The Cryosphere Discuss., 9, 5053–5095, 2015 www.the-cryosphere-discuss.net/9/5053/2015/ doi:10.5194/tcd-9-5053-2015 © Author(s) 2015. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal The Cryosphere (TC). Please refer to the corresponding final paper in TC if available.

A *synthetic* ice core approach to estimate ion relocation in an ice field site experiencing periodical melt; a case study on Lomonosovfonna, Svalbard

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Received: 12 August 2015 – Accepted: 7 September 2015 – Published: 29 September 2015 Correspondence to: C. P. Vega (carmen.vega@geo.uu.se)

Published by Copernicus Publications on behalf of the European Geosciences Union.



Abstract

Physical and chemical properties of four different ice cores (LF-97, LF-08, LF-09 and LF-11) drilled at Lomonosovfonna, Svalbard, were compared to investigate the effects of meltwater percolation on the chemical and physical stratigraphy of these records. ⁵ A synthetic ice core approach was employed as reference record to estimate the ionic relocation and meltwater percolation length at this site during the period 2007-2010. Using this method, the ion elution sequence obtained for Lomonosovfonna was $SO_4^{2-} > NO_3^- > NH_4^+ > Mg^{2+} > CI^-$, $K^+ > Na^+ > Ca^{2+}$, with acidic ions being the most mobile within the snowpack. The relocation length of most of the ions was in the order of 1 m, with the exception of SO_4^{2-} showing relocation lengths > 2 m during this period. 10 In addition, by using both a positive degree day (PDD) and a snow-energy model approaches to estimate the percentage of melt at Lomonosovfonna, we have calculated a melt percentage (MP) of the total annual accumulation within the range between 48 and 70%, for the period between 2007 and 2010 which is above the MP range suggested by the ion relocation evidenced in the LF-syn core (i.e. MP = 30 %). Using a 15 firn-densification model to constrain the melt range, a MP of 30% was found over the same period which is consistent with the results of the synthetic ice core approach, and

a 45% of melt for the last 60 years. Considering the ionic relocation lengths and annual melt percentages, we estimate that the atmospheric ionic signal remains preserved in recently drilled Lomonosovfonna ice cores at an annual or bi-annual resolution.

1 Introduction

Pollutants produced in low- and mid-latitudes are transported to the polar regions where they are included in the snow by different mechanisms, mainly wet and dry deposition, accumulating in glaciers and ice caps. Major ions, such as SO_4^{2-} , NO_3^{-} , NO_4^{-+} , and O_4^{--} are deposited in the answer of and be measured in its and so NO_4^{-+} .

²⁵ Na⁺, and Cl⁻, are deposited in the snowpack and can be measured in ice cores, providing valuable information about their sources, chemical transformations in the atmo-



sphere, and transport patterns to the sampling site (Laj et al., 1992; Goto-Azuma and Koerner, 2001; Kekonen et al., 2002; Hastings et al., 2004, 2009). Nitrate (NO_3^-), for example, has been used as a record for past atmospheric nitrogen oxides ($NO_x = NO_2 + NO$) (Kekonen et al., 2002; Röthlisberger et al., 2002; Hastings et al., 2005, 2009; Vega et al., 2015b). However, this proxy has been difficult to develop since NO_3^- in snow has several sources and experiences post-depositional processes, such as photolysis, diffusion within the ice, evaporation as HNO_3 , or relocation by meltwater (Goto-Azuma et al., 1994; Honrath et al., 1999; Rempel et al., 2002; Röthlisberger et al., 2002). The latter has been an enigma to potential ice core sites since relocation and professes is a protection of abamical apaciac gives an altitudinal and latitudinal threach

- and preferential elution of chemical species gives an altitudinal and latitudinal threshold for potential drilling sites. To make use of environmental data from outside the dry snow zones on glaciers in the polar areas, it is important to give better regional coverage of the atmospheric chemistry outside the large polar ice sheets. For a correct interpretation of the chemical ice core data from drilling sites where significant summer melting occurs, it is necessary to estimate the post-depositional effects of meltwater
- percolation on the chemical content of snow and ice.

It is known that most of the ice core drilling sites at Svalbard experience summer melting, which may damp the chemical signal of ionic species, making difficult to understand the transfer function between ion concentrations in the atmosphere and the snow

- (Goto-Azuma et al., 1994; Isaksson et al., 2001; Moore et al., 2005; Grinsted et al., 2006). Ions do not move uniformly when are removed from the snowpack by meltwater. Instead, they are released following a preferential elution (Goto-Azuma et al., 1994; Eichler et al., 2001; Ginot et al., 2010). The elution of ions is a consequence of sequential grain-scale processes during dry metamorphism (Brimblecombe et al., 1985;
- ²⁵ Schöndorf and Herrmann, 1987; Goto-Azuma et al., 1994) and also influenced by the pH of meltwater (Goto-Azuma et al., 1994). Moore and Grinsted (2009) calculated the elution factors (*e*) of several ions present in snow and ice from an ice core drilled at Lomonosovfonna, Svalbard during 1997 (LF-97). According to their results, the most mobile species in the snow were Ca²⁺, Mg²⁺, SO₄²⁻ and NO₃⁻ with Na⁺, Cl⁻, NH₄⁺ and



 K^+ being eluted later. The elution sequence changed slightly in ice, where NO₃⁻ is the most mobile specie and Mg²⁺ the latest ion to elute. Moore and Grinsted (2009), Ginot et al. (2010) and Eichler et al. (2001) results point to the ionic charge as the control factor in the elution process instead of the acidic character of the ion as reported by Brimblecombe et al. (1985) and Goto-Azuma et al. (1994).

