



Two chloride sources in soils of the McMurdo Dry Valleys, Antarctica

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[1] Sulfate, nitrate, and chloride are major water-soluble anions in soils of the McMurdo Dry Valleys (MDV), Antarctica. We measured the chloride stable isotope composition of 40 soil samples from 16 different soil profiles. The soil profiles come from three different microclimate zones in the MDV: a coastal thaw zone, which fosters a seasonally saturated active layer; a stable upland zone, in which air and soil temperatures are too cold to foster active layers and/or significant snowmelt; and an intermediate, inland mixed zone. Results show that the total water-soluble chloride content is low in both the coastal and the upland zones, but highly variable in the inland mixed zone (average 770 to 11520 ppm). Individual soil $\delta^{37}\text{Cl}$ values range from -2.10‰ to $+0.56\text{‰}$, with profile average $\delta^{37}\text{Cl}$ values broadly decreasing from the coast toward upland valleys. Vertically, the $\delta^{37}\text{Cl}$ increases with depth in soil profiles developed on basal tills but decreases on sublimation tills. We propose that the spatial $[\text{Cl}^-]$ and $\delta^{37}\text{Cl}$ patterns are the result of continuous influx and leaching of two major chloride sources, an airborne sea-salt chloride (SSC) with a $\delta^{37}\text{Cl}$ value $\geq \sim 0.0\text{‰}$ and a secondary atmospheric chloride (SAC) with a $\delta^{37}\text{Cl}$ value $\leq -2.10\text{‰}$. Our model suggests that sublimation tills have their Cl^- input from two boundaries: a till-atmosphere interface at the top and a buried-ice-till interface at the bottom, differing distinctively from basal tills where there is no salt contribution from the bottom. Our model also suggests a higher influx of SSC relative to SAC in the MDV in the past. Overall, characterizing the sources, budgets, and spatial/vertical patterns of chloride constitutes a first step toward unraveling climate, tectonic, and landscape changes archived in MDV soil profiles.

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1. Introduction

[2] The McMurdo Dry Valleys (MDV) are located in the central Transantarctic Mountains, between the East Antarctic Ice Sheet (EAIS) and seasonally open water of the Ross Sea (Figure 1). Local relief is ~ 2800 m. Most surfaces are generally free of ice and there are no vascular plants. Major east-west trending valleys, each ~ 80 km long and up to 15 km wide, extend across the region. A high-elevation bedrock threshold (~ 2000 m) prevents significant influx of the EAIS into the MDV. Two small outlet glaciers, Taylor Glacier and Upper Wright Glacier, just pass over this threshold and terminate 75 to 50 km from the coast; only one outlet glacier reaches the sea (Ferrar Glacier) (Figure 1). Small alpine glaciers, nourished by local precipitation and windblown snow from the Polar Plateau, occur on elevated benches and on plateaus between the main valleys.

[3] Observed and measured variations in weather patterns across the MDV [e.g., *Doran et al.*, 2002] show that the region is best divided into a series of microclimate zones [*Marchant and Denton*, 1996; *Marchant and Head*, 2008]. The simplest zonation includes a coastal thaw zone, an inland mixed zone, and a stable upland zone. Alternative climate subdivisions are possible [e.g., *Bockheim*, 1997, 2002; *Campbell and Claridge*, 1969, 1987], but this three-fold classification captures major trends in soil moisture and geomorphic processes [*Marchant and Denton*, 1996; *Marchant and Head*, 2008].

[4] 1. The first zone is the coastal thaw zone. Modern summertime air temperatures in the coastal thaw zone show a mean season-long temperature of approximately -5°C , and a mean daily maximum of approximately -2°C . Relative humidity (RH) averages $\sim 64\%$; the rather high RH value for this zone is due to the prevalence of southeasterly winds, which carry moisture from the Ross Sea. Because of large variations in surface albedo in the coastal thaw zone (which arise from the presence of numerous tills capped by different lithologies [*Denton and Marchant*, 2000; *Hall et al.*, 1993]), surface and subsurface ground temperatures vary considerably over relatively short horizontal distances of ~ 10 m; in most places, soil temperatures during summer months rise well above 0°C . Snowfall in the coastal thaw zone exceeds 80 mm of water equivalent per year [*Schwerdtfeger*, 1984]. A

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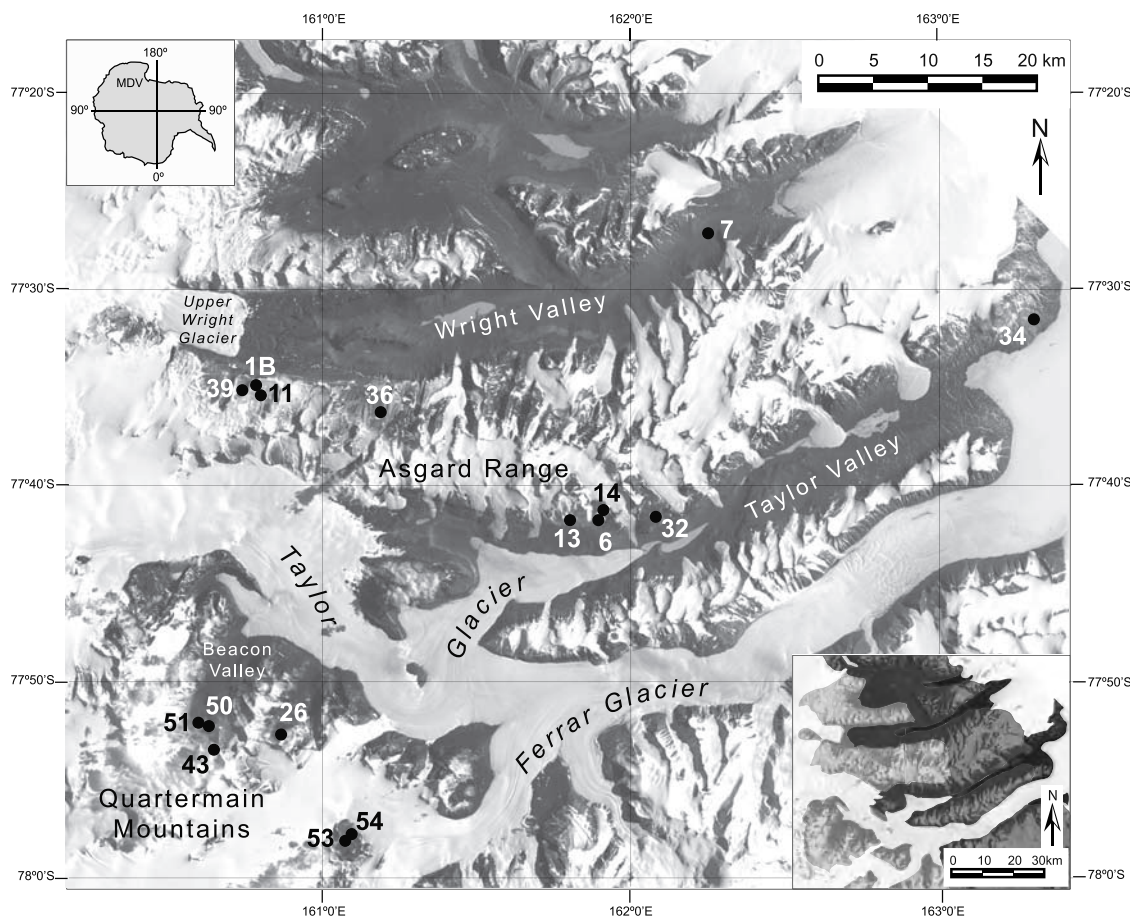


