Deposition, accumulation, and alteration of Cl^- , NO_3^- , ClO_4^- and ClO_3^- salts in a hyper-arid polar environment: mass balance and isotopic constraints

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Abstract

The salt fraction in permafrost soils/sediments 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 soil/sediments in University Valley, located in the ultraxerous 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-cemented soil/sediments, 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 $\text{ClO}_4^-/\text{NO}_3^-$ ratios and NO_3^- isotopic composition with depth and location may reflect both transport related fractionation and depositional history. Low molar ratios of $\text{ClO}_3^-/\text{ClO}_4^-$ 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 kyr near the glacier to 70-200 kyr near the valley mouth. The relatively young age of the salts and relatively low and homogeneous anion concentrations in the ice-cemented sediments 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 aqueous processes 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; 2013). 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-cemented sediments 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 sublimation 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, snow and glacier 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 al., 2010; Jackson et al., 2015). 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 glacier 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 glacier ice. These findings have direct relevance to our understanding of the potential for past episodes of aqueous processes 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 ($77^\circ 52'S$; $160^\circ 45'E$; c.a. 2000 m long, 500-700 m wide and 1600-1800 m a.s.l.), a glacial valley hanging 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 these horizons (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 $-23.4 \pm 8.3^{\circ}\text{C}$ and at no time did 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 0°C linked to higher topographic shadowing; and ii) a seasonally non-cryotic zone where ground surface temperatures $>0^{\circ}\text{C}$ 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 $> 200\text{ka}$ and $>1\text{Ma}$, respectively (Marchant et al., 1993). This interpretation fits the optically stimulated luminescence ages obtained from a 95 cm ice-cemented sediment 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 ($>2.7\text{Ma}$) 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 sediment 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 sediments, 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 sediment (Figure 1). The vertical profiles obtained at 1200 m and 1940 m from the University Glacier 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 μ m). 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^- , NO_3^- (reported as $\text{NO}_3\text{-N}$), ClO_4^- , and ClO_3^- concentrations as described in Jackson et al. (2015). Briefly, ClO_4^- and ClO_3^- 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 2000TM triple quadrupole mass spectrometer equipped

with a Turbo-IonSprayTM source (Rao et al., 2010; Jackson et al., 2015). To overcome matrix effects, all samples were spiked with an oxygen-isotope (¹⁸O) labeled ClO₄⁻ or ClO₃⁻ internal standard. Chloride and NO₃⁻ 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 NO₃⁻ stable isotopic composition. δ¹⁵N and δ¹⁸O in NO₃⁻ were measured by continuous-flow isotope-ratio mass spectrometry on N₂O produced from NO₃⁻ by bacterial reduction (Sigman et al., 2001; Casciotti et al., 2002; Coplen et al., 2004). The data were calibrated by analyzing NO₃⁻ isotopic reference materials using published values (Böhlke et al., 2003). For samples with elevated Δ¹⁷O of NO₃⁻, δ¹⁵N values determined by the bacterial N₂O 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). δ¹⁵N values reported here were not adjusted for this effect because Δ¹⁷O values were not measured in these samples. True δ¹⁵N 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 δ¹⁸O and Δ¹⁷O of atmospheric NO₃⁻ 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 CH₃Cl for IRMS analysis of δ³⁷Cl (Long et al., 1993) at the Environmental Isotope Geochemistry Laboratory, University of Illinois at Chicago. ³⁶Cl abundances in purified Cl⁻ samples were measured by accelerator mass spectrometry at the Purdue Rare Isotope Measurement Lab (Sharma et al., 2000). Tritium (³H) 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 ³H 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 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 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 CsClO_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}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 $1,600 \text{ kg/m}^3$. Concentrations were linearly interpolated between dry soil discrete sample depths. The calculated masses per unit area to a common maximum depth (56cm) were then divided by various deposition measurements as described below.

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

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

Where $\sum \text{Cl}$ is the total Cl^- mass to a given depth per m^2 , Cl_{MW} is the molecular weight of Cl^- , R_u is the $^{36}\text{Cl}/\text{Cl}$ ratio of Cl^- in soils in University Valley (Table 1), and $D_{^{36}\text{Cl}}$ is the deposition rate of ^{36}Cl ($28,000 \text{ atoms/cm}^2\text{-year}$) based on ^{36}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 ($25,000 \pm 1,600 \text{ atoms/cm}^2\text{-year}$) (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.

