

SNOW CHEMISTRY ACROSS ANTARCTICA

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ABSTRACT

An updated compilation of published and new data of major ion (Ca, Cl, K, Mg, Na, NO₃, SO₄) and methylsulfonate (MS) concentrations in snow from 520 Antarctic sites is provided by the national ITASE programmes of Australia, Brazil, China, Germany, Italy, Japan, Korea, New Zealand, Norway, United Kingdom, United States of America, and the national Antarctic programme of Finland. The comparison shows that snow chemistry concentrations vary by up to four orders of magnitude across

Antarctica and exhibit distinct geographical patterns. The Antarctic-wide comparison of glaciochemical records provides a unique opportunity to improve our understanding of the fundamental factors that ultimately control the chemistry of snow or ice samples. This paper aims to initiate data compilation and administration in order to provide a framework for facilitation of Antarctic-wide snow chemistry discussions across all ITASE nations and other contributing groups. The data are made available through the ITASE web page and will be updated with new data as they are provided. In addition, recommendations for future research efforts are summarised.

INTRODUCTION

“Ice cores provide the most direct and highly resolved records of (especially) atmospheric parameters for the last 1,000,000 years” (EPICA Community Members, 2004). While ice core chemistry analyses have revolutionised our knowledge on the working of the climate system and its variability through time (Legrand and Mayewski, 1997; Mayewski and White, 2002), an improved understanding of the fundamental factors that ultimately control the chemistry of a snow or ice sample will allow even more detailed and accurate interpretation of glaciochemical records reconstructing past climate conditions with near-instrumental quality.

To reach this understanding it is necessary to determine individual sources and pathways of aerosols, mechanisms that control precipitation efficiency as well as post-depositional effects (Legrand and Mayewski, 1997). Comparing snow chemistry at different sites and investigating the processes leading to spatial differences in snow chemistry help to improve our understanding of temporal variability and teleconnections. Here, we provide an up-dated summary of available data from 520 sites in Antarctica, developed by the International Trans Antarctic Scientific Expedition (ITASE), with the goal of providing this new dataset along with research recommendations to the wider ice core community and thereby stimulate and focus the discussion towards a more comprehensive data interpretation.

BACKGROUND

ITASE has as its primary aim “... the collection and interpretation of a continental-wide array of environmental parameters assembled through the coordinated efforts of scientists from several nations” (Science and Implementation Plan, 1990, http://www2.umaine.edu/itase/scie_plan/intro.html). During the ISAG 7 meeting in Milano, Italy, 2003, the ITASE community established seven synthesis groups, of which this group – the ITASE Chemistry Synthesis Group – is coordinating the compilation and interpretation of the spatial variability in snow and ice chemistry across the continent to address the knowledge gap on factors governing variability of ice core chemistry in Antarctica. A two-step approach was adopted. Firstly, broad patterns in Antarctic snow chemistry are investigated using all available reliable data (this paper). This will allow formulating the strategy for the second step, in which the group will focus on individual time periods in order to investigate the causes for changes in chemistry patterns (future papers). This will be achieved by contrasting for example El Niño with La Niña years or studying the years before and after volcanic eruptions, such as the recent Mt Pinatubo event.

In this first step we summarise new and previously published data and provide recommendations for future common efforts. The new data are provided by the national ITASE programmes of Australia, Brazil, China, Germany, Italy, Japan, Korea, New

Zealand, Norway, United Kingdom, United States of America, and the national Antarctic programme of Finland.

DATA SELECTION CRITERIA

Previous glaciochemical surveys showed that careful data selection for an Antarctic-wide comparison is important (Mayewski and others, 1992; Mulvaney and Wolff, 1994; Wagenbach, 1996; Legrand and Mayewski, 1997; Wolff and others, 1998a; Wolff and others, 1998b; Kreutz and Mayewski, 1999; Kreutz and others, 1999; Stenberg and others, 1999). Data from 520 sites are summarised here and can be obtained from the ITASE Chemistry Synthesis Group web page (<http://www2.umaine.edu/itase/content/syngroups/index>). While the laboratory procedures of the individual groups are of high standard, no cross-evaluation has yet been undertaken. To obtain further information on individual data sets contact details are provided along with the data.

Because Antarctic glaciochemistry shows large seasonal variability (Gow, 1965; Sigg and Neftel, 1988; Solomon and Keys, 1992; Legrand and Mayewski, 1997; Curran and others, 1998; Wolff and others, 1998b; Kreutz and others, 1999; Bertler and others, 2004b) it is desirable for any continent-wide comparison to use either well-dated (sub-annual) records or multi year averages. The achievable level of age control of ice core records is dependent on many factors, but particularly on annual accumulation (and sampling resolution) and therefore varies greatly across Antarctica. Of the 520 available data sources, 194 records are reliably identified as multiyear samples. The remaining records are predominantly surface snow samples collected along transects and thus are an important contribution to determine aerosol sources. For the comparison of new ITASE data, however, we decided to aim in this first step for 5-year averages. This allows short records to be included while eliminating seasonal variability. A survey of ITASE meta data indicates that the 5-year interval that is represented the most in the currently available data set is 1992 to 1997. At present 45 sites provide well-dated chemistry measurements for this time period. This interval coincides with the Mount Pinatubo volcanic eruption, and provides therefore an opportunity to study the effect of volcanic eruptions in future papers when time series are considered.

A second fundamental decision is whether to use concentration or flux data (Kreutz and others, 2000). Due to the spatially variable influence of dry and wet deposition across Antarctica and the difficulty to obtain reliable, high-resolution annual snow accumulation measurements, concentration data are preferred over flux. However, as more accumulation data will become available, the influence of spatially and temporal varying snow accumulation leading to varying contributions of wet versus dry deposition should be investigated further. This can be achieved by merging the data of this group with the currently compiled data sets of the ITASE/ISMASS Mass Balance and Atmospheric Chemistry Synthesis Groups.

In the meta data survey, information on all glaciochemical analyses have been compiled. Here, we focus on major ions – sodium (Na), magnesium (Mg), calcium (Ca), potassium (K), chloride (Cl), nitrate (NO₃), sulphate (SO₄), and methane sulfonate (MS). An Antarctic-wide comparison of other species, such as trace elements, organic acids, and particles is hampered due to the limited number of data points currently available. However, growing interest and improved analytical methods will enable us to incorporate such data in the near future.

