

The stable isotope composition of halite and sulfate of hyperarid soils and its relation to aqueous transport

Ronald Amundson^{a,*}, Jaime D. Barnes^{b,1}, Stephanie Ewing^{a,2},
Arjun Heimsath^c, Guillermo Chong^d

^a *Division of Ecosystem Sciences, 137 Mulford Hall, University of California, Berkeley, CA 94720, USA*

^b *Department of Earth and Planetary Sciences, MSC03-2040, University of New Mexico, Albuquerque, NM 87131-0001, USA*

^c *School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA*

^d *Departamento de Ciencias Geológicas, Universidad Católica del Norte, Antofagasta, Chile*

Received 29 September 2011; accepted in revised form 21 April 2012; available online 20 June 2012

Abstract

Halite (NaCl) and gypsum or anhydrite (CaSO₄) are water-soluble minerals found in soils of the driest regions of Earth, and only modest attention has been given to the hydrological processes that distribute these salts vertically in soil profiles. The two most notable chloride and sulfate-rich deserts on earth are the Dry Valleys of Antarctica and the Atacama Desert of Chile. While each is hyperarid, they possess very different hydrological regimes. We first show, using previously published S and O isotope data for sulfate minerals, that downward migration of water and sulfate is the primary mechanism responsible for depth profiles of sulfate concentration, and S and O isotopes, in both deserts. In contrast, we found quite different soluble Cl concentration and Cl isotope profiles between the two deserts. For Antarctic soils with an ice layer near the soil surface, the Cl concentrations increase with decreasing soil depth, whereas the ratio of ³⁷Cl/³⁵Cl increases. Based on previous field observations by others, we found that thermally driven upward movement of brine during the winter, described by an advection/diffusion model, qualitatively mimics the observed profiles. In contrast, in the Atacama Desert where rare but relatively large rains drive Cl downward through the profiles, Cl concentrations and ³⁷Cl/³⁵Cl ratios increased with depth. The depth trends in Cl isotopes are more closely explained by a Rayleigh-like model of downward fluid flow. The isotope profiles, and our modeling, reveal the similarities and differences between these two very arid regions on Earth, and are relevant for constraining models of fluid flow in arid zone soil and vadose zone hydrology.

© 2012 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Isotopic studies of water-soluble minerals in hyperarid soils provide insight into the physical processes that operate in these extreme environments. Many studies have explored

isotopes as ways to identify the origin of the elements that comprise the soluble minerals (e.g. NaNO₃, CaSO₄) (Rech et al., 2003; Michalski et al., 2004). However, interpreting the data has ultimately proven to be complex due to isotopic alteration by biological processes (Michalski et al., 2004; Ewing et al., 2007) or abiotic aqueous fractionation processes (Ewing et al., 2008). Very rarely is the isotopic composition of a sample a direct reflection of its source.

Two minerals of special interest in hyperarid soils are gypsum and/or anhydrite (CaSO₄) and halite (NaCl). For both of these salts, there are long standing questions about the sources of the elements that comprise them. In Antarctica, Bao et al. (2000, 2008) considered sea salt, long-range

* Corresponding author.

E-mail addresses: earthy@berkeley.edu (R. Amundson), jdbarnes@jsg.utexas.edu (J.D. Barnes).

¹ Now at Department of Geological Sciences, University of Texas, Austin, TX 78712, USA.

² Now at Department of Land Resources and Environmental Sciences, Montana State University, Bozeman, MT 59717, USA.

atmospheric sources, and underlying permafrost as possible soil salt sources. In the Atacama Desert of Chile, the warm counterpart to the cold Antarctic deserts, Cl and SO₄ can potentially be derived from marine, volcanic, or sedimentary sources. These questions have led to the use of stable isotopes as a way to quantify various salt sources in arid regions (Bao et al., 2000, 2008).

In this paper, we compare depth profiles of S, O, and Cl stable isotopes in the Antarctic and Atacama Deserts, using new and published data. We then focus on determining the underlying processes responsible for the profiles, and derive simple explanatory models for each desert. We show both deserts have sulfate concentration profiles caused by downward migration of waters, but that the two deserts have differing hydrological processes with respect to chloride redistribution. To begin, we examine the geologic characteristics of each desert.

2. FIELD AREAS

2.1. Atacama Desert

The Atacama Desert is the driest warm desert on Earth. The Andes block austral summer precipitation from the Atlantic Ocean. Atmospheric and oceanic circulation prevent the intrusion of Pacific moisture from the west. As a result, large segments of the region receive no rainfall for many years, and the long-term average may be a few mm or less per year (Fig. 1).

The age of the alluvial deposits and their associated soils is largely restricted to two broad time intervals. Large areas of well-preserved Miocene alluvial deposits are found throughout the region, comprising one major age grouping of soils. Inset into the Miocene deposits is a vast region of largely late Pliocene-aged alluvium, the result of a major period of erosion of the older Miocene sedimentary infills. Post-Pliocene (e.g. Quaternary) fluvial modification and deposition is confined to near channel environments, and is thus a small segment of the landscape (Amundson et al., in press).

Soil formation processes in the late Pliocene deposits have been largely constant over time, due to only modest apparent variations in rainfall for the past 2 My (Ewing et al., 2006). Soils lack chemical weathering, and appear to quantitatively retain salts derived from the atmosphere (Ewing et al., 2006). Eighty percent of all nitrate in the soils contains a mass independent O isotope signal imparted during atmospheric oxidation, indicating that it has not undergone biological modification over a multi-million year time period (Ewing et al., 2007). Of relevance to this paper, Ewing et al. (2008) found large Ca, S, and O isotope variations with depth in gypsum and anhydrite. These isotope profiles were explained with a model describing abiotic processes of mineral dissolution and reprecipitation combined with slow (and sporadic) downward transport of solutes with rainfall.

Miocene soils have more complex weathering and soil development histories. The geomorphic surfaces exhibit remarkable preservation, but the soil profiles are more morphologically complicated. Field observations suggest multiple stages of soil formation in very dry conditions, with

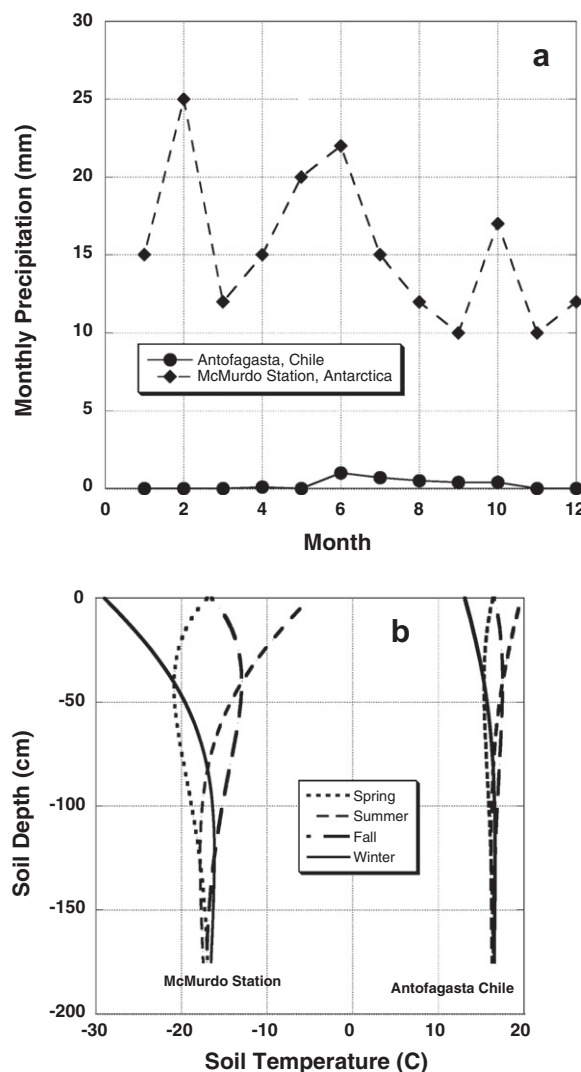


Fig. 1. (a) Monthly mean annual precipitation for McMurdo Station (http://www.antarcticconnection.com/antarctic/weather/hist_wxdata/mcMurdo_station.shtml) and Antofagasta, Chile (<http://www.worldclimate.com/>). (b) Annual range in monthly average air temperatures (temperature at 0 soil depth) for Antarctica and Chile, and projected soil temperature using Eq. (5) in text and a damping depth of 54 cm.

possible humid interludes. In summary, the soils on these landforms are hypothesized to be “poly-genetic”.

In this study, we measured the Cl stable isotopes in (1) a late Pliocene soil which has been the subject of O, S, and Ca isotope investigations of sulfate and nitrate (Ewing et al., 2007, 2008) and (2) a nearby soil in a well-preserved Miocene landscape (Fig. 2a). Both soils formed in an initially salt free, gravely to sandy, fluvial parent material of mixed lithology. The Pliocene soil is largely granitic, whereas the Miocene soil contains more rhyolitic material. Both soils also have significant accumulations of atmospherically derived dust and salt, with corresponding volumetric expansion. The presence of a regional, ~10 cm thick, soft and porous gypsum/anhydrite layer (immediately below a discontinuous desert pavement) is suggestive of a recent period

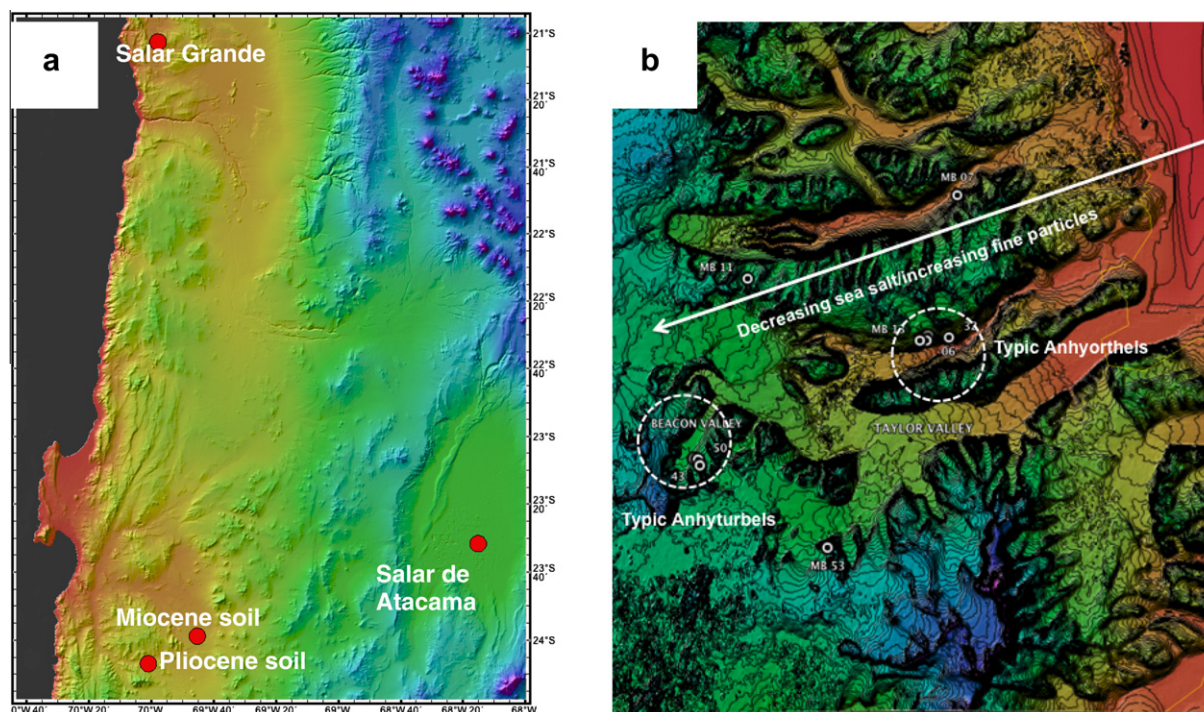


Fig. 2. (a) The location of the sampling sites in the Atacama Desert and (b) The Antarctica.

of intense hyperaridity, with subsequent ineffective movement of surface-deposited sulfates. In the Miocene soil, there is evidence for rainfall events that have produced pools in local micro-depressions, and the pooled waters have infiltrated the salty soil to create piping and subsurface flow. Thus, there are very infrequent events of sufficient magnitude to efficiently move salts vertically and laterally in the soils.

