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Ion Fractionation and Percolation in Ice Cores with Seasonal Melting

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Abstract: We examine the impact that post-depositional change has on ion concentrations in ice cores that suffer limited seasonal melting. We show that the impact in the case of at least one Svalbard ice core is limited to decreasing resolution of signals to about 3 years – a similar accuracy as the best dating can usually provide. We model various effects such as percolation and washout of ions, and show how they can be used to construct useful ice core proxies. The sulfate profile shows how post depositional effects lead to magnesium and nitrate being excellent predictors under normal conditions for sulfate – indicating a difference in the properties of acidic and neutral salt sulfate components. The approach leads to an objective method of detecting volcanic signals in sulfate, even when the signals are much smaller than the sulfate variability caused by other factors. We emphasis the importance of correct statistical analysis the interpretation of ion profiles, taking into account how measurement errors and the distribution of ion chromatography data affects how statistical modelling should be done.

Key words: Svalbard, ice core, ion chemistry, climate change, statistical analysis, diffusion, percolation

List of Symbols and Abbreviations

a	species specific melt rate constant
A,B	concentrations of two chemical species
AR1	first-order autoregressive model coefficient
C_b	Concentrations of ions in bubbly ice
C_p	species initial concentration in fresh snow.
C_s	Concentrations of ions in solid clear ice
D	pre-depositional concentration
EOF	Empirical Orthogonal Function
e	species dependent elution factor
e_{Cmeas}	elution factors for ice core measured
e_{Cmod}	elution factors for ice core corrected
e_p	elution factors for snow pit
K	constant terms in MLR models
k_{AB}	concentration ratio of A and B in fresh snow.
LIA	Little Ice Age
M	dimensionless melt intensity index
m	product of eleution factor and SMI
MLR	Multiple Linear Regression
PC	Principle Component from PCA
PCA	Principle Component Analysis
RC	Reconstructed component from PCA
SMI	Stratigraphic melt index
X	matrix of species, depth in MLR models
Y	target vector of MLR models
w	number of points used in running mean.
Z	Log-normalized concentration of Ca^{2+}, Mg^{2+}, NO_3^- and SO_4^{2-}.
Γ	vector of model coefficients in MLR models

1. Introduction

Ice core records are generally taken from areas where summer melting is nil or very little. The only regions of the world where this condition is met at present are the central regions of the large ice sheets of Antarctica and Greenland, or from a few of the high mountains. These areas represent a spatially limited fraction of the total ice cover of the planet. The extraction of regional scale climate mechanism requires a wider net of observations. To improve this coverage it is necessary to consider the climate data available from less than ideal ice cores from those ice sheets and glaciers where summer melting is significant. Traditionally glaciologists have shied away and treated results from these ice cores with suspicion. This is because of historical difficulties with ice core analysis methods and with the type of data that was expected to come from ice caps with seasonal melt. The objective of this paper is to show that modern analytical methods, combined with advanced ideas on data analysis and a wider range of ice core proxies gives rise to useful climatic interpretations from ice cores that suffer seasonal melting. Indeed several of these methods provide better evidence for some basic ice physics processes than more traditional ice cores can give. This is because the temperatures inside the seasonal melting cores tend to be much warmer, and the ice caps much thinner than those found in the central parts of large ice sheets, so processes such as diffusion occur much more rapidly with much less influence of external climate forcing.

The small, low-altitude ice caps of the Arctic are relatively close to large sources of anthropogenic pollution and may be expected to record a more localized environmental record than that found in the central Greenland ice cores. They are therefore valuable for assessing impacts and source histories in detail over

the period since the industrial revolution [1]. Svalbard is in an interesting geographical position surrounded by Arctic Ocean, Barents Sea and North Atlantic, and located at the southerly edge of the permanent Arctic sea ice.

Several ice cores have been drilled on Svalbard and give records less than 1000 years long. Most of the results that have been presented are stratigraphic studies. The only ion analyses reported were of chloride and sulfate [2], [3]. However the low concentrations in the ice could not be measured very precisely at the time due to imprecise instruments. The Japanese have also drilled several ice cores at other sites in Svalbard since 1987, (e.g.[4], [5], [6]). To date only a few ion records have been published.

2. The Lomonosovfonna ice core

2.1 Geographical setting

The main source of data we have comes from analyses of the central Spitzbergen ice core drilled in 1997. The 121 m long ice core (spanning about the 800 years) comes from Lomonosovfonna, the highest ice field in Svalbard (78° 51' 53"N, 17° 25' 30"E, 1255 m a.s.l.), where the current annual temperature range is from 0 ºC to about -40 ºC. Total ice depth from radar sounding was 123 m, and the site is close to the highest point of the ice cap with roughly radial ice flow. Published data from a previous, lower elevation ice core on Lomonosovfonna drilled in 1976, indicated better preserved stratigraphy than the other sites on Svalbard [7]. Therefore we selected the summit of Lomonosovfonna as our coring site. This ice core was subjected to a fairly standard set of isotopic and chemical analyses. However, in comparison with most cores from seasonal melting ice caps, some fairly novel additions were also done, notably particle analysis using SEM, deuterium excess, samples for ^{14}C dating and bacterial DNA. Perhaps the most interesting results have come from applying advanced statistical methods to modeling the ice core parameters. These methods have allowed estimates of proxies such as summer melting and continentality, and also provided some insights into the nature of the processes that occur during post-depositional melting and subsequent diffusion of chemical ions in ice.

2.2 Ice core dating

The dating of the core was based on a layer thinning model tied with the known dates of prominent reference horizons, (see 8] for details). Dating reliability is estimated to be about 3-5 years over the last 300 years by of comparison the model timescale with independent annual cycle counting, [9]. The accumulation rate for the second half of the 20th century was 0.41 m water equivalent per year (m we. a^{-1}) with a somewhat lower value of 0.31 m we. a^{-1} in the 18th and 19th centuries. Temperatures within the firn pack approach -3 ºC at 15 m depth [10]. Extensive shallow coring and snow pits indicate that any summer melt water is refrozen mostly within the previous winter's snow, and the remainder within the next two or three lower annual layers [11], though some runoff and loss of ions may be occurring in the 21st Century [12].

