Deposition, accumulation, and alteration of Cl⁻, NO₃⁻, ClO₄⁻ and ClO₃⁻ salts in a hyper-arid polar environment: mass balance and isotopic constraints

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Abstract

The salt fraction in permafrost soils of the McMurdo Dry Valleys (MDV) of Antarctica can be used as a proxy for cold desert geochemical processes and paleoclimate reconstruction. Previous analyses of the salt fraction in permafrost soils have largely been conducted in coastal regions where permafrost soils are variably affected by aqueous processes and mixed inputs from marine and stratospheric sources. We expand upon this work by evaluating permafrost soils in University Valley, located in the ultrarxerous zone where both liquid water transport and marine influences are minimal. We determined the abundances of Cl\(^{-}\), NO\(_3\)\(^{-}\), ClO\(_4\)\(^{-}\) and ClO\(_3\)\(^{-}\) in dry and ice-bearing permafrost soils, snow and glacier ice, and also characterized Cl\(^{-}\) and NO\(_3\)\(^{-}\) isotopically. The data are not consistent with salt deposition in a sublimation till, nor with nuclear weapon testing fall-out, and instead point to a dominantly stratospheric source and to varying degrees of post depositional transformation depending on the substrate, from minimal alteration in bare soils to significant alteration (photodegradation and/or volatilization) in snow and glacier ice. Ionic abundances in the dry permafrost layer indicate limited vertical transport under the current climate conditions, likely due to percolation of snowmelt. Subtle changes in ClO\(_4\)\(^{-}\)/NO\(_3\)\(^{-}\) ratios and NO\(_3\)\(^{-}\) isotopic composition with depth and location may reflect both transport related fractionation and depositional history. Low molar ratios of ClO\(_3\)\(^{-}\)/ClO\(_4\)\(^{-}\) in surface soils compared to deposition and other arid systems suggest significant post depositional loss of ClO\(_3\)\(^{-}\), possibly due to reduction by iron minerals, which may have important implications for oxy-chlorine species on Mars. Salt accumulation varies with distance along the valley and apparent accumulation times based on multiple methods range from ~10-30 ky near the glacier to 70-200 ky near the valley mouth. The relatively young age of the salts and relatively low and homogeneous anion concentrations in the ice-bearing permafrost soils point to either a mechanism of recent salt removal, or to relatively modern permafrost soils (< 1 million years). Together, our results show that near surface salts in University Valley serve as an end-member of stratospheric sources not subject to biological processes or extensive remobilization.

1.0 Introduction

The McMurdo Dry Valleys (MDV) of Antarctica are collectively a hyper-arid polar desert environment, but a steep gradient in summer air temperature and water activity exists between the coastal areas and the high elevation valleys (Marchant and Head, 2007). The latter are the
driest, coldest, and oldest in the MDV system (Marchant et al., 2002; Marchant and Head, 2007),
and contain various types of ground ice, ranging from pore ice to massive ground ice bodies
under a layer of dry regolith of variable thickness (Bockheim, 1995; Bockheim and Hall, 2002;
Bockheim, 2007; Bockheim, et al., 2008; Pollard et al., 2012; Lacelle et al., 2011). This upland
region does not develop the same pattern of seasonal active layer as observed in coastal
Antarctica or in Arctic regions (Marchant and Head, 2007). Furthermore, some studies suggest
that the extremely cold climate in the high elevation MDV has dominated for the past 12.5 Ma,
and liquid water has played a negligible role in landscape evolution (e.g., Denton et al., 1971,
1984; Sugden et al., 1995; Marchant et al., 1996; 2013; Swanger et al., 2011). However, recent
investigations suggest that ice-bearing permafrost might have partially thawed during warmer
climate periods in the Quaternary, at least locally (e.g., Dickinson et al., 2012; Lacelle et al.,
2013).

Salts in MDV soils and lakes have been extensively studied (e.g. Bockheim, 1979, 1997;
Campbell and Claridge, 1977; Toner et al., 2013; Kounaves et al., 2010). The abundance and
isotopic composition of anions have been used to evaluate source(s) of anions and their degree
and type of post depositional processing, as well as their implications for paleoenvironmental
conditions (Bao and Marchant, 2006; Bao et al., 2008; Michalski et al., 2005). Chloride has both
direct marine (past flooding events during periods of higher sea level) and atmospheric sources
in the lower MDV while Cl\(^-\) in the upper MDV is due solely to atmospheric deposition (e.g.
Toner et al., 2013). The atmospheric Cl\(^-\) component includes both sea-salt chloride (SSC) and
secondary atmospheric chloride (SAC) with decreasing SSC content away from the coast (Bao et
al., 2008). The soil anion reservoir can include both atmospheric salts deposited directly on the
soil surface and older buried salts released by sublimation of buried glacier ice in sublation
tills. NO\(_3\)\(^-\) is relatively enriched with respect to Cl\(^-\) in the upper MDV due to the ultra-xerous
conditions that allow it to accumulate in surface soils and decreased marine salt deposition flux
(Bockheim, 1997). The isotopic composition of NO\(_3\)\(^-\) in deposition of snow and glacial ice has
been extensively studied, particularly with respect to post depositional processing (e.g. Grannas
et al., 2007; Frey et al., 2009). However, the soil isotopic composition of NO\(_3\)\(^-\) in the MDV has
only been surveyed once (Michalski et al., 2005). ClO\(_4\)\(^-\) has also recently been identified in MDV
soils and is generally enriched with respect to NO\(_3\)\(^-\) compared to less arid systems (Kounaves et
Salt reservoirs in MDV soils have been interpreted to contain substantial information about salt sources and post depositional processes that occur in the MDV, and therefore indirectly about paleoclimatic conditions that led to their current abundance and isotopic composition. However, studies that evaluated both the abundances and isotopic compositions of multiple anions concurrently have been limited.

To gain further insights regarding the source(s), deposition, and chemical and hydrologic alterations of salts in cold hyper-arid systems, we investigated the salt fraction in soils from University Valley, a high elevation glacial valley hanging approximately 400 m above the floor of Beacon Valley, in the Quartermain Mountains. An objective of this study was to use the accumulated salts in these soils to evaluate the paleo-environmental conditions responsible for their distribution and isotopic composition. We combined data on the abundance of Cl\(^-\), NO\(_3^-\), ClO\(_4^-\) and ClO\(_3^-\) in soils, snow and glacial ice, with isotopic measurements of Cl\(^-\), NO\(_3^-\), and ClO\(_4^-\). Our results provide insights regarding the atmospheric deposition of salts and volatile species and their post depositional transformations and transport in soils, snow, and glacial ice. These findings have direct relevance to our understanding of the potential for past episodes of liquid water activity and contribute to a better understanding of the glacial history of the valley.

Salt accumulation in University Valley serves as a model of atmospheric salt dynamics in soils not subject to biological processes. These accumulations have potential relevance for the occurrences of NO\(_3^-\) (Stern et al. 2015) and ClO\(_4^-\) (Hecht et al. 2009) on Mars and the implications for past habitability on that planet, which can be used as a basis for better interpretations of more complex biologically active arid systems.

### 2.0 Sampling and Methods

#### 2.1 Site Description

The study site is situated in University Valley (77°52’S; 160°45’E; c.a. 2000 m long, 500-700 m wide and 1600-1800 m a.s.l.), a hanging glacial valley perched above Beacon Valley in the Quartermain Mountains (Fig. 1). A small glacier is present at the head of University Valley (henceforth named University Glacier) and a few perennial snow patches occupy small circular depressions, 1-2m deep, on the western side of the valley. Widespread interstitial ground ice occurs as part of the permafrost system beneath a layer of dry soil; the depth to the contact
between this horizon (also known as the ice table) generally increases in a down valley direction (McKay 2009; Marinova et al., 2013). The mean annual air temperature recorded during 2010-2012 was -24°C and at no time does the maximum hourly air temperature rise above 0°C (Lacelle et al., 2013). Based on measured ground temperatures and modeled incoming solar radiation the valley can be divided into two zones based on ground surface temperatures: i) a perennially cryotic zone characterized by ground surface temperatures continuously below 0ºC linked to higher topographic shadowing; and ii) a seasonally non-cryotic zone where ground surface temperatures >0°C occur for up to a few hours on clear summer days (Lacelle et al., 2015).