Figure 1. Satellite map of the McMurdo Dry Valleys, Antarctica, and locations of soil profiles reported in this paper. Inset map shows same region with the threefold microclimate classification scheme of *Marchant and Denton* [1996] and *Marchant and Head* [2008]. Dark gray, coastal thaw zone; gray, inland mixed zone; light gray, stable upland zone.

large fraction of this moisture infiltrates soils, yielding gravimetric water contents (GWC) $>30\%$ [*D. I. Campbell et al.*, 1997; *I. B. Campbell et al.*, 1997].

[5] 2. The second zone is the inland mixed zone. Alternating winds passing across the inland mixed zone (westerly katabatic and easterly from the Ross Sea) produce variable RH in the inland mixed zone, but the mean summertime value is close to that of the coast, $\sim 67\%$. Summertime air temperatures show a mean of approximately -7°C , with a mean daily maximum of approximately -4°C . Snowfall is most probably less than that of the coastal thaw zone; the uncertainty lies in the unknown quantity of windblown snow from the Polar Plateau in this region. Apart from regions alongside ephemeral streams and isolated snow patches, near-surface soils contain $<30\%$ GWC [*D. I. Campbell et al.*, 1997; *I. B. Campbell et al.*, 1997].

[6] 3. The third zone is the stable upland zone. The low value of summertime RH for the stable upland zone, $\sim 41\%$, reflects the passage of dry, katabatic winds originating over the EAIS. Summertime air temperatures show a mean of approximately -10°C , with a mean daily maximum of approximately -8°C . Precipitation is limited, but snow blown off the polar plateau may accumulate on small glaciers and feed perennial snow banks. Glaciers and snow

banks lose mass by sublimation and most soils contain $<5\%$ GWC [*I. B. Campbell et al.*, 1997].

[7] Several studies suggest that this threefold microclimate zonation in the MDV has persisted for millions of years, perhaps for as much as 10 to 15 million years [*Marchant and Head*, 2008; *Marchant et al.*, 1996; *Sugden et al.*, 1993]. If so, it seems reasonable to assemble our salt profiles according to this threefold, spatial zonation. We view the salt input and migration as one of the few active and enduring processes in these hyperarid and frigid surfaces. Thus salt profiles bear important information on the history of climate and landscape stability. In order to accurately retrieve these records, a comprehensive and dynamic physical model will have to be constructed to quantify the various salt influxes (deposition) and outfluxes (leaching). Prior to model construction, however, we first need to characterize salt sources and the spatial and vertical distribution of individual salts in MDV soils. Of the three main salt species in the MDV, sulfate, nitrate, and chloride, we focus here on the chloride, particularly its sources and its spatial and vertical variations in concentration and isotope composition. To be sure, our goal is not to determine the precise geographic boundary for each microclimate zone in the MDV, nor to deconvolve the specific climate conditions common in each zone (though our results may help to do so in

the future), but rather our goal is to identify specific chloride sources and the influx and outflux patterns that give rise to observed trends in soil chloride across the region.

[8] The spatial and vertical distribution for sulfate and, to a lesser extent, nitrate have been identified and mapped in the MDV with the assistance of multiple stable isotope compositions [Bao and Marchant, 2004, 2006; Michalski et al., 2005]. Little is known, however, about chloride in MDV soils. Earlier studies noted that chloride was more abundant in coastal and intermediate zones than in plateau fringes or upland valleys [Bockheim, 1979, 1997; Campbell and Claridge, 1968; Claridge and Campbell, 1977]. Most chlorides in the MDV were believed to originate from sea-salt aerosols [Campbell and Claridge, 1968; Claridge and Campbell, 1977; Ugolini, 1966] with minor addition from weathering of parent rocks [Claridge and Campbell, 1977; Linkletter, 1972]. Another potential atmospheric source for chlorides in the MDV is the secondary atmospheric or long-range atmospheric chlorides, including potential stratospheric sources. Volatile chloride compounds such as methyl chloride (CH_3Cl) are generated by biological activities and released into the atmosphere. Sea-salt aerosols, largely in the form of NaCl , also release halogen species into the atmosphere upon acidification. The predominant removal mechanism for atmospheric chlorine is in the form of HCl [Graedel and Keene, 1995]. Therefore secondary atmospheric HCl or chloride salts should be expected in the MDV soils. Similar secondary atmospheric sources have been identified as major components for sulfate and perhaps for all of the nitrate in the MDV soils [Bao and Marchant, 2004, 2006; Michalski et al., 2005].

[9] Building on these earlier reports, our aim here is to use stable chlorine isotope compositions, in combination with chloride concentration data, to examine the hypotheses that chloride in the MDV is a mixture of two major sources, sea-salt chloride (SSC) and secondary atmospheric chloride (SAC). It is expected that SSC and SAC have distinct $\delta^{37}\text{Cl}$ values so that spatial and vertical patterns can be revealed with adequate sampling in the valleys.