We also obtained samples from two salars: the Salar de Atacama, a high elevation (2300 m) salar located at the foot of the Andes, and the Salar Grande, located at 700 m elevation and ~ 10 km from the Pacific Ocean (Fig. 2). Although these two salars are not hydrologically connected, they represent examples of the sources (Salar de Atacama) and terminal sinks (Salar Grande) for the slow migration of both surface and (especially) subsurface water and brine flow from the Andes toward the coast. The Salar de Atacama, the largest salar in Chile, lies at the base of the Andes and downstream of the most recently active volcano (Lascar) in the northern Andes. The andesitic to basaltic composition of the Pliocene to Holocene deposits provide an abundant suite of elements to stream and spring waters which migrate into the Salar (Risacher and Alonso, 2001). The Salar Grande – the closest salar to the ocean in Chile – is an unusual salt deposit consisting of nearly pure NaCl more than 50 m thick and serves as the primary source of Chile's export of NaCl (Chong-Diaz et al., 1999). Based on regional geologic evidence, it appears that the Salar Grande was a regional terminal depositional basin during the Miocene. Faulting and stream re-arrangement isolated the Salar Grande from its up-stream source (Chong-Diaz et al., 1999; Saez et al., 1999). Chong-Diaz et al. (1999)

considered the Salar Grande to be a fossil feature from the Miocene that has undergone subsidence due to dewatering of the underlying sediments. The Salar is subject to strong diurnal on-shore flows with dense fog (Camachas). The onshore wind and fog provides a source of marine-derived Cl, and alters the salar surface through frequent hydration and dehydration cycles.

2.2. Antarctica

The data analyzed here was first reported by Bao and Marchant (2006) and Bao et al. (2008), and details on the sites and sampling are contained in those publications. Briefly, the McMurdo Dry Valleys of Antarctica are cold, nearly lifeless hyperarid deserts. Because of topographic barriers, it is believed that the Valleys have remained largely ice-free for millions of years. Many of the deposits in the region are millions of years old (Bao and Marchant, 2006). Annual precipitation, as snow, is geographically variable, but in the more coastal regions like McMurdo research station, may amount to 80 mm per year (Fig. 1a). Much of this melts during the summer and infiltrates the soils (Hagedorn et al., 2010).

Fig. 2b illustrates the location of the soils reviewed in this study (taken from Fig. 1 in Bao et al., 2008). Based on triple oxygen isotope values ($\Delta^{17}\text{O}$), there is a decline in sea salt contributions to soil sulfates with increasing distance from the coast (and a subsequent increase in non-sea salt sources) (Bao and Marchant, 2006). Additionally, there is a difference in soil processes. Soils examined in the Taylor Valley (MB-06,13,14,32) form in what is mapped largely as dry-frozen ground with permafrost >100 cm in depth

(Bockheim et al., 2008). The lack of near surface ice and recycling of water (discussed below) result in soils without extensive cryoturbation and many are identified largely as Anhyorthels (Bockheim et al., 2008). In contrast, the Beacon Valley contains massive ice under shallow layers of till and other material, and many of these soils exhibit cryoturbation, and are classified as Anhyturbels (Bockheim, 2007). Both Valleys contain exceptions to this general trend.

In Antarctica, where large seasonal surface and soil temperature oscillations (Fig. 1) cause significant gradients in soil water potential, research has shown that thermal processes cause upward movement of brines during the coldest times of the year in soils near a frozen lake in the Wright Valley (Ugolini and Anderson, 1973). More recently, Hagedorn et al. (2007), in the Victoria Valley to the north, examined the partial recycling of sublimating subsurface ice (seasonal upward movement combined with seasonal downward return) to explain the long preservation of the ice. This hydraulic complexity contrasts with that of the warm Atacama Desert, where temperature oscillations are much smaller (Fig 1b) and water flow is largely advective and downward following rainfalls, and all water is lost to the atmosphere via evaporation (Ewing et al., 2008). Although both deserts are dry and >2 million years old, there are distinct differences in the processes that move and distribute soil solutes.

2.3. Stable isotopes in salts of soils and surface environments: model development

Ewing et al. (2008) found large variations in the stable isotope composition of Ca, S and O in gypsum with depth. These patterns were consistent with fractionation by mineral dissolution/precipitation and downward advective transport (Ewing et al., 2008). Sulfur and oxygen isotope values decrease with depth because the heavier isotopes concentrate in solid mineral phases, leaving remaining water depleted in heavy isotopes. The reverse pattern is true for Ca, which for reasons that are still unclear, concentrates lighter isotopes in the solid phase. As a result, warm hyper-arid soils are membranes that isotopically filter ever smaller aqueous solutions with increasing soil depths. Ewing et al. (2008) showed that the Ca, S, and O isotope composition of sulfate in soil is described by a Rayleigh-like model:

$$\delta_{solid}(z) = (\delta_{inputs}(z) + 1000)f^{\alpha_{w-s}-1} - 1000 \quad (1)$$

where δ_{solid} = the δ value for the solid at depth z , δ_{inputs} = the δ value of the dissolved inputs (from above) at depth z , α_{w-s} = aqueous to solid sulfate fractionation factor, and f = the fraction of the total sulfate inventory at depth z relative to the total inventory from z to the base of the soil. The δ_{input} value can be calculated from the following relation:

$$\delta_{input}(z+1) = \frac{[\delta_{input}(z)SO_{4input}(z) - \delta_{solid}(z)SO_{4solid}(z)]}{SO_{4dissolved}} \quad (2)$$

where SO_4 = mass of sulfate/area (or other salt) that is added (input), precipitated (solid), or remaining in a dissolved phase (dissolved) for a soil layer. The input at $z=0$ is the total inventory of salt in the soil and its

weighted mean (relative to salt content) isotopic composition. Ewing et al. (2008) showed that by inserting the appropriate fractionation factor into Eq. (1), and using measured depth profiles of sulfate concentrations, that the measured S and O isotope composition of sulfate in a soil of the warm Atacama Desert was very well replicated. A Rayleigh model implies isotope fraction during precipitation, but none during dissolution or during the aqueous transport of the solutes.

Similarly, in-soil processes can fractionate ^{35}Cl and ^{37}Cl . Cl partitioning between a mineral and an aqueous solution is similar to S and O partitioning described above for sulfate. The equilibrium chlorine isotope fractionation between halite and a saturated solution is $+0.26\text{‰}$ ($\pm 0.07\text{‰}$) at $22 \pm 2^\circ\text{C}$ (Eggenkamp et al., 1995). Halite formed from 0.0‰ seawater is reported to have $\delta^{37}\text{Cl}$ values ranging from -0.6‰ to $+0.4\text{‰}$ solely from equilibrium fractionation and subsequent fractional crystallization (Eastoe et al., 1999; Eastoe and Peryt, 1999). Fractionation due to precipitation and dissolution of evaporite minerals has been identified as a mechanism responsible for the range of $\delta^{37}\text{Cl}$ values observed in the Palo Duro Basin and the Gulf Coast Basin (Eastoe et al., 1999, 2001). This process is potentially important in hyperarid soils, where partial dissolution and reprecipitation of water soluble salts occurs during periodic soil leaching events. However, $\delta^{37}\text{Cl}$ values outside the range of -0.6 to $+0.4\text{‰}$ require additional fractionation mechanisms of formation (Eastoe et al., 1999; Eastoe and Peryt, 1999), which we discuss below.

Eq. (1) works well for sulfate in hyperarid soils because gypsum/anhydrite is only modestly water soluble ($0.205\text{ g}/100\text{ ml H}_2\text{O}$) and the soils in the Atacama Desert (on average) receive only very small quantities of precipitation. Soil solutions thus become quickly saturated with respect to gypsum, and the downward migration of sulfate (as gypsum or anhydrite) is incremental, never involving complete dissolution and rapid advective flow with each rain event (which would cause no observable isotopic discrimination). In contrast, NaCl, due to its much higher water solubility ($36.0\text{ g}/100\text{ ml H}_2\text{O}$), is commonly found concentrated below sulfate in soil. It is possible that during relatively large and rare precipitation events, NaCl is completely dissolved and then advectively transported to a considerable depth, thereby invalidating the use of a Rayleigh model to interpret isotope depth patterns in warm and dry deserts like the Atacama. We discuss this possibility later in the paper.

In the cold deserts of Antarctica, snowmelt is observed to produce downward migrating fluids (Hagedorn et al., 2007). Thus, especially for sulfate, Eqs. (1) and (2) maybe prove useful to interpreting isotope depth profiles of this anion. However, unlike the warm desert of Chile, it has been shown that saline brines also move both upward and downward in these soils along seasonal thermal gradients that control the matric potential of the soil water (Ugolini and Anderson, 1973; Bockheim, 2007; Hagedorn et al., 2007). In a particularly relevant study, Cary and Mayland (1972) conducted lab experiments on homogeneous soil columns containing frozen soil with salt brines. The columns were then exposed to thermal gradients, and the subsequent

water and salt distributions were monitored over a few weeks. Both water and salt moved toward the colder end of the column, although they were not directly coupled. Cary and Mayland (1972) proposed that while both water and salt moved advectively toward the colder regions, the salt molecules diffuse along concentration gradients that partially reverse the advective movement (but given the much slower diffusivity of salt, this only partially moved the salts back toward the warmer end of the column). Cary and Mayland's (1972) model of the processes indicates that at depth z , the flux of salt (J_s) is:

$$J = \underbrace{-C_s K \frac{\partial \tau}{\partial z}}_{\text{advection}} - \underbrace{\gamma \phi D_s \frac{\partial C_s}{\partial z}}_{\text{diffusion}} \quad (3)$$

where J_s is the flux of salt at depth z , τ is the matric potential of water which is a function of temperature, γ is the fraction of unfrozen water in a cross section at depth z , ϕ is the tortuosity, D_s is the diffusion coefficient of salt in water and C_s is the mole fraction of salt.

