

# Patterns and processes of salt efflorescences in the McMurdo region, Antarctica

K. M. Bisson<sup>1,2,5</sup>

K. A. Welch<sup>1,2</sup>

S. A. Welch<sup>1</sup>

J. M. Sheets<sup>1</sup>

W. B. Lyons<sup>1,2</sup>

J. S. Levy<sup>3</sup> and

A. G. Fountain<sup>4</sup>

<sup>1</sup>School of Earth Sciences, Ohio State University, 125 South Oval Mall, Columbus, Ohio 43210, U.S.A.

<sup>2</sup>Byrd Polar Research Center, Ohio State University, 1090 Carmack Road, Columbus, Ohio 43210, U.S.A.

<sup>3</sup>Institute for Geophysics, University of Texas at Austin, 10100 Burnet Road, Austin, Texas 78758-4445, U.S.A.

<sup>4</sup>Department of Geology, Portland State University, P.O. Box 751, Portland, Oregon 97207-0751, U.S.A.

<sup>5</sup>Corresponding author:

kelsey.bisson@lifesci.ucsb.edu

## Abstract

Evaporite salts are abundant around the McMurdo region, Antarctica (~78°S) due to very low precipitation, low relative humidity, and limited overland flow. Hygroscopic salts in the McMurdo Dry Valleys (MDVs) are preferentially formed in locations where liquid water is present in the austral summer, including along ephemeral streams, ice-covered lake boundaries, or shallow groundwater tracks. In this study, we collected salts from the Miers, Garwood, and Taylor Valleys on the Antarctic continent, as well as around McMurdo Station on Ross Island in close proximity to water sources with the goal of understanding salt geochemistry in relationship to the hydrology of the area. Halite is ubiquitous; sodium is the major cation (ranging from 70%–90% of cations by meq kg<sup>-1</sup> sediment) and chloride is the major anion (>50%) in nearly all samples. However, a wide variety of salt phases and morphologies are tentatively identified through scanning electron microscopy (SEM) and X-ray diffraction (XRD) work. We present new data that identifies trona (Na<sub>3</sub>(CO<sub>3</sub>)(HCO<sub>3</sub>)·2H<sub>2</sub>O), tentative gaylussite (Na<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O), and tentative glauberite (Na<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>) in the MDV, of which the later one has not been documented previously. Our work allows for the evaluation of processes that influence brine evolution on a local scale, consequently informing assumptions underlying large-scale processes (such as paleoclimate) in the MDV. Hydrological modeling conducted in FREZCHEM and PHREEQC suggests that a model based on aerosol deposition alone in low elevations on the valley floor inadequately characterizes salt distributions found on the surfaces of the soil because it does not account for other hydrologic inputs/outputs. Implications for the salt distributions include their use as tracers for paleolake levels, geochemical tracers of ephemeral water tracks or “wet patches” in the soil, indicators of chemical weathering products, and potential delineators of ecological communities.

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## Introduction

Antarctica is a land of extremes as Earth's coldest and driest continent, favoring the accumulation of salts. Quantifying salt geochemistry elucidates both regional accumulation patterns and local redistribution processes within Antarctic soils, allowing for the assessment of inorganic salts as a geochemical link in the coupled hydrological-ecological Antarctic landscape. Here, we provide a rigorous examination of the chemical variability observed within a few kilometers in the McMurdo Dry Valleys (MDVs), and we employ specialized SEM analysis to detect a wide variety of salt compositions and morphologies on a micron scale to uncover salt diversity in the McMurdo region.

In this study, we collected visible surface salt samples with the goal of mechanistically understanding salt formation in terms of the general hydrology of the area. Dominant controls on chemical composition include marine aerosol input, snow sublimation, wicking of water around lake and stream boundaries, and chemical weathering (Keys and Williams, 1981; Claridge and Campbell, 1977; Gore et al., 1996; Bockheim, 1997). Other factors such as landscape age, the solubilization of remnant salts from paleolake desiccation (Bao et al., 2008; Toner et al., 2013), rapid changes in relative humidity that affect the salt deliquescence, and cation exchange reactions (Toner and Sletten, 2013) can be geochemically influential.

This investigation builds on earlier studies conducted in the late 1970s (Nishiyama and Kurasawa, 1975; Claridge and Camp-

bell, 1977; Keys and Williams, 1981) to further describe the distribution of salts as well as the key variables that control their formation (see Table 1 for typical MDV salts). It is hypothesized that salts on Ross Island, which is volcanic, will be dominated by weathering products because previous work identified chemical weathering as a present-day process (Gibson et al., 1983). In the MDVs, it is hypothesized that salts closer to the Ross Sea will show a greater marine aerosol influence with higher sodium, sulfate, and chloride content. Finally, we hypothesize that salts can be modeled as evaporitic products of their source waters because we expect them to be geochemically similar to the lakes and streams near which they are collected.

## Geological Setting

The MDVs compose the largest ice-free area (4500 km<sup>2</sup>) in Antarctica (Figs. 1, 2, and 3) (Levy, 2012) and comprise a mosaic of soils, glaciers, ephemeral streams, ice-covered lakes, and exposed bedrock (Fountain et al., 1999). In the areas near McMurdo Station and Scott Base, few natural undisturbed surfaces remain as a result of human occupation since the establishment of the base in the late 1950s.

The MDVs are a region marked by polar climatic conditions, and annual temperature cycles represent a large contrast because during the summer there are 24 hours of daylight and winter receives none. Large variations in surface albedo in the coastal thaw zone cre-

TABLE 1

A list of 10 common salts found in Antarctica (Keys and Williams, 1981), with indications of their presence in our study. We did not identify any nitrate salts, nor have we identified antarctite, likely due to our constrained spatial extent.

| Salt name   | Formula                                                         | Observed in study? |
|-------------|-----------------------------------------------------------------|--------------------|
| Thenardite  | $\text{Na}_2\text{SO}_4$                                        | X                  |
| Gypsum      | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$                       | X                  |
| Halite      | $\text{NaCl}$                                                   | X                  |
| Calcite     | $\text{CaCO}_3$                                                 | X                  |
| Darapskite  | $\text{Na}_3\text{NO}_3\text{SO}_4\text{H}_2\text{O}$           |                    |
| Soda niter  | $\text{NaNO}_3$                                                 |                    |
| Mirabilite  | $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$             | X                  |
| Bloedite    | $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ |                    |
| Epsomite    | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$                       |                    |
| Hexahydrite | $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$                       |                    |

ate considerable variation in subsurface and surface ground temperatures (Doran et al., 2002). Summer air temperatures average  $-5^\circ\text{C}$ , and relative humidity averages 64% (Doran et al., 2002). In the MDV region, katabatic winds with low relative humidity ( $\leq 45\%$ ) descend from the polar plateau from the west onto the valleys to converge with high relative humidity (75%) marine-generated winds from the east (Bull, 1966; Marchant and Denton, 1996). The varied relative humidities converge and possibly promote either rehydration or precipitation, subsequently affecting the geochemical soil environment.

In addition, high sublimation and evaporation rates (Gooseff et al., 2002) coupled with low precipitation rates (3 cm water equivalent  $\text{yr}^{-1}$ , Fountain et al., 2010) lead to desiccation of the soils over long scales of time and space, particularly in areas that do not receive any other hydrological inputs. The soils are frozen but lack sufficient interstitial moisture for cementation, resulting in a layer of dry soil overlying ice-cemented soils. Consequently, soils are susceptible to leaching with small additions of water from the wicking of water at stream edges, melting permafrost, upwelling groundwater, or “wet patches” (Levy et al., 2012).

Though little liquid water is present in the MDVs, chemical weathering is apparent in the discoloration (oxidation) of exposed rock surfaces and is more extensive in the hyporheic zones (wetted areas alongside and beneath streambed) of the streams (Gooseff et al., 2002), which can be enhanced by the warm surface temperatures in the summer (up to  $15^\circ\text{C}$ ). For 6–12 weeks in the austral summer, water flows from the glaciers through defined, permanent stream channels on its way to the lakes (McKnight et al., 1999), the majority of which are closed-basin with no outflows. This glacial melt is the primary source of liquid water to the lakes and streams (Fountain et al., 1999). These streams often have salt crusts on the landward edges of the streams on the wetted margins surrounding the streambed where water is exchanged through the nearby sediments in hyporheic zones.

The precipitation of salts in this desert environment is directly related to the seasonal variation in hydrology and water flow path in these soils. Because only visible surface salts were sampled (Fig. 4), they reflect the sequential nature of evaporating ground water as it percolates through the soils (Levy et al., 2012), preferentially precipitating the most soluble salts last. As water moves slowly down gradient, the least soluble salts are lost from the water first, creating a “chromatography” effect, first described by Wilson (1979). While evaporation or sublimation occurs, the ion activity product of any potential salt can exceed its solubility product and the salt precipitates. In the

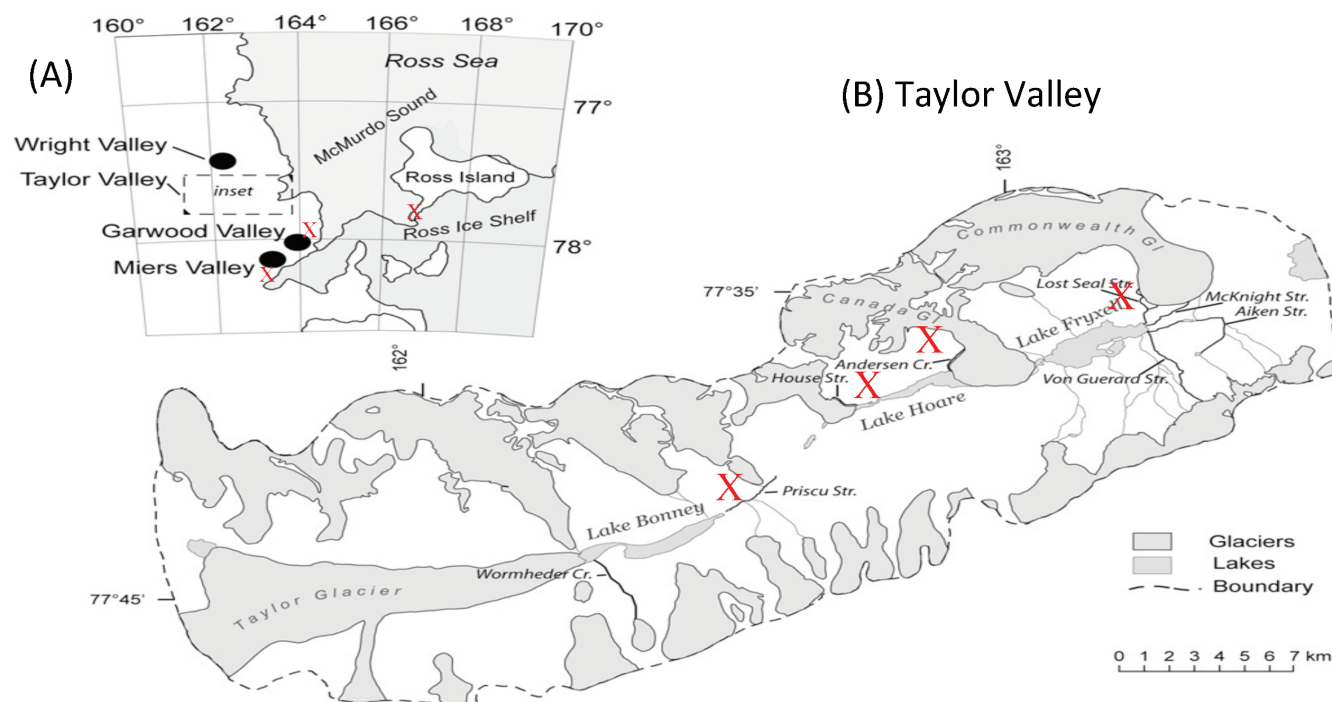
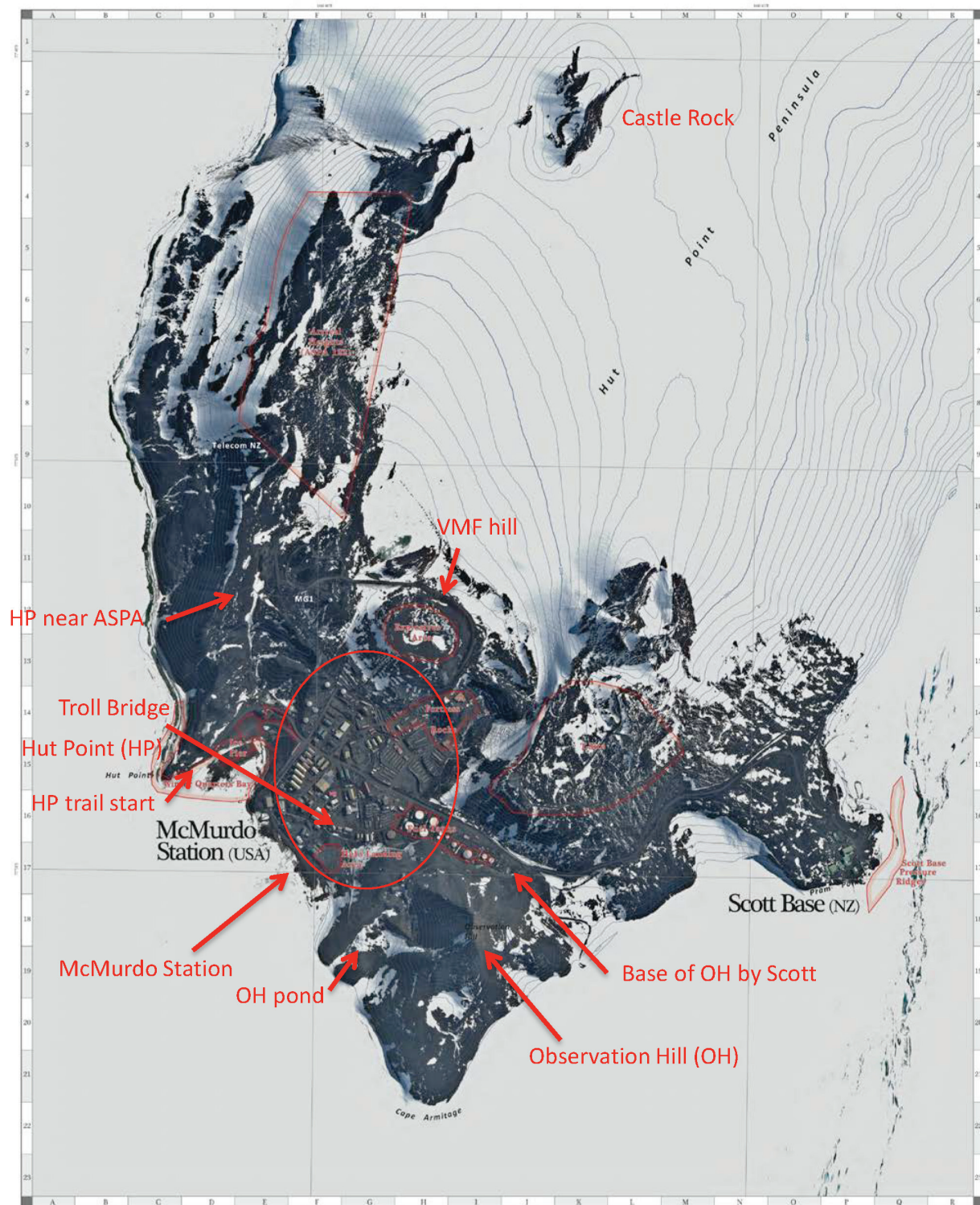