Accumulation times based on total Cl^- accumulation were estimated using the following equation:

$$[2] \quad \text{Accumulation Time} = \sum \text{Cl} / D_i$$

Where D_i is equal to the deposition rate of Cl^- . We evaluated three different methods for evaluating D_i : 1) the maximum and minimum Cl^- deposition rates (D_G) 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 (D_U) measured in this study over a two year period (2010-2012); and 3) the Cl^- deposition rate for Dome Fuji ($D_{\text{Cl-F}}$), adjusted for the larger fraction of non-stratospheric (e.g., marine) Cl^- deposition at University Valley, based on the apparent dilution of $^{36}\text{Cl}/\text{Cl}$ ratios. The adjusted Dome Fuji deposition rate ($D_{\text{Cl-FA}}$) that was calculated using the following equation:

$$[3] \quad D_{\text{Cl-FA}} = D_{\text{Cl-F}} * R_f / R_u$$

where $D_{\text{Cl-F}}$ is equal to the Cl^- deposition rate measured at Dome Fuji, and R_u and R_f are the $^{36}\text{Cl}/\text{Cl}$ ratios of Cl^- at Dome Fuji and University Valley, respectively (Table 1).

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 ($D1_{\text{NO}_3}$ and $D2_{\text{NO}_3}$) reported for low-accumulation MDV glaciers (Witherow et al., 2006); 2) ($D3_{\text{NO}_3}$ and $D4_{\text{NO}_3}$) 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) ($D5_{\text{NO}_3}$) measured total NO_3^- deposition in University Valley (2010-2012) from this study.

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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 $\mu\text{g}/\text{kg}$ 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 (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 sediment. 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_3^- , 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.

$\text{NO}_3^-/\text{Cl}^-$ and $\text{NO}_3^-/\text{ClO}_4^-$ 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-cemented sediment. No such trends with depth were observed for $\text{Cl}^-/\text{ClO}_4^-$ in dry soils. $\text{NO}_3^-/\text{ClO}_4^-$ and $\text{Cl}^-/\text{ClO}_4^-$ but not $\text{NO}_3^-/\text{Cl}^-$ ratios increased with distance from University Glacier (Figure 6). Molar ratios ($\text{NO}_3^-/\text{ClO}_4^-$, $\text{NO}_3^-/\text{Cl}^-$, $\text{Cl}^-/\text{ClO}_4^-$, and $\text{ClO}_3^-/\text{ClO}_4^-$) 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. $\text{NO}_3^-/\text{ClO}_4^-$ and $\text{Cl}^-/\text{ClO}_4^-$ 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-cemented sediment (Figure 6). $\text{NO}_3^-/\text{ClO}_4^-$ and $\text{Cl}^-/\text{ClO}_4^-$ ratios in ice bearing soil were bracketed by ratios in fresh snow. $\text{Cl}^-/\text{ClO}_4^-$ ratios in dry soils were also bracketed by values in fresh snow but $\text{NO}_3^-/\text{ClO}_4^-$ ratios in dry soil generally exceeded those in fresh snow. $\text{NO}_3^-/\text{Cl}^-$ ratios in fresh snow were lower than in total deposition but generally encompassed most soil, snow pack, and glacier ice ratios. Lowest $\text{NO}_3^-/\text{Cl}^-$ ratios were in glacier ice and snow pack and highest ratios in dry soil. $\text{ClO}_3^-/\text{ClO}_4^-$ ratios in dry soils

and ice-cemented sediment were highly variable but consistently lower than all deposition types, snow packs or glacier ice.

3.3 NO_3^- isotopic composition

$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- ($\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$) in dry soils, ice-cemented sediment, glacier ice and perennial snow patches were within the range of values reported previously for various NO_3^- occurrences in Antarctica (Figure 7). Our $\delta^{18}\text{O}$ values (+76 to +84 ‰) overlapped with, but were generally more positive than those reported for other MDV soils (Beacon, Wright, Arena, Mt. Fleming), whereas $\delta^{15}\text{N}$ values were similar to those reported for other MDV soils (Michalski et al., 2005). Snow pack and glacier ice had similar NO_3^- isotopic compositions, and both had lower $\delta^{18}\text{O}$ values and higher $\delta^{15}\text{N}$ values than soils (Figure 7). Fresh snow and total deposition had $\delta^{15}\text{N}$ values similar to soils but lower than perennial snow and glacier ice, and $\delta^{18}\text{O}$ 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 $\delta^{15}\text{N}$ values and high $\delta^{18}\text{O}$ values that were most similar to snow samples collected near the coast. The NO_3^- 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 $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ within and between vertical soil profiles (Figure 7, inset). Within each soil profile, $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ values were significantly positively correlated ($p < 0.05$) and slopes were similar for 3 of the 5 profiles (Table S1). In contrast, $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ values of transect soil samples were significantly inversely correlated. In soil profiles, $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ generally decreased with depth, although the overall change in magnitude was small (< 2 ‰) (Figure 8). The highest $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ values generally coincided with the peak concentration of NO_3^- in dry soil at or near the ground surface. Isotopic trends in the ice-cemented sediment were more variable between profiles. In one profile (750 m), $\text{NO}_3\text{-}\delta^{18}\text{O}$ values decreased with depth below the ice table, while $\text{NO}_3\text{-}\delta^{15}\text{N}$ reached a minimum value at ice table. In another profile (1100 m)