2. Sampling and Analytical Methods

[10] Soil samples were collected during a field campaign led by a team from Louisiana State University (LSU) and Boston University (BU) in 2002–2003. The locations of 16 soil profiles analyzed in this study are shown in Figure 1. All samples were collected from glacial tills, and subdivided further as to whether they came from basal or sublimation tills. Basal tills form at the base of glaciers, either through melt out or plastering; following deposition, the major salt input is from the atmosphere, and initial concentrations are thus highest near the ground surface. The situation is more complex for sublimation tills. Sublimation tills form by the progressive sublimation of debris-rich glacier ice; as ice sublimates, a lag deposit (sublimation till) forms at the top of the remaining ice. Accordingly, two sources of salts influence sublimation tills: an atmospheric source (which for the most part influences the top of the till) and a glacier source, which influences the base of the till. Depending on the location of ice formation, the base of the till may have a salt inventory that differs from the atmospheric inventory at a given locality. Some sublimation tills, still resting on remnant glacier ice in

the stable upland zone, are apparently as old as 8 million years [Marchant et al., 2002; Sugden et al., 1995b].

[11] The vertical sampling resolution for all tills examined in this study ranged from 2 to 15 cm. Extraction of water-soluble ions from each sample was conducted by repeatedly leaching a ~ 300 -mg aliquot (< 2 -mm-sized fraction) with distilled and deionized water. After the solution was filtered through a $0.22 \mu\text{m}$ Whatman syringe filter, the total soluble chlorine ($[\text{Cl}^-]$ ($\pm 5\%$)), together with the concentrations of other water-soluble anions and cations (e.g., SO_4^{2-} , NO_3^- , Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+}), were measured on an Ion Chromatograph (ICS-90) at LSU. For measures of the $\delta^{37}\text{Cl}$, AgCl was precipitated from a solution extracted from a ~ 2 – 5 g soil sample aliquot by the addition of AgNO_3 solution. CH_3Cl was generated in a vacuum by reacting AgCl with CH_3I and further purified by gas chromatography before being introduced to an isotope ratio mass spectrometer (Finnigan MAT Delta Plus XL) [Barnes and Sharp, 2006; Eggenkamp et al., 1995]. AgCl precipitation and chlorine isotope analyses were conducted at University of New Mexico (UNM). The $\delta^{37}\text{Cl}$ is defined as $(R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000\%$, in which R is the ratio of $^{37}\text{Cl}/^{35}\text{Cl}$ and the international reference is Standard Mean Ocean Chlorine (SMOC). The analytical error for $\delta^{37}\text{Cl}$ value is $\pm 0.12\%$ (1σ) on the basis of long-term reproducibility of three in-house references at UNM. This chloride study incorporates four times as many soil profiles as that used in our earlier analyses of sulfate in the MDV (i.e., 16 versus 4) [Bao and Marchant, 2006]. However, the number of samples analyzed at each soil profile was not as great as in our sulfate study; this is due mainly to the relatively laborious procedure involved in measuring $\delta^{37}\text{Cl}$ as compared to measuring sulfur and oxygen isotope data.

[12] Including the 16 soil profiles examined in this study, we have obtained high-resolution ion concentration data for more than thirty soil profiles in the MDV. All water-soluble cations and anions are interconnected by various salt mineral phases and by repeated dissolution/precipitation processes in a soil column. For example, the $[\text{Na}^+]$ is closely related to $[\text{Cl}^-]$ because of a sea-salt source. However, the Na^+ can also form minerals with SO_4^{2-} or NO_3^- , or likewise the Cl^- with K^+ or Mg^{2+} . Therefore the $[\text{Na}^+]$ can only be useful in understanding the Cl^- behavior if postdepositional behaviors for all other soluble cations and anions are jointly considered. We are not, therefore, presenting these high-resolution ion concentration data here because they are only marginally relevant to the goal of this study and are better presented in a separate publication. We will focus on the average $[\text{Cl}^-]$ and, especially, the $\delta^{37}\text{Cl}$ in this report.

3. Results

[13] A quick glance at Figures 2–4 will show large variations in $[\text{Cl}^-]$ within and among individual soil profiles across the MDV. In all soils examined, the $[\text{Cl}^-]$ reaches a maximum at a depth of 10 to 50 cm below the ground surface, as is commonly the case for soil ions in the MDV. However, this $[\text{Cl}^-]$ maximum lies below peak concentration depths measured for SO_4^{2-} (data not shown here, see [Bao and Marchant, 2006]). The average $[\text{Cl}^-]$ normalized with depth for each of the 16 soil profiles is listed in Table 1 (see notes therein for the formula for calculating the

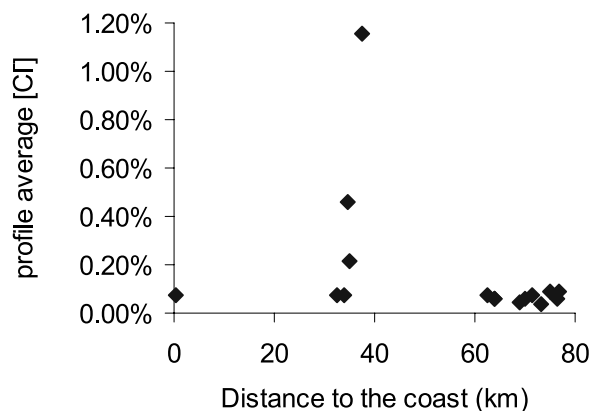


Figure 2. Average water-soluble $[Cl^-]$ in a soil profile (normalized with depth, the last column in Table 1) plotted against distance from the coast across the McMurdo Dry Valleys.

average), together with 40 individual $[Cl^-]-\delta^{37}Cl$ data pairs. Soils ~ 30 to 40 km distant from the coast (i.e., in the inland mixed zone) have the most variable and also the highest chloride content among all samples analyzed, ranging from 770 to 11520 ppm. Soils closer to the coast, as well as those in the stable upland zone ($\sim >60$ km from the coast), are low in their average $[Cl^-]$, ranging from 360 to 910 ppm (Figure 2). Depth-integrated $[Cl^-]$ for soil profiles display a similar pattern (data not shown).