2.3 Chemistry measurements

Ion determinations (Fig. 1) were carried out using a Dionex Dx-120 suppressed ion chromatograph. Four anions, methanesulfonate (MSA), chloride, sulfate and nitrate, were determined using Dionex Ionpack AS15 columns. A total of five cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were determined using Dionex Ionpack CS12 columns. Melted samples were analysed in random order to minimize the effects of any systematic errors.

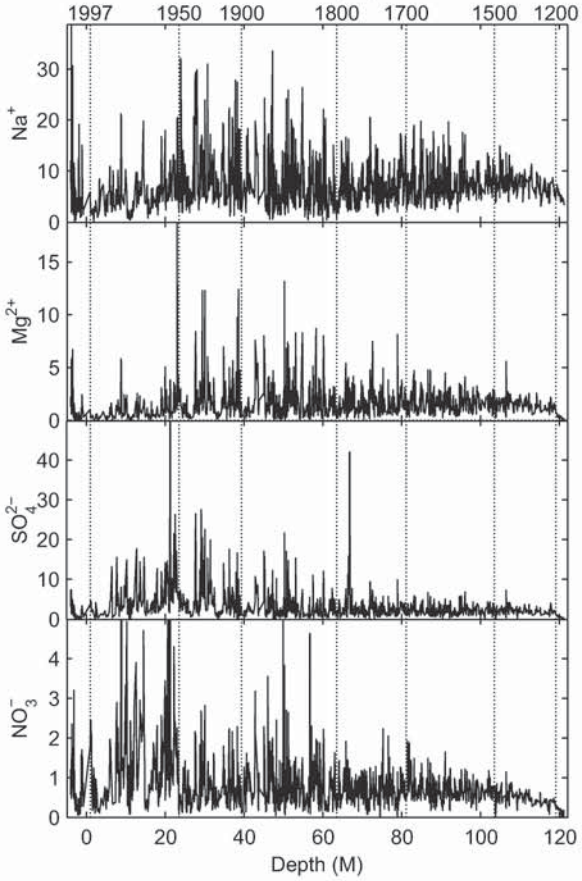

Fig. 1. A 2002 snow pit and the Lomonosovfonna 1997 ice core ion concentrations (μEqL^{-1}) plotted to enable the visual comparison the two data sets. The pit data is plotted from -4 m (spring 2002) to 0 (bottom of the pit is dated as 1999).

Details of the analytical methods are described by *Jauhiainen et al.* [13], *Kekonen et al.* [14, 15] and *Virkkunen* [16]. The general features of the ion profiles are discussed in detail by *Kekonen et al.* [8]. The salient points for the analyses discussed in this paper are: the large spike in sulfate (and tephra, [17]) from the Laki volcanic event in 1783; the general smoothing of the profiles as a function depth; the low concentrations seen in the bottom 5 m of the core; which are also seen in recent years in the snow pit data.

3. Percolation effects

3.1 Ice facies and climate signals

Moore et al. [18] evaluated the effects of post-depositional versus climate factors in determining the ion concentrations in the ice core. An important feature of chemical measurements made using ion chromatography is that the errors in the measurements are proportional to the concentrations, thus a log transformation must be applied to concentrations before using any statistical tests on the data that require Normally distributed errors. This applies, for example, to fitting data with regression models. Additionally before doing Principal Component Analysis (PCA), the ion species concentration probability density functions should be standardized to zero mean and unit variance.

The results from PCA analysis are not immediately interpretable in terms of physically meaningful factors. In order to understand what the derived independent components may represent it is necessary to correlate the reconstructed components (made by projecting the ionic composition on the principle components) with various climate indices or other variables that are suspected to cause significant variability in the record. The great advantage of doing a PCA analysis is that each component is independent thereby, in principle, making separating different forcing signals easier.

Fig. 2 examines the division of ions based on differentiating between types of ice facies the samples originate from. We would expect to see clear differences in the leading EOFs - depicted by their reconstructed components (RC) if the facies type was the dominant determinant of ion concentrations in the core. However fig. 2 shows there are no great differences between the two ice facies. That is the distribution of two facies is evenly distributed, except for the RC1 component. This means that the bubbly or clear ice facies simply affect the mean values of the ionic components, the other independent components do not show separation between facies. This appears to be the case for both the solid ice and the upper firn sections of the core, indicating that even during the late 20th Century when anthropogenic pollution and air temperatures have generally been warmest in the who core record, there is still no significant differentiation of ions by facies type, except in their mean concentrations. This shows that melting and redistribution of ions is not the dominant cause of chemical variations with depth.

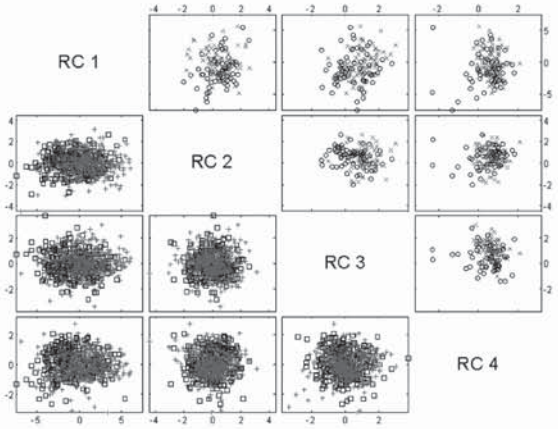

Fig. 2. The leading four reconstructed components (RC 1-4), of the standardized ionic composition of each sample projected on PC 1-4 (which accounts for 67% of total variance). Lower left for the whole upper 80 m of ice core, with bubbly (□) and clear (+) ice marked. Upper right for 1950-97 ice samples with firn and bubbly (○) and clear (x) ice marked.

Next we use PCA analysis to test how significant ion concentrations were changed by the main climatic periods spanned by the core changed relative to the physical evidence of post-depositional effects. Four subsets were created spanning different periods, with approximately the same number of samples in each period: Period I, 1705-1850, which is in the middle of the Little Ice Age (LIA), and is also clearly before any anthropogenic pollution is detectable in the ice core, so can be called pre-industrial; period II, 1866-1920, immediately before the end of the LIA and period III, 1920-1972, immediately after the end of the LIA; period IV, 1950-1997, which is dominated by anthropogenic input. Stratigraphic analysis of the core allowed separation of bubbly and clear ice facies at the cm-scale using the methods of *Pohjola et al.* [19]. Bubbly ice is derived from firn in the usual firnification way with little or no melt water infiltration, and clear ice formed as a result of a firn layer with high porosity that was fully wetted by infiltrating water. The bubbly layers probably correspond to spring and summer snow, and the clear ice layers to autumn and winter snow, being more likely to contain low density depth hoar layers above an impermeable ice layer from late summer.

