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Brine formation in cold desert, shallow groundwater systems: Antarctic Ca-Cl brine chemistry controlled by cation exchange, microclimate, and organic matter

I.C. King, J.T.E. Johnson*, L. Kuang*, S. Naylor, T. Subak*, A.M. Koleszar, and J.S. Levy†
Colgate University, Department of Earth and Environmental Geosciences, 13 Oak Drive, Hamilton, New York 13346, USA

ABSTRACT

Groundwater in the McMurdo Dry Valleys of Antarctica is commonly enriched in calcium and chloride, in contrast to surface and groundwater in temperate regions, where calcium chemistry is largely controlled by the dissolution of carbonates and sulfates. These Antarctic Ca-Cl brines have extremely low freezing points, which leads to moist soil conditions that persist unfrozen and resist evaporation, even in cold, arid conditions. Several hypotheses exist to explain these unusual excess-calcium solutions, including salt deliquescence and differential salt mobility and cation exchange. Although the cation exchange mechanism was shown to explain the chemistry of pore waters in permafrost cores from several meters depth, it has not been evaluated for near-surface groundwater and wetland features (water tracks) in which excess-calcium pore-water solutions are common. Here, we use soluble salt and exchangeable cation concentrations to determine whether excess calcium is present in water-track brines and if cation exchange could be responsible for calcium enrichment in these cold desert groundwaters. We show that calcium enrichment by cation exchange is not occurring universally across the McMurdo Dry Valleys. Instead, evidence of the present-day formation of Ca-Cl–rich brines by cation exchange is focused in a geographically specific location in Taylor Valley, with hydrological position, microclimate, soil depth, and organic matter influencing the spatial extent of cation exchange reactions. Up-valley sites may be too cold and dry for widespread exchange, and warm and wet coastal sites are interpreted to host sediments whose exchange reactions have already gone to completion. We argue that exchangeable cation ratios can be used as a signature of past freeze-concentration of brines and exchange reactions, and thus could be considered a geochemical proxy for past groundwater presence in planetary permafrost settings. Correlations between water-track organic matter, fine sediment concentration, and cation exchange capacity suggest that water tracks may be sites of enhanced biogeochemical cycling in cold desert soils and serve as a model for predicting how active layers in the Antarctic will participate in biogeochemical cycling during periods of future thaw.

1. INTRODUCTION

The McMurdo Dry Valleys are a cold desert region of Antarctica where surface deposits are shaped by biogeochemical processes acting on permafrost-affected soils, glaciers, ice-covered lakes, and ephemeral streams (Moorhead et al., 1999; Lyons et al., 2000; Barrett et al., 2006). With an area of 4500 km^2, the McMurdo Dry Valleys are the largest ice-sheet–free region in Antarctica (Levy, 2013), and are situated along a microclimatic gradient that makes them particularly well-suited for studying the impacts of climate on soil geomorphological, ecological, and hydrological processes (Fountain et al., 2014). The McMurdo Dry Valleys support a surface and near-surface hydrological system consisting of a network of freshwater reservoirs, including glaciers, streams, and ice-covered lakes (Fountain et al., 1999; Gooseff et al., 2011; Levy, 2015), as well as saltwater reservoirs, including hypersaline lakes and deep groundwater conduits (Yamagata et al., 1977; Harris and Cartwright, 1981; Mikucki et al., 2015; Badgeley et al., 2017; Toner et al., 2017), seasonal wetlands and water tracks (Levy et al., 2011), and hypersaline soil patches (Levy et al., 2012; Deutsch et al., 2022; Fig. 1).

Ca-Cl–rich solutions dominate many parts of the saltwater hydrology in the McMurdo Dry Valleys and are found in surficial groundwater (Wilson, 1979; Webster et al., 2003; Levy et al., 2011) and deep groundwater (Cartwright and Harris, 1981), as well as in lakes and ponds (Angino and Armitage, 1963; Healy et al., 2006; Lyons et al., 2012). Ca-Cl–rich brines have been extensively described in Taylor and Wright Valleys (Fig. 1). Though common in the McMurdo Dry Valleys, Ca-Cl–rich brines are uncommon in most hydrological systems in temperate regions (Garrett, 2004), where carbonate and sulfate largely control calcium chemistry. Here, we evaluate which processes may be responsible for concentrating solutes in these geochemically endmember groundwater systems and explore what specifically drives calcium enrichment in Antarctic surface waters, including seasonal wetlands and water tracks.

1.1. Water-Track Characteristics

Water tracks are shallow groundwater-flow features that form a topographically controlled drainage network that routes snow melt and ground-ice melt downslope in permafrost/active-layer environments (Hastings et al., 1989; McNamara et al., 1999; Levy et al., 2011). Water tracks are abundant in the McMurdo Dry Valleys and are characterized by branching linear features that are darker and wetter than adjacent dry soils (Fig. 2). Water tracks are commonly several meters wide and hundreds to thousands of meters long, and as a result, are readily detectable as dark, narrow, linear soil features in satellite and aerial imagery (Kuentz et al., 2022; Fig. 2). Water tracks promote hydrologic connectivity

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J.S. Levy https://orcid.org/0000-0002-6222-139X
†jlevy@colgate.edu

*Present address: J.T.E. Johnson, Multiscale Imaging and Integrative Biophysics Unit, National Institute on Aging, National Institute of Health, 251 Bayview Boulevard, Baltimore, Maryland 21224, USA; L. Kuang, Stony Brook University, Department of Geosciences, 100 Nicolls Road, Stony Brook, New York 11794, USA; T. Subak, Northwestern University, Department of Earth and Planetary Sciences, 2145 Sheridan Road, Evanston, Illinois 60208, USA.

GSA Bulletin;
published online 9 February 2024

https://doi.org/10.1130/B37251.1.

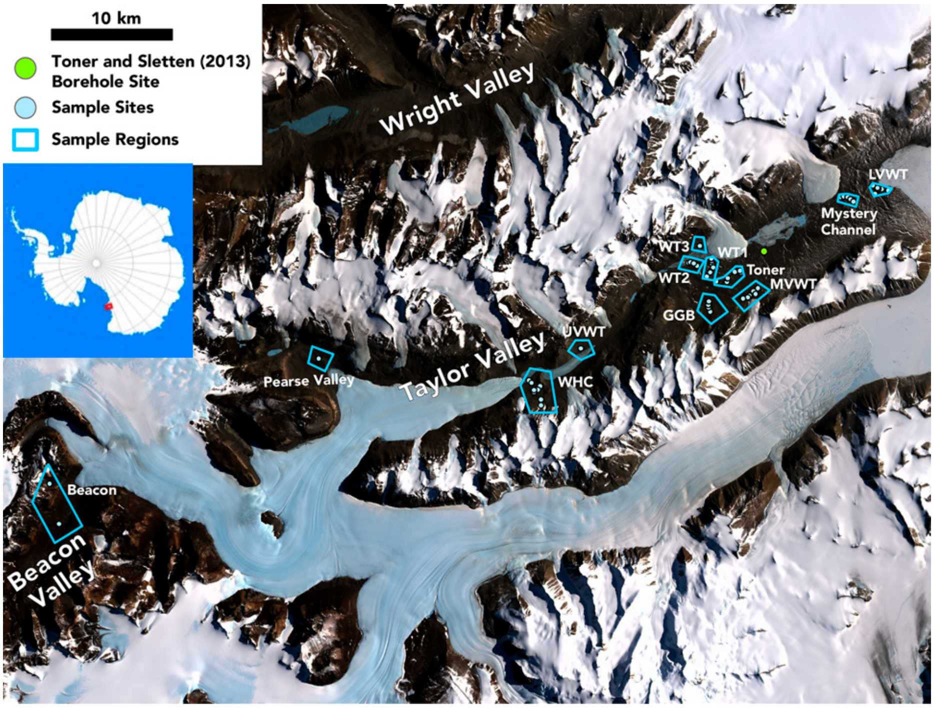

Figure 1. Site map showing the location of McMurdo Dry Valleys, Antarctica, soil sampling regions (blue polygons), soil sampling sites (blue dots), and the borehole site from Toner and Sletten (2013) (green dot). Basemap is the Landsat Image Mosaic of Antarctica (Bindschalder et al., 2008). Sediment samples were collected along a microclimate gradient from the warmer, wetter coastal thaw zone (to right), inland to the upland frozen zone (to left). Map is oriented with north toward the top of the image. GGB—Goldman Glacier Basin; LVWT—Lower-Valley Water Track; MVWT—Mid-Valley Water Track; UVWT—Upper-Valley Water Track; WHC—Wormherder Creek; WT1—Water Track 1; WT2—Water Track 2; WT3—Water Track 3.

throughout the McMurdo Dry Valleys, routing snowmelt, ice melt, and brines downslope from upland terrains to valley floors (Gooseff et al., 2011; Levy, 2015). The water-track hydroperiod (the duration that water tracks are wetted) extends from November to March. This is longer than the December–January period of peak summer snow/ice melting in the McMurdo Dry Valleys, which suggests an important role for soil salts in extending the duration of groundwater flow (Kuentz et al., 2022).

1.2. Ca-Cl Brine Chemistry

Brines are considered Ca-Cl–rich if they contain excess calcium relative to carbonate and sulfate, as indicated by $2Ca^{2+} > HCO^{-} + 2SO_4^{2-}$ (Hardie and Eugster, 1970; Hardie, 1983; Lyons et al., 1998). In most surface waters, calcium carbonate and gypsum precipitate during brine evaporation and/or freezing, which lowers the Ca^{2+} concentration in solution and forms calcium-depleted brines. Conversely, brines rich in Ca^{2+} and Cl^{-} form when insoluble calcium carbonates and sulfates precipitate with excess Ca^{2+} still present, which allows calcium and chloride to remain in solution as highly soluble $CaCl_2$ (Toner and Sletten, 2013).

1.3. Ca-Cl Brine Formation in the McMurdo Dry Valleys

Previous studies suggested formation mechanisms for Ca-Cl–rich brines in the McMurdo Dry Valleys. Wilson (1979) proposed salt deliquescence as a mechanism for salt separation. In this model, when snow sublimates from high on the valley walls, it leaves behind condensation nuclei composed of salts that include Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, SO_4^{-}, and Cl^{-}. During high-humidity conditions (e.g., Levy, 2021), soluble salts such as $CaCl_2$ will deliquesce and become a mobile brine (Dickinson and Rosen, 2003) that moves downslope and enters the groundwater system. In contrast, the other salts in the snow condensation nuclei are less deliquescent and remain as solid soil salts high on the valley walls.