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The special characteristics of snow and firn properties on high altitude ice fields with heterogeneous stratigraphy as Lomonosovfonna are a consequence of the long winter season with air temperatures below the freezing point, enhanced snow drift by strong winds, relatively low annual snow accumulation and cold ground surfaces, punctuated

- ¹⁰ by intermittent melt events. The interaction between the meltwater front formed during episodic melt events and the different stratigraphic horizons form preferential flow patterns and create a secondary stratigraphy if refreezing takes place within colder layers (Colbeck, 1991). The secondary stratigraphy produced by refreezing water will have a large influence in meltwater flow and discharge (Bøggild, 2000). During the intermit-
- tent melt periods, dislocation of water from more superficial layers percolates into the deeper stratigraphy routed as preferential meltwater flow and the formation of solute enriched ice layers during refreeze of the percolated water will affect the chemistry (i.e. ionic concentrations in this study) recorded in ice cores drilled at the high altitude ice fields of Svalbard.
- ²⁰ One estimate to measure if snow melting and percolation have occurred in an ice core stratigraphy is to construct an ion ratio, based on the selection of a pair of ions that originate from the same source but have dissimilar elution coefficients, e.g. Na⁺/Mg²⁺ and Cl⁻/K⁺ as reported by lizuka et al. (2002) and Grinsted et al. (2006). Using the logarithms of the different ionic ratios as melt indices, denoted as W_{NaMg} or W_{CIK} depending upon the pair of ions constructed or process.
- ²⁵ pending upon the pair of ions selected, a reconstruction of the melting history of a particular ice core site can be reconstructed (Grinsted et al., 2006). Pohjola et al. (2002) found that at Lomonosovfonna, about 25 to 55 % of the annual accumulation over the 20th century suffered melt, with meltwater percolating through the snowpack during warm summers. The most mobile ions reported by Pohjola et al. (2002) were NO₃⁻ and



SO₄²⁻, which presented ~ 50 % higher concentrations in ice compared with firn layers. On the other hand, NH₄⁺ presented an even distribution between firn and ice. A percolation mechanism was proposed to have an important role in the redistribution of this specie in the ice crystals after deposition. Pohjola et al. (2002) concluded that although
 some ions may have had a high mobility within the upper part of the LF-97 ice core (0–36 m deep) during anomalously warm summers, the signal was still identifiable, being retained within an annual or biannual resolution.

The aim of this work is to study the temporal change of the snow/firn chemical and physical stratigraphy on the ice field Lomonosovfonna, Svalbard. In this study we will use data from shallow ice cores and snow pits repeatedly studied in 2008, 2009, 2010 and 2011 at Lomonosovfonna to investigate the temporal and vertical change in the stratigraphy and ion composition of the snow/firn column. To manage the sequential

change in ion concentrations we will create a *synthetic* ice core using the top layer (~ 1 year accumulation) of different shallow ice cores and snowpits to have a reference

¹⁵ record to assess the relocation of major ions by meltwater and the percolation length at the site during recent years. In addition, the melt percentage of the annual accumulation at Lomonosovfonna is obtained by using a positive degree day and a snow-energy model approach, and used together with the *synthetic* core to infer the effects of meltwater on the ionic signals present in recent ice cores drilled at Lomonosovfonna.

20 2 Methods

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2.1 Study sites

Four ice cores (LF-97, LF-08, LF-09 and LF-11) and a 1.50 m deep snowpit (SP LF-10) were considered in this study, all retrieved at the Lomonosovfonna ice cap, which is one of the highest glaciated areas in Svalbard with an elevation of \sim 1250 m a.s.l. (Isaksson et al., 2001; Beaudon, 2012; Vega et al., 2015b) (Fig. 1). Lomonosovfonna is located northeast of Longyearbyen, which is the largest settlement in Svalbard, and



Pyramiden, a smaller settlement where coal mining activities were carried out until 1998. Two of the ice cores (LF-97 and LF-08) were drilled at the highest point of the ice cap ca. 100 m apart from each other, while the LF-09 and LF-11 ice cores were drilled ca. 4.5 km east-south-east from the site cored in 1997 and 2008 (Fig. 1, Table 1).

5 2.2 Sampling and analyses

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The cutting, sampling and chemical analyzes of the LF-97 and LF-08 ice cores are reported by Kekonen et al. (2005) and references therein and Beaudon (2012), respectively. The LF-09 and LF-11 ice core cutting and SP LF-10 sampling were done in clean conditions, wearing clean overalls, face masks and powder free gloves. All materials employed to collect the samples were rinsed with ultra-pure water (18 M Ω) and kept in clean plastic bags. Samples and standards were melted and handled under laminar flow hood (class 100) to minimize any contamination from the laboratory environment. Samples and standards were placed in the auto-sampler covered with aluminium foil to avoid any dust contamination. Three sample blanks (made of ultra-

- pure water) were analysed at the beginning and the end of every batch. Sample checks 15 (bulk-snow from Ny-Ålesund or Uppsala) were analysed every ten samples to ensure the replicability of the measurements within a batch. The analytical error was below 5% for each ion. Detection limits (D.L.) for each ion were calculated as the average value of six blanks plus 1.68 times the standard deviation (σ) of the six measurements (i.e. D.L. = average_{blank} + 1.68 × σ_{blank}), being below 0.3 µeq L⁻¹ for all ions.
- Water stable isotopes ($\delta^{18}O-H_2O$) were analysed at the Institute of Geology at Tallinn Technical University, Estonia. The measurements were done with a Picarro L2120-i water isotope analyser (cavity ringdown spectroscopy technology) with a high precision vaporizer A0211. All isotope measurements were calibrated in a two-point scale against the international standards VSMOW (Vienna Standard Mean Ocean Wa-25 ter) and VSLAP (Vienna Standard Light Antarctic Precipitation). The reproducibility of replicate analysis for δ^{18} O–H₂O measurements was estimated to be ±0.1 ‰.



