Stable Isotopes of Nitrate, Sulfate, and Carbonate in Soils From the Transantarctic Mountains, Antarctica: A Record of Atmospheric Deposition and Chemical Weathering

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Soils in ice-free areas in Antarctica are recognized for their high salt concentrations and persistent arid conditions. While previous studies have investigated the distribution of salts and potential sources in the McMurdo Dry Valleys, logistical constraints have limited our investigation and understanding of salt dynamics within the Transantarctic Mountains. We focused on the Shackleton Glacier (85° S, 176° W), a major outlet glacier of the East Antarctic Ice Sheet located in the Central Transantarctic Mountains (CTAM), and collected surface soil samples from 10 ice-free areas. Concentrations of water-soluble nitrate (NO$_3^-$) and sulfate (SO$_4^{2-}$) ranged from <0.2 to ∼150 µmol g$^{-1}$ and <0.02 to ∼450 µmol g$^{-1}$, respectively. In general, salt concentrations increased with distance inland and with elevation. However, concentrations also increased with distance from current glacial ice position. To understand the source and formation of these salts, we measured the stable isotopes of dissolved water-soluble NO$_3^-$ and SO$_4^{2-}$, and soil carbonate (HCO$_3^-$ + CO$_3^{2-}$). $\delta^{15}$N-NO$_3^-$ values ranged from −47.8 to 20.4‰ and, while all $\Delta^{17}$O-NO$_3^-$ values are positive, they ranged from 15.7 to 45.9‰. $\delta^{34}$S-SO$_4^-$ and $\delta^{18}$O-SO$_4^-$ values ranged from 12.5 and 17.9‰ and −14.5 to −7.1‰, respectively. Total inorganic carbon isotopes in bulk soil samples ranged from 0.2 to 8.5‰ for $\delta^{13}$C and −38.8 to −9.6‰ for $\delta^{18}$O. A simple mixing model indicates that NO$_3^-$ is primarily derived from the troposphere (0–70%) and stratosphere (30–100%), SO$_4^{2-}$ is primarily derived from secondary atmospheric sulfate (SAS) by the oxidation of reduced sulfur gases and compounds in the atmosphere by H$_2$O$_2$, carbonyl sulfide (COS), and ozone. Calcite and perhaps nahcolite (NaHCO$_3$) are formed through
INTRODUCTION

Ice-free areas within the Transantarctic Mountains (TAM) have been of scientific interest throughout the 20th and 21st centuries due in part to their unique polar desert soil environments. They are characterized by average annual temperatures below freezing, low amounts of precipitation, and low biomass. Throughout the mid to late Cenozoic, much of the currently exposed areas along the TAM were re-worked by the advance and retreat of the East Antarctic Ice Sheet (EAIS), but some soils are believed to have remained primarily ice-free for possibly millions of years (Mayewski and Goldthwait, 1985; Anderson et al., 2002). As a result of persistent arid conditions since at least the Miocene, salts have accumulated in some Antarctic soils (Marchant and Denton, 1996).

Early geochemical work in the McMurdo Dry Valleys (MDV) (77° S, 162° E), the largest ice-free area in Antarctica, showed that the soil environments in Antarctica are among the most saline systems on Earth (Jones and Faure, 1967; Keys and Williams, 1981). The binary salts, which are primarily nitrate-, sulfate-, chloride-, and carbonate-bearing, have been used for determining relative chronology, and have important implications for habitat suitability and hence soil biodiversity (Claridge and Campbell, 1977; Keys and Williams, 1981; Magalhães et al., 2012; Bockheim and McLeod, 2013; Sun et al., 2015; Lyons et al., 2016). Antarctic ice-free environments are often utilized as Martian analogs, and salt formation processes in Antarctica may aid in our understanding of salt sources and the current and past availability of water on Mars (Wynn-Williams and Edwards, 2000; Vaniman et al., 2004; Bishop et al., 2015).

By interpreting the relationship between the types of salts in the soils, the pH, and the distribution of calcite crusts, Claridge and Campbell (1977) and Keys and Williams (1981) proposed that the majority of MDV salts were derived from marine sources, however, in situ chemical weathering and deposition of oxidized atmospheric compounds are also important. While Cl⁻ salts are generally derived from marine aerosols, and HCO₃⁻ salts from lacustrine deposits and chemical weathering, the origins of NO₃⁻ and SO₄²⁻ salts are more complex (Claridge and Campbell, 1977; Nezat et al., 2001; Bisson et al., 2015). Additionally, when liquid water is present, the dissolution of salts and ion exchange in soils can alter the original salt geochemistry (Toner and Sletten, 2013; Toner et al., 2013).

The measurement of stable isotopes of NO₃⁻, and SO₄²⁻ has greatly improved our understanding of the sources and transport of these salts in Antarctica. Potential sources of NO₃⁻ include deposition from polar stratospheric clouds, tropospheric oxidation of HNO₃ emitted from ice, nitrification and denitrification of nitrogen species by organisms, and oxidation of oceanic organic matter (Savarino et al., 2007; Frey et al., 2009; Campbell et al., 2013; Erbland et al., 2015), while potential sources of SO₄²⁻ include pyrite weathering, marine biogenic sulfate, sea-salt sulfate, and S from volcanic eruptions (Legrand and Delmas, 1984; Patris et al., 2000; Rech et al., 2003; Shaheen et al., 2013). Additional work has used ¹⁷Ο isotopes to attribute NO₃⁻ and SO₄²⁻ salt abundances to the deposition of atmospheric oxidized compounds, particularly in old, high elevation, and hyper-arid environments in Antarctic ice-free areas (Bao et al., 2000; Michalski et al., 2005; Bao and Marchant, 2006).

The majority of isotopic measurements of NO₃⁻ and SO₄²⁻ in Antarctic terrestrial systems have been made on soils from the MDV (e.g., Nakai et al., 1975; Bao et al., 2000; Michalski et al., 2005; Bao and Marchant, 2006; Jackson et al., 2016). Few studies have investigated the geochemistry, distribution, and source of salts from the Central Transantarctic Mountains (CTAM), which are believed to contain some of the most saline soils on Earth (Sun et al., 2015; Lyons et al., 2016). We measured the concentrations and isotopic composition of NO₃⁻, SO₄²⁻, and HCO₃⁻ + CO₂ in samples collected from the Shackleton Glacier region, located in the CTAM, to identify potential salt sources. We show that salt composition varies throughout the region, likely related to differences in the availability of water, and atmospheric deposition is the primary source of both NO₃⁻ and SO₄⁻, while carbonate minerals are formed from the freezing and evaporation/sublimation of water. These data provide insights into the processes that lead to salt formation and accumulation in CTAM soils.