In contrast with fig. 2, Fig. 3 examines the reconstructed components as a function of climatic period. Fig. 3 shows that there are clear differences between the groups seen by the separation of the circles and crosses in RC4 (rightmost column) – showing the changes between the pre and post LIA termination. There are clear differences between squares and plus signs in RC3 (second bottom row) showing chemical differences between post 1950 and pre-industrial ice.

The analysis, elucidated by *Moore et al.* [18] suggests that much information of climatic interest is preserved in the core, even though the physical process of melting causes the largest single change in ion locations.

However, it is the large signal to noise ratio in the chemical analysis of the core [15] that means the lower order EOFs are valuable and not simple noise.

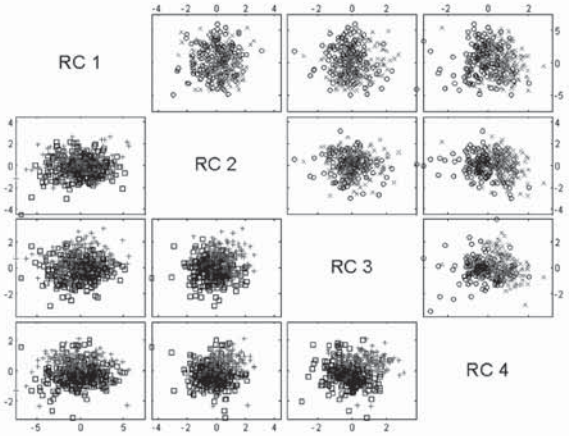

Fig. 3. The leading four reconstructed components (RC 1-4), of standardized ionic composition of each sample projected on PC 1-4 (which accounts for 67% of total variance). Lower left for periods I and IV, with post 1950 (□) and pre 1850 (+) ice samples marked. Upper right for periods II and III with 1866-1920 (○) and 1920-1972 (x) ice samples marked.

It is visually clear that there are differences between EOFs or reconstructed components, but we have not yet shown that they are statistically significant. This is the question we address in the next section.

3.2 Significance testing EOFs

One key element in PCA type of analysis is to determine how significant each of the resolved components are, and hence where to define a noise floor, beyond which interpretation is meaningless. We discuss two methods here. The signal to noise ratio of the chemical ions in our core is about 92-95% - this comes from the analysis of 470 same depth samples with 2 different IC methods of NO_3^-, Cl^- and SO_4^{2-} concentrations [15]. This represents both measurement error and small scale inhomogeneity across the core. Moore et al. [18] used the eigenvectors (EOF vectors) that account for 85% of series variance – that is the first 4. This is one valid way assessing the significance of PCs as far as we are aware (e.g. *Gershenfeld,* [20], p121; and references therein).

A second method is to examine the median and 95% confidence intervals of the PCs (using the median rather than the mean makes for a more robust test). In our case PCs 2,3 and 4 are all significantly different from each other in the 4 time periods we define (see Fig. 2 of *Moore et al.*, [18]). An even better way of testing significance is Monte Carlo testing using suitable noise models. The choice of noise models is quite a complex issue, and at some level becomes purely philosophical as no-one actually knows that the real climate background spectrum actually looks like. Often simple white noise is assumed, which is a rather poor choice given what we do know about the climate (i.e. that there is a memory in the system so that what happens in the present is linked to what happened in the past rather than being purely random. It is common to use a red-noise model based on a series constructed using simple autoregressive order 1 (AR1) characteristics and the same mean and variance of the data to be tested. We have Monte Carlo significance tested the EOFs (Table 1) against white and red noise (AR1=0.5), more than we typically find in our series, e.g. the mean AR1 value in period III is 0.42.

Table 1 Significance testing of EOFs

PC EOF	Variance found[a]	Remaining Variance[b]	P-white[c]	P–red (AR1=.5)[d]
1	57.11	57.11	100	100
2	13.18	30.72	100	100
3	10.62	35.73	100	100
4	6.98	36.57	100	100
5	4.34	35.82	100	100
6	3.26	41.95	100	100
7	2.19	48.51	100	100
8	1.36	58.72	99.17	96.84
9	0.96	100	22.86	0

[a]Variance found is the actual percentage variance we find from the dataset in Period III.
[b]Remaining Variance is the percentage variance remaining after the variance from higher EOFs has been accounted for. E.g. for PC3, Remaining Variance=10.62/(100-57.11-13.18).
[c]P- white ([d]p-red) is the percentage in 10,000 runs of white (red) noise that the Remaining Var EOF was less than we find, i.e. if 100% have Remaining Variance lower, then our found variance is ultra-significant.

What we are looking for is that the EOF in question accounts for more of the fractional variance remaining than would be the case of noise. If the variance accounted for by that EOF was much more than produced randomly then we expect that EOF to be significant. Note that this is a mathematically correct way of estimating significance compared with the simplistic notion that if there are 9 EOFs then each should account for 11% of the variance. This reasoning does not take into the account the variance accounted for by the higher order EOFs which remove much of the total variance in the series. Using this method we find that the first 8 EOFs are extremely highly significant (Table 1).

While table 1 shows that all the leading 8 EOfs are significant, it cannot, as discussed earlier explain their physical significance. In order to understand what the EOFs mean requires an analysis of how they vary with suspected forcing agents. *Moore et al.* [18] showed that there were differences in several components that were associated with changes in climatic period (see previous section for a description of the periods used). This requires that the PCs for individual species compare between periods. Different PCs capture different, independent aspects of source and transport variability.

If the PCs for particular ions are closely grouped during in one period but become widely separated in another period this then indicates that something different has happened to the sources or transport factors that bring the ion species to the ice cap. For example PC4 captures the dramatic changes in SO_4^{2-} and MSA that occurred at the end of the LIA. The pair are located much closer in period III than in period II, probably because of a stronger local source of marine biogenic H_2SO_4 and MSA (and change in their branching ratio from dimethyl sulfate) from increased production in warmer post LIA Barents Sea [21].

