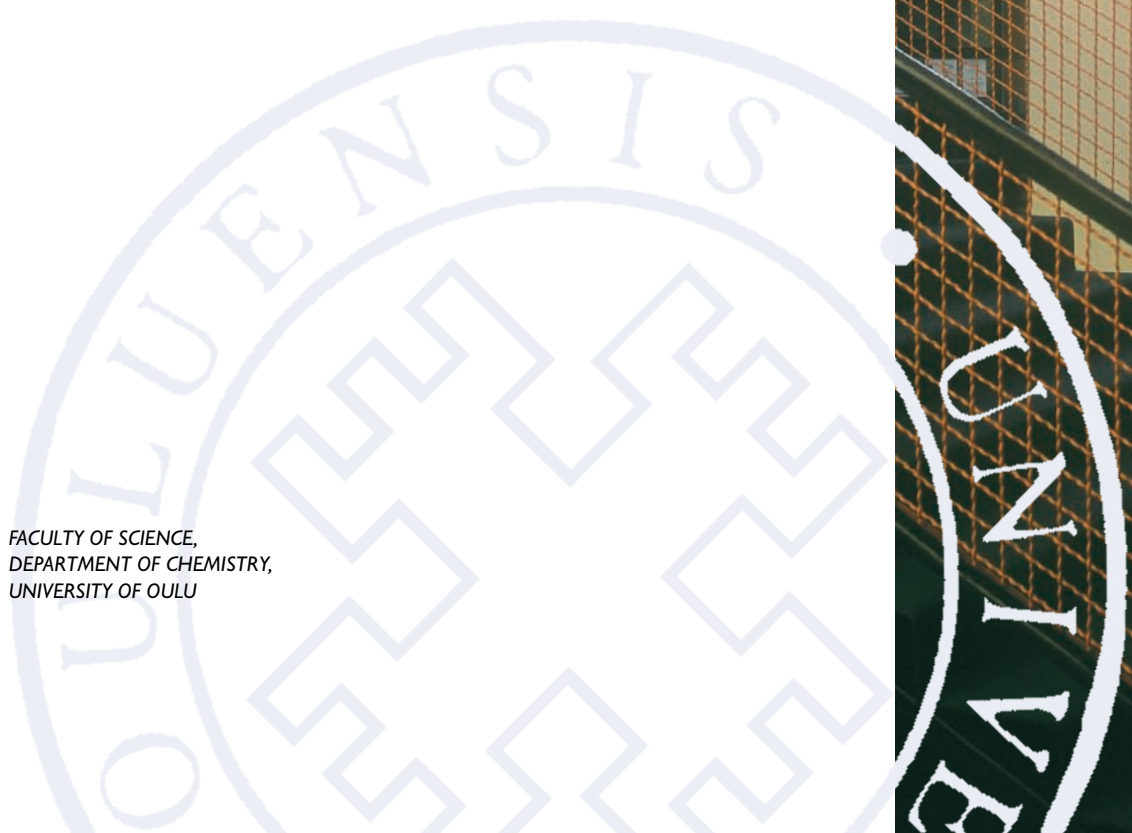*ACTA*

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ENVIRONMENTAL INFORMATION FROM THE SVALBARD ICE CORE FOR THE PAST 800 YEARS

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Abstract

Major water soluble ions (Cl^-, NO_3^-, SO_4^{2-}, $CH_3SO_3^-$, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) were determined and the results interpreted from a 121 m long ice core drilled at the summit of the Lomonosovfonna dome, Svalbard. The core covers about the past 800 years. The reliability of anion chemistry for paleoenvironmental studies, and various insoluble particles were also investigated. The ice core studied in this Thesis is the first relatively deep ice core from the central Svalbard that has been analyzed and the results interpreted and published at high resolution for all major ions.

One of the clearest features of the ion profiles is anthropogenic impact. SO_4^{2-} and NO_3^- concentrations show significant increases by the mid-20th century with slight increases already at the end of the 19th century. In addition excess Cl^- and NH_4^+ from anthropogenic sources are detected arriving after the mid-20th century. Anthropogenically derived SO_4^{2-} and NO_3^- have different sources on Lomonosovfonna. NO_3^- is correlated with NH_4^+ and requires interpretation in terms of both natural and anthropogenic NH_4NO_3 sources.

The ice core ionic load consists mostly of sea salt ions (Na^+, Cl^-, K^+ and Mg^{2+}). Water soluble Ca^{2+} are mostly terrestrial in origin. Ion balance together with the Na^+/Cl^- ratio shows considerable change about 1730 that is most probably due to Na_2CO_3 input to the ice cap before 1730. Marine biogenic $CH_3SO_3^-$ concentrations are high and stable during the Little Ice Age. $CH_3SO_3^-$ concentrations show a clear change in concentrations in 1920, that is the end of the Little Ice Age in Svalbard. Regardless of anthropogenic impact, marine biogenic SO_4^{2-} is appreciable in total SO_4^{2-} budget even in the 20th century.

The Laki volcanic eruption in Iceland in 1783 is identified in the ice core as a volcanic tephra layer and high SO_4^{2-} concentration and acidity peaks. These show that SO_4^{2-} arrived to the Lomonosovfonna ice cap 6–12 months later than insoluble tephra and the SO_4^{2-} aerosol caused a drop in temperature.

The reliability of ice core ion chemistry analyses was estimated – for the first time in an ice core using two different analytical procedures on 500 adjacent samples from the same depth. Small-scale inhomogeneity in ion concentrations shows that information from ice core layers is representative of the regional environmental and suitable for paleoclimate studies.

Keywords: anions, Arctic, cations, ions, Laki, paleoclimate, particles, volcanic eruption

"Il est dans la nature humaine de penser sagement et d'agir d'une façon absurde" -Anatole France

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Finally, my deepest gratitude belongs to my dear husband Janne, and my sons, Aleksanteri and Nestori, who have brought true love and pleasure into my life. You are the most valuable in my life.

Oulu, July 2006   *Teija Kekonen*

Abbreviations

$1\ \mu EqL^{-1}$	$1\ \mu molL^{-1}$ times the charge of the ion
$\delta^{18}O$	is calculated from a formula $(({}^{18}O/{}^{16}O)_{sample}/({}^{18}O/{}^{16}O)_{reference} - 1)$ times 1000, where reference is Standard Mean Ocean Water (SMOW) or Standard Light Antarctic Precipitation (SLAP)
AMAP	Arctic Monitoring and Assessment Programme
a.s.l.	above sea level
CH_3SO_3H	methane sulfonic acid, MSA
$CH_3SO_3^{-}$	methane sulfonate
DMS	dimethyl sulfide, $(CH_3)_2S$
dry deposition	The removal of a substance (gases and particles) from the atmosphere through direct deposition on the Earth's surface.
IC	ion chromatography
IPCC	Intergovernmental Panel on Climate Change
LIA	Little Ice Age
MWP	Medieval Warm Period
nss	non sea salt
PCA	Principal Component Analysis
SEM-EDS	scanning electron microscopy with energy dispersive spectrometer
ss	sea salt
SST	sea surface temperature
wet deposition	The removal of a substance from the atmosphere through being washed out as precipitation: rain, sleet, snow and fog on the Earth's surface
w.eq. a^{-1}	water equivalent per year (w.eq. is snow/firn/ice depth times density)

List of original papers

This Thesis is based on the following publications and manuscript, which are referred to in the text by their Roman numerals:

I   Kekonen T, Perämäki P & Moore J (2004) Comparison of analytical results for chloride, sulfate and nitrate obtained from adjacent ice core samples by two ion chromatographic methods. J Environ Monit 2: 147-152.

II   Kekonen T, Moore J, Perämäki P, Mulvaney R, Isaksson E, Pohjola V & van de Wal R (2005) The 800 year long ion record from the Lomonosovfonna (Svalbard) ice core. J Geophys Res 110: D07304.

III Moore J, Kekonen T, Grinsted A & Isaksson E (2006) Sulfate Source Inventories From a Svalbard Ice Core Record Spanning the Industrial Revolution. J Geophys Res 111: D15307.

IV   Kekonen T, Moore J, Perämäki P & Martma T (2005) The Icelandic Laki volcanic tephra layer in the Lomonosovfonna ice core, Svalbard. Polar Res 24: 33-40.

V   Isaksson E, Kekonen T, Moore J & Mulvaney R (2006) The methanesulphonic acid (MSA) record in a Svalbard ice core. Ann Glaciol 42.

VI   Kekonen T, Moore J, Mulvaney R, Isaksson E, Pohjola V & van de Wal R (2002) An 800 year of nitrate record from the Lomonosovfonna ice core, Svalbard. Ann Glaciol 35: 261-265.

VII Kekonen T, Moore J & Perämäki P (manuscript) Carbonates in the Lomonosovfonna ice core, Svalbard.

VIII Moore J, Grinsted A, Kekonen T & Pohjola V (2005) Separation of melting and environmental signals in an ice core with seasonal melt. Geophys Res Lett 32: L10501.

The research work presented in this Thesis can be divided into three topics. The first includes the original Paper I that shows reliability of ion chemistry using anion data for environmental interpretation. The second reports results and interpretation of ion profiles published in Papers II, III, V, VI and VIII. The third introduces insoluble fraction of the ice core presented in Papers IV and VII.