Thermally driven solute flow can occur both upwards and downwards in Antarctic soils. In addition, there is downward advective flow from melting snow. These competing processes, and their frequent occurrence, might be expected to produce isotope profiles that are complex. However, some soils are reported to be more impacted by certain hydrological processes than others. Bockheim (2007) compared soils in the Beacon and nearby Arena Valleys of Antarctica. The Beacon Valley soils have permafrost near the surface, whereas the Arena Valley soils do not. Bockheim (2007) proposed that Beacon soils are impacted by upward migrating brines along thermal gradients during the austral winter, whereas the Arena soils (lacking ice) are impacted largely by downward migrating water from snowmelt during the summer. Bockheim's work shows that there is considerable spatial heterogeneity in subsurface ice and hydrological processes in this relatively small region.

The goal here is to focus on soils with subsurface ice and brine that are susceptible to upward movement by thermal gradients during the winter. While these soils are also impacted by downward migrating waters in the summer, the purpose is to explore the effect of upward solute movement to determine whether it leaves a distinctive solute concentration and isotope signature. For a lower soil profile boundary condition dictated by the matric potential, water content, and salt concentration of the brine in the ice layer, the steady state solution to Eq. (3) (salt advection = -salt diffusion, i.e., net flux = 0) is:

$$C(\tau) = \frac{C_L}{e^{-K\tau_L/\phi\gamma D}} e^{-K\tau_L/\phi\gamma D} \quad (4)$$

where $C(\tau)$ and $C(L)$ = concentration of a salt at a specific matric potential and at depth (L), respectively; K = hydraulic conductivity (length/time), ϕ = tortuosity (unitless), D = diffusivity of salt in water (length²/time), and τ = soil matric potential.

Eq. (4) describes the total Cl concentration in the soil at a given depth. In order to calculate the $\delta^{37}\text{Cl}$ value, the individual expressions describing the concentration of ^{37}Cl and

^{35}Cl must determined (and divided in order to calculate the δ value). The total Cl in a sample is:

$$\text{Cl}_{\text{total}} = {}^{35}\text{Cl} + {}^{37}\text{Cl} = {}^{35}\text{Cl} + R({}^{35}\text{Cl}),$$

where $R = {}^{37}\text{Cl}/{}^{35}\text{Cl}$. After re-arrangement, this yields ${}^{35}\text{Cl} = (\text{Cl}/1 + R)$ and ${}^{37}\text{Cl} = (\text{Cl}/1 + R)R$. These expressions can be substituted into Eq. (4) to create models suitable for individual isotopes. Finally, the diffusion coefficient (D) for the ^{37}Cl specific equation must be reduced to accommodate the differences in diffusivity of the light and heavy isotopes of Cl. According to Eggenkamp and Coleman (2009), the experimentally determined ratios of the diffusion coefficients for $^{37}\text{Cl}^-$ and $^{35}\text{Cl}^-$ ions in aqueous solutions range from 1.0009 to 1.0028.

In order to evaluate Eq. (4) and compare it to field or laboratory observations, the variation in a number of parameters must be known or calculable. Foremost is the depth profile of soil temperature. From Jury et al. (1991):

$$T(z, t) = T_a + A_0 e^{-z/d} \sin \left[\frac{2\pi(t + t_0)}{365} - \frac{z}{d} - \frac{\pi}{2} \right] \quad (5)$$

where $T(z, t)$ = soil temperature at depth (z) and time (t), T_a = average soil temperature, A_0 = the amplitude of seasonal surface temperature variability, t_0 = time that temperature equals annual average, and d = damping depth (L). The soil temperature of frozen ground determines the vapor pressure of ice in the soil according to the following relationship (Wexler, 1977):

$$\ln(p/p_t) = (a_1\tau + a_2\tau^2 + a_3\tau^3 + a_4\tau^4)T_t/T \quad (6)$$

$T_t = 273.16$ K, T = soil temperature (K), $p_t = 611.657$ Pa, $a_1 = -22.4949$, $a_2 = -0.227$, $a_3 = 0.502$, and $a_4 = 0.564$. In frozen soils, it can be assumed that the vapor pressure of ice controls the total soil water potential (Cary and Mayland, 1972), and the total soil water potential can be calculated by (Scott, 2000):

$$\psi = (RT/M) \ln \frac{e}{e_0} \quad (7)$$

where ψ = soil water potential (P), R = gas constant, T = temp (K), M = mass of a mole of water, e = soil vapor pressure, and e_0 = saturated vapor pressure of pure water, which can be calculated from (WMO, 2008):

$$e_0 = 6.112 e^{(17.62t/(243.12+t))} \quad (8)$$

where e_0 = water vapor pressure in hPa and t = °C.

It has been assumed, in frozen soils, that the total soil water potential is the sum of the matric (τ) and osmotic (ψ_m) potentials. The osmotic potential can be calculated from (Scott, 2000):

$$\psi_o = -miRT \quad (9)$$

where m = molarity of solute, i = Van't Hoff constant (assumed 1 here). The concentration of NaCl in a solution at temperatures below 0 °C can be calculated from the empirical relationship:

$$C = 0.4228 - 0.2385t$$

where C = mol kg⁻¹ water. The fraction of the original liquid water remaining at temperatures below 0 is:

$$f = \frac{C(T_0)}{C(T_i)} \quad (10)$$

where C is the concentration of salt in the original aqueous phase (T_0), and in the brine remaining after some ice has been lost at a lower temperature (T_i). Eq. (4) (and its isotope-specific variants) can be used either with experimentally measured data or with values derived from Eqs. (5)–(10), to evaluate how thermally driven advective and diffusive processes can affect NaCl concentrations and Cl stable isotope ratios.

Desaulniers et al. (1986) identified diffusion as a mechanism to explain large variations in $\delta^{37}\text{Cl}$ values of groundwater, pore fluids, and saline brine with depth (e.g., Desaulniers et al., 1986; Eggenkamp et al., 1994; Eastoe et al., 2001; Godon et al., 2004; Zhang et al., 2007). They observed a decrease in $\delta^{37}\text{Cl}$ values and Cl concentrations in pore fluids with increasing distance from underlying bedrock in a sequence of glacial till deposits, characteristic of diffusion. Ion filtration occurs when a solution is forced through a negatively charged clay membrane. In contrast to diffusion, ion filtration will result in a trend of increasing $\delta^{37}\text{Cl}$ values and a corresponding decrease in Cl concentration. Both ^{35}Cl and ^{37}Cl will be repelled, but since ^{35}Cl is more mobile it will be repelled more effectively than ^{37}Cl , ultimately resulting in a chloride-rich and ^{35}Cl -enriched reservoir on the inflow side of the membrane (Phillips and Bentley, 1987). However, in most hyperarid soils, clay is low (due to the near absence of chemical weathering and in situ clay formation), so ion filtration is not expected to be an important mechanism affecting Cl isotopes.

3. METHODS

3.1. Sample collection

Salar surface salt encrustations were collected during August of 2008. In general, NaCl-rich salars have large, jagged, and irregularly oriented NaCl crystals or forms. Fragments were removed with rock hammers. Soils were examined, described and sampled using standard pedological methods. Full details of the Pliocene soil (Yungay) are presented in Ewing et al. (2006). The Miocene soil was examined and sampled using similar methods. One important sampling distinction, relative to that of Bao et al. (2008), is that samples for chemical and isotopic analyses are aggregated samples of the entire soil horizon, as opposed to point sampling used by Bao et al. (2008). While both methods may have benefits, the aggregate sampling allows us to more easily calculate total mass of salts if bulk density and gravel information is available.

3.2. Chloride concentration and stable chlorine isotope analyses

Chloride concentration and stable isotope analyses were conducted at the University of New Mexico. Approximately 0.5–25 g of soil was leached overnight in 18 M Ω deionized water at room temperature. Samples were filtered and solutions diluted to a known volume. A known aliquot of the solution was reacted with AgNO_3 to extract the

chloride as AgCl (Long et al., 1993; Eggenkamp, 1994; Eggenkamp et al., 1995). The AgCl yield, volume of total solution and aliquot, and mass of leached soil was used to calculate the mg of chloride in a given soil horizon. The AgCl was then reacted with CH_3I in an evacuated Pyrex tube for 2 days in a darkened 80 °C furnace to produce the analyte CH_3Cl , the gas introduced into the mass spectrometer (Eggenkamp, 1994; Eggenkamp et al., 1995). CH_3Cl was purified of excess CH_3I by passage through a gas chromatographic column (GC) before entering the Finnigan Delta XL Plus mass spectrometer (Barnes and Sharp, 2006). $\delta^{37}\text{Cl}$ values are reported in the standard per mil notation versus SMOC (Standard Mean Ocean Chloride). Error on each analysis is $\pm 0.12\text{‰}$ (1σ) based on the long-term laboratory average for in house standards.

4. RESULTS AND DISCUSSION

4.1. Evaluating SO_4 isotope profiles in the two deserts: role of downward infiltration

We begin by comparing SO_4 and Cl concentration profiles in both deserts. The soils of both deserts contain distinctive depth profiles of SO_4 and Cl (Fig. 3). In general, the Atacama soils have higher salt contents, and the Cl is concentrated at deeper depths. Both deserts have SO_4 more enriched nearer the surface, but Chile has more total SO_4 . We begin this section by testing the hypotheses that sulfate transport in both Antarctica and Chile is largely driven by downward migration of liquid water, and that S and O isotope profiles can be explained by the use of Eq. (1). Following this, we then determine if this process also can explain the Cl concentration and Cl isotope profiles in both deserts.

