



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



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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

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“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

water. Our hypothesis is that cations adsorbed to the clay surface form isotopically organized hydration spheres of water around them and thereby sequester these water molecules away from the bulk water. In turn, this has possible implications for interpretations of the O isotope composition of plant waters and pedogenic carbonates, and their relationship to meteoric water.

3. Methods

To study the effects of smectite particles in soil on the oxygen isotope fractionation of soil water, we used Arizona montmorillonite sourced from near Cameron, Arizona (API clay #49-5107) with a CEC of 60.75 cmol_c/kg and Texas montmorillonite sourced from near Gonzalez, Texas (Source Clay STX1-b) with a CEC of 69.5 cmol_c/kg (both measured by Ba-replacement at the University of California, Davis Analytical Laboratory).

Two stocks of Arizona montmorillonite mineral powder were combined with monoionic cation-chloride aqueous solutions of MgCl₂, CaCl₂, and KCl at either 0.05 M or 1 M concentrations, mixed by hand and allowed to equilibrate and gravitationally settle overnight, after which the supernatant saline solutions were manually decanted. Three saline washes at either 0.05 M or 1 M were followed in a similar manner with three deionized water rinses at circumneutral pH. The mineral–water slurries were dried at 70 °C, yielding dry homoionic montmorillonite powders with all available surface adsorption sites occupied by Mg²⁺, Ca²⁺ or K⁺ cations. Iota[®] quartz sand was similarly prepared as a control. While quartz does have a very small (but measurable) CEC due to unsatisfied hydroxyl bonds at mineral cleavage surfaces, it should have almost no ability to adsorb cations and therefore any observable isotope effect should be minimal, if present at all. These samples are referred to herein as “stir and settle” homoionic and were designed to determine if an adsorbed cation isotope effect was present and detectable. Additionally, these experiments test if the effect is still present when smectite clays are exposed to even weakly saline solutions, and therefore simulate saltwater inundated soils in coastal and estuarine settings.

To more precisely constrain and quantify the adsorbed cation isotope effect, a third stock of clay was prepared using the “acidic washing” method. Texas montmorillonite (Source Clay STX1-b) was employed when our supply of Arizona montmorillonite was exhausted and was prepared by washing the mineral powder with acidic (adjusted to pH 3 with HCl) monoionic cation-chloride aqueous solutions (MgCl₂, CaCl₂, NaCl, KCl) at 1 M concentration multiple times (each separated by centrifugation to allow the supernatant to be completely decanted), followed by multiple rinses with acidified 0.01 M saline solution, ethanol rinses to remove chloride anions and residual H⁺ cations, and oven drying at 70 °C. By preparing this smectite material with acidic electrolyte washes in this way, any weathering products that may have been present on the clay surfaces composed mainly of amorphous Al oxyhydroxide materials (proto-boehmite and gibbsite) that are found ubiquitously in soils are dissolved away from the mineral surfaces and removed (Sposito, 2008).

From each of these homoionic smectite materials, sets of mineral–water mixtures were created in autosampler-specific sample vials with butyl rubber septum caps from homoionic dry mineral powder and deionized water of known isotopic composition at 5–32% gravimetric water content (Tables 1 and 2), the same range of soil water proportions that are commonly observed in nature ($n = 1$ replicate per material for “stir and settle” preparation, 3–4 replicates per material for “acidic washing”). Each mineral–water mixture was prepared with the mineral mass scaled to 0.05 g (50 μL) water, thereby reducing size effects in IRMS analyses. The choice of this small amount of water was necessitated by the

relatively large volume of clay powder required to make gravimetric mixtures at 5% water – 95% clay: 0.95 g clay with ~2 mL clay volume in a 12 mL vial is the largest amount of clay that allows for the autosampler needle to be reliably separated from contact with the clay–water mixture. Water volumes of 50 μL still have three orders of magnitude more moles of H₂O for oxygen isotopic equilibration with CO₂ headspace (2.78×10^{-3} mol H₂O: 7.98×10^{-6} mol CO₂ for driest samples), though do require longer equilibration times. Measured δ¹⁸O values on 50 μL pure water samples maintain accuracy and precision similar to samples with larger water volume regularly analyzed on this instrument. Quartz–water mixtures also yield reliable δ¹⁸O values with 50 μL water volumes (discussed below).

Sample vial headspace was purged with 0.2% CO₂ in He and allowed to equilibrate in the vial at room temperature for ca. 5 days (Epstein and Mayeda, 1953) and analysis was subsequently conducted for δ¹⁸O values on a Thermo Delta V mass spectrometer with Thermo Gas Bench II interface (Center for Stable Isotope Biogeochemistry, UC Berkeley). Analyses were started with three injections of tank reference CO₂ to evaluate instrument stability and calculate δ¹⁸O values. Sample gas was injected five times and δ¹⁸O values were calculated on the average of the last four peak heights. Analytical runs included three lab standard reference waters with well constrained δ¹⁸O (VSMOW) values every 6th sample allowing calibration to the VSMOW scale. Long-term external precision on this instrument is ±0.12‰ for δ¹⁸O of water.