DATA EVALUATION AND PRESENTATION

As Antarctica exhibits strong spatial contrasts it is important to evaluate how well the sampled locations represent regional to continent scale gradients. Most parameters, such as elevation, distance from the sea, annual accumulation etc., change simultaneously along many transects and are therefore difficult to assess individually. The comparison between the Antarctic topography as inferred by the RAMP 5km elevation model (Liu and others, 2001) (Fig.1a) and the reconstructed surface using only elevation information from the sampled sites provides a means to evaluate how well Antarctic geographic features are represented by the sampled locations. The reconstructed surfaces in Fig.1b-d are calculated using the interpolation method of linear kriging between sampling sites. In Figure 1b the Antarctic surface is reconstructed using only sites that provide data from the chosen 1992 to 1997 time period (45 data points). While the data are clustered and separated by large geographical gaps, they represent contemporary glaciochemical concentration, generally excluding time-driven factors, such as climate variability. The reconstructed topography lacks many of the significant Antarctic features, e.g. neither ice shelf nor the Antarctic Peninsula are yet represented. A number of sites provide 5-year averages for slightly different time periods or have an associated dating error of more than ± 1 year. Incorporating these sites enlarges the database significantly. In Fig. 1c the reconstructed topography using all multi-year data is shown (194 data points). While main geographical features, such as the East and West Antarctic Ice Sheets, the Ross and Ronne/Filchner Ice Shelves are represented, other significant details, such as the Transantarctic Mountains, the Antarctic Peninsula, and the Lambert Glacier system are poorly or not represented. The reconstructed topography in Fig.1d incorporates all available data (520 data points), including non-annual samples. This is the most comprehensive data set currently available. As the data do not all represent the same time period or might represent only seasons, their interpretation in an Antarctic-wide comparison requires careful attention. Although the reconstructed map incorporating all available data is more detailed than Fig.1c, it still lacks important elements across large regions of the Antarctic continent. Overall this comparison highlights the need for many more traverses to provide better coverage, especially of well dated, multi-year, contemporary time series.

ION CONCENTRATION VERSUS ELEVATION

As discussed above, many site physical characteristics influencing glaciochemistry change simultaneously, either geographically or temporally. These include annual accumulation, elevation, and distance from the sea. Accurate, high resolution annual accumulation data are difficult to obtain, as they require high resolution dating and density measurements. Furthermore, there are no well documented, straightforward linear associations between chemistry and accumulation rate. In order to determine distance from the sea it is necessary to understand the pathway of the precipitating air mass for both wet and dry deposition. Local atmospheric circulation patterns can be highly variable and might change true distance to the sea from 10 kilometres to 1000 kilometres depending on the pathway of the air mass (e.g. Bertler and others, 2004a; Xiao and others, 2004; Kaspari and others, this volume). Furthermore, large seasonal changes in sea-ice cover further complicate the measurement of true distance to the sea. One parameter that is relatively easy to obtain and does not change significantly over short time periods is elevation.

However, as annual accumulation and distance from the sea exhibit a correlation with elevation in Antarctica, any observed patterns are likely to be caused by a varying combination of all three. Correlation between ion concentration and elevation is shown in Fig. 2. Ion concentration variability across Antarctica exhibits an amplitude of up to four orders of magnitude. Therefore, ion concentrations are plotted on logarithmic scales, with the exception of the Cl/Na ratio.

The correlations between elevation and **Na** or **Cl** (Fig. 2a & b) show a statistically significantly inverse relationship (logarithmic) of decreasing ion concentration with increasing altitude of $r=-0.73$ and $r=-0.51$, respectively (Table 1). Furthermore, the scatter in both data sets is larger at lower elevation than at higher locations. When correlating the **Cl/Na** ratio with elevation ($r=0.56$, Table 1), sites below 2000 m predominantly show values close to the marine ratio of ~ 1.8 (Warneck, 1991), while the scatter in the data increases significantly above 2000 m, reaching values of up to 20 (Fig. 2c). This confirms that sites below 2000 m are predominantly influenced by sea-salt and also suggests no significant post-depositional aerosol loss or enrichment. The larger scatter with increasing elevation is indicative of a number of potential processes leading to relative enrichment or depletion of either species (Gayley and Ram, 1985; Mulvaney and Peel, 1988; Mulvaney and Wolff, 1994; De Angelis and Legrand, 1995; Yang and others, 1996a; Legrand and Mayewski, 1997; Kreutz and others, 1998; Stenberg and others, 1998; Wagenbach and others, 1998a; Wolff and others, 1998a; Wolff and others, 1998b; Kreutz and Mayewski, 1999; Udisti and others, 1999; Kreutz and others, 2000; Aristarain and Delmas, 2002; Proposito and others, 2002; Becagli and others, in press; Udisti and others, in press; Benassai and others, this volume).

No statistically significant correlation at the 99.9% significance level exists between elevation and **NO₃** (Fig. 2d). **NO₃** is predominantly a secondary aerosol, produced in the strato- and ionosphere. Processes leading to nitrate production in the higher atmosphere are thought to be stratospheric oxidation of **N₂O**, ionospheric dissociation of **N₂**, and polar stratospheric clouds via **HNO₃**. Additionally, lightning in the mid-latitudes produces the primary **NO₃** aerosol in the troposphere (Parker and others, 1977; Parker and Zeller, 1980; Parker and others, 1981; Parker and others, 1982; McKenzie and Johnston, 1984; Evans and others, 1985; Legrand and Delmas, 1986; Toon and others, 1986; Legrand and Kirchner, 1990; Mayewski and others, 1990; Qin and others, 1992; Solomon and Keys, 1992; Clausen, 1995; Wolff, 1995; Yang and others, 1996a; Yang and others, 1996b; Legrand and Mayewski, 1997; Wagenbach and others, 1998b; Palmer and others, 2001). Higher **NO₃** concentrations are therefore expected within the boundary of the polar vortex due to the influence of upper atmospheric air masses. Furthermore, some post-depositional and photochemical mechanisms lead to **NO₃** loss, especially at low accumulation sites (De Angelis and Legrand, 1995; Legrand and Mayewski, 1997; Mulvaney and others, 1998; Wagnon and others, 1999; Röthlisberger and others, 2000; Jones and others, 2001; Röthlisberger and others, 2002; Wolff and others, 2002; Udisti and others, in press), which partially offsets the trend towards higher **NO₃** in the Antarctic interior. As this effect takes place in the upper few meters of the snow pack it is particularly important not only to compare contemporary **NO₃** data, but also samples derived from similar depths in the snow profile.

The correlation between **SO₄** and elevation also shows no statistically significant trend at the 99.9% significance level (Table 1). While concentration data exhibit a more scattered pattern at lower elevations, total **SO₄** input seems largely independent from elevation. However, **SO₄** has many sources (Delmas and others, 1982; Wolff and Mulvaney, 1991; Mayewski and others, 1992; Mulvaney and Wolff, 1994; Legrand,

1995; Legrand and Mayewski, 1997; Minikin and others, 1998; Udisti and others, 1998; Udisti and others, 1999; Becagli and others, in press) and individual SO₄ species might exhibit significant correlations with elevation. While primary aerosol SO₄ species (sea spray) and secondary marine-biogenic SO₄ should exhibit a rapid decrease with increasing elevation, volcanic SO₄ aerosols enters through the upper atmosphere and therefore should have a stronger signal in the Antarctic interior. Furthermore, the volcanic input of SO₄ often exceeds average SO₄ input (Mayewski and others, 1995; Zielinski and others, 1997; Dixon and others, this volume). Because data used in this comparison represent different time periods, samples containing volcanic SO₄ input have the potential to obscure an existing relationship, especially for the 1992 to 1997 time period, which coincides with the Mount Pinatubo 1991 eruption.