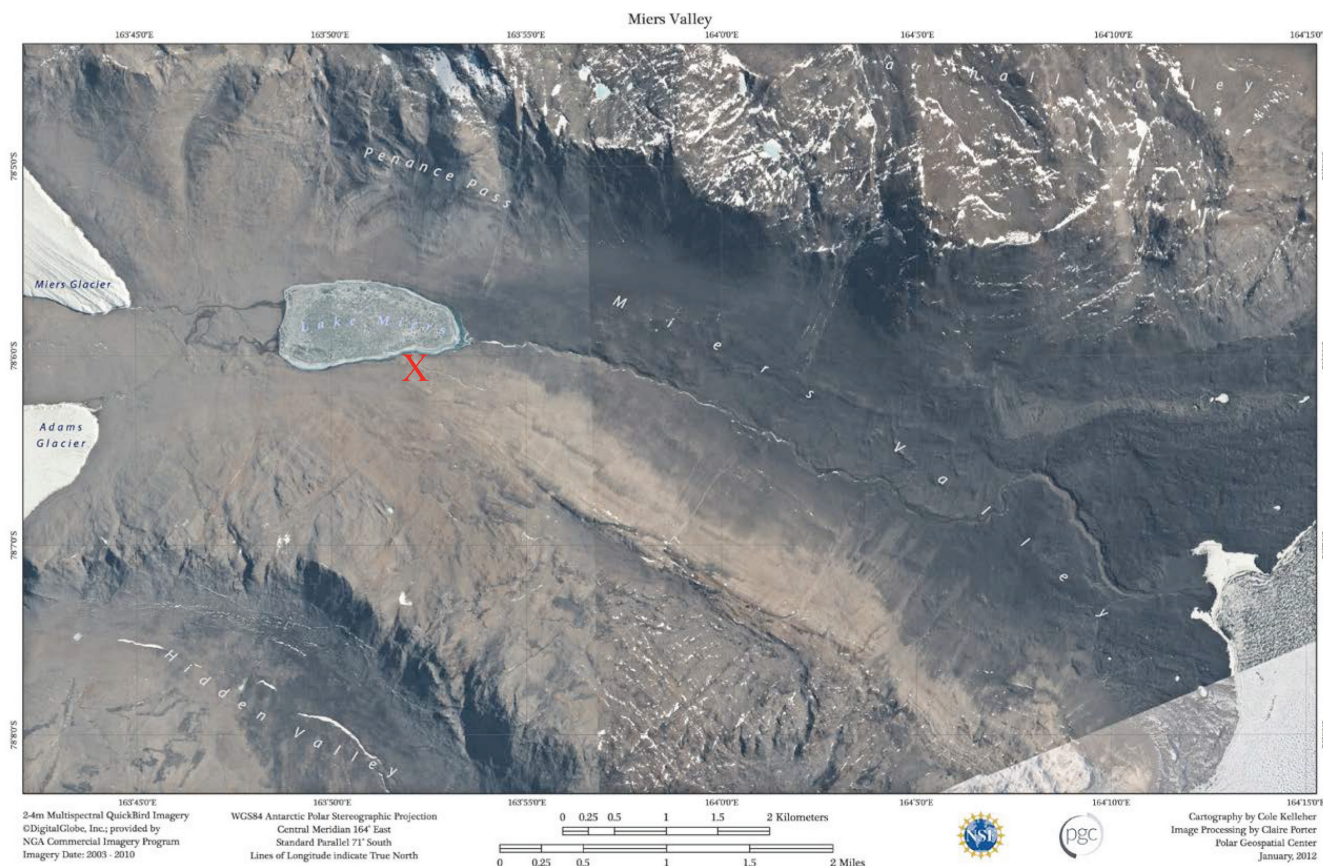
FIGURE 1. (A) Map of sampling area, including Ross Island (site of McMurdo Station), Taylor, Garwood, and Miers Valleys. (B) An enlarged map of Taylor Valley shows Fryxell, Hoare, and Bonney basins with associated inflowing streams. New Harbor is on the far eastern boundary of Taylor Valley. “X” indicates approximate sampling location.



**FIGURE 2.** An enlarged map of Ross Island shows McMurdo Station, Scott Base, and surrounding points of interest. Specific sampling locations from this study are highlighted in red, with building location markers omitted for simplicity.

MDV, water produced by melting ice and snow percolates, dissolving the more soluble salts and leaving the least soluble salts behind (as in Castle Rock salts). Alternatively, if subsurface water (from buried ice or permafrost) is “wicked” up through capillary action (as in Taylor Valley stream and lake samples), the more soluble salts are carried to the soil surface leaving the less soluble at depth. Therefore, the salt dis-

tribution at any one location may reflect local sources of water, notably observed in the Miers Lake salt that is high in  $\text{HCO}_3^-$ . Salts produced from “water tracks” and wet patches (Levy et al., 2012) as opposed to those formed at the edge of streams or lakes exhibit greater chemical variety, which is attributed to these source differences. Depending on the initial amount of water, its direction of flow or source, and the per-



**FIGURE 3.** An enlarged map of Miers Valley shows the approximate sampling location where the most obvious visible salt crust was identified and sampled for analysis.

meability and porosity of the soil (in past determined by grain size), a wide variety of salts could be formed on the surface. We speculate that this process could be very important in salt crust formation because depending on the flow path, the surface crusts could be either the most soluble or least soluble salts in the initial solutions. In addition, if these surfaces are rewetted, only the most soluble salts are redissolved (as originally described by Drever and Smith, 1978), thereby further separating the ions. This phenomenon has been observed previously in Antarctic flow-through ponds (Lyons et al., 2012).

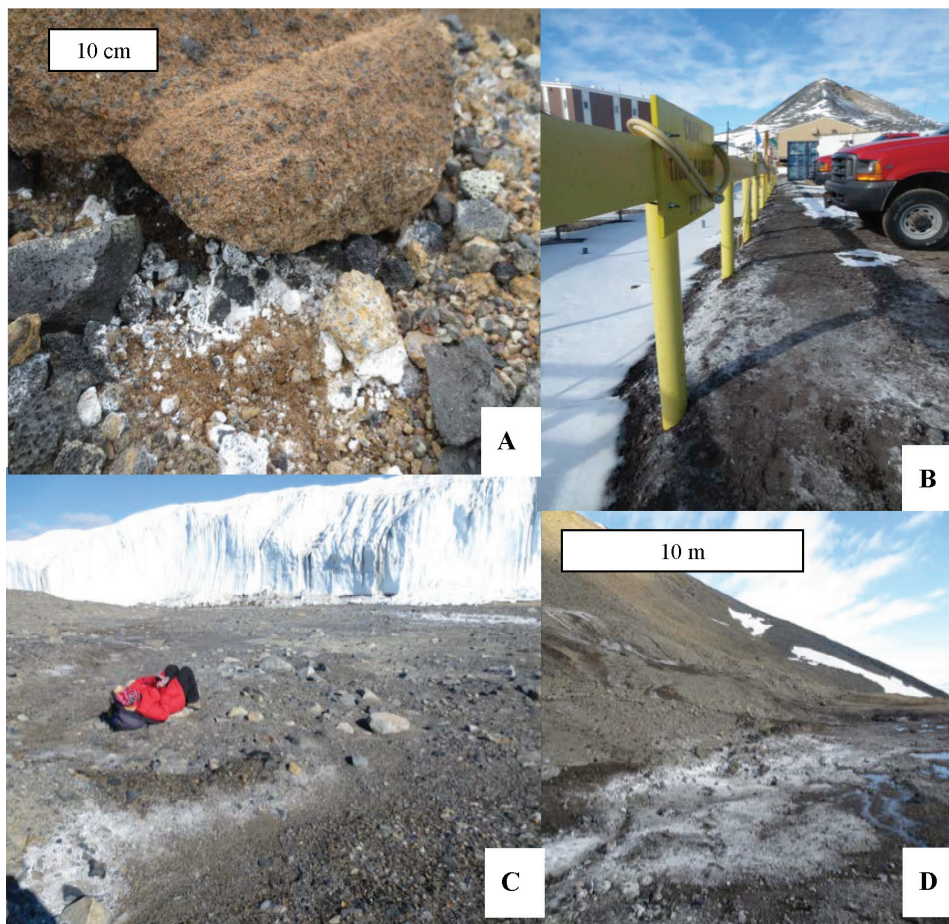
## Experimental Method

Our sampling took place in January and February 2013, and we added samples that were collected from the previous field season by colleagues, taking care to keep a consistent sampling protocol. Salts were selected to represent a large spatial extent over the MDV and McMurdo Station landscape. Coastal and relatively inland salts were sampled, and high elevation salts were collected when present. In this way, the authors feel the sampling is relatively free of methodological bias. The top ~2 cm of each salt crust with underlying soil was collected with a plastic scoop and placed into a 2 oz Whirl-Pak™ bag to be stored at Crary Lab in McMurdo Station at room temperature until analysis (Fig. 4 shows some typical salt efflorescences). Samples were not refrigerated prior to analysis because thermally unstable salts would be destroyed naturally during warm summers. Twenty-four salt samples were collected during the 2012–2013 field season and 18 additional samples from the 2011–2012 season (collected by our colleagues) were added for a total of 42 samples. Using structural and

textural criteria, two types of salt crusts are distinguished: (1) widespread surface crusts with little structure and (2) thicker salt crusts with amorphous shapes that form near boulders.

Total salt content of the crusts was determined by dissolution. A subsample of approximately 10 g of sediment containing salt crusts was weighed and placed into a liter of 18.2 MΩ deionized water, where it was stirred and then let to sit for 30 minutes at room temperature (~20 °C). Preliminary analyses showed that the dissolved ion concentrations did not significantly change after sitting longer than 30 minutes in solution. In a similar study, Toner et al. (2013) demonstrated that gypsum and calcite dissolve more completely after a 1:25 soil to water dissolution. The ratio used for our experiments was effectively 1:100, which should be sufficient for the dissolution of most salt phases considered in this study but did not likely completely dissolve all of the gypsum and calcite. Data were normalized to milliequivalents per kilogram of pre-extraction sample (soil + salt) to facilitate comparison between samples.