Experimental work was mostly accomplished by the author in all the Papers. The calculations, interpretation and writing of the experimental results in Papers I, II, IV, VI and VII were mainly done by the author. The author has contributed to the interpretation of the data for Papers III and V, but writing and sophisticated statistics in these Papers were mostly done by the first author of the Paper. The first draft of the Paper VIII was mostly written by the author except the chapter 5 but the first author of the Paper made the Paper finally to the publishable form.

Contents

1 Introduction

1.1 Overview

The climate of the Earth is changing (IPCC 2002). The global mean temperature has increased by about 0.6ºC during the last century. Models predict that the global mean temperature will rise 3 to 5ºC during the 21st century. Increase in temperatures is reported to be mostly attributable to human activities by the burning of fossil fuels and thus releasing greenhouse gases to the atmosphere (IPCC 2001, Zwiers 2002). The climate changes are more radical and evident in the pristine Polar regions and warming is believed to be more pronounced in polar regions with a decreasing contrast between poles and equator. Arctic snow cover is predicted to decrease and glaciers and ice caps are projected to continue their widespread retreat during the 21st century (IPCC 2001). In addition to increased emissions of greenhouse gases, emissions of other contaminants have been more pronounced during the last half of 20th century. Most of the industrial areas are outside of the Arctic region but contaminants are delivered to Arctic through the atmosphere, sea ice, rivers and ocean (AMAP 2003).

In order to recognize current changes, the past climate and atmospheric composition are essential to be known. Instrumental records do not reach far back in time, therefore proxy records are necessary. Glaciers all over the world store an enormous amount of information about the past. They are the only archives that conserve chemical data almost invariable in the frozen state. Thus ice cores contain one of the best proxy records for the past climatic, atmospheric and environmental studies (e.g. Wolff 1990, Delmas 1992, Legrand & Mayewski 1997). Snow, which has information about the atmosphere, falls to the ground and each snow layer is buried by further precipitation. Lower layers of snow are compressed and slowly transformed to firn and then to solid ice. In the large ice sheets (Greenland and Antarctica) ice core archives can cover timescales of hundreds of thousands of years (Delmas 1992) while the smaller ice caps of the Arctic mostly contain records of a few hundred years, though a very few span the Holocene (Koerner 1997). The small ice caps of the Arctic are situated relatively close to large sources of anthropogenic pollution and they are therefore valuable for assessing impacts and source histories over the period since the industrial revolution (Koerner *et al.* 1999). In many locations in the Arctic some melting and post-depositional change occurs but several ice

cores still contain good record of the original snow fall composition that builds up year by year (Kotlyakov *et al.* 2004).

During the last millennium before the anthropogenic era, two clear climate epochs are reported: The Medieval Warm Period (MWP) and the Little Ice Age (LIA) (Bradley & Jones 1992). The MWP was a relatively warm period associated with the 11th to 14th centuries and the LIA was a relatively cool period associated with the 15th to 19th centuries in the Northern Hemisphere (Grove 1988). The LIA ended at Svalbard about 1920 (Vinje 2001). Cold temperatures during the LIA were more pronounced, especially in North Atlantic region than in the MWP. The LIA is recorded in several northern Greenland ice cores (Fischer *at al.* 1998b).

1.2 Ice core analyses

Ice core samples for chemical analyses are small and concentrations of chemical components determined are generally rather low (Jauhiainen *et al.* 1999, Curran & Palmer 2001). These facts require sophisticated chemical instruments that enable analyses of low concentrations from small sample volumes. Numerous components (e.g. ions, metals, gases, isotopes, organic compounds) can be analyzed and determined from ice cores (e.g. Boutron *et al.* 1991, Anklin *et al.* 1995, Legrand & DeAngelis 1996, Barbante *et al.* 1997, Townsend & Edwards 1998, Masclet *et al.* 2000, Burton *et al.* 2002, Lee *et al.* 2002, Schuster *et al.* 2002). Ions, which are the most commonly studied constituents in ice, are usually determined by IC. The method exhibits high sensitivity and is well suited for the analysis of low concentrations of water soluble ions in ice without sample pretreatment. It also enables analysis of many ions from the same sample in a single run (Buck *et al.* 1992, Legrand *et al.* 1993, Huber *et al.* 2001). Various ion chromatographic techniques using different columns, eluents and methods (gradient, isocratic, suppressed, non-suppressed) are used in glaciochemical analyses (Udisti *et al.* 1994, Ivask & Pentchuk 1997, Ivask & Kaljurand 1999).

Ions provide a lot of information on past atmospheric composition, with both short events (e.g. volcanic eruptions, storms, forest fires) and long-term changes (e.g. anthropogenic input, biogenic production, temperature variations) being recorded (Delmas 1992, Fischer *et al.* 1998b, Wolff *et al.* 2003). Most ions have several sources (e.g. SO_4^{2-}: anthropogenic, marine, terrestrial, biogenic and volcanic), but single source ions are also detected (e.g. $CH_3SO_3^-$: biogenic) (De Angelis *et al.* 1997, Saltzman *et al.* 1997, Bigler *et al.* 2002). In order to make good interpretations of water soluble ion analyses results, the insoluble fraction of samples is really useful (Biscaye *et al.* 1997, Laj *et al.* 1997). Research on the insoluble parts of melted ice core samples has mainly been focused on volcanic particles because of their importance for dating purposes (Fiacco *et al.* 1994, Zielinski *et al.* 1997a). Other marine and terrestrial particles can also provide a lot of knowledge about past climate and atmospheric composition (Zdanowicz *et al.* 2000, Kohfelt & Harrison 2001).

1.3 Svalbard

Svalbard is surrounded by the Arctic Ocean, Barents Sea and North Atlantic (Fig. 1). The Svalbard archipelago has a relatively mild climate considering its northern position. It is located at the southerly edge of the permanent Arctic sea ice and has open ocean to its west even during winter. Svalbard is near to the over-turning point of the North Atlantic thermohaline circulation. The Gulf Stream brings warm water towards to Svalbard and the Barents Sea. Svalbard is influenced by air masses from both west and east (Isaksson *et al.* 2003). Glaciers cover 60% of Svalbard and most of the glaciers in Svalbard are polythermal (a layer of cold-ice on top of the temperate ice layer), (Pälli 2003). Glaciers advanced throughout the LIA to a maximum around 1920 in Svalbard (Svendsen and Mangerud 1997), and have retreated since. A continuous temperature record in Svalbard starts in 1911 (Nordli *et al.* 1996). A temperature minimum is recorded in 1917 and after the late 1960s there has been a significant increase in temperature.

Local industrial activities are coalmines at Barentsburg, Sveagruva, Pyramiden and Longyerbyen. In spite of the relative remoteness, the atmosphere of the Arctic and Svalbard is already disturbed by human activities from industrial areas. (Staebler *et al.* 1999, Goto-Azuma & Koerner 2001, Simões & Zagorodnov 2001, Yalcin & Wake 2001). Air masses bring contaminants from industrial areas to the Arctic especially in the winter and they wash out in precipitation areas (AMAP 2002).

Fig. 1. Map of Svalbard showing the Lomonosovfonna ice core site, and the Snøfjellafonna, Vestfonna and Austfonna ice caps.

1.4 Ion research in other ice cores from Arctic

In addition to Svalbard, other ice cores that have drilled in the Arctic come from Greenland (e.g. Herron 1982, Neftel *et al.* 1985, Fischer *et al.* 1998a, Legrand *et al.* 2002), the Canadian Arctic (e.g. Grumet *et al.* 1998, Koerner *et al.* 1999) and the Russian Arctic (e.g. Kotlyakov *et al.* 2004). The clearest feature that is reported in most of the ice cores is anthropogenic inputs. The earliest increase in SO_4^{2-} concentrations were noticed by Fischer *et al.* (1998a) and Mayewski *et al.* (1990, 1986) from north and south Greenland ice cores, and Goto-Azuma and Koerner (2001) from the Canadian Arctic ice core. Fischer *et al.* (1998a), Mayewski *et al.* (1990, 1986), and Goto-Azuma and Koerner (2001) showed slightly increasing SO_4^{2-} concentrations from around 1890, with marked increases between the 1940s and 1950s. They also reported that after the late 1970s SO_4^{2-} concentrations decreased. Fischer *et al.* (1998a) suggested that the increase in SO_4^{2-} concentrations since the 1950s can be attributed to Eurasian emissions, but in those the first half of the 20th century were dominated by North American sources. NO_3^- concentrations showed an increase since 1950 in north Greenland ice cores and Fischer *et al.* (1998a) supposed that NO_3^- concentrations had a stronger North American source contribution over the 20th century. Neftel *et al.* (1985) reported increase in SO_4^{2-} and NO_3^-

concentrations between the late 1930s and 1950s from south Greenland ice cores. Koerner *et al.* (1999) indicated a marked increase in NO_3^- and SO_4^{2-} concentrations in the mid-20th century in Canadian Arctic ice cores. Their records do not show any decreasing trend in concentrations due to a reduction in emission in industrialized areas. Goto-Azuma and Koerner (2001) concluded that the pollutant sources appear to be North America for south Greenland and the Canadian low Arctic, Eurasia for the Canadian high Arctic and Svalbard, and both North America and Eurasia for central and north Greenland.