Surficial sediments consist of a combination of colluvium and talus cones at the base of the valley walls and undifferentiated alpine drifts and an undifferentiated till on the valley floor (Cox et al., 2012). The alpine drift is restricted to the upper and central parts of the valley and likely is correlated with the Alpine A and B drifts in adjacent Arena Valley, dated to > 200ka and >1Ma, respectively (Marchant et al., 1993). This interpretation fits the optically stimulated luminescence ages obtained from a 95 cm permafrost core in upper University Valley (Lacelle et al., 2013). The undifferentiated till, constrained to the lower part of the valley, contains granite erratics and is likely associated with Taylor 4b Drift (>2.7Ma) or an older glaciation (Cox et al., 2012).

2.2 Sampling

All soil, ice, snow, and atmospheric deposition samples were obtained during three field seasons (2009, 2010, and 2012). Five vertical soil profiles were collected for geochemical analyses along the main axis of the valley, starting at a distance of 370 m from University Glacier and extending 1980 m down valley (Figure 1). Vertical soil profiles were obtained by digging a trench and sampling its walls, whereas samples of ice-cemented permafrost were obtained using a SIPRE (Snow, Ice and Permafrost Research Establishment) corer. The vertical profile closest to University Glacier (370 m, 2 cm ice table depth) was obtained as a 65 cm long core of ice-cemented permafrost, and two vertical profiles (720 m and 1100 m distance from University Glacier) included a layer of dry soil as well as the underlying ice-cemented permafrost (Figure 1). The vertical profiles obtained at 1200 m and 1940 m from University Valley were composed
solely of dry soils and the depth to the ice table was unknown (>40 and >66 cm, respectively). In addition to the profiles, a set of near-surface composite samples of the dry soil layer were collected along a transect from the edge of University Glacier to a distance of 1300 m down valley at 100 m increments. The transect samples (T1-T13) were collected from the surface down to the ice table or to a maximum depth of 20 cm and homogenized prior to subsampling for analysis. In addition, we collected a 1.2 m long core from University Glacier and a 1.0 m core from a perennial snow patch located ~600 m down valley from University Glacier. Samples of fresh snow were also collected during snowfall events in the austral summers of 2010 and 2012. Long-term total atmospheric deposition was collected in a PVC stand pipe (~10 cm diameter and ~1 m above the ground surface) lined with a plastic zip-lock bag. The total atmospheric deposition sampler was deployed in November of 2010 and retrieved in January of 2012. We also evaluated aerosols collected in lower Taylor Valley (2013). Aerosols were sampled by pulling air through filter cartridges containing 25 mm GF/F filters (Whatman 45). The vacuum pump had initial air flow rate of 18 L/min with a filter cartridge attached. Sampling time varied between 3 and 7 days.

2.3 Geochemical analyses
Salts in soil samples were extracted in milli-Q water at water:soil ratios between 5:1 and 10:1 by mass. The extracts were centrifuged for 10 minutes, after which the supernatant water was decanted and filtered (0.2 µm). Ice-bearing samples were sliced frozen into ~2 cm sections. Each section was allowed to thaw after which additional milli-Q water was added and the salts extracted as above. The mass of soil was measured after drying at 105°C. Salt concentrations for all soil samples are expressed as mass/mass of dry soil. All analyzed salts had concentrations less than 10 % of saturation values in the aqueous extracts.

Soil extracts, snow samples, and glacier ice were analyzed for Cl⁻, NO₃⁻ (reported as NO₃-N), ClO₄⁻, and ClO₃⁻ concentrations as described in Jackson et al. (2015). Briefly, ClO₄⁻ and ClO₃⁻ were quantified using an ion chromatograph-tandem mass spectrometry technique (IC-MS/MS) that consisted of a GP50 pump, CD25 conductivity detector, AS40 automated sampler and Dionex IonPac AS20 (250 X 2 mm) analytical column. The IC system was coupled with an Applied Biosystems – MDS SCIEX API 2000™ triple quadrupole mass spectrometer equipped
with a Turbo-IonSpray™ source (Rao et al., 2010; Jackson et al., 2015). To overcome matrix
effects, all samples were spiked with an oxygen-isotope (\(^{18}\)O) labeled ClO\(_4^-\) or ClO\(_3^-\) internal
standard. Chloride and NO\(_3^-\) were analyzed following EPA Method 300.0 using a Dionex LC20,
an IonPac AS14A column (4 X 250 mm), and an Anion Atlas electrolytic suppressor. Individual
sample quantification limits were based on the final dilution of the sample extract. Analytical
uncertainty of all anion measurements is less than ±10% of the measured value.

2.4 Stable isotopes

Subsets of the soil, snow, and ice samples were analyzed for NO\(_3^-\) stable isotopic composition.
\(\delta^{15}\)N and \(\delta^{18}\)O in NO\(_3^-\) were measured by continuous-flow isotope-ratio mass spectrometry on
N\(_2\)O produced from NO\(_3^-\) by bacterial reduction (Sigman et al., 2001; Casciotti et al., 2002;
Coplen et al., 2004). The data were calibrated by analyzing NO\(_3^-\) isotopic reference materials
using published values (Böhlke et al., 2003). For samples with elevated \(\Delta^{17}\)O of NO\(_3^-\), \(\delta^{15}\)N
values determined by the bacterial N\(_2\)O method using conventional normalization equations may
be slightly higher than the true values (Sigman et al., 2001; Böhlke et al., 2003; Coplen et al.,
2004). \(\delta^{15}\)N values reported here were not adjusted for this effect because \(\Delta^{17}\)O values were not
measured in these samples. True \(\delta^{15}\)N values were estimated to be approximately 0.7 to 1.6 ‰
lower than reported values, based on analyses of reference materials and reported correlations
between \(\delta^{18}\)O and \(\Delta^{17}\)O of atmospheric NO\(_3^-\) in Antarctica and elsewhere (Michalski et al., 2003,
2005; Savarino et al., 2007).

Chlorine isotope ratios in Cl\(^-\) were analyzed for a subset of soil, snow, and ice samples. The Cl\(^-\)
was precipitated as AgCl and converted to CH\(_3\)Cl for IRMS analysis of \(\delta^{37}\)Cl (Long et al., 1993)
at the Environmental Isotope Geochemistry Laboratory, University of Illinois at Chicago. \(^{36}\)Cl
abundances in purified Cl\(^-\) samples were measured by accelerator mass spectrometry at the
Purdue Rare Isotope Measurement Lab (Sharma et al., 2000). Tritium (%H) concentrations were
measured in selected core samples from the permanent snow patch and University Glacier.
Samples were prepared by mixing 10 ml of melted snow/ice sample with an equal amount of
Ultragold scintillation cocktail. A PerkinElmer Quantulus 1220 liquid scintillation counter was
used to measure \(^3\)H concentrations in the samples with a detection limit of 1.0 Bq/L (8 TU).
Stable isotope ratios (Cl and O) and $^{36}\text{Cl}/\text{Cl}$ ratios were analyzed for one sample of $\text{ClO}_4^-$ separated from bulk soil (5-15cm) obtained near the soil profiles collected at 720m and 750m. The bulk soil (~50kg) was leached using DDI water and loaded onto a bi-functional anion-exchange resin (Gu et al., 2011). Details of $\text{ClO}_4^-$ extraction, purification, and analysis methods for $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $^{36}\text{Cl}/\text{Cl}$ have been described previously (Gu et al., 2011; Hatzinger et al., 2011). Extraction and purification produced Cs$\text{ClO}_4$ salt, which was decomposed to CsCl and O$_2$. The O$_2$ was analyzed for oxygen isotope ratios ($\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) by isotope-ratio mass spectrometry (IRMS). The CsCl was then converted to AgCl and analyzed for $\delta^{37}\text{Cl}$ and $^{36}\text{Cl}$ as described above.

2.5 Estimation of salt accumulation times

The total masses of Cl$^-$ and NO$_3^-$ per unit area were estimated from the integrated concentrations down to the maximum depth sampled (Figure 2) using a dry soil bulk density of 1,600 kg/m$^3$. Concentrations were linearly interpolated between dry soil discrete sample depths. The calculated masses per unit area were then divided by various deposition measurements as described below.