Oxygen isotope δ¹⁸O values are defined and presented in standard notation:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

where R_{sample} and R_{standard} are the ¹⁸O/¹⁶O ratios for the sample and standard, respectively. All δ¹⁸O data are reported in per mil (‰) relative to VSMOW. The difference between the measured δ¹⁸O values of the homoionic mineral–water mixtures (δ_m) and that of the deionized water used to make the mixtures (δ_0) is calculated as in Sofer and Gat (1972):

$$\Delta\delta^{18}\text{O} = \frac{(\delta_0 - \delta_m)}{(1000 + \delta_m)} \times 1000 \quad (2)$$

Δδ¹⁸O values are somewhat counter intuitive because they are opposite the sign of the observed isotope effect. Δδ¹⁸O values are correction factors and are added to the measured δ¹⁸O values to correct for the isotope effect. Positive Δδ¹⁸O values mean that the measured δ¹⁸O values are depleted in ¹⁸O relative to the input water, and negative Δδ¹⁸O values mean that the measured δ¹⁸O values are enriched in ¹⁸O relative to the input water.

4. Experimental results

With respect to the Arizona montmorillonite prepared with the “stir and settle” homoionic washes ($n = 1$), Mg-montmorillonite shows the largest isotope effect with Δδ¹⁸O values of 3.36‰ at 8% water to 0.90‰ at 32% water when prepared with 1.0 M MgCl₂ washing solution, and 3.14‰ at 8% water to 0.54‰ at 32% water when prepared with 0.05 M MgCl₂ washing solution (Table 1 and Fig. 1A). Ca-montmorillonite shows Δδ¹⁸O values of 2.40‰ at 8% water to 0.84‰ at 32% water when prepared with 1.0 M CaCl₂ washing solution, and 3.37‰ at 8% water to 0.81‰ at 32% water when prepared with 0.05 M CaCl₂ washing solution.

Quartz shows a negligible isotope effect with very small Δδ¹⁸O values that are likely due to limits in analytical precision for the continuous flow IRMS instrument, as well as subtle evaporative effects due to the high surface area to volume ratio of the water in the thin capillary film of water surrounding each quartz grain.

Table 1
Data for mineral–water mixtures prepared with neutral pH “stir and settle” homoionic preparation. The values for the last three columns were determined as discussed in the text. The pure water used to prepare these mixtures had $\delta^{18}\text{O}$ of -12.33‰ (VSMOW).

Cation electrolyte	Mineral	Mineral mass (g)	% H ₂ O (g/g)	$\delta^{18}\text{O}$ (VSMOW)	$\Delta\delta^{18}\text{O}$	Repartitioned cation molarity in added H ₂ O	$\Delta\delta^{18}\text{O}$ due to repartitioned cations in added H ₂ O	% $\Delta\delta^{18}\text{O}$ due to repartitioned cations in added H ₂ O
MgCl ₂ [1.0 M]	Montmorillonite	0.580	7.9	-15.63	3.36	0.104	0.116	3.5
		0.265	15.9	-14.00	1.70	0.048	0.053	3.1
		0.108	31.7	-13.21	0.90	0.019	0.022	2.4
MgCl ₂ [0.05 M]	Montmorillonite	0.575	8.0	-15.42	3.14	0.103	0.115	3.7
		0.265	15.9	-13.71	1.40	0.048	0.053	3.8
		0.106	32.0	-12.86	0.54	0.019	0.021	3.9
CaCl ₂ [1.0 M]	Montmorillonite	0.576	8.0	-14.70	2.40	0.143	0.067	2.8
		0.265	15.9	-13.72	1.41	0.066	0.031	2.2
		0.106	32.2	-13.16	0.84	0.026	0.012	1.5
CaCl ₂ [0.05 M]	Montmorillonite	0.578	8.0	-15.64	3.37	0.143	0.067	2.0
		0.264	15.9	-14.34	2.04	0.065	0.031	1.5
		0.111	31.1	-13.13	0.81	0.028	0.013	1.6
MgCl ₂ [1.0 M]	Quartz	0.577	8.0	-12.38	0.05	–	–	–
		0.264	15.9	-12.24	-0.09	–	–	–
		0.107	31.8	-12.31	-0.02	–	–	–
MgCl ₂ [0.05 M]	Quartz	0.579	7.9	-12.09	-0.24	–	–	–
		0.264	15.9	-12.23	-0.10	–	–	–
		0.109	31.5	-12.13	-0.20	–	–	–
CaCl ₂ [1.0 M]	Quartz	0.574	8.0	-12.06	-0.27	–	–	–
		0.262	16.0	-12.18	-0.16	–	–	–
		0.105	32.2	-12.08	-0.25	–	–	–
CaCl ₂ [0.05 M]	Quartz	0.576	8.0	-12.23	-0.10	–	–	–
		0.262	16.0	-12.07	-0.26	–	–	–
		0.106	32.1	-11.94	-0.39	–	–	–

This is as expected, given the near complete absence of a structural charge on which to adsorb cations.