The ice layer and grain size were inspected in each core section by visual examination on a lighted bench located in the cold laboratory $(-20 \degree C)$ at the Norwegian Polar Institute. Bulk density was calculated by scaling and measuring each ice core piece. The stratigraphic melt index was calculated as the percentage of clear ice present in the ice core (considering the ice core length in m w.e. (m water equivalent)).

2.3 Synthetic ice core construction

In order to estimate the effects of meltwater percolation on the chemical record at Lomonosovfonna, a *synthetic* ice core approach was implemented. This consists in building an unperturbed ice core using only the top meter snowpack record from differ-¹⁰ ent ice cores (top meters of the LF-08 and LF-09 cores corresponding to approx. 3/4 of the year previous to the drilling date) and the SP LF-10 snowpit, thus, constructing a snow-firn record covering over early spring, previous winter and fall of each year of the period 2007–2010 (Table 2).

2.4 Calculation of the meltwater

¹⁵ In order to quantify the meltwater produced at Lomonosovfonna, two independent approaches were used: a simple positive degree day (PDD) model using instrumental temperature data from stations near Lomonosovfonna; and a coupled snow-energy balance model (van Pelt et al., 2012) that delivers snowmelt as output.

2.4.1 PDD model

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²⁰ We considered temperature instrumental data from three different sites in Svalbard: Longyearbyen Airport, Sveagruva and Ny-Ålesund (data from the Norwegian Meteorological Institute, http://met.no). To estimate the number of positive degree days (PDD) at Lomonosovfonna, a lapse rate of -0.0044 °C m⁻¹ was used (Pohjola et al., 2002). An annual average number of 37 PDD at Lomonosovfonna was calculated when using the ²⁵ combined temperature records of Longyearbyen Airport, Sveagruva and Ny-Ålesund



(i.e. average value of daily temperatures from the three stations), during the period between 1989–2010. The meltwater production was calculated as described by Pohjola et al. (2002), using the melt capacity of snow as function of the PDD at Lomonosovfonna, considering the degree day factor (DDF) as 3.0 mm water °C⁻¹ day⁻¹ found at Svalbard after calibration against stake measurements (Nuth et al., 2012). In a recent study by Claremar (2013), that employs Polar Weather Research and Forecast (Polar WRF, Skamarock et al., 2008; Wilson et al., 2011) modelled temperatures, a value for DDF of 25 mm °C⁻¹ day⁻¹ of water was found at Lomonosovfonna. However, this DDF value has proven to be too high due to the poor modelling of the net mass balance at Lomonosovfonna when using polar WRF temperatures and snow accumulation rates for the last decades (Claremar, 2013). Consequently, to calculate the meltwater we employed the DDF value proposed by Nuth et al. (2012) which is more realistic for Lomonosovfonna.

2.4.2 Coupled snow-energy balance model

The coupled model was developed to simulate the surface energy balance and subsurface conditions, in order to predict melt, refreezing and runoff at Nordenskiöldbreen, Svalbard and it is described by van Pelt et al. (2012, 2014). The meltwater refreezing output of the grid point located at 1200 ma.s.l. was used in this study to account for melting at the Lomonosovfonna ice core site. At this elevation runoff does not occur;
which implies that all the available water at the surface (from melt and rain) refreezes within the snow/firn pack.

3 Results and discussion

3.1 Dating of the ice cores

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The LF-97 ice core has been dated by different methods (e.g. radioactive horizons, δ^{18} O-H₂O cycles counting, volcanic horizons) having a time scale that covers the



past 800 years (Isaksson et al., 2001; Pohjola et al., 2002). An updated time scale for this ice core has been recently published by Divine et al. (2011).

During the 2009 drilling campaign at Lomonosovfonna, two parallel ice cores were drilled: the LF-09 (36 m deep, this study) and a longer core LF-09_{deep} (149.5 m deep)

- ⁵ (Wendl et al., 2015). Tritium (³H) measurements done in the LF-09_{deep} ice core estimate the 1963 ³H horizon (Pinglot et al., 1999) at 23.6 m w.e., with a resulting accumulation rate of 0.51 m yr⁻¹ w.e. between the ³H radioactive horizon and the top of the ice core (Wendl et al., 2015). In addition, the high resolution chemical data available for the LF-09 ice core (samples taken each 8 cm) allowed the use of a multilinear regression
- ¹⁰ method (MLR) developed by Moore et al. (2012) to account for volcanic layers in the non-sea salt sulfate concentrations. A detailed description on the usage of the MLR method on the dating of the LF-09 ice core can be found in Vega et al. (2015b). In addition to the MLR method, an automated $\delta^{18}O-H_2O$ cycles counting routine was used in the dating. This method counted $\delta^{18}O-H_2O$ annual cycles that had an amplitude ¹⁵ A > 0.1 % ($\delta^{18}O$ uncertainty in the SMOW scale) and a frequency in the sub-annual
- ¹⁵ A > 0.1% (*b* C) uncertainty in the SMOW scale) and a frequency in the sub-annual cycle (λ_{seas}) larger than 1/3 the accumulation rate (Pohjola et al., 2002). Using both methods, the time scale for the LF-09 core was estimated to span between 1957–2009 (Vega et al., 2015b).