MATERIALS AND METHODS

Study Site

During the 2017–2018 austral summer, a multi-disciplinary field camp was established at the Shackleton Glacier (~84.5°S), a major outlet glacier of the EAIS in the CTAM. The Shackleton Glacier flows between several exposed peaks of the Queen Maud Mountains, which are the basis of this study (Figure 1). Though climate data for the region are sparse, winter temperatures are well below freezing and summer months

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FIGURE 1 | Map of Antarctica highlighting the Shackleton Glacier (SG; yellow box) in relation to the McMurdo Dry Valleys (MDV) and Beardmore Glacier (BG) (gray boxes) (a). The Shackleton Glacier is the focus of this study and flows from the Polar Plateau to the Ross Ice Shelf (b). Soil samples were collected from 11 features along the glacier: Roberts Massif (c), Schroeder Hill (d), Mt. Augustana (e), Bennett Platform (f), Mt. Heekin (g), Taylor Nunatak (h), Thanksgiving Valley (i), Mt. Wasko (j), Nielsen Peak (k), Mt. Speed (l), and Mt. Franke (not shown). The symbols represent sampling locations, though no accurate GPS coordinate could be recorded from Mt. Wasko. Images of the Shackleton Glacier were acquired from the Polar Geospatial Center (PGC).

are closer to 0°C (LaPrade, 1984). Elevations of the ice-free areas range from ~150 m.a.s.l. toward the Ross Ice Shelf to >3,500 m.a.s.l. further inland. The soils in this study were collected between ~300 m.a.s.l. and 2,100 m.a.s.l. (Table 1). The geologic basement consists of gneiss, schist, slate, and quartzite formed from sedimentary and igneous strata which were intruded by granitoid batholiths in the Ross Orogeny. Devonian to Triassic rocks of the Beacon Supergroup overlie the basement, which have been cut by dolerite/basaltic sills (Elliot and Fanning, 2008). Near the Ross Ice Shelf, the exposed surfaces are primarily comprised of metamorphic and igneous rocks, while the Beacon Supergroup and Ferrar Dolerite are more abundant toward the Polar Plateau along with sediments from the Sirius Group. These rocks serve as primary sources of weathering products for salt formation (e.g., carbonates and cations).
Sample Collection

The top 5 cm of soil was collected from 11 locations along the Shackleton Glacier (total of 27 samples) using a clean plastic scoop, stored in Whirlpak bags, and shipped at $-20^\circ$C to The Ohio State University (Figure 1). We attempted to collect three samples in transects perpendicular to the Shackleton Glacier or local tributary/alpine glaciers at each of the 11 locations. One sample was collected near the glacier, one near our estimate of the glacier's trim line during the Last Glacial Maximum (LGM), and the third further inland to represent long-term exposure. The soil ages are not known, but samples from the southern portion of the region, such as Roberts Massif, are likely at the glacier's trim line during the Last Glacial Maximum (LGM), the distance to the nearest glacier (Table 1). In the latter measurement, the term “glacier” was used to represent any glacier, including the Shackleton Glacier, tributary glaciers, alpine glaciers, etc. While this distance does not account for topography, it can be used as an estimate of potential modern and past hydrologic influence and impact on salt formation and mobility.

Water-Soluble Leaches

The soil samples were leached at a 1:5 soil to water ratio for 24 h, following procedures previously described (Nkem et al., 2006; Diaz et al., 2018). The leachate was filtered through 0.4 $\mu$m Nucleopore membrane filters using a polyether sulfone (PES) filter funnel that was thoroughly cleaned with deionized (DI) water between samples. The leachate was stored in the dark at $+4^\circ$C until sample analysis. Filter blanks were collected and analyzed to account for any possible contamination from the filtration and storage process.

Major Ions

Concentrations of water-soluble Cl$^-$ and SO$_4^{2-}$ were measured using a Dionex ICS-2100 ion chromatograph and an AS-DV automated sampler, as originally described by Welch et al. (2010).
Water-soluble cations ($K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$) were measured on a PerkinElmer Optima 8300 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) at The Ohio State University Trace Element Research Laboratory (TERL). Nitrate ($NO_3^- + NO_2^-$) concentrations were measured on a Skalar San++ Automated Wet Chemistry Analyzer with an SA 1050 Random Access Auto-sampler. The precision of replicated check standards and samples was better than 10% for all anions, cations and nutrients. Accuracy was better than 5% for all analytes, as determined by the NIST1643e external reference standard and the 2015 USGS interlaboratory calibration standard (M-216).

**Nitrogen and Oxygen Isotope Analysis of Nitrate**

Aliquots of the sample leachates were analyzed for $\Delta^{17}O$ and $\delta^{15}N$ of nitrate at Purdue University following procedures described by Michalski et al. (2005). Dissolved nitrate solutions were first injected into air-tight vials and the headspace was flushed with Ar. The nitrate in the solutions were reduced to $N_2O$ using $TiCl_4$ (Altabet et al., 2019), then the isotopic composition of $N_2O$ was analyzed on a Finnigan-Mat 251 isotope ratio mass spectrometer (IRMS). Mass independent fractionation of oxygen isotopes, calculated by $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$ ($\Delta^{17}O \pm 1.0\%$), are reported in units of per mille ($\%$) with respect to Vienna Standard Mean Ocean Water (VSMOW) and nitrogen isotopes ($\delta^{15}N \pm 0.3\%$) are reported with respect to $N_2$. Nitrate concentrations were high enough for isotopic analysis on 21 of 27 samples attempted. Though the relationship between $\delta^{18}O$ and $\delta^{17}O$ was used in the $\Delta^{17}O$ calculation, the absolute values of these isotopes could not be determined.

**Sulfur and Oxygen Isotope Analysis of Sulfate**

The same samples that were analyzed for $\Delta^{17}O$ and $\delta^{15}N$ of nitrate were analyzed for $\delta^{18}O$ and $\delta^{34}S$ of sulfate at the University of Tennessee Knoxville. The leachates were acidified with HCl to pH ~2 to remove any dissolved carbonate/bicarbonate ions. Sulfate was then precipitated as $BaSO_4$, after the addition of BaCl$_2$ (~10% wt/vol). The precipitate was rinsed several times with DI water and dried at 80°C. The $\delta^{34}S$ and $\delta^{18}O$ values of $BaSO_4$ were determined using a Costech Elemental Analyzer and a Thermo Finnigan TC/EA, respectively, coupled to a Thermo Finnigan Delta Plus XL mass spectrometer at the Stable Isotope Laboratory at University of Tennessee (e.g., Szynkiewicz et al., 2020). Isotopic values are reported in units of $\%$ with respect to Vienna Canyon Diablo Trolite (VCDT) for $\delta^{34}S$ and VSMOW for $\delta^{18}O$ with analytical precision < 0.4$\%$ based on replicate measurements. Sulfur sequential extractions for $\delta^{34}S$ of sedimentary sulfur were performed on seven dried, bulk soils from seven locations following methods from Szynkiewicz et al. (2009). The samples were ground and treated with 30 ml of 6 N HCl to measure acid-soluble $SO_4^{2-}$. Then the samples were treated with 20 ml of 12 N HCl and 20 ml of 1 M $CrCl_3 \cdot 6H_2O$ under $N_2$ to dissolve disulfide to measure Cr-reducible sulfide. Of the 27 initially prepared for $\delta^{34}S$ and $\delta^{18}O$ analysis, eight samples had sulfate concentrations too low for sufficient precipitation of BaSO$_4$. Therefore, in these samples, $\delta^{34}S$ was analyzed using a Nu Instruments multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the US Geological Survey High Resolution ICP-MS laboratory, Denver with analytical precision < 0.3$\%$ (Pribil et al., 2015).

**Carbon and Oxygen Isotope Analysis of Carbonate**

Between 5 and 10 g of bulk soil from five locations (Roberts Massif, Bennett Platform, Mt. Heekin, Taylor Nunatak, and Nilsen Peak) were dried and ground to fine powder using a ceramic mortar and pestle for carbonate isotope analysis at the Stable Isotope Laboratory at Southern Methodist University. Total inorganic carbon (TIC) was measured by adding phosphoric acid kept at 90°C to the sample, liberating the carbonate as CO$_2$. The $\delta^{13}C$ and $\delta^{18}O$ composition of the CO$_2$ was measured using a dual-inlet Finnigan MAT 252 mass spectrometer. $\delta^{13}C$ and $\delta^{18}O$ are reported in units of $\%$ with respect to Peedee belemnite (PDB) with an overall analytical precision of ±0.2$\%$ or better.