Solution aliquots were collected and filtered prior to analysis from each sample using Whatman Puradisc polyethersulfone syringe filters (25 mm, 0.45 μm). Major cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and anions ( $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) were analyzed using a Dionex DX-120 ion chromatograph (IC) with an AS40 automated autosampler as described by Welch et al. (2010). At the beginning of each run, seven incrementally increasing standards were measured to construct a calibration curve from which sample concentrations were later calculated. After every ten sample runs, a verification standard and duplicate sample were analyzed to determine precision while accounting for any instrument drift. Alkalinity ( $\text{HCO}_3^-$ ) was calculated through charge balance according to the following:



**FIGURE 4.** Various photos selected to show sample site variability. (A) Base of Castle Rock, west side by approach. Salts form underside of rock face (heat island effect). (B) Crary Lab Truck Area. Salt forms near areas of high human traffic and activity. (C) Salts form alongside Green Creek, within its hyporheic zone. (D) Widespread salts on western side of Observation Hill, roughly 30 m from Ross Sea.

$$\text{HCO}_3^- (\text{meq kg}^{-1} \text{ soil}) = \sum \text{cations} (\text{meq kg}^{-1} \text{ soil}) - \sum \text{anions} (\text{meq kg}^{-1} \text{ soil}). \quad (1)$$

The average error between calculated and measured alkalinity values in over 900 Dry Valley stream samples from multiple summer seasons has been calculated to be  $\pm 14\%$ , and this is the best estimate for the precision of alkalinity determined from this charge balance method (Lyons et al., 2012).

Because the leaching experiments only yield bulk salt composition, selected samples with high salt concentrations were characterized by SEM and XRD to further elucidate chemical and mineralogical compositions of individual phases. Of the 42 samples that were analyzed for major ions, 15 were selected for SEM using an FEI Quanta FEG 250 SEM equipped with a Bruker X-Flash 5030 energy dispersive X-ray spectrometer for imaging. Analysis conditions of 15 keV accelerating voltage and 13 mm working distance allowed for suitable conditions for chemical analysis. Salt crusts were scraped off the soils with sterile dental tools, placed on carbon tape adhered to aluminum sample stubs, and finally coated with gold/palladium. SEM imaging of the salts was conducted using both secondary electrons (Everhart-Thornley detector ETD) and backscattered electron detectors (BSE) to identify salts that were not apparent from the bulk leach analysis. Energy dispersive X-ray spectroscopy (EDS) was used to determine qualitative chemical information from individual phases, and ultimately to inform the bulk ion analysis by correlating chemical composition and crystal habit. In this way, minerals not apparent from the salt leach or detected by the XRD could be identified. Elemental

mapping was used to highlight specific assemblages, making various salts apparent in the image (as seen later in Fig. 9, part C).

Assessments of crystalline salt phases (in the past determined by XRD) have resolved only the dominant salt species. Following SEM analysis, selected salt samples with complex chemistries were analyzed using a PANalytical X'Pert Pro X-ray Diffractometer equipped with X'pert High Score Plus software and PDF 4+ database. Samples for XRD were prepared by scraping in a similar manner as for the SEM samples; grains were secured on carbon tape and mounted on a glass slide. XRD scans were acquired with a step size of 0.02-degree 2-theta, and a counting time of 4 seconds per step.

Selected carbon-rich salt samples were analyzed for  $\delta^{13}\text{C}$  in the carbonate fraction of the salts using a Picarro cavity ring-down spectrometer (CRDS) Carbon Isotopic analyzer (G1111-i) equipped with an Automated Autoprep device. Several milligrams of salt samples were placed in capped autosampler vials, and they were treated with phosphoric acid by the Autoprep device.  $\text{CO}_2$  released from the samples was subsequently analyzed by the CRDS. The  $\delta^{13}\text{C}$  are reported here with respect to the Pee Dee Belemnite standard.

## Results

### EXTRACTION RESULTS

Results of salt leach analyses are reported in Table 2 and depicted in Figures 5, 6, 7, and 8. The total salt leached by weight from the samples was typically on the order of a few percent and ranged from a low of  $\sim 0.01\%$  for a sample collected near Castle

TABLE 2

Results of ion chromatograph (IC) analysis are displayed in milli-equivalents per kilogram of soil sampled.

| Area of Interest               | Latitude       | Longitude    | Na     | K     | Mg    | Ca    | F    | Cl     | NO <sub>3</sub> | SO <sub>4</sub> | HCO <sub>3</sub> | % Na  | % K  | % Mg | % Ca  | % F  | % Cl  | % NO <sub>3</sub> | % SO <sub>4</sub> | % HCO <sub>3</sub> |
|--------------------------------|----------------|--------------|--------|-------|-------|-------|------|--------|-----------------|-----------------|------------------|-------|------|------|-------|------|-------|-------------------|-------------------|--------------------|
| <i>McMurdo Region</i>          |                |              |        |       |       |       |      |        |                 |                 |                  |       |      |      |       |      |       |                   |                   |                    |
| Building 160 (HF)              | S 77<br>50.885 | E 166 40.618 | 56.03  | 3.02  | 1.96  | 2.13  | 0.35 | 24.15  | 0.00            | 26.71           | 13.24            | 88.73 | 4.79 | 3.11 | 3.37  | 0.54 | 37.47 | 0.00              | 41.44             | 20.55              |
| 1/2 OH (HF)                    | S 77<br>51.070 | E 166 41.353 | 117.46 | 8.64  | 2.21  | 7.34  | 1.50 | 12.82  | 0.70            | 109.27          | 12.89            | 86.59 | 6.37 | 1.63 | 5.41  | 1.09 | 9.34  | 0.51              | 79.66             | 9.39               |
| Top of OH                      | S 77<br>51.123 | E 166 41.665 | 16.75  | 1.81  | 1.46  | 2.08  | 0.46 | 10.82  | 2.01            | 4.98            | 4.81             | 75.80 | 8.18 | 6.61 | 9.40  | 1.97 | 46.89 | 8.71              | 21.57             | 20.85              |
| W of OH near pond              | S 77<br>51.096 | E 166 40.927 | 292.41 | 7.47  | 1.34  | 37.87 | 0.37 | 17.12  | 0.83            | 313.72          | 8.25             | 86.24 | 2.20 | 0.40 | 11.17 | 0.11 | 5.03  | 0.24              | 92.19             | 2.43               |
| Base of OH near Scott Base     | S 77<br>51.047 | E 166 42.386 | 234.73 | 5.28  | 1.54  | 58.69 | 0.34 | 28.23  | 0.84            | 248.87          | 23.40            | 78.18 | 1.76 | 0.51 | 19.55 | 0.11 | 9.36  | 0.28              | 82.50             | 7.76               |
| HP Trail Start                 | S 77<br>50.700 | E 166 36.528 | 353.42 | 4.55  | 1.47  | 5.26  | 2.38 | 122.23 | 1.26            | 99.27           | 140.59           | 96.91 | 1.25 | 0.40 | 1.44  | 0.65 | 33.42 | 0.34              | 27.14             | 38.44              |
| HP Trail near ASPA             | S 77<br>50.241 | E 166 39.962 | 565.20 | 4.63  | 13.10 | 22.05 | 0.39 | 68.19  | 2.84            | 543.78          | 0.00             | 93.42 | 0.77 | 2.17 | 3.65  | 0.06 | 11.08 | 0.46              | 88.39             | 0.00               |
| Base of OH near cylinders (HF) | S 77<br>50.927 | E 166 40.831 | 612.53 | 27.47 | 11.91 | 38.26 | 1.07 | 210.44 | 6.32            | 496.21          | 0.00             | 88.75 | 3.98 | 1.73 | 5.54  | 0.15 | 29.47 | 0.88              | 69.49             | 0.00               |
| Outside galley smoker (HF)     | S 77<br>50.803 | E 166 40.071 | 154.57 | 7.45  | 2.64  | 15.51 | 0.24 | 47.30  | 1.11            | 130.07          | 3.31             | 85.79 | 4.13 | 1.47 | 8.61  | 0.13 | 25.98 | 0.61              | 71.45             | 1.82               |
| Troll Bridge (HF)              | S 77<br>50.817 | E 166 40.037 | 267.82 | 16.78 | 2.98  | 10.60 | 1.98 | 91.24  | 2.54            | 171.55          | 32.95            | 89.82 | 5.63 | 1.00 | 3.55  | 0.66 | 30.39 | 0.85              | 57.13             | 10.97              |
| JSOC stairs (HF)               | S 77<br>50.822 | E 166 39.893 | 406.20 | 5.55  | 3.83  | 12.19 | 0.24 | 100.21 | 2.24            | 329.75          | 0.00             | 94.96 | 1.30 | 0.89 | 2.85  | 0.06 | 23.17 | 0.52              | 76.25             | 0.00               |
| Crary Truck Area (HF)          | S 77<br>50.822 | E 166 40.033 | 589.95 | 10.74 | 4.86  | 12.19 | 1.07 | 200.56 | 6.07            | 405.43          | 8.02             | 95.50 | 1.74 | 0.79 | 1.97  | 0.17 | 32.29 | 0.98              | 65.27             | 1.29               |
| Southern Exposure Bridge (HF)  | S 77<br>50.815 | E 166 39.981 | 82.21  | 1.45  | 1.44  | 11.29 | 0.00 | 15.09  | 0.27            | 78.32           | 3.75             | 85.29 | 1.51 | 1.49 | 11.71 | 0.00 | 15.48 | 0.28              | 80.39             | 3.85               |
| Underneath Crary Phase 1       | S 77<br>50.835 | E 166 40.041 | 79.40  | 2.88  | 2.68  | 15.04 | 0.36 | 13.87  | 1.64            | 79.30           | 6.69             | 79.40 | 2.88 | 2.68 | 15.04 | 0.35 | 13.62 | 1.61              | 77.84             | 6.57               |
| Base of Castle Rock East       | S 77<br>48.075 | E 166 46.705 | 62.99  | 1.58  | 1.05  | 12.05 | 0.48 | 26.61  | 1.00            | 39.05           | 11.29            | 81.10 | 2.04 | 1.35 | 15.51 | 0.62 | 33.93 | 1.28              | 49.78             | 14.39              |
| Castle Rock Summit             | S 77<br>48.059 | E 166 46.483 | 1.58   | 0.06  |       | 0.56  | 0.00 | 0.27   | 0.00            | 0.30            |                  | 71.87 | 2.59 | 0.00 | 25.54 | 0.00 | 47.25 | 0.00              | 52.75             | 0.00               |

