Atmospheric Environment 120 (2015) 137-143

EISEVIED

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Mineral dust and major ion concentrations in snowpit samples from the NEEM site, Greenland



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HIGHLIGHTS

• We provide mineral dust and major ion records in a 3.2-m snowpit from Greenland.

• The snowpit covers a six-year period from spring 2003 to summer 2009.

• An anomalous dust event was occurred at the winter-spring 2005/2006 period.

• A back trajectory analysis suggests possible Asian dust source regions.

ARTICLE INFO

Article history: Received 10 April 2015 Received in revised form 20 August 2015 Accepted 21 August 2015 Available online 24 August 2015

Keywords: Atmospheric mineral dust Major ions Seasonal variation Greenland

ABSTRACT

Polar ice sheets conserve atmospheric aerosols at the time of snowfall, which can be used to reconstruct past climate and environmental conditions. We investigated mineral dust and major ion records in snowpit samples obtained from the northwestern Greenland ice sheet near the North Greenland Eemian Ice Drilling (NEEM) camp in June 2009. We analyzed the samples for mineral dust concentrations as well as stable water isotopes ($\delta^{18}O$, δD , and deuterium excess) and major ions (Cl⁻, SO₄²⁻, methanesulfonic acid (MSA), Na⁺, and Ca²⁺). Seasonal $\delta^{18}O$ and δD cycles indicate that the snowpit samples covered a six-year period from spring 2003 to early summer 2009. Concentrations of mineral dust, nss-Ca²⁺, and nss-SO₄²⁻ showed seasonal deposition events with maxima in the winter—spring layers. On the other hand, the Cl⁻/Na⁺ ratio and the concentrations of MSA exhibited maxima in the summer layers, making them useful indicators for the summer season. Moreover, an anomalous atmospheric mineral dust event was recorded at a depth of 165–170 cm corresponding to late winter 2005 to spring 2006. A back trajectory analysis suggests that a major contributor to the Greenland aerosol was an air mass passing over the Canadian Arctic and North America. Several trajectories point to Asian regions as a dust source. The mineral dust deposited at NEEM was strongly influenced by long-range atmospheric transport and dust input from arid source areas in northern China and Mongolia.

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1. Introduction

Past climate and environmental records imprinted in the polar ice sheets reflect the atmospheric conditions at the time of snowfall. Numerous studies of snow chemistry and mineral dust in snow

http://dx.doi.org/10.1016/j.atmosenv.2015.08.062 1352-2310/© 2015 Elsevier Ltd. All rights reserved. and ice have been carried out on ice cores and snowpit samples from the Greenland ice sheet to provide information about past climate and environmental changes (Dansgaard et al., 1993; Mayewski et al., 1993; Steffensen, 1997). In particular, the strong correlation between mineral dust concentrations and climate variability in Greenland ice cores indicates an increase of dust concentrations during the last glacial period, which can be influenced by characteristics of the source regions and atmospheric transport patterns (Biscaye et al., 1997; Fischer et al., 2007; Ruth et al., 2003).

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Greenland, as well as Antarctica, are important regions for ice core science because both areas provide unique access to past climates and environments (Jouzel, 2013). Since the 1950s, intensive efforts have been made to extract deep ice cores from the Greenland ice sheet, beginning with the Camp Century ice core and continuing with the recent North Greenland Eemian Ice Drilling (NEEM) ice core. The NEEM project is an international ice core research project designed to obtain a new and undisturbed ice core climate record reaching back through the previous interglacial period, the Eemian (130-115 ka BP). The project successfully completed a 2540-m long ice core, several shallow cores, snowpit studies, and meteorological monitoring during the 2008-2012 field campaigns. The deep ice core contains valuable information about past climate throughout the previous interglacial period. The oldest climate record extracted from the NEEM ice core now reaches to 128.5 ka BP (NEEM Community Members, 2013).

In this paper, as a part of the NEEM snowpit study, we present data acquired from a snowpit in June 2009. The study focuses on the determination of seasonally resolved stable water isotopes, major ions, and mineral dust records from the NEEM for the period from 2003 to 2009. In a previous study, seasonal variations of snow chemistry at NEEM were investigated on samples taken close to our site, but no mineral dust record was studied (Kuramoto et al., 2011). The presented study of the relationship between snow chemistry and mineral dust in the Greenland ice sheet will contribute to a better understanding of processes controlling Greenland's climate and environment.