**Scanning Electron Microscopy**

One sample from Schroeder Hill (SH3-2) was analyzed using a FEI Quanta FEG 250 Field Emission scanning electron microscope (SEM) equipped with a backscattered electron detector for imaging and a Bruker energy dispersive x-ray (EDX) detector for spot chemical analysis. The sample was allowed to air dry and was then affixed to an aluminum stub with carbon tape. The stub was coated using Au-Pd with a Denton Desk V precious metal coater before analysis by SEM.

**RESULTS**

**Major Ion Concentrations**

The concentrations of all measured water-soluble ions are variable across the sampling locations and span up to six orders of magnitude for $SO_4^{2-}$ (Table 1). In general, the most abundant anion is $SO_4^{2-}$, however $Cl^-$ is the most dominant species in samples closest to the Ross Ice Shelf, such as those at Mt. Speed and Mt. Wasko (Table 1 and Figure 2). $NO_3^-$ concentrations vary with distance from the coast, but also within individual sample locations (Table 1). For example, concentrations at Mt. Augustana vary from ~1 to 23 $\mu$mol g$^{-1}$. The most abundant cation is $Ca^{2+}$ for nearly all soils, except for the Schroeder Hill samples, where $Na^+$ is the most abundant and concentrations approach 700 $\mu$mol g$^{-1}$. Additionally, the two Schroeder Hill samples furthest from the glacier have the lowest $Ca$: $Mg$ molar ratios (0.52–0.30), indicating an enrichment of $Mg^{2+}$ compared to $Ca^{2+}$, while most other samples are dominated by $Ca^{2+}$. Concentrations of $K^+$ range from <0.03 $\mu$mol g$^{-1}$ at Thanksgiving Valley to 6.85 $\mu$mol g$^{-1}$ at Schroeder Hill (Table 1).

**Trends in Salt Distributions**

Molar ratios of $NO_3^-/Cl^-$, $SO_4^{2-}/Cl^-$, and $NO_3^-/SO_4^{2-}$ with distance from the Ross Ice Shelf are compared for
FIGURE 2 | Molar ratios of major anion species typically associated with salts in high latitude, polar desert soils [(a) \( \text{NO}_3^- / \text{Cl}^- \), (b) \( \text{SO}_4^{2-} / \text{Cl}^- \), and (c) \( \text{NO}_3^- / \text{SO}_4^{2-} \)] compared to distance from the coast of the Ross Ice Shelf. The black dotted lines represent general trends in the data, while the red solid line represents equal molar proportions of the anions and the blue line represents the \( \text{SO}_4^{2-} / \text{Cl}^- \) molar ratio in seawater.

the different locations in Figure 2. Between the coast and approximately halfway up the Shackleton Glacier, \( \text{NO}_3^- \) and \( \text{Cl}^- \) are in approximately equal proportions, but nitrate-bearing salts become more dominant closer to the Polar Plateau (Figure 2a). The trend for sulfate-bearing salts is similar. Near the coast, chloride is about two orders of magnitude higher in concentration than sulfate. However, \( \text{SO}_4^{2-} \) becomes the dominant species for most locations beyond 50 km inland, and
concentrations increase to nearly four orders of magnitude higher than Cl\(^-\) (Figure 2b). The molar ratio of NO\(_3^-\)/SO\(_4^{2-}\) with distance from the coast exhibits an inverse trend compared to the species normalized to Cl\(^-\) (Figure 2c), where the ratio is highest near the coast. As observed with the SO\(_4^{2-}\)/Cl\(^-\) ratio, approximately 50 km inland, sulfate becomes dominant. The relative enrichment of SO\(_4^{2-}\) increases further away from the coast and closer to the Polar Plateau. In general, both nitrate and sulfate have a positive relationship with distance from the Ross Ice Shelf. These results show that, contrary to trends observed in the MDV and the Beardmore Glacier region (83\(^\circ\)4\’ S, 171\(^\circ\)0\’ E) where NO\(_3^-\) was the dominant salt for inland and high elevation locations, sulfate is instead the most abundant in the Shackleton Glacier region (Keys and Williams, 1981; Lyons et al., 2016).

### \(\delta^{15}N\) and \(\Delta^{17}O\) of Nitrate

Values of \(\delta^{15}N\) and \(\Delta^{17}O\) are widely variable within and between the different locations. \(\delta^{15}N\) values range from −47.8 to 20.4\%\(_e\) and while all \(\Delta^{17}O\) values are positive, they range from 15.7 to 45.9\%\(_e\) (Table 2). The highest \(\Delta^{17}O\) and \(\delta^{15}N\) values were at Mt. Augustana and Thanksgiving Valley, respectively. The isotopic composition of NO\(_3^-\) does not appear directly related to elevation and distance from the coast, though there is a slight \((R^2 = 0.20, p\text{-value} = 0.05)\) positive relationship between \(\delta^{15}N\) and distance from the glacier (Figures 3a–c).

### \(\delta^{34}S\) and \(\delta^{18}O\) of Sulfate

Despite a wide range of SO\(_4^{2-}\) concentrations, \(\delta^{34}S\) values are well constrained between 12.5 and 15.8\%\(_e\), even for the low SO\(_4^{2-}\) concentration samples that were analyzed by MC-ICP-MS (Table 2). \(\delta^{18}O\) values are slightly more variable, though all values are negative and range from −14.5 to −6.8\%\(_e\). The highest \(\delta^{34}S\) value is from Mt. Heekin and the most negative \(\delta^{18}O\) value is from Schroeder Hill. Values of \(\delta^{34}S\) do not vary significantly with geography, however \(\delta^{18}O\) exhibits negative trends with elevation and distance from the glacier (Figures 3d–f).

### Inorganic \(\delta^{13}C\) and \(\delta^{18}O\) of Carbonate

Although dissolved inorganic carbon species were not directly measured for the soil extracts in this work, carbonate and bicarbonate minerals have been identified throughout the MDV, and therefore, these minerals are assumed to also be present in CTAM soils (Bisson et al., 2015; Lyons et al., 2020). The amount of carbonate in the nine bulk soil samples analyzed ranges from 0.07% at Roberts Massif near the Polar Plateau to 2.5% at Taylor Nunatak further North (Table 3). \(\delta^{13}C\) values are positive for all samples, ranging from 0.2 to 8.5\%\(_e\), with the exception of Bennett Platform, which has a value of −13.0\%\(_e\). All \(\delta^{18}O\) values are negative and range from −38.8 to −9.6\%\(_e\). One sample from Taylor Nunatak (TN-1-6), noted in Table 3, yielded NO gas which froze out of the system and interfered with the \(\delta^{18}O\) analysis.

### DISCUSSION

These Shackleton Glacier region data represent the highest southern latitude \(\delta^{15}N\) and \(\Delta^{17}O\) of NO\(_3^-\), \(\delta^{34}S\) and \(\delta^{18}O\) of SO\(_4^{2-}\), and \(\delta^{13}C\) and \(\delta^{18}O\) of HCO\(_3^-\) measurements made on soils and soil leaches. We evaluate water-soluble ion concentrations and compare the isotopic compositions to potential source reservoirs to understand the types of salts, sources of salts, and possible post-deposition alteration in remote, hyper-arid Antarctic terrestrial environments.

