Suppressed ion chromatography methods for the routine determination of ultra low level anions and cations in ice cores

Mark A.J. Curran[a],*, Anne S. Palmer[b]

[a]Antarctic CRC and Australian Antarctic Division, GPO Box 252-80, Hobart, Tasmania 7001, Australia
[b]Institute of Antarctic and Southern Ocean Studies, University of Tasmania, Hobart, Tasmania, Australia

Abstract

The concentration of trace ionic species in snow and ice samples was determined using suppressed ion chromatography (IC) with conductivity detection and ultra-clean sample preparation techniques. Trace anion species were determined in a single 24-min run by combining sample preconcentration with gradient elution using $Na_2B_4O_7$ eluent. The detection limits (ranging from 0.001 to 0.006 μM) are the lowest reported in the literature. Cation species were analysed by direct injection of 0.25 ml and isocratic elution with a H_2SO_4 eluent. The clean preparation techniques showed no evidence of a difference (Student's t-test) between Milli-Q water samples analysed directly and processed Milli-Q ice samples. These robust, ultra-clean IC methods were routinely applied to the analysis of large number of samples to produce a high-resolution trace ion ice core record from Law Dome, East Antarctica. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ice cores; Anions; Cations

1. Introduction

The Antarctic ice sheet holds a unique archive of the chemical composition of the Earth's atmosphere that can be acquired by analysing ice cores. Ice core environmental records assist with past climatic reconstruction, and in turn can be used in climate models to predict future conditions. The measurement of trace chemical ionic species is a necessary tool for ice core palaeoclimatology. The major ions of interest include Na^+, K^+, Mg^{2+}, Ca^{2+}, $CH_3SO_3^-$, Cl^-, NO_3^- and SO_4^{2-}. Obtaining a high resolution record of these ions from an ice core presents a number of challenges, including low concentrations, limited sample volumes, clean preparation procedures and throughput of large sample numbers.

Ion chromatography (IC) is widely used for the determination of ionic species in melt water from snow and ice samples [1–4]. A number of modified IC techniques have been used to attain the low detection levels required, including suppressed IC [2–5], non suppressed IC [5,6] and non suppressed correlation chromatography [7]. Recently, capillary electrophoresis with a modified sample stacking injection method has been developed for trace ion analysis [8]. Some of these techniques, while having desirable detection limits, require a large effort (in terms of run time or signal processing) per sample and are not practical for routine ice core analysis with a large sample throughput. Also, there have

*Corresponding author. Tel.: +61-3-6226-1876; fax: +61-3-6226-2902.

E-mail address: mark.curran@utas.edu.au (M.A.J. Curran).

been difficulties in obtaining an anion method that can suitably separate trace quantities of $CH_3SO_3^-$ and Cl^- (weak eluting species) and elute NO_3^- and SO_4^{2-} in a single run, within a reasonable time. Suppressed IC with gradient elution has been suggested as the best method to achieve this separation [5]. Another consideration with analysis of $CH_3SO_3^-$ and Cl^- in Antarctic ice samples is that these ions usually vary inversely throughout an annual cycle (i.e. in winter Cl^- concentrations are highest and $CH_3SO_3^-$ concentrations are close to detection limits). Separation and analysis of very low levels of $CH_3SO_3^-$ is difficult in the presence of relatively high Cl^- levels.

The extraction of trace ion records from Antarctic ice cores is susceptible to contamination from many sources. A stringent protocol must be followed when preparing clean samples for analysis, particularly for ions that are easily contaminated, such as Na^+, K^+, Ca^{2+} and Cl^-. The sources of contamination are widespread and include the operator, the outer surfaces of the core, the atmosphere and laboratory equipment. The most important stage of the analytical procedure is removing the outer surfaces of the core or sample and this may be achieved in a number of ways. These include melting and washing with Milli-Q water [9,10], melting and recovering the inner portion [11,12], re-coring samples with clean vials [4], cutting with a Lexan or flame-hardened steel blade [2], shaving with a lathe [3] and scraping with a stainless steel blade [1,5].

This manuscript describes ultra-clean sample preparation procedures and suppressed IC techniques developed for the determination of trace ion species in ice cores. This study specifically addresses the problem of separating trace $CH_3SO_3^-$ amounts from relatively high Cl^- levels, while also eluting NO_3^- and SO_4^{2-} in the same run, within a reasonable time. The method is further challenged by sample volume limitations that are necessary for the production of high-resolution ice core records.