[14] The $\delta^{37}Cl$ values for soil chloride range from -2.10‰ to $+0.56\text{‰}$ ($n = 40$). There is a significant variation in single soil profiles with depth and also among different soil profiles across the MDV (Table 1 and Figure 3). Considering the low vertical data resolution, we compare different soil profiles using two different data sets: (1) the $\delta^{37}Cl$ measured in the soil profile horizon with the highest $[Cl^-]$ and (2) the average $\delta^{37}Cl$ value normalized by both $[Cl^-]$ and depth for an entire profile (see formula in Table 1). Both approaches result in similar trends, although there is significant scatter in profile averages for the $\delta^{37}Cl$. Overall, however, soils in the stable upland zone have lower $\delta^{37}Cl$ values than do those in the

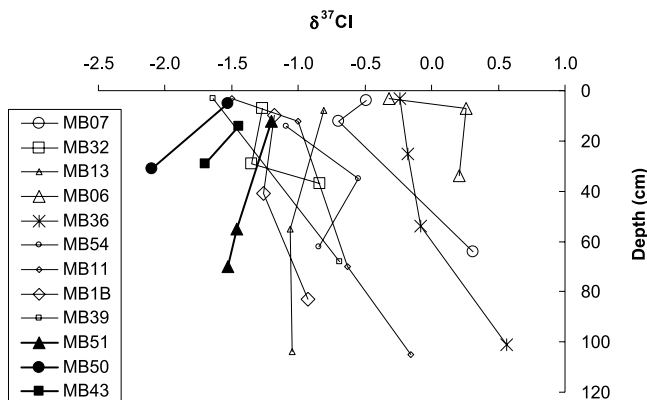


Figure 3. Plot showing $\delta^{37}Cl$ versus depth for 13 individual soil profiles (profile names are given in Table 1). Note that $\delta^{37}Cl$ increases with depth for most profiles developed on basal tills, whereas it decreases for all three sublimation tills (bold lines, MB51, 50, 43).

inland mixed zone (Figure 4). Averaging soil profiles within each microclimate zone, the $\delta^{37}Cl$ value for the stable upland zone is -1.07‰ (using data set 1) or -1.11‰ (using data set 2) and for the inland mixed zone it is -0.47‰ (using data set 1) or -0.60‰ (using data set 2). The $\delta^{37}Cl$ difference is larger if profile MB36 is treated as an outlier. The coastal site (MB34-7) shows a slightly positive $\delta^{37}Cl$ ($+0.18\text{‰}$).

[15] Vertically, the $\delta^{37}Cl$ data fall into two separate groups that are defined by the type of till sampled, basal or sublimation. For the 13 profiles developed on basal tills, the $\delta^{37}Cl$ values are distinctively greater at depth, excepting two soils (e.g., MB13 and MB54) that appeared unusually moist (Table 1 and Figure 3). This trend is highly robust considering the texture, lithology, and age heterogeneity among these soils. In sharp contrast, the $\delta^{37}Cl$ in all measured sublimation tills decreases with increasing soil depths, a trend opposite to that found in basal tills. Regardless of whether the samples are from basal or sublimation tills, however, we find that the range of $\delta^{37}Cl$ values in individual soil profiles varies from 0.09‰ to 1.34‰ , and is typically greatest for soils in the stable upland zone.

4. Discussion

[16] Here we propose a conceptual model for the sources and spatial distribution of chloride in MDV soils to account

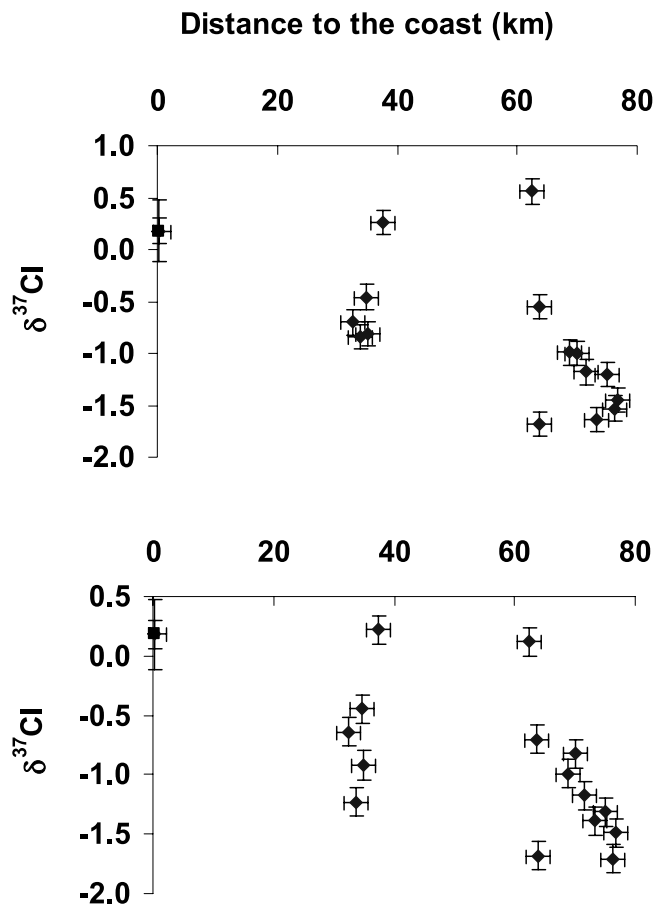


Figure 4. Plots showing $\delta^{37}Cl$ values as a function distance from the coast using (top) data set 1 and (bottom) data set 2. See text and Table 1 for explanation.