### Water-Soluble Salt Compositions

Molar ratios of water-soluble ions and SEM images suggest that a variety of salts exist within the soils of the Shackleton Glacier region. Salt dissolution diagrams indicate that the major nitrate salt is Na(K)NO\(_3\), though some samples, such as those from the high elevation and distant locations of Roberts Massif and Schroeder Hill, have Na\(^+\) + K\(^+\) concentrations that are higher than the 1:1 dissolution line (Figure 4a). These samples likely have some Na\(^+\)(K\(^+\)) associated with HCO\(_3^-\) (forming nahcolite, trona, thermonatrite and/or sodium bicarbonate), as observed in MDV and Beardmore Glacier region (Bisson et al., 2015; Sun et al., 2015), or possibly bloedite [Na\(_2\)Mg(SO\(_4\))\(_2\)-4H\(_2\)O] in...
and Williams, 1981; Bisson et al., 2015; Diaz et al., 2018) and been identified in soils and aeolian material in the MDV (Keys (Na
Schroeder Hill (\

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addition to Na(K)-NO
3, which is observed in the SEM images of Schroeder Hill (Figure 5).

There appear to be a range of possible sulfate salts across the region and within individual samples. Anhydrite and/or gypsum (CaSO
4 or CaSO
4 · 2H2O) have been previously identified in MDV soils (Keys and Williams, 1981; Bisson et al., 2015) and some of the Shackleton samples plot on the salt dissolution line, consistent with the dissolution of Ca-SO
4 salts. Mirabilite (Na2SO
4 · 10H2O) and thenardite (Na2SO4), however, have also been identified in soils and aeolian material in the MDV (Keys and Williams, 1981; Bisson et al., 2015; Diaz et al., 2018) and high Na
+ and SO
4 2− concentrations which are outside the stoichiometric lines for gypsum/anhydrite are likely due to the dissolution of these salts (Figures 5c,d). The Schroeder Hill SEM images and EDX spot analysis show that SO
4 2− from this location is likely from the dissolution of gypsum or anhydrite, epsomite (MgSO
4 · 7H2O), thenardite or mirabilite, and/or glauberite [Na2Ca(SO4)2]. Mg-SO
4 salts are also suggested to be abundant in Martian soils and may reflect the water content potential of the soils (Clark and Van Hart, 1981; Vaniman et al., 2004). We also identify an unusually abundant Na–Mg–SO
4 salt, possibly bloedite (Na2Mg(SO4)2 · 4H2O), which, along with the other salts observed at Schroeder Hill, was previously described at Roberts Massif (Claridge and Campbell, 1968) (Figure 5). We did not observe any HCO
3 or CO
3 salts in the Schroeder Hill SEM images. The variability in the salt concentrations and compositions is likely due to the heterogeneous lithology of the Shackleton Glacier region, and differences in salt solubilities. While sulfate salts, such as gypsum do not readily solublize even with multiple wetting events, nitrate salts, such as soda niter (NaNO
3), are highly soluble and only form in hyper-arid soils (Toner et al., 2013). The presence of NaNO
3 and Na2SO4 salts in the high elevation and inland samples indicates that these soils likely have had prolonged arid conditions.

**Stratospheric and Photochemical Processes as Sources of NO
3−**

The δ
15N and Δ
17O composition of NO
3− in our samples suggests that NO
3− is derived primarily from the atmosphere, with a component derived from photolysis in snowpack or another post-deposition alteration process. Atmospheric NO
3−
FIGURE 4 | Salt dissolution diagrams for the major NO$_3^-$ (a,b) and SO$_4^{2-}$ (c,d) salts typically observed in high latitude polar desert soils. The solid black lines are dissolution lines, suggesting that samples which fall on the lines likely have salts derived from the ions represented on the x and y axes.

has a distinct isotopic signature, with a $\delta^{15}$N value of 0‰ if derived from N$_2$, or $\sim -6$ to 7‰, if derived from multiple N species, and $\Delta^{17}$O values $> 15\%$ (Moore, 1977; Michalski et al., 2003). However, upon deposition to the surface, $\delta^{15}$N values of NO$_3^-$ can be altered by photolysis (the breakdown of molecules due to intense and prolonged UV radiation) and volatilization in the absence of biologic activity, which could cause $\delta^{15}$N to either increase or decrease depending on HNO$_3$ equilibrium between the aqueous solution and vapor (Walters and Michalski, 2015). The range of our $\delta^{15}$N values suggests that the NO$_3^-$ is not simply from oxidized N$_2$.

All of the Shackleton Glacier region samples have $\Delta^{17}$O values $> 15\%$, indicating an atmospheric source (Figure 6). Positive $\Delta^{17}$O values are an indicator of NO$_3^-$ derived from ozone and ozone-derived oxygen in the atmosphere, which has a high non-mass dependent $^{17}$O enrichment. The $^{17}$O signal is preserved in NO$_3^-$ and is believed to only be altered by denitrification (Reich and Bao, 2018). However, because biological denitrification is thought to be a minor process in Antarctic soils (Cary et al., 2010), the $\Delta^{17}$O compositions are likely minimally altered.

Isotopic variations of N and O in NO$_3^-$ have been previously measured in exposed sediments from the MDV and the Beardmore Glacier region to elucidate the source of NO$_3^-$ to these systems. We compared the Shackleton Glacier region samples to these data, and while our isotopic values are not as well constrained, they generally plot near the MDV and Beardmore samples (Figure 6). These variations are also independent of NO$_3^-$ concentration (Figure 6b). In the MDV, $\delta^{15}$N values ranged from $-9.5$ to $-26.2\%$ and $\Delta^{17}$O ranged from 28.9 to 32.7‰ (Michalski et al., 2005; Jackson et al., 2015, 2016). Further south, isotopic compositions of NO$_3^-$ along the Beardmore Glacier ranged from 1.8 to 8.8‰ and 28.4 to 33.5‰ for $\delta^{15}$N and $\Delta^{17}$O, respectively (Lyons et al., 2016). Between the two locations, $\Delta^{17}$O values are identical, but $\delta^{15}$N values are not similar. The $\delta^{15}$N and $\Delta^{17}$O range for the Beardmore overlaps
with measured values of atmospheric NO$_3^-$ (Moore, 1977; Michalski et al., 2003) (Figure 6), and Lyons et al. (2016) suggested that approximately 50% of the NO$_3^-$ was produced in the troposphere and 50% in the stratosphere based on the high $\Delta^{17}$O values. In other words, the NO$_3^-$ in Beadmore Glacier region soils, as in the Shackleton Glacier region, is entirely atmospheric in origin and has preserved the atmosphere isotopic signature.

Post-depositional Alteration and Snowpack Emission of NO$_3^-$ in Antarctica

Though the Shackleton Glacier samples are likely initially derived from the atmosphere, the $\delta^{15}$N values differ from the $\delta^{15}$N range of atmospheric NO$_3^-$ (Figure 4). While not measured in this study, our data suggest that post-depositional alteration of NO$_3^-$ likely occurs in CTAM soils, potentially due to photolysis or local oxidation of N species (either modern or ancient). Previous studies have used both direct measurements and theoretical models to argue that the isotopic composition of NO$_3^-$ at the Antarctic surface can be affected by post-depositional fractionation processes, particularly re-emission of NO$_x$ (NO + NO$_2$) from snowpack due to photolysis and evaporation of HNO$_3$ (Savarino et al., 2007; Frey et al., 2009; Morin et al., 2009). Photolysis has been previously documented in glacial environments in both Greenland and Antarctica where snow accumulation rates are low (Honrath et al., 1999; Jones et al., 2001), and in photochemical experiments using snow and NO$_3^-$ which show direct production of NO$_x$ when exposed to sunlight (Honrath et al., 2000). Savarino et al. (2007) estimated the emission flux of NO$_x$ [NO + NO$_2$ + HNO$_3$ + HONO + 2 x (N$_2$O$_5$), etc.] from oxidized NO$_x$ species to be $\Delta N = 1.2 \times 10^7$ kg year$^{-1}$, which is similar to the flux from polar stratospheric clouds at $\Delta N = 6.3 \times 10^7$ kg year$^{-1}$ (Muscari et al., 2003). In other words, photolysis and NO$_x$ emission is an important source of NO$_3^-$ to the Antarctic N cycle.