Toner and Sletten (2013) propose that Ca-Cl–rich brine formation in the McMurdo Dry Valleys is a consequence of cation exchange reactions. In this model, Na^{+}-rich brines originate from sea spray and then exchange with Ca^{2+} and Mg^{2+} that are bound to exchange sites on clays. Divalent cations typically bind more strongly than monovalent cations to exchange sites; however, Toner and Sletten (2013) showed experimentally that divalent cations will preferentially enter solution by cation exchange in concentrated brines due to the ratio law. The ratio law is a concentration effect that can be understood using the Rothmund-Kornfeld equation for binary cation exchange reactions (Bond, 1995), which is modified here specifically to show Ca-Na exchange:

$$K^{\mathrm{Ca,Na}} = \frac{A_{\mathrm{Ca}}}{A_{\mathrm{Na}}^{2}}\left[\frac{a_{\mathrm{Na}}^{2}}{a_{\mathrm{Ca}}}\right]^{n^{\mathrm{Ca,Na}}}. \tag{1}$$

K is the Rothmund-Kornfeld parameter (equilibrium constant) for the Ca-Na exchange example, A is the exchangeable cation activity for Ca^{2+} and Na^{+}, a is the solution cation activity for Ca^{2+} and Na^{+}, and n is an empirical exponent for Ca-Na exchange. As the solution cation activity ratio increases during processes such as freezing or evaporation, the charge balance between the divalent calcium and monovalent sodium requires that the exchangeable cation activity ratio decreases by removing Ca^{2+} from exchange sites. Therefore, the ratio law models conditions where the exchange of sodium and calcium from concentrated groundwater solutions will result in the enrichment of calcium in the solution and adsorption of sodium onto soil exchange sites.

Based on this effect, Toner and Sletten (2013) provided evidence of cation exchange in the McMurdo Dry Valleys using brine and soluble salt geochemistry from a 210-cm-deep borehole. Their deep sampling method focused on the analysis of ice-cemented soil and argued that cation-exchanged brines may flow episodically through the ice-cemented soil and ultimately to other parts of the hydrological system of the McMurdo Dry Valleys, since the brines are highly mobile with low eutectic temperatures (Wilson, 1979; Marion, 1997). However, pore waters with excess Ca^{2+} are also present at shallow depths (<60 cm) in the McMurdo Dry Valleys, most commonly in water tracks and wetlands fed by water tracks. Water tracks contain clays in the soil matrix and concentrated pore-water solutions (Levy et al., 2013, 2011), which makes them possible locations for cation exchange that could create the excess-calcium brines observed in the near surface.

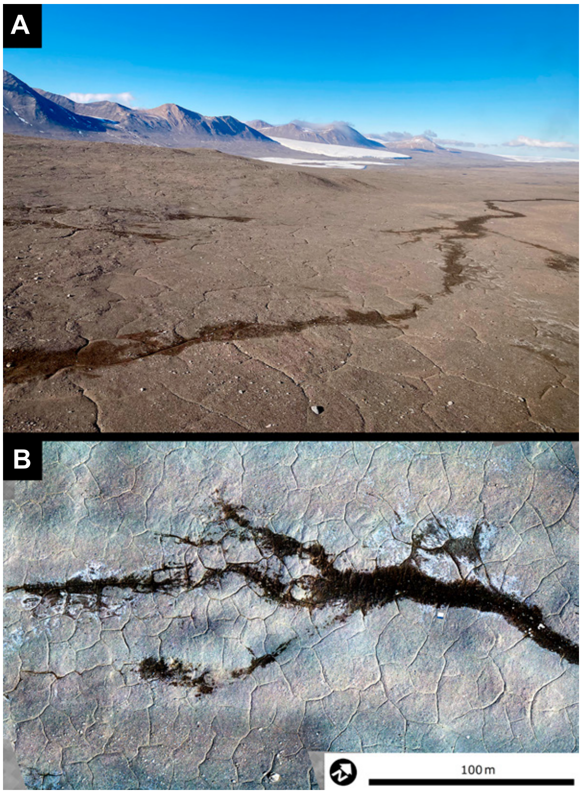

Figure 2. (A) Field photograph of Mid-Valley Water Track (MVWT), Antarctica, and (B) drone-collected ortho-image of the same feature. In part A, downslope is toward the right. Field of view is ∼250 m in the foreground. In part B, downslope is toward the right.

2. RESEARCH QUESTIONS, HYPOTHESES, AND PREDICTIONS

Previous work on deep pore waters by Toner and Sletten (2013) motivates the following research questions: (1) Are excess-calcium brines found in water tracks across the McMurdo Dry Valleys, and is the presence of excess calcium in water tracks recorded in the soluble salt chemistry? (2) Can we explain the presence of Ca-Cl–rich brines in water tracks with the Toner and Sletten (2013) cation exchange mechanism? (3) What factors control potential cation exchange signatures in Antarctic soils that could provide insight into biogeochemical or climatic processes at work here and in similar cold deserts?

We look for evidence of cation exchange that results in the depletion of Ca^{2+} and enrichment of Na^+ at soil exchange sites in water-track soils that show calcium enrichment in pore waters and/or soluble salt extracts. We predict that wetted water-track and wetland soils will show evidence of cation exchange that produced calcium-rich pore waters, leaving exchange sites with low exchangeable Ca^{2+} and high exchangeable Na^+ (and producing a low exchangeable Ca^{2+}/Na^+ ratio). In contrast, soils from adjacent, dry, "off-track" soils do not have the opportunity to interact with concentrated pore-water solutions, and therefore should not be sites where cation exchange reactions occur. We predict that off-track soils should not exhibit an exchange signature and therefore should have higher exchangeable Ca^{2+}/Na^+ ratios, which would indicate that calcium is still bound to the exchange sites and was not lost to groundwater.

The questions and hypotheses we put forth are important for understanding salt processes in the cold desert environment of Antarctica, where Ca-Cl–rich brine compositions are distinct from other global surface waters. The soils of this environment may serve as a model for similar cold desert groundwater processes operating elsewhere. For example, modern Mars is a cold desert where freezing and evaporative processes dominate; therefore, we may be able to use insights regarding brine geochemistry from the McMurdo Dry Valleys to evaluate salt formation and distribution mechanisms that have operated on Mars (Gibson, 1980; Osterloo et al., 2008; Deutsch et al., 2022).

3. MATERIALS AND METHODS

3.1. Research Site

The McMurdo Dry Valleys are an ice sheet-free region in Antarctica that sits between the Transantarctic Mountains of southern Victoria Land and the Ross Sea. The McMurdo Dry Valleys have a mean annual temperature of -18 °C (Doran et al., 2002) and experience 3–50 mm water-equivalent annual precipitation (Fountain et al., 2010). The cold temperatures in the region create perennially frozen permafrost from the surface to a depth of ∼200–600 m (McGinnis and Jensen, 1971). Active layers are typically 10–60 cm thick in the McMurdo Dry Valleys (Bockheim et al., 2007; Adlam et al., 2010), which permits water tracks and seasonal wetlands to expand in response to snowmelt, ground-ice melt, and salt deliquescence (Kuentz et al., 2022).

The McMurdo Dry Valleys experience a coast-to-inland climatic gradient, which produces microclimatic zones with different geomorphic processes and resulting landscape features (Marchant and Head, 2007; Fountain et al., 2014). The coastal thaw zone along the Ross Sea has a mean summer temperature of ~ -5 °C and high relative humidity due to southeasterly winds carrying moisture (Marchant and Head, 2007). Inland, the intermediate mixed zone has a mean summer temperature of ~ -7 °C and a variable relative humidity due to alternating west katabatic winds and easterly winds from the Ross Sea (Marchant and Head, 2007), which results in more limited fluvial activity than in the coastal thaw zone. In the most inland and highest portions of the valleys, the upland frozen zone has a mean summer temperature of ~ -8 °C and low relative humidity; it is composed largely of glacial and melt-free landforms (Marchant and Head, 2007).

The study sites for this investigation are located in Beacon (upland frozen zone), Pearse (intermediate mixed zone), and Taylor valleys (coastal thaw zone to intermediate mixed zone) in the McMurdo Dry Valleys (77.69°S, 162.62°E). To capture the variability in microclimates, our study sites span the coastal, intermediate, and upland microclimates and vary in elevation, slope, azimuth, and distance to the Ross Sea. The sites are the Lower-Valley Water Track (LVWT); Mystery Channel (Mystery or MC); Mid-Valley Water Track (MVWT), near Toner and Sletten (2013)'s borehole (Toner); Water Track 1 (WT1); Water Track 2 (WT2); Water Track 3 (WT3); Goldman Glacier Basin (GGB); Upper-Valley Water Track (UVWT); Wormherder Creek (WHC); Beacon Cirque (Beacon); and Pearse Valley (Fig. 1).

3.2. Sampling

Ninety-five soil samples were collected from the active layer during the 2012–2013 and 2015–2016 field seasons. The sediments are mostly near-surface samples from the upper 10 cm of the soil column; however, some samples from

TABLE 1. MEDIAN UNCERTAINTY FOR SOLUBLE IONS ANALYZED BY ION CHROMATOGRAPH (IC) AND EXCHANGEABLE IONS ANALYZED BY INDUCTIVELY COUPLED PLASMA–OPTICAL EMISSION SPECTROMETER (ICP-OES)

Ion	IC uncertainty	ICP-OES uncertainty
Anions		
F^-	±2.8%	
Cl^-	±1.3%	
NO_2^-	±0.7%	
Br^-	±1.0%	
NO_3^-	±1.0%	
PO_4^{3-}	±2.1%	
SO_4^{2-}	±0.7%	
ClO_4^-	±2.4%	
Cations		
Li^+	±1.0%	
NH_4^+	±1.0%	
Na^+	±0.9%	±3.2%
K^+	±0.9%	±1.3%
Mg^{2+}	±1.2%	±3.7%
Ca^{2+}	±11%	±3.8%

deeper in the active layer were also analyzed. Where depths are reported, samples are from the subsurface; where depths are not reported, samples are from the near-surface in the upper 10 cm of the soil column. In this paper, we consider "on-track" samples to be those collected from the darkened and wetted section of the water track. "Off-track" samples were collected from the lighter-toned and drier sediments adjacent to the water track (within 5–10 m of the on-track sampling point). At each sampling site, ~300 g of soil was collected using a clean scoop and placed into a clean Whirl-Pak bag. The samples were then transported to McMurdo Station, where they were weighed, dried in a 105 °C oven, and then weighed again. The dried samples were transported to the United States at room temperature and were stored at room temperature until this study.

Water samples were also collected directly from the active layer during the 2012–2013 and 2015–2016 field seasons. They were collected using sterile polyethylene syringes and were filtered in the field using 0.45 µm HT Tuffryn membrane syringe filters and stored in pre-cleaned bottles. Water samples were kept refrigerated at all times.