Experiments with the “stir and settle” homoionic preparation method show a larger isotope effect than the homoionic samples prepared with acidic washing and centrifugation, and therefore may be complicated by the incomplete removal of residual salts from the electrolyte cation-loading solutions. Even with this additional complication, these samples demonstrate the efficacy of cation loading solution concentrations equivalent to those found in nature (seawater [Mg] = 0.05 M) and these soil analogs are similar to soil or sediment samples found in the field, i.e. clay-rich soils in semiarid climates or within coastline or estuarine settings that have been inundated by saline or brackish waters.

$\Delta\delta^{18}\text{O}$ values for mineral–water mixtures composed of Texas montmorillonite prepared with the acidic homoionic washing are shown in Table 2 and Fig. 1B. Mg-montmorillonite shows the largest isotope effect with $\Delta\delta^{18}\text{O}$ values from 0.96‰ to 1.55‰ (Ave = 1.20‰, S.D. = 0.31, $n = 3$) at 5% water content to $\Delta\delta^{18}\text{O}$ values of 0.49‰ to 0.70‰ (Ave = 0.60‰, S.D. = 0.11, $n = 3$) at 30% water. Ca-montmorillonite had an isotope effect nearly as large as Mg, with $\Delta\delta^{18}\text{O}$ values from 0.74‰ to 1.01‰ (Ave = 0.92‰, S.D. = 0.15, $n = 3$) at 5% water content to $\Delta\delta^{18}\text{O}$ values from 0.33‰ to 0.39‰ (Ave = 0.35‰, S.D. = 0.03, $n = 3$) at 30% water. K-montmorillonite shows $\Delta\delta^{18}\text{O}$ values from -0.51‰ to -0.86‰ (Ave = -0.69‰ , S.D. = 0.17, $n = 3$) at 5% water content to $\Delta\delta^{18}\text{O}$ values of -0.11‰ to -0.27‰ (Ave = -0.21‰ , S.D. = 0.08, $n = 3$) at 30% water. Na-montmorillonite shows $\Delta\delta^{18}\text{O}$ values from 0.01‰ to -0.24‰ (Ave = -0.09‰ , S.D. = 0.12, $n = 4$) at 5% water content to -0.03‰ to -0.16‰ (Ave = -0.10‰ , S.D. = 0.06, $n = 3$) at 30% water.

5. Discussion

These experiments affirm the fact that smectite minerals are not an isotopically inert medium for water. Pure water that is exposed to homoionic smectite will undergo reactions with the solid phase that ultimately changes the stable isotope composition

of the more energetically free water that remains. The reactions are clearly impacted by the concentration and valence of the adsorbed cation phases, and also likely reflect additional, but poorly understood, effects of water–mineral interactions.

When pure water is added to the homoionic smectite, two processes occur simultaneously. First, the exchangeable cations on the clay surfaces hydrate and reconfigure into the inner- and outer-sphere complexes of the electrical double layer, while some portion of the cations become fully solvated and go into solution where they exert the isotope effects previously discussed as the ‘salinity effect’. Second, those cations that remain in the inner- and outer-sphere complexes that are adsorbed to the clay surfaces and are not fully solvated, form hydration spheres around them and exert a different fractionation effect on the bulk water, see Fig. 2 for a conceptual depiction of this process. The $\Delta\delta^{18}\text{O}$ values measured on mineral–water mixtures are a combination of these two effects and their respective contributions to the net observed effect. Separating out the magnitude of each component’s contribution to the net isotope effect can yield information on the nature of the adsorbed cation effect.

Following equilibration with pure water, the concentration of cations desorbed from the clay and now are solvated in solution is calculated by multiplying the initial quantity of cations adsorbed on the clay by the partition coefficient (K_D): $K_D = A/C$, where A is the amount of cations adsorbed on the clay and C is the amount of cations in solution. K_D values available in the literature for base cations in clay soils are shown in Table 3 (Baes and Sharp, 1983). K_D values for Na are unavailable and so an estimated value of 9 mL/g is used, based on the value for K and its relative similarity in ionic properties to Na. To express K_D values as a dimensionless ratio (K_D^*), K_D (mL/g) is multiplied by the density of montmorillonite (2.5 g/cm^3) (Appelo and Postma, 1999). The molarity of the equilibrated water in each mineral–water mixture after cation repartitioning is shown in Tables 1 and 2, and calculated as follows.