NO₃-δ¹⁸O values were relatively constant below the ice table, while NO₃-δ¹⁵N showed an increase (~1 ‰ within 1 cm) at the ice table, and decreased with depth.

There was a strong correlation between NO₃-δ¹⁸O and NO₃-δ¹⁵N values in dry soils and distance down valley from University Glacier (p=0.005 for NO₃-δ¹⁸O and <0.001 for NO₃-δ¹⁵N) (Figure 6 and Table S1). The correlation was positive in the case of NO₃-δ¹⁸O and negative in the case of NO₃-δ¹⁵N. Spatial variations in average NO₃-δ¹⁸O and NO₃-δ¹⁵N values between soil profiles were approximately 5 ‰ and 4 ‰, respectively; these were larger than the variations with depth in each profile. Variations of NO₃⁻ stable isotopic composition in dry soils generally were directly related to measures of NO₃⁻ abundance (Figure 9 and Table S1). NO₃-δ¹⁸O values within soil profiles, transect samples, and for all data were negatively correlated to 1/NO₃⁻ concentrations and to Cl⁻/NO₃⁻ and ClO₄⁻/NO₃⁻ molar ratios. For the profiles there were generally consistent relationships between isotope ratios and each of the indicators of NO₃⁻ stability; relations with ClO₄⁻/NO₃⁻ ratios were the most consistent. δ¹⁵N values of soil profiles were not as consistently related to NO₃⁻ concentrations (1/NO₃⁻) but generally were significantly negatively correlated to both Cl/NO₃⁻ and ClO₄⁻/NO₃⁻ molar ratios (Figure 9). It should be noted that while NO₃-δ¹⁵N values of transect samples were significantly correlated to both 1/NO₃⁻ and ClO₄⁻/NO₃⁻ 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 NO₃⁻ isotope composition in the dry soils (see Discussion). Variations with depth in soil profiles (increasing δ¹⁵N and δ¹⁸O with decreasing relative NO₃⁻ abundance) could be consistent with isotopic fractionation or mixing, whereas spatial variations along the valley floor (increasing δ¹⁸O with decreasing δ¹⁵N and relative NO₃⁻ abundance) may indicate different sources or depositional environments. Finally, perennial snow and glacier ice had similar NO₃⁻ isotopic compositions, with lower δ¹⁸O values and higher δ¹⁵N values than soils (Figure 7). The trend was reversed with respect to fresh snow and total atmospheric deposition, the latter being depleted in δ¹⁵N but enriched in δ¹⁸O.

3.4 Cl⁻ isotopic composition

δ³⁷Cl values of Cl⁻ (Cl-δ³⁷Cl) 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-δ³⁷Cl 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 sediment (Figure 10). Only in the profile closest to University Glacier, composed solely of ice-cemented sediment, did values of $\text{Cl}-\delta^{37}\text{Cl}$ decrease with depth (by $<1\text{‰}$ over 60 cm). $\text{Cl}-\delta^{37}\text{Cl}$ values in soil samples were lower by $\sim 1\text{-}2\text{‰}$ than in the snow pack or glacier ice.