MS shows a statistically significant decrease with increasing elevation (Fig. 2f) of $r=-0.42$ (Table 1). While most ion species have multiple sources, MS is thought to have a single marine source and is derived via oxidation from plankton-produced DMS (Dimethylsulfonate) in polar oceans (Mulvaney and others, 1992), which explains its anti-correlation with elevation. MS is observed to peak in summer, when biological activity is highest (Welch and others, 1993; Saltzman, 1995; Saltzman and others, 1997; Meyerson and others, 2002). Delmas and others (2003) and Wellers and others (2004) describe a mechanism by which MS is lost to interstitial gaseous phase in the Antarctic interior, which might partially be responsible for the observed trend in Fig. 3f. As for NO₃ it is therefore important to investigate MS data in relationship to snow depth of the sample.

Ca, **Mg**, and **K** show an inverse relationship with decreasing concentration at higher elevation sites (Fig. 3g, h) with $r=-0.70$ and $r=-0.73$, $r=-0.52$ respectively. Furthermore, the scatter in the data sets appears higher at lower elevations sites, especially for Ca. These species have local and global terrestrial, as well as marine sources. In the vicinity of ice-free areas, such as the McMurdo Dry Valleys, ion concentration is influenced from those local sources (Gayley and Ram, 1985; Aristarain and Delmas, 2002; Bertler and others, 2004b). Elsewhere, the input is dominated by sea-salt and global dust input (Shaw, 1979), with the former producing orders of magnitude higher concentrations than the latter, thus explaining the overall inverse relationship with elevation

SPATIAL ION CONCENTRATION VARIABILITY

To further investigate the relationships observed in Fig. 2, the geographical variability is discussed in Fig. 3 to 11. The data for each species have been clustered into colour-coded classes. Due to the large amplitude of variability in ion concentration the classes are not linearly distributed but, rather, according to data distribution. This is necessary as coastal regions for example show Na concentrations that are four orders of magnitude higher than those in the Antarctic interior (Fig.3). As a result a linear scale would under represent the variability with only one class for the entire Antarctic interior or for coastal sites. To compare sites within the Antarctic interior, or various coastlines, it is necessary to tune the classes so that variability at low *and* high concentrations can be observed. The legend shows the percentage and number of data points contained in each class. Furthermore, data have been distinguished into three groups: well dated data representing 1992-1997 time period (solid circles), all other multi-year samples (solid triangles), and undated or non-annual samples (crosses). The colour coding for concentration classes is the same for all three groups.

Spatial variability of **Na** concentration is shown in Fig. 3, ranging from 2 ppb to 14,680 ppb. As expected the East Antarctic interior shows significantly lower values (~2 ppb to ~30 ppb) than the coastal sites (~75 ppb to 14,680 ppb). However, high values have also been reported from Marie Byrd Land at high elevation, and low concentrations in the vicinity of the East Antarctic coastlines (Kaiser Wilhelm Land and Terra Adelie). Furthermore, the change from very low to very high concentrations seems to occur within a narrow band in the vicinity of the coast. While high Na deposition is readily explained in coastal areas due to high sea-salt input, the narrow zone of marine air mass intrusions (meso-scale cyclonic activity) coincides with the rapid decrease of Na concentrations in the Antarctic interior. Here the katabatic wind streams, transporting Na-depleted air masses from the interior towards the coast, compete with the Na-rich coastal air masses. In contrast, the Antarctic Peninsula shows overall high values and no trends, caused by strong sea-salt input all around and a secondary non-sea-salt contribution from ice-free mountain peaks. However it is important to note that most of the data points located on the Antarctic Peninsula are surface samples representing winter snow. As Na peaks in most regions of Antarctica during winter, the higher Na concentrations reported from the Antarctic Peninsula are partially explained by this bias.

Cl variability exhibits a similar pattern to Na (Fig. 4), ranging from ~1 ppb to 27,740 ppb. The highest values are observed at coastal sites (~150 ppb to ~27,740 ppb) and lower values in the interior (1 ppb to ~150 ppb). The Antarctic Peninsula again shows overall high values and no significant trend with elevation. Furthermore, Cl shows high concentrations in the centre of the East Antarctic interior, which is also observed in the Na data, but to a lesser degree. In Fig. 5 the spatial variability of the **Cl/Na** ratio is shown, ranging from 0.2 to 19.3. While most sites show a near seawater ratio of 1.8 (Warneck, 1991), in the Antarctic interior the ratio increases to an average value of 4.3, with data ranging from 2 to 9. Whereas coastal sites are likely to show seawater Cl/Na ratios due to the direct input, elevated Cl/Na ratio in the low accumulation zones of the Antarctic interior are suggestive of secondary Cl precipitation through HCl (De Angelis and Legrand, 1995), which might be partially off-set by HCl re-emission from the upper layers of the snow pack (Udisti and others, in press; Benassai and others, this volume). Overall, Antarctic interior Cl and Na concentrations are depleted in comparison to coastal values (Fig. 3 & 4). However, in the East Antarctic interior Cl seems relatively less depleted than Na, causing an increase in the Cl/Na ratio.

Figure 6 shows the spatial variability of **NO₃**, ranging from ~4 ppb to ~800 ppb. Highest values can be observed in Enderby, Dronning Maud, and Victoria Land, ranging from ~30 ppb to 800 ppb. Intermediate values are reported from Marie Byrd Land, Ronne Ice Shelf, South Pole region and Northern Victoria Land (~35 ppb to ~100 ppb), while the lowest values are observed on the Antarctic Peninsula and in Kaiser Wilhelm II Land (~0 ppb to ~20ppb). While NO₃ has been shown to be effected by postdepositional loss in low accumulation sites (Mayewski and Legrand, 1990; De Angelis and Legrand, 1995; Legrand and Mayewski, 1997; Mulvaney and others, 1998), the lowest values for NO₃ have been observed at sites with relatively high annual accumulation – the Antarctic Peninsula and Kaiser Wilhelm II Land. Samples from those sites are collected from the snow surface during August/September 1989 and February 1990, respectively, and contrast to snow surface samples from Enderby Land collected during October 1997, which show some of the highest values in entire data set. This suggests that postdepositional loss of NO₃ is strongly dependent on site-specific characteristics.