Stable S and O isotope values in sulfate generally decrease with increasing depth in Antarctica (Bao et al., 2000; Bao and Marchant, 2006) and Chile (Ewing et al., 2008). Ewing et al. (2008) demonstrated that Eq. (1) adequately described these depth profiles in the Atacama Desert, and here we begin by testing its applicability to Antarctica. Four Antarctic soils have detailed sulfate chemistry with depth (Bao and Marchant, 2006) – and have much less detailed Cl isotope data that we will consider later (Bao et al., 2008). These soils are reported to have formed on basal glacial till – tills without sublimating ice at depth (soils MB07, MB-13, MB-11, MB-53). Fig. 4(a–h) shows the measured vs. the modeled $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of the sulfate. While the Rayleigh model describes the first order variation in oxygen and sulfur isotope ratios with depth, we were required to reduce the $\alpha_{\text{sulfate-gypsum}}$ values by 50% in order to obtain this fit. This differs from the soils in Chile (Ewing et al., 2008), where published equilibrium fractionation factors result in good fits with the observed soil isotope patterns (Ewing et al., 2008). Because the Antarctic sulfate is concentrated near the soil surface, it is unlikely that a portion of the sulfate has been moved downward advectively by large, non-fractionating snowmelts. Rather, given the previous research on fluid flow, upward migration of brines is likely involved to some degree in the sulfate transport, creating some discrepancy with the simple Rayleigh model.

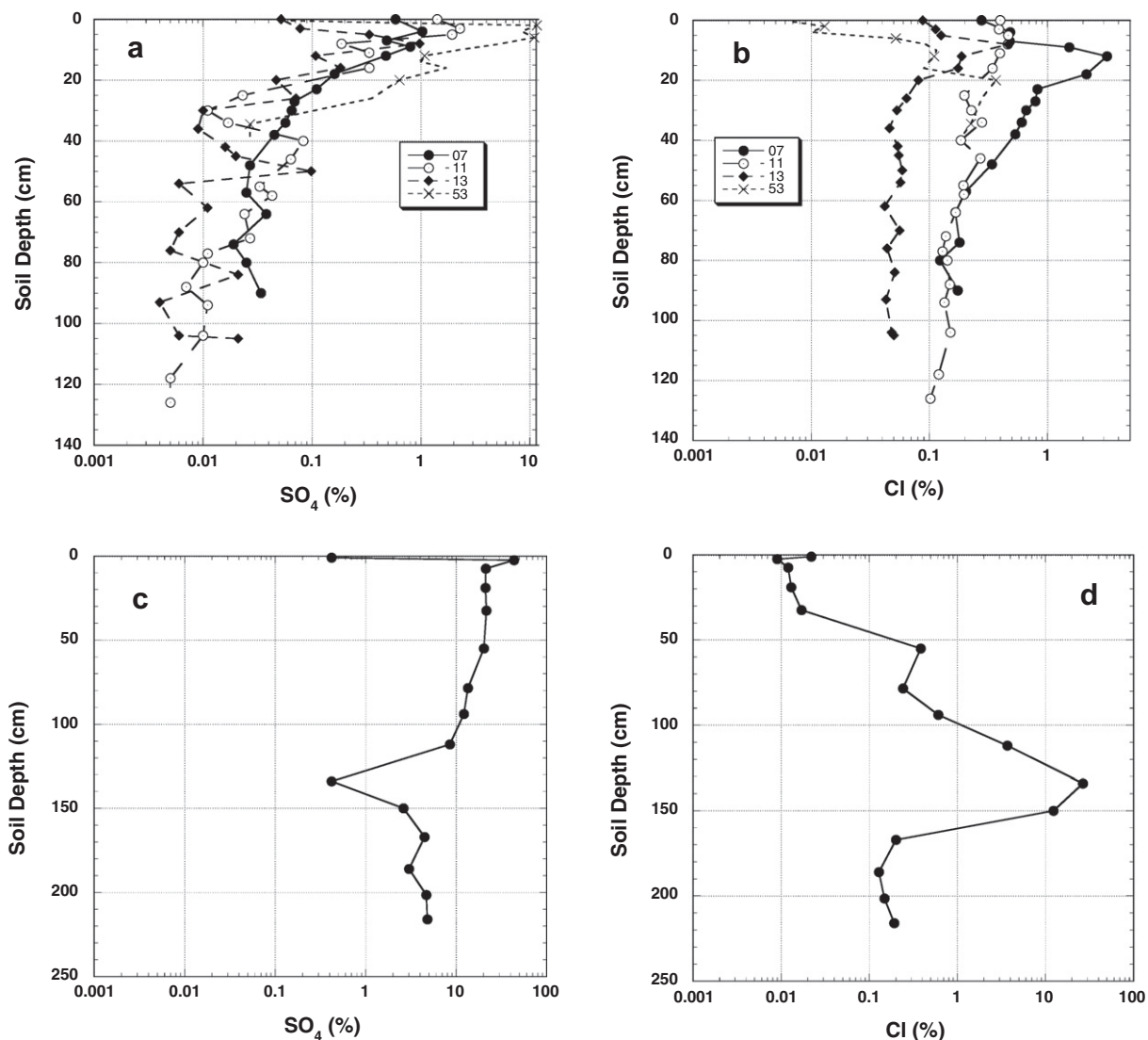


Fig. 3. Depth distribution of SO₄ and Cl in soils from Antarctica (a and b) (Bao and Marchant, 2006) and the Atacama Desert (c and d) (Ewing et al., 2006). Cl and SO₄ are in weight percent.

An additional indicator of mass dependent fractionation of the Antarctic sulfates is the slope of the relationships between their $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values. If mass dependent processes caused the variations, the slope should be the ratio of the fractionation factors, $\sim 1.2 \pm 0.2\%$ (Ewing et al., 2008). For three out of the four Antarctic soils (the exception being MB-53), the slopes approach this value, supporting the presence of mass dependent processes (Fig. 4I). Because of the relatively small fluid amounts in brines, and the low SO₄ solubility, the processes associated with brine movement (discussed below) appear to be secondary to the downward advection and dissolution/precipitation on the isotope profiles.

4.2. Evaluating Cl isotope profiles in the two deserts: role of downward infiltration

Next, we ask if processes described by a Rayleigh model can describe the Cl isotope profiles in the two deserts. We

begin with the soils of the Atacama Desert, where S and O isotope values in sulfate are well replicated by this model.

The Pliocene Atacama soil examined by Ewing et al. (2006, 2008) was shown to retain nearly all atmospheric salt deposition within the upper 175 cm, including a halite cemented layer at the base of the profile (Fig. 3d). There is a significant redistribution of the salts with depth: (1) sulfate largely confined to the surface horizons (Fig. 3c) and (2) chloride and nitrate concentrated at about 1.5 m in depth (Fig. 3d). The stable Cl isotope values of the Pliocene soil decline somewhat erratically with depth ($R = 0.57$), with a weighted soil average value of -0.67% (Table 1). This value is well within the ranges for the salars and various sources discussed below. It is clear from the profile that as salt concentration increases greatly, the $\delta^{37}\text{Cl}$ values decrease slightly. The Cl profile is consistent with a downward trajectory of fluids. Thus, in Fig 5, we use the data in Table 1, along with the Rayleigh model, to determine if the model mimics Cl isotopes as effectively as it has the O

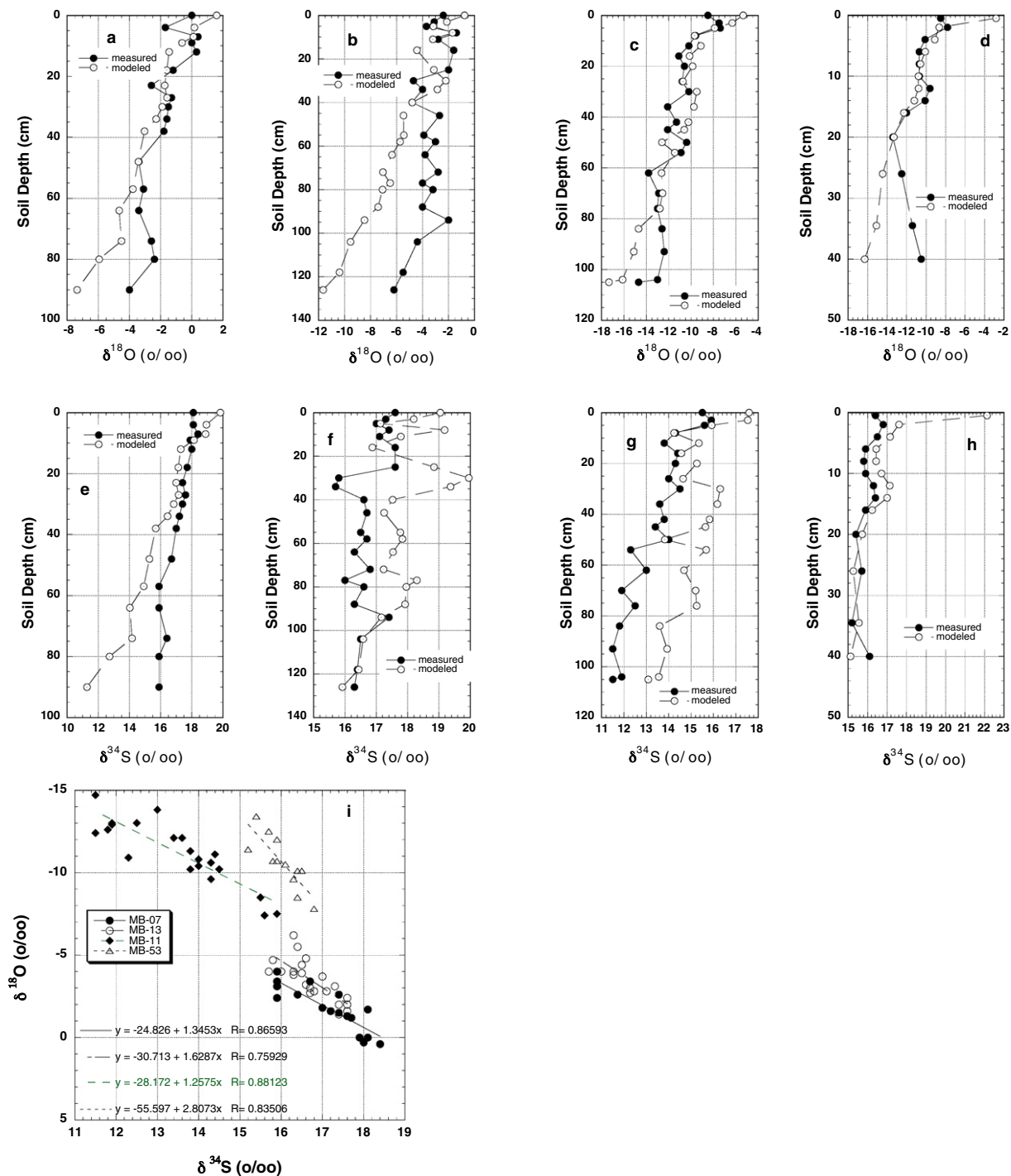


Fig. 4. Measured and model O isotopes (a–d) and S isotopes (e–h) for soils 7, 13, 11, and 53, respectively, as reported by Bao and Marchant (2006). Modeled values were made using Eqs. (1) and (2), and SO_4 to gypsum fractionation factors of 1.0001 for O, and 1.0008 for S. (i) A plot of measured S and O isotopes for sulfates from the four Antarctic soils.

and S isotope values for SO_4 . The results show that for the upper 150 cm, there is a fair relationship between measured and modeled values. In particular, the model captures the small near-surface decline in $\delta^{37}\text{Cl}$ values, and the small decrease with depth there-after. We note that the three lowest layers in the Pliocene soil appear to lie below all geochem-

ical accumulations during the period of soil formation, and occur in fine-laminated sediments devoid of weathering (with the exception of some Cl accumulation). It is possible that the Cl here reflects Cl accumulated in a fluvial environment before the onset of soil formation that has subsequently occurred. Therefore, we recalculated the Rayleigh

Table 1
Cl and Cl isotope data for samples from the Atacama Desert.