2. Experimental section

2.1. Sampling and sample preparation

As a part of the NEEM project, we excavated a snowpit on 26 June 2009 at the NEEM study site in northwestern Greenland (Fig. 1). As the dominant wind direction at the NEEM site is south, we selected a sampling site approximately 1.0 km southeast of the NEEM camp (77°26'N, 51°03'W, 2461 m a.s.l.) to minimize the influence of human activities. We followed clean protocols and took great precautions during all steps of all laboratory and field activities including bottle preparation, sample collection, handling, and storage to prevent sample contamination (Hong et al., 2000; Hur et al., 2007). Briefly, we cleaned the sample bottles four times using reagent grade nitric acid, 25% Suprapur grade nitric acid (Merck Millipore, USA) and twice with 0.1% Optima grade nitric acid (Fisher Scientific, Canada). We then washed the bottles three times with Milli-Q water and twice with sub-boiled water, and dried the bottles in a Class 10 clean bench. During the field campaign, all personnel wore full clean room suits, polyethylene gloves, and particle masks. We dug a 3.2-m snowpit using metal shovels and then removed snow from the wall of the pit using pre-cleaned LDPE shovels, obtaining a continuous series of 70 snow samples with an acid-cleaned PTFE tube and hammer. The snow samples were transferred into acid-cleaned 1 L LDPE bottles. All sample bottles were double-sealed in polyethylene bags and transported back to the laboratory at the Korea Polar Research Institute (KOPRI). The samples were kept frozen at -20 °C until analysis. To prevent contamination during sample preparation, aliquots were prepared using a Class 10 clean bench in a Class 1000 clean room at KOPRI. Samples were melted in the clean bench at room temperature. The samples were then transferred to 20 mL high-density polyethylene vials (Wheaton, USA) for stable water isotopes and ion analysis and 25 mL polystyrene Accuvette cups (Beckman Coulter, USA) for dust analysis. All vials and cups were washed three times with Milli-Q water (Merck Millipore, USA) before use.



Fig. 1. Location map of NEEM and other deep ice coring sites in Greenland.

2.2. Instrumental analysis

Stable water isotopes were analyzed using a Picarro L1102-*i* wavelength-scanned cavity ring-down spectrometer (WS-CRDS) (Picarro Inc., USA). Each sample was filtered using a 0.45 μ m PVDF syringe filter (Merck Millipore, USA) and then transferred to a 2 mL glass vial. The vial was cleaned three times with Milli-Q water and dried for 24 h at 80 °C before use. Samples were injected using a syringe and vaporized at 110 °C. Vienna Standard Mean Ocean Water (VSMOW2), Greenland Ice Sheet Precipitation (GISP), and Standard Light Antarctic Precipitation (SLAP2) were used as certificated reference materials (CRMs) to correct for measurement biases. The isotopic measurements were converted to the VSMOW-SLAP scale by measuring standards of known isotopic composition. To correct for drifts, GISP was measured every five samples. The measurement accuracies for δ^{18} O and δ D were 0.08 and 0.15‰, respectively.

Major ions (Cl⁻, methanesulfonic acid (MSA), Na⁺, Ca²⁺, and SO_4^{2-}) in the snowpit were analyzed by ion chromatography using Dionex ICS-2000 and ICS-2100 systems (Thermo Fisher Scientific Inc., USA). Anions were measured using a Dionex model ICS-2000 with an IonPac AS 15 column and KOH eluent (6–55 mM). Cations were measured using a Dionex model ICS-2100 with an IonPac CS 12A column and MSA eluent (20 mM). Detection limits of major ions were calculated as three times the standard deviation of blank measurements, which ranged from 0.01 to 0.26 ng mL⁻¹. Diluted BCR-408 (1:1000) certified reference material (simulated rain water) was used to test the accuracy of the measurements (Hong et al., 2015).

The analytical procedure for dust concentration and size distribution was adopted from previous studies with minor modifications (Delmonte and Maggi, 2002; Steffensen, 1997). The measurements of dust concentration and size distribution were performed using a Multisizer 3 Coulter Counter (Beckmann Coulter, USA) with a 50 um diameter aperture tube in a Class 100 clean booth. The melted snow sample was made conductive by the addition of a pre-filtered 20% NaCl solution to obtain a 2% electrolyte solution. The samples were continuously stirred before analysis to avoid dust sedimentation in the Accuvette cups. Three consecutive measurements were performed on each 500 µL volume. The Coulter Counter was calibrated using a Coulter CC Size Standard L5 (Beckmann Coulter, USA) with nominal 5.0 µm diameter polystyrene latex beads. The instrument was set for measurements of particles with diameters between 1.0 and 30.0 µm in 300 channels on a logarithmic size scale. Particle size is expressed by the diameter of a sphere of equivalent volume and particle mass was calculated from the measured volume assuming a mean crustal particle density of 2.5 g cm^{-3} .