Spatial and temporal variations in the $\delta^{15}$N composition of Antarctic snow are similar to the variability in the Shackleton Glacier soils, reflecting both stratospheric and tropospheric production of NO$_3^-$ . Savarino et al. (2007) found that the composition of NO$_3^-$ in coastal Antarctic snowpack was dependent on the season, where winter was dominated by deposition of NO$_3^-$ from polar stratospheric clouds ($\delta^{15}$N $\approx 19\%o$) and the summer and late-spring composition was influenced by snow reemissions of NO$_x$ and HNO$_3$ from further.
enriched cause gaseous loss of that NO$_3^-$ is positive and argue that subsequent photolysis and evaporation

δN distribution of NO$_3^-$ is still poorly

released to the atmosphere, which is later re-deposited elsewhere on the continent, including soils, as HNO$_3$.

It should be noted that no studies have directly investigated or measured post-depositional fractionation of δ$^{15}$N and Δ$^{17}$O in NO$_3^-$ in Antarctic soils. Jackson et al. (2016) argued that the isotopic signature of NO$_3^-$ in MDV soils is preserved and more resistant to post-depositional alteration, likely due to acid neutralization by soil carbonate minerals and limited light penetration into soils. These authors assumed that NO$_3^-$ which was deposited directly on soil surfaces from the atmosphere was not influenced by volatilization, photolysis, or water exchange. Instead, they suggested that the soil δ$^{15}$N values of NO$_3^-$ were affected by post-depositional alteration when overlain by ephemerual snow and near glaciers due to photolysis in the snowpack, as supported by decreasing δ$^{15}$N values further from the glacier. We do not observe a trend of decreasing δ$^{15}$N values further from snow and ice in our samples. However, considering the range of δ$^{15}$N values and positive Δ$^{17}$O values along the Shackleton Glacier, we hypothesize that our samples contain a mixture of NO$_3^-$ produced in the stratosphere (sedimentation from polar stratospheric clouds, oxidation of NO$_x$ by ozone) and the troposphere (oxidation of HNO$_3$ by ozone, snowpack remission, and long range transport of gases and aerosols), both of which could be affected by evaporation and photolysis upon deposition on soils.

Estimating the Atmospheric Contribution of NO$_3^-$ to Shackleton Glacier Region Soils

Production, transport and alteration of NO$_3^-$ in soils requires further investigation to effectively determine the relative fraction of NO$_3^-$ derived from both stratospheric and tropospheric sources. However, we estimate the fluxes from the two reservoirs following conceptual and theoretical models from Savarino et al. (2007), Frey et al. (2009), and Erbland et al. (2015). Our data suggest that for inland locations in Antarctica, NO$_3^-$ is deposited from the stratosphere onto the surface of the EAIS and soils of the TAM, and initially maintains a stratospheric signal (typically δ$^{15}$N near 0‰ and δ$^{17}$O > 15‰). Intense UV radiation induces photolysis and mobilization of HNO$_3$ plus other reduced N species, especially in snow, which are later re-oxidized by tropospheric ozone and re-introduced to the surface through wet and dry deposition. This mechanism is further supported by results from Jackson et al. (2016), who found that δ$^{15}$N values in soils from the MDV were similar to values from aerosols near Dumont d’Urville in the coastal Antarctic (Savarino et al., 2007).

δ$^{15}$N$_{soil} = f \cdot \delta ^{15}N_{strat} + f \cdot \delta ^{15}N_{trop(emit)} \pm f \cdot \delta ^{15}N_{post-dep}$  (1)

\[f_{strat} + f_{trop(emit)} = 1\]  (2)

A simple mixing model using Equations 1 and 2 can be solved to determine the relative fractions of the different atmospheric sources to the Shackleton soils. In Equation 1, the δ$^{15}$N composition of NO$_3^-$ is derived from the fractions (f) of δ$^{15}$N from the stratosphere (strat), photolytic emission from snowpack to the troposphere [trop(emit)], and post-depositional processes (post-dep). Post-depositional alteration of NO$_3^-$ is still poorly

inland (δ$^{15}$N ≈ −34‰). Frey et al. (2009) measured the spatial distribution of NO$_3^-$ concentrations and δ$^{15}$N and Δ$^{17}$O values of NO$_3^-$ between the Antarctic coast and the interior. They found that δ$^{15}$N values were highly positive in the interior, with values > 200‰, and highly negative on the coast, with values as low as −15‰. Frey et al. (2009) and Erbland et al. (2013) show that the δ$^{15}$N-NO$_3^-$ of snowpack in the interior of the continent is positive and argue that subsequent photolysis and evaporation cause gaseous loss of that NO$_3^-$ as NO$_x$. This process results in enriched δ$^{15}$N in the remaining snow, and a lighter δ$^{15}$N of NO$_x$
FIGURE 7 | Isotopic composition of $SO_4^{2-}$ (a) and the variation of $\delta^{34}S$ with inverse sulfate concentrations (b). The shapes and colors representing the different sampling locations correlate with the key in Figure 2. The solid circles represent MB11 samples (Asgard Tills) from the McMurdo Dry Valleys (Bao and Marchant, 2006). The solid red box shows the distribution of the samples at a higher resolution. The solid and dotted black boxes represent potential $SO_4^{2-}$ sources and the blue star is the $SO_4^{2-}$ isotopic composition of modern seawater (Holser and Kaplan, 1966; Faure and Felder, 1981; Calhoun and Chadson, 1991; Legrand et al., 1991; Alexander et al., 2003; Pruett et al., 2004; Jonsell et al., 2005; Bao and Marchant, 2006; Baroni et al., 2008; Tostevin et al., 2014).
understood in soils, but over prolonged periods of exposure, we anticipate that the modern influence on isotopic composition would be minimal. Therefore, we simplify the Equation 1 and assume that stratospheric deposition and emission to the troposphere (followed by redeposition) are the primary sources of NO$_3^-$ in Equation 2. We use end-member values of $\delta^{15}$N $\approx$ 19‰ for deposition from polar stratospheric clouds to represent the stratospheric deposition and $\delta^{15}$N $\approx$ −34‰ for NO$_3^-$ species liberated by photolysis to represent tropospheric deposition (Savarino et al., 2007). Solving these equations, we estimate between 30 and 100% of NO$_3^-$ is from the stratosphere and up to 70% is from the troposphere, with the exception of one sample from Nilsen Peak which appears entirely derived from the troposphere (Table 4). Slightly negative fraction values for Nilsen Peak and Thanksgiving Valley are likely due to minor variations in the source isotopic compositions. However, Mt. Speed has an anomalously low $\delta^{15}$N value of $-47.8\%$, which cannot be explained by our simple model.

**Primary and Secondary Atmospheric, and Chemical Weathering Derived SO$_4^{2-}$ Sulfide Weathering as a Source of SO$_4^{2-}$**

The $\delta^{34}$S and $\delta^{18}$O isotopic values of SO$_4^{2-}$ indicate that sulfide weathering is likely a minor source of SO$_4^{2-}$ to the Shackleton Glacier region compared to other sources, such as atmospheric deposition. Though the $\delta^{18}$O values are similar between the sulfide end-member and the Shackleton soil leaches, the Shackleton $\delta^{34}$S values are greater (Figure 7). This is probably due to the low abundance of sulfide minerals in the local lithology since the $\delta^{34}$S signature is preserved during sulfide weathering (Balci et al., 2007).