Sample	Depth (cm)	Midpoint depth (cm)	Density (g/cm ³)	Cl concentration (mg Cl/g soil)	$\delta^{37}\text{Cl}$ (‰)
<i>Pliocene soil</i>					
YNG 1	0–2	1	1.4	0.41	–0.26
YNG 2	2–3	2.5	0.8	0.13	–0.51
YNG 3	3–12	7.5	0.6	0.21	–0.94
YNG 4	12–26	19	1.2	0.26	–0.66
YNG 5	26–39	32.5	1.5	0.34	–0.86
YNG 6	39–71	55	1.3	6.58	–0.49
YNG 7A	71–85	78.5	1.2	4.17	–0.59
YNG 7B	85–102	94	1.2	9.37	–0.95
YNG 8	102–122	112	1.5	57.34	–0.63
YNG 9	122–146	134	1.7	410.55	–0.64
YNG 10	146–154	150	1.7	190.59	–0.56
YNG 11	154–180	167	1.7	3.12	–1.23
YNG 12	180–192	186	1.6	2.08	–1.03
YNG 13	192–211	201.5	1.7	2.34	–1.14
YNG 14	211–232	216	1.7	2.96	–0.99
<i>Miocene soil</i>					
<i>Major Soil Horizons</i>					
0–2 fine	0–2	1	n.d.	0.11	–0.28
8–10 whole	8–10	6	n.d.	0.07	–0.06
8–35 whole	8–35	22.5	n.d.	1.47	–1.07
35–100 whole	35–100	67.5	n.d.	38.77	–0.59
108–135 whole	108–135	117.5	n.d.	15.19	–0.30
Replicate			n.d.	17.61	
135–200 fine	135–200	167.5	n.d.	91.60	–0.58
Replicate			n.d.	96.24	
200–280 fine	200–280	240	n.d.	21.46	–0.29
Replicate			n.d.	21.64	
280–340 fine	280–340	310	n.d.	31.65	–0.51
<i>Special Features within Miocene Soil</i>					
35–100 crack	35–100	67.5	n.d.	17.63	–0.58
Replicate			n.d.	19.67	
100–110 fine	100–110	105	n.d.	16.27	–0.73
108–135 crack	108–135	121.5	n.d.	56.30	–0.85
130–170 wedge	130–170	150	n.d.	81.33	–0.95
135–200 crack	135–200	167.5	n.d.	34.35	–0.43
Replicate			n.d.	33.63	
Replicate			n.d.	35.27	
Replicate			n.d.	33.39	
Replicate			n.d.	35.81	
<i>Salar de Atacama</i>					
WP258					–0.16
Replicate					–0.36
Replicate					–0.22
Replicate					–0.09
WP259					–0.25
Replicate					–0.12
Replicate					–0.02
<i>Salar Grande</i>					
WP 287					–0.38
Replicate					0.24*
Replicate					–0.18

model down to a depth of 150 cm to exclude these horizons from the calculations. As the results show, there is a slightly better fit with the observed values (Fig. 5). We interpret this as indicating that the Cl is slowly winnowed downward via aqueous processes. However, it is clear there are processes that occur in addition to that implied by the simple model.

One key process not captured in the Rayleigh model is large but rare rain events. The large quantities of NaCl at about 150 cm in depth (a halite cemented zone) require significant quantities of water to move the salt to this depth (at high concentrations). Many of these events were likely needed, over millions of years, to completely dissolve all

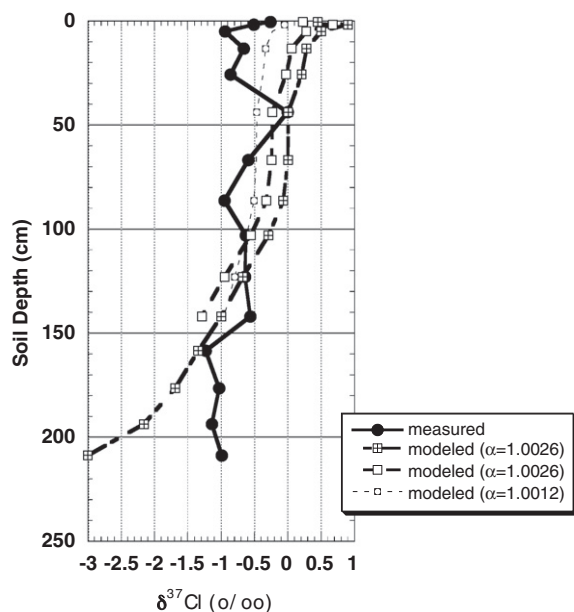


Fig. 5. Depth profiles of $\delta^{37}\text{Cl}$ values for a Pliocene soil in the Atacama Desert (Ewing et al., 2006, 2008). Modeled fits were made using Eqs. (1) and (2) and the fractionation factors indicated.

near surface NaCl (derived from atmospheric deposition), and advectively transport it to greater depths. Again, if dissolution is complete (and reprecipitation occurs largely at one depth), the isotopic effects are largely eliminated or greatly subdued. This would explain the small depth dependency of isotope ratios, with the enormous depth dependency of total Cl. Since the net effect of this mechanism

reduces the effective fractionation factor, we redid the calculations by reducing the fractionation factor by half (to 1.0012), but still within experimentally observed values. This in effect made the fit between the modeled and observed values stronger, as expected (Fig. 5) ($R = 0.53$, slope = 0.8).

The Cl concentration and Cl isotope profile of the Miocene age soil is shown in Fig. 6. Fig. 6a is a photograph of the profile. The field evidence is suggestive of three major phases of soil development: (1) pre-Pliocene dust and salt accumulation, with the development of gypsum polygons similar to post-Pliocene soils, (2) a phase of some degradation of the soil surface (and partial dissolution of the sulfate polygon tops), followed by (3) the post Pliocene soil processes (dust and salt) responsible for the Pliocene soil discussed above. We, thus, hypothesize that the profile consists of a lower, older soil with a younger soil “welded” to its top. This interpretation is supported by the 2 layers of sulfate polygons, and the bimodal distribution of both SO_4 (not shown here) and Cl concentration with depth (Fig. 6b). Thus, to examine and model the Cl isotope profiles, we divided the soil into 2 layers (horizons above 100 cm, and those below). One question we were interested in is whether the Cl sources for two soils, separated by a significant time interval, were the same. The weighted mean average $\delta^{37}\text{Cl}$ values of each soil was calculated, and they were quite similar: -0.60‰ and -0.51‰ for the upper and lower soils, respectively. Next, we explored whether the same processes would explain the isotope distribution with depth. Using Cl inventories and these input values, the Rayleigh model was used to project $\delta^{37}\text{Cl}$ profiles for both large and small fractionation factors (Fig. 6c). The modeled results capture some of the depth features of the

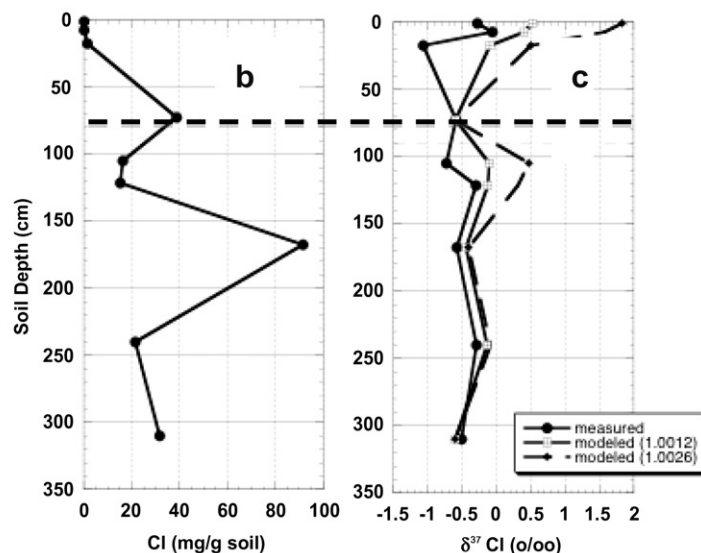
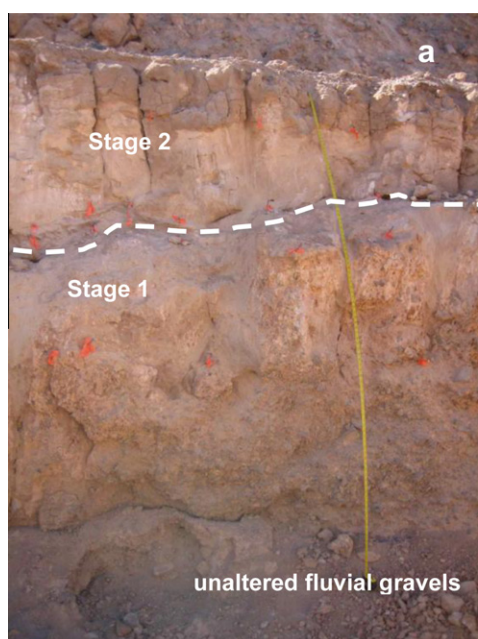


Fig. 6. Depth profiles of (b) Cl concentration and (c) $\delta^{37}\text{Cl}$ values for a Miocene soil in the Atacama Desert. Modeled fits in (c) were made using Eq. (1) and the fractionation factors indicated. The dashed line in (a) indicates the interpreted boundary between Miocene soil (below) and a post Pliocene soil (above).

