systems, we created a series of monomineralic–water mixtures at gravimetric water contents ranging from 5% to 32%, consisting of pure deionized water of known isotopic composition with homoionic (Mg, Ca, Na, K) montmorillonite. Similar mixtures were also created with quartz to determine the isotope effect of non-, or very minimally-, charged mineral surfaces. The $\delta^{18}\text{O}$ value of the water in these monomineralic soil analogs was then measured by isotope ratio mass spectrometry (IRMS) after direct headspace CO_2 equilibration. Mg- and Ca-exchanged homoionic montmorillonite depleted measured $\delta^{18}\text{O}$ values up to 1.55‰ relative to pure water at 5% water content, declining to 0.49‰ depletion at 30% water content. K-montmorillonite enriched measured $\delta^{18}\text{O}$ values up to 0.86‰ at 5% water content, declining to 0.11‰ enrichment at 30% water. Na-montmorillonite produces no measurable isotope effect. The isotope effects observed in these experiments may be present in natural, high-clay soils and sediments. These findings have relevance to the interpretation of results of direct CO_2 –water equilibration approaches to the measurement of the $\delta^{18}\text{O}$ value of soil water. The adsorbed cation isotope effect may bear consideration in studies of pedogenic carbonate, plant–soil water use and soil–atmosphere interaction. Finally, the observed isotope effects may prove useful as molecular scale probes of the nature of mineral–water interactions.

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1. Introduction

In isotope-based approaches to hydrology, soil and sediment have been implicitly considered to be an inert matrix through which water passes. Yet, this assumption is inconsistent with the fact that soils contain a wide range of solutes and highly variable concentrations of chemically reactive clay particles (Sposito, 2008), all of which may react with bulk water to create regions of water molecules with different coordination environments and varying isotope compositions.

Previous researchers have postulated the existence of various “pools” of water with differing oxygen isotope compositions in

soils (Ingraham and Shadel, 1992; Araguas-Araguas et al., 1995; Hsieh et al., 1998), but it has only been recently that a growing body of evidence has emerged supporting this hypothesis (c.f. Brooks et al., 2010; Soderberg et al., 2012). The mechanisms for the formation and retention, as well as the locations, of these pools remains largely unexplored, particularly in light of both macro- and molecular-scale considerations of soil mineralogy and physical chemistry.

Soil solutions commonly have high solid to fluid ratios in a matrix of minerals with diverse structures and electrical charges. Based on molecular scale modeling of the organization of water molecules at and near electronegatively charged particle surfaces (Bourg and Sposito, 2011), we anticipate that isotope effects should be produced and be experimentally observable, especially at lower water contents where the ratio between the isotopically

* Corresponding author. Tel.: +1 303 990 1499.

E-mail address: erik.oerter@berkeley.edu (E. Oerter).

“perturbed” water is high relative to free water. The magnitude of these effects should be most evident in soils with high cation exchange capacity (CEC) combined with specific cations adsorbed to the clay particles. Here we conduct laboratory experiments to explore the potential existence of such isotope effects as a first step in a more detailed consideration of the role of stable isotopes in mineral–water interactions.

2. Background

2.1. Ionic solutions

Water that passes through soils physically interacts with an array of solutes, as well as with solids (here, we consider colloidal suspensions as part of the water–solid interaction). The effects of solutes on oxygen isotopes have a long history of study in stable isotope geochemistry (Feder and Taube, 1952, Taube, 1954; Sofer and Gat, 1972, 1975). In general, oxygen isotope fractionation in aqueous saline solutions varies with dissolved cation concentration, and the sign and magnitude of the effect is cation-specific, largely correlating with the “ionic potential” (charge/ionic radius) of the ion in solution and its corresponding polar coordination with water molecules resulting in the formation of hydration spheres around each cation (O’Neil and Truesdell, 1991). The isotopes of oxygen in the water molecules associated with hydration spheres around dissolved ions can be either enriched or depleted in the heavy oxygen isotopes of water, with a corresponding effect on the bulk water. This is the so-called salinity effect.

The most favorable theory explaining the fractionation of water oxygen isotopes by cations in solution is based on the notion of cations with a high ionic potential (e.g. Mg^{2+} , Ca^{2+} herein) creating a more structured organization of water molecules around each cation, as compared to the bulk water. Conversely, cations with lower ionic potential (e.g. K^+) disrupt the water structure around them. Frank and Wen (1957) first observed these macroscopic effects and discussed the structure-making and structure-breaking effects of electrolytes in aqueous solution. More recent studies have both confirmed the effects of cations on the structure of water (Marcus, 2010) and cast doubt on its molecular-scale underpinnings (Turton et al., 2011). This uncertainty does not preclude the use of the structure making and breaking concept to describe the macroscale behavior of water oxygen isotopes in saline solutions. We adopt the operational definition of O’Neil and Truesdell (1991), who articulated that from an oxygen isotope perspective, structure makers have the effect of depleting the bulk water in ^{18}O , while structure breakers yield bulk water with an enriched ^{18}O composition. They justify this definition with the observation of positive isotopic fractionation between ice (highly structured) and liquid water (O’Neil, 1968), and negative isotopic fractionation between vapor (no structure) and liquid water (Majoube, 1971). These simple cases are analogous to water in hydration spheres around cations because these water isotopologues are sequestered away from the bulk water in a similar sense to how they would be in ice crystals.