In sedimentary rocks, sulfide is almost exclusively found as the mineral pyrite (FeS$_2$). Pyrite has been observed and characterized in the metasandstone of both Bowers Terrane (Molar Formation and Pyrite Pass) and Robertson Bay Terrane near the MDV. Further South, till found on Mt. Sirius in the Beardmore Glacier region contained detrital pyrite, which is likely the major source of pyrite for the TAM (Hagen et al., 1990). Tills of the Sirius Group can be found throughout much of the TAM at high and low elevations, but along the Shackleton Glacier the till was most abundant at Roberts Massif and Bennett Platform, with smaller outcrops observed at Schroeder Hill (Hambrey et al., 2003). Pyrite-bearing tills have been identified in these regions, but their distributions and isotopic compositions are variable (Holser and Kaplan, 1966; Balci et al., 2007; Pisapia et al., 2007; Bao, 2015).

The SO$_4^{2-}$ isotopic composition of the Shackleton soils is not reflect of a predominately pyrite source. Sulfur sequential extractions were performed on seven samples representing the range of elevations, local lithology, and glacial histories found along the Shackleton Glacier to investigate pyrite weathering as a potential source of S. Percentages of acid-soluble sulfate and Cr-reducible sulfide (i.e., pyrite) were generally low for nearly all samples with less than 0.5 and 0.003% (≈150 to 1 µmol-S g$^{-1}$), respectively (Table 5). Concentrations of acid-soluble sulfate were of sufficient mass for $\delta^{34}$S analysis only for the high elevation and further inland locations of Roberts Massif, Mt. Augustana and Schroeder Hill. Interestingly, the acid-soluble $\delta^{34}$S values are only 0.2–0.3‰ higher than the water-soluble $\delta^{34}$S values, which is within our analytical error. We suggest that this extractable phase may be primarily from gypsum/anhydrite dissolution in acid and therefore is of a common source with the water-soluble SO$_4^{2-}$ since the acid extraction solubilizes both the water and acid soluble constituents. For the Cr-reducible phase, S concentrations were sufficient for $\delta^{34}$S analysis for two samples, Mt. Heekin and Nilsen Peak. These $\delta^{34}$S values are more negative than both the

![Table 4](image-url)

| Sample  | f(strat) | f(trop(emit)) |
|---------|----------|---------------|
| AV2-1   | 0.29     | 0.71          |
| AV2-5   | 0.31     | 0.69          |
| AV2-8   | 0.46     | 0.54          |
| BP2-1   | 0.47     | 0.53          |
| BP2-5   | 0.56     | 0.44          |
| BP2-8   | 0.47     | 0.53          |
| MH3-1   | 0.81     | 0.19          |
| MH3-5   | 0.62     | 0.38          |
| MSP4-2  | −0.26*   | 1.26          |
| NP3-4   | −0.02*   | 1.02          |
| RM2-1   | 0.53     | 0.47          |
| RM2-5   | 0.49     | 0.51          |
| RM2-8   | 0.55     | 0.45          |
| SH3-2   | 0.57     | 0.43          |
| SH3-3   | 0.42     | 0.58          |
| SH3-8   | 0.52     | 0.48          |
| TGV2-1  | 1.03     | −0.03*        |
| TGV2-5  | 0.66     | 0.34          |
| TGV2-8  | 0.71     | 0.29          |
| TN2-1   | 0.83     | 0.17          |
| TN2-8   | 0.55     | 0.45          |

End-member values of $\delta^{15}$N from stratospheric clouds (strat) (19‰) and tropospheric remission (trop(emit)) (−34‰) were originally reported by Savarino et al. (2007). Negative values are indicated (*), which identify samples where the model parameters were insufficient.

![Table 5](image-url)

| Sample  | Acid-soluble SO$_4$ | Cr-reducible sulfide | Acid-soluble SO$_4$ | Cr-reducible sulfide |
|---------|---------------------|----------------------|---------------------|----------------------|
| TGV2-1  | <0.001              | <0.001               | b.d.l.              | b.d.l.               |
| TN2-1   | <0.001              | <0.001               | b.d.l.              | b.d.l.               |
| MH3-5   | 0.001               | 0.0003               | b.d.l.              | −2.3                 |
| AV2-1   | 0.268               | <0.001               | 14.6                | b.d.l.               |
| NP3-4   | 0.001               | 0.002                | b.d.l.              | 12.1                 |
| RM2-8   | 0.432               | <0.001               | 14.3                | b.d.l.               |
| SH3-2   | 0.87                | <0.001               | 13.3                | b.d.l.               |

Samples that were below the analytical detection limit are listed as b.d.l.
water-soluble and acid-soluble values at −2.3 and 12.1‰. As a comparison, Sirius Group tills had δ34S values ranging from −1.4 to +3.1‰, representing an isotopic composition similar to elemental sulfur (S0), though it is well-known that sedimentary sulfides are isotopically variable (Hagen et al., 1990).

Our data show that some Shackleton Glacier region soils contain sulfide (likely as pyrite), however, sulfide weathering is unlikely to be a major source of SO42−. The concentrations of water-soluble SO42− in our samples are as high as 450 µmol g−1, while most samples had sulfide concentrations too low for analysis (<0.001% or 0.3 µmol·S g−1). Though Mt. Heekin had quantifiable sulfide, the concentration was only 0.003% (~1 µmol·S g−1), compared to 0.19% (~50 µmol·S g−1) for water-soluble S. Unless the sulfide reservoirs were at least 100x greater in the past and experienced complete oxidation, the majority of our SO42− was derived from another source, likely the atmosphere as we proposed previously. Additionally, the distinct trends between SO42− concentrations and isotopic composition with elevation, distance from the coast, and distance from the nearest glacier suggest that similar processes are controlling SO42− formation throughout the region. Finally, the δ34S values of the Cr-reducible sulfide from Mt. Heekin and Nilsen Peak are too negative to explain the isotopic composition of the water-soluble SO42−. All the available information suggest that chemical weathering of pyrite may occur in some Shackleton Glacier region soils, but it is a minor process and is overwhelmed by an atmospheric source.

### Atmospheric Sulfate as the Primary Source of SO42−

We used end-member values of δ34S and δ18O for non-sea salt secondary atmospheric sulfate (SAS) (δ34S = 12.0%, δ18O = −16.0‰), sea salt sulfate (SS) (δ34S = 22.0%, δ18O = 10.0‰), and terrestrial sulfate from sulfides (TS) (δ34S = 5.0%, δ18O = −20.0‰) reported by Bao and Marchant (2006) to estimate the contributions of each source to the Shackleton Glacier region soils. We solved a three-component mixing model (Equations 3–5) for the fractions of SAS, SS, and TS comprising the observed SO42− isotopic composition. With the exception of one sample from Mt. Heekin, the SO42− in our samples appears predominately derived from an SAS source, followed by SS, and lastly TS (Table 6). In particular, the higher elevation and furthest inland locations, such as Schroeder Hill and Roberts Massif, have the highest contributions from SAS (>70%). These results are similar to those from high and inland locations in the MDV (Bao and Marchant, 2006). Though the isotopic composition of most samples can be explained by a combination of the three end members, our simple model was not sufficient for two Thanksgiving Valley samples and three additional samples from Mt. Heekin, Taylor Nunatak, and Schroeder Hill, probably due to unaccounted variability in the values for the SAS and TS end-members. As stated in section “Sulfide Weathering as a Source of SO42−,” the sulfide isotopic composition in terrestrial systems is highly variable, but the least constrained end-member is likely SAS.