The concentration of adsorbed cations per unit mass of dry homoionic montmorillonite can be determined by reasoning that

Table 2

Data for Texas montmorillonite mineral–water mixtures prepared with acidic homoionic preparation. The values for the last three columns were determined as discussed in the text. The pure water used to prepare these mixtures had $\delta^{18}\text{O}$ of -11.74‰ (VSMOW).

Cation	Mineral mass (g)	% H ₂ O (g/g)	$\delta^{18}\text{O}$ measured (VSMOW)	$\Delta\delta^{18}\text{O}$	Repartitioned cation molarity into added H ₂ O	$\Delta\delta^{18}\text{O}$ due to repartitioned cations into added H ₂ O	% $\Delta\delta^{18}\text{O}$ due to repartitioned cations into added H ₂ O
Mg ²⁺	0.960	5.0	-13.27	1.55	0.198	0.219	14.1
	0.940	5.1	-12.69	0.96	0.194	0.215	22.3
	0.950	5.0	-12.80	1.08	0.196	0.217	20.2
	0.470	9.6	-12.90	1.18	0.097	0.107	12.5
	0.440	10.2	-12.78	1.06	0.091	0.101	9.1
	0.460	9.8	-12.59	0.86	0.095	0.105	9.2
	0.283	15.0	-12.92	1.19	0.058	0.065	4.6
	0.287	14.8	-12.69	0.97	0.059	0.066	4.6
	0.284	15.0	-12.68	0.96	0.058	0.065	3.8
	0.204	19.7	-12.68	0.95	0.042	0.047	3.4
	0.201	19.9	-12.58	0.85	0.041	0.046	3.0
	0.201	19.9	-12.62	0.89	0.041	0.046	2.7
	0.113	30.7	-12.22	0.49	0.023	0.026	2.6
	0.113	30.7	-12.43	0.70	0.023	0.026	3.8
	0.114	30.5	-12.34	0.60	0.023	0.026	2.7
	Ca ²⁺	0.953	5.0	-12.47	0.74	0.196	0.092
0.951		5.0	-12.74	1.01	0.196	0.092	12.5
0.952		5.0	-12.73	1.00	0.196	0.092	12.7
0.452		10.0	-12.67	0.94	0.093	0.044	6.4
0.454		9.9	-12.68	0.95	0.093	0.044	6.4
0.455		9.9	-12.90	1.17	0.094	0.044	5.2
0.284		15.0	-12.54	0.81	0.058	0.027	4.7
0.283		15.0	-12.63	0.90	0.058	0.027	4.2
0.283		15.0	-12.73	1.00	0.058	0.027	3.8
0.200		20.0	-12.48	0.75	0.041	0.019	3.5
0.200		20.0	-12.24	0.51	0.041	0.019	5.2
0.200		20.0	-12.44	0.71	0.041	0.019	3.8
0.120		29.4	-12.07	0.33	0.025	0.012	4.8
0.114		30.5	-12.07	0.34	0.023	0.011	4.5
0.117		29.9	-12.12	0.39	0.024	0.011	4.0
K ⁺		0.949	5.0	-10.89	-0.86	0.391	-0.063
	0.947	5.0	-11.03	-0.71	0.390	-0.062	8.8
	0.947	5.0	-11.23	-0.51	0.390	-0.062	12.1
	0.453	9.9	-11.17	-0.58	0.187	-0.030	5.2
	0.449	10.0	-11.57	-0.17	0.185	-0.030	17.1
	0.449	10.0	-11.18	-0.57	0.185	-0.030	5.2
	0.281	15.1	-11.42	-0.32	0.116	-0.019	5.8
	0.282	15.1	-11.65	-0.09	0.116	-0.019	20.7
	0.282	15.1	-11.52	-0.22	0.116	-0.019	8.4
	0.199	20.1	-11.51	-0.23	0.082	-0.013	5.7
	0.200	20.0	-11.70	-0.04	0.082	-0.013	31.8
	0.200	20.0	-11.62	-0.13	0.082	-0.013	10.5
	0.118	29.8	-11.51	-0.24	0.049	-0.008	3.3
	0.116	30.1	-11.48	-0.27	0.048	-0.008	2.9
	0.115	30.3	-11.63	-0.11	0.047	-0.008	6.7
	Na ⁺	0.951	5.0	-11.60	-0.15	0.392	0
0.950		5.0	-11.50	-0.24	0.391	0	0
0.950		5.0	-11.75	0.01	0.391	0	0
0.950		5.0	-11.74	0.01	0.391	0	0
0.452		10.0	-11.96	0.23	0.186	0	0
0.451		10.0	-11.70	-0.04	0.186	0	0
0.450		10.0	-11.89	0.15	0.185	0	0
0.451		10.0	-11.80	0.06	0.186	0	0
0.283		15.0	-11.81	0.07	0.117	0	0
0.282		15.1	-11.84	0.10	0.116	0	0
0.284		15.0	-11.83	0.09	0.117	0	0
0.284		15.0	-11.73	-0.01	0.117	0	0
0.198		20.2	-11.90	0.16	0.082	0	0
0.199		20.1	-11.82	0.08	0.082	0	0
0.199		20.1	-11.68	-0.06	0.082	0	0
0.200		20.0	-11.70	-0.04	0.082	0	0
0.118	29.8	-11.67	-0.07	0.049	0	0	
0.118	29.8	-11.58	-0.16	0.049	0	0	
0.117	29.9	-11.71	-0.03	0.048	0	0	
0.116	30.1	-11.63	-0.12	0.048	0	0	