3.3. Soil Processing

Soil samples were analyzed for soil electrical conductivity, ash-free dry mass or organic matter content, gravimetric water content, volumetric water content, soluble salt major ions (F^-, Cl^-, NO_2^-, Br^-, NO_3^{3-}, PO_4^{3-}, SO_4^{2-}, HCO_3^-, Li^+, Na^+, NH_4^+,K^+, Mg^{2+}, and Ca^{2+}), and exchangeable cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}).

Gravimetric water content was determined by dividing the mass of water in the sample (calculated by subtracting dry weight from wet weight) by the dry weight. Volumetric water content was then calculated by dividing the gravimetric water content by the average bulk density of Lake Hoare basin soils (1.8 g/cm^3).

For the measurement of soil electrical conductivity, major ions, and exchangeable ions, soil samples were processed using a 1:10 soil-water extraction by mass. Soils were subsampled in triplicate, and each aliquot was processed fully independently following the methods of Levy et al. (2011). For each subsample, 5 g of soil were shaken and centrifuged with 50 mL of ultrapure water (18.2 MΩ cm at 25 °C) in pre-cleaned bottles. The soluble salt extract solution was decanted into another set of pre-cleaned bottles for analysis. The 5 g of soil was then shaken and centrifuged for a second time using 50 mL of ultrapure water to ensure that it was free of soluble salts prior to cation exchange experiments.

3.4. Soil Soluble Salt Processing

The soluble salt extract solution was vacuum filtrated through a 0.45 µm filter and measured for electrical conductivity. The brine was diluted to below 150 ppm equivalent conductivity with ultrapure water. Ion chromatography was used to determine the major ion concentrations (F^-, Cl^-, NO_2^-, Br^-, NO_3^{3-}, PO_4^{3-}, SO_4^{2-}, Li^+, Na^+, NH_4^+,K^+, Mg^{2+}, and Ca^{2+}) with a Metrohm 930 ion chromatograph (Table 1). The concentration of HCO_3^- was calculated by completing a charge balance for each sample (all samples are circum-neutral in pH).

3.5. Cation Exchange Experiments

To evaluate evidence for the cation exchange mechanism proposed by Toner and Sletten (2013), we performed cation exchange extraction on our washed soil samples. The washed soils were dried in a 45 °C oven and then flushed with 50 mL of 1 M ammonium chloride, shaken for 1 h, and then centrifuged. The exchange extract was passed through a 0.45 µm membrane syringe filter into a pre-cleaned bottle. The exchanged cation concentrations were measured using inductively coupled plasma–optical emission spectrometry (ICP-OES) at the SUNY College of Environmental Science and Forestry Baker Laboratory in Syracuse, New York, USA.

3.6. Organic Matter Processing

The ash-free dry mass of each sediment sample was measured using combustion analysis. The soils were weighed in a crucible and dried in a 150 °C oven for 24 h, then were weighed again and placed in a desiccator with a 1 M HCl acid fog for 24 h to remove any remaining inorganic $CaCO_3$ on the soil grains. Additionally, 1 mL of 1 M HCl was added to each sample to dissolve calcium carbonate not removed by the fogging. After the samples were acidified, they were redried in the oven at 150 °C for 24 h and weighed again. Finally, the samples were heated in a muffle furnace at 500 °C for 2 h, cooled, and then weighed to determine the organic matter loss on ignition.

4. RESULTS

4.1. Do Water Tracks Contain Abundant Ca and Cl⁻ Salts?

The distribution of soluble salt ions is reported in Piper diagrams (Piper, 1944), in which our samples span multiple geochemical facies (Figs. 3 and 4). The Piper diagram for directly sampled waters shows that water-track

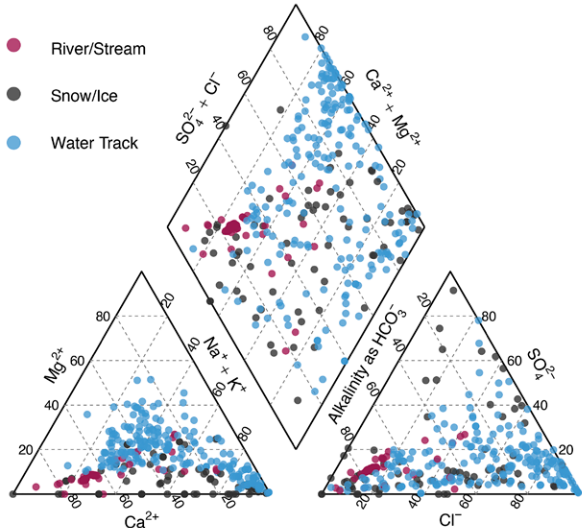

Figure 3. Piper diagram of river/stream, snow/ice, and water-track pore water samples from Beacon and Taylor Valleys, Antarctica. Water-track samples are mixed-chloride and mixed-bicarbonate dominant. Water tracks differ from other water reservoirs such as rivers/streams and snow/ice, which are bicarbonate dominant.

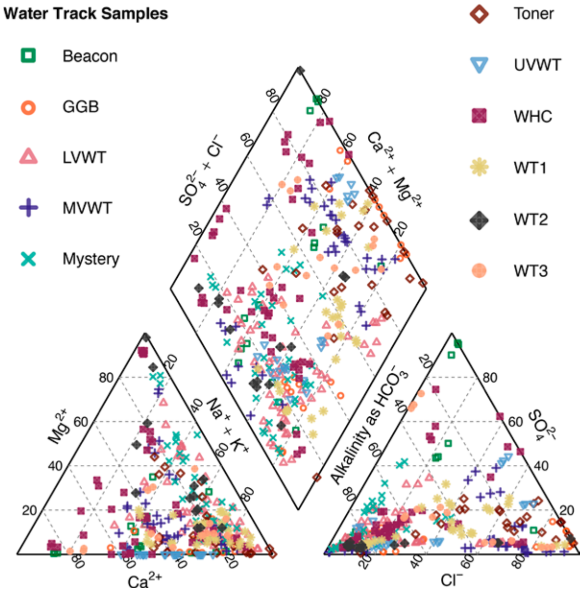

Figure 4. Piper diagram of water-track soluble salt samples from Antarctic sites: Beacon and Pearse Valley (Beacon), Goldman Glacier Basin (GGB), Lower-Valley Water Track (LVWT), Mid-Valley Water Track (MVWT), Mystery Channel (Mystery), near Toner and Sletten's (2013) borehole (Toner), Upper-Valley Water Track (UVWT), Wormherder Creek (WHC), Water Track 1 (WT1), Water Track 2 (WT2), and Water Track 3 (WT3). Water-track soluble salt compositions are variable and plot mainly in the mixed-carbonate and mixed-chloride facies.

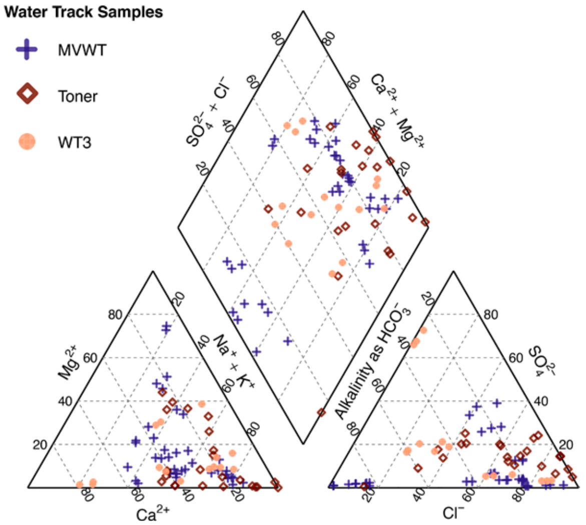

Figure 5. Piper diagram of soluble salt extracts from Mid-Valley Water Track (MVWT), Antarctica, near Toner and Sletten's (2013) borehole (Toner), and Water Track 3 (WT3). These samples are largely within the mixed-chloride facies.

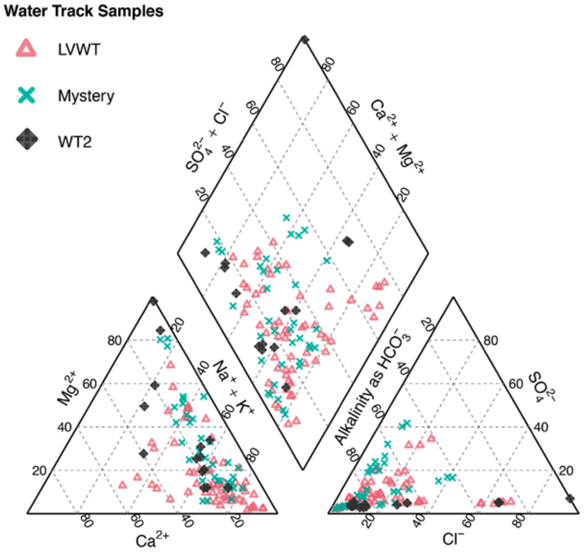

Figure 6. Piper diagram of soluble salt extracts from Antarctic sites: Lower-Valley Water Track (LVWT), Mystery Channel (Mystery), and Water Track 2 (WT2). These samples are largely within the mixed-bicarbonate facies.

samples are found in the calcium chloride- and calcium carbonate-dominant facies, whereas rivers/streams cluster in the calcium bicarbonate facies and snow/ice cluster in the sodium chloride facies. Water-track samples are enriched in Ca^{2+} and Cl^- in comparison to snow, ice, rivers, and streams.

In contrast, the soil-salt extract Piper diagram (Fig. 4) shows that soluble salts in water-track soils span several geochemical facies, including the mixed-carbonate facies and mixed-chloride facies. Although some water-track soluble salts plot in the calcium chloride facies, a majority of the sampled salts reflect mixed-carbonate composition.

Breaking down the salt-soil extract data by composition, three groups of water track sites emerge: (1) samples from the Mid-Valley Water Track (MVWT), Toner, and Water Track 3 (WT3) sites plot largely within the mixed chloride facies (Fig. 5); (2) samples from the Lower-Valley Water Track (LVWT), Mystery Channel, and Water Track 2 (WT2) sites plot largely within the mixed-carbonate facies (Fig. 6); and (3) samples from the remaining sites plot in both the chloride and bicarbonate facies (Fig. 7). The most chloride-dominated samples are spatially proximal to each other (Mid-Valley Water Track [MVWT] and Toner) and/or drain from watersheds that extend high above the valley floor (Water Track 3 [WT3], Wormherder Creek [WHC], Goldman Glacier Basin [GGB], etc.).