$$\delta^{34}S_{\text{SO}_4} = f \cdot \delta^{34}S_{\text{SAS}} + f \cdot \delta^{34}S_{\text{SS}} \pm f \cdot \delta^{34}S_{\text{TS}} \quad (3)$$

$$\delta^{18}O_{\text{SO}_4} = f \cdot \delta^{18}O_{\text{SAS}} + f \cdot \delta^{18}O_{\text{SS}} \pm f \cdot \delta^{18}O_{\text{TS}} \quad (4)$$

$$f_{\text{SAS}} + f_{\text{SS}} + f_{\text{TS}} = 1 \quad (5)$$

SAS can have a large range of δ34S, δ18O, and Δ17O values due to differences in the initial source of S and the chemical composition of the oxidizing compounds. Sulfur gases in the atmosphere (SO2) are derived from volcanic emissions, DMS oxidation from the ocean, and anthropogenic emissions. The latter is thought to comprise the least important source for Antarctica. SO2 can be oxidized by both ozone and H2O2 to form SAS in the troposphere and stratosphere, where the oxygenic isotopic transfer is one oxygen (0.25) and two oxygen (0.5) of the total four oxygen atoms in SO42− for ozone and H2O2, respectively, which produces a positive Δ17O anomaly in SO42− and a wide range of δ18O values (Savarino et al., 2000; Uemura et al., 2010; Bao, 2015). Additionally, SAS can be produced in the stratosphere by photolysis of carbonyl sulfide (COS), the most abundant sulfur gas in the atmosphere, and by SO2 oxidation by OH radicals, which also produce positive Δ17O anomalies (Kunasek et al., 2010; Brühl et al., 2012). Though we could not determine the Δ17O composition of the Shackleton Glacier region SO42−, we suspect Δ17O would be positive and similar to the MDV and Beardmore Glacier region (Bao et al., 2000; Bao and Marchant, 2006; Sun et al., 2015). Future measurements

**Table 6** | Three-component mixing model to determine relative contributions of different sources of SO42−.

| Sample     | f(SAS) | f(SS) | f(TS) |
|------------|--------|-------|-------|
| AV2-1      | 0.73   | 0.25  | 0.03  |
| AV2-5      | 0.68   | 0.27  | 0.06  |
| AV2-8      | 0.58   | 0.33  | 0.19  |
| BP2-1      | 0.58   | 0.28  | 0.15  |
| BP2-8      | 0.48   | 0.33  | 0.19  |
| MH3-1      | 0.50   | 0.34  | 0.16  |
| MH3-5      | 0.34   | 0.39  | 0.27  |
| MH3-8      | 0.99   | 0.13  | −0.11*|
| NP3-4      | 0.58   | 0.35  | 0.07  |
| RM2-1      | 0.58   | 0.25  | 0.16  |
| RM2-5      | 0.59   | 0.27  | 0.13  |
| RM2-8      | 0.77   | 0.22  | 0.01  |
| SH3-2      | 1.03   | 0.06  | −0.08*|
| SH3-5      | 0.71   | 0.18  | 0.10  |
| SH3-8      | 0.65   | 0.24  | 0.10  |
| TGV2-1     | 1.02   | 0.06  | −0.07*|
| TGV2-5     | 0.97   | 0.23  | −0.20*|
| TN2-1      | 0.64   | 0.34  | 0.02  |
| TN2-5      | 0.64   | 0.31  | 0.05  |
| TN2-8      | 0.73   | 0.29  | −0.02*|

End-member values of δ34S and δ18O for non-sea salt secondary atmospheric sulfate (SAS) (12.0 and −16.0‰), sea salt sulfate (SS) (22 and 10‰), and terrestrial sulfate from sulfides (TS) (5 and −20‰) were originally reported by Bao and Marchant (2006). Negative values are indicated (*), which identify samples where the model parameters were insufficient.
of $\Delta^{17}$O in SO$_4^{2-}$ would provide additional evidence for SAS accumulation in CTAM soils.

Accumulation of Secondary Atmospheric Sulfate (SAS) and Wetting History

The relatively small variability in $\delta^{34}$S values indicates that the SO$_4^{2-}$ in the Shackleton Glacier region is derived from a common, large-scale source, such as the atmosphere. Additionally, when compared to the concentrations of SO$_4^{2-}$ in the water leaches, $\delta^{34}$S does not vary systematically indicating that the variability is not due to differences in source, but instead from varying accumulation periods (Figure 7b).

Though exposure ages have yet to be determined for these areas in the Shackleton Glacier region, modeling studies have shown that the height of the Shackleton Glacier was probably higher than current levels during the LGM (MacKintosh et al., 2011; Golledge et al., 2013), and likely inundated much of the currently ice-free areas near the Ross Ice Shelf. While these surfaces were inundated, some soils closer to the Polar Plateau may have been ice-free and would have accumulated salts from the atmospheric deposition of SAS. When the EAIS retreated in the late Pleistocene/early Holocene, the recently exposed soils could begin accumulating salts again. The small variations in $\delta^{34}$S values likely reflect isotopic changes of SAS through time due to changes in volcanic activity and DMS and/or MSA production, and changes in the concentrations of ozone, OH, COS, and H$_2$O$_2$ in the atmosphere, as reflected in the wide-range of values for Antarctic background sources in Figure 7a (Legrand et al., 1991; Bao, 2015). The variability in $\delta^{18}$O values is possibly due to the removal of $^{18}$O during atmospheric transport, changes in temperature, changes in the ocean isotopic composition during glacial and interglacial periods, and/or differences in the relative abundance of oxidizing atmospheric compounds. However, without the ability to decipher the difference between contemporary and paleo SO$_4^{2-}$ deposits, these mechanisms remain speculative.

Cryogenic Carbonate Mineral Formation and Isotope Equilibrium

Pedogenic carbonates in Antarctic soils are thought to be formed by authigenesis in the presence of liquid water. It is assumed that Ca$^{2+}$ ions for carbonate formation are derived from the weathering of Ca-rich aluminosilicate minerals, the dissolution of primary calcite within the soils, and/or calcium associated with aeolian dust (Lyons et al., 2020). In solution, carbonate minerals are precipitated during dissolved Ca-HCO$_3$/CO$_3$ saturation when the ion activity product is greater than the solubility product. In polar region soils, this typically occurs during evaporation/sublimation or cryoconcentration due to freezing of soil solutions or films (Courty et al., 1994; Vogt and Corte, 1996; Burgener et al., 2018).

The isotopic composition of HCO$_3$ + CO$_3$ in the Shackleton Glacier region bulk soil samples suggests that the carbonate is originally formed by cryogenic processes, such as rapid freezing and evaporation/sublimation, with possible kinetic isotope effects (KIE) (Figure 8). Previous studies have shown that the formation of authigenic calcite deposits is controlled by dissolved CO$_2$ concentrations and carbonate alkalinity of Ca-HCO$_3$ solutions (Nakai et al., 1975; Lacelle et al., 2006; Lacelle, 2007; Burgener et al., 2018). The $\delta^{13}$C and $\delta^{18}$O isotopic composition of carbonate minerals is dependent on the isotopic composition and temperature of the formation fluid when in equilibrium with both the fluid and atmosphere (Lacelle, 2007). Further, the $\delta^{18}$O isotopic composition of the fluid is influenced by evaporation/sublimation, which depletes the fluid of the lighter oxygen isotope, and freezing, which incorporates the heavier isotope in ice (Jouzel and Souchez, 1982). However, during rapid dehydration, freezing, and carbonate dissolution, KIE can result in temperature-independent fractionation and isotopically variable carbonate species (Clark and Lauriol, 1992; Skidmore et al., 2004; Burgener et al., 2018).