The $^{36}\text{Cl}/\text{Cl}$ ratios of Cl^- in soils from University Valley (1800×10^{-15} to 2400×10^{-15}) were higher than those reported for other MDV soils (400×10^{-15} to 1200×10^{-15}), but lower than those in Dome Fuji ice ($\sim 4500 \times 10^{-15}$) 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 ($\sim 2400 \times 10^{-15}$). $^{36}\text{Cl}/\text{Cl}$ ratios in glacier ice and perennial snow (composite samples between 0-125 cm) were 880×10^{-15} and 510×10^{-15} , respectively, and much lower than those in soils, but were similar to values (123×10^{-15} to 592×10^{-15}) in fresh snow from Taylor Dome (Lyons et al., 1998). Perennial snow patch samples contained both pre- and post-nuclear weapon testing (bomb) deposition, as indicated by a measurable ^3H peak (23 TU) at a depth of 45 cm, whereas glacier ice appeared to be mainly pre-bomb, as there was no detectable ^3H (<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}Cl in these soil profiles. The relatively low $^{36}\text{Cl}/\text{Cl}^-$ ratios and relatively high $\delta^{37}\text{Cl}$ 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}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 sediments overlain by a layer of dry soil whose thickness tends to increase toward the mouth of the valley (McKay, 2009; Marinova et al., 2013). 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-cemented sediments, 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 $\text{NO}_3^-/\text{Cl}^-$ 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). $\text{NO}_3^-/\text{ClO}_4^-$ 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 $\text{NO}_3^-/\text{ClO}_4^-$ 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 $\delta^{18}\text{O}$ value of -4.9 ‰ and a $\Delta^{17}\text{O}$ 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 $\Delta^{17}\text{O}$ value was slightly elevated (by 2-3 ‰) compared to those of any other ClO_4^- samples with similar $\delta^{18}\text{O}$ values (Jackson et al., 2010). In contrast, the $\delta^{37}\text{Cl}$ value of University Valley ClO_4^- (+1.3 ‰) was similar to those of many other indigenous natural ClO_4^- occurrences, but significantly higher than those of Atacama ClO_4^- , and the $^{36}\text{Cl}/\text{Cl}$ ratio ($33,000 \times 10^{-15}$) 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 $\text{NO}_3^-/\text{Cl}^-$ 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). $\text{ClO}_3^-/\text{ClO}_4^-$ 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 $\text{ClO}_3^-/\text{ClO}_4^-$ ratios of the order of 1 or higher have been reported (Rao et al., 2010; Kounaves et al., 2014; Jackson et al., 2015). Lower $\text{ClO}_3^-/\text{ClO}_4^-$ 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.

The negative $\delta^{37}\text{Cl}$ values and elevated $^{36}\text{Cl}/\text{Cl}$ 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 $\delta^{37}\text{Cl}$ values with

depth due to the contribution of buried glacier ice. The buried glacier ice, whose origin was attributed to windblown polar plateau snow, was assumed to have very negative $\delta^{37}\text{Cl}$ value. A two-component mixing model (Figure 11A) reasonably describes the variation in $\delta^{37}\text{Cl}$ and $^{36}\text{Cl}/\text{Cl}$ values, assuming the stratospheric component had end member values of -4 ‰ (based on northern hemisphere precipitation; Koehler and Wassenaar, 2010) and 4500×10^{-15} (average value at Dome Fuji), respectively, and the SSC component had end member values of 0 ‰ and 1×10^{-15} (sea water), respectively. Correlations of both $\delta^{37}\text{Cl}$ and $^{36}\text{Cl}/\text{Cl}$ values with inverse Cl^- concentration (Figure 11B,C) further support this two-component mixing model. Glacier ice and snow had higher $\delta^{37}\text{Cl}$ values compared to soil values, contrary to past assertions that the glacier ice in the stable upland zone should have the lowest $\delta^{37}\text{Cl}$ values as the ice source is windblown snow from the Polar Plateau (Bao et al. 2008). $\text{Cl}-\delta^{37}\text{Cl}$ 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 $\text{Cl}-\delta^{37}\text{Cl}$ variation with depth and the lower $\text{Cl}-\delta^{37}\text{Cl}$ 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 glacier ice, although some such residual components may be present.