every available charge site to adsorb a cation is occupied after the homoionic clay preparation. For monovalent cations this amount is simply the measured CEC of the mineral (Arizona Montmorillonite:

60.8 cmol_c/kg; Texas montmorillonite: 69.5 cmol_c/kg), and for divalent cations it is half this number, as each divalent cation balances two structural charge sites. The total amount of cation

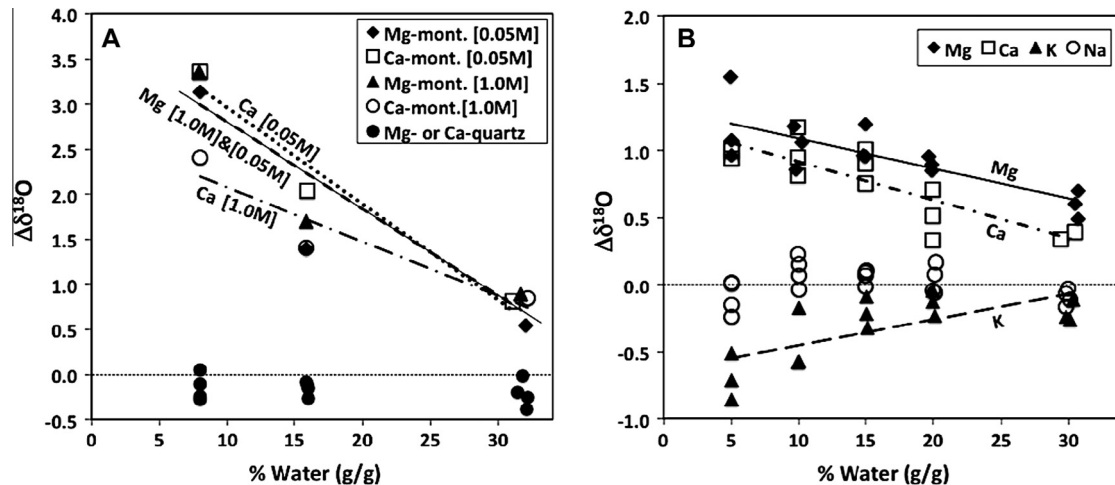


Fig. 1. The relationship of $\Delta\delta^{18}\text{O}$ to gravimetric water content for (A) Mg- and Ca-montmorillonite-water, and quartz-water, mixtures prepared with the “stir and settle” washing method with varying cation concentration, and (B) Mg-, Ca-, K-, Na-montmorillonite-water mixtures prepared with the acidic washing method.

adsorbed to clay particles in a gravimetric sample is then easily determined by multiplying the CEC by the mass of mineral.

The portion of the observed $\Delta\delta^{18}\text{O}$ values that are attributable to the isotope salinity effect, which is due to the fractionation of water molecules into hydration spheres around fully solvated cations compared to the pure water used to make the solutions, can be determined by multiplying the equilibrated solution molarity by the salinity effect per molarity unit as characterized by [Sofer and Gat \(1972\)](#): 1.11‰ for Mg^{2+} , 0.47‰ for Ca^{2+} , 0‰ for Na^+ , $-0.16‰$ for K^+ . The component of $\Delta\delta^{18}\text{O}$ values for each mineral–water mixture that is directly attributable to the salinity effect of repartitioned cations into the aqueous phase is shown in [Tables 1 and 2](#).

The magnitude of the isotope effect due to adsorbed cations can be determined by subtracting the salinity effect component from the observed $\Delta\delta^{18}\text{O}$ value. In general, the salinity effect exerted by cations in solution are on the order of 7–22% of the total observed for the driest mineral–water mixtures (5% water), and are less than 10% of the observed $\Delta\delta^{18}\text{O}$ values for wetter samples with 8% or more water. The balance of the isotope effect and observed $\Delta\delta^{18}\text{O}$ values is therefore attributable either solely to that exerted by adsorbed cations on the bulk water or by a combination of the adsorbed cations and some other factor(s), such as reactions with the mineral surface itself.