Spatial variability of SO_4 is shown in Fig. 7. The data range from 0.1 ppb to 3,800 ppb. It is important to note that SO_4 is particularly prone to sporadic input through volcanic events. As the data set represents different time periods, some of which coincide with volcanic eruptions, it is necessary to interpret SO_4 variability carefully. However, many data points in Marie Byrd, Victoria and Dronning Maud Land are contemporary data from 1992-1997 (Fig. 7, solid circles). The SO_4 concentrations of those data are higher at Victoria and Dronning Maud Land (~30 ppb to 3,800 ppb) than at Marie Byrd Land (~30 ppb to 90 ppb). Furthermore, the transect leading from the Antarctic Peninsula to Kaiser Wilhelm II Land shows large variability. The Antarctic Peninsula is characterised by low values (~10 ppb to 30 ppb), with higher values only at coastal sites (~75 to 1000 ppb). Also the data in Kaiser Wilhelm II Land are relatively low with 15 ppb to 70 ppb. The centre part of the transect, however, shows in comparison high values (~70 ppb to 100 ppb). In addition, the Enderby Land transect also shows an increase in SO_4 concentration with elevation (from ~10 ppb to 30 ppb). This could be influenced by local accumulation rates and variable SO_4 sources.

In Fig. 8 spatial variability of MS data are shown, ranging from 3 ppb to 166 ppb. In contrast to NO_3 and SO_4 , MS is thought to be predominantly derived through wet deposition due to its high Henry constant (Udisti and others, 1998; Becagli and others, this volume). Overall the data show highest concentration at coastal sites with decreasing trends inland, with the exception of two areas: the coastal sites at King George and Livingston islands and the transect at Enderby Land. While MS concentrations in the former are unusually low in comparison to other coastal sites (~0 ppb to 2 ppb), the latter shows a trend from low MS values (0 ppb to 14 ppb) at low elevation to high MS concentrations (14 ppb to 50 ppb) further inland. A similar, but less pronounced increase in concentration along the Enderby Land transect is also observed in the SO_4 and NO_3 data.

Ca, **Mg**, and **K** are shown in Fig. 9, 10, and 11, respectively. Concentration values range from 0.1 ppb to 740 ppb for Ca, from 0.2 ppb to 1,930 ppb for Mg, and from 0.1 ppb to 600 ppb for K. All three species show overall low concentration values across Antarctica with a few distinctive exceptions. Local dust sources such as the McMurdo Dry Valleys, a strong marine influence such as Terra Nova, or coastal sites at the Antarctic Peninsula cause orders of magnitude higher concentrations. Intermediate concentration levels are rare. The continent-wide pattern might therefore be used to distinguish typical 'global' or hemispherical dust content from local Antarctic sources.

SUGGESTIONS FOR FUTURE WORK

The primary objectives of this paper are to provide an updated summary of available chemistry data from Antarctica and make recommendations for future efforts. The observed variability across Antarctica clearly shows the need for an improved understanding of the mechanisms that ultimately control the chemistry of a snow or ice sample. By making this data set available, we invite and encourage the wider science community to participate in this continent-wide effort.

Based on our findings and on previous papers, we aim for the following research outputs as the next step for the ITASE Chemistry Synthesis Group:

- Investigation of the snow chemistry signal migration and spatial variability of significant climate events and oscillating and non-oscillating climate drivers
 - This can be achieved by intercontinental comparison of snow chemistry variability contrasting e.g. El Niño with La Niña years, high index Antarctic Oscillation years with low index years, and the snow chemistry signal before, during and after volcanic eruptions
 - Furthermore, cross-correlation of snow chemistry data with reanalysis data, such as NCEP/NCAR and ERA-40 will allow us to link characteristic geographic chemistry patterns to typical climate modes, establishing transfer functions, and to identify Antarctic teleconnections and their variability through time.
 - Tuning general circulation models to reconstruct snow chemistry patterns in reoccurring synoptic and meso-scale climate events using contemporary chemistry data as a training set will allow us to use these models in reverse, to output climate events using chemistry data further back in time
- Investigation of the relationship between atmospheric aerosol loading and contemporary snow chemistry.
 - Quantification of contemporary aerosol precipitation and deposition efficiency by linking surface snow chemistry concentration with atmospheric aerosol loading measurements can be established in collaboration with the ITASE Atmospheric Chemistry Synthesis Group. Furthermore, this will assist in investigating the processes that lead to post-depositional ion concentration changes. It is important to compare samples of similar age as well as of similar snow depths.
 - Investigation of dry versus wet deposition is particularly important when comparing coastal sites with the Antarctic interior. Here progress can be achieved in collaboration with the ITASE/ISMASS Mass Balance Synthesis Group and the ITASE Atmospheric Chemistry Synthesis Group
 - Incorporate new analytical techniques allowing the measurement of trace elements and their isotopic signatures, as well as organic acids, and particles
- Laboratory inter-comparison
 - We suggest a laboratory inter-comparison in order to demonstrate the compatibility of snow chemistry data across all laboratories.
- Data Availability
 - The data described here are made available through the ITASE Synthesis Groups web page. The data set will be updated as new data and data sets are provided.

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Table 1: Correlation between elevation and ion concentration of multi-year samples

Species	Number of samples	Correlation formula	r	t	p
Na	150	$y = -503 \bullet \ln(x) + 4078$	-0.73	13.18	>0.999
Cl	172	$y = -421 \bullet \ln(x) + 4040$	-0.51	7.21	>0.999
Cl/Na	144	$y = +1120 \bullet \ln(x) + 1288$	+0.56	8.08	>0.999
NO ₃	166	not significant >0.999			
SO ₄	160	not significant >0.999			
MS	89	$y = -793 \bullet \ln(x) + 3994$	-0.42	4.37	>0.999
Ca	116	$y = -429 \bullet \ln(x) + 3030$	-0.70	10.47	>0.999
Mg	122	$y = -474 \bullet \ln(x) + 2966$	-0.73	11.87	>0.999
K	76	$y = -294 \bullet \ln(x) + 2388$	-0.52	5.23	>0.999

r=correlation coefficient , t=double-sided student 't' test, p=level of significance