Fischer (2001) found significant excess Cl^- for the last few decades in northern Greenland ice cores and they believed it to be due to anthropogenic emission. In pre-industrial era ice Na^+/Cl^- ratio showed a very close ratio to that of seawater (Fischer 2001). In addition Fischer (2001) reported that 600 year sea salt record showed an increase during the 19th century that was interpreted as an enhancement of sea salt export from the Pacific region.

$CH_3SO_3^-$ concentrations are widely reported from Greenland ice cores (Hansson & Saltzman 1993, Jaffrezo *et al.* 1994, Whung *et al.* 1994, Legrand *et al.* 1997, Saltzman *et al.* 1997). Seasonal cycles, sea surface temperatures and climatic eras are sometimes interpreted from $CH_3SO_3^-$ concentrations.

Even though water soluble ions are commonly determined from ice cores, only a few complete ice core ion records have been published from Svalbard (Table 1). The researchers from the former Soviet Union drilled several ice cores on Svalbard between 1975 and 1987 (Punning *et al.* 1987). Mainly Cl^- concentrations were determined (Kotlyakov *et al.* 2004). The reliability of results is questionable because of lack of sophisticated instruments during that time. The Japanese have also drilled several ice cores at other sites than Lomonosovfonna in Svalbard since 1987 (e.g. Goto-Azuma *et al.* 1995, Watanabe *et al.* 2001, Matoba *et al.* 2002). Only a few ion records have been published because most of the ice cores have not yet been analyzed. The most significant ion results from the ice cores show increases in SO_4^{2-} and NO_3^- concentrations in the mid-20th century in Snøfjellafonna (Goto-Azuma *et al.* 1995), Austfonna (Watanabe *et al.* 2001) and Vestfonna (Matoba *et al.* 2002) ice caps (Fig. 1).

Table 1. Ice cores drilled in Svalbard and have been subject to ion analyses (Isaksson et al. 2001, Watanabe et al. 2001, Kotlyakov et al. 2004).

Drilling site	Year	Published ion analyses	Reference
Grønfjordbreen	1975	Cl^-(*)	Punning *et al.* (1987)
Lomonosovfonna	1976	Cl^-, SO_4^{2-}	Punning *et al.* (1987), Punning & Vaikmäe (1985)
Fridtjovbreen	1979	Cl^-(no data given)	Kotlyakov *et al.* (2004)
Amundsenisen	1980	Cl^-(*)	Punning *et al.* (1987), Punning & Vaikmäe (1985)
Vestfonna	1981	Cl^-	Punning *et al.* (1987), Vaikmäe (1990)
Austfonna	1985	Cl^-(*), Na^+(*), K^+(*)	Punning *et al.* (1987)
Snøfjellafonna	1992	Na^+, Cl^-, NO_3^-, SO_4^{2-}	Goto-Azuma *et al.* (1995)
Vesfonna	1995	Na^+(¤), Cl^-(¤), NO_3^-, SO_4^{2-}, Ca^{2+}(*)	Watanabe *et al.* (2001), Matoba et al (2002)
Austfonna	1998	Na^+(*), Ca^{2+}(*), NO_3^-(*), SO_4^{2-}(*)	Watanabe *et al.* (2001)
Austfonna	1999	Na^+, Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}(*)	Watanabe *et al.* (2001)

* Only few meters data or mean concentration published. ¤ Data published at coarse resolution.

1.5 Ions: Sources and pathways

Ions in the ice cores are mainly marine, terrestrial, anthropogenic, biogenic and volcanic (Table 2) (e.g. Delmas 1992, Legrand & Mayewski 1997). At low accumulation sites dry deposition is often dominant, whereas at high accumulation sites wet deposition dominates (Fischer *et al.* 1998b, Sommer *et al.* 2000a). Bulk sea salt ratio of ions (Table 3) is an important factor for detecting origin of ions for ice cores drilled from coastal areas (Stenberg *et al.* 1998). Comparison between ion profiles and temperature and sea ice edge variations can reveal connections between ions and climatic signals (Rankin *et al.* 2002). Volcanic eruptions can be found in single SO_4^{2-}, Cl^- and F^- concentration peaks and sometimes a tephra layer is found near the peaks. Seasonal variations of e.g. Na^+ and Ca^{2+} concentrations can be detectable especially in high accumulation rate ice cores (Whitlow *et al.* 1992, Hall & Wolff 1998, Iizuka *et al.* 2004).

Emission trends of countries and continents are useful for searching origin of anthropogenic signal of ions (Goto-Azuma & Koerner 2001). The ways that anthropogenic SO_4^{2-}, NO_3^-, NH_4^+ and Cl^- are delivered to the Arctic are strongly influenced by climate variability. Water soluble gaseous compounds are emitted to the atmosphere, transported and reacted, and then deposited to the Earth's surface generally as wet deposition. The main pathway for contaminants in winter is from mid-latitudes into to Arctic but in summer northward transport decreases (AMAP 1998). North American sources are not as well connected to the Arctic by air transport as Eurasian sources. However, industrialized regions of eastern North America, Europe and southeastern Asia are main source areas for the distribution of anthropogenic SO_2 and NO_x emissions over the northern hemisphere (Benkovitz *et al.* 1995).

Table 2. Potential sources of ions. Modified from Legrand and Mayewski (1997) and Delmas (1992).

Ion	Source
Na^+	marine, terrestrial
Cl^-	marine, anthropogenic, volcanic
K^+	marine, terrestrial
Mg^{2+}	marine, terrestrial
SO_4^{2-}	anthropogenic, biogenic, marine, terrestrial, volcanic
$CH_3SO_3^-$	biogenic
NO_3^-	anthropogenic, continental emission, marine, atmospheric
NH_4^+	anthropogenic, continental emission, forest fires
Ca^{2+}	terrestrial, marine

Na^+, Cl^-, Mg^{2+}, SO_4^{2-}, Ca^{2+} and K^+ are all present in bulk sea water (Table 3) (Wilson 1975). All these ions also have terrestrial sources but Na^+ and Cl^- are especially considered as the clearest sea salt ions (Legrand & Mayewski 1997). Comparison with Na^+/Cl^- ratio of ice core and the bulk sea salt ratio shows how large a source the ocean is for all sea salt ions (Mulvaney & Peel 1988). Sometimes post-depositional processes confuse the expected ratio (Davies *et al.* 1982). Na^+ is generally the best sea salt marker and it is not as sensitive to post-depositional processes as Cl^- (Legrand & Delmas 1988, Davies *et al.* 1982). Cl^- may be affected by anthropogenic input (Legrand *et al.* 2002). Nss-Cl^- observations may be often explained by a larger influx of HCl from anthropogenic origin sources (Fischer 2001). Loss of Cl^- as volatile HCl is also possible and it is created by the reaction of sea-salt aerosols (NaCl) with atmospheric acids (HNO_3, H_2SO_4) (Legrand & Delmas 1988, Wagnon *et al.* 1999, Maupetit & Delmas 1994). Classifying sources for K^+ and Mg^{2+} are much more complicated because they are minor ions in bulk sea salt water and can be dominated by input from terrestrial sources (Mulvaney & Peel 1988, Wagenbach *et al.* 1998, Clausen *et al.* 2001, Kang *et al.* 2003). Mg^{2+}/Na^+ can be used as an indicator of seasonal melting at ice core and snow samples (Iizuka *et al.* 2002).

Table 3. The major inorganic ions of bulk seawater (Wilson 1975).

Ion	gkg^{-1}
Cl^-	19.4
Na^+	10.8
SO_4^{2-}	2.7
Mg^{2+}	1.3
Ca^{2+}	0.4
K^+	0.4

SO_4^{2-} has the largest number of different sources: anthropogenic, marine, terrestrial, biogenic and volcanic (Legrand *et al.* 1997, Fischer *et al.* 1998a, Wolff 1990, Delmas 1992). At present the main SO_4^{2-} precursors are SO_2 from anthropogenic sources and volcanoes, and DMS from biogenic sources, especially marine plankton (IPCC 2001). For many ice cores anthropogenic SO_4^{2-} is the most substantial part of the total SO_4^{2-}

budget after industrialization. The combustion of fossil fuels in electric power plants is the most important source of anthropogenic SO_2 emissions (AMAP 1998). SO_2 reacts with the oxygen in the air to form SO_3 and after reaction with H_2O it is rained down as a H_2SO_4. H_2SO_4 can react with NH_3 or $CaCO_3$ to form $(NH_4)_2SO_4$ and NH_4HSO_4 or $CaSO_4$. ss-SO_4^{2-} concentrations can be defined by using the bulk sea salt ratio of SO_4^{2-} to Na^+ or Cl^- concentrations. Terrestrial SO_4^{2-} is often associated with Ca^{2+} and/or Mg^{2+} derived from weathering of rocks. Production of SO_2 and SO_4^{2-} via conversion of DMS from marine organism is a source of biogenically derived SO_4^{2-} (Legrand & Mayewski 1997). DMS comes from local seas at coastal ice coring sites, and from distant oceanic sources. Many ice cores show well preserved records of large volcanic eruptions (Robock & Free 1995) that can be detected by just the SO_4^{2-} concentration peak or in some ice cores by Cl^- or F^- concentrations and a tephra layer near the SO_4^{2-} concentration peak.