TABLE 2  
Continued

| Area of Interest       | Latitude       | Longitude    | Na      | K     | Mg    | Ca    | F    | Cl     | NO <sub>3</sub> | SO <sub>4</sub> | HCO <sub>3</sub> | % Na   | % K   | % Mg | % Ca  | % F  | % Cl  | % NO <sub>3</sub> | % SO <sub>4</sub> | % HCO <sub>3</sub> |
|------------------------|----------------|--------------|---------|-------|-------|-------|------|--------|-----------------|-----------------|------------------|--------|-------|------|-------|------|-------|-------------------|-------------------|--------------------|
| Hill Near YMF (HF)     | S 77<br>50.556 | E 166 41.388 | 464.45  | 8.58  | 1.44  | 13.57 | 0.44 | 263.90 | 0.81            | 211.84          | 12.14            | 95.17  | 1.76  | 0.29 | 2.78  | 0.09 | 53.95 | 0.17              | 43.31             | 2.48               |
| Dorm 208               |                |              |         |       |       |       |      |        |                 |                 |                  |        |       |      |       |      |       |                   |                   |                    |
| Pierside (HF)          |                |              | 163.20  | 9.11  | 3.50  | 4.87  | 0.26 | 77.63  | 1.09            | 103.92          | 0.14             | 90.33  | 5.04  | 1.94 | 2.69  | 0.14 | 42.41 | 0.60              | 56.78             | 0.07               |
| Hamshack (HF)          |                |              | 163.47  | 23.94 | 0.76  | 16.64 | 0.75 | 68.52  | 3.72            | 98.45           | 34.00            | 79.82  | 11.69 | 0.37 | 8.12  | 0.36 | 33.35 | 1.81              | 47.92             | 16.55              |
| JSOC B165 (HF)         |                |              | 235.97  | 3.36  | 7.06  | 10.13 | 0.20 | 151.21 | 2.07            | 106.03          | 1.74             | 91.99  | 1.31  | 2.75 | 3.95  | 0.08 | 57.88 | 0.79              | 40.58             | 0.67               |
| Side of B175 (HF)      |                |              | 357.32  | 4.58  | 3.50  | 5.68  | 0.40 | 9.39   | 0.11            | 363.77          | 0.00             | 96.29  | 1.24  | 0.94 | 1.53  | 0.11 | 2.51  | 0.03              | 97.35             | 0.00               |
| Garwood Valley         |                |              |         |       |       |       |      |        |                 |                 |                  |        |       |      |       |      |       |                   |                   |                    |
| #10 Lower Garwood      |                |              | 192.63  | 1.77  | 2.02  | 4.04  | 1.49 | 68.43  | 2.62            | 15.08           | 114.18           | 96.09  | 0.89  | 1.01 | 2.02  | 0.74 | 33.91 | 1.30              | 7.47              | 56.58              |
| Garwood Valley Salt    |                |              | 7129.50 |       |       |       | 0.00 | 0.00   | 0.00            | 7125.34         |                  | 100.00 | 0.00  | 0.00 | 0.00  | 0.00 | 0.00  | 0.00              | 100.00            | 0.00               |
| JLS 011412 SALT #2     |                |              | 30.68   | 0.55  | 0.00  | 1.34  | 0.00 | 0.85   | 0.00            | 31.42           | 0.33             | 94.19  | 1.68  | 0.01 | 4.12  | 0.00 | 2.61  | 0.00              | 96.39             | 1.01               |
| Taylor Valley          |                |              |         |       |       |       |      |        |                 |                 |                  |        |       |      |       |      |       |                   |                   |                    |
| Priscu stream 1        | S 77<br>43.277 | E 162 16.137 |         |       |       |       | 0.15 | 15.86  | 0.88            | 35.71           | 0.00             |        |       |      |       | 0.28 | 30.16 | 1.66              | 67.90             | 0.00               |
| Priscu stream 2        | S 77<br>43.277 | E 162 16.137 | 26.17   | 0.85  | 1.84  | 18.10 | 0.33 | 11.57  | 0.44            | 26.34           | 9.62             | 55.72  | 1.82  | 3.93 | 38.54 | 0.68 | 23.95 | 0.92              | 54.54             | 19.91              |
| #1 Lake Hoare          |                |              | 767.03  | 2.68  | 7.38  | 8.01  | 5.68 | 167.16 | 4.04            | 314.67          | 298.56           | 97.70  | 0.34  | 0.94 | 1.02  | 0.72 | 21.16 | 0.51              | 39.83             | 37.79              |
| #2 Lake Hoare          |                |              | 43.12   | 5.03  | 4.26  | 6.18  | 0.42 | 23.61  | 0.10            | 37.16           | 0.16             | 73.59  | 8.59  | 7.27 | 10.54 | 0.68 | 38.42 | 0.16              | 60.48             | 0.26               |
| #3 Lake Hoare Camp     |                |              | 52.96   | 4.41  | 1.13  | 7.52  | 0.00 | 25.29  | 0.26            | 30.33           | 10.94            | 80.21  | 6.68  | 1.71 | 11.39 | 0.00 | 37.84 | 0.39              | 45.39             | 16.37              |
| #4 Lake Hoare          |                |              | 407.60  | 27.71 | 0.21  | 9.60  | 0.31 | 346.60 | 0.90            | 47.02           | 50.49            | 91.57  | 6.22  | 0.05 | 2.16  | 0.07 | 77.83 | 0.20              | 10.56             | 11.34              |
| #5 New Harbor          |                |              | 573.10  | 2.49  | 13.33 | 23.75 | 0.18 | 24.30  | 0.00            | 536.87          | 60.42            | 93.54  | 0.41  | 2.18 | 3.88  | 0.03 | 3.91  | 0.00              | 86.34             | 9.72               |
| #5 New Harbor 2hr Soak |                |              | 598.11  | 2.84  | 13.89 | 28.45 | 0.20 | 25.29  | 0.00            | 563.40          | 63.91            | 92.98  | 0.44  | 2.16 | 4.42  | 0.03 | 3.87  | 0.00              | 86.30             | 9.79               |
| #6 New Harbor          |                |              | 548.65  | 6.95  | 6.15  | 12.51 | 0.86 | 405.91 | 1.71            | 60.42           | 109.47           | 95.54  | 1.21  | 1.07 | 2.18  | 0.15 | 70.18 | 0.30              | 10.45             | 18.93              |
| #7 New Harbor          |                |              | 277.94  | 6.32  | 2.22  | 18.23 | 0.69 | 113.46 | 0.00            | 22.88           | 169.22           | 91.22  | 2.07  | 0.73 | 5.98  | 0.23 | 37.05 | 0.00              | 7.47              | 55.25              |
| #8 F6 Camp             |                |              | 1647.81 | 24.81 | 10.51 | 6.76  | 3.65 | 900.95 | 17.69           | 248.76          | 525.83           | 97.51  | 1.47  | 0.62 | 0.40  | 0.21 | 53.09 | 1.04              | 14.66             | 30.99              |
| #9 F6 Camp             |                |              | 169.67  | 2.13  | 0.00  | 3.06  | 0.34 | 95.14  | 0.27            | 17.67           | 61.45            | 97.03  | 1.22  | 0.00 | 1.75  | 0.19 | 54.41 | 0.16              | 10.11             | 35.14              |

414 / ARCTIC, ANTARCTIC, AND ALPINE RESEARCH

| Area of Interest             | Latitude | Longitude    | Na     | K    | Mg   | Ca   | F    | Cl     | NO <sub>3</sub> | SO <sub>4</sub> | HCO <sub>3</sub> | % Na  | % K  | % Mg  | % Ca  | % F  | % Cl  | % NO <sub>3</sub> | % SO <sub>4</sub> | % HCO <sub>3</sub> | % |
|------------------------------|----------|--------------|--------|------|------|------|------|--------|-----------------|-----------------|------------------|-------|------|-------|-------|------|-------|-------------------|-------------------|--------------------|---|
|                              |          |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
| Delta Stream near Howard gl. | S 77     |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
|                              | 39.387   | E 163 05.845 | 405.92 | 8.98 | 1.14 | 5.31 | 1.31 | 277.73 | 0.83            | 34.07           | 108.18           | 96.34 | 2.13 | 0.27  | 1.26  | 0.31 | 65.79 | 0.20              | 8.07              | 25.63              |   |
| Small pond by Howard gl.     | S 77     |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
|                              | 39.493   | E 163 06.080 | 584.81 | 7.84 | 1.77 | 6.81 | 2.22 | 304.83 | 2.05            | 110.94          | 182.42           | 97.27 | 1.30 | 0.30  | 1.13  | 0.37 | 50.60 | 0.34              | 18.41             | 30.28              |   |
| Green creek/Canada gl.       | S 77     |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
|                              | 37.566   | E 163 02.952 | 499.12 | 6.69 | 1.51 | 5.81 | 1.96 | 262.19 | 7.16            | 20.63           | 222.22           | 97.27 | 1.30 | 0.30  | 1.13  | 0.38 | 50.99 | 1.39              | 4.01              | 43.22              |   |
| New mouth of Green           | S 77     |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
|                              | 37.433   | E 163 03.800 | 285.73 | 2.32 | 0.86 | 2.72 | 0.95 | 191.67 | 0.14            | 13.43           | 86.02            | 97.98 | 0.80 | 0.29  | 0.93  | 0.32 | 65.59 | 0.05              | 4.60              | 29.44              |   |
| Lost Seal                    | S 77     |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
|                              | 35.747   | E 163 14.666 | 520.14 | 3.59 | 1.37 | 4.33 | 2.69 | 283.56 | 0.57            | 31.54           | 211.99           | 98.25 | 0.68 | 0.26  | 0.82  | 0.51 | 53.47 | 0.11              | 5.95              | 39.97              |   |
| <i>Miers Valley</i>          |          |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
| Miers near moat              | S 78     |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
|                              | 05.977   | E 163 53.209 | 311.02 | 9.35 | 1.28 | 5.04 | 1.18 | 71.53  | 0.54            | 43.81           | 210.51           | 95.20 | 2.86 | 0.39  | 1.54  | 0.36 | 21.84 | 0.17              | 13.37             | 64.27              |   |
| Taylor Valley Snow           |          |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
|                              |          |              |        |      |      |      |      |        |                 |                 |                  | 62.1  | 2.7  | 15.70 | 19.60 |      | 68.80 |                   | 33.00             | 0.00               |   |
| McMurdo Snow                 |          |              |        |      |      |      |      |        |                 |                 |                  |       |      |       |       |      |       |                   |                   |                    |   |
|                              |          |              |        |      |      |      |      |        |                 |                 |                  | 16.3  | 1.6  | 2.2   | 80    |      | 6.8   |                   | 13.9              | 79.4               |   |

Rock on Ross Island to a high of over 50% for a salt crust collected in the Garwood Valley. For the hydrous salts (gypsum, mirabilite) this probably represents a minimum value.  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{=}$  are the most abundant ions by percent, the three of which are rapidly leachable in distilled water (Drever and Smith, 1978). For the extractions with low salinity, the high water-soil ratio makes cation exchange effects important, which could reduce  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations and increase  $\text{Na}^+$  and  $\text{K}^+$  (Toner et al., 2013). In all samples analyzed in the leaching experiments,  $\text{Na}^+$  is the dominant cation (in meq), comprising >50% of the total.  $\text{Mg}^{2+}$  and  $\text{K}^+$  are minor constituents and  $\text{Ca}^{2+}$  varies, with higher contributions generally found around McMurdo Station and in the western basins of Taylor Valley. Anions ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{=}$ ) contained in the salts are variable, though in general samples collected around McMurdo Station or the coastal New Harbor sites tend to have elevated  $\text{SO}_4^{=}$  and samples collected in the MDVs tend to be dominated by bicarbonate/carbonate (alkalinity). In general, the salts that were analyzed from McMurdo Station have higher ionic  $\text{SO}_4^{=}$  contributions (40%–95% of anions) compared to seawater (5%) or average snow composition (14%, Leslie, 2013).

Alkalinity ( $\text{HCO}_3^-$ ) concentrations in the samples vary from 0 to  $\sim 520$  meq  $\text{kg}^{-1}$  soil or 0% to 64% of the total anion milliequivalents. In general, the samples with the highest percentage of alkalinity from our study were observed in the hyporeic zone salt samples collected in close proximity to the ephemeral streams in the MDV.

### SEM/XRD RESULTS

The most striking observation from the SEM analysis is the variability of mineralogy, composition, and morphology of the salts (Figs. 9–11), which reflects compositionally varied water sources as well as the water flux out of the soils. Still, halite is ubiquitous in all the analyzed samples and occurs in cubic crystal form as well as anhedral masses. Characteristic sulfate salts are depicted in Figure 9. Gypsum is observed in several samples, though its distribution is sparse (Fig. 9, part A). Sodium sulfate salts are observed in nearly all the samples and exhibit a large range in morphology from anhedral masses (Fig. 9, part B) to elongate needle-like crystals (Figs. 9, parts C and F) to euhedral prisms (Fig. 9, part D) to flat hexagonal crystals (Fig. 9, part E) suggesting the presence of several sodium sulfate minerals, presumably thenardite and mirabilite. Bicarbonate/carbonate-based salts are also quite common (Fig. 10), and like the sulfate salts, they exhibit a variety of crystal forms, elongate needles, and tabular forms. Spot analysis with the EDS detector reveals a range in the peak intensities of Na, C, and O indicating different hydrous states of the sodium bicarbonate/carbonate minerals. Other salts observed through SEM images include amorphous urea (Fig. 11, part A), octahedral prisms of  $\text{MgCl}_2$  (probably  $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ , Fig. 9, part B), elongate needles of glauconite, and K-rich rims on glauconite.

Thenardite (mirabilite) is very abundant in most of the salt samples, as seen in its euhedral mirabilite crystals in a matrix of subhedral halite grains (Fig. 9, part B) in the Garwood samples. This salt deposit was not associated with a lake or stream like our other samples. Of the TV samples, the salts at New Harbor, closest to the coast, exhibit the most diverse range in geochemistry, mineralogy, and mineral morphology (Table 2, Figs. 11, parts E and F). Other notable  $\text{SO}_4$  salts identified include the salt crust near the edge of Lake Miers, which displays a flat, cylindrical form of  $\text{Na}_2\text{SO}_4$  (Fig. 9, part E), in close association with what appears to be weathered volcanic glass. Sodium sulfate salts are observed to be elongate “spiky sticks” (Figs. 9, parts C and F), smaller prolate spheroids (Fig. 9, part B),

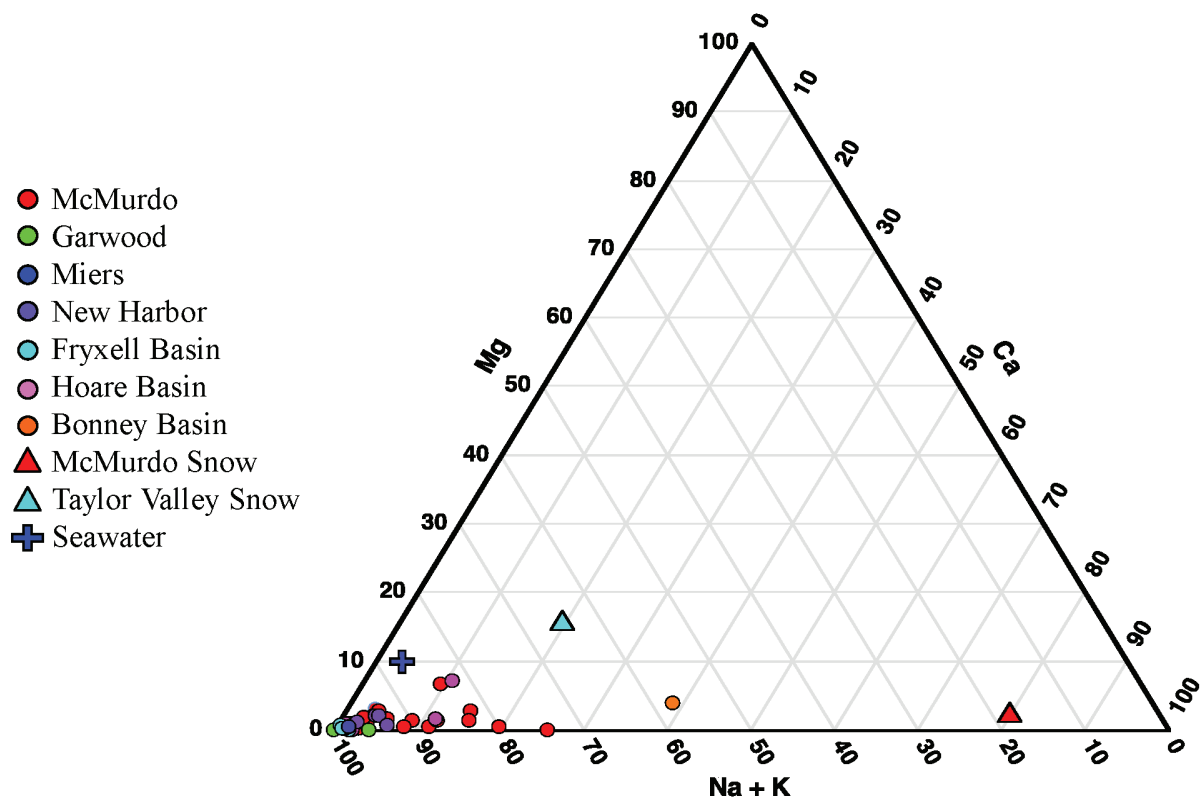


FIGURE 5. A Piper diagram illustrates the dominance of Na ions in the extracted solutions, indicating Na is a major cation in the salts. (comparisons in milliequivalents [meq])