Figures

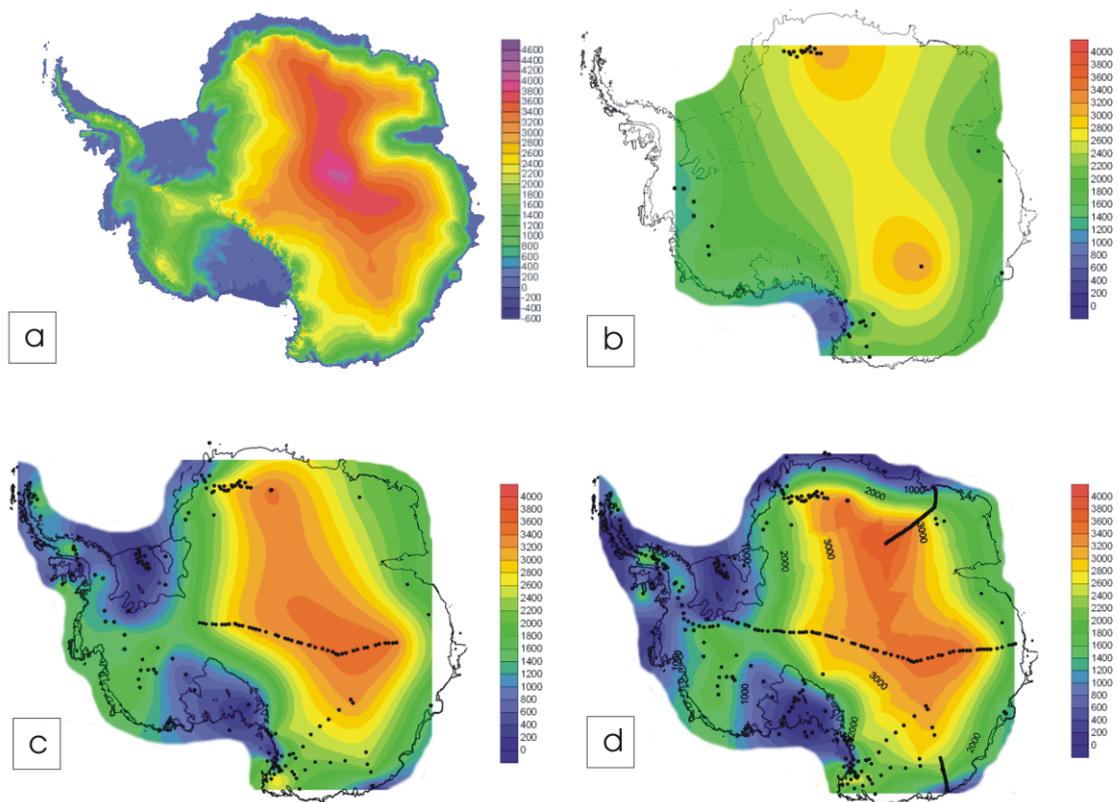


Figure 1: Reconstructed topography of Antarctica, derived from **a)** RAMP 5km elevation model (Liu and others, 2001), **b)** sample locations providing data for the 1992-1997 time period, **c)** sample locations providing multi-year averages, **d)** all glaciological sample locations.

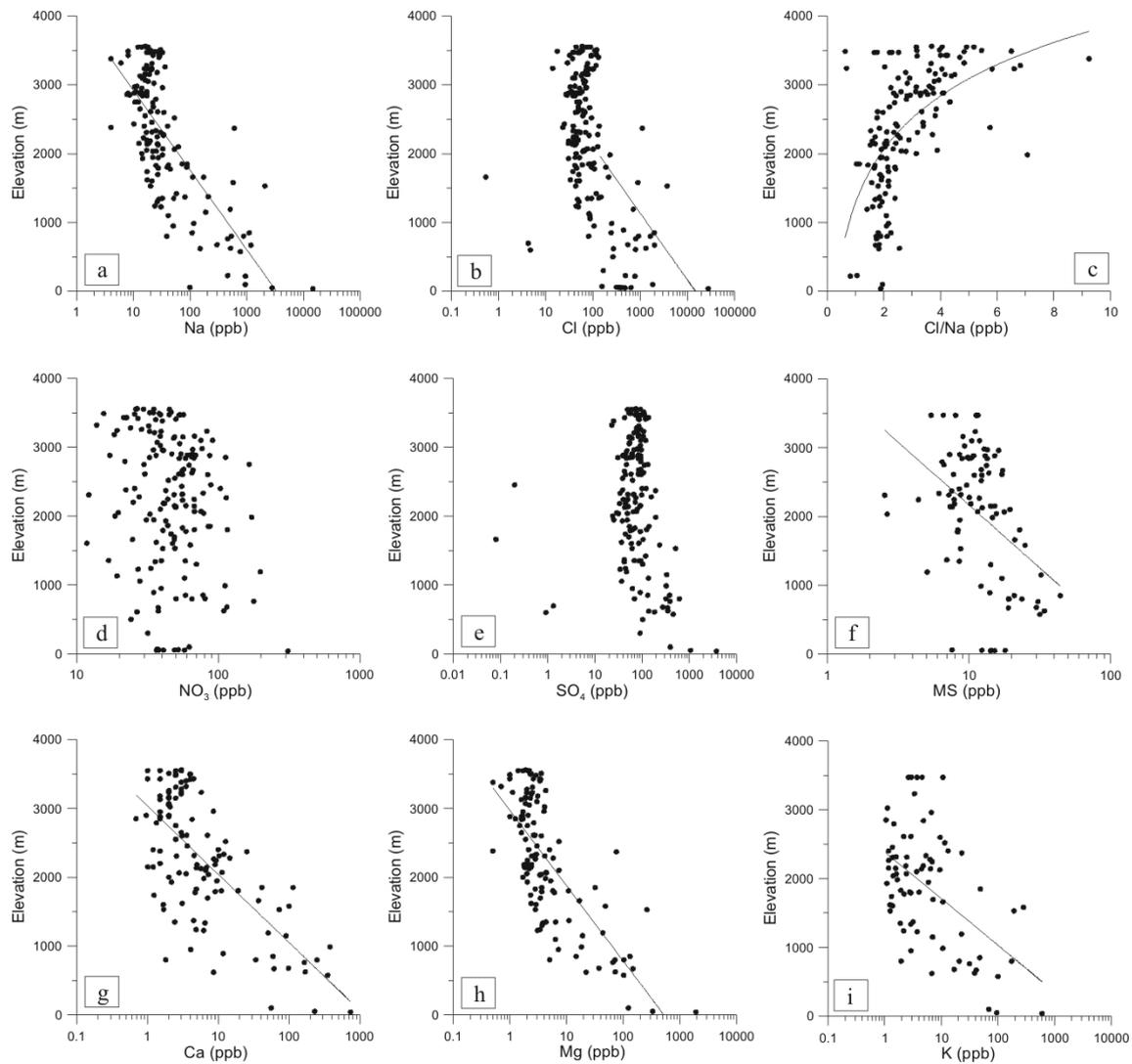


Figure 2: Relationship between multi-year ion concentration data and elevation. Please note, all species are plotted on logarithmic scale, with the exception of Cl to Na ratio, which is plotted on a linear scale. The logarithmic trends shown are significant on the 99.9% level.