Our data indicate that variations in soil $\text{Cl}-\delta^{37}\text{Cl}$ and $^{36}\text{Cl}/\text{Cl}$ 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 $\delta^{37}\text{Cl}$ 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 $\text{Cl}-\delta^{37}\text{Cl}$ 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, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 HNO_3 . Previous studies in Antarctica indicate NO_3^- photolysis and partial re-oxidation may be responsible for large increases in $\delta^{15}\text{N}$ and moderate decreases in $\delta^{18}\text{O}$ of NO_3^- in snow and ice (Frey et al., 2009; Erbland et al., 2013). Our snow and ice data are qualitatively consistent with such effects, but the magnitudes of changes in our data appear to be relatively smaller for $\delta^{15}\text{N}$ and larger for $\delta^{18}\text{O}$ compared to effects commonly attributed to photolysis (Figure 7). Other potential fractionating processes of NO_3^- loss include HNO_3 volatilization, which could cause variable isotope effects depending on the relative importance of either equilibrium or kinetic fractionations associated with aqueous speciation ($\text{NO}_3^-_{(\text{aq})}$ - $\text{HNO}_{3(\text{aq})}$) and vapor emission ($\text{HNO}_{3(\text{aq})}$ - $\text{HNO}_{3(\text{g})}$). For example, Frey et al. (2009) summarize theoretical calculations indicating HNO_3 may have higher $\delta^{15}\text{N}$ than NO_3^- at equilibrium. In this case, if $\text{HNO}_3 < \text{NO}_3^-$ in the perennial snow, and if other fractionating mechanisms were not dominant, then $\delta^{15}\text{N}$ of HNO_3 could be higher than that of total ($\text{HNO}_3 + \text{NO}_3^-$) and emission of HNO_3 could leave behind NO_3^- with relatively low $\delta^{15}\text{N}$, which would not be consistent with $\delta^{15}\text{N}$ enrichments observed in perennial snow packs (Frey et al., 2009). However, if $\text{HNO}_3 > \text{NO}_3^-$, then the isotopic composition of HNO_3 would be similar to that of ($\text{HNO}_3 + \text{NO}_3^-$) and isotope effects could be dominated by effects of HNO_3 emission. Erbland et al. (2013) report experiments indicating “physical release” of HNO_3 caused an increase in $\delta^{15}\text{N}$ of residual NO_3^- in snow, with an apparent fractionation much smaller than that associated with photolysis. Walters and Michalski (2015) summarize theoretical calculations indicating $\delta^{15}\text{N}[\text{HNO}_{3(\text{aq})}] < \delta^{15}\text{N}[\text{NO}_3^-_{(\text{aq})}] < \delta^{15}\text{N}[\text{HNO}_{3(\text{g})}]$ at equilibrium, with fractionation factors of the order of 2-4 ‰, permitting a variety of effects depending on conditions, possibly including ^{15}N enrichment of residual NO_3^- especially if volatilization is associated with a substantial kinetic fractionation. . Further, if conditions in concentrated aqueous films were strongly acidic, then O exchange could occur between HNO_3 and H_2O with low $\delta^{18}\text{O}$, causing $\delta^{18}\text{O}$ of HNO_3 to decrease (Böhlke et al., 2003; Kaneko and Poulson, 2013). In this case,

volatilization and exchange could conceivably cause $\delta^{15}\text{N}$ to increase and $\delta^{18}\text{O}$ to decrease in residual HNO_3 in the perennial snow, as was observed. Variation in the perennial snow and glacier ice NO_3^- isotopic composition did not appear to be related to NO_3^- concentration, $\text{Cl}^-/\text{NO}_3^-$, $\text{ClO}_4^-/\text{NO}_3^-$, or depth. However, the much higher $\text{NO}_3^-/\text{Cl}^-$ ratios in soil compared to the perennial snow and glacier ice suggest that either the deposition rate and/or capture rate of NO_3^- and Cl^- were different between ice and soil, or NO_3^- was lost from the perennial snow and ice. HCl has a higher vapor pressure than HNO_3 but it also has a much lower dissociation constant.

In contrast to the perennial snow and glacier ice, soil NO_3^- apparently was more resistant to post-deposition processes affecting its relative abundance and isotopic composition. Major differences between these environments include acid neutralization by reaction with minerals in soil (less photolysis, volatilization, and isotopic exchange) and less light penetration in soil (less photolysis; i.e., Tester et al., 1987). These results indicate NO_3^- 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 dry 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 $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ (transect samples), and the strong overall relations between $\delta^{18}\text{O}$, $\delta^{15}\text{N}$, and measures of NO_3^- loss (e.g. $\text{ClO}_4^-/\text{NO}_3^-$ molar ratio and $1/\text{NO}_3^-$) (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 $\text{NO}_3^-/\text{Cl}^-$ and $\text{NO}_3^-/\text{ClO}_4^-$ ratios with depth down to the ice table (Figure 5), 2) decreasing $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ with depth and simultaneously with NO_3^- relative abundance, as indicated by $1/\text{NO}_3^-$, $\text{Cl}^-/\text{NO}_3^-$, and $\text{ClO}_4^-/\text{NO}_3^-$ (Figure 8 and 9), and 3) co-variation of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ within profiles that is consistent with isotope fractionation effects (Figure 7). These relations are similar to those reported for $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ 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 underlying ice-cemented sediment. Mixing could be qualitatively consistent with a series of positive $\delta^{15}\text{N}$ - $\delta^{18}\text{O}$ 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 ($\sim 10\times$) in ice-cemented sediment 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 ($2\times$) between the surface of the ice-cemented sediment and the overlying dry soil ($\sim 1\text{cm}$).