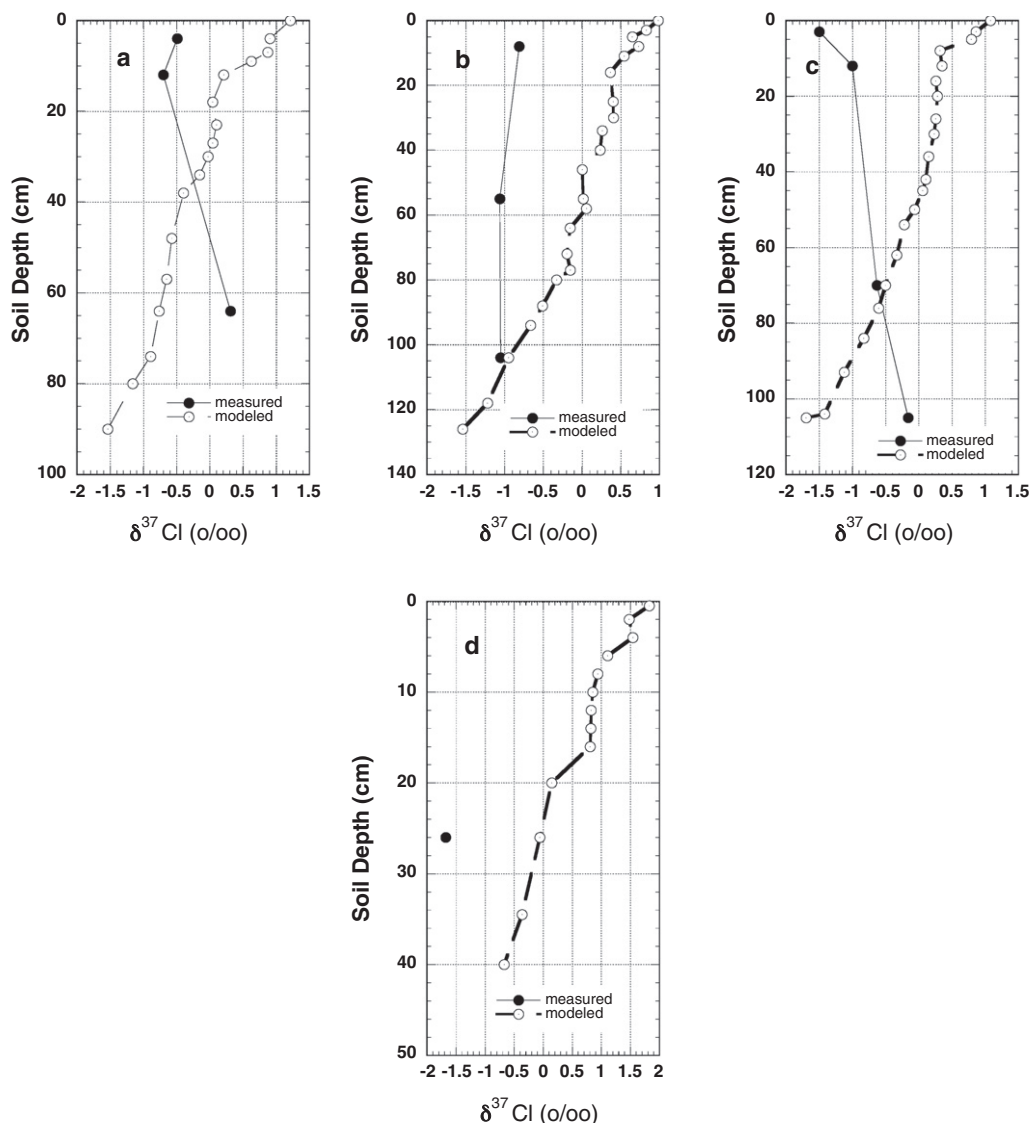


Fig. 7. Measured vs. modeled (Eqs. (1) and (2)) Cl isotope values for Antarctic soils 7, 13, 11, and 53 respectively (a–d). Measured data from Bao et al. (2008). Model results made assuming (1) Na concentrations (from Bao and Marchant, 2006) are proportional to Cl, (2) input $\delta^{37}\text{Cl} = 0\text{‰}$ (the per mil symbol on the x-axis is funny same in Fig. 3), and (3) a fractionation factor of 1.00026.

upper soil, and fit very well with the observed values in the lower soil. Thus, as for the Pliocene soil, Cl isotopes at least partially conform to a Rayleigh type process, with deviations likely due to its high solubility and responsiveness to large infrequent rain events.

We determined if the Rayleigh model is applicable to Antarctica. If we assume that the soluble Na content (reported by Bao and Marchant, 2006) is proportional to Cl concentrations (only a few Cl concentrations are reported), the $\delta^{37}\text{Cl}$ values vs. depth can be calculated and compared with the reported Cl isotope data (Bao et al., 2008). As Fig. 7(a–d) demonstrates, unlike the results for O and S isotope values (or compositions) in the Antarctic sulfate, there is a poor or inverse relationship between the modeled and measured Cl isotope data. Thus, the Cl isotope profiles have resulted from very different mechanisms. Next, we examine the impact of diffusion.

4.3. Evaluating Cl isotope profiles in Antarctica: role of thermally driven aqueous transport and molecular diffusion

In order to examine how thermally driven brine movement and diffusion might affect salt and isotope composition in cold desert soils, we begin by examining the steady state result of a thermally driven transport model. Eqs. (4)–(10) are used to examine how winter temperature profiles, and resulting salt and isotope profiles, might look in an Antarctic soil with a brine source at some depth below the surface. In this exercise, velocity and effective diffusivity are not constant with depth, better representing soil conditions in nature. Fig. 8a shows the winter temperature profiles for a soil with an assumed ice layer at 1 m and annual surface temperature oscillation of $\pm 5\text{ °C}$. Assuming that significant brine moves only upward during the winter temperature extreme, this very simple model scenario shows

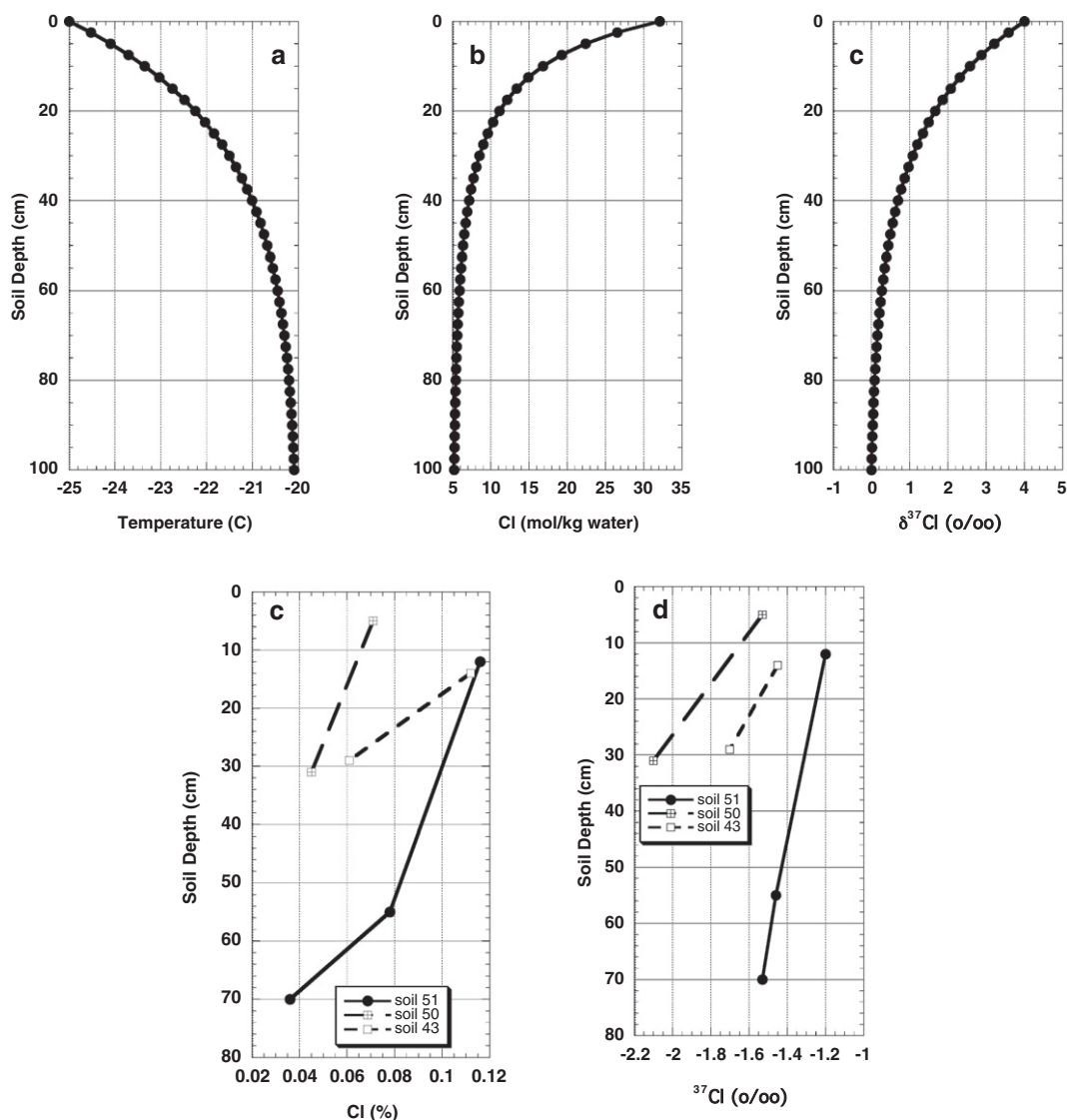


Fig. 8. A modeled analysis of an Antarctic soil with upward migrating brines during winter. (a) calculated temperatures (assuming MAT = -20°C), (b) Cl concentrations (assuming a brine in equilibrium with MAT @ 100 cm), (c) $\delta^{37}\text{Cl}$ profile assuming input at 100 cm = 0 o/oo, and (d and e) measured Cl and Cl isotope data for 3 soils formed above shallow ground ice (Bao et al., 2008).

significant increases in both total Cl concentration (Fig. 8b) and enrichment of ^{37}Cl (Fig. 8c) near the surface. Fig. 8d and e show the Cl concentration and $\delta^{37}\text{Cl}$ profiles for the Beacon Valley soils with reported near surface ice. Although the sparse data makes it impossible to determine the exact shape of the profiles, qualitatively they follow the patterns predicted by the modeled results.