$^{36}\text{Cl}$ accumulation times were estimated using the following equation:

$$\text{Accumulation Time} = \sum\text{Cl}/\text{Cl}_{\text{MW}} \times 6.023 \times 10^{23} \times R_u / D_{36\text{Cl}}$$

Where $\sum\text{Cl}$ is the total Cl$^-$ mass to a given depth per m$^2$, $\text{Cl}_{\text{MW}}$ is the molecular weight of Cl$^-$, $R_u$ is the $^{36}\text{Cl}/\text{Cl}$ ratio of Cl$^-$ in soils in University Valley, and $D_{36\text{Cl}}$ is the deposition rate of $^{36}\text{Cl}$. The $^{36}\text{Cl}$ deposition rate (28,000 atoms/cm$^2$-year) was based on $^{36}\text{Cl}$ deposition rates in Dome Fuji for 10 kyr B.P. and 22 kyr B.P. (Sasa et al., 2010). The Dome Fuji deposition rates were similar for both time periods evaluated and regardless of the snow accumulation rate, which changed between the LGM and the Holocene by a factor of ~2.4 (Table 1). The Dome Fuji deposition rates match well with other published rates estimated from latitude-dependent modeling (25,000 ±1,600 atoms/cm$^2$-year) (Synal et al., 1990). The $^{36}\text{Cl}/\text{Cl}$ ratios of Cl$^-$ in University Valley were fairly constant with depth and between locations, reducing the error imparted by the relatively low number of measured $^{36}\text{Cl}/\text{Cl}$ ratios.

Total Cl$^-$ accumulation times were estimated using the following equation:
Accumulation Time = \sum Cl / D_{Cl}

Where D_{Cl} is equal to the deposition rate of Cl\(^-\). We evaluated three different methods for evaluating D_{Cl}: 1) the maximum and minimum Cl\(^-\) deposition rates for low-accumulation glaciers in the MDV, based on snow pits that generally represent deposition since 1948 (Witherow et al., 2006); 2) the measured total Cl\(^-\) deposition rate in University Valley measured in this study over a two year period (2010-2012); and 3) the Cl\(^-\) deposition rate for Dome Fuji, adjusted for the larger fraction of non-stratospheric (e.g., marine) Cl\(^-\) deposition at University Valley, based on the apparent dilution of \(^{36}\)Cl/Cl ratios. The adjusted Dome Fuji deposition rate (D_{Cl-FA}) that was calculated using the following equation:

\[ D_{Cl-FA} = D_{Cl-F} * R_f/R_u \]

where D_{Cl-F} is equal to the Cl\(^-\) deposition rate measured at Dome Fuji, and R_u and R_f are the \(^{36}\)Cl/Cl ratios of Cl\(^-\) at Dome Fuji and University Valley, respectively.

\(^{NO_3^-}\) accumulation times were estimated using a modified version of Equation 2. \(^{NO_3^-}\) deposition rates (Table 2) were based on the following reported or measured values: 1) the range reported for low-accumulation MDV glaciers (Witherow et al., 2006); 2) the relation between snow and \(^{NO_3^-}\) accumulation developed by Traversi et al. (2012) assuming dry deposition only (no contribution from snow), and a maximum snow deposition rate of 10 cm/year, which should serve as an upper bound given the limited snow fall in Upper MDV valleys (Fountain et al., 1999); and 3) measured total \(^{NO_3^-}\) deposition in University Valley (2010-2012) from this study.

3.0 Results

3.1 Concentration and distribution of Cl\(^-\), \(^{NO_3^-}\), \(^{ClO_4^-}\) and \(^{ClO_3^-}\) salts

Chloride and \(^{NO_3^-}\) concentrations ranged between 10 and 1,000 mg/kg of dry soil mass, whereas \(^{ClO_4^-}\) and \(^{ClO_3^-}\) concentrations were in the \(\mu\)g/kg range. In all vertical dry soil profiles, anion concentrations generally peaked between 5 and 15 cm depth and then decreased downward toward the ice table (where present) (Figure 2). Concentrations of all soluble ions decreased by a factor of \(~2\) immediately below the ice table and remained constant with depth within the ice-cemented permafrost. Concentrations varied between vertical soil profiles by a factor of 2 to 4, even at decameter scales. \(^{NO_3^-}\) was significantly correlated with \(^{ClO_4^-}\) (p<0.05) in all depth
profiles. Cl' was significantly correlated with NO_3^- and ClO_4^-, except in the profile at 1200 m (Jackson et al., 2015). Soluble ion concentrations in glacier ice and perennial snow were comparable to those in fresh snow, approximately 1000 times lower than in soils, and relatively constant with depth, except in the case of ClO_4^-, which was more variable (Figure 3).

In general, the total mass of Cl', NO_3^-, and ClO_4^- salts per unit area increased with distance from University Glacier for any given depth sampled (Figure 4A, B and Table 1 and 2). Dry soils contained the majority (>70%) of the total mass of anions, with the exception of the profile closest to University Glacier that was composed entirely of ice-cemented sediment. The rate of mass increase with distance from University Glacier was nearly constant for Cl' and NO_3^-, while the rate of mass increase for ClO_4^- decreased with distance down valley (Figure 4B).

3.2 Variations in ratios of measured anions with respect to location and deposition.

NO_3^-/Cl' and NO_3^-/ClO_4^- ratios decreased with depth in the dry soils by 40-60% compared to the peak ratio at the concentration maximum at or near the surface (Figure 5 and S1) but were constant with depth in the underlying ice-bearing soil. No such trends with depth were observed for Cl'/ClO_4^- in dry soils. NO_3^-/ClO_4^- and Cl'/ClO_4^- but not NO_3^-/Cl ratios increased with distance from University Glacier (Figure 6). Molar ratios (NO_3^-/ClO_4^-, NO_3^-/Cl', Cl'/ClO_4^-, and ClO_3^-/ClO_4^-) in fresh snow were higher than in total deposition or in aerosols suggesting enrichment of ClO_4^- in dry deposition compared to wet deposition, which is supported by the enrichment in ClO_4^- of aerosols. NO_3^-/ClO_4^- and Cl'/ClO_4^- ratios of glacier ice and snow pack were generally higher than in total deposition and highly variable exceeding the upper range of fresh snow and total variation in dry soil and ice-bearing soil (Figure 6). NO_3^-/ClO_4^- and Cl'/ClO_4^- ratios in ice bearing soil were bracketed by ratios in fresh snow. Cl'/ClO_4^- ratios in dry soils were also bracketed by values in fresh snow but NO_3^-/ClO_4^- ratios in dry soil generally exceeded those in fresh snow. NO_3^-/Cl' ratios in fresh snow were lower than in total deposition but generally encompassed most soil, snow pack, and glacier ice ratios. Lowest NO_3^-/Cl' ratios were in glacier ice and snow pack and highest ratios in dry soil. ClO_3^-/ClO_4^- ratios in dry soils and ice-bearing soils were highly variable but consistently lower than all deposition types, snow packs or glacier ice.

3.3 NO_3^- isotopic composition
δ\textsuperscript{15}N and δ\textsuperscript{18}O values of NO\textsubscript{3}\textsuperscript{−} (NO\textsubscript{3}-δ\textsuperscript{15}N and NO\textsubscript{3}-δ\textsuperscript{18}O) in dry soils, ice-cemented permafrost soils, glacier ice and perennial snow patches were within the range of values reported previously for various NO\textsubscript{3}\textsuperscript{−} occurrences in Antarctica (Figure 7). Our δ\textsuperscript{18}O values (+76 to +84 ‰) overlapped with, but were generally more positive than those reported for other MDV soils (Beacon, Wright, Arena, Mt. Fleming), whereas δ\textsuperscript{15}N values were similar to those reported for other MDV soils (Michalski et al., 2005). Snow pack and glacier ice had similar NO\textsubscript{3}\textsuperscript{−} isotopic compositions, and both had lower δ\textsuperscript{18}O values and higher δ\textsuperscript{15}N values than soils (Figure 7). Fresh snow and total deposition had δ\textsuperscript{15}N values similar to soils but lower than perennial snow and glacier ice, and δ\textsuperscript{18}O values higher than snow pack and glacier ice but lower than soils. Compared with previously reported snow values from a traverse on the Polar plateau between Dome C and Dumont d’Urville stations (Frey et al., 2009), soils from University Valley had relatively low δ\textsuperscript{15}N values and high δ\textsuperscript{18}O values that were most similar to snow samples collected near the coast. The NO\textsubscript{3}\textsuperscript{−} isotopic composition in the dry soil was comparable to aerosols from Dome C and Dumont d’Urville, and near the seasonal mass-averaged aerosol values for Dumont d’Urville (Savarino et al., 2007, Frey et al., 2009).