CH_3SO_3H is an atmospheric oxidation product of gaseous biogenic DMS emissions that is produced mainly in oceanic waters by marine organisms (Dacey & Wakeham 1986). Biogenic marine sources (e.g. benthic and planktonic) form DMS, which is oxidized in the atmosphere to SO_2, SO_4^{2-} and CH_3SO_3H. DMS emissions are seasonal and diurnal and are dependent on location. $CH_3SO_3^-$ concentrations are a proxy for marine biogenic productivity in the ice cores (e.g. Hansson & Saltzman 1993, Saltzman *et al.* 1997) because it does not have any other source than DMS (Jaffrezo *et al.* 1994). In polar waters the DMS production is strongly influenced by the sea ice. The highest concentrations of DMS are found in open water at the ice edge, and the lowest concentrations beneath heavy pack ice (Leck & Persson 1996). Therefore, the $CH_3SO_3^-$ concentration record from ice cores has been suggested as a potential sea ice proxy (Pasteur *et al.* 1995, Legrand *et al.* 1997, O'Dwyer *et al.* 2000, Curran *et al.* 2003, Wolff 2003).

Anthropogenic NO_3^- dominates the NO_3^- budget after the mid-20th century in many ice cores. Automobiles are the most important sources of anthropogenic NO_x (= NO_2 + NO) (AMAP 1998). The main natural sources are assumed to be oceans, atmosphere (e.g. lightning) and continental emissions. Much of the NO_3^- precursors are transported as a gas (Legrand & Kirchner 1990, Hara *et al.* 1999, Palmer *et al.* 2001). NO_3^- is also subject to several post-depositional processes (Mayewski & Legrand 1990, Röthlisberger *et al.* 2000) and therefore the linkage between gaseous compounds and ice is not entirely clear (Honrath *et al.* 1999, Laird *et al.* 1999). Gaseous NO_x react in the presence of water vapor in the atmosphere to HNO_3 and particulate NO_3^- (NH_4NO_3 and HNO_3 reacted with sea salt aerosols) and deposit dry or wet to the Earth's surface (Seinfeld 1986, Clausen & Langway 1989). There are different reaction pathways that dominate in the light and dark periods. NO_3^- originates from a broad geographical area (Mayewski *et al.* 1990).

NH_4^+ budget is related to continental emissions such as soil exhalation (Hansson & Holmén 2001). Other sources are biomass burning (Hegg *et al.* 1988, Legrand *et al.* 1992, Whitlow *et al.* 1994), forest fires and animals (Legrand & Mayewski 1997). NH_3 can react with H_2SO_4 and HNO_3 to form $(NH_4)_2SO_4$ and NH_4HSO_4 and NH_4NO_3. NH_4NO_3 has an enhanced transport out of the emission areas because it has a lower rate of deposition than gaseous HNO_3 (Hov & Hjøllo 1994). NH_4^+ that is associated with NO_3^- and SO_4^{2-} (Silvente & Legrand 1993, Legrand *et al.* 1996) is often related to Arctic Haze (Heintzenberg 1989). Arctic Haze is visible and consists of submicron size aerosols

that contain significant levels of SO_4^{2-}, carbonaceous soot, soil, and marine aerosols (Heintzenberg 1980). Some NH_3 also dissolves from laboratory air during melting and analyses, which has to be taken into account in calculating final concentrations of NH_4^+.

Ca^{2+} is present in bulk sea water but is more dominant in terrestrial sources (Mulvaney & Peel 1988, Laj *et al.* 1997, Sommer *et al.* 2000b, Ruth *et al.* 2002, Röthlisberger *et al.* 2002) and thus Ca^{2+} is generally considered as a terrestrial marker (Steffensen *et al.* 2001). Seasonal cycles of Ca^{2+} in high accumulation rate ice cores are used for dating. Röthlisberger *et al.* (2000) reported that Ca^{2+} can be associated with NO_3^- via the stabilizing effect of dust particles. However, aerosol samples in Ny-Ålesund show that NO_3^- is bound to terrestrial particles during the summertime and therefore NO_3^- and Ca^{2+} has a local source in the Arctic (Teinilä *et al.* 2003).

1.6 Insoluble fraction of ice cores

The insoluble fraction of an ice core can include e.g. terrestrial, marine and volcanic tephra particles. The amount and type of particles varies greatly depending on climatic and stochastic effects such as wind speed, snow and sea ice cover, and volcanic eruptions. Terrestrial sand and silt particles and marine silica particles can be easily detected but many salt particles are much more difficult because of their high solubility (Steffensen 1997). Distinguishing between soluble and insoluble particles is not always unambiguous. The distribution between soluble and insoluble fraction can vary as a function of ice core depth as it depends on the temperature and pH of the precipitation when deposition occurred (Laj *et al.* 1997).

Volcanic eruptions produce a large volume of SO_2 gas, lava, ash and rock. Volcanic material can travel high into the atmosphere and mix with the air masses that circulate the world (Palais *et al.* 1992, Basile *et al.* 2001, Clausen *et al.* 1997). The particles eventually come back down to earth in falling rain. A volcanic eruption can bring such a lot of tephra to glaciers that a particle layer can be visible even by eye in the frozen ice core. Each volcano produces volcanic ash particles with specific percentages of elements, thereby producing its own chemical fingerprint by which its ash can be identified (e.g. Fiacco *et al.* 1993, Zielinski *et al.* 1995, Zielinski *et al.* 1997a). Volcanic ash particles can be detected from ice cores and they are important for dating (Palais *et al.* 1990, Zielinski *et al.* 1997b, Zielinski *et al.* 1998). The largest basaltic fissure eruption in historic times was Laki (1783 AD) in Southern Iceland (Thordarson & Self 2003). A strong SO_4^{2-} and H^+ signal corresponding to an age of 1783 has been reported in many ice cores from the Northern hemisphere (Fiacco *et al.* 1994, Zielinski *et al.* 1994, Thordarson *et al.* 1996).

2 Objectives of the Thesis

The main objectives of this Thesis were to determine water soluble ion concentrations and analyze insoluble particles from the ice core, to investigate the reliability of ion results, and to evaluate the significance of data from a climatic and environmental point of view. The research site of this Thesis was Lomonosovfonna ice cap on Svalbard (Fig. 1), and this Thesis was based on a 121 m long ice core drilled from the highest ice field at the summit of the Lomonosovfonna dome (78° 51' 53"N, 17° 25' 30"E, 1255 m a.s.l.) in 1997. The ice core covers approximately the past 800 years. More specifically, the main aims were:

1) to prove that ice core ion concentrations are comparable using different ion chromatographic methods and adjacent samples, and therefore are appropriate for paleoclimate and environmental studies. This is the first time that duplicate chemical analyses have done for such large number of samples. Adjacent samples from an ice core at the same depth are generally assumed to give the same information even though the concentrations of ions are extremely low, and the effects of snow accumulation, snow drifting and partial melting are known to vary of over lengths comparable to the diameter of an ice core (~10 cm).

2) to examine the origin of the ions and to assess the distribution of sources. To interpret the past, the composition and origin of chemical impurities deposited in Arctic snow must be known. Sources are generally marine, terrestrial, anthropogenic, biogenic and volcanic.

3) to evaluate climatic, environmental and post-depositional changes from ice core ion results. Different climatic periods and anthropogenic effects are sometimes possible to detect using long term ion profiles because ions provide information on past atmospheric composition. The LIA and the end of the LIA (in Svalbard 1920) and industrialization should be observed in this ice core because it covers about the past 800 years.

4) to characterize the insoluble fraction of ice core samples. Svalbard ice cores have not been subject to particle analysis before. Analyses give valuable information for interpretation of ion results and have intrinsic value in themselves.

3 Experimental

Sampling, sample handling and chemical analyses of ice cores demands a lot of consideration to obtain reliable results. All possible changes in ion concentrations or particle composition were minimized when the ice core was transported and stored in frozen state until analyses. The ice core was drilled with an electromechanical drill on Lomonosovfonna (Fig. 1) in April 1997 by a multinational drilling team. The ice core was carried in the frozen state first to Norway, and then to Finland. The ice core was sampled and cleaned in a cold room (-22°C) under a laminar flow hood with strict contamination control. It was cut into 5 cm sections along its length (Fig. 2). Outer parts of the samples (the possibly contaminated parts) were removed, and the inner part then subsampled into smaller pieces. All the sample vials and caps, bottles and other containers were cleaned using ultra pure water (Millipore Milli-Q water) twice and left to soak over 24 hours. Then the equipment was placed in an ultrasonic bath for 15 min and rinsed three times with ultra pure water. Prior to use, all the equipment was rinsed once again and dried under the laminar flow hood. Samples were melted and, together with standard solutions and control samples, prepared just before analyses to prevent contamination. Clean suits, masks and plastic gloves were worn in the cold and clean rooms at all times during sampling and preparation of the samples and standard solutions.