Soils where *upwards* transport (vs. downward snow-melt) might be most dominant are those with shallow ice, and three of the Beacon Valley soils considered earlier (MB51, 50 and 43) have those characteristics. We also examined Cl concentration vs. Cl isotope depth profiles in other locations to see if other sites might strongly reflect upward processes (increasing total Cl concentration and increasing $\delta^{37}\text{Cl}$ value with decreasing depth) vs. that of downward movement (the opposite relationship). In particular, it appears that the Taylor Valley soils also share

patterns similar to Beacon Valley soils in terms of Cl geochemistry. As noted in the site description section, there is no near-surface ice reported for the soils in the Taylor Valley (Bao et al., 2008), but cryoturbated soils are mapped close by (Bockheim et al., 2008), so it is possible that there may be some brine movement in this area as well. If they are all impacted by this process, the data (even if we do not know all the temperature and hydrological parameters for these sites) *must* yield the ratio of the diffusion coefficients of the two Cl isotopes by the following method, which provides a strong quantitative check as to whether diffusion is truly impacting the Cl concentration and Cl isotope distribution. Eq. (4) can be simplified to constant diffusive and advective transport with depth (Scott, 2000):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad (11)$$

where v = velocity. At steady state, for the boundary conditions $\frac{\partial C}{\partial z} = -vC|_{z=0} = vC_0$, the solution is:

$$C(z) = 2C_0e^{vz/D} - C_0 \quad (12)$$

where C_0 is considered to be the source of brine that migrates along a thermal gradient at some depth (either soil surface if downward, or at some depth (z) if viewed as brine movement from a ice layer upward in the winter). Eq. (12) is introduced because it offers a simple opportunity to test whether Cl profiles may reflect steady state upward flow. Using the observed data, one can calculate the apparent diffusional fractionation factor (the ratio of the diffusion coefficients) from soil observations using a re-arrangement of Eq. (12) and its ^{35}Cl and ^{37}Cl equivalents. This gives the following relationship:

$$\alpha = \frac{\ln(^{37}\text{Cl}_z + ^{37}\text{Cl}_o) - \ln(^{237}\text{Cl}_o)}{\ln(^{35}\text{Cl}_z + ^{35}\text{Cl}_o) - \ln(^{235}\text{Cl}_o)} \quad (13)$$

Thus, if the calculated fractionation factor based on measured values approaches that of the experimentally determined value, it provides support for the relevance of Eq. (4) as a viable model for these soils. Applying this relationship to sublimation till soils MB51, 50 and 43 in Beacon Valley (Bao et al., 2008) and all soils from Taylor Valley gives α values for diffusion between 1.0002 to 1.0011 (individual soils or aggregated data) (the relationship between the ln of Cl concentration and $\delta^{37}\text{Cl}$ values, which illustrates this trend slightly differently, is shown in Fig. 9). The calculated values are smaller than a recently experimentally determined value of 1.0028 at 2 °C, but within the range of reported values in other studies (1.0009–1.00128) (Eggenkamp and Coleman, 2009). The fact that the values based on observations are possibly smaller is not unexpected, since the salt profile must also be impacted by snow-melt that moves both total salt, and ^{37}Cl , downward. This reduces the depth gradients of both total salt and isotope ratios caused by thermal processes. Nonethe-

less, the sign and numerical similarity (fractionation factors that are between and factor of 1–10 of the reported value) are suggestive that thermally driven brine movement is important in creating the distinctive Cl concentration and Cl isotope profiles in these soils.

4.4. Comparison of Cl isotope patterns in warm and cold deserts

To summarize the observations and interpretations, Antarctica is indeed “dry”, but receives consistent snowfall which slowly melts and move downward during the summer. Remaining brines from this surface source, as well as more substantial brines from near-surface ice in some locations, provides an upward moving salt-bearing fluid in the winter – particularly in response to the large seasonal surface temperature variations. Sulfate, which is relatively less soluble, appears to largely reflect downward dissolution/precipitation and transport – with the caveat that the observed S and O isotope fractionation is smaller than predicted, suggesting some winter remodification of the profiles by upward water movement. In contrast, Cl which is very water soluble, appears to cluster into two endmembers: (1) soils with near-surface ice have decreasing $\delta^{37}\text{Cl}$ values and decreasing Cl concentrations with increasing depth and (2) soils affected by downward moving snowmelt waters have decreasing $\delta^{37}\text{Cl}$ values and increasing Cl concentrations with increasing depth. Endmember 1 is explainable by advection/diffusion modeling while Endmember 2 is explainable by a Rayleigh-type model. Many soils, particularly in Antarctica, may lie somewhere between these endmembers. Given that our interpretations hinge on data and reports that are by nature somewhat preliminary and fragmentary, there is clearly an opportunity for field work designed specifically to more thoroughly test some of the hypotheses generated here.

The Atacama Desert, in contrast to Antarctica, receives much less precipitation. Compared to Antarctica, it has a smaller amplitude of seasonal air temperature variation. The Atacama also has the unique hydrological characteristic that the infrequent moisture may occur in relatively large events. Soils are never frozen, and thermally driven brines are not a process of significance. In general, downward aqueous migration of salt combined with mineral dissolution and reprecipitation drives both S and O isotope patterns in sulfate and Cl isotope patterns in halite.

Walvoord (2002) examined the hydrological characteristics of an arid to semi-arid site in the Chihuahuan Desert of western Texas (see also Walvoord and Phillips, 2004). This location, like many in the Southwestern US, has vadose zones that reflect a response to Holocene drying and the emplacement of a no-flux boundary for infiltrating water at the base of the rooting zone. Thus, soils/vadose zones show a large bulge of both Cl and NO_3 due to accumulation at this boundary (Fig. 10a). At the desert scrub A site (Walvoord and Phillips, 2004), Walvoord (2002) measured Cl isotope composition of soil halite at several depths in the upper 10 m. Here, we assume (as Walvoord does) that the Cl above and including the bulge is a Holocene response to aridification, and represents downward fluid and salt

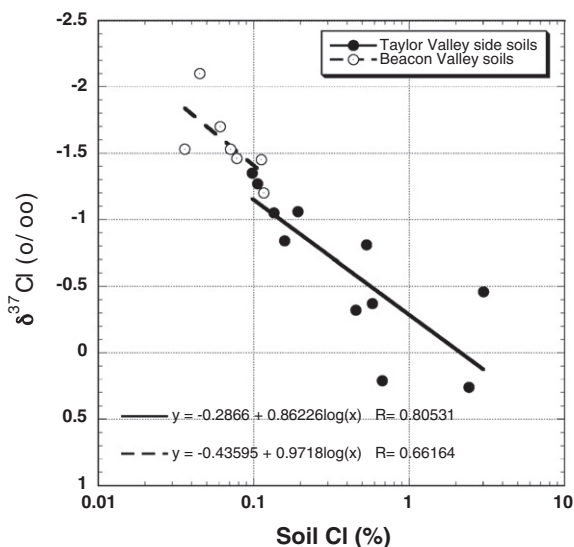


Fig. 9. A plot of $\delta^{37}\text{Cl}$ values vs. Cl wt.% for Beacon Valley and Taylor Valley soils in Antarctica (Bao et al., 2008).

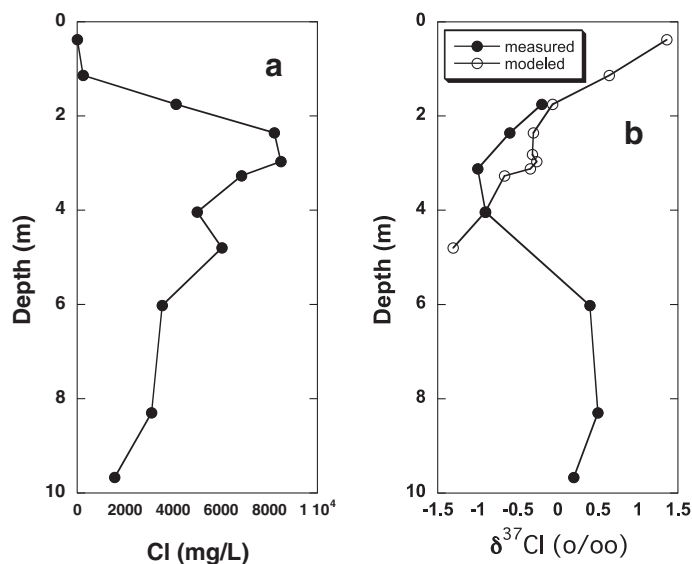


Fig. 10. (a) Pore water Cl concentrations vs depth and (b) $\delta^{37}\text{Cl}$ values of the Cl (and modeled values using Eqs. (1) and (2) in text) for the SA core at the McKee desert scrub site in the Chihuahuan desert of Texas (Walvoord, 2002). Modeled data extend to the approximate base of the Cl bulge, which is interpreted to largely represent Holocene hydrological conditions.

flow (but over much greater distance than the shallow accumulation in the Atacama Desert). Using the Cl data in Fig. 10a, and the mean $\delta^{37}\text{Cl}$ value of all samples, we used the Rayleigh model to calculate the depth trend of Cl isotopes (Fig. 10b). The relationship between the observed and the modeled values is quite good, indicating that this transport process may have wider applicability to a range of environments and hydrological histories. In particular, the Cl isotope profile provides an important constraint on the hydrological processes occurring within a vadose zone. For example, Walvoord (2002) found that a numerical vadose zone model could explain much of the water potential and Cl concentration profiles in an arid site in Texas (Fig. 10a), but the underlying diffusion mechanism assumed to be operative led to Cl isotope profiles largely the opposite of those observed. While we had some success (using a Rayleigh model) describing the Holocene dominated upper portion of the Cl profile (Fig. 10b), the underlying causes of the Cl isotope distribution below this zone remain unexplained. As Walvoord (2002) noted, in addition to unidentified processes, there is the additional problem of an isotopic legacy of past climate conditions and associated processes.

4.5. Implications for earth and planetary science research

The most important result of this comparison of two very different deserts on Earth is that there is a large variation in the isotope composition of salts with soil (or vadose zone) depth. This variation is driven by physical processes that cause isotope fractionation of the atmospheric inputs, and samples collected at any given depth will be unlikely to provide insight into the isotopic composition of the source of the salt. However, these isotopic depth trends have important implications for understanding the aqueous processes in the soils. Downward, Rayleigh type processes will

largely result in a decline in $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\delta^{37}\text{Cl}$ value in the direction of fluid flow. In contrast, salts impacted by combined advection and diffusion (e.g. migration of brines) will have delta values that increase in the direction of fluid and net salt movement. In this paper, we have been able to identify deserts that have soils that appear to generally fit these two extremes. However, we anticipate that more complex soils exist (particularly in Antarctica) that exhibit seasonal shifts in processes, and combinations of mechanisms, that will require more research.

In Chile, while the soil profiles largely exhibit downward fluid flow following rare rains, the landscape surface (particularly near the coast) is impacted by fog that is likely to cause surficial diagenesis and isotopic fractionation more akin to that observed in some Antarctic soils. We sampled surface crust from two salars in Chile. The $\delta^{37}\text{Cl}$ values of two samples from the the Salar de Atacama (adjacent to the Andes) average $-0.21 \pm 0.11\text{‰}$ ($n = 4$) and $-0.13 \pm 0.12\text{‰}$ ($n = 3$). The Salar Grande (adjacent to the Pacific) has an average $\delta^{37}\text{Cl}$ value of $-0.28 \pm 0.14\text{‰}$ ($n = 2$, excluding one outlier). Taking into account analytical error, these two localities are isotopically indistinguishable from one another and, in a broad perspective, close to marine or recycled-marine sources.