4.2. Cation Exchange Properties at the Surface (0–10 cm)

Data from the cation exchange experiments do not generally show Ca^{2+} depletion and Na^+ enrichment (lower Ca^{2+}/Na^+ ratios) for on-track samples where cation exchange was hypothesized to occur (Fig. 8). Additionally, higher Ca^{2+}/Na^+ ratios are not generally present in off-track soils where minimal cation exchange was hypothesized to occur. Three sample sites break from this general trend; Mid-Valley Water Track and Water Track 3 show a clear distinction between low on-track Ca^{2+}/Na^+ ratios and comparatively high off-track Ca^{2+}/Na^+ ratios. On-track samples at the Toner site also show low exchangeable Ca^{2+}/Na^+ ratios, although no off-track paired samples exist at this sampling site for direct comparison.

The exchangeable Ca^{2+}/Na^+ ratios we measured (Fig. 8) are generally higher and span a larger range than those of Toner and Sletten (2013). Toner and Sletten (2013) reported exchangeable Ca^{2+}/Na^+ ratios from ~0.6 to 2. Therefore, in the following sections, we describe exchangeable Ca^{2+}/Na^+ ratios as "high" or

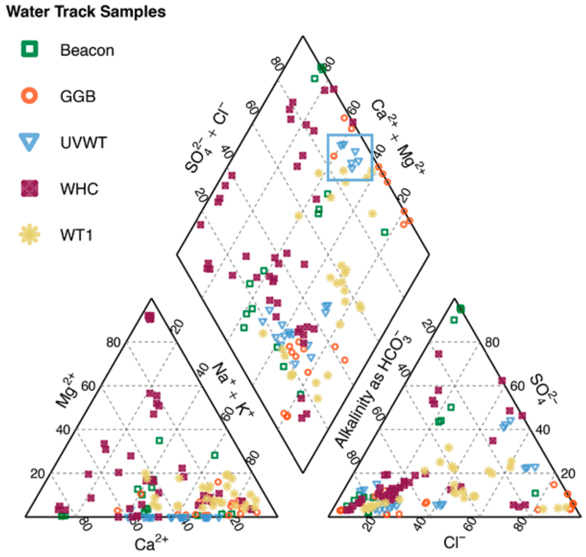

Figure 7. Piper diagram of soluble salt extracts from Antarctic water tracks: Beacon and Pearse Valley (Beacon), Goldman Glacier Basin (GGB), Upper-Valley Water Track (UVWT), Wormherder Creek (WHC), and Water Track 1 (WT1). Beacon, GGB, UVWT, WHC, and WT1 span the mixed-chloride and mixed-bicarbonate facies. Ca-Cl–rich samples in UVWT (light blue box) are surface samples, unlike bicarbonate-dominated samples from UVWT, which were collected deeper in the soil column (>10–20 cm).

"low" depending on how on- and off-track samples compare at each site, not relative to particular ratios measured by Toner and Sletten (2013).

4.3. Cation Exchange Properties with Depth (0–40 cm)

Exchangeable Ca^{2+}/Na^{+} ratios were measured along depth profiles at three sites and vary based on water-track location (Fig. 9). At Lower-Valley Water Track, both on and off-track samples show low Ca^{2+}/Na^{+} ratios regardless of depth. At Mid-Valley Water Track, the exchangeable Ca^{2+}/Na^{+} ratios for on-track samples reach a minimum value at ~20 cm below the surface and are bracketed by higher Ca^{2+}/Na^{+} ratios above and below. However, the exchangeable Ca^{2+}/Na^{+} ratios for off-track samples in the Mid-Valley Water Track remain high, from 0 cm to 10 cm. In the Upper-Valley Water Track, the exchangeable Ca^{2+}/Na^{+} ratios for on-track samples increase with depth. The Ca^{2+}/Na^{+} ratios for off-track samples in the Upper-Valley Water Track, however, do not increase or decrease with depth.

The cation exchange capacity (CEC) of our samples ranges from 200 meq kg^{-1} to 2910 meq kg^{-1}, with an average of 900 meq kg^{-1} ($1\sigma = 541$ meq kg^{-1}). At depth, the CEC is lower in the Mid-Valley Water Track and Upper-Valley Water Track (Fig. 10). However, in the Lower-Valley Water Track, the CEC is higher at depth (Fig. 10).

4.4. Organic Matter Content

Organic matter is more abundant on-track than off-track in most of the sample sites. The Mid-Valley Water Track is the only site where organic matter concentration is universally higher off-track than on-track. In Goldman Glacier Basin, Lower-Valley Water Track, Upper-Valley Water Track, Wormherder Creek, and Water Track 1, organic matter is generally more abundant in on-track samples than off-track samples (Fig. 11), though all sites yielded some off-track samples containing high organic matter content (e.g., at Wormherder Creek).

5. DISCUSSION

Using the distribution of soluble salts and exchangeable cations in the water tracks described above, we consider the following questions: (1) Are excess-calcium brines found in water tracks across the McMurdo Dry Valleys, and is the presence of excess calcium in water tracks recorded in the soluble salt chemistry? (2) Can we explain the presence of Ca-Cl–rich brines in water tracks with the Toner and Sletten (2013) cation exchange mechanism? (3) What factors control potential cation exchange signatures in Antarctic soils that could provide insight into biogeochemical or climatic processes at work here and in similar cold deserts?

5.1. Are Excess Calcium Brines Found in Water Tracks across the McMurdo Dry Valleys, and Is the Presence of Excess Calcium in Water Tracks Recorded in the Soluble Salt Chemistry?

Although some water-track solutions contain excess calcium, none of the water-track soil salts sampled in this study contain excess Ca^{2+} ($2Ca^{2+} > HCO_3^- + 2SO_4^{2-}$). As seen in the Piper diagrams presented above (Figs. 4–6), some of the samples do fall in the calcium chloride and mixed-chloride facies (particularly Mid-Valley Water Track, Toner, and Water Track 3), which suggests calcium enrichment of water-track solutions (Fig. 4). Indeed, when pore waters of water tracks were sampled directly (Levy, 2023b), water tracks in several parts of the McMurdo Dry Valleys showed evidence of excess calcium in pore waters (Fig. 12). Our soluble salt findings raise the question, why is there no evidence of excess calcium in the soluble salt extracts?

In many cases, our samples' soluble salt concentrations are higher than those of Toner and Sletten (2013; Table 2). These differences could be due to several factors. One possibility is a difference in sample depth and location, which is indicative of multiple salt sources. For example, near-surface samples could be dominated by sea spray or atmospheric fallout of salts versus chemical weathering at depth (Claridge, 1965; Claridge and Campbell, 1977; Bao and Marchant, 2006). Another possibility is evapoconcentration in water tracks (Barrett et al., 2009); water tracks are wetter than adjacent, off-track soils and allow for considerably enhanced salt mobility as solutes are carried downslope from the water-track watershed and concentrated near the surface as a consequence of evaporation (Dickinson and Rosen, 2003; Levy et al., 2011). These salts build up in water-track soils.

Although our samples are more concentrated than the values Toner and Sletten (2013) reported, we still do not detect excess calcium in our soluble salt extracts. The sites where we most clearly observe Ca^{2+} enrichment are Mid-Valley Water Track, Water Track 3, and Toner, with some additional evidence for mixed chlorides and carbonates in Water Track 1 and Goldman Glacier Basin (Fig. 7). The most plausible explanation is that our soluble salt data reflect both water-track pore-water chemistry and salt-crust chemistry. Efflorescent salt crusts are common around the margins of water tracks (Bisson et al., 2015; Gough et al., 2017) and result from the saturation of pore waters at the surface evaporation front. Where near-surface samples include abundant precipitated pedogenic carbonates (salt crusts), soluble salt extract data may reflect a combination of pore-water chemistry at the time of collection as well as accumulated salt-crust carbonates preserved from successive years of evaporative emplacement at the surface of the soil column. This combination of precipitated carbonates and chlorides that were originally in solution is consistent with sites showing samples in both the carbonate and chloride facies of the Piper plots and may mask evidence of excess calcium relative to carbonate and sulfate in water-track pore solutions.

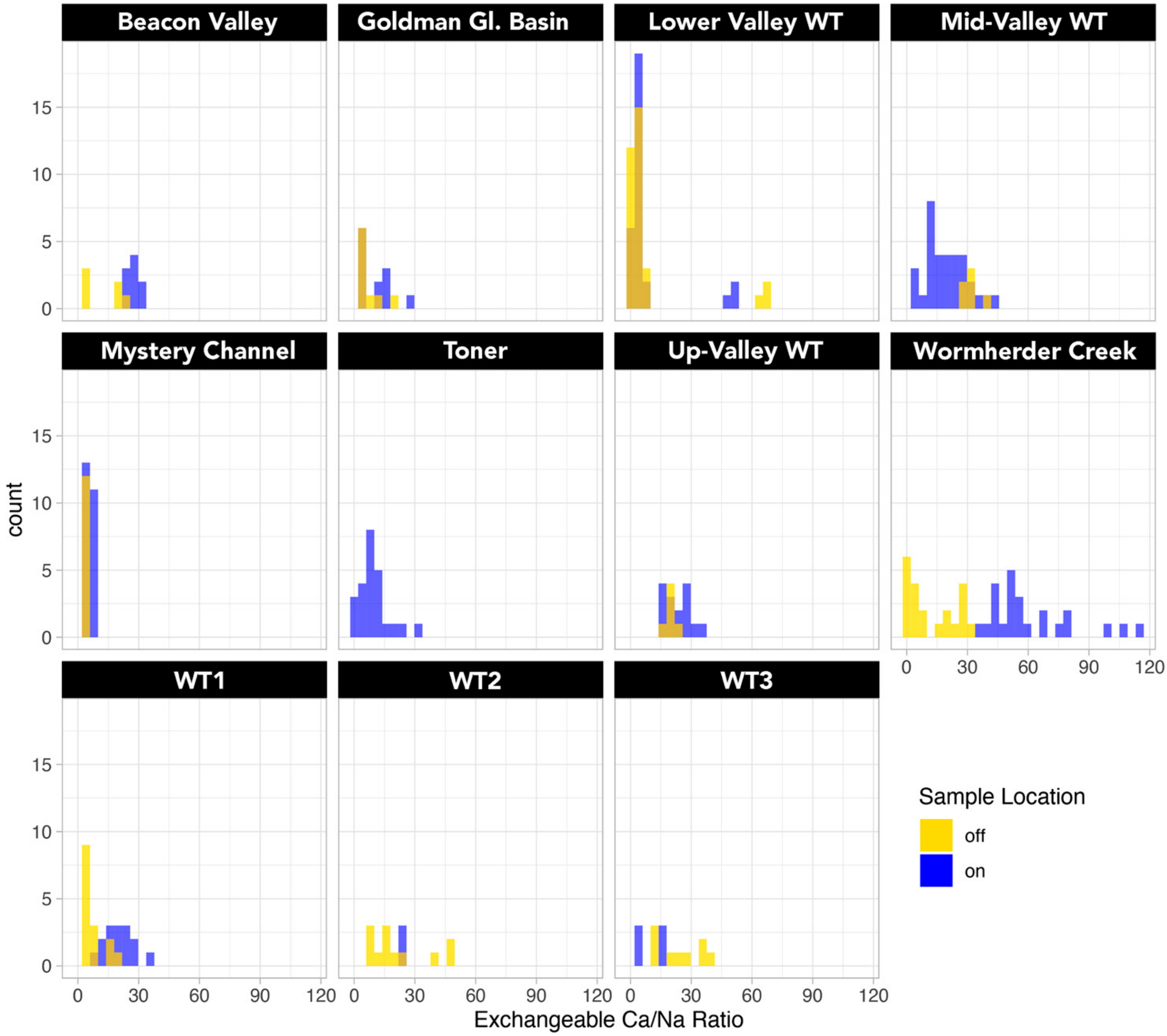

Figure 8. Exchangeable Ca^{2+}/Na^+ ratio (meq/meq) histograms by Antarctic sampling site: Beacon and Pearse Valley (Beacon), Goldman Glacier Basin (GGB), Lower-Valley Water Track (LVWT), Mid-Valley Water Track (MVWT), Mystery Channel (Mystery), near Toner and Sletten's (2013) borehole (Toner), Upper-Valley Water Track (UVWT), Wormherder Creek (WHC), Water Track 1 (WT1), Water Track 2 (WT2), and Water Track 3 (WT3). Only sites MVWT, Toner, and WT3 show high Ca^{2+}/Na^+ ratios for off-track soils and low Ca^{2+}/Na^+ ratios for on-track wetted soils.