Considering the mass balance of water added to the mineral–water mixtures can help elucidate the observed trend of increasing adsorbed cation effect with decreasing water content. The total amount of water molecules coordinated in hydration spheres around cations adsorbed to clay surfaces can be found by multiplying the number of water molecules per hydration sphere (“hydration number” in [Table 3](#); [Ohtaki and Radnai, 1993](#)) by the CEC of the mineral (assuming adsorbed cations have the same coordination arrangement when adsorbed compared to in solution). For the case of Mg exchanged Texas montmorillonite, this is

$6 \times 69.5 \text{ meq}/100 \text{ g} = 417 \text{ mmol}/100 \text{ g}$. This quantity of coordinated water is then multiplied by the molar mass of water (18 g/mol) and converted into mol from mmol, yielding 7.506 g water per 100 g clay, or 7.5% water content. Above this threshold, the increasing proportion of bulk to adsorbed water will diminish the influence of the adsorbed cation effect.

Though it is somewhat approximate, the relationship of the adsorbed isotope effect component to the concentration of cations remaining adsorbed (in a net equilibration sense) to the clay particles in the mineral–water mixtures (which is, analogous to adsorbed cation molarity), is 0.96‰ per mole of adsorbed cation for Mg^{2+} , 1.19‰ for Ca^{2+} and $-0.9‰$ for K^+ ([Table 4](#)). Not surprisingly, and similar to its behavior in solution, Na^+ does not show an isotopic effect when adsorbed to smectite surfaces ([Fig. 3A and B](#)).

The effects of Mg, both adsorbed and in solution, are relatively similar on a per mole basis. However, Ca shows a twice-greater effect when adsorbed, as compared to in solution, and is comparable to that of Mg. [Xu et al. \(2000\)](#), using infrared spectroscopy, found that as the water content of Mg- and Ca-montmorillonite decreases to <10 water molecules per exchangeable cation (~12.5% water for Texas montmorillonite in this study), the water molecules are clustered around the adsorbed cation and are restricted in their ability to form hydrogen bonds with the surrounding bulk water, a condition that would seem to favor water structure making and the attendant isotopic effects. Interestingly, both Mg- and Ca-montmorillonite behaved in a similar manner in the study of [Xu et al. \(2000\)](#), suggesting that once the clay surface is saturated by adsorbed cations, divalent base cations regardless of identity exert a similar effect on the structure of water. This may explain why the adsorbed cation isotope effects for Mg and Ca seen in this study are similar to each other in magnitude.

Somewhat surprisingly, K shows an effect more than 5 times greater when it is adsorbed compared to when in solution

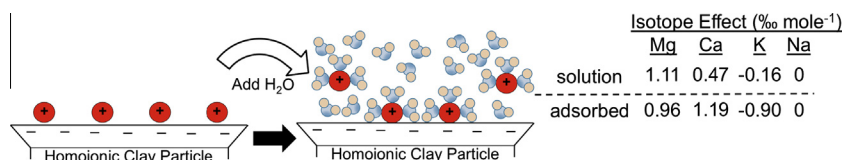


Fig. 2. Conceptual depiction of cation repartitioning when homoionic clay is exposed to liquid water and the corresponding isotope effect attributable to each component. Solution data from [Sofer and Gat \(1972\)](#), adsorbed data this study.

Table 3

Ionic properties for materials used in this study. Hydration numbers from Ohtaki and Radnai (1993).

Cation	Hydration #	K_D (mL/g)	K_D^*	Adsorbed cation molarity (mol/kg)	
				AZ	TX
				montmorillonite	montmorillonite
Mg ²⁺	6	13.5	33.75	0.30375	0.3475
Ca ²⁺	6	9.8	24.5	0.30375	0.3475
K ⁺	4	9	22.5	0.6075	0.695
Na ⁺	4	9	22.5	0.6075	0.695

(Fig. 3B: -0.9‰ mole⁻¹ for adsorbed K, Fig. 1B: -0.16‰ mole⁻¹ for K in solution). This disproportionate effect suggests that there is likely another mechanism present that enhances the inclusion of isotopically light water in the vicinity of K-montmorillonite surfaces, thereby enriching the bulk water in H₂¹⁸O. That is, the net effect of the structure-breaking cation seems to be enhanced. An aspect of the K⁺ ion that may be relevant is that its ionic size allows it to fit into the open crystal structure of phyllosilicate mineral sheets (Sposito, 2008). This ability to create a relatively “satisfied” surface both electrically and texturally may enhance the ability of the surface to create regions of hydrogen bonded water near to it, as discussed below.

The isotopic fractionation factor per unit mole between water surrounding desorbed cations in solution and water associated with adsorbed cations on clay surfaces can be calculated from the per mole δ values by the relationship:

$$\alpha_{\text{aq-ad}} = (1000 + \delta_{\text{aq}})/(1000 + \delta_{\text{ad}}) \quad (3)$$

where δ_{aq} and δ_{ad} are the molar components of the measured δ values as described above. Fractionation factors for the cations in this study are listed in Table 4, and expressed as $1000\ln\alpha$ for utility.