2. Methods

2.1. Ice core sample preparation and handling

Precautions were taken to minimise contamination

during core handling, sample preparation and analysis. Polyethylene gloves were worn at all times and cleaned plasticware was used throughout the laboratory. All plasticware was rinsed three times with deionised Milli-Q water (Q-water; resistivity$>$18 MΩ-cm), filled and left to soak overnight and then rinsed a further three times. Autosampler vials and caps (Dionex, California) were stored in regularly-changed Q-water, while all other plasticware was dried in a laminar flow hood and stored in plastic sealable bags until use. Prior to use, all plasticware, including polyvials and caps, were further rinsed with Q-water.

Q-water and Q-ice samples were analysed routinely to assess background or procedural blanks. Blank Q-ice was prepared in a clean 4 l container, 3/4-filled with Q-water, and placed in the freezer at $-18°C$ overnight. This ice was cut into 3 cm by 3 cm sticks, and processed in the same manner as ice core material. Three Q-ice samples were cut and cleaned before each individual ice core section was processed.

Ice cores (~1 m) were cut longitudinally using a band saw, and a 3 cm by 3 cm stick was taken from close to the centre of each core. The sticks were scored at the required sample length (e.g. 5 cm) and held in a clean vice preventing movement and breakage during decontamination. The vice was within a laminar flow hood, which directed filtered clean air over the ice. The outer 3 mm of ice were removed along the length of each sample by scraping with a precleaned (with Q-ice) microtome blade. The sample was then transferred into a 10 ml accuvette (Coulter) and stored for later analysis. All ice core processing was completed in a freezer laboratory at $-18°C$.

2.2. Standards and eluents

A single stock standard containing a mixture of all ions of interest was prepared from solutions of NaCl (Merck), K_2SO_4 (Merck), $Mg(NO_3)_2$ (Aldrich), $CaCl_2$ (Aldrich) and CH_3SO_3H (Aldrich). These solutions were prepared from AR grade salts using Q-water, and CH_3SO_3H was diluted from a 99.0% solution. The ion concentrations in the stock standard were similar to levels expected in ice cores from previous studies [13] and are shown in Table 1. The

Table 1
Concentrations of ions in the primary standard

Ion	Concentration (μM)
Na^+	44.90
K^+	7.44
Mg^{2+}	4.25
Ca^{2+}	7.31
$CH_3SO_3^-$	0.89
Cl^-	59.50
NO_3^-	8.50
SO_4^{2-}	3.72

stock standard was diluted to give a range of five working calibration standards for analysis.

A stock solution of $Na_2B_4O_7$ (anion eluent) was prepared from a 99.998% purity salt (Aldrich), and H_2SO_4 (cation eluent) was prepared from concentrated AR grade solution (98.0%, Merck). When required, these eluents were diluted to working concentrations and degassed using high purity helium (BOC gases) in an ultrasonic bath.

Gravimetric techniques were used at each stage of standard and eluent preparation, and all stock solutions were stored in a refrigerator at 4°C.

2.3. Ion chromatography system

A DX500 microbore (2 mm) ion chromatograph with a CD20 conductivity detector and GP40 gradient pump (Dionex, California) was used for ion separation and detection. Commercially available Ionpac CG12A guard and CS12A analytical columns (Dionex, California) with carboxylic–phosphonic acid functional groups were used for cation analysis. Ionpac AG14 guard and AS14 analytical columns (Dionex, California) with quaternary ammonium functional groups were used for anion separation. Eluents were stored in 1 l vessels pressurised at 8 p.s.i. using high purity helium (BOC gases), and flow-rates were maintained at 0.45 ml/min for anions and 0.40 ml/min for cations using a GP40 gradient pump (Dionex, California). Samples were loaded from an AS40 automated sampler (Dionex, California).

2.4. Analysis

Prior to analysis, samples (ice core and Q-ice)

were removed from the freezer and allowed to thaw at room temperature. Thawed samples, along with Q-water and working calibration standards were then transferred to autosampler polyvials using a micropipette (Eppendorf) within a laminar flow hood. Low volume (0.5 ml) polyvials were used for direct analysis using a sample loop and larger volume (5 ml) vials were used for preconcentration analysis. Typically, a full calibration (five standards) was run daily, with a Q-water, a high standard and a low standard run every 20 samples. The Q-ice samples were treated the same as real ice samples during the analysis stage.