2.3. Backward air trajectories

In order to assess the origin of air masses arriving at the sampling site, 10-day backward air trajectories for one year between September 2005 and August 2006 were calculated using HYSPLIT 4 (http://www.arl.noaa.gov/ready/hysplit4.html). Trajectories were calculated once a day at 0000 UTC (Coordinated Universal Time).

3. Results and discussion

3.1. Dating of the snowpit using seasonal variations of stable water isotopes

Fig. 2 shows vertical profiles of stable water isotopes ($\delta^{18}O$, δD) and deuterium-excess (d-excess; d-excess = $\delta D - 8 \delta^{18} O$) of samples from the NEEM snowpit. The isotopic signal of the snowpit record integrated meteorological information weighted by air mass deposition (Krinner and Werner, 2003). The δ^{18} O values vary between -41.7 and -23.3% with a mean of -32.9%. The δD values range between -332.0 and -179.8‰ with a mean value of -258.2%. The d-excess is characterized by values between -0.4and 11.0% with a mean value of 4.8%. The mean annual δ^{18} O composition of the NEEM firn ice core drilled in 2008 was -33.0% (Steen-Larsen et al., 2011), with a mean δ^{18} O value over the past millennium of -33.6% (NEEM Community Members, 2013). The mean d-excess value in our study was quite low compared to the average d-excess level of the NEEM firn core drilled in 2007. Unusually low d-excess values could be caused by the re-evaporation of snow crystals during precipitation or low kinetic effects, which are expected if evaporation occurs over a cool ocean surface with high surface air relative humidity. The low d-excess of precipitation samples from NEEM in 2008 coincided with an Arctic northward air mass origin (Steen-Larsen et al., 2011).

The δ^{18} O and δ D depth profiles fluctuate in phase and represent recognizable seasonal patterns (Fig. 2). As both δ^{18} O and δ D are strongly correlated with temperature, the δ^{18} O and δ D data were used as temperature proxies and provide information about the temperature during snow deposition (Dansgaard, 1964). These seasonal isotope patterns were used to define seasonal layers as summer maximum and winter minimum. As our 3.2-m snowpit contained six δ^{18} O and δ D maxima and minima, we assumed six years of snow deposition, from spring 2003 to early summer 2009. This assumption is consistent with data from a 2.0-m snowpit dug at the NEEM site, which covered a four-year period from 2005 to 2009 (Kuramoto et al., 2011). A 10-m snowpit from the Summit



Fig. 2. Vertical profiles of stable water isotopes and d-excess (dashed red lines represent winter layers). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

region excavated during the 1987 field season showed a seasonal variability of δ^{18} O with summer-maximum and winter-minimum peaks (Mayewski et al., 1990). The δ^{18} O profile of a 3.35-m snowpit obtained from the Dye3 site in South Greenland also showed clear seasonal variations over a three-year period, with limited summer melt (Steffensen, 1985). The d-excess values, which depend on sea surface temperature and evaporation processes in the vapor source region (Masson-Delmotte et al., 2005), also show seasonal cycles, but are not in phase with the $\delta^{18}O$ and δD variations. The d-excess peaks are shifted compared to those of δ^{18} O and δD, with the d-excess minima occurring in spring–early summer and the d-excess maxima in the fall. The phase lag between dexcess and $\delta^{18}O$ and δD is affected by diffusion, with d-excess values driven by evaporation over the ocean, subsequent transportation to Greenland, and condensation of water vapor when snow forms (Sodemann et al., 2008). Whereas δ^{18} O and δ D in polar snow depends primarily on local temperature, d-excess in polar snow is largely influenced by the source temperature. This seasonal dexcess variation is similar to that reported for ice and snow samples from the high-altitude regions of the Greenland ice sheet (Johnsen et al., 1989; Kuramoto et al., 2011).