5.2. Is Cation Exchange Responsible for Ca-Cl–Rich Brine Formation in Water Tracks?

Based on the Toner and Sletten (2013) hypothesis that brine-driven cation exchange enriches pore-water solutions of the McMurdo Dry Valleys by releasing calcium from exchange sites and replacing it with sodium, our prediction was that on-track samples would exhibit a cation exchange signature (low exchangeable Ca^{2+}/Na^+ ratios), while adjacent, dry, off-track soils would not show evidence of exchange (high exchangeable Ca^{2+}/Na^+ ratios). However, the on-track samples do not universally exhibit a lower exchangeable Ca^{2+}/Na^+ ratio than adjacent off-track samples. In this context, lower and higher are relative to adjacent on- and off-track samples within a given watershed because different watersheds may have experienced different pre-exposure of clay grains due to the flow of near-surface water with different initial compositions.

Interestingly, we find an average CEC of 900 meq kg^{-1} across our samples, which is much higher than the CEC reported by Toner and Sletten (2013) in deeper (0–200 cm) borehole samples. Toner and Sletten (2013) report an average CEC of 25 meq kg^{-1}, with CEC reaching a maximum value of 60 meq kg^{-1} at

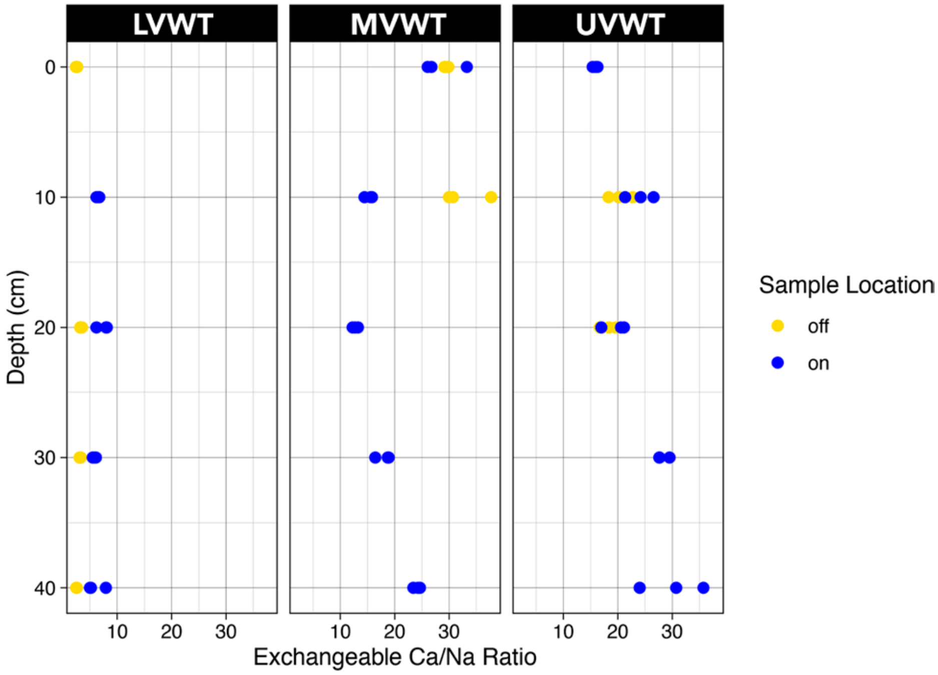

Figure 9. Exchangeable Ca^{2+}/Na^{+} ratio (meq/meq) with depth (cm) in Antarctic Lower-Valley Water Track (LVWT), Mid-Valley Water Track (MVWT), and Upper-Valley Water Track (UVWT) samples.

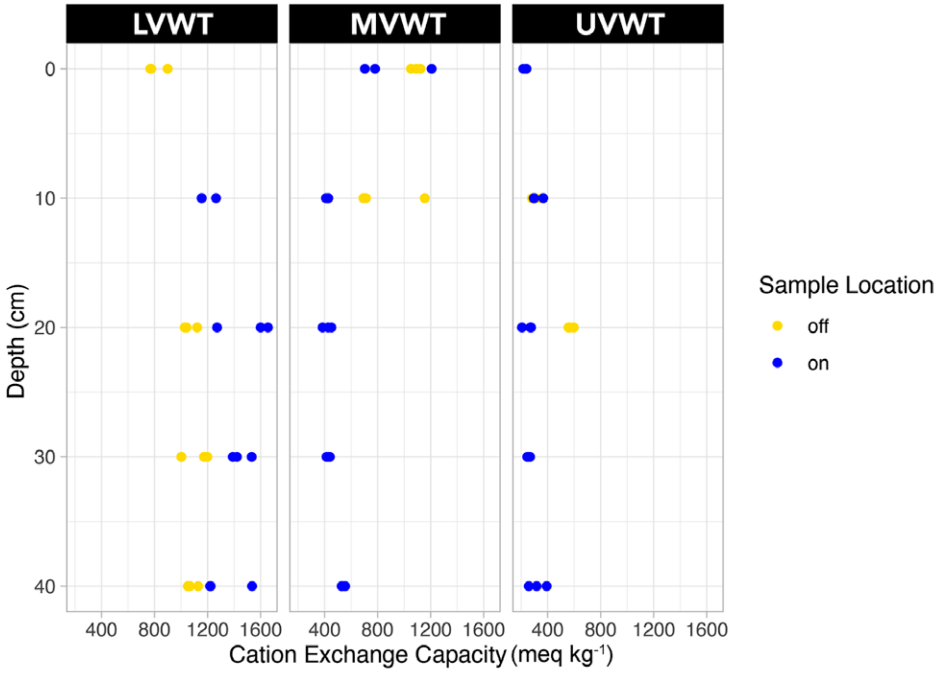

Figure 10. Cation exchange capacity (meq kg^{-1}) with depth (cm) at Antarctic Lower-Valley Water Track (LVWT), Mid-Valley Water Track (MVWT), and Upper-Valley Water Track (UVWT).

200 cm depth, deep in the ice-cemented portion of the permafrost borehole. The difference in CEC between our samples and that of Toner and Sletten (2013) may reflect a difference in host sediment, as they analyzed samples from a borehole in sandy to gravelly paleolake foreset/fluvial terrace deposits. We document higher CEC in water tracks where near-surface soils are derived largely from glacial tills and are commonly enriched in clay (Levy et al., 2014).

One possible explanation for the high Ca^{2+}/Na^{+} ratios we observed on water tracks could be that the high clay content and high CEC of water tracks means that, in some cases, they have not yet fully exchanged away their Ca^{2+} due to the large number of sites available for cation binding in the clay-enriched sediment. In contrast, clay-poor sands like those analyzed by Toner and Sletten (2013) may be expected to have fewer sites at which cations can bind, producing a large change in the Ca^{2+}/Na^{+} ratio when a comparatively small number of cations undergoes exchange (Fig. 13). However, the highest exchangeable Ca^{2+}/Na^{+} ratios we saw were in low-CEC soils, and soils with CEC values higher than ~1500 meq kg^{-1} typically have low exchangeable Ca^{2+}/Na^{+} ratios. This suggests a second possible explanation: the most clay-enriched soils, or the soils with the most cation exchange sites, may have been the most hydrologically modified by water-track flow, which increased the clay content in the soils and exported calcium to pore-water solutions by cation exchange, reducing their exchangeable Ca^{2+}/Na^{+} ratio. This suggests that the exchangeable Ca^{2+}/Na^{+} ratio may reflect climatic or hydrological processes at work in the McMurdo Dry Valleys.

5.3. Cation Exchange Properties with Depth (0–40 cm)

How does the exchangeable Ca^{2+}/Na^{+} ratio change with depth, and what does that suggest about how cation exchange in water tracks may drive Ca^{2+} enrichment of pore-water solutions? In the lower reaches of Taylor Valley, the Lower-Valley Water Track site has the lowest exchangeable Ca^{2+}/Na^{+} ratios of our three depth profiles, and these ratios largely do not change with depth. However, the CEC values at the Lower-Valley Water Track are the highest of our three depth profiles (Figs. 9 and 10). The Lower-Valley Water Track is located close to the Ross Sea in the coastal thaw zone, and therefore experiences higher precipitation, warmer surface temperatures, and higher relative humidity than other sites in our study (Marchant and Head, 2007). The soils close to the Ross Sea are also dominated by fine-grained clays from the Ross Sea Drift, and their comparatively high fines content also may increase CEC (Schmidt and Levy, 2017). On its face, the consistently low exchangeable Ca^{2+}/Na^{+} ratios at the Lower-Valley Water Track for both wetted and dry soils suggests that cation exchange does not preferentially occur in water-track soils at this study site or at the proximal Mystery Channel site, based on similarly low on- and off-track exchangeable Ca^{2+}/Na^{+} ratios at both sites.