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 ice or snow packs, but not those based on total deposition, were higher than those based on Cl^- . The lower NO_3^- deposition rates from glacier and snow studies are likely due to the greater tendency for NO_3^- post-depositional processing (photo-transformation and volatilization), which is supported by low $\text{NO}_3^-/\text{Cl}^-$ ratios in University Valley snow pack and glacier ice, and by altered NO_3^- stable isotopic composition in snow pack and glacier ice but not in soil NO_3^- . Salt accumulation times are consistent with the lack of variation in $^{36}\text{Cl}/\text{Cl}^-$ ratios which would have been only minimally impacted by radioactive 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.

Differences in the estimated salt accumulation times along the valley 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 kyr, 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 kyr, 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 sediments

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 sediment; 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 with 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. Such process has been observed in glaciers (e.g., Fisher, 1987).

Finally, the low abundance and homogenous distribution of salts in the ice-cemented sediment could be due to a rapid sedimentation in a scenario of glacier retreat, leading to the deposition of a 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 epigenetic permafrost and ground ice would prevent further infiltration of salt from the atmosphere. The mass balance of salts in the soil and the ^{36}Cl data suggest that such an event would have happened during the last several hundred thousand years. While there is no independent evidence supporting this event, it has been suggested that 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 relatively dilute salt profiles 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 might result in a salt-rich layer 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 sediment will likely provide important insights regarding the formation and evolution of ground ice in this extremely cold and dry environment. Deeper sampling, along with 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 $^{36}\text{Cl}/\text{Cl}^-$ ratios and $\delta^{37}\text{Cl}^-$ 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 $^{36}\text{Cl}/\text{Cl}^-$ ratios are not due to nuclear bomb fallout, but rather may be characteristic of the natural deposition (wet or dry) source of Cl^- . Soil NO_3^- isotopic compositions largely reflect unaltered atmospheric deposition and likely represent some of the best preserved atmospheric NO_3^- occurrences on earth. Small but systematic variations in NO_3^- 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 resulted in differing degrees of post depositional transformation. We also propose that ratios of NO_3^- to other conserved species, particularly ClO_4^- , appear to be useful indicators of NO_3^- loss and NO_3^- isotopic alteration and should be considered in other studies in addition to evaluating changes in NO_3^- concentration directly. The isotopic composition of ClO_4^- 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

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 ClO_4^- and ClO_3^- in these soils along with the very limited transport, hyper-arid conditions, and cold temperatures, support the use of University Valley as a possible Earth analog of Mars processes. SAM data indicate a constant ratio of $\text{NO}_3^-/\text{ClO}_4^-$ in Martian soil (Stern et al., 2015). The loss of ClO_3^- in University Valley soils is of particular interest as it could suggest that the ratio of $\text{ClO}_3^-/\text{ClO}_4^-$ in Martian soils may be an indicator of water availability, although further work is required to understand the exact conditions that lead to ClO_3^- 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.

Profile	Distance From Glacier	Total Depth	ΣCl	R _U	R _F	Accumulation Time				
University Valley Measured Values					Sasa et al., 2010			Whitherow et al., 2006 MDV		Measured Total Deposition
				³⁶ Cl/Cl*10 ⁻¹⁵ Avg(Stdev)	³⁶ Cl/Cl*10 ⁻¹⁵ Avg(Stdev)	³⁶ D _{36Cl} ^a ³⁶ Cl Deposition (28,000±1,600 atoms/cm ² -year)	³⁶ D _{Cl-FA} ^b Cl Deposition normalized for ³⁶ Cl ratio (3.8±0.4 mg/m2-y)*R _F /R _U	³⁶ D _G ^c Estimated Cl ⁻ Deposition from Glaciers		³⁶ D _U ^d University Valley (2 year cumulative Collection) ^d
								2.9 mg/m ² -y	6 mg/m ² -y	2.4 mg/m ² -y
	(m)	(cm)	(mg/m ²)	(Atom/Atom)	(Atom/Atom)	Years				
1	370	56	80,470	1,990 (96)	4,512 (789)	9,800	9,400	28,100	13,400	33,500
3	720	56	189,000	1, 920 (56)	4,512 (789)	22,300	21,200	66,100	31,500	79,000
4	1100	56	349,000	2,200 (260)	4,512 (789)	47,200	45,000	122,000	58,200	145,000
5	1980	56	525,000	2,200(260)	4,512 (789)	71,000	68,000	184,000	87,500	219,000

- a. ³⁶Cl deposition rate for Dome Fuji between 10,000 and 22,000 years ago from Sasa et al., 2010. (see section 2.5 for method)
- b. Cl deposition 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/Cl at each site. (see section 2.5 for method)
- c. Cl deposition rate reported (Witherow et al., 2006) for the range of MDV low accumulation glaciers. (see section 2.5 for method)
- d. Total Deposition rate measured for a two year period (2010-2012) from this study. (see section 2.5 for method)

Table 2. Ranges of NO_3^- accumulation time in profiles along University Valley based on deposition rates.