3.2. Mineral dust deposition records

Mineral dust in snow or ice cores consists of the insoluble fraction of atmospheric aerosols deposited on the surface of the polar ice sheets (Steffensen, 1985). As the concentration of mineral dust in snow depends on the primary supply from a source region by long-range atmospheric transport as well as depositional processes, the mass concentration of mineral dust in snow can be linked to climate variability (Drab et al., 2002). Fig. 3 shows vertical profiles of the number of particles and volume and mass



Fig. 3. Vertical profiles of mineral dust (a) number, (b) volume, and (c) mass concentrations (dashed red lines represent winter layers). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

concentrations of mineral dust in the NEEM snowpit. Mineral dust concentrations are plotted for the 1.0–6.0 μ m particle size interval. The quantity of mineral dust deposited on the Greenland ice sheet is highly variable from season to season and year to year (Steffensen, 1987). Number concentrations of the mineral dust range from 330 to 16,097 particles mL⁻¹ with a mean value of 2370 particles mL⁻¹. Volume concentrations of the mineral dust range from 1850 to 100,686 μ m³ mL⁻¹ with a mean value of 15,234 μ m³ mL⁻¹. Mass concentrations range from 4.6 to 252 ng mL⁻¹ with a mean value of 38.1 ng mL⁻¹. Mean dust mass concentrations are similar to results from analyses of the GRIP ice core from the surface to 2.75 m depth, where average mass concentrations were 46.2 ng mL⁻¹ (Steffensen, 1997).

The mineral dust profiles in our snowpit show dust deposition events with seasonal spikes (Fig. 3). The seasonal spikes usually occur in winter–spring layers due to the presence of one or two high-concentration dust samples. Relatively high dust concentrations are present in the summer layers of 2005, 2007, and 2008. At present, Greenland dust deposition shows clear seasonal variability with most of the dust being deposited during springtime, which was identified using high-resolution trace element records (Banta et al., 2008; Drab et al., 2002). The ice core study revealed that winter–spring layers are characterized by a high mineral dust content leading to high Ca²⁺ ion concentrations (Ruth et al., 2002). Seasonally resolved measurements of various mineral dust proxies show that this winter–spring pattern can be traced throughout the Holocene period (Rasmussen et al., 2006).

An anomalous atmospheric dust event is recorded at a depth of 165-170 cm, corresponding to the period between late winter 2005 and spring 2006. The mean mass concentrations are 179 ng mL⁻¹, which is approximately seven times higher than the dust concentrations of the other seasons (26.5 ng mL⁻¹). All measured ion concentrations also show maxima at the same depth (Fig. 5).

Aerosol sources for summer 2005 to spring 2006 were identified as various source-related aerosol types such as Asian dust, Saharan dust, industrial combustion, marine aerosols with combustion tracers, and well-mixed background Arctic haze (VanCuren et al., 2012). In order to investigate the origin of the dust, the HYSPLIT model was used to generate air mass backward trajectories for the NEEM site. Seasonal (SON, DJF, MAM, and JJA) and monthly trajectories (December 2005, January, February, and March 2006) are presented in Fig. 4 and Fig. S1 in the supporting information. The 10-day backward trajectories were calculated once a day at 0000 UTC (Coordinated Universal Time) for one year (September 2005-August 2006). The back trajectories arrived from various directions, including the Canadian Arctic, North America, and the North Atlantic (Fig. 4). The back trajectory analysis suggests that the major contributor to Greenland aerosols was an air mass passing over the Canadian Arctic and North America during the winterspring seasons. In addition, the back trajectories indicate a weak influence of Asian dust on the NEEM site. Several back trajectories point to Asian dust source regions in northern China and Mongolia. This attribution is supported by the results of a dust analysis of snowpit samples at NGRIP during 1998-1999 that indicated at least two eastern Asian sources for Greenland dust (Bory et al., 2002). These dust sources are believed to exist to the present day. Moreover, the dust deposition event could be explained by precipitation formed under arctic haze conditions in the atmosphere over the Greenland ice sheet (Steffensen, 1985). Arctic haze observed over the Greenland ice sheet shows a weak seasonal signal, which is associated with the weak seasonality of our dust record (Dibb et al., 2007). Potential source areas for Greenland dust can be characterized by different tracers such as Pb isotopes, isotopic ratios of Nd and Sr, and trace elements (Bory et al., 2003; Grousset and Biscaye, 2005), which will be discussed in a forthcoming manuscript.

3.3. Seasonal variations of major ions

Vertical concentration profiles of anions and cations (Na⁺, Ca²⁺, Cl⁻, SO²₄-, MSA) are shown in Fig. 5. The sample analysis from the snowpit indicates a strong maximum for all major ions at a depth of 160–175 cm.