Previous studies have measured the isotopic composition of soil carbonate minerals from the MDV and have elucidated the formation mechanisms for cryogenic carbonates (see Lacelle, 2007). In summary, isotopic values of soil carbonate in Taylor and Victoria Valleys in the MDV ranged from 6.73 to 11.02‰ for $\delta^{13}$C and −8.13 to −20.34‰ for $\delta^{18}$O (VPDB) (Burgener et al., 2018; Lyons et al., 2020). Nakai et al. (1975) measured $\delta^{13}$C and $\delta^{18}$O of carbonate coatings on rocks in the Lake Vanda Basin, MDV, and their $\delta^{13}$C values ranged from 1.5 to 17.6‰ while their $\delta^{18}$O ranged from −9.2 to −31.2‰ (VPDB). Lacelle (2007) argued that the Lake Vanda basin carbonates were cryogenic in
origin, forming from bicarbonate dehydration and subsequent CO₂ degassing in isotopic disequilibrium. Disequilibrium during rapid evaporation/sublimation or freezing results in more positive δ¹³C and δ¹⁸O values relative to equilibrium carbonate formation (Clark and Lauriol, 1992; Lacelle et al., 2007). Using a clumped isotope method, Burgener et al. (2018) arrived at similar conclusions regarding disequilibrium during carbonate formation. The authors suggested that negative Δ₄₇ (notation from clumped isotopes of mass 47) with positive δ¹⁸O anomalies, and positive δ¹³C values with respect to equilibrium were consistent with cryogenic calcite formation and KIE from CO₂ degassing during bicarbonate dehydration. Additionally, δ¹³C values from Taylor Valley carbonates, which were sampled as mineral coatings on rocks, were near 7.4‰ indicating an atmospheric origin of CO₂ (Lyons et al., 2020), and were similar to the values reported by Burgener et al. (2018).

The Shackleton samples are generally within the range of δ¹³C for cryogenic carbonate in equilibrium with the atmosphere (Figure 8) (Lacelle et al., 2006; Lacelle, 2007). Since we collected surface samples (up to 5 cm at depth), the carbonates were formed under conditions allowing for rapid exchange of CO₂. However, some samples have lower δ¹⁸O values, possibly due to KIE, and rapid freezing and evaporation/sublimation. As stated previously, the formation of carbonate minerals in soils from rapid evaporation/sublimation of glacial meltwater results in a relatively heavier δ¹⁸O signature compared to the ice isotopic composition (Lacelle et al., 2006; Lyons et al., 2020). While the isotopic composition of ice in the Shackleton Glacier region is unknown, due to its distance inland, we expect δ¹³C values ~ -45‰ (Mayewski et al., 1990; Gooseff et al., 2006). Evaporation/sublimation carbonate formation from this water may explain the relatively more positive δ¹⁸O values in the Shackleton soils compared to glacial ice. Most of our data can be explained by these mechanisms, but one sample from Bennett Platform and a second from Mt. Heekin have highly negative δ¹⁸O values, and the Bennett Platform sample is the only sample we measured with a negative δ¹³C value (Figure 8). These outliers demonstrate the need for more geochemical data from CTAM ice-free areas to definitively elucidate carbonate formation and kinetics in ice-free Antarctic environments.

CONCLUSION

Ice-free areas from the Shackleton Glacier region, Antarctica represent polar desert environments that have been modified throughout the Cenozoic, which is reflected in the variable salt geochemistry. Along a transect moving inland and up in elevation along the Shackleton Glacier toward the Polar Plateau, water-soluble salt concentrations increased, and the dominant salt species also changed. Near the Ross Ice Shelf, Cl⁻ was the dominant salt, while NO₃⁻ and SO₄²⁻ were more abundant further inland. High NO₃⁻ and SO₄²⁻ concentrations are likely associated with soda niter (NaNO₃), anhydrite or gypsum (CaSO₄ or CaSO₄ · 2H₂O), epsomite (MgSO₄ · 7H₂O), thenardite or mirabilite (Na₂SO₄ or Na₂SO₄ · 10H₂O) and glauberite (Na₂Ca(SO₄)₂). We also identified abundant Na–Mg–SO₄ salts at Schroeder Hill, potentially bloedite.

The δ¹⁵N and Δ¹⁷O isotopic composition of NO₃⁻ indicated that NO₃⁻ is primarily derived from the atmosphere, with varying contributions from the troposphere (0–70%) and stratosphere (30–100%). Neither δ¹⁵N nor Δ¹⁷O exhibited trends with elevation, distance from the coast of the Ross Ice Shelf, or distance from the glacier. We argue that post-depositional alteration of NO₃⁻, potentially due to photolysis or volatilization, likely occurs in CTAM soils and possibly explains the variability in the NO₃⁻ isotopic composition. However, the occurrence and degree of soil photolysis of NO₃⁻ is unknown and requires further investigation.

Results from a three-component mixing model suggested that SO₄²⁻ in Shackleton Glacier region soils was predominately deposited as secondary atmospheric sulfate (SAS) and derived from the oxidation of SO₂, H₂S, and/or dimethyl sulfide by H₂O₂, COS, and ozone in the atmosphere. While there is evidence to suggest that some SO₄²⁻ was produced by the weathering of pyrite and other sulfide minerals, the atmospheric source was likely much more important, especially in soils which have been exposed for prolonged periods at higher elevations and near the Polar Plateau.

While SO₄²⁻ and NO₃⁻ were primarily derived from atmospheric deposition, carbonate minerals were formed at the surface as cryogenic carbonate. Based on the δ¹³C and δ¹⁸O values of soil total inorganic carbon (TIC), we conclude that both equilibrium and disequilibrium occur through slow and rapid evaporation/sublimation or freezing of fluids. Disequilibrium between the fluid and the precipitated carbonate resulted in the negative δ¹⁸O values observed due to bicarbonate dehydration.

Our analysis and interpretation of the isotopic composition of NO₃⁻, SO₄²⁻, and HCO₃⁻ + CO₃²⁻ show that atmospheric deposition and chemical weathering at the soil surface are important for salt formation in Antarctica. While NO₃⁻ and SO₄²⁻ are both oxyanions and thought to maintain their isotopic composition post-deposition, post-depositional processes, such as volatilization and photolysis, may alter both N and O in NO₃⁻, while SO₄²⁻ appears less affected by these processes. As a result, the isotopic composition of NO₃⁻ can potentially be used to constrain NO₃⁻ recycling in soils, SO₄²⁻ can be used as an indicator of past atmospheric oxidation processes, and carbonate can be used to understand current and past availability of water. We suggest that similar processes likely occur(ed) for other hyper-arid environments in the CTAM and Mars.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/Supplementary Material.

AUTHOR CONTRIBUTIONS

BA, DW, IH, NF, and WL designed and funded the project. BA, DW, IH, NF, and MD conducted the fieldwork. JL, GM, and MD analyzed the samples for N and O isotope ratios in nitrate. MD
prepared the samples for S and O isotopic analysis in sulfate. TD and MD analyzed the samples for C and O isotope ratios in carbonate. SW, CG, and MD analyzed the samples for water-soluble ions. MD wrote the manuscript with contributions and edits from all authors. All authors contributed to the article and approved the submitted version.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2020.00341/full#supplementary-material

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