Profile	Distance From Glacier	Total Depth	$\Sigma \text{NO}_3\text{-N}$	Estimated Accumulation time Based on Various NO_3 Deposition Values				
				MDV Low Accumulation Glaciers (Whitherow et al., 2006))		Snow ITASE Traverse (Traversi et al., 2012)		University Valley Measured Total Deposition University Valley Measured Total Deposition
				^a D1 _{NO3} (0.55 mg/cm ² -year)	^a D2 _{NO3} (0.87 mg/cm ² -year)	^a D3 _{NO3} (0.67 mg/m ² -year)	^a D4 _{NO3} (1.1 mg/m ² -year)	
	(m)	(cm)	(mg/m ²)	Years				^b D5 _{NO3} (3.6 mg/m ² -year)
1	370	56	66,000	121,000	76,000	99,000	59,000	18,000
3	720	56	146,000	267,000	168,000	218,000	130,000	41,000
4	1100	56	268,000	491,000	309,000	400,000	239,000	74,000
5	1980	56	534,000	978,000	615,000	797,000	477,000	148,000

a. Deposition rates reported for the range of MDV low accumulation glaciers (Whitherow et al., 2006) or the relationship developed for NO_3 accumulation and snow accumulation assuming either dry deposition only or a maximum snow accumulation rate of 10cm w.e. /year as an upper bound given there is no snow accumulation in University Valley. (see section 2.5 for method)

b. Total Deposition rate measured for a two year period (2010-2012) from this study. (see section 2.5 for method)

Table S1. Statistical relationships (r^2 , P values, and slopes) between $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of NO_3 with various variables. Note that for Transect samples location in Valley is replaced with depth of sample.

Profile	$\delta^{18}\text{O}-\text{NO}_3$ (‰)														
	r^2					Slope					P				
	Cl/NO_3	$1/\text{NO}_3$	NO_3/ClO_4	Depth/ Location *	$\delta^{18}\text{O}-\text{NO}_3$	Cl/NO_3	$1/\text{NO}_3$	NO_3/ClO_4	Depth/ Location*	$\delta^{18}\text{O}-\text{NO}_3$	Cl/NO_3	$1/\text{NO}_3$	NO_3/ClO_4	Depth/ Location *	$\delta^{18}\text{O}-\text{NO}_3$
(m)	(mol/mol)	(kg/mg)	(mol/mol)	(‰/cm) or (‰/m)*	‰/‰	(‰*mol/ mol)	(‰*mg/kg)	(‰*mol/mol)	(‰/cm) or (‰/m)*	‰/‰	(mol/mol)	(kg/mg)	(mol/mol)	(‰/cm) or (‰/m)	‰/‰
720	0.87	0.90	0.23	0.62		-6.7	-420	-26,000	-.065		0.008	<.001	0.22	0.02	
750	0.45	0.30	0.51	0.66		-3.1	-208	-23,000	-.032		0.14	0.256	0.11	<.001	
1000	0.91	0.76	0.77	0.42		-4.3	-190	-51,000	-.017		0.03	0.05	0.05	0.24	
1100	0.93	0.57	0.93	0.57		-3.6	-297	-31,000	-.041		<.001	0.012	<.001	0.001	
1980	0.92	0.62	0.8	0.22		-3.2	-420	-33,000	-.017		0.001	0.02	0.003	0.24	
Transect	0.003	0.60	0.9	0.5*		0.8	-350	-57,000	-.003*		0.84	0.001	<.001	0.004*	
All	0.28	0.30	0.76	0.4*		-2.4	-180	-46,000	-.003*		0.05	<.001	<.001	0.005*	
	$\delta^{15}\text{N}-\text{NO}_3$														
720	0.92	0.22	0.7	0.87	0.55	-2.1	-99	-18,000	-.030	0.37	0.008	0.13	0.009	<.001	0.09
750	0.67	0.53	0.73	0.48	0.02	-2.4	-26	-8,600	-.0084	0.04	0.015	0.005	<.001	0.008	0.72
1000	0.99	0.71	0.92	0.84	0.78	-3.0	-120	-35,000	-.016	0.57	<.001	0.07	0.01	0.028	0.047
1100	0.95	0.09	0.43	0.51	0.88	-3.2	-39	-17,000	-.035	0.82	<.001	0.19	0.001	0.003	<.001
1980	0.78	0.50	0.50	0.27	0.87	-2.5	-350	-24,000	-.018	0.86	0.021	0.05	0.05	0.19	<.001
Transect	0.21	0.3	0.53	0.63	0.63	-9.5	400	70,000	-.006	-1.3	0.10	0.04	0.003	<.001	<.001
All	0.35	0.04	0.03	0.56		-7.6	87	-12,000	-.005		<.001	0.10	0.16	<.001