3.3 Percolation model

The analysis of *Moore et al.* [18] and that in Fig. 2 shows that facies type is only reflected in PC1, suggesting that a simple linear model of percolation with just a single parameter in combination with melt will be sufficient. A physically plausible representation of this is use the elution rate found for each species (Table 2) multiplied by the stratigraphic melt index (SMI), envisaging a mechanism whereby melt infiltrates the layer beneath in a exponentially decaying fashion. We define elution rate,

$$e = 1 - \exp((\overline{\ln C_b} - \overline{\ln C_s}))$$

where C_b and C_s are the concentrations of a species in bubbly ice (melt <30%) and clear ice (melt >70%).

Elution factors for the snow pit (Table 2) were calculated by comparing concentrations in the same layer of snow before (winter surface snow in 2001 snowpits) and after summer melting (layer spanning autumns 2001-2000). The least eluted species are sodium, chloride, ammonium and potassium. The charge on the ion seems to play an important role during elution, since except for NO_3^-, divalent ions (Ca^{2+}, Mg^{2+} and SO_4^{2-}) have the highest elution factors. This contrasts with earlier data that found anions of strong acids were eluted first (e.g. [22]) but observations in more recent studies (e.g. [23]) are very similar to ours. Also at Austfonna the dry snow had lower pH values (5.2-5.3) than the wet snow (5.6-5.6). Therefore some elution of hydrogen ions obviously occurs during melting.

The elution factor of NH_4^+ is not as reliable as that for other species in the snowpit. The winter surface snow in 2001 snowpits does not include layers with the highest NH_4^+ concentrations since ammonium is expected to peak during warm periods, especially in late summer and autumn, when there are often large forest fires in the Northern Hemisphere and biogenic emissions are greater [24]. However, our estimate of elution factor seems fairly reasonable since NH_4^+ is one of the least eluting species in both the Lomonosovfonna and Austfonna [25] snow pits and the 1997 ice core.

Moore et al., [18] originally calculated elution factors based on the assumption that during melting many ions elute from the snowpack and are trapped in clear ice layers as the water is refrozen. Thus the layer where the ions were originally located (bubbly ice) has lower concentrations. The order of elution factors based on ice core data and snow pit concentrations are fairly similar but the values are different. For most of the ions the elution factors are 2-3 times higher in the snowpit than in the ice core. This most probably indicates how serious the melting was during the 2000-2001 summers and that an unusually large proportion of ions was lost by deep percolation or runoff. Due to its much lower altitude Austfonna ice cap is more affected by melting than Lomonosovfonna and this can also be seen in the elution factors that were calculated based on the concentrations in dry and wet snow in 1998 [25]. The values of the elution factors are similar even though the values at Lomonosovfonna represent layers with serious melting while the some summers affecting the formation of 'wet' snow layers at Austfonna were not noted as especially warm summers.

Table 2 Elution factors (e) for ion species in the pit and in the 1997 ice core Cmeas [18]. Cmod takes into account that not all the bubbly layers have necessarily experienced melting in the 1997 Lomonosovfonna ice core record. Elution factors for Austfonna glacier in 1998, e_A, were calculated based on the concentrations in wet and dry snow [25].

e_{pit}	NH_4^+	Na^+	Cl^-	K^+	NO_3^-	Mg^{2+}	Ca^{2+}	SO_4^{2-}
	0.18	0.49	0.58	0.70	0.85	0.86	0.88	0.88
e_{Cmeas}	Mg^{2+}	NH_4^+	Na^+	Cl^-	K^+	Ca^{2+}	SO_4^{2-}	NO_3^-
	0.27	0.28	0.28	0.31	0.35	0.37	0.43	0.47
e_{Cmod}	NH_4^+	K^+	Na^+	Cl^-	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}
	0.25	0.36	0.43	0.44	0.51	0.56	0.61	0.61
e_A	NH_4^+	K^+	Na^+	Cl^-	Ca^{2+}	NO_3^-	SO_4^{2-}	Mg^{2+}
	0.37	0.71	0.73	0.75	0.77	0.79	0.88	0.93

The most significant difference between the elution factors in the snowpits and those in the ice core 1997 is the location of magnesium in the elution order. According to the ice core data this ion is the most stable ion in the snowpack during the melting. In the snowpit record, however, magnesium elutes with melt water similar to other divalent ions and nitrate. As the use of the $\log([Na^+]/[Mg^{2+}])$ melt indicator (see section 4.1) is based on the assumption of different elution rates for magnesium and sodium, there is an apparent contradiction, that can however, be resolved. Not all the bubbly layers in the ice core have necessarily experienced melting. If we restrict the calculation to regions where the smoothed (7 point moving average) stratigraphic melt index, SMI, has a steep slope (absolute gradient larger than 10% per sample) then we get modified elution factors, C_{mod}, which are much more consistent with those of the pit (see Table 2). Values of the elution factors are higher than before but still not as high as in the pit with unusually heavy melting, and the location of Mg^{2+} in the elution order is similar to the other records.

The limited re-distribution of ions acts a low-pass filter on the concentration data enhancing ion autocorrelation functions. If we want to produce a record that is rather more like the original atmospheric composition than we now have measured in the post-depositionally altered ice layers, effectively deconvoluting the signal with a filter representing post depositional effects. We do this assuming that the measured concentration C_i in each annual layer i, is a result of some loss of ions to the $i+j$th layer below, so that a smooth approximation to the ionic concentration D_{i+j} for a particular species in the original precipitation may be given as:

$$C_i = (1-m)\sum_{j=0}^{\infty} m_i^j \; D_{i+j}$$

However this is not possible to solve for variable m_i. So we use a local inverse filter to extract the

$$D_i = (1+x)C_i - xC_{i-1}$$

where

$$x = (m_i^{-1} - 1)^{-1}$$

and m_i is the product of the elution factor for each species and the local SMI taken from the detailed stratigraphic analyses of the ice core. The model uses variable melt index, but it is held constant within each short (8 year) convolution window. We choose an 8-year window as that is the multiple of 2 that seems likely to be closest to any plausible depth of penetration of melt water based on observations of shallow ice cores melt layers and borehole temperature profiling [11]. The local distribution of melt layers changes over short horizontal distances [11] even though the upper parts of the firn pack must be isothermal in summer, and experience the same climate conditions. Thus the model allows melt index to change over an 8 year window, but not for each thin melt layer.