There is some evidence that smectite surfaces themselves may exert an isotope effect on water by creating a very thin film of structurally broken water at the mineral surface. Bourg and Sposito (2011) conducted molecular dynamics simulations of the organization of water near smectite surfaces and found several regions with a higher density of water molecules in the electrical double layer at the mineral–water interface. Immediately adjacent to the clay (2.7 Å from surface), the density of water molecules in the first statistical water monolayer is more than three times larger than that in the bulk water, and that these molecules are hydrogen bonded to surface O atoms. In the region of the second statistical water monolayer (6.4 Å), water molecule density is between 1 and 3 times that of the bulk water. Their calculations reveal that diffusion of both water molecules and ions within these high water density regions is rapid enough to indicate that this water is not rigidly structured in an “ice-like” manner (Bourg and Sposito, 2011). The presence of regions of hydrogen bonded water and the lack of rigid structure in the vicinity of smectite surfaces seem to indicate that there is the potential for water isotope fractionation between this high water density region and the bulk water in a manner akin to that observed in aqueous solutions of structure breaking cations like K⁺. The effects associated with smectite

Table 4

Measured isotope values and fraction factors per unit mole. All δ units are ‰ per mole of cation desorbed in solution (aq) or adsorbed to mineral surfaces (ad).

Cation	δ_{aq}	δ_{ad}	$1000\ln\alpha$
Mg ²⁺	1.11	0.96	0.15
Ca ²⁺	0.47	1.19	-0.72
K ⁺	-0.16	-0.9	0.74
Na ⁺	0	0	0

surfaces may be present in the interlayer space between phyllosilicate crystal structures and may be contributing to the macroscopic isotope effect that is observed in the bulk water. Moreover, the effects of the smectite clay surface may enhance the magnitude of the isotopic effects of the structure breaking cations when adsorbed to smectite surfaces.

Beyond these fundamental physical interactions there are practical implications of our observed effects on the use of stable isotopes in terrestrial ecosystem hydrology. First, the analytical method chosen to assess soil water oxygen isotope composition must be considered in view of the intended “pools” of soil water to be measured. Direct equilibration, used here, clearly measures a portion of soil water that is free for equilibration with CO₂, in contrast to water extracted by various methods which reflect the total soil water isotope composition. While direct equilibration of CO₂ with in situ soil water will not reflect the total soil water composition, it may in turn be a more reliable guide to the composition of water that is biologically available or reactive in mineral precipitation (such as calcite). Additionally, a spatial distribution of various pools of soil water may be analytically accessible through the use of the screening effect that the limited CO₂ diffusive path length in various soil water environments presents. The use of direct equilibration techniques has greatly increased in recent years for laboratory IRMS (e.g. Scrimgeour, 1995; Hsieh et al., 1998; Ignatev et al., 2013) and IRIS analyses (Wassenaar et al., 2008), as well as in field analyses (Breecker and Sharp, 2008; Herbstritt et al., 2012; Rothfuss et al., 2013).

An especially vigorous area of research in ecohydrological science revolves around investigations into plant water use and its spatiotemporal variability. These approaches generally rely on variation in the isotopic profile of soil water as a function of depth in the soil horizon, which occurs when dry conditions drive soil surface evaporation (Barnes and Allison, 1988; Braud et al., 2009). These dry conditions are where we observe the greatest adsorbed cation fractionation effect. Research on plant water use utilizing both oxygen and hydrogen isotopes has recently demonstrated the possibility of two distinct soil water pools: a more mobile pool of water that resembles the precipitation and stream water associated with the local meteoric water line, as well as a second and less mobile pool of water that is consistent with plant water use (Brooks et al., 2010; Goldsmith et al., 2012). The adsorbed cation isotope effect presented here may be relevant to the isotopic composition of plant available water in soils with some component of high-CEC clay and when soil water conditions are drying. Our experimental results combined with observations of aberrant soil water isotope signatures in field soils (Orlowski et al., 2013; Meißner et al., 2014) suggests that soil mineralogy may warrant greater consideration in isotopic studies of soil and plant water.

The results here are also relevant to interpreting the stable isotope composition of secondary, pedogenic carbonate in paleosols. Clay-rich soils (Vertisols, soils with a minimum of 40% expandable clay) are found on outcrops of clay rich rock or sediment, coastal or estuarine environments, basin deposits, or outcrops of shale or mudstone (Soil Survey Staff, 1999). Additionally, outcrops of basalt or ultramafic rock commonly weather, especially in semiarid settings, into clay rich Vertisols. Fossil Vertisols (buried clay-rich soils) are especially prominent in the geological record since they form at the distal ends of large subsiding basins. Additionally, these fossil soils are commonly rich in pedogenic carbonate (CaCO₃), and thus are similar to the Ca-rich smectite experiments in Table 2 and Fig. 1B. It appears that the water recorded by the oxygen isotopes in carbonate forming in equilibrium with soil water may be about 1 per mil more depleted than that which would be recorded by carbonate forming in equilibrium with the meteoric waters that entered the soil, since pedogenic carbonate minerals precipitate when soils are at their driest (Breecker et al., 2009), soil moisture