The LF-08 and LF-11 ice cores were dated using the automated $\delta^{18}O-H_2O$ annual cycles counting routine and by comparing the Cl⁻ record with the respective LF-09 ice core profile. The time scales for the cores were estimated to cover the 1989–2008 and 2004–2011 periods for the LF-08 and LF-11 (Vega et al., 2015a) ice cores, respectively. The time scale of the SP LF-10 snowpit was obtained by assuming a constant snow accumulation rate over the depth-scale, resulting in a time coverage between 2009.4– 2010.4.



3.2 Major ions

All the ionic concentrations were binned to annual averages to obtain equally spaced time series of one year resolution, which can be compared in between the different ice cores. Having all the chemical species as annual averages, their concentrations (c_i) were normalized to the mean value for each specie in each ice core record, during the total overlapping period (1957–2009) to compare the variations of the ions in the

different ice cores (Eq. 1).

$$c_{\rm N} = \frac{c_i - c_{\rm mean}}{\sigma},$$

where $c_{\rm N}$ is the normalized concentration of a given ion, $c_{\rm mean}$ is the ion mean in the specific ice core or strata, and σ is the standard deviation of the series.

When comparing the annual average concentrations between the different ice cores, some of the peaks show a lag between the different records which likely is associated to the uncertainty on the dating of the three different ice cores. We applied a 5 year moving average smoothing to the annual chemical data (Fig. 2). The dating error of the LF-08 and LF-09, in respect to the LF-97 ice core, was estimated as ± 2 years. We found

and LF-09, in respect to the LF-97 ice core, was estimated as ±2 years. We found that similar temporal variations experienced by the different ions were registered in the different Lomonosovfonna ice cores during the overlapping period studied (Fig. 2).

Table 3 shows the Pearson *R* values between the different species in the LF-97 and LF-09 ice cores and the LF-09 and LF-09 ice cores, smoothed out with 5 year moving averages. The *R* values between the LF-97 and LF-08 ice cores were not calculated since the overlapping period using 5 year moving average was too short. The *R* values in Table 3 suggest that the LF-97 and LF-09 ice cores have comparable records for all ions. However, the correlation coefficients measured in the LF-08 and LF-09 ice cores are not significant at the 95% confidence interval (with the exception of Mg²⁺, R = -0.53).



(1)

3.3 Ionic distribution in the snowpack

In order to investigate to what degree ions are eluted from the snowpack when meltwater percolates, we first compared the log-transformed concentrations (log(*c*)) of the different species measured in the LF-09 and LF-11 ice cores at different snowpack facies: i.e. snow, ice, and firn. The chemical record of the LF-09 ice core was considered only during the period 2004–2009 when it overlaps with the LF-11 ice core.

Figure 3 shows that log(c) of ions in the LF-09 ice core is higher in the snow compared to ice and firn for all species. Moreover, concentrations show similar means in firn and ice. On the other hand, Fig. 4 shows that ion concentrations in the LF-11 ice core are higher in the snow compared to ice and firn for most of the ions, with the exception of NO_3^- and NH_4^+ . NO_3^- presents even concentrations in all the strata, while NH_4^+ shows a higher mean concentration in ice compared to firn and snow.

Previous work by Pohjola et al. (2002) focused on the effect of periodic melting in the chemical record of an ice core drilled at Lomonosovfonna (LF-97) shows that the

- ¹⁵ average ionic concentrations of the different ionic species were higher in the ice facies than in the firn layers. We observed this only for Br⁻ and NH⁺₄ measured in the LF-09 ice core and F⁻ and NH⁺₄ measured in the LF-11 ice core. Since all ions in the LF-09 and LF-11 ice cores within the period 2004–2011 (10 m deep) are mostly distributed between the snow and firn, we infer that ions in this section of the ice cores have not been beauly releasted by moltwater periodation. Since the amount of moltwater
- not been heavily relocated by meltwater percolation. Since the amount of meltwater production at the summit of Lomonosovfonna is unknown for the studied years, three different approaches were used in order to estimate and relate it to ionic snowpack redistribution (see Sect. 3.5.).

In order to elucidate the evolution of meltwater production over time, the chemical ²⁵ melt index (W_{NaM}), defined as log(Na⁺)/(Mg²⁺) (using ionic concentrations in µeqL⁻¹) (lizuka et al., 2002; Grinsted et al., 2006) was calculated in the different Lomonosovfonna ice cores (Fig. 5). This chemical approach is based on the selection of a pair of ions that have the same source but dissimilar elution coefficients within the snowpack,



e.g. Na⁺/Mg²⁺ and Cl⁻/K⁺ (Grinsted et al., 2006). Positive W_{NaMg} values indicate that melting is most probably confined to a particular time period. This is the case of the four Lomonosovfonna ice cores (Fig. 5) which show positive melt indices during the last 60 years. As observed in Fig. 5, melting at the drilling site is far from being constant; a period of particular high melt is evident during mid-1980s to mid-1990s which is concomitant with a period of relatively high number of PDDs at Lomonosovfonna. Although

the above mentioned method is useful to infer melting regimes at Lomonosovionna. Although large time scales (i.e. decadal to centennial), it is not suitable to infer melting at sub-, and multi-annual resolutions; therefore, the *synthetic* ice core approach described in this study presents a suitable option.