This model may be used to remove the effects of percolation to reconstruct the original species concentrations. If the objective is to recover a climate signal then it does not matter much that the ions are blurred in location, as long as the original distribution can be estimated. Our model does not seek to explain the exact details of percolation in our core, which we accept must sometimes have occasional "pipe" type percolation. The point is that it does not happen very often in any *particular place*, so that *on average* the simple model we suggest does actually suffice for any particular place such as the ice core site. This is self-consistent with the PCA analysis that does show only simple differences in PC1 between ice with different melt histories. This simple behavior proves that there is no need *on average* to consider more complex models of percolation, as we can still explain 85% of the signal we have with the simple model.

The model differs from simple diffusion processes in several respects: the percolation distribution is single-sided reflecting that percolation takes place only downwards, and secondly that the concentrations decay exponentially with distance rather than following a Gaussian curve with diffusion. This means that the tails of the percolation distribution are thinner than the Gaussian, which is a consequence of the Brownian motion random-walks in diffusion compared with uni-directional motion in percolation. Thus the impact of percolation in this model is therefore less dramatic than a diffusion-type model would produce.

4. Chemical fractionation

4.1 Melt index

Many studies have found that particular ions are preferentially washed out of the ice during seasonal melt (e.g. [26], [25]). However, details of specific ion elution rates depend on the incorporation of ions in the ice during grain growth and so are certainly affected by processes that occur prior to the onset of melting [23]. While microphysical processes governing the removal of ions are poorly understood, it is reasonable to assume, following *Grinsted et al.* [27] that the ions are removed fractionally as the melt progresses, and so we can write

$$\frac{\partial C}{\partial M} = -a \cdot C \; and \; C(0) = C_p \Leftrightarrow C(M) = C_p \cdot e^{-aM}$$

where M is a dimensionless melt intensity index specifying the total amount of melt, C is the concentration of a chemical species, a specifies the rate constant for a species as ions are lost from the snow and C_p is the species initial concentration in the fresh snow. The rate constant a is related to the elution rate of a species, but it is dimensionless and will be later scaled by observed melt degree in the 20th Century, and so is not numerically equal to the elution rates in Table 2. Here we have implicitly assumed that the reservoir volume for the ions is constant, i.e. the increase in concentration due to a reduced volume caused by run-off is negligible, which is different from the situation in a seasonal snow pack. The concentration ratio of two ionic species in a sample has been proposed as a melt indicator by *Iizuka et al.* [25] using another Svalbard ice core from Austfonna.

If we define A and B to be the concentrations of two such chemical species, then $A_p = k_{AB} B_p$, where A_p and B_p are the concentrations of X and Y prior to melt, and k_{AB} is their ratio in fresh snow. It is clear that the logarithmic ratio of the concentrations after melting is linear in M.

$$\log\left(\frac{A}{B}\right) = \log\left(\frac{A_p \cdot e^{-a_A M}}{B_p \cdot e^{-a_B M}}\right) = \log(k_{AB}) + (a_B - a_A) M \; .$$

Hence we can derive a melt index provided that the two rate constants a_A and a_B differ significantly. Note that this holds even for a finite reservoir that is depleted during the melt season, as happens with significant run-off. A good melt indicator should have several properties: species need to have different elution rates and they should come mainly from the same source. Additionally the ratio used as the melt indicator should be relatively constant in dry snow and should be spatially and inter-annually stable. *Iizuka et al.* [25] show that there are high correlations (>.95) between the

concentrations of Na^+, Cl^-, K^+ and Mg^{2+} in Svalbard dry snow from Austfonna. However, all these correlations break down in wet snow, except that between Na^+ and Cl^-. Hence, the washout rates for Na^+, K^+ and Mg^{2+} must differ widely, whereas they are the similar for Na^+ and Cl^-. Because of these differences in washout rates, we can construct two independent chemical melt indices M_{NaMg} and M_{ClK} based on $\log(Na^+/Mg^{2+})$ and $\log(Cl^-/K^+)$, Fig. 4.

We consider M_{NaMg} to be superior to M_{ClK} since relative measurement errors in K^+ are much larger than in Mg^{2+} [14] and further K^+ has a tendency to have large peaks that are seemingly unrelated to other ions in high resolution pit data [25]. Using sea water ratios in μgL^{-1} we get k_{NaMg}=8.3 and k_{ClK}=49. To avoid difficulties with percolation between layers [19], [18], we use 15-year mean concentrations. To compare M_{NaMg} and M_{ClK} we scale the dimensionless indices by their mean values over the 20th century.

4.2 Washout factors

Virkunen et al. [12] considered recent pit samples taken since the Lomonosovfonna ice core was drilled. These pit samples show behaviour qualitatively different from most of the ice core – with several parts of the pit, representing the 2001 and 2002 years having very low concentrations. Our hypothesis is that the warm summers led to post-depositional removal of ions and not simple percolation as was discussed in the previous section. This phenomenon is rare but perhaps also occasionally recorded in the ice core – which would indicate periods when summer temperatures were as anomalously high as in 2001 and 2002. We therefore investigate how unique is the pit sample chemistry compared with the ice core record by computing a washout factor. Since in this case we are looking for periods not only of melting, but when ions were lost by run-off we use both melt indices proposed by *Grinsted et al.* [22]: $\log([Na^+]/[Mg^{2+}])$ and $\log([Cl^-]/[K^+])$ – see section 4.1. We observe in the snow pits that the concentrations of divalent ions and nitrate, are preferentially eluted in the core and snow pit (Table 2). We therefore compute a washout index that includes both the washout factors and the ion loss factors (logged to take account of the Log Normal distribution of the ion data), [21] such that at each depth (d), the washout factor Λ_d is:

$$\Lambda_d = -\overline{Z}_d M_{,NaMg,d} M_{,ClK,d}$$

where M are the two standardized melt indices (section 4.1), and Z is Log-normalized concentration of the species: Ca^{2+}, Mg^{2+}, NO_3^- and SO_4^{2-}. We find that multiplication of the melt indices produces a more spiked distribution for Λ_d than simply summing the melt indices. Since we are attempting to find rare and extreme events, spiky non-Normal distributions are preferred.