Ion analyses were made using a Dionex ion chromatograph with conductivity detector and suppressor housed in a clean laboratory. Four major anions (Cl^-, NO_3^-, SO_4^{2-}, $CH_3SO_3^-$) and five major cations (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) in the ice core were determined. pH was measured by using a Radiometer Copenhagen pH meter and combined pH electrode. For pH measurements samples were melted under nitrogen atmosphere to prevent carbon dioxide dissolution. H^+ concentrations were calculated assuming that the activity coefficient is one. Insoluble particles were analyzed for major elements by using a Jeol scanning electron microscope combined with a Link ISIS or INCA energy dispersive spectrometer (SEM-EDS). All methods have been presented in detail in the original papers.
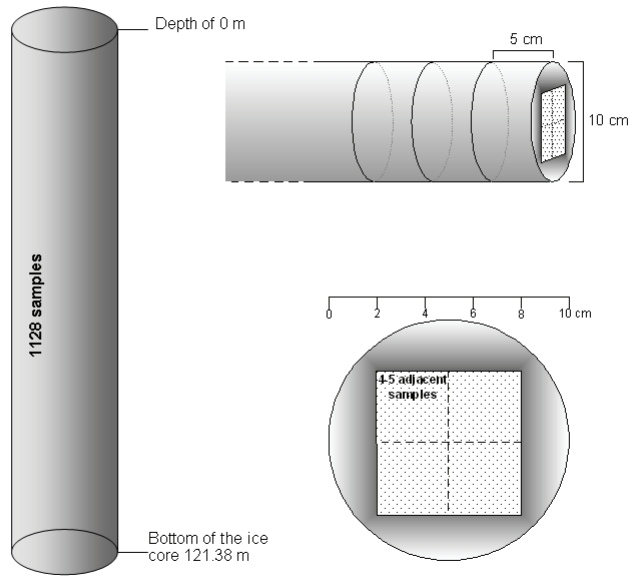
Fig. 2. The 121 m deep ice core. The 10 cm diameter ice core was first cut into 5 cm long pieces. The outer part of the core was then removed and the inner part cut into small pieces.

4 Dating

The dating of an ice core can be established using different models depending on character of the ice core. The time scale can be based on several reference horizons (volcanic eruptions, radioactive layers) and seasonal cycles of some ion or $\delta^{18}O$. The relative abundance of oxygen isotopes in ice represents mainly air temperature. Various dating methods can be used together or independently depending on frequency of reference horizons and the accumulation rates in the ice core.

The time scale of the Lomonosovfonna ice core presented in this Thesis is based on an ice layer thinning model (Nye 1963) tied with the known dates of prominent reference horizons (1963 radioactive ^{137}Cs layer (Pinglot *et al.* 1999) and 1783 Laki volcanic SO_4^{2-} layer and volcanic tephra layer). The ice core is well dated to ⅔ depth using reference horizons (Fig. 3). The upper part of the ice core also agrees with annual cycle counting (Pohjola *et al.* 2002b). About ⅓ of total ice thickness has no direct dating, however there are a number of observations that give confidence to simple flow modeling: the basal ice layers show no disturbances in stratigraphy and no basal debris bands are observed. The accumulation rate is 0.41 m w.eq. a^{-1} for 1963-1997 and 0.31 m w.eq. a^{-1} for earlier periods. 5 cm spans 1/8 of a year near the surface but a whole year at 90 m depth. A detailed description of the dating can be found in Paper II and further credence for the timescale based on dating of volcanic signals back to 1259AD can be found by analysis the SO_4^{2-} record in paper III.
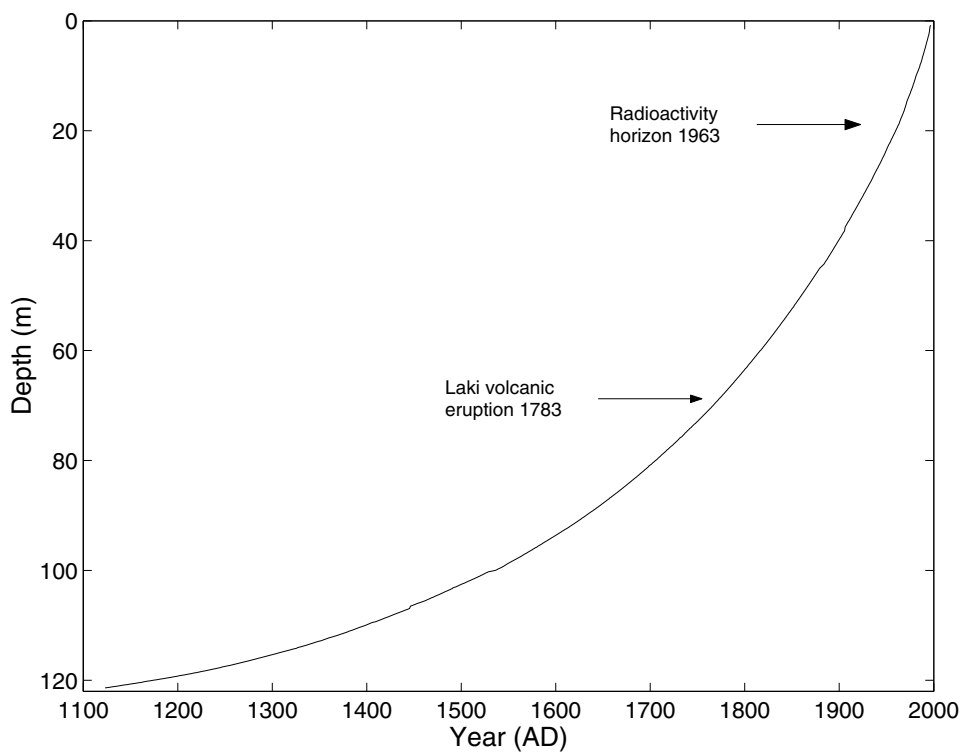
Fig. 3. The time scale of the ice core. Reference horizons are marked in the figure: 1963 radioactive ^{137}Cs layer and 1783 Laki volcanic SO_4^{2-} layer.

5 Results and discussion

5.1 Reliability of ice core anion results (Paper I)

Reliability of ion results was investigated by analyzing anions (Cl^-, SO_4^{2-}, NO_3^-) of adjacent ice core samples in nearly 500 pairs from the same depth (from the deepest 60 m of the ice core) using two different columns and eluents. Sets of analyses were performed entirely independently of each other and all samples were analyzed in random depth order. The two methods had different detection limits for every anion.

The anion results showed that there were small but statistically significant differences in the mean concentrations from the adjacent samples in Cl^- and SO_4^{2-} (5-6 μgL^{-1}) but not in NO_3^-. The Dionex AS15 column showed higher mean concentration for Cl^- whereas the Dionex AS9 column had higher for SO_4^{2-}. NO_3^- had the closest correspondence between two samples from the same depth. NO_3^- is known to be rather mobile due to post-depositional processes and hence had most likely a truly more equal distribution in the core than Cl^- and SO_4^{2-}. 2% of all samples had very high concentration differences (> 3σ) between the adjacent samples. The distribution of the large concentration differences appears random. This was probably result of real glaciological effects due to chemical components being adsorbed onto particle surfaces rather than any flaw in the IC measurement.

Even though single adjacent samples did not record exactly the same concentration and ion chromatographic methods showed some differences in concentrations, ions still provided reasonably comparable results for time series analyses and can therefore be used with confidence to detect the chemical composition of the atmosphere in the past (Fig. 4).
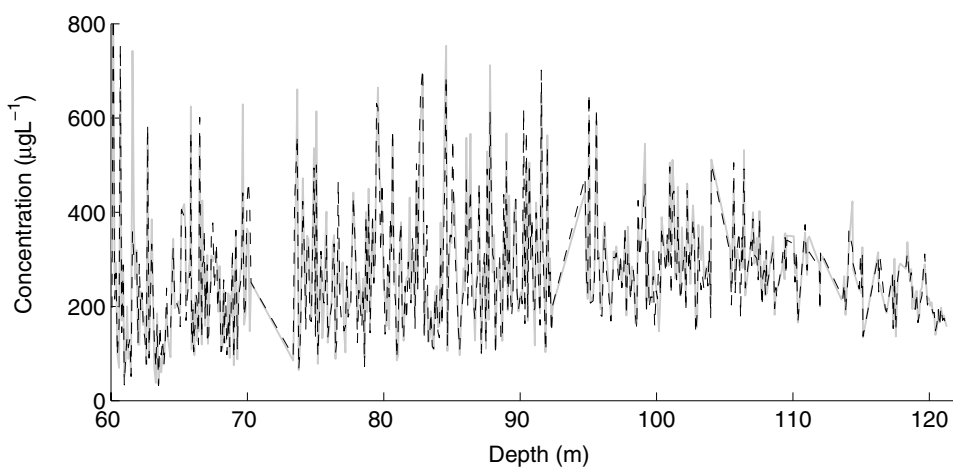
Fig. 4. Cl⁻ concentrations in adjacent ice core samples using two different IC methods Dionex AS9 (dotted line) and AS15 (solid line).