3.4 Synthetic ice core

Assuming that snowmelt does not occur during winter, and considering that precipitation records of different Svalbard sites show that most of the precipitation is registered during the winter and autumn seasons (Førland et al., 2011), it is expected that the synthetic ice core (LF-syn) captures the unperturbed chemistry of the autumn-winter and early spring seasons between spring 2007–2010. Figure 6 shows the annual precipitation cycle at Longyearbyen airport and Ny-Ålesund stations and the precipitation amount and snow accumulation from the two stations and the LF-syn core during the period 2007–2011. Both, the meteorological and the ice core records are coherent with each other, depicting higher accumulation rates during the autumn/winter period than

- 20 each other, depicting higher accumulation rates during the autumn/winter period than spring/summer. Consequently, it is expected that the LF-syn ice core is representative of the snow accumulation regime at Lomonosovfonna during 2007–2010. The flat accumulation observable during the winter 2010 is due to the assumption of a linear time scale when dating each snow layer of the snowpit dug out in 2010 (SP LF-10). In
- addition, the average annual mass loading of each ion was calculated for the period 1980–2009 by averaging the annual ion loads calculated in the LF-97 and LF-09 cores. This procedure averaged out the possible effects of percolation and relocation of ions



between the strata corresponding to different years. This estimate was then compared with the mass loading of the different ions corresponding to individual years in the LF-syn core (i.e. 2007–2010) which are assumed to represent cumulative autumn-winter-early spring snow accumulation unaltered by meltwater percolation or ion relocation. It

- ⁵ was found that the 5 year LF-syn record represents between 70–200 % of the 30 year average ion mass loading with NH_4^+ and Mg^{2+} located at the bottom and top percentage boundaries, respectively, and NO_3^- and SO_4^{2-} representing 94 and 111 % of the average, respectively. Having in mind that the mass loading for most of the ions show increasing values since 2005 (not shown), thus, influencing the percentage of aver-
- age mass loading in the LF-syn core, we consider that this synthetic core is adequate to investigate ion relocation during the period 2007–2011. The F-syn core was then compared with the LF-11 core to evaluate the effects of ion elution/deposition between 2007–2010 (recorded in the LF-11 ice core) compared to the unperturbed LF-syn ice core (Fig. 7). To avoid any bias caused for the snow accumulated after the spring 2010
- ¹⁵ and 2011, this period was not considered in the normalization of the LF-11 ionic concentrations. Figure 7 shows that the LF-11 record has noticeable large $c_{\rm N}$ peaks, e.g. around summer 2009, that can be associated to the increase in ionic concentrations by the relocation of ions by the refreezing of percolation water. Figure 8 shows the differences between $c_{\rm N}$ in both ice cores (LF-11 – LF-syn) calculated after interpolating
- ²⁰ the records at 0.01 year time steps to homogenize the data. We considered a relocation peak when the differences in c_N are higher than twice the standard deviation of the normalized concentrations of each ion (dashed red line in Fig. 8; the zero values are shown as a dashed black line). Positive differences indicate higher ionic concentrations in the LF-11 ice core with respect to the LF-syn ice core, therefore, ice-firn layers
- ²⁵ enhanced in ions due to relocation by percolation water. Negative differences indicate ionic elution happening at that layer. From Fig. 8 it can be observed that ions such as Cl^- , Na^+ and NO_3^- present clear deposition/elution c_N peaks. On the other hand, SO_4^{2-} only shows a deposition peak with an elution zone, rather than a single elution peak.



This can be interpreted as SO_4^{2-} eluting steadily and further down the snowpack than the other ions during this period (Fig. 8).

We estimate a *minimum* ionic relocation length as the difference in depth between the maximun/minimun (deposition/elution) $c_{\rm N}$ peaks, as shown in Fig. 8 and presented

- ⁵ in Table 4. The relocation length was calculated for all ions, with the exception of $SO_4^{2^-}$ which does not show an elution peak that is significant within the time window studied. For the ions that show more than one significant deposition/elution peak, the relocation length calculated considering the second maximun/minimun c_N peak is also shown in Table 4.
- ¹⁰ Considering the deposition/elution c_N peaks estimated above, the ionic elution scheme at Lomonosovfonna for the last 5 years results in SO²⁻₄ being the most mobile ion and NO⁻₃ the least mobile one. This elution scheme differs with previous studies done at Lomonosovfonna (Moore and Grinsted, 2009) mainly in locating NO⁻₃ at the end of the elution sequence. However, it should be noticed that we estimated two
- ¹⁵ possible relocation lengths based in the depth difference between deposition/elution peaks (as explained before). Therefore, considering a NO_3^- relocation length of 1.16 m, the elution sequence agrees with previous findings by Moore and Grinsted (2009), locating the acidic ions (SO_4^{2-} and NO_3^-) as more mobile than the others ions. The elution sequence and ion relocation lengths shown in Table 4, suggest that the less
- ²⁰ mobile ions are relocated by the meltwater at short lengths, probably trapped in thin and medium-thick ice layers present within the ice column observable in the LF-97, LF-09 and LF-11 cores (Fig. 9), or in refrozen water that soaks the firn column filling the pore space. More mobile ions may percolate further down in the snowpack and get trapped in medium-thick to thick ice layer which start to form at about 3–10 m deep in the ice column as observable in the LF-97 and LF-09 cores (Fig. 9).

In order to estimate how the ionic relocation length during 2007–2010 is connected to meltwater percolation length and snowpack melting, we have estimated the melt percentage at Lomonosovfonna using two different methods, as shown in the following section.