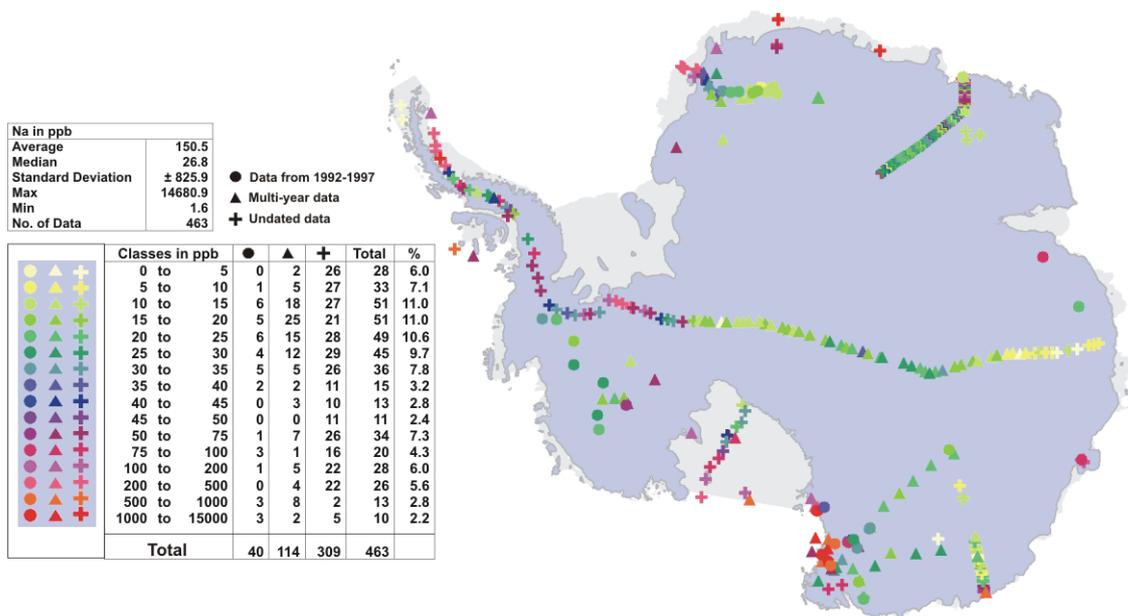


Figure 3: Spatial variability of Na concentration measured in ppb. Solid circles represent data from 1992-1997. Solid triangles represent all other multi-year data. Crosses represent non-annual or undated samples

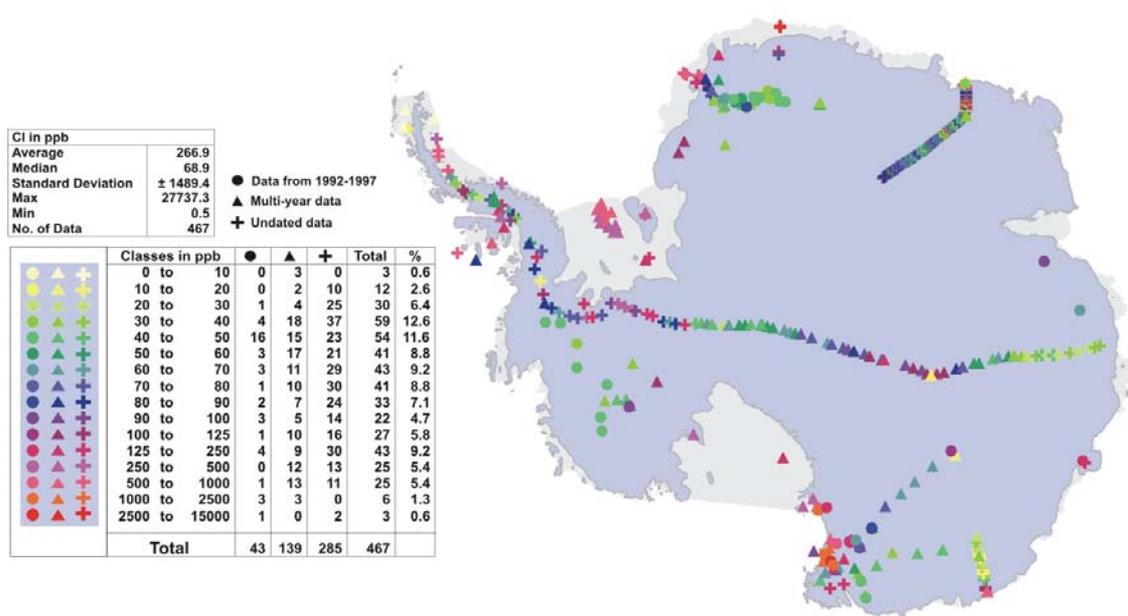


Figure 4: Spatial variability of Cl concentration measured in ppb.

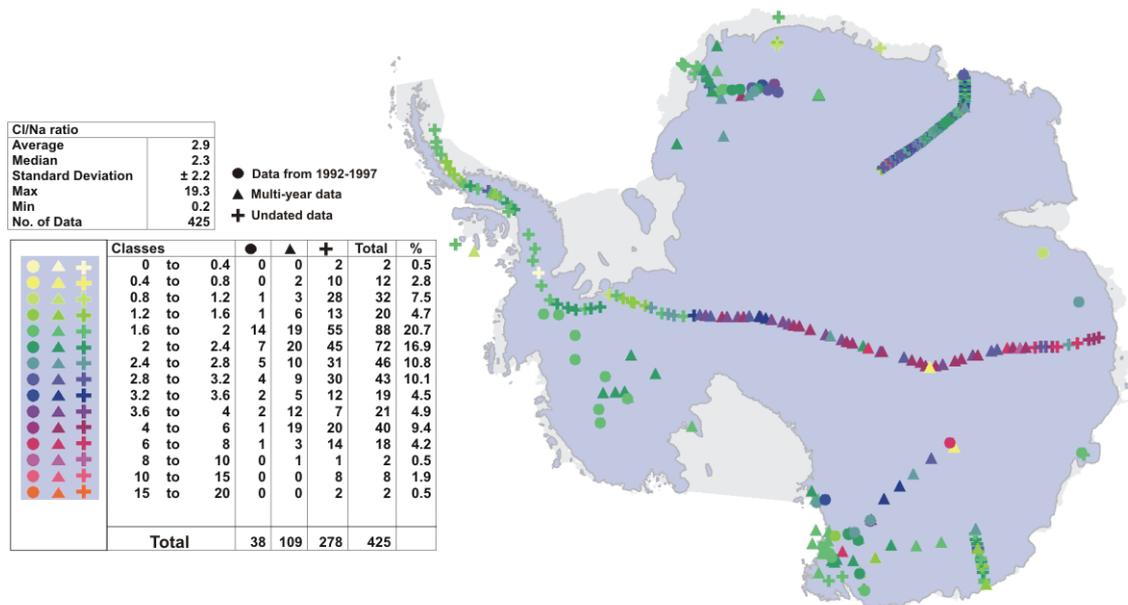


Figure 5: Spatial variability of Cl/Na ratio.