Table 1. Geographic Parameters, Sample Depth, $[\text{Cl}^-]$, $\delta^{37}\text{Cl}$, and Average $[\text{Cl}^-]$ and $\delta^{37}\text{Cl}$ for Individual Soil Profiles in the McMurdo Dry Valleys, Antarctica

Sample	Location	Distance to the Coast, km	Elevation, m ± 20 m	Depth, cm ± 2 cm	$[\text{Cl}^-]$, wt% $\pm 5\%$	$\delta^{37}\text{Cl}$, ‰ $\pm 0.12\%$	Profile $\delta^{37}\text{Cl}$, ^a Average	Profile $[\text{Cl}^-]$, ^b Average
MB34-7	Taylor Valley, coast	0.2	50	16	0.096%	0.18 ^c	0.18	0.072%
MB07-16	Wright Valley, side	32.5	295	4	0.659%	-0.49	-0.64	0.075%
MB07-13				12	4.527%	-0.70		
MB07-4				64	0.316%	0.31		
MB32-15	Taylor Valley, side	33.75	1070	7	0.106%	-1.27	-1.23	0.077%
MB32-9				29	0.098%	-1.35		
MB32-6				37	0.158%	-0.84		
MB14-16	Taylor Valley, side	34.75	915	8	3.009%	-0.46	-0.45	0.462%
MB14-11				26	0.581%	-0.37		
MB13-19	Taylor Valley, side	35	880	8	0.532%	-0.81	-0.92	0.213%
MB13-11				55	0.193%	-1.06		
MB13-3				104	0.135%	-1.05		
MB06-10	Taylor Valley, side	37.5	1045	3	0.454%	-0.32	0.22	1.152%
MB06-8				7	2.423%	0.26		
MB06-2				34	0.672%	0.21		
MB36-18	Asgard, Cirque 8	62.5	1515	3	0.104%	-0.24	0.12	0.071%
MB36-14				25	0.053%	-0.18		
MB36-8				54	0.055%	-0.08		
MB36-2				101	0.127%	0.56		
MB54-12	Pivot Peak	63.75	1515	14	0.025%	-1.09	-0.70	0.060%
MB54-6				35	0.097%	-0.55		
MB54-1				62	0.053%	-0.85		
MB53-4	Pivot Peak	63.8	1515	23	0.079%	-1.68	-1.68	0.056%
MB26-4	Arena Valley	68.75	1350	25	0.078%	-0.99	-0.99	0.047%
MB11-20	Asgard, Cirque 4	70	1490	3	0.064%	-1.50	-0.82	0.060%
MB11-17				12	0.097%	-1.00		
MB11-6				70	0.057%	-0.63		
MB11-1				105	0.036%	-0.16		
MB1B-11	Asgard, Cirque 4	71.5	1550	10	0.174%	-1.18	-1.18	0.075%
MB1B-7				41	0.074%	-1.26		
MB1B-3				83	0.045%	-0.93		
MB39-11	Asgard, Cirque 3	73.25	1525	3	0.083%	-1.64	-1.39	0.036%
MB39-1				68	0.033%	-0.69		
MB51-8	Beacon Valley	75	1330	12	0.116%	-1.20	-1.31	0.091%
MB51-4	(sublimation till)			55	0.078%	-1.46		
MB51-1				70	0.036%	-1.53		
MB50-2	Beacon Valley	76.25	1360	5	0.071%	-1.53	-1.71	0.057%
MB50-5	(sublimation till)			31	0.045%	-2.10		
MB43-4	Beacon Valley	76.75	1575	14	0.112%	-1.45	-1.49	0.088%
MB43-7	(sublimation till)			29	0.061%	-1.70		

^aAveraged over both concentration and profile depth, i.e.,

$$\delta^{37}\text{Cl}_{\text{profile average}} = \frac{\sum_{i=1}^n \left(\frac{C_i \delta_i + C_{i+1} \delta_{i+1}}{2} \right) (d_{i+1} - d_i)}{\sum_{i=1}^n \left(\frac{C_i + C_{i+1}}{2} \right) (d_{i+1} - d_i)}, \text{ in which } C_i \text{ is the } [\text{Cl}^-] \text{ at a horizon of depth } d_i \text{ with } \delta^{37}\text{Cl} \text{ value at } \delta_i.$$

^bAveraged over an entire profile depth (up to 120 cm depending on soil pits) based on high-resolution $[\text{Cl}^-]$ data (not shown here), i.e.,

$$[\text{Cl}^-]_{\text{profile average}} = \frac{\sum_{i=1}^n C_i (d_{i+1} - d_i)}{D}, \text{ in which } C_i \text{ is the } [\text{Cl}^-] \text{ at a horizon of depth } d_i \text{ in a soil profile with a total depth of } D.$$

^cAnalytical error at $\pm 0.30\%$ due to a small sample size.

for the observed variations in $[\text{Cl}^-]$ and $\delta^{37}\text{Cl}$. Two central points in the model are (1) that there are two major sources of chloride, SSC and SAC, and (2) that the long-term quantity and vertical distribution of chloride in hyperarid, desert soils is a function of both input (deposition) and migration (leaching).

4.1. Soil Chloride Concentration

[17] Spatially, the influx of SSC in soils decreases inland, as is expected from sea salt's limited transport distance determined by its relatively large particle size range (1 to 2 μm). Ion data from firn core, snow pit, and 1-m integrated superficial snow samples along coast-inland traverses in Antarctica reveal a two-order-of-magnitude decrease in sea-salt content in the first 200 km from the sea [Benassai et al.,

2005]. In addition, a study on the transport of marine aerosols across southern Sweden, one of the few actual aerosol measurements along a transport trajectory in the field, reveals an overall exponential decrease of sea-salt content toward inland sites there, with an enhancement by relative air humidity [Gustafsson and Franzen, 2000; Rossknecht et al., 1973]. In contrast with the SSC, SAC should exhibit a uniform depositional flux throughout the valleys because of its secondary atmospheric origin. On the other hand, the outflux (i.e., leaching) is positively correlated with the moisture content and temperature. It is conceivable, therefore, that the outflux of soil chloride should decrease exponentially landward because of increasing hyperaridity with increasing distance and elevation from the coast (Table 1). Thus a conceptual model can help to understand the $[\text{Cl}^-]$ distribu-

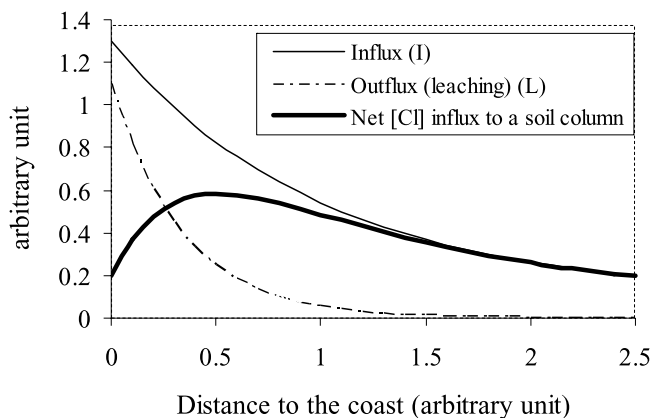


Figure 5. Schematic diagram with arbitrary scales illustrating how the integrated influx (I indicates atmospheric deposition) and outflux (L indicates leaching) of soil chloride along a coast-to-inland transect in the MDV can result in the observed chloride concentration pattern R (bold line). A bell-shaped curve with elevated concentrations in the intermediate zone is only possible when the rate of leaching (outflux) decreases faster inland than does the rate of deposition (influx).