3.5 Meltwater production at Lomonosovfonna

The produced meltwater obtained by using the PDD and snow-energy model approaches are shown in Fig. 10 for the period 1979–2012 (calculated using PDD and instrumental temperatures), and 1989–2010 (using the snow-energy model). The production of meltwater at the summit of Lomonosovfonna has increased at a rate of +0.0011 m yr⁻¹ w.e. toward the last decades (corresponding to the linear trend of meltwater production calculated with the PDD and instrumental temperatures approach, Fig. 10). The meltwater production shows a minimum around 1995, which is present when using both approaches (Fig. 10). The average melting between 1989–2010 was
calculated as 0.17 m w.e. when using the PDD and instrumental temperature approach. When considering the period between 2007–2010 (Fig. 11), the melting shows stable values with alternated warmer and colder years (2007/09, and 2008/10, respectively), with meltwater average values of 0.19 and 0.27 m w.e. when using the instrumental temperature, melt-

- ¹⁵ water production was also calculated by using modelled temperatures obtained with the Polar WRF model at the summit of Lomonosovfonna and a DDF of 3.0 mm water °C day⁻¹. An average meltwater production of 0.07 and 0.05 m w.e. were obtained for the periods 1989–2010 and 2007–2010, respectively when using the Polar WRF modelled temperatures. The meltwater production obtained by the Polar WRF approach
- ²⁰ gives values that are significantly lower than the meltwater obtained by using both the PDD and snow-energy model approaches which is a consequence of the less number of PDDs per year estimated at the summit of Lomonosovfonna when using the Polar WRF model (i.e. 18 PDDs per year between 1989–2010) explained by the fact that the Polar WRF model produces lower surface temperatures compared to the lapse-rate
- ²⁵ based temperatures at this site. Therefore, the meltwater calculated by using Polar WRF modelled temperatures were not considered in this study.

In order to estimate the impact of melting on the snowpack ionic content at the summit of Lomonosovfonna, the percentages of the annual snow accumulation that melts



(Table 5) were calculated using the results in Figs. 10 and 11 and the annual accumulation rate between 2007–2010 at Lomonosovfonna obtained from the LF-09 and LF-11 cores. The melt percentage (MP) obtained by using the instrumental temperatures (48 % for the period 2007–2010) was in the order of previously reported values

- of 47 % of melt during the warmest years and 28 % during the coldest, during the period 1976–1995 (Pohjola et al., 2002). The relatively high MP values obtained in this study for the period 2007–2010 can be explained by the increase in temperatures at the site with a consequent steady increase of the number of PDD at the summit of Lomonosovfonna at a rate of 0.4 day yr⁻¹ for the period 1979–2012 in which instru mental temperatures exist in all the three stations used, Sveagruva, Ny-Ålesund and
- ¹⁰ mental temperatures exist in all the three stations used, Sveagruva, Ny-Alesund and Longyearbyen airport; the MPs calculated using the PDD approach over the period 1979–2010 show a steady increase of $1 \% \text{ yr}^{-1}$ in line with the trend in decreasing the annual snow accumulation in -0.01 m yr^{-1} w.e. during the same period (accumulation data from the LF-09 ice core).
- However, the calculated MPs using the PDD approach and the snow-energy do not agree with the results obtained by the synthetic core approach which suggest moderate melting during the 2007–2010 period which is also supported by the stratigraphy observed in the LF-09 and LF-11 cores (Fig. 9).

Due to the dissimilar results of MP obtained using the PDD and snow-energy model approaches (Table 5), we compared the density profiles of the shallow ice cores used in this study (LF-08, LF-09 and LF-11) with the total layer density values obtained using a simple firn-densification model (Reeh et al., 2005). The ice core density profiles were binned in annual averages in order to be comparable with the output of the firn-densification model. As described by Reeh et al. (2005), the model requires both annual average temperatures and snow accumulation at the study site as input, which were set as -18.3 °C and 0.39 m w.e., according to instrumental temperatures from

Sveagruva, Svalbard Airport and Ny-Ålesund (the lapse rate employed to calculate the temperatures at the Lomonosovfonna summit was -0.0044 °Cm⁻¹), and average accumulation rates obtained from the LF-09 and LF-11 ice cores, respectively, for the pe-



riod between 2007–2010. The firn-densification model also requires the surface snow density, which was set as 350 kg m⁻³, and a defined spatial resolution, set as 0.5 m. The firn-densification model considers the percentage of melting as one of the input variables, showing output density values vs. depth. Output densities of 900 kg m⁻³ are expected when the percentage of melt reaches 100%. Four different melt scenarios where considered: MP equal to (a) 20%, (b) 30%, (c) 45%, and (d) 70%. The re-

sults of the comparison between the real ice core density profiles and the output of the firn-densification model are shown in Fig. 12.

According to Fig. 12, the firn-densification model shows better agreement with the

- ¹⁰ measured density profiles in the top 10 m when the MP was set between 20 and 30 %. This agrees with the physical melt index of the LF-09 ice core (22%), calculated as the percentage of clear ice present in the ice core (considering the ice core length in m w.e.). However, the agreement between the firn-densification model and the density profiles is poor for depths deeper than 10 m (Fig. 12a and b) considering this range or
- ¹⁵ MP. Figure 12c and d, show the comparison between the firn-densification model and the density profiles using a MP of 45 and 70%. The agreement between the model and the measurements is better through the whole depth profile when setting the MP to 45% (Fig. 12c). This agrees with the physical melt index of the LF-97 ice core (50%), calculated between 1957 and 1997, however, it is not consistent with the physical melt index of the LF-09 ice core (25%), calculated for the same period.