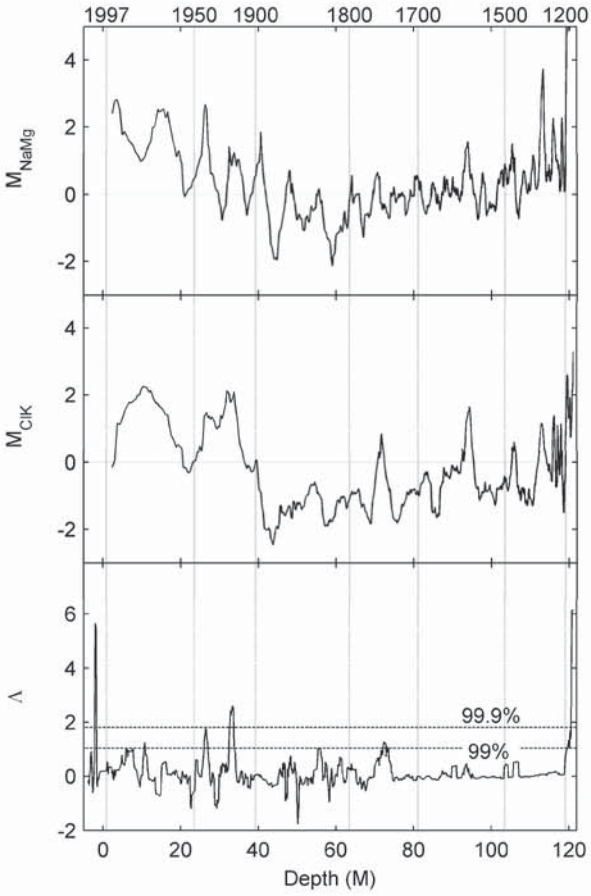

Fig. 4. Melt indices M and washout factor Λ for the Lomonosovfonna ice core. Melt indices are computed using 15 year running means of concentrations to emphasize general climatic trends and remove short period spikes, while washout factor is computed using 11-point means (given higher resolution closer to the surface), and is designed to find short periods of intense melting.

One of the advantages of computing a washout index similar to ours is that significance testing can be easily done as described in section 3.2. The significance of Λ was computed using Monte Carlo methods based on 200 000 noise samples having the same autocorrelation and same cross-correlation as the real data. Figure 4 shows a plot of Λ as a function of depth in a snow pit from 2002 and the ice core, with an 11 point boxcar smoothing window. It is clear that the snow pit samples have exceptional washout factors that only compare with data from the bottom few metres of core. There are a few intervals where Λ is significant at the 99% and single place where it passes the 99.9% significance level (33 m). Ice core dating [8], shows that 33 m corresponds to the year 1920 when abrupt warming occurred in the Svalbard temperature record [28].

4.3 Sulfate ion modeling

We now turn to a detailed analysis of the sulfate ion record. Sulfate is of great interest as it has several important sources: anthropogenic pollution, marine

biogenic, terrestrial dust, sea salt and volcanic fallout. To investigate the different contributions to the sulfate budget along the core *Moore et al.* [21] introduced a novel approach based on multiple linear regression analysis, (MLR) between sulfate and the other ions in the core. MLR models are well understood and have well-defined best-fit criteria – the F-statistic that ensures that the optimum number of parameters is used to avoid over-fitting the data (e.g [29]). The models fit an equation of the form:

$$Y = X\Gamma + K$$

in the least squares sense. The variable X is a matrix of ions and Γ is a vector of coefficients, Y is the sulfate data and K is a constant. To fulfil the requirement of the fit being the best in the least squares sense, and to test the statistical significance of the regression, it is required that the errors in X and Y data are Normally distributed. If ion concentration data were used, the high concentration spikes (with large absolute measurement errors) would disproportionately weight the regression models. Because of the log transformation the regression coefficients are not simple multipliers of concentrations, but exponents, so that in concentration space the regression models look like:

$$\left[SO_4^{2-}\right] = K\left[Mg^{2+}\right]^{\Gamma_1}\left[NO_3^-\right]^{\Gamma_2}\cdots$$

where the [] denote concentrations. This means that the Γ coefficients cannot be compared directly with e.g. sea salt ratios. However, we should point out that while this formulation is non-standard in glacio-chemistry, it is physically quite realistic as the Log-normal distribution is ubiquitous in nature, e.g. rainfall (and accumulation rates in this ice core, [*27*]) are Log-normally distributed, as are air pollution indices in many US cities [30].

We make no assumptions about what ions should be in X, we begin with all ions and remove them one by one until the F-statistics suggests an optimum fit. We also allow both Γ and K to change over time (e.g. in response to climate changes), however as the data are lag 1 auto-correlated, they must be kept in time or depth order. This is done by running the MLR model in a moving window of data 100 points long, with an F-statistic calculated for each model. An intrinsic assumption in using a 100 point widow for modeling is that changes in Γ due to changing climate are smooth, with no dramatic step changes. The MLR models therefore determine how the relations preserved in the core between the different ions change over time. Prior to the MLR analysis we smooth the ion data with 3-point running means to reduce short wavelength, species-dependent elution rate variations. This is a progressively longer smoothing time interval with depth due to compression of ice layers. A simple running mean reduces the number of degrees of freedom of the data by a factor $1.5/w$ where w is the number of points used in the running mean. So for 3 point running means we reduce our effective number of data points by factor of 2. This is taken into account when calculating the F-statistic and significance levels of the Γ coefficients. The single most obvious sulfate signal in the core is the Laki volcanic peak in 1783 (Fig. 1). Indeed it is such a dominant signal in the pre-20th century record that we remove the entire ion data between 66 and 67 m depth from the modeling, although the clearly volcanic sulfate deposit only affects about 15 cm within that metre [17]. By removing a full metre of data we try to ensure that the typically 2-3 year impact of a volcano on the atmosphere are removed, however, possible longer term changes associated with the eruption (such as suggested by *Kekonen et al*., [17]) will still be present if they persisted for a decade or so.