tion in the MDV soils. Chloride influx (I) ($\text{mg}/\text{cm}^2/\text{a}$) in soils with a distance x to the coast can be described as

$$I = M + Ae^{-ax}, \quad (1)$$

where M is the uniform SAC influx and Ae^{-ax} the SSC influx that decreases exponentially toward inland sites. The coefficient A evaluates the quantity of SSC input parameter and a is determined by climatic, meteoric, and topographic conditions of the MDV. Similarly, chloride outflux due to leaching (L) ($\text{mg}/\text{cm}^2/\text{a}$) in soils with a distance x to the coast is described as

$$L = Be^{-bx}, \quad (2)$$

in which the coefficient B evaluates the quantity of leached chloride and b is determined by climatic, meteoric, and topographic conditions. Thus the remaining $[\text{Cl}^-]$ (mg/cm^2) (R) in a particular soil profile is the time-integrated difference in chloride influx and outflux,

$$R = \int_0^t (I - L)dt = \int_0^t (M + Ae^{-ax} - Be^{-bx})dt. \quad (3)$$

[18] The x here ranges from 0 to ~ 100 km and t from 0 to $\sim >15$ million years in the MDV [Sugden *et al.*, 1993]. There is a general positive correlation between x_i and t_i since the oldest soils are found furthest inland in the MDV [Denton *et al.*, 1993; Marchant and Denton, 1996; Marchant *et al.*, 2002]. In principle, for any soil profile designated by x_i and t_i , we have an estimate of total $[\text{Cl}^-]$ in that profile. Note that in this model the MDV soil is treated as a single layer.

[19] This conceptual model (equation (3)) explains the observed spatial $[\text{Cl}^-]$ pattern, which shows that both the

coastal thaw zone and the stable upland zone have lower $[\text{Cl}^-]$ than does the inland mixed zone (Figures 2 and 5). A low influx of chloride in the upland zone and a high outflux (leaching) in the coastal zone are most likely responsible for these zones' low $[\text{Cl}^-]$. The average soil $[\text{Cl}^-]$ or the depth-integrated $[\text{Cl}^-]$ is highly variable among soils in the inland mixed zone, consistent with the high heterogeneity in soil ages, materials, and alternating weather conditions in this zone [Marchant and Denton, 1996; Prentice *et al.*, 1998; Sugden *et al.*, 1993]. Despite the fact that more data are needed to constrain the parameter M , A , and B in the model (equation (3)), the observed spatial $[\text{Cl}^-]$ pattern requires that a has to be less than b in equation (3) (Figure 5). The important conclusion is that along a coast-to-upland transect in the MDV, the decrease of chloride outflux through leaching is faster than the decrease of SSC influx.

4.2. Chlorine Isotope Composition of Soil Chloride

[20] $\delta^{37}\text{Cl}$ values in the MDV vary significantly, both within single soil profiles and spatially across microclimate zones. The variations are most likely related to changes in the chloride sources and fluxes, as discussed above, as well as to processes affecting chloride's isotope composition. We propose that the seemingly complex pattern of $\delta^{37}\text{Cl}$ values is largely the result of the mixing of two major chloride sources, SSC and SAC, that respectively have $\delta^{37}\text{Cl}$ values of $>+0.0\%$ and $<-2.1\%$. Two additional factors may also play roles in shaping the observed vertical $\delta^{37}\text{Cl}$ pattern in soil profiles: (1) the potential for secular (long-term) chloride-source variations and (2) the different boundary conditions for chloride fluxes in basal and sublimation tills.

4.2.1. SSC

[21] SSC originates from ocean waves, or from brine or frost flowers on sea ice [Rankin and Wolff, 2003]. The $\delta^{37}\text{Cl}$ between solid NaCl and that of a chloride saturated aqueous solution is small, $0.26 \pm 0.09\%$ at $22 \pm 2^\circ\text{C}$ [Eggenkamp *et al.*, 1995]. Because of other kinetic effects, chloride salts formed from the 0.0% seawater chloride can have $\delta^{37}\text{Cl}$ values in the range of -0.6 to $+0.5\%$ [Eastoe *et al.*, 1999]. It is, therefore, reasonable to believe that SSC has a $\delta^{37}\text{Cl}$ value close to 0.0% when initially formed. The measured $\delta^{37}\text{Cl}$ value of $+0.18\%$ at a coastal site sample (MB34-7) (Table 1) supports this assertion.

[22] Chlorine isotope fractionation occurs during atmospheric transport of SSC. A series of chemical reactions involving H_2SO_4 and HNO_3 occur on sea-salt particle surfaces and result in the formation of volatile HCl, a main mechanism for observed "chlorine depletion" for sea salt in inland sites [Chameides and Stelson, 1992; Erickson *et al.*, 1999]. Chloride loss has been demonstrated on atmospheric aerosols collected in coastal stations in Antarctica [e.g., Jourdain and Legrand, 2002; Kerminen *et al.*, 2000]. The first measurement of $\delta^{37}\text{Cl}$ values on atmospheric aerosols was conducted on marine aerosols from Bermuda (western Atlantic Ocean) [Volpe and Spivack, 1994]. The Bermudan aerosols all had positive $\delta^{37}\text{Cl}$ values ($+0.42$ to $+2.53\%$), which are strongly correlated with chlorine deficit and non-sea-salt sulfate content. This result is consistent with a mechanism that the gaseous HCl generated by the acidification of sea-salt particle preferentially takes ^{35}Cl , a mechanism substantiated by a set of seawater acidification and evaporation experiments [Volpe and Spivack, 1994]. Volpe

et al. [1998] also conducted a size-segregated aerosol sampling study in the central equatorial Pacific to examine potential sampling artifacts on the chlorine deficit and particle-to-gas or gas-to-particle conversion processes on bulk filters. They found that whereas midsize aerosols were enriched in ^{37}Cl , behaving similar to the bulk sample, coarse aerosols (Stage 1 and 2 of a Sierra cascade impactor) were depleted in ^{37}Cl relative to that of the seawater chloride. These authors speculated that the apparent inverse isotope effect, a depletion of the heavier isotope in the solid phase in the coarse aerosol fraction, is related to “the formation of a bound reactive chlorine species”. While further investigation is needed in this matter, we assume that the bulk SSC at inland and high-elevation sites bear a similar or slightly higher $\delta^{37}\text{Cl}$ value than does the initial seawater chloride after having traveled tens to hundreds of kilometers from the source (open water or sea ice). Therefore, if SSC were the only source of chloride in the MDV soils, we would have seen an increase in $\delta^{37}\text{Cl}$ toward inland elevated sites, a spatial pattern opposite to that observed (Figure 4).