5.2 Na$^+$, Cl$^-$, K$^+$ and Mg^{2+} (Papers II and VII)

Na$^+$ and Cl$^-$ accounted for about 63% of all ions in the whole of the Lomonosovfonna ice core (Fig. 5). The maritime location of the ice core and the fact that the mean Na$^+$/Cl$^-$ ratio (0.93 calculated in μeqL^{-1}) was near that of bulk seawater (0.86) indicated that both Na$^+$ and Cl$^-$ were mostly of marine origin. Detailed study of Na$^+$/Cl$^-$ ratio (Fig. 6) showed that some anthropogenically derived Cl$^-$ was detected between 1970 and 1990, and it was most probably as an influx of HCl. From the 1900s to the 1960s and 1985-90 loss of Cl$^-$ was observed. Volatile HCl can be created by the reaction of sea salt aerosols with atmospheric acids (HNO$_3$, H$_2$SO$_4$). Mean ion balance (Fig. 5) showed that there is unmeasured anion in the ice core and detailed ion balance and Na$^+$/Cl$^-$ ratio indicated some small amount of terrestrial Na$^+$ (probably Na$_2$CO$_3$) before 1730 (Fig. 6).
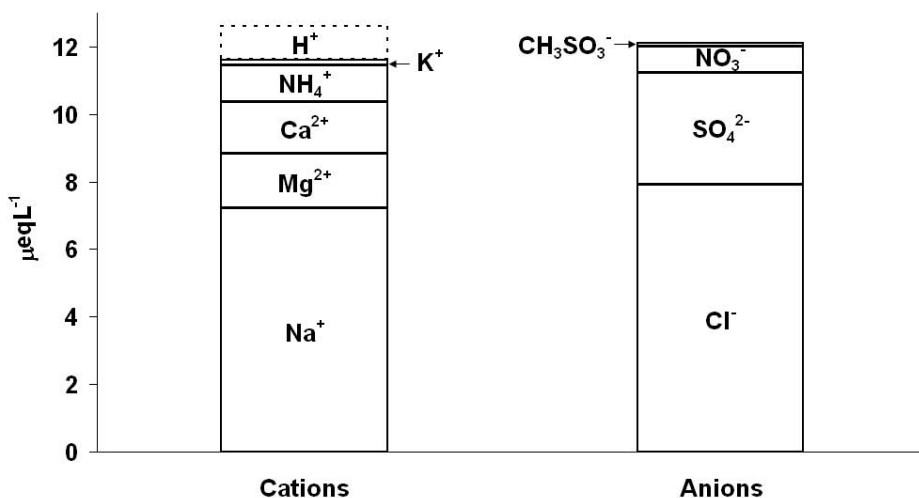
Fig. 5. Mean ion concentrations covering the whole ice core. H$^+$ concentrations have been measured only from the deepest 60 m of the ice core.
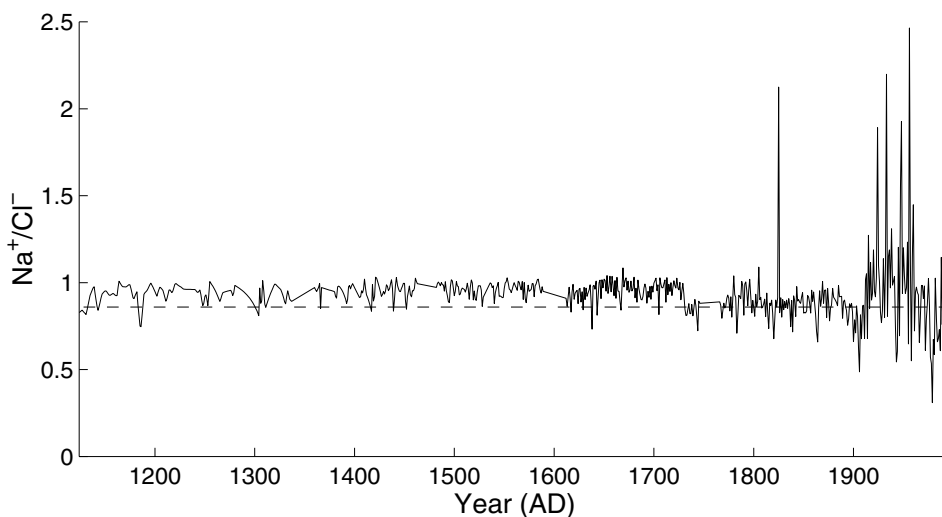
Fig. 6. The yearly values of Na$^+$/Cl$^-$ ratio calculated in µeqL^{-1}. The bulk sea salt ratio is marked by the dashed line.

All of Mg^{2+} and 92% of K$^+$ were derived from sea salt aerosols based on sea salt ratio, assuming that all Na$^+$ comes from sea water (Wilson 1975). Some Mg^{2+} was depleted by elution from the snow pack especially during the 20th century and before 1400 (Fig. 7). Mg^{2+} is reported to be rather mobile and has affected by migration and post-depositional movement (Kreutz *et al.* 1998, Iizuka *et al.* 2002). Despite the high sea salt percentage Mg^{2+} certainly also had terrestrial sources in this ice core because it correlated with SO$_4^{2-}$

and not sea salts. Broad features of the $\delta^{18}O$ profile and nss-Mg^{2+} indicated correlation, with low $\delta^{18}O$ values (cold) associated with positive nss-Mg^{2+} and high $\delta^{18}O$ values (warm) associated with negative nss-Mg^{2+}. Iizuka *et al.* (2002) reported that nss-Mg^{2+} can be used as an indicator of melt and hence warm temperatures consistent with the Lomonosovfonna ice core.
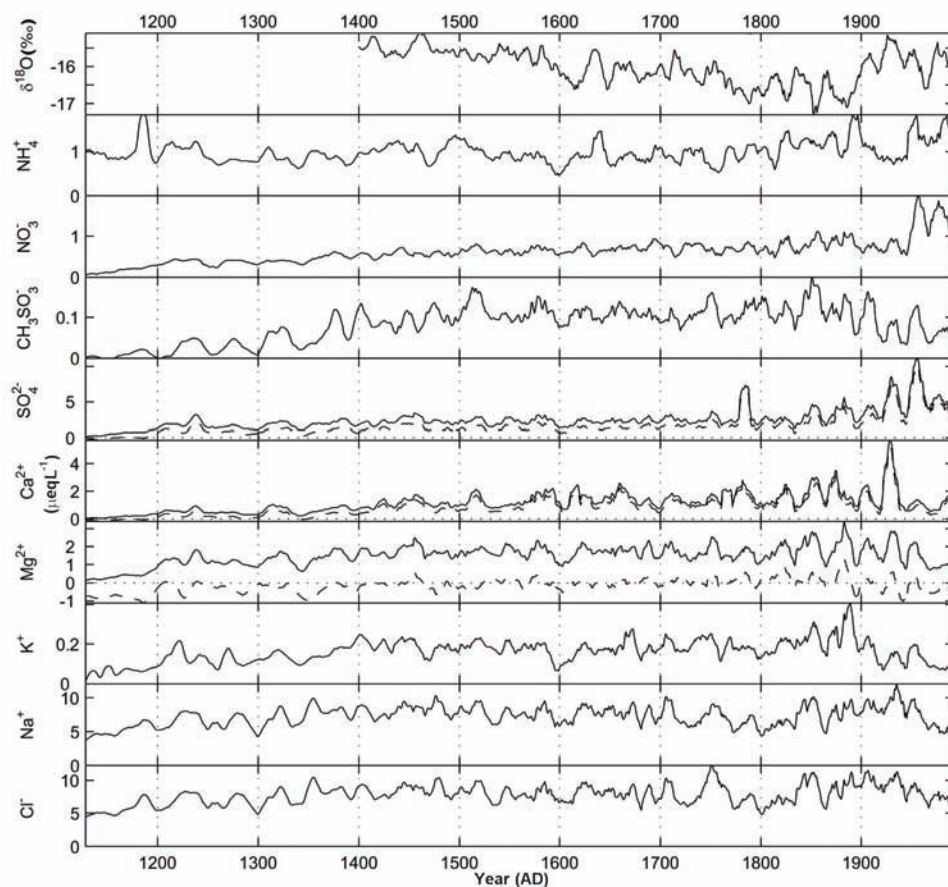
Fig. 7. Time series of water soluble ion concentrations. Yearly values were calculated from the original 5-10 cm resolution data and 10 years running means were taken. Nss-Mg^{2+}, nss-Ca^{2+} and nss-SO_4^{2-} are marked by dashed lines and $\delta^{18}O$ profile is adapted from Isaksson *et al.* (2003).

All major sea salt ion concentrations (Na^+, Cl^-, K^+ and Mg^{2+}) started to decrease after the beginning of the 20th century but after 1950 concentrations were even lower. Melting and elution could have been an explanation for the decrease of these ions, with K^+ and Mg^{2+} more easily lost from the core than Na^+, as had been observed elsewhere (Iizuka *et al.* 2002, Davies *et al.* 1982, Pohjola *et al.* 2002a, Tsiouris *et al.* 1985). However, SO_4^{2-}, NO_3^- and NH_4^+, that are also easily lost, have high concentrations during 20th century. Snow pit samples, collected from Lomonosovfonna in spring before any summer melting

affected concentrations, show the same concentration range as found in the ice core during the 1990s. This strongly suggests that concentrations are actually lower in the 1980s and 1990s than in the mid-20th century (Virkkunen 2004).

In general Na^+, Cl^-, K^+ and Mg^{2+} concentrations along the entire core illustrated rather similar concentration profiles in the Lomonosovfonna ice core (Fig. 7) and were rather variable with complex association to climatic variations.

5.3 SO_4^{2-} (Papers II and III)

In the Lomonosovfonna ice core SO_4^{2-} was the next abundant ion after Na^+ and Cl^- and represented about 14% of total ions (Fig. 5). Sea salt and non-sea salt fractions are shown in Fig. 7 and clearly nss-SO_4^{2-} was the dominant fraction. 74% of total SO_4^{2-} was nss-SO_4^{2-} and since 1950 over 88%. Only one volcanic eruption, the Laki, was easily detected (Section 5.3.1) and terrestrial SO_4^{2-} usually was present together with Ca^{2+} (Section 5.6) and/or Mg^{2+}. Therefore in the pre-anthropogenic period, most of the SO_4^{2-} was from marine biogenic production (Section 5.4). In the 20th century CH_3SO_3H and SO_4^{2-} concentrations had correlations over decadal periods (Fig. 7), such obvious co-variation indicated that biogenic SO_4^{2-} is a major SO_4^{2-} source even though anthropogenic inputs were already present. Models of the SO_4^{2-} record also suggest that even in the 20th century marine biogenic sources were dominant accounting 30-55% of total SO_4^{2-} budget.