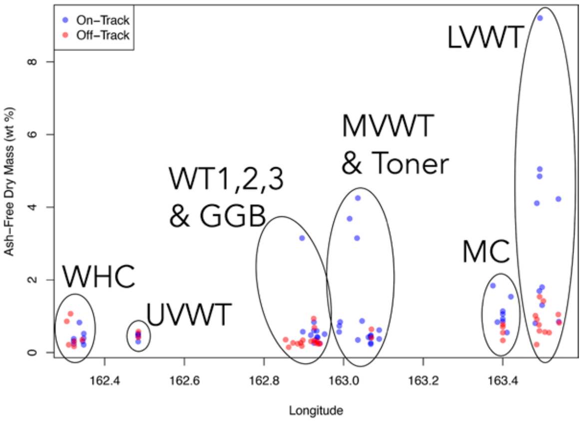

Figure 11. Organic matter as ash-free dry mass for on-track and off-track sampling sites in Taylor Valley, Antarctica. In general, organic matter is higher on-track than off-track and increases toward the east (toward the coast). GGB—Goldman Glacier Basin; LVWT—Lower-Valley Water Track; MC—Mystery Channel; MVWT—Mid-Valley Water Track; UVWT—Upper-Valley Water Track; WHC—Wormherder Creek; WT1—Water Track 1; WT2—Water Track 2; WT3—Water Track 3.

The low exchangeable Ca^{2+}/Na^{+} ratios at these warm, wet coastal sites could be the result of cation exchange reactions that have nearly gone to completion in both on- and off-track soils. Abundant and widespread soil moisture in the coastal thaw zone could allow cation-exchange reactions to occur across the near-surface environment during the fall freeze-up concentration of soil water droplets, regardless of hydrological position (on- or off-track), driving calcium off coastal thaw zone sediments and into brines that are lost to the subsurface (e.g., Toner and Sletten, 2013).

At the other extreme, samples from a depth profile in the up-valley, inland reach of Taylor Valley, at the Upper-Valley Water Track site, show the highest exchangeable Ca^{2+}/Na^{+} ratios and the lowest total CEC (Figs. 9 and 10). The Upper-Valley Water Track has a low exchangeable Ca^{2+}/Na^{+} ratio at the surface that increases at depth, which suggests that perhaps exchange of Ca^{2+} into seasonal brines does occur, but only in the warmest, wettest part of the soil column affected by a thin active layer. At depth, sediments may be too dry or too cold for exchange reactions to reliably occur, leaving calcium preferentially bound to exchange sites. The Upper-Valley Water Track is in the inland mixed climatic zone on a pole-facing slope, which experiences colder temperatures than other parts of the Taylor Valley (Marchant and Head, 2007). The interpretation that cation exchange is limited to the near-surface in the Upper-Valley Water Track is supported by the Piper diagram (Fig. 7), where samples from the Upper-Valley Water Track span both the bicarbonate and calcium chloride facies. The calcium chloride-dominant samples were collected closer to the surface (highlighted in the light blue box in Fig. 7) than the bicarbonate-dominant samples, which were collected from deeper in the soil column. Meltwater may not be penetrating deep into the subsurface at the Upper-Valley Water Track, causing a freeze-drying effect that limits the formation of Ca-Cl–rich brines except in the warmest and wettest part of the soil column.

We would then interpret the soil column in the central portion of Taylor Valley at the Mid-Valley Water Track site to reflect processes intermediate between the two extremes of the Lower-Valley Water Track and Upper-Valley Water Track. The Mid-Valley Water Track site has moderate exchangeable Ca^{2+}/Na^{+} ratios that vary with depth, as well as intermediate values of CEC between those of the Upper-Valley and Lower-Valley sites. In the Mid-Valley Water Track site profile, exchangeable Ca^{2+}/Na^{+} ratios are high at the surface (0 cm) and at the base of the soil column (40 cm) but reach a minimum on-track at ~20 cm depth, which suggests that preferential exchange could be occurring in the active layer in this water track. This aligns closely to the local minimum in exchangeable Ca^{2+}/Na^{+} ratio reported by Toner and Sletten (2013) in the active layer at their site at ~20 cm depth

TABLE 2. SOLUBLE SALT CONCENTRATION RANGES (IN MMOL KG^{-1}) FOR SOIL EXTRACTS FROM THIS STUDY AND TONER AND SLETTEN (2013)

Soluble salt ion	This study	Toner and Sletten (2013)
Ca^{2+}	0–60	0–3
Mg^{2+}	0–160	0–1.5
Na^{+}	0–490	0–12
K^{+}	0–130	0–1
Cl^{-}	0–440	0–12
SO_4^{2-}	0–80	0–0.5
NO_3^{-}	0–10	0–0.1
HCO_3^{-}	0–700	0–5

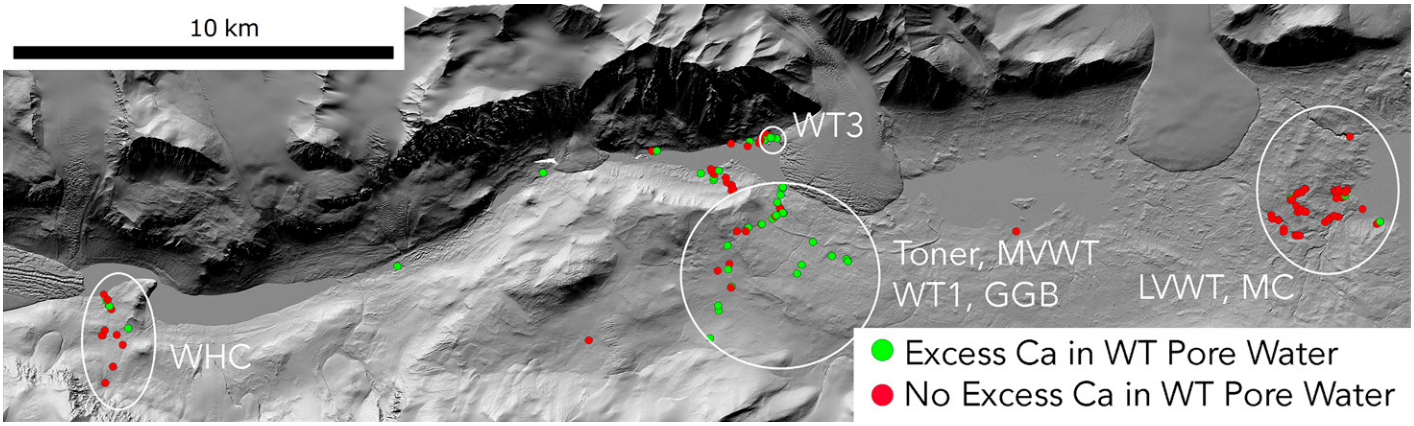

Figure 12. Water-track pore-water sampling sites in Antarctica showing evidence of excess calcium. Sample data are from Levy et al. (2023b). Sites where we see calcium enrichment in soluble salt extract data as well as potential evidence for on-track cation exchange reactions (e.g., Toner, Mid-Valley Water Track [MVWT], and Water Track 3 [WT3]) are the same locations where excess calcium in water-track pore waters is most common. GGB—Goldman Glacier Basin; LVWT—Lower-Valley Water Track; MC—Mystery Channel; WHC—Wormherder Creek; WT1—Water Track 1.

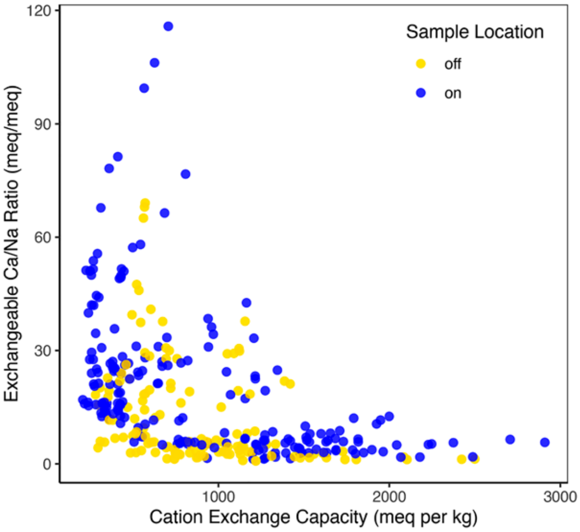

Figure 13. Cation exchange capacity (meq kg^{-1}) versus exchangeable Ca^{2+}/Na^{+} ratio (meq/meq). Soils with few exchange sites show the highest range of exchangeable Ca^{2+}/Na^{+} ratio.

(although the majority of that study focused on analyses of brines from the underlying ice-cemented soil down to 2 m depth).

Accordingly, we interpret the local minimum in exchangeable Ca^{2+}/Na^{+} ratio at 20 cm as evidence of the active exchange of calcium from exchange sites in the seasonally saturated portion of the active layer. This suggests the presence of an optimal depth at which there is enough brine to freeze concentrate while it is still wet enough from the late water-track summer thaw to avoid freeze-drying in autumn (Kuentz et al., 2022).

It is also important to note that the Mid-Valley Water Track sample site is within the same watershed and inland microclimate as the samples collected by Toner and Sletten (2013): the Howard Glacier/Crescent Stream watershed. It is possible that unique mineralogical properties or a unique source of meltwater in this watershed could explain why samples from our study and the Toner and Sletten (2013) project indicate Ca-enriching cation exchange reactions within the active layer in this portion of the valley. However, the observation that excess-calcium brines are flowing through water tracks in the vicinity of the Mid-Valley Water Track, the Toner and Sletten (2013) borehole site, and geographically proximal (but not hydrologically linked) water-track watersheds such as Water Track 1 and Water Track 3 (Fig. 12) suggests that this region may be experiencing optimum conditions for the generation of excess-calcium pore waters through cation exchange reactions in water-track and active wetland layers. The sites in the middle reaches of Taylor Valley experience warm enough and wet enough conditions (Fountain et al., 2014) for exchange reactions to occur in water tracks, and the sediments have undergone sufficient chemical weathering to generate abundant exchange sites (Fig. 10), but surface soils outside of water tracks are seasonally too dry (and/or too cold) for exchange reactions to remove calcium from exchange sites in off-track locations.

5.4. Is Organic Matter Influencing Cation Exchange in Water Tracks?

One possible explanation for why we do not detect a clear cation exchange signature in the form of lower exchangeable Ca^{2+}/Na^{+} ratios across all on-track surface soil samples (0–10 cm) could be the presence of organic matter. Organic matter bonds to smectite clays by Ca^{2+} and Al^{3+} cation bridges (Oades, 1989), which can cause calcium to preferentially remain bound to exchange sites and not enter the pore-water solution. In our samples, the Mid-Valley Water Track is the only site where we detect lower organic matter in on-track samples than in off-track samples. It is also one of the few sites where we observe the anticipated cation exchange signature (lower exchangeable Ca^{2+}/Na^{+} ratio) in on-track samples. In samples from Beacon, Goldman Glacier Basin, Lower-Valley Water Track, Upper-Valley Water Track, Wormherder Creek, and Water Track 1, we find the opposite pattern, in which there is higher organic matter and no cation exchange signature for on-track samples (i.e., the exchangeable Ca^{2+}/Na^{+} ratio remains high). We interpret this to suggest that organic matter may be inhibiting the exchange of calcium away from exchange sites in many on-track samples. Higher organic matter content causes calcium to remain bound at exchange sites, leading to a higher exchangeable Ca^{2+}/Na^{+} ratio. The Mid-Valley Water Track may show a clearer cation exchange signal owing to the low organic matter content at the profile site, which is insufficient to inhibit the exchange of calcium.