4.2.2. SAC

[23] There are additional lines of evidence supporting the presence of a $\delta^{37}\text{Cl}$ -negative chloride source, SAC. First, the ratio of SAC/SSC is expected to be much higher in the upland soils, where (1) sea-salt particles are less frequently reached and (2) salt influx introduced by sublimation of snow drifts from the East Antarctic Ice Sheet is greater than in the coastal zone. Polar snows or ices are known to have variable chloride concentrations [Legrand and Delmas, 1988]. In order to generate the observed isotope spatial pattern in which chloride in the stable upland zone has lower $\delta^{37}\text{Cl}$ values than do those in the inland mixed or coastal thaw zones (Figure 4), a negative $\delta^{37}\text{Cl}$ is required for the SAC source. Second, the $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ values for secondary atmospheric nitrate and sulfate in Antarctica are both significantly lower than those of the initial source value, such as those of NO_x or dimethylsulfide (DMS) [Bao and Marchant, 2006; Michalski *et al.*, 2005; Wada *et al.*, 1981]. A common cause for these significantly lower isotope compositions among secondary atmospheric anions is a Rayleigh distillation process during long-distance transport, a mechanism still requiring further test by observations and models. Nevertheless, a very negative $\delta^{37}\text{Cl}$ for SAC would be consistent with this pattern. The $\delta^{37}\text{Cl}$ data suggest that SAC has a $\delta^{37}\text{Cl}$ value equal to or lower than -2.10‰ , the most negative value encountered in the MDV soils.

4.2.3. Chloride From Weathering and Volcanic Emission

[24] Weathering is a potential source of chloride in the MDV soils. However, weathering is only significant in the relatively warm and wet coastal zone [Campbell and Claridge, 1987], where the sea-salt influx and the outflux (leaching) are also highest, making the relative contribution from weathering less significant. We have not measured the $\delta^{37}\text{Cl}$ value of all glacial materials in the MDV, but as tills are often composed of well-mixed and recycled crustal materials their $\delta^{37}\text{Cl}$ values are likely to be at $\sim 0.0 \pm 0.5\text{‰}$ [Stewart and Spivack, 2004]. As long as the relative portion of weathering-generated chloride to other sources of chloride are small throughout the MDV, weathering-gener-

ated chloride will not affect the observed spatial $\delta^{37}\text{Cl}$ pattern significantly.

[25] A contribution difficult to quantify at this time is chloride emission from Mount Erebus. Mt. Erebus, situated ~ 50 km east of the MDV, can be an important chloride contributor to the Antarctic atmosphere (6.9 to 13.3 Gg a^{-1}) [Zreda-Gostynska *et al.*, 1993, 1997]. Since the volcano is located just off the coast, its chloride input into the valleys can be treated similarly as the SSC influx with an exponentially decreasing $[\text{Cl}^-]$ and an increasing $\delta^{37}\text{Cl}$ away from the coast. In other words, this uncertainty does not change the fact that we still require a ^{37}Cl -depleted SAC source to interpret the observed spatial pattern.

4.2.4. Chlorine Isotope Fractionation Associated With Leaching

[26] Dissolution of chloride salts results in ^{35}Cl being preferentially incorporated into the liquid or brine phase and thus migrating preferentially to deeper horizons than the residual ^{37}Cl -enriched solid chlorides. The net vertical chlorine isotope difference caused by repeated leaching, however, depends on the magnitude and frequency of the wetting events as well as the influx of chloride in a soil profile. For example, one can imagine that a heavily leached profile would have little vertical $\delta^{37}\text{Cl}$ difference. Qualitatively, leaching is more intense in the coastal thaw zone than in the stable upland zone. The observed larger vertical range in $\delta^{37}\text{Cl}$ values for soils of the upland zone, as compared to those of the inland mixed zone, fits this pattern. However, the observation that most basal till soil profiles have higher $\delta^{37}\text{Cl}$ values at depth than nearer the ground surface suggests that the vertical $\delta^{37}\text{Cl}$ trend is due to reasons other than a leaching-induced isotope fractionation.

4.2.5. Secular Change in SSC Influx

[27] One potential cause of the observed downward increase in $\delta^{37}\text{Cl}$ values within a single profile is that the atmospheric chloride in the MDV had a higher $\delta^{37}\text{Cl}$ value in the past, and because of leaching, the older chloride resides at deeper horizons. Either a lower elevation for the overall MDV or a warmer climate (with less sea ice coverage in the Ross Sea) in the past could facilitate this scenario. Landscape models based on fission track data and $^{40}\text{Ar}/^{39}\text{Ar}$ dating of surface ashfall deposits [Sugden *et al.*, 1995a] suggest modest surface uplift (~ 350 m) in the MDV during the last 10–15 Ma. However, fjords may have occupied portions of Wright and Taylor Valleys up until Pliocene time [Denton and Sugden, 2005; Hall *et al.*, 1993; Sugden *et al.*, 1995a]. One could argue that the trend toward cooler conditions throughout the late Cenozoic [Zachos *et al.*, 2001] is accompanied by an increase in fringing sea ice around Antarctica, resulting in a decreasing SSC/SAC ratio in chloride influx to the MDV over time. Alternatively, a warm episode in the Pliocene (~ 3 Ma) [e.g., Harwood and Webb, 1994] could account for the vertical trend, especially among the younger soil profiles. We emphasize, however, that the warmth envisioned by Harwood and Webb [1994], sufficient to melt most of the East Antarctic Ice Sheet, is excessive and a much more modest potential warming of $\leq 3^\circ\text{C}$ is envisioned here [Marchant *et al.*, 1993]. Resolving whether gradual Cenozoic cooling or a relatively short lived warm interval in the Pliocene might be causes for the observed variations in $\delta^{37}\text{Cl}$ requires a much higher spatial and vertical sampling resolution than presented in this study,

as it requires knowledge of the precipitation and dissolution behavior of chloride salts and the dynamics of salt migration (including accompanied sulfate or nitrate salts) in the hyperarid and frigid soil matrices. The $^{36}\text{Cl}/\text{Cl}$ ratio, bearing information on chloride age and source [Carlson *et al.*, 1990], may also shed light on the vertical $\delta^{37}\text{Cl}$ trend, but is a topic beyond the scope of this study.