SO_4^{2-} concentration dependence on regional emission records (Stern 2005, Tuovinen *et al.* 1993), suggests that the only anthropogenic source is from Western Europe, and that it accounted for 10-25% of total SO_4^{2-} in the 20th century (Fig. 8). Comparison with other SO_4^{2-} concentration data in Svalbard indicated that Lomonosovfonna ice cap was dominated more by SO_4^{2-} enriched air masses from the Barents Sea direction (East) than Vestfonna ice cap (Matoba *et al.* 2002), but clearly less than Ny-Ålesund area (Teinilä *et al.* 2003, 2004).
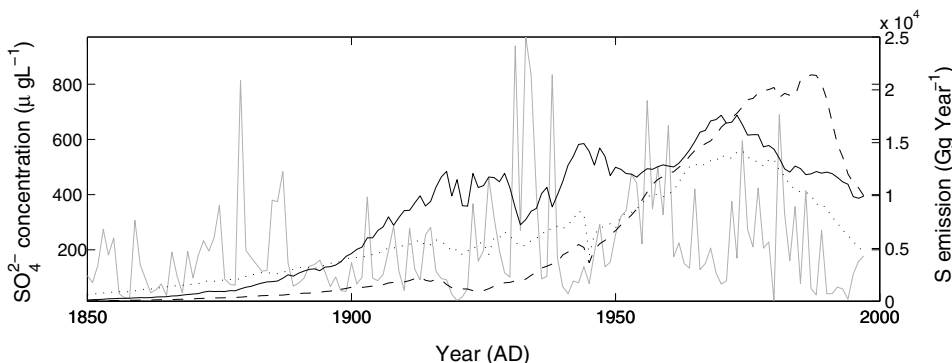

Fig. 8. The regional SO_2 emissions for North America (black), Eastern Europe (dashed) and Western Europe (dotted) (Stern 2005), and the yearly values of SO_4^{2-} concentration of the ice core (grey).

5.3.1 Volcanic tephra layer (Papers IV and III)

A clear feature in the SO_4^{2-} and H^+ concentration profiles was the large peak at a depth of 66.79 m (Fig. 9). A volcanic tephra layer of basaltic composition was found 10-20 cm deeper than where the high SO_4^{2-} and H^+ concentration peaks were observed. The tephra layer consisted mostly of sand and silt particles (approximately half a million in 10 ml meltwater) showing very clearly that not only light ash particles were transported from the eruption site. The relative locations of the acid and particle layers showed that tephra arrived to ice cap 6-12 months earlier than gaseous SO_2 was deposited on the ice cap as H_2SO_4. The H_2SO_4 precipitation lasted 9-15 months. Immediately after the high SO_4^{2-} concentration peak, the $\delta^{18}O$ record indicated a sudden drop of temperatures of about 2°C.

A volcanic ash particle analyzed using SEM-EDS had the same chemical composition as reported earlier from Icelandic Laki volcanic ash particles in the 1783 eruption (Fiacco *et al.* 1994). In contrast to many ice core records, other volcanic signals were not clearly present in the Lomonosovfonna SO_4^{2-} concentration record. This was apparently because of the maritime conditions around Svalbard leading to fluxes of both sea salt and marine biogenic SO_4^{2-}, together with relatively high annual precipitation diluting volcanic SO_4^{2-} input. However, the residuals from Multiple Regression Analysis models displayed occasional very large positive spikes that are likely volcanic eruptions.
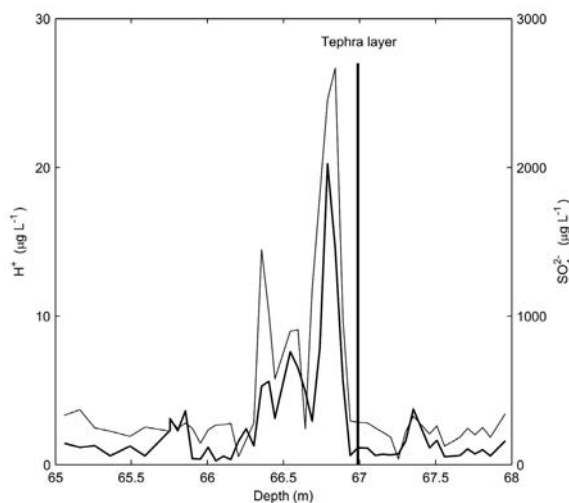

Fig. 9. SO_4^{2-} (thick) and H^+ (thin) concentrations near by Laki eruption. Tephra layer is marked in vertical line.

5.4 $CH_3SO_3^-$ (Papers V and II)

$CH_3SO_3^-$ was the minor ion of total ion budget as it is generally in most ice cores (Fig. 5). Prior to the end of the LIA the $CH_3SO_3^-$ concentrations were about 100% higher than after it (Fig. 7). During the LIA the sea ice coverage was more widespread than after it and $CH_3SO_3^-$ concentrations indicated that periods with large sea ice extent seem to coincide with high CH_3SO_3H content. $CH_3SO_3^-$ concentrations were rather stable during the LIA, so a constant flux of biogenic production seems likely. The decrease of $CH_3SO_3^-$ concentrations after the end of the LIA reflected the reduction in sea ice around Svalbard in about 1920 (Vinje 2001), which certainly caused changes in the local biogenic production. However, O'Dwyer *et al.* (2000) reported that between 1920 and 1997 there was a negative correlation between sea ice, SST in the Barents Sea and CH_3SO_3H on the sub-decadal scale in the Lomonosovfonna ice core. Hence the $CH_3SO_3^-$ concentration record reflects both a record of sea ice variability on multi-decadal scales and SST-sea ice on the sub-decadal scale. Presumably lower concentrations prior the 15th century reflected simple loss of ions by elution because $CH_3SO_3^-$ is relatively easily eluted, rather than less sea ice around Svalbard.

5.5 NO_3^- and NH_4^+ (Papers VI and II)

NO_3^- and NH_4^+ represented about 3% and 5% of total ions, respectively (Fig. 5). The NO_3^- record shows a rise in concentrations from the 12th century to the mid-16th century, reasonably stable concentrations until the mid-19th century and a rise in concentrations into the 20th century. The most obvious feature is the increase of NO_3^- concentrations in the mid-20th century which was surely due to increasing industrial emission. The record of global NO_x emissions show slight increases from the 1860s and sharp rises around the mid-20th century (Klimenko *et al.* 2000). The rise in NO_3^- concentrations was consistent with the rapid growth of NO_x emissions in Eurasia and North America (Erisman & Draaijers 1995) (Fig. 10). Maximum concentrations in the ice core were reached in the mid-1970s and mid-1980s. From the mid-1980s to 1997, NO_3^- concentration dropped rapidly, which could have been an effect of the strict pollution controls on NO_x.

NO_3^- and NH_4^+ concentrations showed more similar profiles than NO_3^- and SO_4^{2-} even though they all have anthropogenic sources. NO_3^- concentrations showed the most dramatic increase later than SO_4^{2-}, and NO_3^- also showed a large peak mid-1980s when SO_4^{2-} concentrations were relatively low (Fig. 7). NH_4^+ showed a slight increase in the mid-20th century that was probably due to anthropogenic inputs. However, NH_4^+ concentrations were rather high along the entire core and therefore the increase was not as considerable as for SO_4^{2-} and NO_3^-.

The correlation between NH_4^+ and NO_3^- concentrations indicated that NH_4NO_3 has been common at Lomonosovfonna before 1920 and after 1960. In recent years this was presumably related to anthropogenic inputs but the correlation during the earlier period suggested naturally significant sources of NH_4NO_3.

The close stoichiometric ratio suggested there was $Ca(NO_3)_2$ in the core. Röthlisberger *et al.* (2000) suggested that Ca^{2+} might be associated with NO_3^- via the stabilizing effect

of dust particles. Aerosol samples in Ny-Ålesund showed that NO_3^- was bound to terrestrial particles during the summertime (Teinilä *et al.* 2003) and Teinilä *et al.* (2003) assumed that NO_3^- and Ca^{2+} had a local source during the Arctic summer. Thus later studies suggested that Ca^{2+} and NO_3^- were bound together before deposition rather than as a result of post-depositional movement.
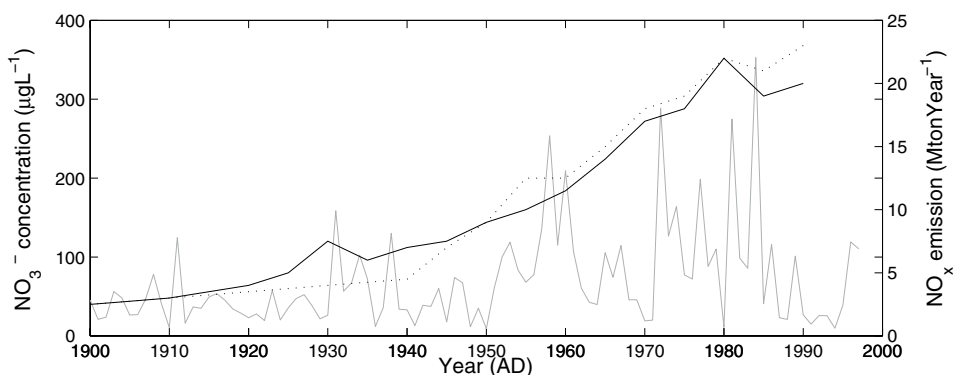

Fig. 10. Trends in emissions of NO_x in North America (black) and Eurasia (dotted) (Erisman & Draaijers 1995), and the yearly values of NO_3^- concentration of the ice core (grey).