The residuals from the MLR models are not quite Normally distributed in the log transformed data as there are correlations between data points (e.g. [29]). However, we can use a normalization procedure to convert the residuals for each 100 point model back to concentration data by standardizing by the standard error of the model coefficient matrix, and then anti-logging the residual. One-tailed confidence intervals are also estimated from the anti-log of the standard deviation of the original residual distribution. We can improve the signal/noise ratio in any MLR model by computing "joint models", found by adding the residuals from MLR models with no common X variables in log space (equivalent to multiplication in concentration data space), and by weighting the models by their F-statistic. In addition to the F-statistic weighting, this procedure also has the advantage of avoiding over-fitting which would occur if a single MLR model with all plausible X were used to find residuals. It is obviously tempting to assign these residuals to volcanic events. Unlike all other attempts to assign spikes in sulfate or electrical stratigraphy of ice cores to volcanic signals, the object of the MLR modeling was to attempt to describe the usual variability of the sulfate data, not to extract volcanic spikes. The significance test of the residuals is also a correctly specified Student's t-test and not based on the standard deviation of the raw sulfate data, which are statistically meaningless as the raw concentration data are not Normally distributed – and which could also vary for many reasons other than volcanic acid input.

Results from MLR modeling of the whole core record (Fig. 5) suggests that sulfate may be predicted by an acid and a neutral salt species predictor set that can account for about 80% of the sulfate variance. The empirically found ions that best do this are nitrate and magnesium. This is most likely because of co-location of acidic nitrate and sulfate components in the ice, and similar affiliation between magnesium and neutral salt forms of sulfate (both from marine and terrestrial sources). While there may be a co-deposition of magnesium or nitrate with sulfate, we suppose that it more likely to be post-depositional co-elution during percolation processes that leads to the observed relationship between the ions [18].

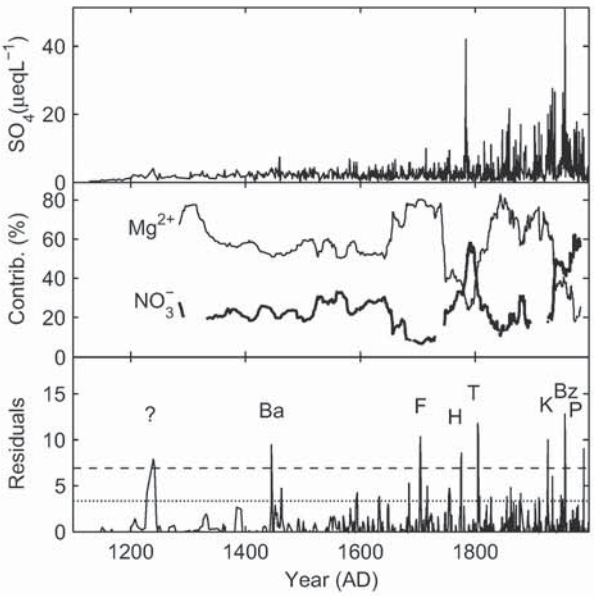

Fig. 5. Sufate concentration (including the large Laki signal in 1783). Laki was removed and then the sufate curve was fitted by MLR models, with the best one having magnesium and nitrate as parameters. Their contributions show that it is mainly the neutral salt component that dominates except for the 20th Century and for a 30 year period around the Laki eruption – this is also seen if the Laki signal is kept in the analysis. The bottom panel shows the residuals to a joint model using magnesium and nitrate weighted twice as highly as NaCl, MSA and calcium parameters. The dotted and dashed lines are 95 and 99% significance levels based on 1-sided t-testing of the residuals. The large, highly significant spikes are close to dates of significant volcanic eruptions (? Is the 1259 event, Ba is 1477 Bardarbunga, F is 1707 Fuji, H is 1766 Hekla, T is 1815 Tambora, K is 1933 Kharimkotan, Bz is 1956 Bezymianny, P is 1991 Pinatubo).

In contrast to the results found empirically, using an Expected model based on *a priori* assumptions of sulfate sources, defining an *X* variable field of Ca^{2+}, MSA and NaCl shows similar results, but fits much less well than the Mg^{2+} and NO_3^-empirical model. In the Expected model MSA plays the role of acid predictor. Much of the core, especially the bottom is well predicted by magnesium or salt, suggesting that neutral sulfate species dominated in general. However, the 30 year period around Laki in 1783 was quite different than the rest of the record, with acidic components dominating. The post LIA is also dominated by acidic sulfate, and in the Expected model, MSA becomes a much more important predictor of sulfate than earlier. The Ca^{2+} predictor for sulfate is not significant at the 5% level in any of the MLR models, however detailed analysis of the time-frequency structure of the sulfate and calcium records shows that there are close relationships between the two for parts of the record in the LIA, with strong suggestions of a 25-35 year quasi-periodic signature [21], [8].

5. Diffusion

Virkunen et al. [12] compared their pit samples taken in the early 2000s with the core drilled in 1997. The most strikingly similar part of the 800 year record is the 119 m – core bottom section. This section is dated by flow modelling [8], but also supported by the observation of a highly significant anomalous sulfate signal at 117.6 m depth (Fig. 5) that *Moore et al.* [21] show is likely to be the AD1259 volcanic eruption often seen in ice core records. The flow model date for this signal is AD1244, suggesting that the dating is good to a few percent to the 13th century. All ions except NH_4^+, Na^+ and Cl^- drop to values close to zero as the core bottom is approached, even lower than seen in the autumn 2001-1999 layer , (Fig. 1). We have considered the possible impact of diffusion on the ion record and find it an implausible explanation for the decreasing ion profile measured. Diffusion would remove all short period signals in the ion records before the formation of the long wavelength drop in ion levels observed. However the record in Figs. 1 and 5 shows significant short period structure in many ions in the bottom 5 m of the record, ruling out diffusion as a mechanism.

Alternative mechanisms for ion removal can be envisaged. However *Kekonen et al.* [8] mention that Darcy flow cannot occur in the basal ice layer given the grain size, impurity concentrations and temperature gradients [10] presently observed. Though the grain sizes near the base of the core are rather large, which would certainly aid a Darcy type drainage mechanism, driving via the observed temperature gradients is extremely small. *Rempel et al.* [31] proposed a novel mode of migration of ions based on the hypothesis that the impurities were to a large degree in concentrated liquid form at triple grain junctions in the ice. Draining of ions to the bed is possible by this kind of diffusion, though the speed depends sensitively on the nature of the bed – especially its permeability. We do not have sufficient information to calculate a *Rempel et al.* [31] diffusion rate, nor do we have any information on the composition of the bed underneath the ice cap. This is needed to determine if *Rempel*-diffusion could remove impurities from the ice in times as short as a millennium. Of course it is possible to produce values for the temperature profile and solute loading and grain size variation over time that could lead to significant loss of ions, but that would be wild speculation. All we can say is that given observed conditions, loss of ions through the grain boundary network does not occur.