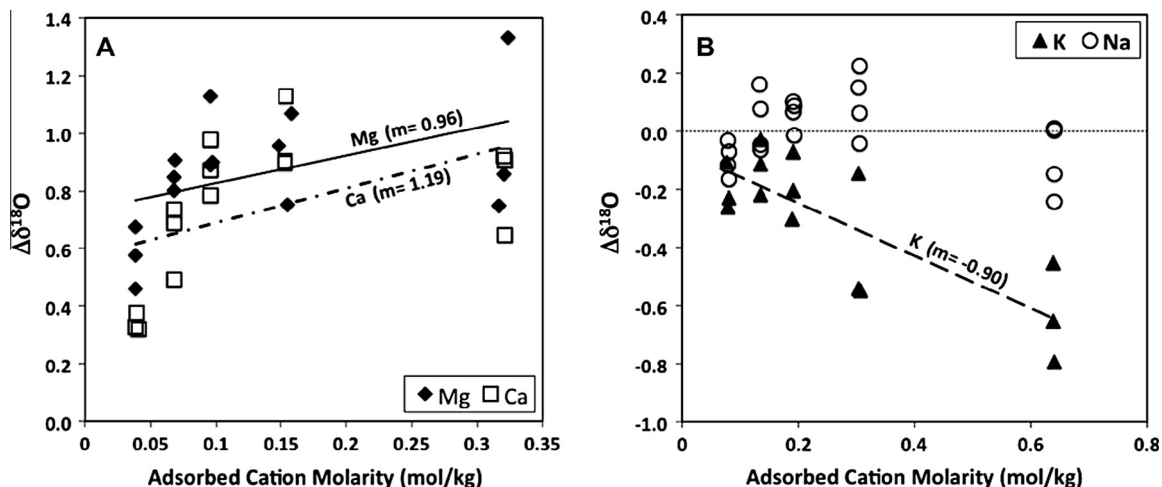


Fig. 3. The relationship of $\Delta\delta^{18}\text{O}$ to the concentration of adsorbed cation concentration for (A) Mg- and Ca-montmorillonite-water mixtures prepared by the acidic homoionic washing method and (B) K- and Na-montmorillonite-water mixtures prepared by the acidic homoionic washing method.

contents analogous to <15% in Fig. 1B. While the net effect is likely modest, it may have significance in certain paleo-interpretations.

The biggest impact of these findings may be on the evolving efforts to use the O isotope composition of atmospheric CO_2 to serve as a probe of gross primary production and ecosystem exchange (e.g. Werner et al., 2012). One of the most complex parameters in these efforts is the net effect of soil respiration and abiotic exchange with the atmosphere (Stern et al., 2001). The additional issue of meteoric water reactions with soil minerals and salts adds yet an additional challenge for this approach, and even a few per mil shift in the soil water value on a global scale, has enormous impacts on global estimates of GPP (Stern et al., 2001; Yakir and Sternberg, 2000). The influence of soil on the $\delta^{18}\text{O}$ composition of the atmosphere has been investigated by analytic and numeric modeling studies, and one conclusion of this work is that some component of the atmospheric oxygen isotope composition is determined by the global-scale direct equilibration of atmospheric CO_2 with soil water (Tans, 1998; Stern et al., 1999).

As mentioned, soils that may be especially reactive in an oxygen isotope sense with atmospheric CO_2 are Vertisols, which are rich in fine-grained, smectite clays and undergo intense shrink/swell behavior with desiccation cracks opening during the drying season to depths greater than 50 cm (Soil Survey Staff, 2010). These cracks increase the area of the soil-atmosphere interface, promoting isotopic exchange between soil water and the atmosphere. This enhanced atmospheric perfusion to considerable depths, coupled with the occurrence of Vertisols across 2.4% of Earth's surface (Dudal and Eswaran, 1988), suggests that adsorbed cation isotope effects on the $\delta^{18}\text{O}$ composition of the atmosphere may warrant further investigation.

6. Conclusions

We show that cations adsorbed to high-CEC clay mineral particles can create isotopically distinct “pools” of water that may not readily mix with each other or the bulk water in the soil solution. The measured $\delta^{18}\text{O}$ values of soil water in the vicinity of high-CEC clay minerals may therefore only be reflecting a portion of the total soil water. Investigations of oxygen isotope dynamics in soil water are of interest to a variety of disciplines ranging from soil science to stable isotope ecology to the study of global biogeochemical fluxes. Our ability to observe and accurately predict the role of clay mineralogy on soil water oxygen isotopes is a critical step towards

the eventual evaluation of this isotope effect in natural soils and for incorporating the effect in biophysical applications.

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