5.6 Ca^{2+} (Papers II and VII)

Nss-Ca^{2+} amounted to 80% of total Ca^{2+} (Fig. 7) and Ca^{2+} accounted for about 7% respectively of the total ions (Fig. 5). Ca^{2+} had high concentrations and displayed great variability from the mid-18th to the mid-20th century, which includes the coldest part of the LIA according to the Lomonosovfonna $\delta^{18}O$ profile (Fig. 7) (Isaksson *et al.* 2005a, 2005b). Ca^{2+} and SO_4^{2-} sometimes peaked together independently of Na^+, K^+ and Mg^{2+}, for example in the second half of the 18th century. SO_4^{2-} and Ca^{2+} also exhibited 25-33 year quasicoperiodicity that reflected a terrestrial $CaSO_4$ source. Ca^{2+} showed a clear decrease in concentrations since 1950, possibly due to an increase in accumulation preventing wind erosion of local dust sources, because Ca^{2+} is relatively unaffected by melt.

Snow pit samples showed high Ca^{2+} concentration close to the summer melt layer on Lomonosovfonna (Virkkunen 2004), and Ca^{2+} in aerosols at Ny-Ålesund (Fig. 1) had larger Ca^{2+} concentrations during summer periods (Teinilä *et al.* 2004, 2003). This strongly supported the Ca^{2+} sources are mainly from local rock surfaces with seasonal snow cover and are sensitive to wind speed and extent of snow free source area. However, the lack of any relationship with accumulation, suggested that wind speed might be more important (Steffensen 1997).

5.6.1 CaCO₃ (Paper VII)

Insoluble fractions from the melted ice core samples indicated that $CaCO_3$ particles were present in this ice core. According to the morphology of particles (by SEM imagery) some of the $CaCO_3$ particles were calcite and aragonite. In addition some spherical shaped particles were identified as probably vaterite, which were in the process of changing to calcite. We found only small particles which were therefore wind blown dust from local evaporite areas, rather than formed on the glacier from situ spring melt water. The Gipsdalen evaporite region (consisting of marine carbonates and evaporites) is present in Billefjorden, near the Lomonosovfonna ice cap which would provide a ready source of $CaCO_3$ particles. The rare and generally unstable hexagonal vaterite form had only previously been detected in nature in the Canadian High Arctic (Grasby 2003).

5.7 Ion sources at different time periods (Paper VIII)

The ice core ion data can be naturally split into four groups: pre-industrial period that was in the middle of the LIA, period immediately before the end of the LIA (before 1920), period immediately after the end of the LIA (after 1920), and period after 1950 dominated by anthropogenic input. Performing Principal Component Analysis (PCA) on each group brought out the impact of bubbly and clear ice facies (caused by changes in seasonal melting) and the nature of relationships between ions. PCA indicated that climate variability is more dominant in the ice core as source of ionic variations than melt water percolation. PCA showed that Na^+ and Cl^- were clearly from the same source in the pre-industrial period. In the anthropogenic period Na^+ and Cl^- indicated excess Cl^- from anthropogenic sources. SO_4^{2-} and NO_3^- were closer associated in the anthropogenic period than pre-industrial period and this suggested anthropogenic pollution even though ions were not from identical sources (Section 5.5). Before and after the end of the LIA periods clear changes concerning $CH_3SO_3^-$ and SO_4^{2-} can be seen. Change was also noticed in concentration ratios (Section 5.4).

6 Conclusions

This Thesis and original papers show a new and detailed ice core study. The ice core suffers from modest seasonal melt but environmental information is more dominant in the ice core as source of ionic variations than melt water percolation. Continuous and accurate ion history with particle analyses from central Svalbard provides an additional knowledge for climate and environmental studies.

The 121m long ice core spans the last 800 years and includes several different periods. Changes in concentrations of soluble ions are clearly visible in different sections of the ice core. The two largest changes are the sudden termination of the Little Ice Age (determined by the retreat of sea ice cover around Svalbard in 1920), and the sharp rise in anthropogenic sources from the mid-20th century. NO_3^- and SO_4^{2-} concentrations show anthropogenic impacts starting at the end of the 19th century and a sharp increase after the mid-20th century. $CH_3SO_3^-$ concentrations are remarkably stable between the 15th and mid-18th centuries suggesting constant marine biogenic input during the Little Ice Age. At the end of the Little Ice Age $CH_3SO_3^-$ and SO_4^{2-} show sharp changes in ratios. $CH_3SO_3^-$ concentrations are much higher before the end of the Little Ice Age than after it despite the more extensive sea ice cover during the Little Ice Age. In this ice core $CH_3SO_3^-$ concentrations indicate both sea surface temperature-sea ice on sub-decadal scale and sea ice variability on multi-decadal scale. Ca^{2+} has higher and very variable concentrations from mid-18th to the mid-20th century which may be explained by higher wind speeds during the coldest part of Little Ice Age. All sea salt and terrestrial ion concentrations (Na^+, Cl^-, K^+, Mg^{2+} and Ca^{2+}) start to decrease in the mid-20th century but SO_4^{2-}, NO_3^- and NH_4^+ concentrations are still high after the mid-20th century. Therefore concentrations are in fact lower and the decreases are not due to melting and loss of ions by run-off. The bottom 10 m of the core shows anomalously low concentrations compared with the rest of the core, and this probably indicates loss of ions either during the original transformation of the snow-pack to solid ice, or by loss of ions from the ice to the bed over a much longer period.

The ice core is dominated by the large contribution from sea salt aerosol. Na^+, Cl^-, K^+ and Mg^{2+} concentrations account for about 70% of the whole ice core water soluble ion concentrations. Sea salt ratios show that Ca^{2+} is mostly a terrestrial ion and primarily from local sources. Ca^{2+} exhibited 25-33 quasicoperiodicity with SO_4^{2-} showing a $CaSO_4$ source but no correspondence with known climatic events has yet been found. SO_4^{2-} is

mainly from marine biogenic sources in the pre-industrial period and also plays a considerable role in the 20th century. After the mid-20th century the significant source for SO_4^{2-} is the anthropogenic as one, it is also for NO_3^-, and partly for NH_4^+ and Cl^-. Even though SO_4^{2-} and NO_3^- are both anthropogenic they show different source origins. NH_4^+ concentrations show more similarities with NO_3^- indicating a NH_4NO_3 source. Emission profile models of SO_2 show that anthropogenic SO_4^{2-} originates only from Western European sources. Emission profiles of NO_x are compared with NO_3^- but deficiencies in the emission profiles mean that source area is not so clear.

The main interest in the study of insoluble particles was to get more information on the high SO_4^{2-} concentration and acidity peak at the depth of 66.69-66.89 m that is due to the Laki volcanic eruption. The analysis indicated a volcanic tephra layer near to this layer. The tephra layer includes a huge amount of sand and silt particles which suggests that not only light ash particles travel a long distances, but also much heavier sand and silt particles. Tephra arrived at the ice cap about 6-12 months earlier than gaseous SO_2. After H_2SO_4 deposition, the $\delta^{18}O$ record displays a sudden drop in temperature. The geochemical compositions of volcanic tephra are basaltic, and the geochemical signature of an ash particle shows derivation from the Icelandic Laki volcanic eruption in 1783.

Ice core samples that were studied at the same depth as high Ca^{2+} concentrations by using SEM showed insoluble $CaCO_3$ particles. The morphology of $CaCO_3$ particles shows several polymorphs: calcite, aragonite and probably the unusual vaterite. A possible source for the particles is the Gipsdalen evaporites in Billefjorden near Lomonosovfonna ice cap. The water soluble Na^+/Cl^- ratio shows CO_3^{2-} is also associated with Na^+. Particle analysis and ion concentrations indicate that both Na_2CO_3 and $CaCO_3$ are present in this ice core. Na^+/Cl^- ratio shows a considerable and abrupt change around 1730 which suggests inaccessibility of source evaporites due to a change in snow cover, no other known climatic factor has been found.

Ion concentrations in ice cores are so small that, from a chemistry point of view, there is always doubt how accurate concentrations are. Therefore the reliability of anions concentrations is an important part of the Thesis. It was shown that there are statistically significant differences in mean concentrations for Cl^- and SO_4^{2-} , which are however, explainable if only 2% of the samples have large differences in concentrations over a distance of about 10 cm. This comparison also shows that glaciological noise level is not remarkable, and it is less than the typical accuracy of IC measurements. Despite some differences in concentrations, long term anion profiles are almost equal and therefore adjacent samples measured by using two different procedures are repeatable and ice core ion results are sound for paleoclimate and environmental studies.

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