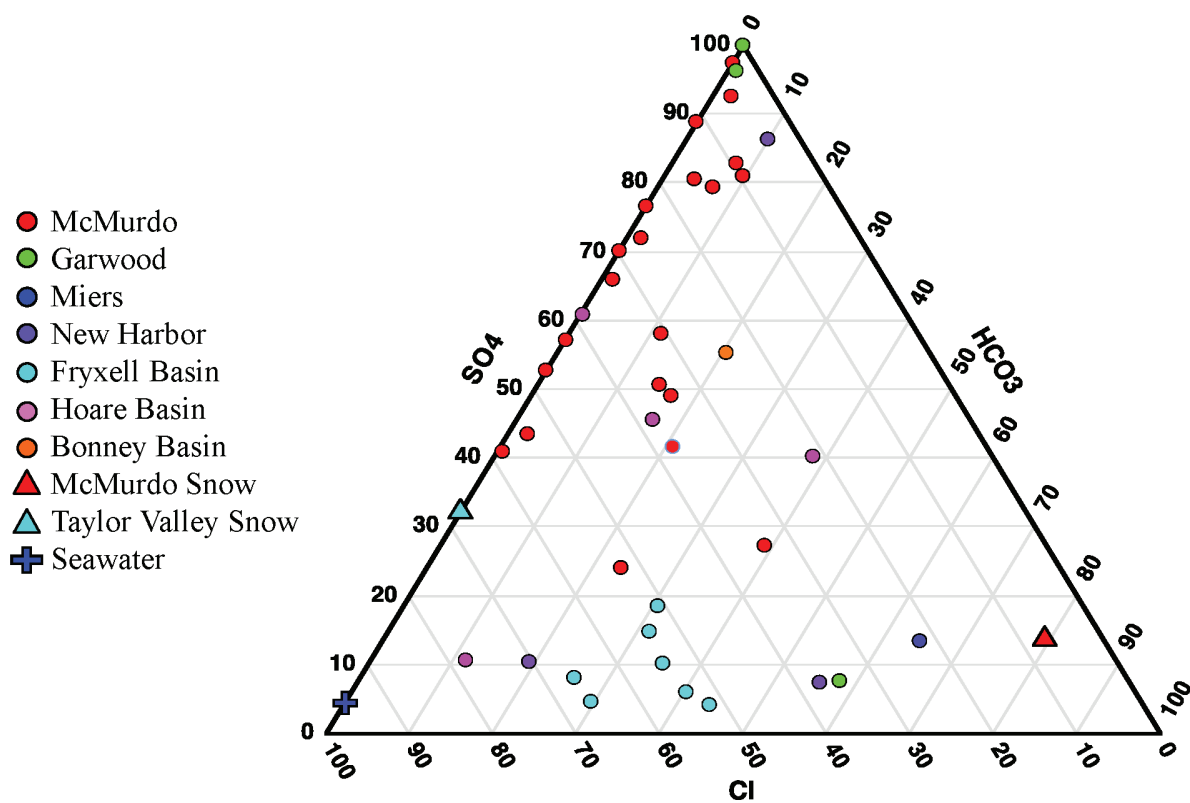
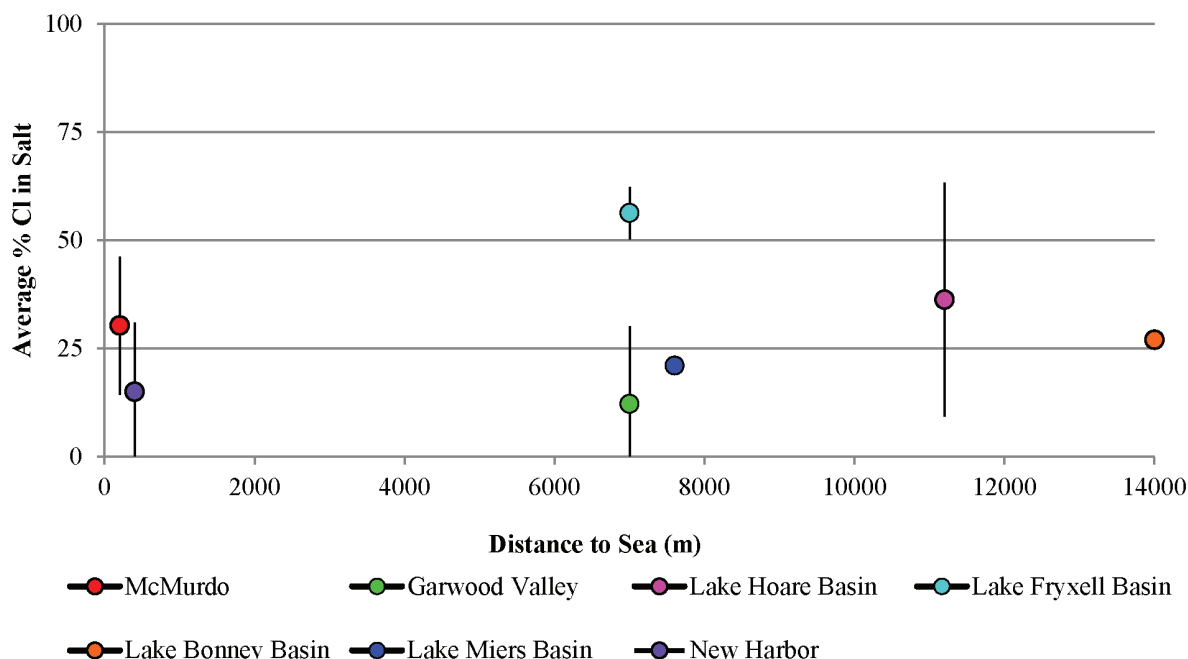


FIGURE 6. A ternary plot of anions measured through ion chromatography (IC) on the salt leaches reveals the variability of anions in the salts present, with geographical associations or otherwise further highlighted by basin color assemblages. Comparisons were made in meq.

## Cl in Salt vs. Distance to Ocean

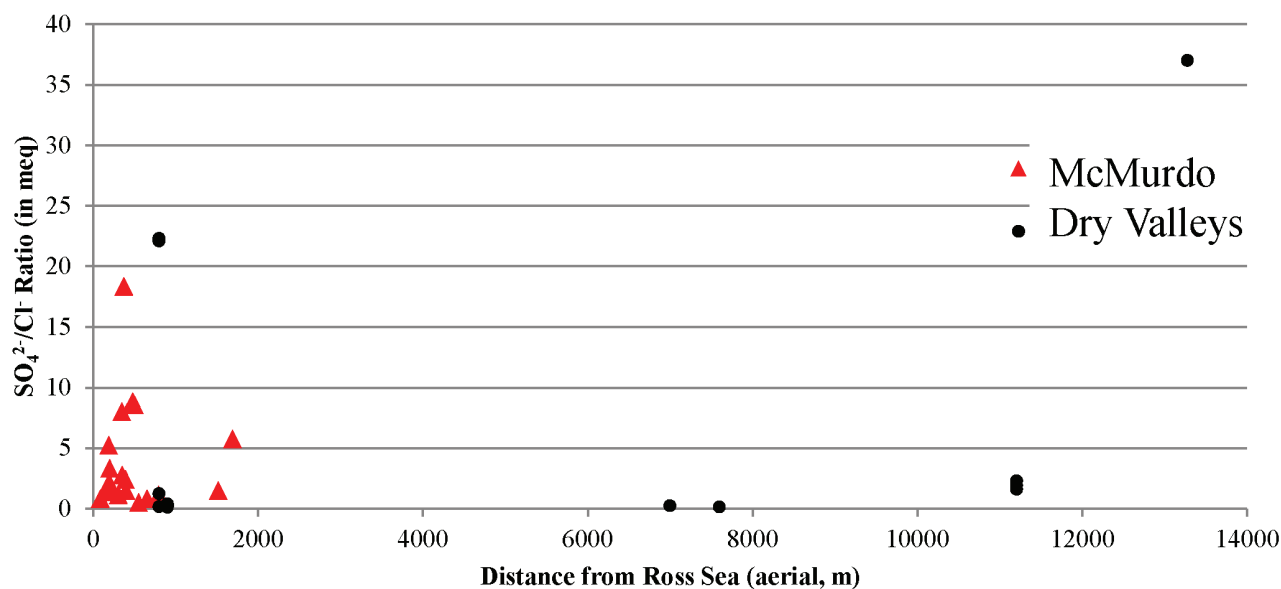


**FIGURE 7.** Chloride contribution to salts is plotted versus linear distance to the ocean. No significant trend is observed in Cl content (in equivalents) with distance from the sea, a finding that reveals differences in basin geochemistry rather than distance from the sea may influence salt chemistry.

and discoidal crystals (Fig. 9, part E). Mineralogical form of the salts is not clearly explained by chemical composition, indicating that hydrological processes may influence morphology.

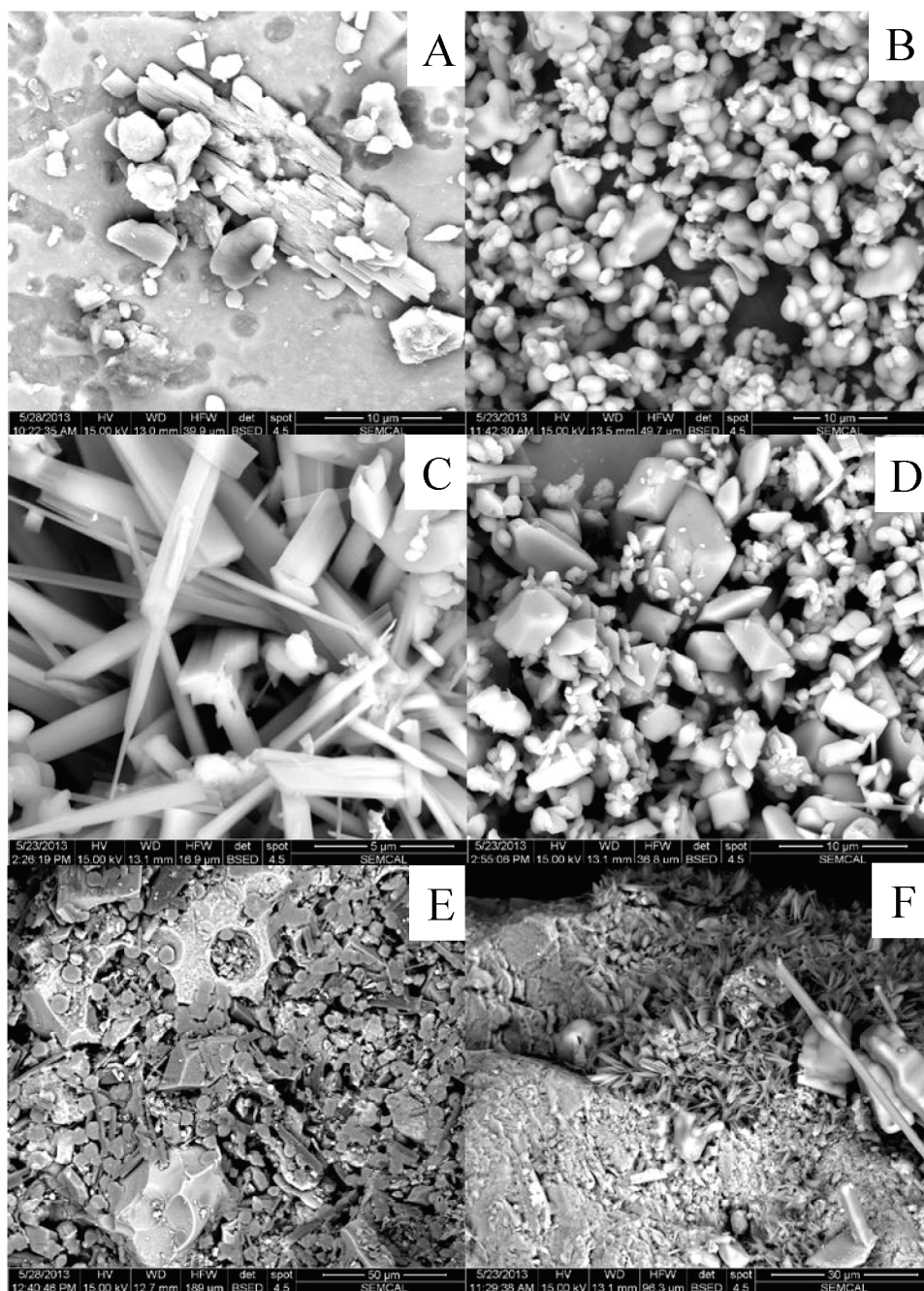
While mirabilite is the most common  $\text{SO}_4$  salt observed in Dry Valley samples, gypsum was observed in several McMurdo Station samples, including the base of Castle Rock (under a boulder, Fig.