There were small but systematic variations in NO\textsubscript{3}-δ\textsuperscript{15}N and NO\textsubscript{3}-δ\textsuperscript{18}O within and between vertical soil profiles (Figure 7, inset). Within each soil profile, NO\textsubscript{3}-δ\textsuperscript{15}N and NO\textsubscript{3}-δ\textsuperscript{18}O values were significantly positively correlated (p<0.05) and slopes were similar for 3 of the 5 profiles (Table S1). In contrast, NO\textsubscript{3}-δ\textsuperscript{15}N and NO\textsubscript{3}-δ\textsuperscript{18}O values of transect soil samples were significantly inversely correlated. In soil profiles, NO\textsubscript{3}-δ\textsuperscript{15}N and NO\textsubscript{3}-δ\textsuperscript{18}O generally decreased with depth, although the overall change in magnitude was small (<2 ‰) (Figure 8). The highest NO\textsubscript{3}-δ\textsuperscript{15}N and NO\textsubscript{3}-δ\textsuperscript{18}O values generally coincided with the peak concentration of NO\textsubscript{3}\textsuperscript{−} in dry soil at or near the ground surface. Isotopic trends in the ice-bearing soils were more variable between profiles. In one profile (750 m) NO\textsubscript{3}-δ\textsuperscript{18}O values decreased with depth below the ice table, while NO\textsubscript{3}-δ\textsuperscript{15}N reached a minimum value at ice table. In another profile (1100 m) NO\textsubscript{3}-δ\textsuperscript{18}O values were relatively constant below the ice table, while NO\textsubscript{3}-δ\textsuperscript{15}N showed an increase (~1 ‰ within 1 cm) at the ice table, and decreased with depth.

There was a strong correlation between NO\textsubscript{3}-δ\textsuperscript{18}O and NO\textsubscript{3}-δ\textsuperscript{15}N values in dry soils and distance down valley from University Glacier (p=0.005 for NO\textsubscript{3}-δ\textsuperscript{18}O and <0.001 for NO\textsubscript{3}-δ\textsuperscript{15}N) (Figure 6.
and Table S1). The correlation was positive in the case of \( \text{NO}_3^\text{-d}^{18}\text{O} \) and negative in the case of \( \text{NO}_3^\text{-d}^{15}\text{N} \). Spatial variations in average \( \text{NO}_3^\text{-d}^{18}\text{O} \) and \( \text{NO}_3^\text{-d}^{15}\text{N} \) values between soil profiles were approximately 5 % and 4 %, respectively; these were larger than the variations with depth in each profile. Variations of \( \text{NO}_3^- \) stable isotopic composition in dry soils generally were directly related to measures of \( \text{NO}_3^- \) abundance (Figure 9 and Table S1). \( \text{NO}_3^\text{-d}^{18}\text{O} \) values within soil profiles, transect samples, and for all data were negatively correlated to \( 1/\text{NO}_3^- \)

concentrations and to \( \text{Cl}/\text{NO}_3^- \) and \( \text{ClO}_4^-/\text{NO}_3^- \) molar ratios. For the profiles there were generally consistent relationships between isotope ratios and each of the indicators of \( \text{NO}_3^- \) stability; relations with \( \text{ClO}_4^-/\text{NO}_3^- \) ratios were the most consistent. \( \text{d}^{15}\text{N} \) values of soil profiles were not as consistently related to \( \text{NO}_3^- \) concentrations (\( 1/\text{NO}_3^- \)) but generally were significantly negatively correlated to both \( \text{Cl}/\text{NO}_3^- \) and \( \text{ClO}_4^-/\text{NO}_3^- \) molar ratios (Figure 9). It should be noted that while \( \text{NO}_3^\text{-d}^{15}\text{N} \) values of transect samples were significantly correlated to both \( 1/\text{NO}_3^- \) and \( \text{ClO}_4^-/\text{NO}_3^- \) molar ratios, the slopes of these relationships were of opposite sign compared to those of individual profiles, pointing to at least two distinct processes affecting \( \text{NO}_3^- \) isotope composition in the dry soils (see Discussion). Variations with depth in soil profiles (increasing \( \text{d}^{15}\text{N} \) and \( \text{d}^{18}\text{O} \) with decreasing relative \( \text{NO}_3^- \) abundance) could be consistent with isotopic fractionation or mixing, whereas spatial variations along the valley floor (increasing \( \text{d}^{18}\text{O} \) with decreasing \( \text{d}^{15}\text{N} \) and relative \( \text{NO}_3^- \) abundance) may indicate different sources or depositional environments. Finally, perennial snow and glacier ice had similar \( \text{NO}_3^- \) isotopic compositions, with lower \( \text{d}^{18}\text{O} \) values and higher \( \text{d}^{15}\text{N} \) values than soils (Figure 7). The trend was reversed with respect to fresh snow and total atmospheric deposition, the latter being depleted in \( \text{d}^{15}\text{N} \) but enriched in \( \text{d}^{18}\text{O} \).

3.4 Cl isotopic composition

\( \text{d}^{37}\text{Cl} \) values of Cl (Cl-\( \text{d}^{37}\text{Cl} \)) in soils ranged from -3.0 % to -1.3 %, generally lower than those reported by Bao et al. (2008) for soils throughout the MDV including Beacon Valley. In the dry soil profiles, Cl-\( \text{d}^{37}\text{Cl} \) values were generally lowest at the surface and increased by ~1 % immediately below the surface and then were constant with depth both in the dry soil and into the underlying ice-cemented permafrost (Figure 10). Only in the profile closest to University Glacier, composed solely of ice-cemented permafrost, did values of Cl-\( \text{d}^{37}\text{Cl} \) decrease with depth (by <1 % over 60 cm). Cl-\( \text{d}^{37}\text{Cl} \) values in soil samples were lower by ~1-2 % than in the snow pack or glacier ice.
The $^{36}\text{Cl}/\text{Cl}$ ratios of Cl$^-$ in soils from University Valley (1800 x $10^{15}$ to 2400 x$10^{15}$) were higher than those reported for other MDV soils (400 x $10^{15}$ to 1200 x $10^{15}$), but lower than those in Dome Fuji ice (~4500 x $10^{15}$) deposited 10-22 kyr ago (Figure 10) (Carlson et al., 1990; Lyons et al., 1998; Sasa et al., 2010). The $^{36}\text{Cl}/\text{Cl}$ ratios in soil profiles were approximately constant with depth, although two surface samples had the highest measured ratios (~2400 x $10^{15}$). $^{36}\text{Cl}/\text{Cl}$ ratios in glacier ice and perennial snow (composite samples between 0-125 cm) were 880 x $10^{-15}$ and 510 x$10^{-15}$, respectively, and much lower than those in soils, but were similar to values (123 x $10^{-15}$ to 592 x $10^{-15}$) in fresh snow from Taylor Dome (Lyons et al., 1998). Perennial snow patch samples contained both pre- and post-bomb deposition, as indicated by a measurable $^3\text{H}$ peak (23 TU) at a depth of 45 cm, whereas glacier ice appeared to be mainly pre-bomb, as there was no detectable $^3\text{H}$ (<8 TU) (Figure S2). The similarity of $^{36}\text{Cl}/\text{Cl}$ ratios in pre- and post-bomb deposition snow and ice, combined with the large Cl$^-$ mass/area in soils compared to deposition rates, suggests little or no influence of bomb $^{36}\text{Cl}$ in these soil profiles. The relatively low $^{36}\text{Cl}/\text{Cl}$ ratios and relatively high $^{37}\text{Cl}$ values in ice and snow samples, compared to those in soil samples, may indicate a larger fraction of sea salt Cl in snow and ice (see Discussion).

3.5 Salt accumulation times

Maximum accumulation times for Cl$^-$ in the dry soil for a constant depth (56cm) at each location varied by a factor of ~3 depending on the method used to calculate Cl$^-$ deposition rates (Table 1). The accumulation times increased with distance from the glacier (9,400-33,500 years near the glacier to 68,000-218,000 years furthest from the glacier). Accumulation times based on $^{36}\text{Cl}$ deposition rates increased with distance from the glacier and ranged from 10,000-71,000 years. Accumulation times for NO$_3^-$ had a similar overall pattern, but were generally greater by a factor of 2-4 (Table 2). The lowest accumulation times based on NO$_3^-$ were calculated using the short-term total NO$_3^-$ deposition rate in University Valley measured in the current study. Other NO$_3^-$ deposition rates were all based on deposition rates measured for snow and glacier ice.