4.2.6. Sublimation Till: A Different Boundary Condition for Chloride Influx [28] The measured downward $\delta^{37}\text{Cl}$ decrease in sublimation tills is opposite the trend for basal tills (Figure 3). This phenomenon is consistent with the fact that salt input for sublimation tills is not only from the top via atmospheric deposition but also from the bottom via glacier sublimation. The chloride in glacier ice from the stable upland zone (where sublimation tills form) is expected to have the highest SAC/SSC ratio; this is because one of the main sources for glacier ice is windblown snow from the Polar Plateau (East Antarctic Ice Sheet). Accordingly, the $\delta^{37}\text{Cl}$ at the bottom of sublimation till most closely approaches the SAC value. The survival of this opposite vertical $\delta^{37}\text{Cl}$ trend attests to very dry soil conditions, with limited leaching and vertical ion migration.

4.3. Other Chloride-Related Studies in the MDV

[29] Different $\delta^{37}\text{Cl}$ compositions and depth profiles were reported for chlorine dissolved in three perennially ice-covered lakes (Bonney, Fryxell, and Hoare) in Taylor Valley [Lyons *et al.*, 1999]. The $\delta^{37}\text{Cl}$ ranges from +0.32‰ to -1.07‰, values which fall within our range of measured soil $\delta^{37}\text{Cl}$. There is not, however, a well-defined trend for lake $\delta^{37}\text{Cl}$ from coastal to inland sites. In addition to atmospheric fallout, the chloride in these lakes is known to have contributions from relict seawater, streams, and deep groundwater sources [Carlson *et al.*, 1990; Lyons *et al.*, 1999; Takamatsu *et al.*, 1998], and is therefore more complex than chloride in soils. The desiccation of the lakes in the past can contribute chloride to nearby soils and thus introduce complexity to our two-source mixing model and contribute to the $\delta^{37}\text{Cl}$ variability observed in the MDV. This process is for the most part only expected to impact low-elevation sites in the coastal thaw and inland mixed zones.

[30] Data on modern aerosol transport for the MDV are lacking. As yet, a network of on-site aerosol collectors that could be used to examine seasonal variations in sea-salt chloride input and/or monitor the effect of sea-ice extent on chloride input is not established. However, recent glacio-chemical data, including $[\text{Cl}^-]$, from snow pits [e.g., Witherow *et al.*, 2006] have demonstrated a high degree of heterogeneity in ion and elemental concentrations in coastal Antarctica. Ions in snow and firn, however, behave differently from those in soils, and so the snow and firn data are not immediately transferable to our soil study. Moreover, the chemical data from snowfall and firn span only the last few hundred years, and so these data too have only limited relevance to the long-term source, budget, and spatial/vertical patterns of chloride input observed in the multimillion year old MDV soils.

5. Conclusions

[31] Although many aspects of chlorine isotope fractionation and systematics are still not well defined, especially

those involving atmospheric and leaching processes, we have been able to present an internally consistent model that describes complex spatial and vertical variations in $[\text{Cl}^-]$ and $\delta^{37}\text{Cl}$ in the MDV soils. Our results are consistent with the notion of a threefold microclimate zonation in the MDV, including a relatively wet coastal thaw zone, a very dry stable upland zone, and an intermediate inland mixed zone [e.g., Marchant and Head, 2008]. The MDV chloride budget in all microclimate zones is largely the result of continuous influx from atmospheric deposition and variable outflux through leaching. There are two major atmospheric sources for chloride: sea-salt chloride (SSC) with a $\delta^{37}\text{Cl}$ value of $\sim 0.0\text{‰}$ or higher and secondary atmospheric chloride (SAC) with a $\delta^{37}\text{Cl}$ value of $\leq -2.10\text{‰}$. In terms of spatial variation in MDV soils, the SAC/SSC ratio increases landward, reaching its highest levels in the dry, stable upland zone; this variation is due largely to the restricted transport distance for SSC particles. Measured values for $[\text{Cl}^-]$ also show a predictable variation. Soils in the stable upland zone show relatively low $[\text{Cl}^-]$ because input from SSC is low far inland from the coast. Perhaps unexpectedly, $[\text{Cl}^-]$ values are also relatively low near the coast; the reason for the low values is best explained by excessive moisture and soil leaching (outflux) in the coastal thaw zone. $[\text{Cl}^-]$ values reach a maximum in the inland mixed zone.

[32] Vertical trends in $\delta^{37}\text{Cl}$ can also be explained through deposition by variable atmospheric transport pathways (SSC and SAC) and subsequent modification by expected soil/geomorphic processes endemic to each microclimate zone. For example, the observed increase in $\delta^{37}\text{Cl}$ with depth in basal tills is explained by a higher SSC/SAC ratio in chloride influxes in the past, a trend consistent with either general climate cooling (for example increasing sea-ice extent over the Late Cenozoic) or, paradoxically, a short-lived climate amelioration, perhaps during mid-Pliocene time. The decreasing $\delta^{37}\text{Cl}$ with depth observed in sublimation tills is consistent with a second influx of SAC-rich chloride from the bottom of the tills via glacier sublimation. The survival of this vertical $\delta^{37}\text{Cl}$ trend in sublimation tills over extant buried ice, opposing the trend seen for basal tills in this study, attests to very dry soil conditions, with limited leaching and vertical ion migration. Our initial characterization of the sources, budgets, and spatial/vertical patterns of chloride in MDV soils constitutes a first step toward unraveling climate, tectonic, and landscape changes archived in MDV soils.

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