Ca²⁺ is commonly used as a mineral dust proxy when direct measurements of mineral dust using a coulter counter or a laser counter are unavailable (Ruth et al., 2002). Concentrations of Ca²⁺ in the NEEM snowpit show seasonal variations similar to those of Na^+ and Cl^- . High Ca^{2+} concentrations can be observed in the winter-spring layers, which is in good agreement with data from the Summit site (Dibb et al., 2007). As Ca²⁺ is also present in seasalt aerosols, inputs from marine air masses may disturb the Ca²⁺ signal in coastal regions. However, because the NEEM site is distant from the ocean, the non-sea-salt (nss) fraction of Ca^{2+} is expected to be abundant. Concentrations of nss-Ca²⁺ were calculated with the equation, $[nss-Ca^{2+}] = [Ca^{2+}]-(Ca^{2+}/Na^{+})_{sea} \times [Na^{+}]$, where $(Ca^{2+}/Na^{+})_{sea}$ is using seawater ratios 0.038 (w/w). The concentrations of nss-Ca²⁺ ranged from 0.1 to 49.5 ng mL⁻¹ with an average value of 6.0 ng mL⁻¹. The average non-sea-salt fractions of Ca²⁺ were 95%. A major source of nss-Ca²⁺ would be mineral dust input by atmospheric transport from local, regional, or hemispheric source regions. Dust layers have been observed in winter-spring layers over wide areas of the Greenland ice sheet (Drab et al., 2002; Steffensen, 1987). Large deserts and arid areas in Asia such as the Gobi Desert could be natural dust sources for the Greenland ice sheet. Kuramoto et al. (2011) insisted that nss-Ca²⁺ transported to the NEEM had originated from Asian dust sources. However, the dust provenance should be confirmed by analyzing the isotopic composition of Nd and Sr or Pb of the mineral dust (Bory et al., 2003; Grousset and Biscaye, 2005).



Fig. 4. Backward trajectories of air masses arriving at NEEM for the autumn (SON), winter (DJF), spring (MAM), and summer (JJA) seasons of one year (September 2005-August 2006).



Fig. 5. Vertical profiles of major ion concentrations and Cl⁻/Na⁺ ratios (dashed red lines represent winter layers). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

The SO_4^{2-} concentrations of the Greenland ice sheet are influenced by a complex array of sources, including sea-salt aerosols, volcanic activity, marine biogenic activity, mineral dust, and burning of fossil fuels (Jaffrezo et al., 1994; Legrand and Mayewski, 1997). Concentrations of nss- SO_4^{2-} range from 0.7 to 443 ng mL⁻¹ with a mean value of 82.7 ng mL⁻¹, with average non-sea-salt

fractions of SO_4^{2-} being 98%. The nss- SO_4^{2-} record exhibits seasonal variations with maxima in the winter–spring layers. Many previous studies have reported winter–spring SO_4^{2-} peaks and seasonal variations of SO_4^{2-} from Greenland sites (Finkel et al., 1986; Mayewski et al., 1990; Whitlow et al., 1992). Geographically, the seasonal SO_4^{2-} amplitude is five times higher in the northern parts of

the ice sheet than in central Greenland (Fischer et al., 1998). The winter–spring SO_4^2 -peak at NEEM may be attributed to an inflow of air pollutants produced by fossil fuel combustion as well as natural sources (Kuramoto et al., 2011). Particularly, the winter–spring layer at 160–175 cm depth could be associated with an episode of increased mineral dust inputs. Our MSA and SO_4^2 - records indicate that DMS is not a predominant source of SO_4^2 - at NEEM due to the offset of SO_4^2 - and MSA peaks. In most cases, spring maxima of SO_4^2 - overlap with maxima in Ca^{2+} and mineral dust. The correlation coefficients of nss- SO_4^2 - with dust and nss- Ca^{2+} are 0.74 and 0.54, respectively (p < 0.01), indicating nss- SO_4^2 - inflow into Greenland together with mineral dust. However, SO_4^2 - concentrations were constantly low during a period from the end of 2007 through 2008, which may have been caused by reduced emissions of air pollutants from distant Asian source regions (Wang et al., 2010).