However, we are uncertain to what degree these values reflect the geological sources vs. physical partitioning by transport or diagenesis. For example, the Salar Grande is located within a dense coastal fog belt. Any Cl-bearing sediment exposed to fog becomes wet due to the deliquescence of halite (Davila et al., 2008), and during the daylight hours, the brine appears to move toward the soil surface where solar driven drying is occurring, forming a dense, nearly pure halite crust. The corresponding effects of mineral dissolution/reprecipitation and/or diffusion are unknown, but might be expected to be significant. While the higher elevation (and much further from the coast) Salar

de Atacama does not appear to have these types of crust forming processes, occasional rains may result in some isotope fractionation. In summary, given the degree of isotope fractionation observed during soil hydrological processes, careful attention to the effect of these processes on surficial deposits seems warranted. On the other hand, Cl isotopes may prove useful to test models describing the formation of the halite crusts and their interaction with fog water, particularly since the crusts provide unique habitats for microbial life in an otherwise inhospitable environment (Wierzcchos et al., 2006).

5. SUMMARY

In the past decade, isotopic studies of salts in hyperarid soils have revealed unsuspected insights into the modest aqueous processes that occur in these dry regions. Antarctica and Chile offer fascinating comparative research areas due to differences in temperature and moisture delivery. Most simply, in the warm Atacama Desert salt is largely moved downward by infiltrating water. In Antarctica, the hydrology appears temporally and spatially variable, with a sometimes strong upward signal that produces distinctive salt and isotope patterns. Both deserts are ripe for integrated hydrological and geochemical studies that will greatly develop, or even reject, some of the interpretations made here. Additionally, the adaptation of more complex numerical models (e.g. Walvoord, 2002) is needed to explore the combined effects of seasonally driven hydrological processes. A full understanding of salt movement under varying boundary conditions is important to predict the fate of contaminants in arid regions, and Cl stable isotopes offer a useful means of testing and constraining models and interpretations of solute profiles in arid zone hydrology.

REFERENCES

- Amundson, R., Dietrich W., Bellugi D., Ewing S., Nishiizumi K., Chong G., Ebling A., Owen J., Finkel R., A. Heimsath, Stewart B. and Caffee M. (in press) Geomorphic evidence for late Pliocene onset of hyperaridity in the Atacama Desert. *Geol. Soc. Am. Bull.*
- Bao H., Barnes J. D., Sharp Z. D. and Marchant D. R. (2008) Two chloride sources in soils of the McMurdo Dry Valleys, Antarctica. *J. Geophys. Res.* **113** (D03301).
- Bao H. and Marchant D. R. (2006) Quantifying sulfate components and their variations in soils of the McMurdo Dry Valleys, Antarctica. *J. Geophys. Res.* **111** (D16301).
- Bao H., Campbell D. A., Bockheim J. G. and Thiemens M. H. (2000) Origins of sulphate in Antarctic dry-valley soils as deduced from anomalous ^{17}O compositions. *Nature* **407**, 499–502.
- Barnes J. D. and Sharp Z. D. (2006) A chlorine isotope study of DSDP/ODP serpentinized ultramafic rocks: insights into the serpentinization process. *Chem. Geol.* **228**, 246–265.
- Bockheim J. (2007) Soil processes and development rates in the Quartermain Mountains, Upper Taylor Glacier Region, Antarctica. *Geogr. Ann.* **A(13)**, 153–165.
- Bockheim J., Prentice M. L. and McLeod M. (2008) Distribution of glacial deposits, soils, and permafrost in Taylor Valley, Antarctica. *Arctic Antarctic Alpine Res.* **40**, 279–286.
- Cary J. W. and Mayland H. F. (1972) Salt and water movement in unsaturated frozen soil. *Soil Sci. Soc. Am. Proc.* **36**, 549–555.
- Chong-Diaz G., Mendoza M., García-Veigas J., Pueyo J. J. and Turner P. (1999) Evolution and geochemical signatures in a Neogene forearc evaporitic basin: the Salar Grande (Central Andes of Chile). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **151**, 39–54.
- Davila A. F., Gomez-Silva B., de los Rios A., Ascaso C., Olivares H., McKay C. P. and Wierzcchos J. (2008) Facilitation of endolithic microbial survival in the hyperarid core of the Atacama Desert by mineral deliquescence. *J. Geophys. Res.* **113**, G01028. <http://dx.doi.org/10.1029/2007JG000561>.
- Desaulniers D. E., Kaufmann R. S., Cherry J. A. and Bentley H. W. (1986) ^{37}Cl – ^{35}Cl variations in a diffusion-controlled groundwater system. *Geochim. Cosmochim. Acta* **50**, 1757–1764.
- Eastoe C. J., Long A. and Knauth L. P. (1999) Stable chlorine isotopes in the Palo Duro Basin, Texas: evidence for preservation of Permian evaporite brines. *Geochim. Cosmochim. Acta* **63**(9), 1375–1382.
- Eastoe C. J., Long A., Land L. S. and Kyle J. R. (2001) Stable chlorine isotopes in halite and brine from the Gulf Coast Basin: brine genesis and evolution. *Chem. Geol.* **176**, 343–360.
- Eastoe C. J. and Peryt T. (1999) Stable chlorine isotope evidence for non-marine chloride in Badenian evaporites, Carpathian mountain region. *Terra Nova* **11**(2/3), 118–123.
- Eggenkamp H. G. M. (1994) The geochemistry of chlorine isotopes. In: vol. Universiteit Utrecht, p. 151.
- Eggenkamp H. G. M. and Coleman M. L. (2009) The effect of aqueous diffusion on the fractionation of chlorine and bromine stable isotopes. *Geochim. Cosmochim. Acta* **73**, 3539–3548.
- Eggenkamp H. G. M., Kreulen R. and Koster van Groos A. F. (1995) Chloride stable isotope fractionation in evaporites. *Geochim. Cosmochim. Acta* **59**(24), 5169–5175.
- Eggenkamp H. G. M., Middelburg J. J. and Kreulen R. (1994) Preferential diffusion of ^{35}Cl relative to ^{37}Cl in sediments of Kau Bay, Halmahera, Indonesia. *Chem. Geol.* **116**, 317–325.
- Ewing S. A., Michalski G., Theimens M., Quinn R. C., Macalady J. L., McKay C. P. and Amundson R. (2007) Rainfall limit of the N cycle on Earth. *Global Biochem. Cycles* **21** (GB3009).
- Ewing S. A., Sutter B., Amundson R., Owen J., Nishiizumi K., Sharp W., Cliff S. S., Perry K., Dietrich W. E. and McKay C. P. (2006) A threshold in soil formation at Earth's arid-hyperarid transition. *Geochim. Cosmochim. Acta* **70**, 5293–5322.
- Ewing S. A., Yang W., DePaolo D. J., Michalski G., Kendall C., Stewart B. W., Theimens M. and Amundson R. (2008) Non-biological fractionation of stable Ca isotopes in soils of the Atacama Desert, Chile. *Geochim. Cosmochim. Acta* **72**, 1096–1110.
- Godon A., Jendrzewski N., Castrec-Rouelle M., Dia A., Pineau F., Boulègue J. and Javoy M. (2004) Origin and evolution of fluids from mud volcanoes in the Barbados accretionary complex. *Geochim. Cosmochim. Acta* **68**(9), 2153–2165.
- Hagedorn B., Sletten R. S. and Hallet B. (2007) Sublimation and ice condensation in hyperarid soils: Modeling results using field data from Victoria Valley, Antarctica. *J. Geophys. Res.* **112**, F03017.
- Hagedorn B., Sletten R. S., Hallet B., McTeague D. F. and Steig E. J. (2010) Ground ice recharge via brine transport in frozen soils of Victoria Valley, Antarctica: insights from modeling $\delta^{18}\text{O}$ and δD profiles. *Geochim. Cosmochim. Acta* **74**, 435–448.
- Jury W. A., Gardner W. R. and Gardner W. H. (1991) *Soil Physics*, fifth ed. John Wiley & Sons, New York.
- Long A., Eastoe C. J., Kaufmann C. J., Martin J. G., Wirt L. and Finley J. B. (1993) Stable chlorine isotopes in hydrothermal systems. *Geochim. Cosmochim. Acta* **56**, 4247–4255.

- Michalski G., Böhlke J. K. and Theimens M. (2004) Long term atmospheric deposition as the source of nitrate and other salts in the Atacama Desert, Chile: new evidence from mass-independent oxygen isotopic compositions. *Geochim. Cosmochim. Acta* **68**, 4023–4038.
- Phillips F. and Bentley H. (1987) Isotopic fractionation during ion filtration: I: theory. *Geochem. Cosmochim. Acta* **51**, 683–695.
- Rech J. A., Quade J. and Hart W. S. (2003) Isotopic evidence for the source of Ca and S in soil gypsum, anhydrite and calcite in the Atacama Desert, Chile. *Geochim. Cosmochim. Acta*, 575–586.
- Risacher F. and Alonso H. (2001) Geochemistry of ash leachates from the 1993 Lascar eruption, northern Chile. Implication for recycling of ancient evaporites. *J. Volcanol. Geother. Res.* **109**, 319–337.
- Saez A., Cabrera L., Jensen A. and Chong G. (1999) Late Neogene lacustrine record and palaeogeography in the Quillagua-Llamara basin, Central Andean fore-arc (northern Chile). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **151**, 5–37.
- Scott H. D. (2000) *Soil Physics. Agricultural and Environmental Applications*. Iowa State University Press, Ames.
- Ugolini F. C. and Anderson D. W. (1973) Ionic migration and weathering in frozen Antarctic soils. *Soil Science* **115**, 461–470.
- Walvoord M. A. (2002) *A unifying conceptual model of water, vapor and solute movement in deep arid vadose zones*. PhD Dissertation, New Mexico Tech, Socorro, NM.
- Walvoord M. A. and Phillips F. M. (2004) Identifying areas of basin-floor recharge in the Trans-Pecos region and the link to vegetation. *J. Hydrol.* **292**, 59–74.
- Wierzchos J., Ascaso C. and McKay C. P. (2006) Endolithic cyanobacteria in halite rocks from the hyperarid core of the Atacama Desert. *Astrobiology* **6**, 415–422.
- Wexler A. (1977) Vapor-pressure formulation for ice. *J. Res. Natl Bureau Standards Sect. A – Phys. Chem.* **81**, 5–20.
- World Meteorological Organization (WMO), Guide to Meteorological Instruments and Methods of Observation, Appendix 4B, WMO-No. 8 (CIMO Guide), Geneva 2008.
- Zhang M., Frapre S. K., Love A. J., Herczeg A. L., Lehmann B. E., Beyerle U. and Purtschert R. (2007) Chlorine stable isotope studies of old groundwater, southwestern Great Artesian Basin, Australia. *Appl. Geochem.* **22**, 557–574.

Associate editor: Jon Chorover