4.0 Discussion

The undifferentiated alpine drift in University Valley consists of ice-cemented permafrost soils overlain by a layer of dry soil whose thickness tends to increase toward the mouth of the valley.
The soluble salt fraction in both horizons was dominated by Cl\(^-\) and NO\(_3^-\) (SO\(_4^{2-}\) is not discussed in this paper), but there was a marked difference in salt distribution and abundance between the dry soils and the ice-cemented sediments. To better characterize these differences, each of those horizons is discussed separately below.

4.1 Salts in the dry soils: modern atmospheric sources, post-depositional transformations and transport

Salt concentrations in the dry soils are higher than in the ice-bearing permafrost, and more variable with depth and with distance from University Glacier. Total salt concentration in this layer is generally lower than in the low elevation valleys of the MDV, or in Beacon Valley, particularly for deeper soil horizons (Bao et al., 2008; Kounaves et al., 2010). Salt concentrations generally peak at a depth of 10-15 cm, which likely reflects the maximum depth of snowmelt percolation during clear summer days following the accumulation of a thin snow cover, as was visually observed (Figure 2).

In contrast to total salt concentrations, NO\(_3^-\) and ClO\(_4^-\) concentrations and NO\(_3^-\)/Cl\(^-\) ratios in the dry soils are generally higher than in the lower MDV and similar to Beacon Valley (Kounaves et al., 2010; Bockheim et al. 1997). ClO\(_4^-\) concentrations in University Valley soils are 10 to 100 times higher than in soils from other arid regions on earth, excluding areas with high-grade surface NO\(_3^-\) deposits (e.g. Atacama Desert, Mojave Clay Hills, and Turpan Hami) (Jackson et al., 2015). NO\(_3^-\)/ClO\(_4^-\) molar ratios are lower than in all other known ClO\(_4^-\) occurrences except for the Atacama (~10 times lower) and Turpan Hami (similar). Our data support the contention that low NO\(_3^-\)/ClO\(_4^-\) ratios are due to preservation of atmospheric deposition and lack of input from biological NO\(_3^-\) production as proposed by Jackson et al., (2015).

ClO\(_4^-\) separated from a single dry soil sample had a \(\delta^{18}\)O value of -4.9 \(\%\) and a \(\Delta^{17}\)O value of +12.8 \(\%\). These are roughly within the range of values reported for ClO\(_4^-\) from the Atacama and Mojave Death Valley NO\(_3^-\) deposits, although the University Valley \(\Delta^{17}\)O value was slightly elevated (by 2-3 \(\%\)) compared to those of any other ClO\(_4^-\) samples with similar \(\delta^{18}\)O values (Jackson et al., 2010). In contrast, the \(\delta^{33}\)Cl value of University Valley ClO\(_4^-\) (+1.3 \(\%\)) was similar to those of many other indigenous natural ClO\(_4^-\) occurrences, but significantly higher.
those of Atacama ClO$_4^-$, and the $^{36}$Cl/Cl ratio (33,000 x $10^{-15}$) was among the highest reported for ClO$_4^-$ in soils and caliches from any location. The strong correlation between Cl$^-$, NO$_3^-$ and ClO$_4^-$ concentrations, along with the elevated NO$_3^-$/Cl$^-$ molar ratios and the isotopic compositions of Cl$^-$, NO$_3^-$, and ClO$_4^-$ are consistent with atmospheric (possibly stratospheric) sources, limited post depositional transport, and scarce biological activity, as suggested previously for these ions in other MDV soils (Michalski et al., 2005; Savarino et al., 2007; Kounaves et al., 2010; Jackson et al., 2015).

ClO$_3^-$ has not previously been reported for soils from Antarctica, although it is present in the MDV lakes and other surface waters (Jackson et al., 2012). ClO$_3^-$/ClO$_4^-$ ratios in University Valley dry soils were less than 1 and commonly were of the order of 0.1, in contrast to other terrestrial arid soils, Mars meteorites, asteroidal meteorites, and lunar samples, for which ClO$_3^-$ /ClO$_4^-$ ratios of the order of 1 or higher have been reported (Rao et al., 2010; Kounaves et al., 2014; Jackson et al., 2015). Lower ClO$_3^-$/ClO$_4^-$ ratios in soils compared to those in fresh snow, total deposition, aerosols, glacier ice, and perennial snow suggest that soil ClO$_3^-$ may have been subjected to abiotic post-depositional transformations. Partial ClO$_3^-$ loss from soils may have occurred by a mechanism similar to iron-mediated reduction of NO$_3^-$ in MDV ponds and lakes (Samarkin et al., 2010; Murray et al., 2012) but taking place on soil particles, perhaps in thin aqueous films. Alternatively, photochemical oxidation of ClO$_3^-$ to ClO$_4^-$ may have occurred.

The negative $\delta^{37}$Cl values and elevated $^{36}$Cl/Cl ratios of Cl$^-$ in the dry soils indicate that salt input was largely from atmospheric deposition and may have had a substantial (~50%) stratospheric component. Bao et al. (2008) proposed a model in which MDV soil Cl$^-$ is dominated by sea salt chloride (SSC) in valleys near the coast and by secondary aerosol chlorides (SAC) at locations far from the coast, and that sublimation tills should have increasingly negative $\delta^{37}$Cl values with depth due to the contribution of buried glacial ice. The buried glacial ice, whose origin was attributed to windblown polar plateau snow, was assumed to have very negative $\delta^{37}$Cl value. A two-component mixing model (Figure 11A) reasonably describes the variation in $\delta^{37}$Cl and $^{36}$Cl/Cl values, assuming the stratospheric component had end member values of -4 ‰ (based on northern hemisphere precipitation; Koehler and Wassenaar, 2010) and 4500 x $10^{-15}$ (average value at Dome Fuji), respectively, and the tropospheric component had end member values of 0
and $1 \times 10^{-15}$ (sea water), respectively. Correlations of both $\delta^{37}$Cl and $^{36}$Cl/Cl values with inverse Cl$^-$ concentration (Figure 11B,C) further support this two-component mixing model. Glacial ice and snow had higher $\delta^{37}$Cl values compared to soil values, contrary to past assertions that the glacial ice in the stable upland zone should have the lowest $\delta^{37}$Cl values as the ice source is windblown snow from the Polar Plateau (Bao et al. 2008). Cl-$\delta^{37}$Cl values in vertical soil profiles were not increasingly negative with depth, as has been proposed for sublimation tills (Bao et al., 2008). Based on the lack of Cl-$\delta^{37}$Cl variation with depth and the lower Cl-$\delta^{37}$Cl values in soil than snow or ice, there is no indication from our study that salts were concentrated in the dry soils by sublimation of buried glacial ice, although some such residual components may be present.

Our data suggest that variations in soil Cl-$\delta^{37}$Cl and $^{36}$Cl/Cl may also be related to relative contributions of wet and dry deposition and that wet deposition contains a larger SSC than dry deposition. This could be due to wet deposition having a larger marine component or that snow/ice accumulates less HCl (stratospheric Cl) than non-acid forms of Cl$^-$. Our $\delta^{37}$Cl values are generally more negative than those reported for Beacon Valley, which is the same distance from the coast. This may suggest that elevation plays a role in the relative contributions of deposition types and Cl$^-$ sources (e.g., larger wet deposition contribution in Beacon). Alternatively, as suggested by Bao et al. (2008), the relative contributions of SAC and SSC may have changed over time as Beacon Valley has older soil ages. However, for changes in Cl$^-$ deposition type over time to be responsible for the higher reported Cl-$\delta^{37}$Cl values in Beacon Valley soils, the Cl$^-$ would need to be well mixed (older Cl$^-$ mixing with younger Cl$^-$ at surface) which is not consistent with isotopic variations observed with depth in Beacon Valley (Bao et al., 2008).