While the specific molecular-scale mechanism(s) for the reorganization of oxygen isotopes around cations in solution remain uncertain, the prevailing theory (i.e. O’Neil and Truesdell, 1991) is that structure making cations (Mg^{2+} , Ca^{2+}) create organized water by forming two hydration regions around the cation. In the inner sphere, water molecules are strongly bound by the cation’s ionic charge and are structured with their dipoles oriented radially to the cation by an intense electrostatic attraction. The more diffuse outer region is where water molecules are hydrogen bonded to each other and more weakly bound to the cation. The inner, strongly bonded region preferentially incorporates $H_2^{18}O$ with its

shorter intramolecular bonds, while the outer, hydrogen bonded region concentrates $H_2^{16}O$. It is the net balance of the effects of these hydration regions that determines the characteristic cation-specific fractionation effect, with the inner sphere dominating the net effect of the divalent Mg^{2+} and Ca^{2+} ions. In contrast, water structure breaking ions with lower ionic potential (K^+) create a single hydration region of water molecules that are organized by hydrogen bonding. This region of hydrogen-bonded water appears to preferentially incorporate $H_2^{16}O$ molecules, thereby enriching the bulk water outside of the hydration region in $H_2^{18}O$.

In the special case of Na^+ , which does not exhibit net oxygen-fractionating effects, there seem to be two potential mechanisms for the lack of fractionation: if Na^+ creates two hydration spheres around itself, they appear to have largely mutually cancelling effects (Phillips and Bentley, 1987), or that Na^+ creates a region of very mild hydrogen bonded water that does not exert a strong enough influence on the bulk water surrounding it to be observable (Nag et al., 2008). In either mechanistic case, a macroscopic oxygen isotope effect is not seen for Na^+ in aqueous solution.

2.2. Clay mineral interactions with water

Soil is largely a heterogeneous mixture of silicate minerals. The sand (0.05–2 mm) and silt (0.002–0.05 mm) fractions tend to be dominated by primary silicates of low surface area to mass ratios and have a negligible electrostatic charge. In contrast, the clay fraction (<0.002 mm) is commonly dominated by secondary phyllosilicates with high surface area to mass ratios and a considerable permanent negative charge. This negative charge gives rise to a mineral’s cation exchange capacity (CEC), a measure of how many cations (typically Ca^{2+} , Mg^{2+} , K^+ , Na^+) from the surrounding soil solution adsorb to the mineral surface to balance its negative structural charge (Schoonheydt and Johnston, 2013). The most common reactive mineral group within the phyllosilicates (clays) is the smectites, and montmorillonite is a common smectite. These cations adsorbed to clay particles attract water in the form of hydration spheres, and infrared spectroscopic studies of Mg- and Ca-montmorillonite reveal that the properties of the surrounding water are distinct from the bulk water and strongly influenced by the identity of the adsorbed cation (Burgess, 1978; Johnston et al., 1992; Xu et al., 2000).

A comprehensive body of research exists on the effects of clays on water isotope fractionation at higher temperatures and pore water pressures than are found in soils. This work is intended to emulate underground settings such as confined aquifers and geothermal reservoirs and has concluded that diffusive gradients concentrate the heavy isotopic species behind clay membranes, irrespective of cation identity and ionic potential (e.g. Coplen and Hanshaw, 1973; Phillips and Bentley, 1987; Hu and Clayton, 2003). These results differ markedly from observations of oxygen isotope fraction at ambient pressures which are the conditions found in soils and we therefore interpret these high temperature and pressure oxygen isotope effects to be due to mechanisms and processes not present in soils.

Given the large and predictable ionic–water isotope interactions described above, it follows that a more in depth investigation of oxygen isotope fractionation from water–solid interactions is warranted. These water–solid interaction processes likely manifest themselves in nature, particularly in soils with high salt contents, or more generally in any soil with a significant proportion of charged clay minerals (e.g. Vertisols, soils with at least 40% expandable clay and associated high CEC).

In this paper, we examine the effect of monomineralic homionic smectite–water mixtures on the oxygen isotope composition of soil water measurable by CO_2 exchange. This research tests the assumption that soil is essentially an inert matrix for infiltrating

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