## $\text{SO}_4^{2-}/\text{Cl}^-$ Vs Distance to Sea



**FIGURE 8.** No clear trend is observed in sulfate:chloride ratios (in equivalents) with distance from the sea, indicating that marine aerosol deposition is not a dominant influence on salt chemistry. Rather, the large variability within “coastal” salts collected around McMurdo Station reveals that local variations in water geochemistry and snowmelt overprint regional aerosol chemistries.

## SO<sub>4</sub> – Dominated Salt Assemblages

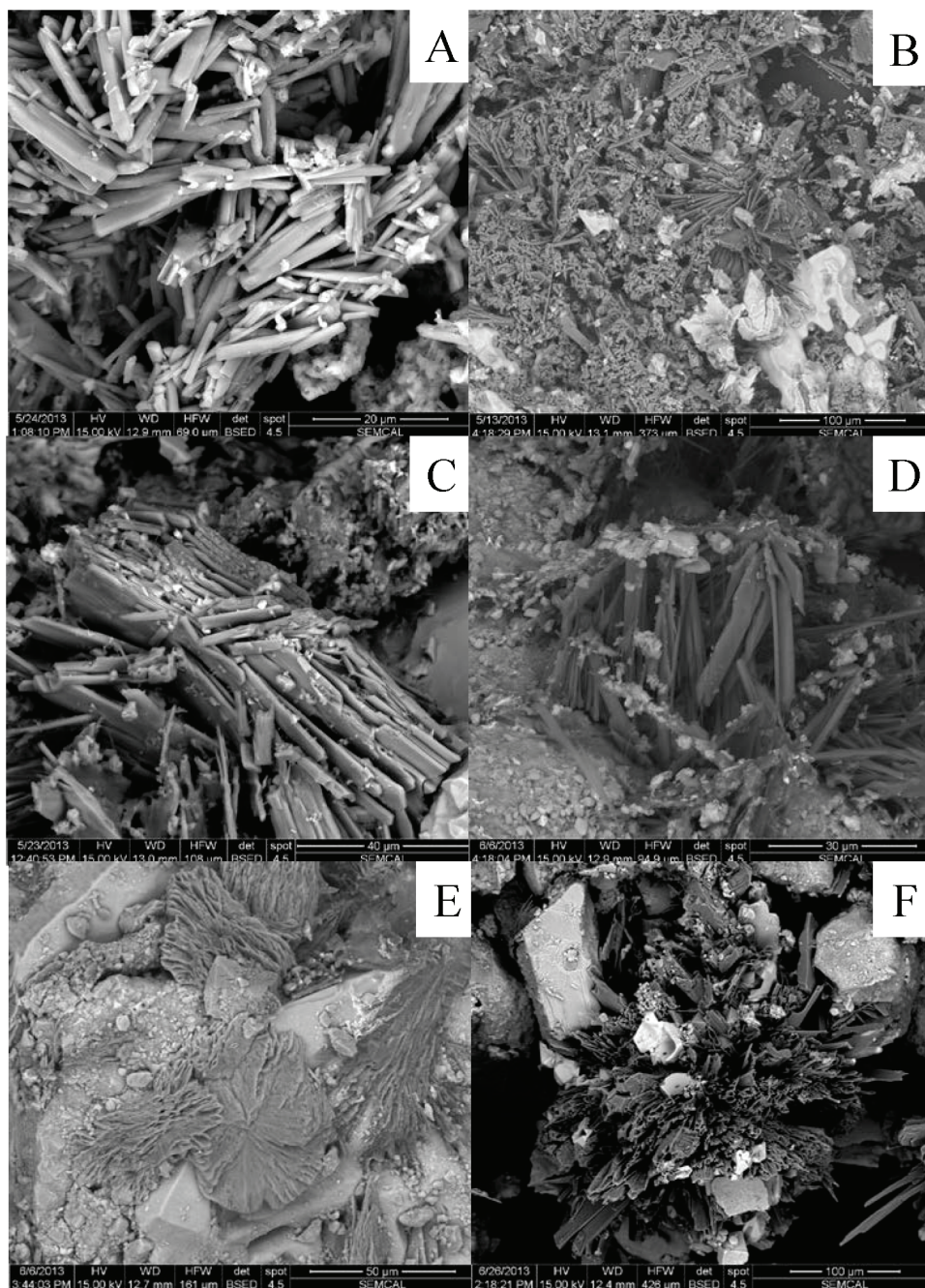


**FIGURE 9.** Selected photos show variation in the morphology of SO<sub>4</sub> based salts. (A) Gypsum from Castle Rock Base. (B) Garwood Valley mirabilite. (C) Glauberite sticks from Lake Hoare #2. (D) Mirabilite and glauberite from Lake Hoare #2. (E) Mirabilite discs among volcanic ash from Lake Miers Moat. (F) Gypsum and halite (far right, long sticks) from Priscu.

9, part A), a distinctive high-elevation (~400 m) feature on the Hut Point Peninsula of Ross Island, and near a small snow melt pond alongside Observation Hill (located on Hut Point Peninsula). At the base of Castle Rock, the gypsum is set against a weathering texture resembling cells (Fig. 9, part A), indicating a potential influence for microbiological communities. Gypsum is also found on the Castle Rock summit, where fog and marine moisture input is common. Gypsum is found only in one TV sample, near Priscu Stream in the Bonney Basin, which is the most western basin and contains more soluble Ca<sup>2+</sup> and higher Cl<sup>-</sup> and SO<sub>4</sub><sup>=</sup> relative to HCO<sub>3</sub><sup>-</sup> in soils (Toner et al., 2013). This basin also has the oldest surface of our samples.

It was not possible to quantitatively identify the mineralogy of the sodium bicarbonate/carbonate salts present using the SEM; however, the variability in the peak intensities of Na, C, and O in the EDS spectra, and the differences in the grayscale intensity of Na-, C-, O-bearing minerals, along with the variation in morphology observed, suggest that several different sodium bicarbonate/carbonate minerals exist in these soils. The salts are most likely nahcolite (NaHCO<sub>3</sub>) or trona (Na<sub>3</sub>(CO<sub>3</sub>)(HCO<sub>3</sub>)·2H<sub>2</sub>O), which were found in association with halite and thenardite (Fig. 10), but these phases only comprise <10% of the sample, making XRD a difficult technique to confirm the phase. Because the bicarbonate/carbonate phase cannot exactly be

## CO<sub>3</sub> – Dominated Salt Assemblages



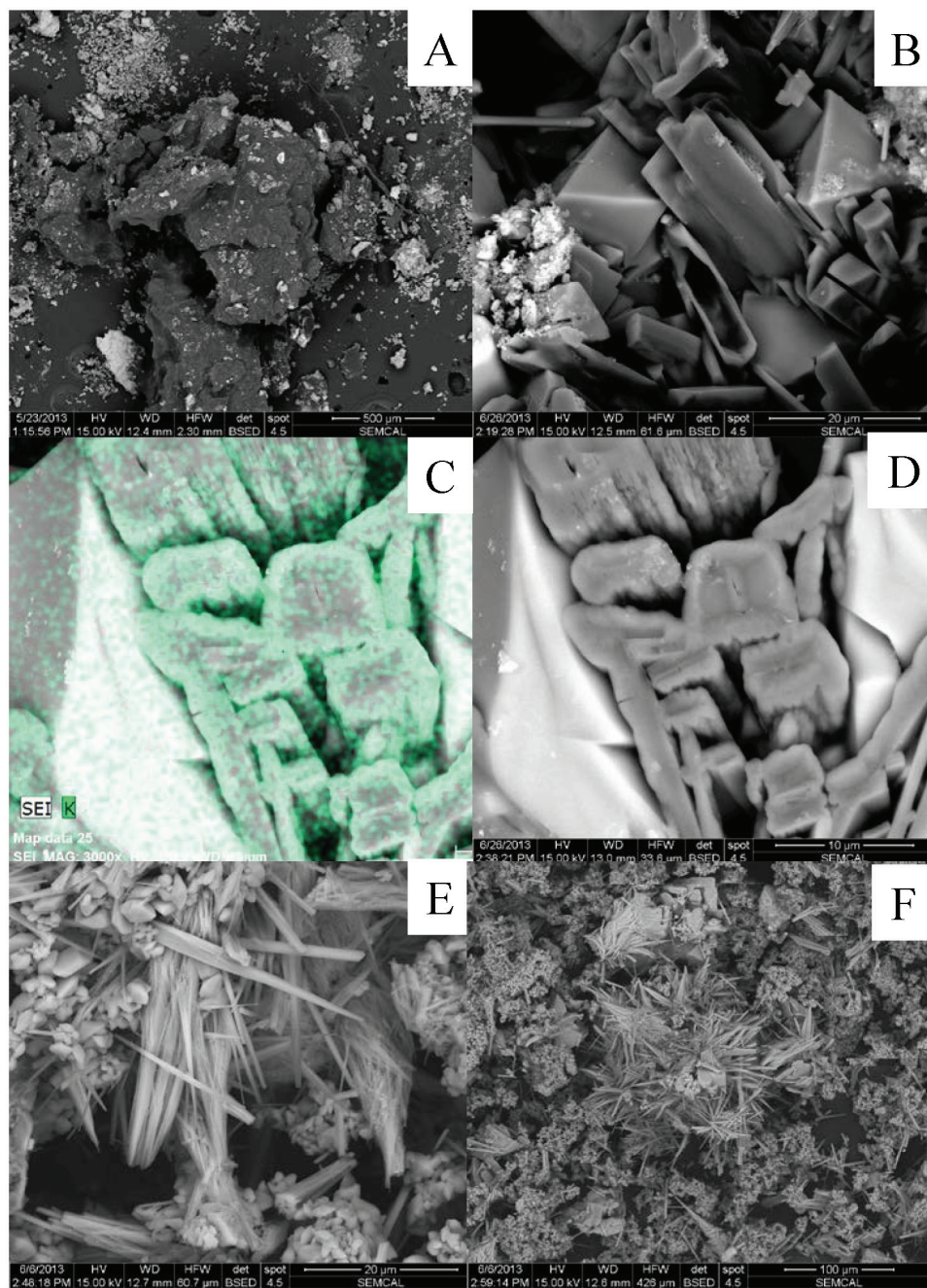
**FIGURE 10.** Various images of trona are shown to reflect source differences and relatively consistent form, easily identified by its darker color. (A) Trona showing different composition colored ends from site 8/F6. (B) Low magnification of trona from Green Creek showing halite as well. (C) Cluster of trona sticks from Green Creek. (D) Trona growth from side of mineral from small pond by Howard Glacier. (E) Radial growth trona from Hut Point Trail. (F) Evaporitic textured trona with magnesium chloride pyramids and halite from New Harbor # 5.

determined, we will refer to it as trona (Fig. 10, part A). Salts containing this mineral include those sampled near Green Creek in TV, Lake Miers in Miers Valley, Hut Point on Ross Island, Howard Glacier in TV, Lake Fryxell in TV, and Lost Seal Stream in TV, which is a spatially similar distribution of the soluble salts by Toner et al. (2013). Characteristic size and form of trona we observe are shown in Figure 8, part A, from the Fryxell Basin. The Lost Seal sample is from an evaporitic environment along a low gradient stream's hyporheic zone and is dominated by large euhedral tabular crystals of trona ranging from microns to hundreds of microns in size, with intergrowth into

larger, anhedral halite. Trona found in Green stream (Figs. 10, parts B and C, and 12, part B) is a similar size but different morphology (elongate needles), and the crystals have a different intensity in grayscale on the backscattering electron detector, suggesting a more hydrous phase. The trona sample collected near the Howard Glacier has long needles that appear to have grown from mineral surfaces (Fig. 10, part D). HCO<sub>3</sub><sup>-</sup> was the largest anion constituent in the sample taken near the moat of Lake Miers, and it exists as massive NaHCO<sub>3</sub> crystals.