The basal ice does not have any basal debris material entrained within it, nor are there bands of clear and bubbly ice, nor ice containing enriched ion content, hence it is not a basal ice facies of the types sometimes seen in temperate glaciers (e.g.[32]). The lowest metres of ice appear very similar to the ice at other depths, except that the crystals are bigger and the layers of clear and bubbly ice are thinner – which is to be expected. These observations suggest that ice has not become tainted by elution of ions from melting in contact with

the bed of the glacier. So we are left with the same mechanism as seems to have occurred in the autumn 2001 – autumn 1999 layer: loss of ions either by percolation or run-off. As the core reached to within 2 m of the bed and there is no sign of higher concentrations closer to the bed, we suppose that run-off must have occurred.

Present estimates of ion diffusion rates differ by several orders of magnitude depending on how the estimate is made. Typically data come from laboratory work performed on microscale at extremely cold temperatures. Other estimates have been made from the evolution of peak-shape in chemical profiles from ice cores [33]. However *Barnes et al.* [33] approach had several difficulties which make their estimates prone to uncertainty. The main one being that they select the peak slope as being the best factor to measure, but hold the spectrum of the peak constant over time. It is clear that in classic diffusion that the largest sensitivity on diffusion rate is to period of the wave being diffused, hence it cannot be realistic to hold the spectrum of the peaks constant over time. We suggest that a better estimate of diffusion from ice core analysis may be made by considering the background level of ion concentration – though here changes in climate may well introduce changes in mean background.

It may also be noted that if back-diffusion is used to reconstruct peak-heights, or the similar exponential percolation model is de-convoluted to recover an original amplitude concentration signal, then errors in measurement, and errors in diffusion rates become amplified mitigating any advantage of back-diffusion in these cases. A better way of isolating significant signals comes from the regression model analysis discussed earlier whereby the residuals from fitting e.g. sulfate time series are examined for large peaks. A good example is the 1259 event, which appears very insignificant in the sulfate profile, but which is a very large excess sulfate signal compared with what could be predicted by other ionic species (Fig. 5).

6. Conclusions

We highlight the great significance of data analysis before performing advanced statistical analysis, in particular the correction of the data to ensure that errors are Normally distributed, and that the data themselves are appropriately distributed for the kind of statistical modelling being attempted.

We have developed useful models of melting processes in ice that allow present day measurements on snow pits and cores to be compared with data from the Medieval Warm Period, and show that for a proxy of summer melting, that the post-2000 era is significantly warmer than the previous 600 years.

The melting phenomena actually appears to beneficial for ice core analysis in the sense that it leads to an increase in signal to noise ratio in the core. This can be explained by ion movement and formation of associations between them that we show are consistent over time. The external environment can change those associations, as is shown by the change in the importance of acidic and salt predictors to the sulfate budget. Surprisingly this analysis shows that the period around the exceptionally large Laki 1783 volcanic eruption is similar to the impact of the change from Little Ice Age to 20th Century. This kind of result has not been seen in traditional ice core analysis from Greenland, but is consistent with the impacts of volcanic eruptions on large scale atmospheric circulation patterns, and with the enormous damage now slowly being recognized that the Laki eruption did to the European environment.

The sulfate ion modelling also provides a method of locating spikes in concentration that can be identified as volcanic signatures in a way that is philosophically superior than other methods of estimating signal significance. This superiority comes from the idea of not trying to search for peaks, but rather attempt to eliminate the entire signal by fitting the sulfate profile with no *a priori* notions of sulfate sources of inappropriate budgeting in normal (that is un-logged) sulfate concentration space. The residuals from the best fit models can then be significance tested using standard methods, this allows volcanic signals to be found even though on average the volcanic sulfate fraction amounts to only 5-10% of total sulfate, and almost none of the sulfate peaks assigned to volcanic signals are visible in the raw sulfate profile.

This paper is mainly a review of the statistical methods that have allowed us to demonstrate that ice cores from seasonal melting environments can provide rich archives of climate history. Although we have only sufficient data for a comprehensive analysis from a single ice core: Lomonosovfonna, we hope that the methods outlined here are generally applicable to other cores from seasonal melting ice caps. A suitable candidate from the other Arctic ice caps may be Vestfonna where a new core will be drilled by Arctic Centre in 2008 and subjected to all the analyses outlined here. It is clear that in order to maximize the interpretation of the record that a full set of chemical and physical stratigraphic analyses are done. This is essential so that the chemical relationships can be shown to preserve a degree of independence of physical processes such as the seasonal melt and bubbly-clear ice facies formation. While gross redistribution of ions leading to differences in mean concentrations is not sufficient to loose a climate or environmental signal, it is clear that too much loss of ions by run off would degrade the climate signal. Hence computation of washout index and examination of the core to check if there are many periods when the ice core has lost ions would be an essential step in the interpretation of any new cores.

The Canadian ice caps have been subject to ice coring for many years. Some of the data sets show quite large differences from the Lomonosovfonna core. The large body of work by Fritz Koerner shows that melt layers carries useful indications of summer temperatures on

the Canadian ice caps. This seems to be not the case on Lomonosovfonna, presumably because of differences in post-depositional process converting firn to ice. Another source of confusion in interpretability of seasonal melting cores comes from comparison of pairs of cores from the same ice cap. *Goto-Azuma et al.* [34] performed an analysis of variability between two core 2.5 m apart on Penny Ice Cap, Canada and concluded that low correlations at high resolution meant that about 50% of the ionic variability is simply noise. However, all cores, even those from dry snow zones, contain accurate (to within measurement errors) records only of what has happened at that site. Although no location can capture the full variability of climate on regional scales, the whole record at any site contains additional regional-scale information when site-specific effects are deconvoluted. This implies that for many Arctic ice cores, despite percolation and "worryingly" high melt ratios, much of ion chemical stratigraphy is retained and we argue these records are almost as reliable as those from dry snow sites. Of course the true test of the relationships we outline must be that they work on other ice cores, and so we encourage other glaciologists to apply the same techniques in future.

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