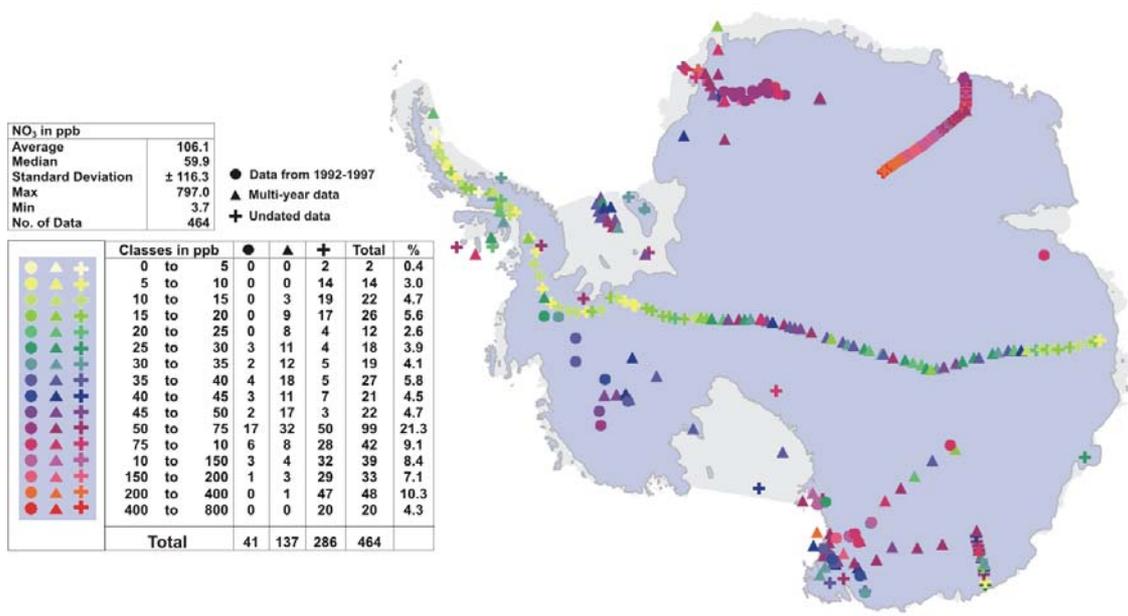


Figure 6: Spatial variability of NO₃ concentration measured in ppb.

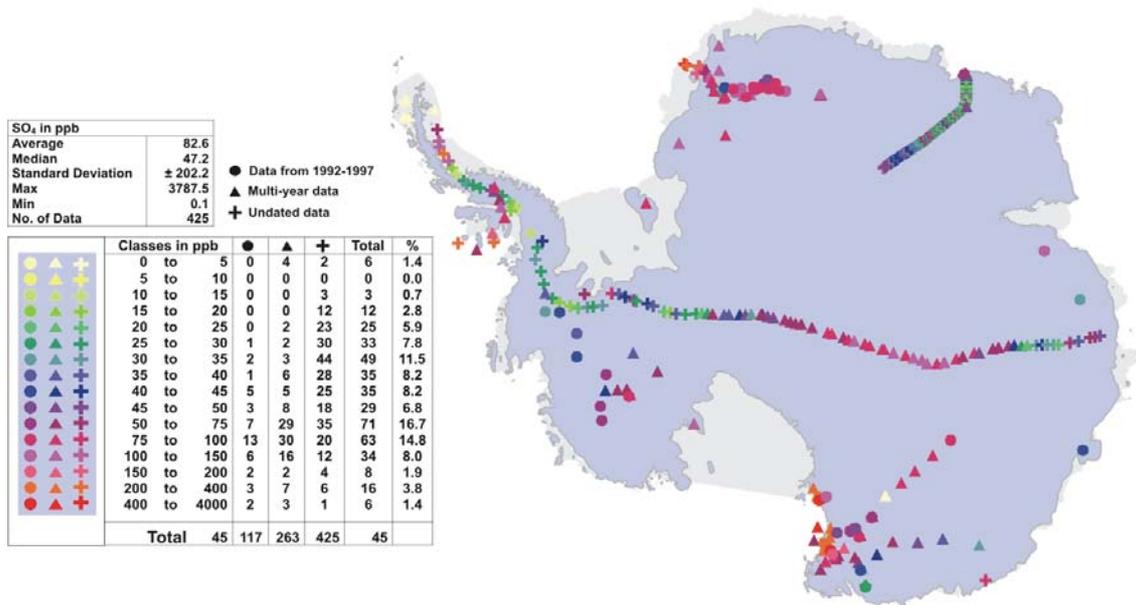


Figure 7: Spatial variability of SO₄ concentration measured in ppb.

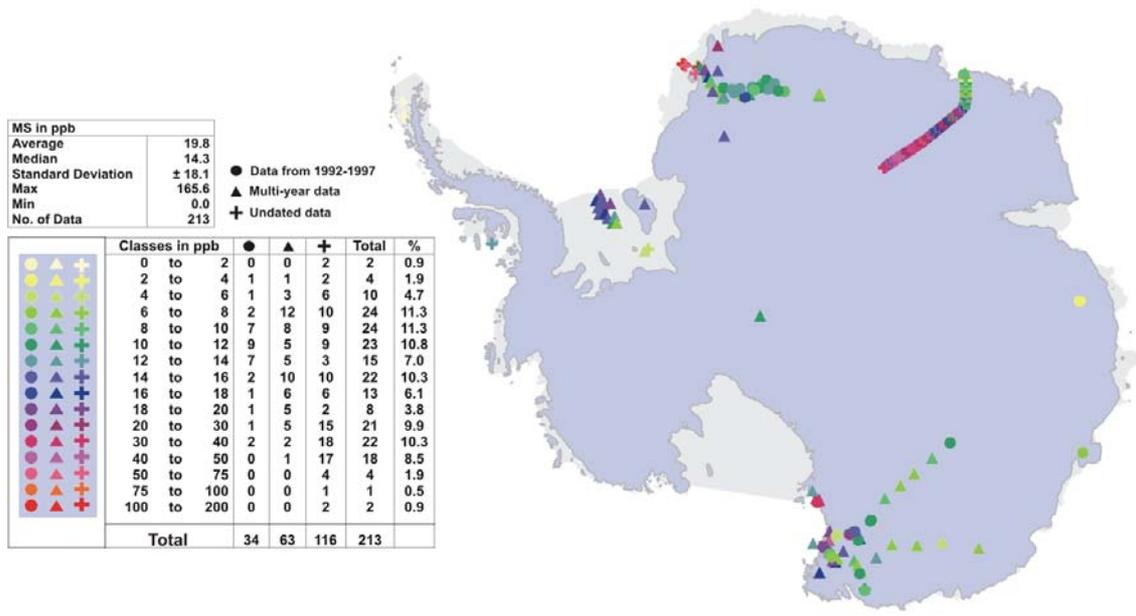


Figure 8: Spatial variability of MS concentration measured in ppb.