Variations in NO$_3^-$ stable isotopic composition, both with depth and valley location, revealed important clues about processing of deposited NO$_3^-$ by volatilization, transport, and/or photolysis. Importantly, $\delta^{15}$N and $\delta^{18}$O values of NO$_3^-$ in dry soil were similar to those of aerosols and total deposition, but significantly different from those in perennial snow and glacier ice. We interpret the NO$_3^-$ stable isotopic composition of perennial snow and glacier ice as evidence of varying degrees of post depositional fractionation due to combinations of photo-
processing, O exchange, and/or volatilization of HNO₃. Previous studies in Antarctica indicate
NO₃⁻ photolysis and partial re-oxidation may be responsible for large increases in δ¹⁵N and
moderate decreases in δ¹⁸O of NO₃⁻ in snow and ice (Frey et al., 2009; Erbland et al., 2013). Our
snow and ice data could be considered qualitatively consistent with such effects, but the relative
magnitudes of changes in δ¹⁵N (smaller) and δ¹⁸O (larger) appear to be somewhat different.
HNO₃ volatilization may cause variable isotope effects depending on relative importance of
fractionations associated with aqueous speciation and vapor emission. Theoretical calculations
indicate HNO₃ has higher δ¹⁸O and δ¹⁵N than NO₃⁻ at equilibrium (Frey et al. 2009; Monse et al.
1969). In this case, if NO₃⁻ > HNO₃ in the perennial snow, then δ¹⁸O and δ¹⁵N of HNO₃ would
be higher than those of total (HNO₃+NO₃⁻) and emission of HNO₃ could leave behind NO₃⁻ with
relatively low δ¹⁸O and δ¹⁵N and would not be consistent with δ¹⁵N enrichments observed in
perennial snow packs. However, if HNO₃ > NO₃⁻, then the isotopic composition of HNO₃ would
be similar to that of (HNO₃+NO₃⁻) and isotope effects could be dominated by kinetic effects of
HNO₃ emission, which could leave behind HNO₃ with higher δ¹⁸O and δ¹⁵N (Erbland et al.,
2013). Further, if conditions in concentrated aqueous films were strongly acidic and HNO₃ was
the dominant species, then O exchange could occur between HNO₃ and H₂O with low δ¹⁸O,
causing δ¹⁸O of HNO₃ to decrease. In this case, volatilization and exchange could conceivably
cause δ¹⁵N to increase and δ¹⁸O to decrease in residual HNO₃ in the perennial snow, as was
observed. Variation in the perennial snow and glacier ice NO₃⁻ isotopic composition did not
appear to be related to NO₃⁻ concentration, Cl⁻/NO₃⁻, ClO₄⁻/NO₃⁻, or depth. However, the much
higher NO₃⁻/Cl⁻ ratios in soil compared to the perennial snow and glacier ice suggest that either
the deposition rate and/or capture rate of NO₃⁻ and Cl⁻ were different between ice and soil, or
NO₃⁻ was lost from the perennial snow and ice. HCl has a higher vapor pressure than HNO₃ but
it also has a much lower dissociation constant.

In contrast to the perennial snow and glacial ice, soil NO₃⁻ apparently was more resistant to post-
deposition processes affecting its relative abundance and isotopic composition. Major differences
between these environments include less light penetration in soil (less photolysis) and acid
neutralization by reaction with minerals in soil (less photolysis, volatilization, and isotopic
exchange). These results indicate NO₃⁻ retained in the shallow regolith may be a better monitor
of the isotopic composition of atmospheric deposition than NO$_3^-$ retained in ice cores in some hyper-arid environments, though this would not be the case where soils were biologically active.

Apart from major contrasts between relatively well preserved NO$_3^-$ in soils and more altered NO$_3^-$ in perennial snow and glacier ice, our data also indicate at least two separate processes may have interacted to cause minor variations in NO$_3^-$ stable isotopic composition within the soils. First, isotopic variation with distance from University Glacier could be consistent with varying degrees of processing on ephemeral overlying snow and ice prior to incorporation in the soil. McKay (2009) argued that a decrease in snow recurrence with down-valley distance from University Glacier could explain the observed trend in ice-table depth. We assume that NO$_3^-$ deposited directly onto exposed soil would not be subject to volatilization, photolysis, or water exchange, whereas NO$_3^-$ deposited onto overlying snow and ice would be subject to such post depositional processes. Therefore the relative amount of NO$_3^-$ deposited on snow and ice rather than directly on soil and the relative amount of time that NO$_3^-$ spends in the snow and ice before being transported into the soil could determine the bulk NO$_3^-$ isotopic composition in the soil at each location. If soils near University Glacier were covered by snow more often than soils farther down the valley, then accumulated soil NO$_3^-$ nearer the glacier ought to be more affected by photolysis, volatilization, or O exchange because it was less rapidly neutralized and protected from light exposure. Data supporting this conceptual model include changes in NO$_3^-$ stable isotopic composition with respect to location in the valley, the overall inverse relation between δ$^{18}$O and δ$^{15}$N (transect samples), and the strong overall relations between δ$^{18}$O, δ$^{15}$N, and measures of NO$_3^-$ loss (e.g. ClO$_4$/NO$_3$ molar ratio and 1/NO$_3$) (Figures 6, 7, 9).

While down-valley trends were evident in the shallow soil samples (Figure 6), the profile data indicate NO$_3^-$ isotopic composition may have been altered further by processes occurring during vertical transport (dissolution, advection, crystallization) and/or mixing with NO$_3^-$ released from underlying ice-cemented sediments by sublimation at the ice table (Figure 8). Observations supporting an impact from crystallization and transport include: 1) decreasing NO$_3^-$/Cl$^-$ and NO$_3^-$ /ClO$_4^-$ ratios with depth down to the ice table (Figure 5), 2) decreasing δ$^{18}$O and δ$^{15}$N with depth and simultaneously with NO$_3^-$ relative abundance, as indicated by 1/NO$_3^-$, Cl$^-$/NO$_3^-$, and ClO$_4^-$/NO$_3^-$ (Figure 8 and 9), and 3) co-variation of δ$^{18}$O and δ$^{15}$N within profiles that is consistent
with isotope fractionation effects (Figure 7). These relations are similar to those reported for
\( \delta^{18}O \) and \( \delta^{34}S \) in SO\(_4\)\(^{2-} \) in MDV soil profiles and attributed to downward migration and
crystallization/transport fractionation effects (Amundsen et al., 2012). However, it is also
possible that some of the isotopic variation was due to mixing of relatively new atmospheric
NO\(_3\)\(^-\) and old NO\(_3\)\(^-\) released from the ice-cemented permafrost. Mixing could be qualitatively
consistent with a series of positive \( \delta^{15}N \)- \( \delta^{18}O \) trends between local deep ground ice values and
local shallow soil transect values (Figure 7 inset). However, this effect should be relatively
minor given 1) the low NO\(_3\)\(^-\) concentrations (~10X) in ice-cemented permafrost compared to the
overlying dry soil; 2) the observation that isotopic values are not always the most positive at the
surface but rather at the concentration maximum, nor are they always the least positive at the ice
table; and 3) the sharp transition in anion concentration (2X) between the surface of the ice-
cemented permafrost soil and the overlying dry soil (~1cm).

4.2 Salt accumulation times

Our results suggest that salts in University Valley permafrost soils are mostly derived from direct
atmospheric deposition and not from lateral remobilization or sublimation of tills. Our calculated
salt accumulation times to a depth of 56 cm using deposition rates of Cl\(^-\), NO\(_3\)\(^-\), and \(^{36}\)Cl (Table 1
and Table 2) consistently increased with distance from the glacier and were generally consistent
between calculation methods, although most estimates based on NO\(_3\)\(^-\) accumulation in glacier or
snow packs but not those based on total deposition were higher than all methods based on Cl\(^-\).
The lower NO\(_3\)\(^-\) deposition rates from glacial and snow studies are likely due to NO\(_3\)\(^-\) greater
tendency for post-depositional processing (photo-transformation and volatilization) which is
supported by the low NO\(_3\)\(^-\)/Cl\(^-\) ratios in University Valley snow pack and glacial ice, and altered
NO\(_3\)\(^-\) stable isotope composition in snow packs, glacial ice but not soil NO\(_3\)\(^-\). Salt accumulation
times are consistent with the lack of variation in \(^{36}\)Cl/Cl\(^-\) ratios which would have been only
minimally impacted by decay over the last 100K-200K years particularly considering the large
mass of Cl\(^-\) accumulated near the surface allowing mixing of older and newer Cl\(^-\) deposition. It
should be noted that we have no information regarding the mass of salts present below our
sample depths and so our discussion only pertains to the salts in the upper 56 cm. We also do not
eliminate the possibility that the current salt accumulations are partially due to sublimation of
ground ice and deflation of soils with concentration due to limited downward migration of salts from transient melt events. While none of our data directly support this interpretation, it does not change the accumulation time required to account for the accumulated salts observed assuming the salts are atmospheric in origin. These estimated accumulation times are subject to various interpretations.