Concentrations of Na⁺ and Cl⁻ in polar snow and ice are used as a sea salt aerosol proxy, because they originate primarily from sea spray aerosols (Legrand and Mayewski, 1997). Na⁺ and Cl⁻ in our snowpit show seasonal variations and high concentrations in the winter-spring layers. High concentrations of Na⁺ and Cl⁻ indicate winter-spring inputs from air masses of marine origin above Greenland due to increased cyclogenesis in the North Atlantic (Drab et al., 2002). The correlation coefficient between Na⁺ and Cl⁻ is 0.621 (p < 0.01), resulting from the same provenance of the marine source. The winter-spring peaks and seasonal variations for Na⁺ and Cl⁻ are consistent with previous studies carried out at Greenland sites, including Dye3, Summit, and NEEM (Beer et al., 1991: Dibb et al., 2007: Kuramoto et al., 2011). The Cl⁻/Na⁺ ratio shows high peaks in the summer layers, as the Na⁺ concentration in seawater is lower compared to the Cl⁻ concentration (Domine et al., 2004). The peak of the Cl^{-}/Na^{+} ratio in summer supports a contribution of nss-Cl⁻ derived from gaseous HCl or anthropogenic emissions, which becomes dominant when the sea salt aerosol contribution is very low. Exchange between NaCl and H₂SO₄ or HNO₃ produces gaseous HCl when an aerosol is enriched in acidic species (Legrand et al., 2002). The summertime Arctic troposphere is an acidic environment with carboxylic acids and sulfate aerosols, and is generally contaminated with low levels of anthropogenic pollutants even during the summer season (Talbot et al., 1992). Similar to the summer maxima of δ^{18} O and δ D, the Cl⁻/Na⁺ ratio in the Greenland snowpit could be used as an indicator of the summer season.

Presence of MSA in polar snow and ice indicate marine biogenic activity (Abram et al., 2013). Concentrations of MSA show seasonal variations with maximum values mainly in the summer-fall layers of the NEEM snowpit. These seasonal variations are in good agreement with the changes in atmospheric MSA concentration from the central Greenland ice sheet (Jaffrezo et al., 1994; Li et al., 1993). The seasonal cycle is dominantly influenced by marine biogenic activities. During spring and summer, marine phytoplankton, marine algae, and benthic diatoms begin to produce dimethylsulfide (DMS), which is rapidly oxidized by hydroxyl and halogen radicals in the atmosphere and yields MSA and SO₂ (Legrand and Mayewski, 1997; Ravishankara et al., 1997). On the other hand, high MSA concentrations are present in the 2005/2006 and 2006/2007 winter layers. It is unclear why high concentrations of MSA may have occurred during the winter season, as biogenic activity is low in winter. Although MSA is believed a useful tracer of marine biogenic emissions, atmospheric MSA signals are largely perturbed by anthropogenic inputs, particularly during winter and spring with the formation of Arctic haze (Jaffrezo et al., 1994). Because mineral dust form long-range atmospheric transport occurs together with the winter MSA spikes, it is probable that MSA originated in mid-latitude oceanic regions, where phytoplankton activity has a less seasonal character (Li et al., 1993).

In conclusion, as part of an ongoing effort to develop an aerosol record at the NEEM site, seasonal records of mineral dust along with major anion and cation concentrations were presented. Our study revealed an anomalous dust deposition event with high rates of mineral dust deposition during the period from late winter 2005 to spring 2006. Measured ion concentrations also showed maximum concentrations during the same seasons. A back trajectory analysis suggests that a major contributor to Greenland aerosols was an air mass passing over the Canadian Arctic and North America. Moreover, several trajectories point to Asian dust source regions in northern China and Mongolia. These results will contribute to an improved understanding of the snow chemistry of ice cores, transport pathway variations, and will provide additional clues about what caused the dramatic variations in mineral dust conditions in Greenland over the past climate cycle.

Acknowledgments

This work was supported by a research grant (PE15010) from the Korea Polar Research Institute (KOPRI). We are thankful for the efforts of all field personnel involved in sampling during the NEEM deep ice core drilling project. The NEEM project was directed and organized by the Center for Ice and Climate at the Niels Bohr Institute and the Polar Programs office of the US national Science Foundation. The project was supported by funding agencies and institutions in Belgium (FNRS-CFB and FWO), Canada (NRCan/GSC), China (CAS), Denmark (FIST), France (IPEV, CNRS/INSU, CEA and ANR), Germany (AWI), Iceland (Rannls), Japan (NIPR), Korea (KOPRI), Netherlands (NOW/ALW), Sweden (VR), Switzerland (SNF), the UK (NERC), and the USA (US NSF OPP). The authors wish to thank the anonymous reviewers for providing helpful comments which improved the manuscript.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.08.062.

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