Considering the results shown in Table 5 and the firn-densification model output shown in Fig. 12a–d, it is plausible to think that the MP at Lomonosovfonna is not straight forward to estimate either using a simple PDD or the snow-energy model approach. Moreover, the use of Polar WRF temperatures at Lomonosovfonna as input to

obtain the MP at the site is ruled out since it predicts MP values considerably lower than the values suggested by the density profiles both measured and modelled (i.e. an average MP of 12 % for the period 2007–2010 when Polar WRF modeled temperatures and a DDF of 3.0 mm water °C day⁻¹ are used to calculate the meltwater production). It also needs to be considered that the firn-densification model assumes a constant melt



index during the ice core time span. Therefore, the firn-densification model does not include the variability in meltwater production at Lomonosovfonna through time which is key to the understanding of ion relocation within the snowpack at long time scales; however, the MP estimated here are suitable to understand the ionic relocation and ⁵ water percolation during the period 2007–2010.

Figure 13 shows a comparison between the LF-11 and the LF-syn ice core depthtime scale. It is clear from Fig. 13 that the depth differences between the ice cores (black and grey lines) can be related to a partial melting of the snowpack and refreezing of the meltwater taking place between the 2007-2011 period, as evidenced by the ionic relocation. An estimate of the decrease in depth of the LF-syn ice core 10 by the effects of snowpack melting considering a MP = 20, 30, 48 and 70% during 2007-2010 as suggested by the firn-densification model, MPs obtained using the PDD approach (using instrumental temperatures) and the snow-energy model is shown in Fig. 13. It can be observed that a MP = 20-30 % results in a LF-syn ice core depth-time scale highly similar to the depth-time scale of the LF-11 ice core during the 2007–2010 15 period, confirming that the MP during that period is coherent with the results of the firn-densification model but not with the PDD results shown in Table 5. This relatively low MP reinforces the fact that during this period, ion relocation took place at moderate depths (0.5-2 m) and that the meltwater percolation depth was most probably in the same order, with refreezing of meltwater within the snowpack pore space or by forming

20 same order, with refreezing of meltwater within the snowpack pore space or by forming thin ice layers (0.03–0.15 m) (Fig. 9).

4 Conclusions

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By comparing different ice cores from Lomonosovfonna and using a *synthetic* ice core approach, we have been able to estimate the elution signal and relocation length of different ions measured at the study site, in order to assess the transfer function between the atmospheric ionic concentrations and the concentration in snow and ice.



Our results show good agreement between the ionic records of three different ice cores drilled during different years, using normalized concentrations and five year moving averages. Therefore, we reiterate that the different ice core records from Lomonosovfonna all share the same climatic and chemical features, despite the fact that cores have been retrieved in different years, were sampled at different resolutions, and were analyzed at different laboratories. Our conclusion is that summer melting

does not degrade the climatic signals. By using the *synthetic* ice core approach, we could estimate an elution sequence for the summit of Lomonosovfonna, as $SO_4^{2-} > NO_3^- > NH_4^+ > Mg^{2+} > CI^-$, $K^+ > Na^+ >$

- ¹⁰ Ca²⁺, which agrees with previous reports. This elution sequence points towards the acidic ions as being the most mobile within the Lomonosovfonna snowpack. Considering the differences between the LF-11 and the LF-syn ice cores, we conclude that the relocation length of most the ions during the 2007–2010 period is in the order of 1 m, therefore, the ions are eluted and re-deposited within the annual snow layer,
- ¹⁵ considering present average accumulation rate at Lomonosovfonna (i.e. < 1 m of snow per year). According to our results, only SO_4^{2-} shows percolation lengths that could potentially reach deeper than the previous year of snow accumulation (> 2 m), which affects the annual atmospheric signal and prevents any high resolution (seasonal, annual) analysis to be possible in Lomonosovfonna ice cores. However, as we have con-
- ²⁰ cluded before, using 5 year moving averages of the ionic data allows having comparable records when different ice cores are used.

By using the PDD and the snow-energy model approaches to estimate the percentage of melt (MP) at Lomonosovfonna, we have estimated average annual MP in the range of 48 to 70% for the period between 2007–2010, in contrast to the moderate melting suggested by the LF-syn core for the same period. In order to constrain the MP, we have compared different density profiles obtained at the Lomonosovfonna drilling sites with a simple firn-densification model, obtaining a most probable average annual MP of 30% for the 2007–2010 period which is consistent with the results of the synthetic ice core approach, and 45% of melt for the last 60 years. The lower melting

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percentages inferred for the 2007–2010 period compared with the whole period covered by the LF-09 core are most probably a result of a combination of relatively high snow accumulation rates and reduced PDD during the 2007–2010 period despite of the warmer conditions registered during the last decades.

- ⁵ Considering our findings, we conclude that despite of the warmer conditions and higher number of PDD registered at Lomonosovfonna during the last decades, the ionic signal affected by melting is retained within the same year of deposition for all major ions, with the exception of SO_4^{2-} which can possibly be re-deposited in previous annual layers.
- Acknowledgements. The authors want to thank the Lomonosovfonna 1997, 2008 and 2009 drilling teams and NPI field logistics for their support, C. Zdanowicz and G. Engström, Uppsala University, J. Moore, Arctic Centre, J. Zábori, Stockholm University, and S. Bejai, SLU for their comments and sharing of analytical lab facilities. This work was supported within the Marie Curie Initial Training Network NSINK ITN-2007.1.1, ENV., 215503 with complementary
 economic support by Ymer-80, the Arctic Fieldwork Grant by the Svalbard Science Forum, Uppsala Geographical Association, Sweden, and to the EU Regional Development Foundation, project 3.2.0801.12-0044.