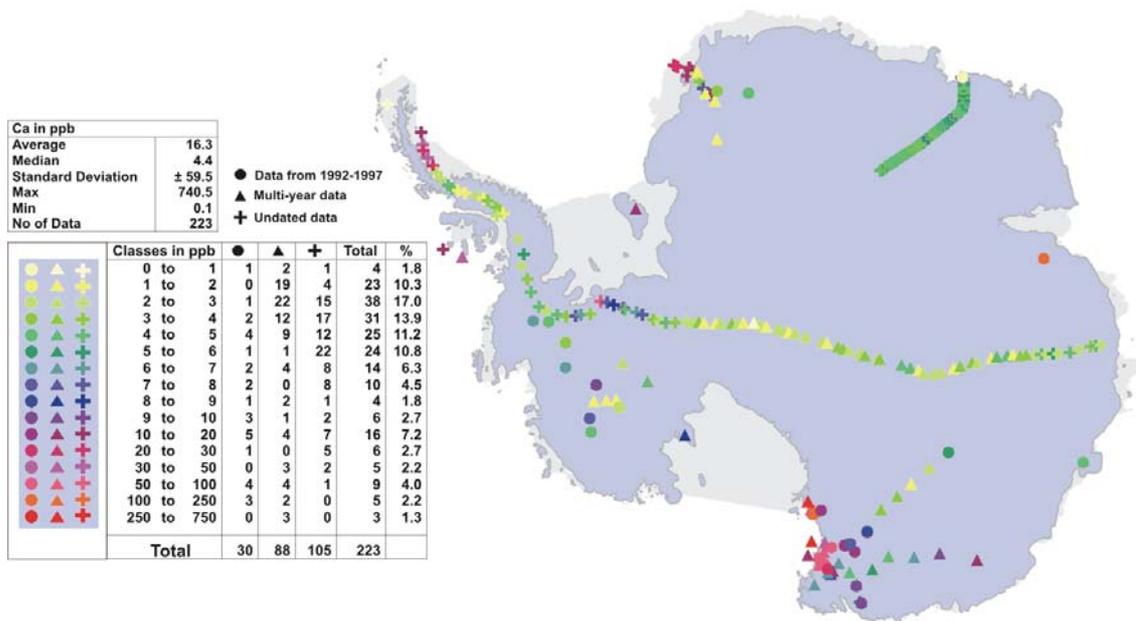


Figure 9: Spatial variability of Ca concentration measured in ppb.

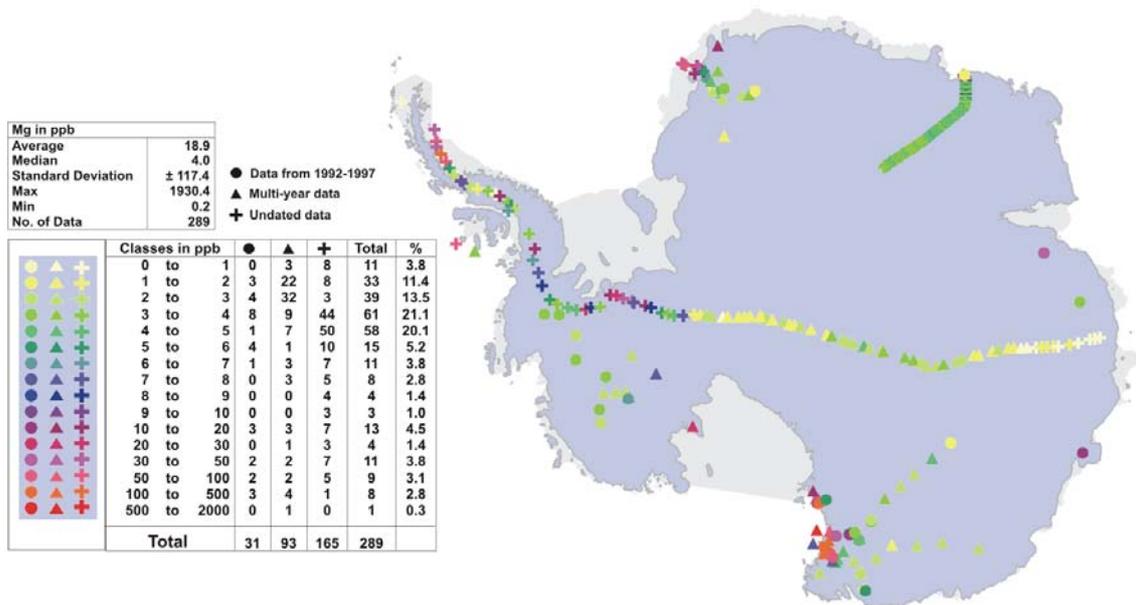


Figure 10: Spatial variability of Mg concentration measured in ppb.

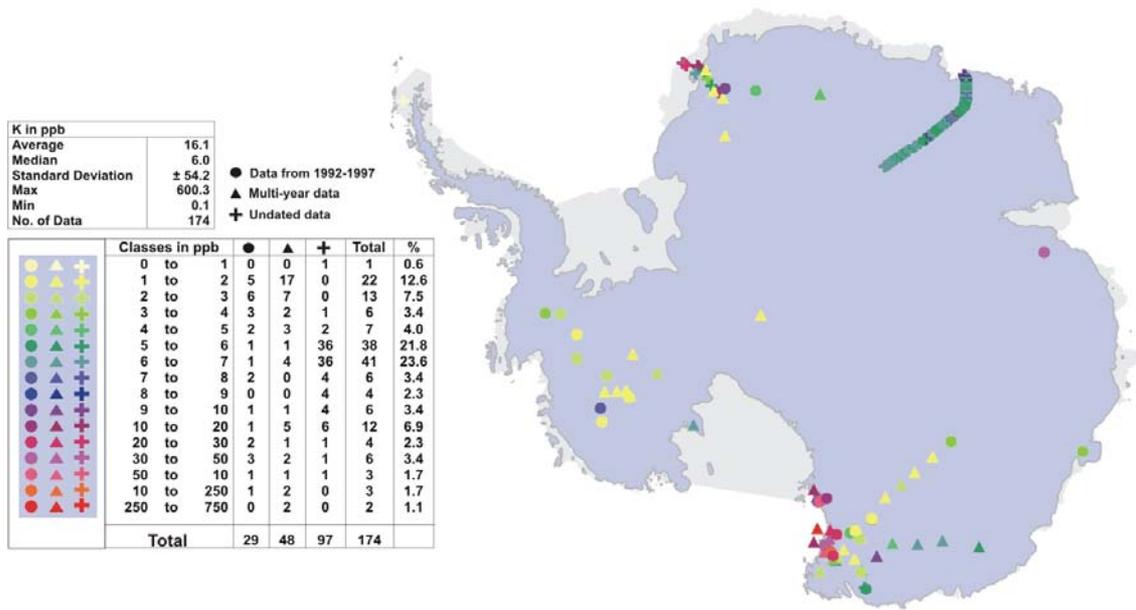


Figure 11: Spatial variability of K concentration measured in ppb.