Figure 1. A) Map showing the location of University Valley relative to Beacon Valley within the McMurdo Dry Valleys (MDV) of Antarctica; B) Map of University Valley showing locations of soil transect samples (T1-T13) and soil profile samples at various distances from University Glacier; and C) Schematic longitudinal vertical section of University Valley showing relative positions of ice, snow, and soil profile samples, with the approximate location of the boundary between dry soil and ice cemented sediment.

Figure 2- Depth profiles of anion concentrations in University Valley soils at various distances downgradient from University Glacier (Figure 1C). Filled symbols indicate values in dry cryotic soil and open symbols indicate values in ice-cemented sediment. Horizontal lines indicate the depth to the top of ice-cemented sediment (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 sediment. B) Variation in Cl^- , NO_3^- -N, and ClO_4^- mass per area at four distances from the glacier (370 m, 720 m, 1100 m, 1980 m). Total masses are given for the upper 56 cm of the profiles (maximum common depth). Hatched boxes indicate the portions of the masses attributable to the ice cemented parts of the profile.

Figure 5. Depth profiles of $\text{NO}_3^-/\text{ClO}_4^-$, $\text{Cl}^-/\text{ClO}_4^-$, and $\text{NO}_3^-/\text{Cl}^-$ 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 sediment (ice table) where known.

Figure 6. Variation of anion molar ratios and NO_3^- stable isotopic composition in snow, ice, and soils with distance from University Glacier. Horizontal lines indicate mean values in aerosols 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 data from dry cryotic soils (solid symbols) and open symbols represent ice cemented sediment (not included in regressions). References in legend are: ¹ (Frey et al., 2009), ² (Savarino et al., 2007), ³ (Michalski et al., 2005)

Figure 8. Variation of NO₃ 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 sediment. Boxes indicate samples with the maximum NO₃⁻ concentration in each profile. Horizontal lines (green, red, and blue) indicate the depth to the top of ice-cemented sediment (ice table).

Figure 9. Comparison of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of NO_3 with measures of relative NO_3 abundance as reflected by $\text{NO}_3\text{-N}$ concentration ($1/\text{NO}_3$) and molar ratios of $\text{ClO}_4^-/\text{NO}_3^-$ and $\text{Cl}^-/\text{NO}_3^-$. Colored lines indicate regressions for dry cryotic soils with similar colored data points (solid symbols). Open symbols represent values of ice cemented soil below dry cryotic soil and are not included in regressions. Black lines indicate overall regressions for all of the dry cryotic soil data in each plot.

Figure 10. Variation of $^{36}\text{Cl}/\text{Cl}$ and $\delta^{37}\text{Cl}$ values in soil Cl^- with respect to depth and location in University Valley. Filled symbols indicate values in dry cryotic soil and open symbols indicate values in ice-cemented sediment. Composite values for snow pack and glacier ice are also shown. Horizontal lines indicate the depth to the top of ice-cemented sediment (ice table).

Figure 11. A) Variation in $^{36}\text{Cl}/\text{Cl}$ ratio with respect to $\delta^{37}\text{Cl}$ of Cl^- in samples from University Valley. Filled symbols indicate values in dry cryotic soil and open symbols indicate values in ice-cemented sediment. The curve represents a hypothetical mixing model between stratospheric and SSC 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) and C) Variation in $^{36}\text{Cl}/\text{Cl}$ and $\delta^{37}\text{Cl}$ with respect to Cl abundance ($1/\text{Cl}^-$). Black lines represent regression line.

Figure S1. Relative ratios of NO_3^- , Cl^- , and ClO_4^- in soil profiles at various distances from University Glacier. Measured ratios (shown in Figure 2) were arbitrarily normalized to the surface ratio in each profile to better illustrate relative changes with depth. Horizontal black lines indicate the depth to the top of ice-cemented sediment (ice table).

Figure S2. Concentrations of tritium (^3H in tritium units, TU) in vertical profiles from University Glacier and University Valley snow pack. The solid line represents the detection limit (8TU). The snow pack data are not from the same core used to generate the chemical profiles in this study but are from the same snow pack.