Glauberite, a salt undescribed by previous studies, has been tentatively identified and described here (Figs. 11, parts E and F,

# Atypical Salts and Assemblages



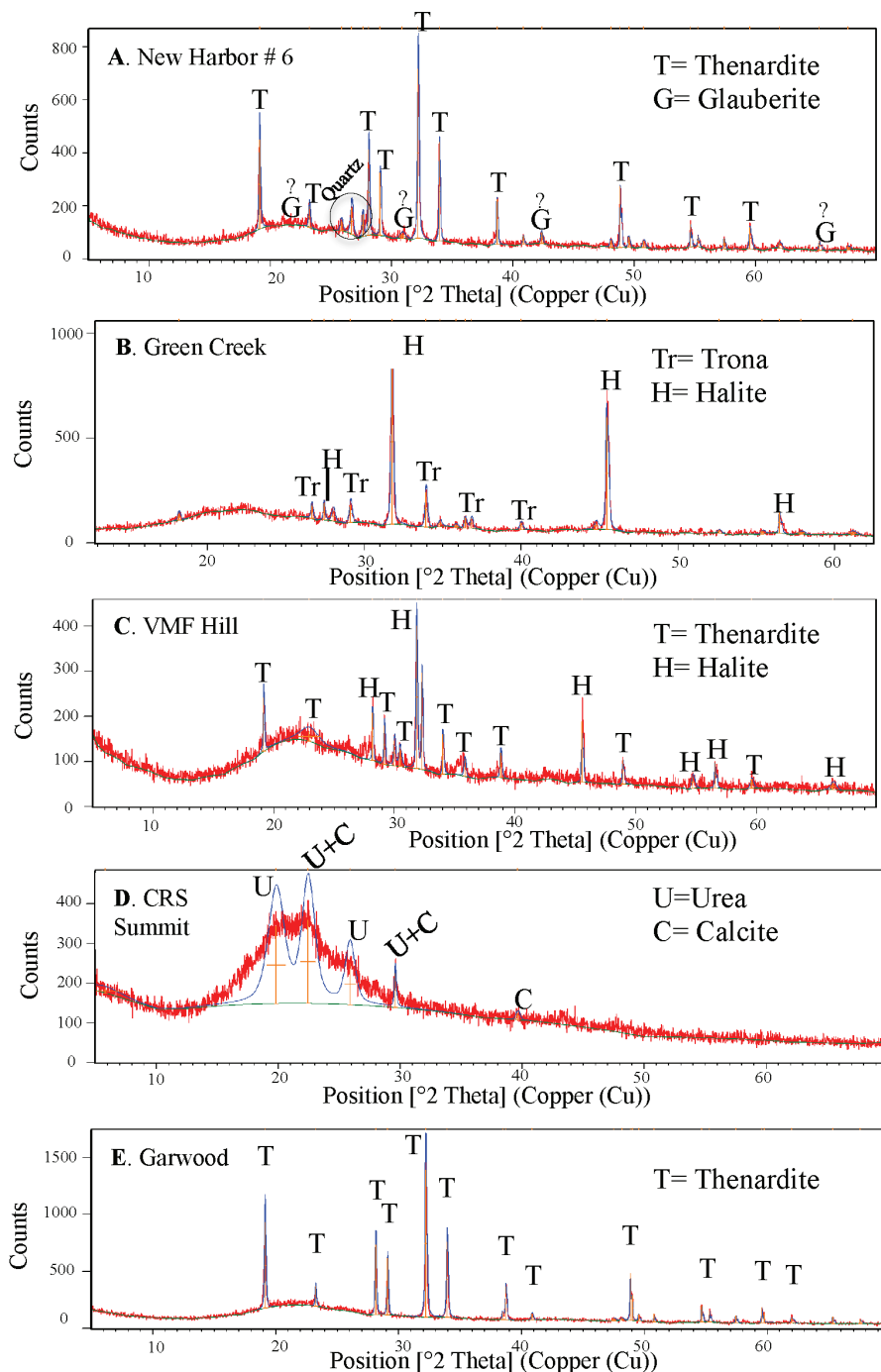
**FIGURE 11. Unusual salt forms and chemical differences selected to highlight the variability within the relatively small study area. (A) Urea from the Castle Rock Summit. (B)  $\text{MgCl}_2$  pyramids from New Harbor #6. (C) Potassium coating on glauberite from Lake Hoare #2 is highlighted in green. (D) Compositional K rims from Lake Hoare #2. (E) Glauberite from New Harbor #7 with smaller mirabilite crystals. (F) Low magnification glauberite from New Harbor #7.**

and 12, part A). Glauberite occurs in association with other minerals, notably halite and thenardite, in subhedral to euhedral elongate crystals ranging from tens to hundreds of microns in size. Its shape in some samples resembles bundles of fibers or hair that are woven together in a semicylindrical fashion, and in others exists as pointy translucent sticks, possibly indicating its relative hydration state.

High potassium levels in a Lake Hoare salt reveal a compositionally atypical salt form (Figs. 11, parts C and D) with potassium coating longer shafts of what is believed to be glauberite ( $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ ) or eugsterite ( $\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2(\text{H}_2\text{O})$ ). The SEM analysis cannot resolve the mineralogy of the sodium calcium sulfate mineral, so it will be

referred to as glauberite because its XRD peak intensities match glauberite more so than those of eugsterite (Fig. 12, part A).

XRD analysis of selected salt samples was used to confirm the minerals that were inferred from the bulk leach and EDS elemental compositions (Fig. 12). Halite and thenardite were commonly observed in the XRD spectra. Because most of the uncommon salts exist as accessory phases, the XRD data are not as robust for determination of those salts. Still, individual analysis of smaller peaks suggests intensities for the minerals targeted through SEM analysis (glauberite, trona), demonstrating that they are present but in smaller quantities than halite and thenardite (Fig. 12).



**FIGURE 12.** Intensity curves from XRD analyses are shown to confirm the presence of various phases as indicated. Note axes limit changes.

## Discussion

### THE ROLE OF WEATHERING AND ANTHROPOGENIC INPUT IN MCMURDO STATION SALTS

The environments of McMurdo Station and the MDV are distinctive and geochemically different due to the prevailing atmospheric conditions and lithologic diversity. The MDV have more geologic variability due to past glaciations and more felsic bedrock (including the Beacon sandstone formation that overlies the Ferrar dolerite), while McMurdo Station bedrock is basinite. Considering these differences, it is appropriate to compare McMurdo Station salts to those of the MDV.

There has been speculation about the extent to which chemical weathering plays a role in salt formation on Ross Island (Keys and Williams, 1981; Jones et al., 1983; Gibson et al., 1983). We hypothesized that salts precipitated on Ross Island are derived from chemical weathering, potentially containing higher carbonate than those originating in the MDV. Though calcite has been observed associated with marine volcanic rocks in TV (Miller, 2006), this was not observed in our study. Calcite is observed infrequently in samples, and it was only identified on the summit of Castle Rock and at the Hut Point trail entrance at the southwestern tip of the peninsula. The role of weathering may be locally constrained and

regionally variable, because  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of surface salt crusts used to determine origin differ greatly (from 0.70344 at the Castle Rock Summit to 0.70861 at Cape Royds) around Ross Island Peninsula (Jones et al., 1983). All of these values are less radiogenic than current seawater, indicating that the strontium is not derived from marine aerosol ( $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.70906), but rather from weathering products of the mafic bedrock.

Though the focus of this study is primarily inorganic, binary salts, urea was identified from salt obtained on the summit of Castle Rock (Figs. 11, part A, and 12, part D) on Ross Island, which has regular human recreational activity in the Austral summer months. Urea is attributed to human activity here because the Castle Rock summit is a highly improbable location for penguins and the presence of skua is nearly nonexistent. Anthropogenic activity is a contributing factor to salt genesis in the McMurdo area, and since the establishment of McMurdo Station and Scott Base on the Hut Point peninsula, very few natural surfaces remain.

#### GEOCHEMICAL AND MORPHOLOGICAL VARIABILITY WITHIN DRY VALLEY SALTS

None of the salt samples plot near the average snow chemistry for either McMurdo Station or the MDV sites (Fig. 6), indicating the salts are not merely the precipitate of sublimated snow. To examine the influence of location on salt chemistry, a simple two-sample t-test was conducted based on watershed groupings. The results did not show significant differences in the ion chemistry ( $p = .05$ ). In contrast to Keys and Williams (1981), who identified strong trends in the distribution of chloride in salts with distance from the coast, our data show that the  $\text{Cl}^-$  content does not decrease in the western areas of the valley (Fig. 7). The spatial extent of our study is much smaller than that of Keys and Williams (1981) and includes only visible salt accumulations at the surface. The variations we observe in  $\text{Cl}^-$  are likely a function of marine aerosol input, hydrologic dynamics, stream, and lake water in the coastal localities that contain abundant salts. These results suggest that  $\text{Cl}^-$  salts are abundant in visible salt crusts, independent of location in McMurdo Station or the MDV locations.

We did not observe a systematic trend in the  $\text{Cl}^-$  distribution and the  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio in salts versus distance from the ocean (Figs. 7 and 8). With the exception of one sulfate-rich salt collected in the Garwood Valley, the largest variation in  $\text{SO}_4^{2-}/\text{Cl}^-$  was observed in samples collected in close proximity to the coast. Toner et al. (2013) found ionic  $\text{SO}_4^{2-}/\text{Cl}^-$  ratios of .161 (TV mouth), .402 (Fryxell Basin), and .444 (Bonney Basin) in the soluble salts of the soils (compared to .051 of dissolved  $\text{SO}_4^{2-}/\text{Cl}^-$  [moles] in seawater), showing an increase westward, which is consistent with the findings of Keys and Williams (1981). Neither of these studies observed the extreme values ( $\text{SO}_4/\text{Cl} > 1$ ) observed by us, but it is difficult to quantify a marine influence in this context because marine aerosol inputs will not necessarily reflect the geochemistry of the ocean. In particular, chemical reactions can alter the signature of the aerosol through the production of oxidized species of dimethyl sulfide. The variability in salt composition within Taylor Valley is significant because adjacent basins do not show similar chemistries, and none of the salts plot near the average precipitation value. The widespread presence of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in salt crusts, ranging from 4 to 7000 meq  $\text{kg}^{-1}$  sediment, is indicative of some contribution of marine origin (Keys and Williams, 1981). However, the  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio (meq) in our samples varies from .07 to ~40, with the highest values and greatest variability observed in samples collected close to the ocean, indicating there must be other

input sources or that there has been a major fractionation of the origin salts that concentrate the  $\text{SO}_4^{2-}$  component. These elevated sulfate levels could be attributed to proximity to Mount Erebus and volcanic sulfate aerosols (Ilyinskaya et al., 2010; Nishiyama and Kurasawa, 1975), or the salts we sampled could have more soluble  $\text{Cl}^-$  salts leached away from them prior to sampling, causing the high ratio we observe.

Furthermore, all salts are enriched in sodium relative to seawater. Antarctic aerosol consists of primary (sea salt) and secondary (biogenic) marine components in addition to emissions from penguin rookeries, volcanic outgassing, and continental dust (Wagenbach et al., 1998). Heterogeneous reactions with  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{SO}_3^{2-}$ , and  $\text{NO}_3^-$  can alter the chemical signature of the sea-salt aerosols during transport (Hara et al., 2004), and cation exchange reactions in the soil could also exert an important influence (Toner et al., 2013). In the Austral summer in Antarctica, high values of Na, Cl, Mg, Ca, and  $\text{NH}_4$  have been observed in aerosols (Fattori et al., 2005).

Total soluble salt contents in the Taylor Valley soils increase inland (Toner et al., 2013), with Lake Bonney soils representing a different environment than that of Fryxell or Hoare. Salts are heavily influenced by glacier retreat and soil exposure age, as soluble salt concentrations are generally consistent with differences in soil age and past glaciations (Toner et al., 2013). Another factor determining salt composition is vertical distance from the valley floor. A high elevation environment could potentially support the more soluble, nitrate salts. A high elevation salt sample in Taylor Valley plots very closely to the snow chemistry, suggesting that salts from marine aerosol deposition do accumulate in the MDV. However, if lower elevation salts were fundamentally a product of aerosol deposition, it would be expected that they would show similar  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$  values (which they do not), suggesting moisture distribution, freeze-thaw dynamics, water contact, and other soil interactions play a larger role in contributing to salt chemistries.

#### $\text{SO}_4$ SALTS

While the salts in the McMurdo Region have been hypothesized to form primarily through the accumulation of weathering products and the precipitation of marine aerosols, work by Bowser et al. (1970) indicates mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) is common in the coastal areas of the MDV. It was probably formed by the freezing of seawater because mirabilite precipitates from a freezing seawater sequence through the Ringer-Nelson-Thompson pathway at  $-8.2^\circ\text{C}$  (Marion and Kargel, 2008). Our results show that several samples collected at the New Harbor site close to the coast are dominated by  $\text{Na}_2\text{SO}_4$ . At previous oceanic high stands or at times when the advancing West Antarctic Ice Sheet “pushed” seawater into the valley, Garwood Valley has recorded the extent of the marine high stand in the form of mirabilite deposits observed on the eastern edge (coastal side) of the valley, seen in the ion chemistry for the Garwood salts.  $\text{Na}_2\text{SO}_4$  is the major sulfate salt identified in the salt crusts there, but other  $\text{SO}_4$  salts are also widespread, including calcium sulfate (presumably gypsum [Fig. 9, part A]), and Na- and Ca-bearing sulfate salts (glauberite), each with distinctive morphologies (Fig. 9 and Figs. 11, parts E and F), reflecting differences in formation and likely small chemical substitutions.