One possible explanation for the increasing salt accumulation time with distance from University Glacier could be the differential stability of HCl and HNO$_3$ in snow and ice compared to bare soils. If current conditions of snow recurrence in University Valley, with more stable and permanent snow cover towards the head of the valley, persisted during the past 100-200 kyrs, then soils near the head of the valley would be expected to be depleted in Cl$^-$ and NO$_3^-$ due to photolysis and volatilization in snow/ice, compared to bare soils towards the mouth of the valley. The result would be a lower accumulated salt mass near University Glacier, resulting in a lower calculated salt accumulation time even though the true salt accumulation times might have been similar throughout the valley.

Another possible scenario might be glacier retreat resulting in the progressive deposition/exposure of permafrost soils in an up-valley direction during the past 100-200 kyrs, a timing that roughly coincides with the age of Alpine A drifts in adjacent Arena Valley, dated to $>200$ ka (Marchant et al., 1993). However, there is no conclusive evidence yet of glaciation in University Valley during the Quaternary, or of a significant change in climate regime that would support this scenario.

4.3 Salts in ice-cemented permafrost sediments (or soils)

Contrary to the dry soils, the abundance, distribution, and isotopic composition of soluble anions in the ice-cemented sediments were relatively monotonous throughout the valley and with depth, with the exception of NO$_3^-$ isotopes, which showed some spatial variation (Figure 2, 6, and 8). To our knowledge such distribution of soluble ions in ground ice has not been reported in the literature previously. There are several mechanisms that could explain the relatively low abundance and homogenous distribution of salts in the ice-cemented permafrost; however, our data are inconclusive.
Commonly, soils with low salt abundances and featureless vertical salt profiles reflect flushing events whereby percolation of surface water dissolves and carries soluble ions towards deeper soil layers. However, under current conditions, liquid water plays a minimal role in landscape evolution in University Valley, and this has likely been the norm throughout the Quaternary, and perhaps longer (Marchant et al., 2013). Relatively warmer and wetter conditions could have occurred during past interglacial periods triggered by orbital changes, but these are unlikely to cause complete thawing and refreezing of the ice-cemented layer. In addition, stable water isotope analyses show that some of the ground ice in University Valley formed from vapor diffusion and freezing (Lacelle et al., 2013), a result that is incompatible with significant vertical liquid water transport in the soil column, at least locally. The low abundance and homogenous distribution of salts could also be due to cryoturbation and soil mixing, but this also requires partial thawing and refreezing of the ground ice, again inconsistent with the stable isotope data. We note also that other morphological features commonly associated to cryoturbation such as frost heave (sorting) or solifluction lobes are absent in University Valley.

An alternative explanation would be strain induced cycles of ice recrystallization due to daily and seasonal temperature fluctuations. Ice recrystallization can cause chemical impurities (i.e. salts) to concentrate at grain boundaries, possibly resulting in thin briny films with lower freezing points, which can then migrate along the network of grain boundaries and smooth out any initial chemical layering (Fisher, 1987).

Finally, the low abundance and homogenous distribution of salts in the ice-cemented permafrost could be due to a very fast sedimentation in a scenario of rapid glacier retreat, leading to the deposition of a glacial till across the valley. In that scenario, melting at the snout of the glacier during its retreat could leach salts deposited with the till, and the subsequent formation of ground ice would prevent further salt deposition from the atmosphere. The mass balance of salts in the soil and the $^{36}$Cl data suggest that such event would have happened during the last several hundred thousand years. While there is no independent evidence that can support this event, small alpine glaciers in the McMurdo Sound region respond more quickly to climate variations than do the major glaciers fed from the central plateau (Campbell and Claridge, 1987). In the Beacon Valley area there are five recognized advances of the Taylor Glacier from the north and
five recognized advances of Alpine-type glaciers (Linkletter et al., 1973), but the timing of these events has not yet been fully constrained. If the distribution and abundance of the salt fraction in permafrost soils in University Valley indeed points to the last period of advance and retreat of University Glacier, then our age estimates would place this event at approximately 150-200 kyr ago.

The ultimate mechanism responsible for the salt profile in the ice-cemented soils critically depends on whether there has been a net loss of salt in the sampled profile since the formation of the soil layer. A flushing event or the vertical movement of liquid water would result in a salt-rich layer with depth, which might be below the maximum sampling depth. Such a salt-rich layer would be absent in a scenario of fast sediment deposition followed by ice-accumulation, or mixing due to strain induced cycles of ice recrystallization. While we cannot conclusively rule out any of the above scenarios, the explanation of the observed salt profile in the ice-cemented permafrost will likely provide important insights regarding the formation and evolution of ground ice in this extremely cold and dry environment. Current efforts to establish OSL ages along the valley may help to resolve which scenario is correct.

5.0 Conclusions

This study used the abundances and spatial distributions of soluble anions and the isotopic compositions of a subset of these anions to evaluate the salt sources and post depositional alterations in a high-elevation cold hyper-arid valley of Antarctica. We demonstrated that Cl\(^-\), NO\(_3^-\), ClO\(_3^-\), and ClO\(_4^-\) in this valley were dominated by atmospheric deposition to the soil surface and varying degrees of post depositional transformation and limited vertical transport. Unlike lower-elevation MDV soils there does not appear to be a substantial contribution of salts from periods before the current accumulation period nor has extensive remobilization occurred based on salt profiles and isotopic composition. As such the salts in University Valley soils may be more robust indicators of past climate conditions and deposition sources.

We propose the large variations in NO\(_3^-\) and Cl\(^-\) isotopic composition in perennial snow and glacier ice compared to soils reflect enhanced preservation of isotopic composition in soils as well as differences in the proportion of dry and wet deposition. While the \(^{36}\)Cl/Cl\(^-\) ratios and
δ³⁷Cl⁻ values support previous conclusions that deposition of sea-salt chloride decreases with distance from the coast, our data are not congruent with past interpretations of depth-dependent changes attributed to the presence or absence of sublimation tills. Our data also indicate that elevated ³⁶Cl/Cl ratios are not due to nuclear bomb fallout, but rather may be characteristic of the natural deposition (wet or dry) source of Cl⁻. Soil NO₃⁻ isotopic compositions largely reflect unaltered atmospheric deposition and likely represent some of the best preserved atmospheric NO₃⁻ occurrences on earth. Small but systematic variations in NO₃⁻ isotopic composition with depth are likely due to downward transport-related fractionation, while changes with respect to location in University Valley are more likely due to changes in the amount and stability of snow cover in the valley that lead to differing degrees of post depositional transformation. We also propose that ratios of NO₃⁻ to other conserved species, particularly ClO₄⁻, appear to be good indicators of NO₃⁻ loss and therefore of NO₃⁻ isotopic fractionation and should be considered in other studies in addition to evaluating changes in concentration directly. The isotopic composition of ClO₄⁻ in University Valley soil appears consistent with a stratospheric source although smaller amounts of surface production cannot be ruled out.

The abundance and distribution of salts in the ice-cemented sediments, along with the estimated age of salt deposition, point to either a mechanism of recent salt removal (e.g. water leaching), or to the formation of permafrost soils in relatively modern times (< 500 kyr). Hence, this type of study can provide important insights regarding the hydrology and glacial history of this extremely cold and dry environment.

The occurrence of both ClO₄⁻ and ClO₃⁻ in these soils along with the very limited transport, hyper-arid conditions, and cold temperatures, support the use of this valley as a possible Earth analog of Mars processes. SAM data indicate a constant ratio of NO₃⁻/ClO₄⁻ in Martian soil (Stern et al., 2015). The stability of ClO₃⁻ in these soils is of particular interest as it could suggest that the ratio of ClO₃⁻/ClO₄⁻ in Martian soils may be a predictor of water availability, although further work is required to understand the exact conditions that lead to ClO₃⁻ loss in University Valley soils.

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Table 1. Ranges of Cl accumulation time in profiles along University Valley based on Cl or 36Cl deposition rates.

<table>
<thead>
<tr>
<th>Profile from Glacier</th>
<th>Distance From Glacier (m)</th>
<th>Total Depth (cm)</th>
<th>Estimated Ages (Years)</th>
<th>Estimated Cl Deposition from Glaciers (mg/m²/year)</th>
<th>Measured Total Deposition (mg/m²)</th>
<th>MDV Measured Values</th>
<th>Whitherow et al., 2006</th>
<th>This Study</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
</table>

4. Age estimated based on the total Cl in each profile and the measured total Cl deposition rate measured in University Valley from 2010-2012.