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 Table 1. Drilling site and ice core description for the three different cores used in this study.

Ice core	Drilling date	Location	Elevation (ma.s.l.)	Length (m)	Reference
LF-97	May 1997	78°51′ N, 17°25′ E	1250	121.6	Isaksson et al. (2001)
LF-08	Mar 2008	78°51′ N, 17°24′ E	1250	10.0	Beaudon (2012)
LF-09	Mar 2009	78°49′ N, 17°25′ E	1200	36.0	Vega et al. (2015b)
SP LF-10	Mar 2010	78°49′ N, 17°25′ E	1200	1.5	This work
LF-11	Apr 2011	78°49' N, 17°25' E	1200	7.6	Vega et al. (2015a)

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Table 2. Synthetic ice core construction using the different Lomonosovfonna shallow cores (LF-08 and LF-09) and SP LF-10 snowpit.

*The top meter of the LF-11 was not used to construct the synthetic ice core but it is shown here as reference to account for the final depth of the synthetic core.

Table 3. Pearson coefficients (*R*) at a 95% confidence interval, between the different ions measured in the LF-97 and LF-09 ice cores (normalized concentrations and smoothed out as 5 year running averages). Significant values (p < 0.05) are shown in italics. The overlapping period is 1957–1997.

LF-97 and LF-09 ice cores								
lon R	Cl [−] 0.46	NO ₃ 0.64	SO ₄ ²⁻ 0.56	Na ⁺ 0.49	NH ₄ ⁺ 0.77	K ⁺ 0.66	Ca ²⁺ 0.36	Mg ²⁺ 0.72
LF-08 and LF-09 ice cores								
R	-0.21	0.02	0	-0.30	0.32	-0.16	-0.23	-0.53



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Table 4. Relocation length estimated for each ion measured in the LF-11 ice core. Secondary relocation peaks are also depicted.

lon	SO_4^{2-}	NH_4^+	Mg ²⁺	CI⁻	K ⁺	Na ⁺	Ca ²⁺	NO ₃
Relocation length (m)	> 2.05	1.28	1.09	0.89	0.89	0.79	0.78	0.66
Peak (year) Secondary	2009.5	2008.2–2009.6	2008.6-2009.5	2008.8–2009.5 1.16	2007.8–2009.5	2008.8–2009.5 1.16	2007.7–2008.7 2.97	2008.9–2009.5 1.16
peak (m) Secondary peak (year)				2007.4–2008.8		2007.4–2008.8	2007.7–2010.3	2008.9–2009.8

Table 5. Percentages of melted annual snow accumulation (MP) calculated with the PDD approach (Pohjola et al., 2002; Nuth et al., 2012) using instrumental temperatures, and the snowenergy model (van Pelt et al., 2012).

	MP (%)				
Year	Instrumental temperatures	Snow-energy model			
2010	34	52			
2009	55	81			
2008	34	68			
2007	69	78			
Average	48	70			





Figure 1. Map of Svalbard showing the main settlements: Longyearbyen, Ny-Ålesund and Pyramiden, and the LF-97, LF-08, LF-09 and LF-11drilling sites at Lomonosovfonna.























Figure 5. Melt index W_{NaMg} calculated in the different Lomonosovfonna ice cores. The values correspond to 5 year moving averages. The dashed rectangle indicates a high melting period during mid-80s to mid-90s.











Figure 7. Comparison between a *synthetic* ice core (LF-syn, black) and the LF-11 ice core (grey). Ionic concentrations are normalized (c_N) to mean values according to the LF-syn ice core time scale.





Figure 8. Difference between the normalized ionic concentrations (c_N) in the LF-11 and the LF-syn ice cores (black line). Twice the standard deviation (dashed red line) and zero values (dashed black line) are also shown. Deposition is a positive excursion and elution zones are negative excursions from the mean in each diagram.







Figure 9. Number of ice layers found at different depths in the: LF-97 (left panel), LF-09 (centre panel) and LF-11 (right panel) ice cores. The ice layers were divided in three classes according to their thickness: thin layers (*), medium-thick layers (∇) and thick layers (•).



Figure 10. Produced meltwater calculated at Lomonosovfonna using the PDD (black) and snow-energy model (dashed red) approaches. The linear trend of meltwater calculated with the PDD approach and instrumental temperatures is also shown over the 1979–2012 period (grey).





Figure 11. Meltwater calculated at Lomonosovfonna during the period 2007–2010 using the different approaches: PDD and instrumental temperatures (black); and the snow-energy model (dashed red). The percentages above each line represent the average melt percentage (MP) during the studied period, estimated by the different approaches.





Figure 12. Comparison between the LF-08, LF-09 and LF-11 ice core density profiles (annual averages) and the output of the firn-densification model (Reeh et al. 2005), considering: (a) 20% of melt, (b) 30% of melt, (c) 45% of melt, and (d) 70% of melt.





Figure 13. Depth–time scales for the LF-11 and LF-syn ice cores during 2007–2011 (black and grey lines, respectively). Blue dashed, black-dot-dashed, green and red lines represent the synthetic core depth–time scale considering a MP of 20, 30, 48 and 70 %, respectively.