To determine the role of organic matter in more broadly shaping cation exchange in McMurdo Dry Valleys soils, we report two multiple linear regression models in which we fit the concentration of organic matter found in on-track and off-track samples to nine hydro-geochemical variables (water content by mass, electrical conductivity, exchangeable Ca^{2+}, exchangeable Mg^{2+}, exchangeable Na^{+}, exchangeable K^{+}, longitude, soluble Cl^{-}, and soluble PO_4^{-}). For on-track samples, organic matter negatively correlates with longitude; more organic matter is not necessarily found in on-track soils closer to the Ross Sea (Table 3). Instead, organic matter positively and strongly correlates with exchangeable Na^{+}, Ca^{2+}, and Mg^{2+} in on-track samples (Table 3). Likewise, organic matter content only marginally correlates with soil moisture content (gravimetric water content) in on-track soils, which suggests that once a soil moisture threshold has been surpassed within water-track soils, additional soil moisture does not lead to increased organic matter content. In contrast, the organic matter content of off-track sediments is dependent on the location in the valley (i.e., longitude) as well as soil moisture content (Table 4). There is a slight positive correlation with organic matter and exchangeable Ca^{2+} in off-track samples (Table 4). We interpret this multiple linear regression to indicate that for dry, off-track soils, even small additions of soil moisture to the sediment can have large impacts on primary productivity in the soil, which is moderated by valley-scale spatial patterns of surface temperature.

TABLE 3. MULTIPLE BEST-FIT LINEAR MODELS FOR ON-TRACK SAMPLES WHERE THE DEPENDENT VARIABLE IS ORGANIC MATTER

Variables	Estimate	Standard error	t value	P value	Significance
(Intercept)	3.85	1.14	3.38	2.15E-03	**
GWC	6.28E-07	3.30E-07	1.90	6.73E-02	.
EC	–1.01E-04	3.42E-05	–2.96	6.17E-03	**
Exchangeable Ca^{2+}	2.12E-03	6.06E-04	3.50	1.57E-03	**
Exchangeable Na^{+}	3.03E-02	3.49E-03	8.68	1.99E-09	***
Exchangeable K^{+}	–5.04E-03	4.35E-03	1.16	2.56E-01	
Exchangeable Mg^{2+}	–1.68E-02	5.41E-03	–3.11	4.25E-03	**
Longitude	–2.35E-02	6.97E-03	–3.37	2.19E-03	**
Soluble Cl^{-}	3.22E-04	1.25E-04	2.57	1.57E-02	*
Soluble PO_4^{-}	–3.20E-04	1.25E-04	–2.56	1.62E-02	*

Note: GWC—gravimetric water content; EC—electrical conductivity. Significance codes: ***—(0 to 0.001); **—(0.001 to 0.01); *—(0.01 to 0.05), .—(0.1 to 1). Multiple $R^2 = 0.94$.

TABLE 4. MULTIPLE BEST-FIT LINEAR MODELS FOR OFF-TRACK SAMPLES WHERE THE DEPENDENT VARIABLE IS ORGANIC MATTER

Variables	Estimate	Standard error	t value	P value	Significance
(Intercept)	–7.24E-01	2.24E-01	–3.23	7.20E-03	**
GWX	1.73E-07	7.92E-08	2.19	4.93E-02	*
EC	1.87E-06	8.83E-07	2.12	5.56E-02	.
Exchangeable Ca^{2+}	2.82E-04	1.09E-04	2.58	2.39E-02	*
Exchangeable Na^{+}	–1.18E-03	1.02E-03	–1.16	2.70E-01	
Exchangeable K^{+}	2.15E-03	2.52E-03	0.85	4.11E-01	
Exchangeable Mg^{2+}	4.32E-03	4.84E-03	0.89	3.90E-01	
Longitude	4.45E-03	1.37E-03	3.24	7.06E-03	**
Soluble Cl^{-}	–2.29E-05	5.48E-05	–0.42	6.83E-01	
Soluble PO_4^{-}	2.30E-05	5.48E-05	0.42	6.82E-01	

Note: GWC—gravimetric water content; EC—electrical conductivity. Significance codes: ***—(0, 0.001); **—(0.001, 0.01); *—(0.01, 0.05); .—(0.1,1). Multiple $R^2 = 0.9601$.

These multiple linear regression models produce R^2 values of 0.94 for the on-track organic matter measurements and 0.96 for the off-track values.

As may be expected, organic matter seems to increase the number of cation exchange sites in McMurdo Dry Valleys soils, particularly in on-track samples, in which organic matter is commonly more abundant. In both on- and off-track soils, total cation exchange capacity is positively correlated with organic matter content. For off-track soils, longitude—position in the valley—is the most significant predictor of organic matter content, with organic matter content increasing with proximity to the coast. These differences between on- and off-track soils suggest that both organic matter formation and cation exchange reactions are governed by hydrological position (soil location on or off a water track) overlain on regional soil moisture and temperature gradients.

5.5. Could Other Water/Rock Reactions Be Modifying Groundwater Chemistry?

Laboratory studies of clay-brine interactions (e.g., Wilson and Bish, 2011) and reactions between clays and vapor-derived soil films (e.g., Geyer et al., 2023) showed that insoluble calcium sulfate phases can rapidly form due to cation exchange reactions when sulfate is present in the soil matrix. These reactions remove sulfate and calcium from soil brines, increase solution chloride content, and decrease the freezing point of the brine, while also removing calcium from exchange sites. Could such reactions also be occurring in water tracks or in McMurdo Dry Valleys off-track soils?

Calcium-sulfate–generating exchange reactions occur in McMurdo Dry Valleys soils owing to the presence of abundant near-surface sulfate from marine and atmospheric aerosol deposition (Bao and Marchant, 2006), the presence of clays in the glacial soils, and the regular presence of intergranular soil brines that form during episodes of relative humidity (e.g., Levy, 2021; Deutsch et al., 2022). However, two lines of evidence argue against the widespread generation of insoluble calcium sulfates in water-track soils. First, while water-track solutions are commonly chloride-rich—consistent with depletion of soluble sulfate by precipitation—they are also commonly enriched in calcium, to the point of showing calcium excess, where calcium exceeds soluble bicarbonate and sulfate (e.g., Levy et al., 2011; Toner and Sletten, 2013). This suggests that exchanged calcium is not being consumed by sulfate precipitation in water-track and permafrost groundwater solutions. Second, where water-track silt and clay fraction mineralogical measurements exist (e.g., Levy et al., 2014), the water-track fine fraction does not show volumetrically abundant gypsum or other calcium sulfates. Instead, illite, smectite, chlorite, aragonite, calcite, sepiolite, talc, and vermiculite dominate the fines fraction of these soils.

However, exchange reactions between clays and vapor-derived soil brines do pose an intriguing explanation for the depletion of exchangeable calcium in near-surface, off-track soils (Fig. 8). Removal of calcium from off-track exchange sites by exchange reactions facilitated by episodic soil brine presence, and the delivery of exchanged calcium to largely immobile, insoluble, surface sulfate grains could help explain the depletion of calcium on these otherwise dry soil exchange sites, while also not contributing calcium-depleted fluids to McMurdo Dry Valleys groundwater systems. More detailed examinations of off-track silt and clay mineral composition could help evaluate this mechanism for exchange reactions in dry soils.

5.6. Cation Exchange Signatures as a Possible Hydroclimate Marker in the Cold Desert

Our initial hypothesis was that the seasonal presence of soil moisture in water tracks would produce low exchangeable Ca^{2+}/Na^{+} ratios in wetted soils, as calcium was exchanged away to form excess-calcium soil brines, while adjacent, off-track (dry) soils would preserve calcium bound at exchange sites, producing a higher exchangeable Ca^{2+}/Na^{+} ratio. As the preceding discussion shows, this is not universally the case across the McMurdo Dry Valleys. Instead, we suggest that exchangeable Ca^{2+}/Na^{+} ratios, coupled with soil CEC values, reveal a regional hydroclimatic gradient in which McMurdo Dry Valleys microclimate is recorded in soil properties, and in which water-track hydrological position is most important for soils at the hydroclimatic boundary between warm and wet soils and cold and dry soils.

Geological and hydroclimatic gradients are well-described in the McMurdo Dry Valleys. Glacial till soils increase in age from Holocene at the coast (Stuiver et al., 1981; Hall and Denton, 2000), through a series of increasingly old Quaternary tills up-valley and inland (Hendy et al., 1979; Higgins et al., 2000), to the oldest soils in the McMurdo Dry Valleys, which are Miocene in age (Sugden et al., 1995; Fig. 14). The young coastal tills are silt- and clay-rich, with fines content decreasing in older tills up-valley and inland (Schmidt and Levy, 2017). Likewise, microclimatic conditions become colder and drier with distance from the coast (Doran et al., 2002; Fountain et al., 2014).