3. Age estimated based on the total Cl in each profile and the Cl deposition rate reported (Whitherow et al., 2006) for the range of MDV low.

2. Age estimated based on the total Cl in each profile and the Cl deposition rate estimated from the Dome Fuji deposition rate adjusted for dilution of non-stratospheric Cl based on the ratios of 36Cl at each site. ($\frac{36Cl}{Cl_{Ri}} \times \frac{Cl_{RF}}{Cl_{RU}}$).

1. Age estimated based on the total Cl in each profile and the Cl deposition rate estimated from the total Cl deposition rate for Dome Fuji deposition rate for the range of MDV low.

|$\sum Cl \times Cl_{MW} \times Cl_{RU} / D_{36Cl}$.
Table 2 Ranges of NO\textsubscript{3} accumulation time in profiles along University Valley based on deposition rates.

<table>
<thead>
<tr>
<th>Profile Distance from Glacier (m)</th>
<th>Total Depth (cm)</th>
<th>∑NO\textsubscript{3}-N (mg/m\textsuperscript{2} - year)</th>
<th>Estimated Ages Based on Various NO\textsubscript{3} Deposition Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>14800</td>
<td>0</td>
<td>0.55</td>
<td>170 years, 56,000 years</td>
</tr>
<tr>
<td>14000</td>
<td>0</td>
<td>0.87</td>
<td>289 years, 171 years</td>
</tr>
<tr>
<td>14000</td>
<td>0</td>
<td>0.67</td>
<td>575 years, 56,000 years</td>
</tr>
<tr>
<td>14800</td>
<td>0</td>
<td>0.87</td>
<td>289 years, 171 years</td>
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<tr>
<td>14000</td>
<td>0</td>
<td>0.87</td>
<td>289 years, 171 years</td>
</tr>
</tbody>
</table>

a. Age estimated based on the total NO\textsubscript{3} in each profile and the deposition rate reported for the range of MDV low accumulation glaciers (Whitherow et al., 2006).

b. Age estimated based on the total NO\textsubscript{3} in each profile and the measured total NO\textsubscript{3} deposition rate measured in University Valley from 2010-2012.
Table S1. Statistical relationships ($r^2$, $P$ values, and slopes) between $\delta^{18}O$ and $\delta^{15}N$ of NO$_3$ with various variables.

<table>
<thead>
<tr>
<th>Depth/Location</th>
<th>$\delta^{18}O$-NO$_3$ (‰)</th>
<th>$r^2$</th>
<th>Slope</th>
<th>$P$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 600 m</td>
<td>720 0.87 0.90 0.23 0.62 6.7</td>
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</tr>
<tr>
<td>750 - 1000 m</td>
<td>750 0.45 0.30 0.51 0.66 3.1</td>
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<td></td>
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</tr>
<tr>
<td>1000 - 1100 m</td>
<td>1100 0.93 0.57 0.93 0.57 3.6</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1100 - 1980 m</td>
<td>1980 0.92 0.62 0.8 0.22 3.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transect</td>
<td>0.003 0.60 0.9 0.5* 0.5* 3.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All</td>
<td>0.28 0.30 0.76 0.4* 0.24 2.4</td>
<td></td>
<td></td>
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</tbody>
</table>
Figure 1. A) Location of University Valley relative to Beacon Valley within the Mdv; B) Location of soil profiles with University Valley; and C) a conceptual cross section of University Valley.
Figure 2 - Depth profiles of anion concentrations in University Valley soils at various distances downgradient from University Glacier. Filled symbols indicate values in dry cryotic soil and open symbols indicate values in ice-cemented soil. Horizontal lines indicate the depth to the top of ice-cemented soil (ice table). All concentrations are given in units of mass per kg of dry soil equivalent (i.e., after removal of water).
Figure 3: Depth profiles of anion concentrations in glacier ice, snow pack, and fresh snow from University Valley.
Figure 4. A) Cumulative Cl mass with depth in University Valley soils at various distances downgradient from University Glacier. Filled symbols indicate values in dry cryotic soil and open symbols indicate values in ice-cemented soil. B) Variation in Cl, NO$_3$-N, and ClO$_4$- mass per area with distance from glacier. Hatched box represents the mass attributable to ice-cemented soil below dry cryotic soil. Mass is the cumulative mass to 56 cm, the maximum common depth.
Figure 5: Depth profiles of NO$_3$/ClO$_4$ and NO$_3$/Cl molar ratios at various distances downgradient from University Glacier when sampled in 2010. Filled symbols indicate values in dry cryotic soil and open symbols indicate values in ice-cemented soil. Horizontal lines indicate the depth to the top of ice-cemented soil (ice table) where known.
Figure 6. Variation of anion molar ratios and $NO_3^-$ stable isotopic composition in snow, ice, soils with distance from University Glacier. Horizontal lines indicate mean values in aerosol and deposition samples. Aerosols collected from Taylor Valley (2013).
Figure 7. Variation of NO$_3^-$ stable isotopic composition in soil profiles, transect soil samples, snow pack, glacier ice, fresh snow, and total deposition from University Valley. Also shown are previously reported data for MDV soils (Michalski et al., 2005), snow samples including pit and traverse samples from Dome C to Dumont d’Urville (Frey et al., 2009), and aerosol measurements (Savarino et al., 2007). Aerosol mass average values were calculated from one year of data (n=27) at Dumont d’Urville (Savarino et al., 2007). Dashed arrows indicate qualitative directional changes that could be caused by photo-decomposition and oxygen exchange with water. The inset figure gives an enlarged view of variations in University Valley soils; colored lines indicate regressions for subsets of the data and open symbols represent ice cemented permafrost below dry soil. References in legend are: $^1$ (Frey et al., 2009), $^2$(Savarino et al., 2007), $^3$ (Michalski et al., 2005)
Figure 8. Variation in NO$_3^-$ stable isotope composition in University Valley soils at various distances down gradient from University Glacier. Filled symbols indicate values in dry cryotic soil and open symbols indicate values in ice-cemented soil. Boxes indicate maximum NO$_3^-$ concentration for each profile. Horizontal lines indicate the depth to the top of ice-cemented soil (ice table).
Figure 9. Relationship between δ^{18}O and δ^{15}N of NO\textsubscript{3} with NO\textsubscript{3} abundance as reflected by NO\textsubscript{3}-N concentration (1/NO\textsubscript{3}) and molar ratios of ClO\textsubscript{4}/NO\textsubscript{3} and Cl/NO\textsubscript{3}. Colored lines reflect regression plots for similar colored data points. Open circles represent values of ice cemented soil below cryotic soil and are not included in regression analysis. The black line depicts the overall regression plot for all data excluding open symbols in plot.
Figure 10. Variation of $^{36}\text{Cl}/^{35}\text{Cl}$ and $\delta^{37}\text{Cl}$ values in soil $\text{Cl}$- with respect to depth and location in University Valley. Filled symbols indicate values in dry cryoetic soil and open symbols indicate values in ice-cemented soil. Composite values for snow pack and glacier ice are also shown. Horizontal lines indicate the depth to the top of ice-cemented soil (ice table).
Figure 11. A) Variation in $^{36}\text{Cl}/\text{Cl}$ ratio with respect to $\delta^{37}\text{Cl}$ of samples in University Valley. Filled symbols indicate values in dry cryotic soil and open symbols indicate values in ice-cemented soil. The curve represents a hypothetical mixing model between stratospheric and tropospheric components (see text for endmember values). Fractions of the stratospheric component (high $^{36}\text{Cl}/\text{Cl}$, low $\delta^{37}\text{Cl}$) are indicated with tick marks. B) Variation in $^{36}\text{Cl}/\text{Cl}$ and C) $\delta^{37}\text{Cl}$ with respect to Cl abundance ($1/\text{Cl}$). Black lines represent regression line.
Figure S1. Relative ratios of NO3 and Cl to ClO4 and NO3 to Cl in depth profiles. Ratios (Figure 2) were arbitrarily normalized to the surface ratio to better illustrate relative changes with depth. Horizontal black lines demark interface of ice cemented soil.
Figure S2. Tritium profiles for the University Valley Glacier and snow pack. Solid line represents the detection limit (8TU). Data is derived from independent cores than those used to determine concentrations of anions.