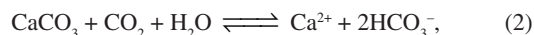
In the laboratory, we noted the instability of mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and made our best efforts to store samples under conditions to minimize this. However, the conversion of mirabilite to thenardite is rapid (30 minutes, Liu et al., 2015) under room temperature conditions and therefore it is difficult to preserve the

mirabilite phase under standard lab conditions. Thus, our analysis yielding thenardite phases was most likely its precursor phase (mirabilite) at the time of collection. This notion is supported by previous studies (Bowser et al., 1970; Keys and Williams, 1981; Claridge and Campbell, 1977).

The lack of moisture further inland may support the preservation of gypsum. Gypsum was not observed in any sample where calcite (also relatively insoluble) was found, perhaps suggesting that the least soluble salt in this case, calcite, controls the calcium concentrations in these salt precipitating solutions. Due to gypsum's relative insolubility, it is likely that it would persist through variations in relative humidity, whereas on the valley floors abundant moisture would solubilize it. There exists no clear relationship between the presence of gypsum and the presence of either halite or thenardite (far more soluble by comparison).

### CO<sub>3</sub>/HCO<sub>3</sub> SALTS

With the exception of the Miers lake sample (which was most likely formed by "evapoconcentration" whereby lake water evaporates near the soil surface and concentrates lake-derived salts in the upper soil column [Barrett et al., 2009]), the salts rich in bicarbonate/carbonate are found in the eastern (coastal) region of TV near streams. Bicarbonate/carbonate salts are not found west of the Fryxell basin, which is consistent with the findings of Claridge and Campbell (1977) because a lower pH in soils westward is attributed to the accumulation of alkaline marine aerosols near the coast and acidic aerosols near the East Antarctic Ice Sheet. Toner et al. (2013) described the development of NaHCO<sub>3</sub> in eastern TV as a series of steps that start with a Na-rich solution (NaCl), where Na<sup>+</sup> moves downward into the soils and exchanges via exchange reactions for Ca<sup>2+</sup>, from



and exchangeable Ca can be calculated according to

$$\text{Ca}_{\text{exch}} = \left( \text{Ca}_{\text{sat}} - \frac{\text{HCO}_3}{2} - \text{Ca} \times \frac{V_{\text{eq}}}{V_{\text{sat}}} \right) \times \frac{V_{\text{sat}}}{\text{soil}(g)} \quad (3)$$

Ca<sub>exch</sub> is exchangeable Ca, V<sub>sat</sub>, and V<sub>eq</sub> (mL) are the volume of saturating and equilibrating solutions, and Ca<sub>sat</sub> is the concentration of Ca in the saturating and equilibrating solutions to form nahcolite and thenardite (Na<sub>2</sub>CO<sub>3</sub>·2H<sub>2</sub>O) after subsequent evaporation and precipitation at/near the surface (Nishiyama and Kurasawa, 1975; Toner et al., 2013). Because the process of NaHCO<sub>3</sub> production is dependent upon leaching and saturation of the soil, it must occur in regions with either high precipitation or nearby water sources. Keys and Williams (1981) attributed the presence of bicarbonate to the biological activity in the eastern Taylor Valley (Lake Fryxell basin containing Lost Seal and Green streams), but excess bicarbonate can also be a product of aluminosilicate weathering or remineralization of organic material. In the context of our study, this process is limited to salts near streams, lakes, and water tracks, though conditions could also promote NaHCO<sub>3</sub> formation under a boulder face where snow is trapped. Due to the morphology of the trona (Figs. 10, parts E and F), it is likely that it formed very slowly through evaporation, promoting the formation of elongate needles in association with halite. Calcite was also identified near Lake Miers and was probably formed by the nearby alkaline wa-

ters and process of evapoconcentration. In this study, the samples with the highest alkalinity are from areas in close proximity to a water source in the eastern Taylor Valley (Lost Seal, Green, and Delta streams), which could sustain organisms or produce HCO<sub>3</sub><sup>-</sup> through weathering processes (Gooseff et al., 2002; Treonis and Wall, 2005). Salts with high HCO<sub>3</sub><sup>-</sup> content were analyzed for δ<sup>13</sup>C and ranged from δ<sup>13</sup>C of ~0.5‰ to 3‰, with the sample collected from the moat of Lake Miers as the heaviest. In the Taylor Valley, pedogenic carbonates have a δ<sup>13</sup>C that ranges from +5.7‰ to +11‰ and ancient lacustrine carbonates range from +2.4‰ to +6.8‰ (Hendy et al., 1979). The lighter δ<sup>13</sup>C of these salts may indicate some input of biologically fixed carbon.

The δ<sup>13</sup>C of HCO<sub>3</sub><sup>-</sup> in the Taylor Valley streams do not, however, indicate a biogenic source of C to these aquatic systems suggesting that the HCO<sub>3</sub><sup>-</sup> comes from CO<sub>2</sub> in the atmosphere and perhaps chemical weathering (Lyons et al., 2013).

### ATYPICAL SALTS

A mineral whose main constituents are sodium, calcium, and carbonate, most probably gaylussite (Na<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O) was found in the Lake Miers moat sample, Hut Point trail start, and along the Lost Seal Stream edges. It has been detected using the EDS detector. Commonalities in the three sites include a close proximity to water (lake, ocean, stream) and either volcanic soil or soil rich in calcium, readily available for dissolution. Bischoff et al. (1991) found the supersaturation of gaylussite in Mono Lake, California, occurs when salinity is in excess of 80‰, a level that is not attained in the streams but could be reached through cryoconcentration in the hyporheic zone regions. Gaylussite solubility is strongly affected by temperature and thus its formation in Antarctica is probably promoted by cold waters and freeze-thaw cycles, causing an increase in salinity and thus precipitation of the salt.

Euhedral magnesium chloride hexahydrate has been found in at least one sample (Fig. 11, part B) from New Harbor within a trona matrix. According to both the Gitterman and the Ringer-Nelson-Thompson pathways for seawater freezing, MgCl<sub>2</sub>·12H<sub>2</sub>O is the last salt to precipitate at the eutectic temperature for seawater freezing (-36.2 °C and -36 °C, respectively), a temperature not reached in streams during the Austral summer (Marion et al., 1999) but that can be attained during the year at many locations within the MDV (Doran et al., 2002). The magnesium salt identified in New Harbor could be residual from sea ice as it is so close to the ocean, but it is likely unstable in Antarctic summer temperatures. More probably, marine aerosol supplied Mg<sup>2+</sup> to the environment and magnesium chloride precipitated slowly as evaporation concentrated the waters, suggested by the shape of the mineral cluster in which the magnesium salt is found (seen in Fig. 9, part F, to the right of the roughly centered halite crystal). In general, because K<sup>+</sup> salts are more soluble than Na<sup>+</sup>, it is possible that K<sup>+</sup> precipitated out of subsurface water from Lake Hoare onto crystals of glauberite during formation. A salt with only potassium, calcium, sodium, and sulfate has not previously been identified in Antarctica. Possibly, the potassium phase coating the sticks is arcanite (K<sub>2</sub>SO<sub>4</sub>), as it has been tentatively documented in the interior of Antarctica (Fitzpatrick et al., 1990).

## Geochemical Modeling

Meltwater generation and subsequent hydrologic evolution has been explored successfully through geochemical modeling to

predict flow pathways in simple environments (Lyons et al., 2005; Toner and Sletten, 2013). Despite these modeling successes, mechanisms of salt movement in cold desert soils are still poorly understood because ionic transport is affected by the abundance of moisture and temperature, which can vary significantly on the order of a few hours. A FORTRAN based computer model (FREZCHEM, FREZing CHEMistry, <<http://www.frezchem.dri.edu>>) was used to test a hypothesis that salts are the product of evaporating subsurface flow (water similar in chemistry to hyporheic zones of streams, lake water, permafrost, and snow melt). Despite numerous simulations with geochemically and climatically appropriate starting quantities, the predicted and observed phases do not agree under a fractional crystallization regime. Overwhelmingly, the model predicts that calcite and gypsum should form under conditions ranging from  $-10^{\circ}\text{C}$  to  $10^{\circ}\text{C}$ . Minerals predicted by the model are not corroborated by our SEM analysis, as calcite and gypsum were rarely observed in the SEM analysis of the salt crusts and were also not abundant based on the logical extrapolations of our salt leach experiments. Relative humidity is not a parameter, which, although simplifying the processes promoting salt accumulation, makes the model less applicable to the observed dynamics of salt formation in the MDV.

Similar modeling strategies were used to predict the geochemical evolution of water using PHREEQC but did not provide insight into the exotic salts we observe in this study. This suggests that a combination of weathering and other processes (upward percolating melted permafrost in the subsurface, modification of brines due to dissolution and then subsequent preferential solubilization) contribute to the observed salt composition. Cation exchange can be another process by which surface salt composition does not reflect a simple evolution of water through the soil column, and these reactions are not captured in simple hydrologic models. However, the extent to which cation exchange is influential in salt formation is controlled in part by marine aerosol input into the soil as well as by subsurface water inputs from melting permafrost and groundwater tracks.

Toner and Sletten (2013) found that cation exchange reactions can form Ca-Cl rich brines when  $2\text{Ca}^{2+} > \text{HCO}_3^- + 2\text{SO}_4^{2-}$ , a condition not met by the majority of surface waters in this study. However, despite the high concentrations of Na- $\text{HCO}_3$  salts that we observe, a Ca-Cl brine can develop (Toner and Sletten, 2013) by exchanging aqueous  $\text{Na}^+$  with exchangeable  $\text{Ca}^{2+}$ , influencing the subsequent geochemistry of surface salts (Toner and Sletten, 2013). Modeled cation exchange soils saturated with water from streams have higher  $\text{Ca}^{2+}$  than  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ , while those near lakes contain higher proportions of exchangeable  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  (Toner and Sletten, 2013), a distinction that in practice has obvious implications for the observed surface geochemical diversity. Myriad water sources combine with marine aerosol inputs on irregular spatio-temporal scales throughout the MDV. It is not surprising that the FREZCHEM model fails to predict the observed phases because it does not explicitly account for cation exchange or perturbations in the form of additional water inputs, such as marine aerosol. In this study, it is likely that both surface and subsurface waters leach the soils and contribute to a solution that evolves depending on the initial source of the water and its direction in the soil column. In our study, the exotic salts we observe could develop from a decoupling of the brine from the surrounding soil during formation (Toner and Sletten, 2013), as work in PHREEQC has shown that the inclusion of cation-exchange reactions in models yields different phase predictions.

One of the primary goals of this research is to evaluate our results within the framework of the established larger (spatially)

studies of Keys and Williams (1981) and Claridge and Campbell (1977). Our results further suggest that a model based on aerosol deposition as the major process alone in low elevations on the valley floor is not appropriate to characterize salt distributions found on the surfaces of the soil. Rather, we found that small changes in hydrological processes and water inputs from various sources largely overprint the primary processes behind evaporating stream water, ultimately complicating the salt chemistry.

## Concluding Remarks

Salt crusts in soils are preferentially formed near wetted areas in the MDVs and on Ross Island, which includes stream beds, “wet patches,” lake edges, in “heat islands” produced under boulders that trap snow, and near the coast where precipitation is prevalent. Understanding the location and chemical composition of visible salts provides important insights for variations in atmospheric chemical input, the possible influence of water sources (including melting permafrost in the austral summer, stream input, hyporheic zone interactions), marine legacy effects, and in situ changes regarding relative solubilities of major salts and chemical weathering. Our results differ from those in the 1970s studies because the  $\text{SO}_4/\text{Cl}$  ratios do not increase with distance away from the coast, but all of the samples were taken within the coastal zone, suggesting marine aerosol condensation could be a contributing, though not major, process in controlling salt formation. Our results suggest that salts are not solely the product of marine aerosol deposition. Our modeling efforts show that the cryoconcentration of snow, stream, and lake water from the MCM-LTER database does not predict the variety of salt phases identified by SEM, implying intermediate processes affecting salt formation. Although the Keys and Williams work spans a much larger spatial scale, we demonstrate here that smaller scale variations in hydrologic conditions can clearly have an important impact on surface salt accumulations. Recent work by Toner et al. (2013) also supports the idea that water dynamics have a great impact on salt accumulation on a basin scale.

As lake levels rise with climate change, increasing the connectivity of hydrodynamic systems in the Dry Valleys, the relationship between mobilized salts and ecological environments will be important. Experiments to study the interactions of salt dissolution with biological communities could improve an understanding of the seasonal nature of populations, because salts are important both for potentially contributing nutrients (sulfur, nitrogen) and energy ( $\text{HCO}_3^-$ ) that sustain ecosystems (Treonis and Wall, 2005; Barrett et al., 2007) and for habitat suitability of organisms (Virginia and Wall, 1999).

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