These regional factors provide a framework for interpreting the exchangeable Ca^{2+}/Na^{+} ratios and CEC measurements determined in this study. Generally, the cation exchange capacity of McMurdo Dry Valleys soils increases from west to east, with higher CEC closer to the coast, in younger, warmer, and wetter sediments (Fig. 14). Exchangeable Ca^{2+}/Na^{+} ratios decrease from west to east, with higher values inland, intermediate values near the Mid-Valley Water Track site, Toner and Sletten's (2013) borehole, etc., and low values at coastal sites (Fig. 14). One possible interpretation of this regional trend is that exchangeable Ca^{2+}/Na^{+} ratios are low in coastal settings for both on- and off-track soils because relatively abundant soil moisture from snowfall and summertime melting permitted cation exchange reactions to remove calcium nearly completely from these exchange sites. Coupled with abundant pore-water sodium from sea spray, these sites may represent a warm and wet endmember of cold desert cation exchange chemistry. In contrast, inland sites may be largely too cold, with insufficient soil moisture (e.g., abundant dry permafrost; Bockheim et al., 2007; McKay, 2009), to permit regular pore water–grain interactions. These sites could preserve high exchangeable Ca^{2+}/Na^{+} ratios if little to no moisture is available to form intergranular brines that could drive calcium-depleting exchange reactions. We interpret the high calcium content of the Upper-Valley Water Track and Wormherder Creek to potentially reflect access to calcium from paleo-

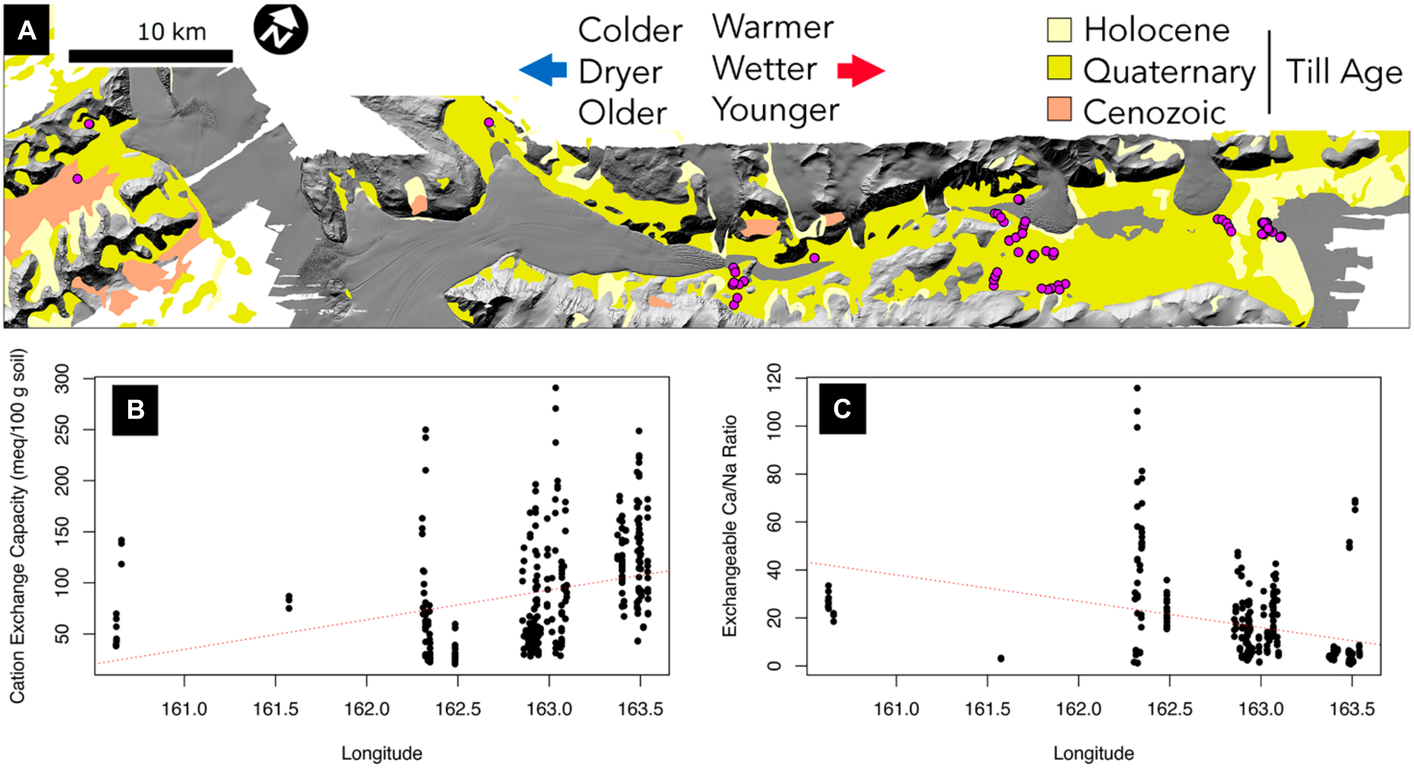

Figure 14. Conceptual summary of cation exchange processes as a hydroclimate marker in cold desert environments. (A) Regional map showing soil sample locations (purple dots) across the McMurdo Dry Valleys, Antarctica. Surface soils (tills) increase in age from east to west, while climatic conditions are warmer and wetter toward the east and colder and dryer inland toward the west (Fountain et al., 2014). Map data are courtesy of Cox et al. (2023). (B) Cation exchange capacity of soils increases from west to east across sample sites (linear model P << 0.01). (C) Exchangeable Ca^{2+}/Na^{+} ratio in sediment samples decreases from west to east, with higher values inland, intermediate values near Mid-Valley Water Track (MVWT), and low values at coastal sites (linear model P << 0.01).

fjord conditions in the McMurdo Dry Valleys, which allows access to ancient marine calcium. This is not possible for extreme inland sites (e.g., Beacon Valley), which in turn have high, but comparatively lower, exchangeable Ca^{2+}/Na^{+} ratios (Fig. 14). Finally, these cold and dry inland sites may experience too low an intensity of chemical weathering to generate clays and/or too little organic matter enrichment to generate large numbers of exchange sites and have low CEC as a result.

How do intermediate sites fit into this regional interpretation? The Mid-Valley Water Track, Toner, and Water Track 3 were the only sites where on-track samples showed the expected low exchangeable Ca^{2+}/Na^{+} ratios and off-track sites showed the expected high exchangeable Ca^{2+}/Na^{+} ratios; Water Track 1 and Goldman Glacier Basin also showed some evidence for calcium enrichment in soluble soil salts. These sampling sites span the main regions of Taylor Valley, in which excess-calcium pore waters were directly measured (Fig. 12). Together, this suggests that at these centrally located sampling sites, active, seasonal cation exchange reactions like those described by Toner and Sletten (2013) presently occur in water tracks. Regularly wetted soils, like those at depth in the Mid-Valley Water Track, are at an optimal hydroclimatic and geological position for brine concentration during winter freeze-up to promote calcium removal from exchange sites, allowing calcium to enter pore waters and create the directly sampled excess-calcium brines. These intermediate microclimatic sites are wet enough on-track that exchange reactions can occur, but not so wet that the reactions can occur regularly in off-track soils.

Taken together, the spatial trends in cation-exchange capacity, soil moisture, and organic matter content may suggest that water tracks and seasonal wetlands are sites of enhanced soil development in the Antarctic polar desert. It is notable that indicators of biogeochemical activity in glacial sediments all increase from the cold, dry inland portion of Taylor Valley toward the warmer, wetter coast, including cation-exchange capacity, fines content, organic matter content, and the spatial density of water tracks. Together, this suggests that water tracks and seasonal wetlands may be sites of a positive feedback loop in soil development, and that enhanced soil moisture for extended periods of the Antarctic summer melt season leads to enhanced chemical weathering of soils to generate clays with enhanced growth of soil organic matter. Enrichments in soil organic matter and fine-grained sediments, accompanied by enhanced soil pore-water solute concentrations from weathering reactions and dissolution of soil salts, may lead to increased resistance to active-layer freezing, extending the water-track thaw period. If so, water tracks and seasonal wetlands may serve as a model for how Antarctic permafrost will participate in biogeochemical cycling during periods of future thaw if wet active layers expand in the Antarctic desert.

5.7. Planetary Implications

Water tracks were proposed as a groundwater analog for recurring slope lineae (RSL) sites on Mars (McEwen et al., 2011; Levy, 2012; Stillman et al., 2014). Similar to water tracks, RSL are seasonal, dark albedo features that lengthen downslope during the warm season and fade during the cold season (McEwen et al., 2011). There are both "wet" models (Grimm et al., 2014; Huber et al., 2020) and dry models (Schmidt et al., 2017; Dundas et al., 2017, p. 201) for RSL formation; wet models rely on liquid water or intergranular brines in the formation of RSL features, whereas dry models do not involve liquid water or brines. A third possibility for RSL formation is that they are related to subsurface soil salts that undergo hydration and/or deliquescence, but not modern flow of liquid water (Gough et al., 2011; Wang et al., 2019).

Exchangeable cation ratios may be a tool for evaluating the past presence of soil brines at martian RSL sites, even if those soils are not currently wetted today, as exchangeable cation ratios would likely be preserved in the modern dry climate. Importantly, our observations highlight the importance of sampling at depth throughout the soil column. Samples from the Mid-Valley Water Track and Water Track 3, which are the largest and saltiest water tracks in our sample set, show some evidence of Ca-Na cation exchange at the surface but most clearly at depths near $\sim$20 cm. The depletion of calcium on exchange sites is not necessarily widespread on water tracks in the upper 5–10 cm of the soil column but does become apparent at hydroclimatically optimum sites such as the Mid-Valley Water Track. This suggests that future efforts to sample RSL to look for signatures of past brine flow should consider sampling at depth, not just from surface-sediments, where the albedo change is observable from orbital imagers. Surface solutions may not be persistent enough or long-lived enough, or salty enough, or the soils rich enough in fine sediments, to support clear evidence of Ca^{2+}-Na^{+} exchange. Evidence of past active-layer porewater flow may only become more apparent deeper in the putative martian active layer.

6. CONCLUSIONS

We hypothesized that cation exchange signatures (lower exchangeable Ca^{2+}/Na^{+} ratios) would be evident in wetted and saline water-track soil samples, and that cation exchange signatures would not be evident in dry off-track samples (with higher exchangeable Ca^{2+}/Na^{+} ratios). We found that cation exchange signatures are present in wetted and concentrated on-track samples in the Mid-Valley Water Track, Toner, and Water Track 3, and that evidence of the removal of bound calcium to generate excess-calcium pore waters is most apparent at the Mid-Valley Water Track at a depth of 20 cm. In contrast, coastal soils were found to have universally lower exchangeable Ca^{2+}/Na^{+} ratios, and inland soils were found to have universally higher exchangeable Ca^{2+}/Na^{+} ratios. This suggests that the Toner and Sletten (2013) model for cation exchange as a mechanism for generating Ca-Cl–rich brines is active across the McMurdo Dry Valleys and is moderated by both hydrological position (on/off water track) and regional microclimate. Soils from warm, wet coastal regions may have had calcium removed from exchange sites due to exchange reactions occurring in seasonally wetted soils, whereas up-valley soils preserve high exchangeable Ca^{2+}/Na^{+} ratios due to low soil moisture and low temperatures inhibiting exchange. Middle-valley water tracks show evidence of sodium-for-calcium exchange and are spatially proximal to active locations of excess-calcium brine flow, which suggests that in these climatically intermediate soils, hydrological position determines whether exchange reactions will or will not occur. We suggest that the cation exchange signature could serve as a tool for providing evidence of past brine flow in other cold deserts, including those on Mars.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation award OPP-1847067 to J.S. Levy. We thank the Colgate Martians undergraduate soil processing team, Aidan Guller, and M.C. Rapoza for assistance in sample preparation, and Bill Rice for development of the Piper plotting R scripts used in this project and available at https://wcrice.github.io/2019-07-23-Piper-Diagram/. J.T.E. Johnson is supported by the Intramural Research Program of the National Institute on Aging. Publication support provided in part by the Colgate University Research Council.

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Science Editor: Brad Singer
Associate Editor: Shasta Marrero

Manuscript Received 21 July 2023
Revised Manuscript Received 7 December 2023
Manuscript Accepted 8 January 2024