3. Results and discussion

3.1. Cations

Optimum separation of cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) was obtained using 11 mM H_2SO_4 eluent, with a total run time of 10 min (Fig. 1a). This eluent

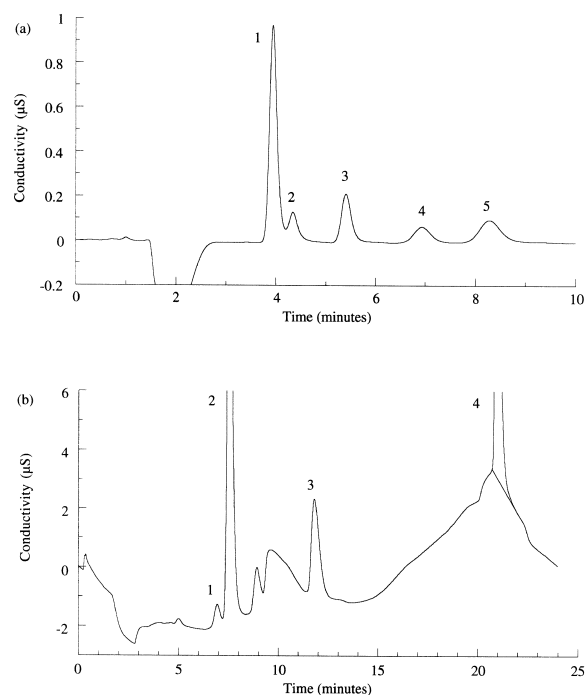Fig. 1. (a) cation chromatogram [1, Na^+; 2, NH_4^+; 3, K^+; 4, Mg^{2+}; 5, Ca^{2+}] and (b) anion chromatogram [1, $CH_3SO_3^-$; 2, Cl^-; 3, NO_3^-; 4, SO_4^{2-}].

Table 2
Calibration parameters, detection limits, precision and Q-ice tests for the final cation (loop) and anion (gradient/preconcentration) methods

Ion	Na^+	K^+	Mg^{2+}	Ca^{2+}	$CH_3SO_3^-$	Cl^-	NO_3^-	SO_4^{2-}
Range (μM)	0.3–22	0.05–3.6	0.03–2.1	0.05–3.6	0.006–0.42	0.4–28.0	0.06–4.0	0.03–1.8
Regression	$S=0.004+0.15c$	$S=0.046+0.87c$	$S=0.025+0.77c$	$S=0.056+0.44c$	$S=-0.0004+7.53c$	$S=0.005+0.15c$	$S=0.095+1.16c$	$S=0.11+0.80c$
STDE S	0.03	0.07	0.06	0.04	0.04	0.02	0.04	0.03
r^2	0.9990	0.9951	0.9961	0.9985	0.9988	0.9998	0.9979	0.9989
DL (μM)	0.01	0.01	0.02	0.01	0.001	0.006	0.005	0.004
P	0.02	0.07	0.07	0.12	0.04	0.006	0.03	0.03
Q t-test	0.85	0.52	0.91	0.12	nd	0.26	0.38	0.32

S, peak area (relative units); *c*, concentration (μM); STDE S, standard error of estimation of *S*; r^2, regression coefficient; DL, detection limit (μM) is the concentration of an ion giving a signal-to-noise ratio equal to three; *P*, precision for 20 repeats of a standard; Q *t*-test, probability from a Student's *t*-test with the null hypothesis being that the concentration distributions have the same mean; nd, non-detectable.

strength was found to give a good balance between suitable Na^+/NH_4^+ (interfering ion) resolution, minimum peak broadening for Mg^{2+} and Ca^{2+}, and run time. This method was run continuously, using the autosampler, with over 1000 samples analysed for cations every 7 days. The calibration ranges, regression equations, errors of estimation and correlation coefficients are given in Table 2. Acceptable precision values were obtained, ranging from 2 to 12% for 20 replicates of a single standard (Table 2). Suitable detection limits (0.01–0.02 μM) were achieved with a 0.25 ml sample loop (Table 2), and compare well with reported detection limits (Table 3). The differences in detection limits listed in Table 3 are mainly due to differences in injection volumes, with the exception being those reported by Doscher et al. [4]. The volumes used by Doscher et al. [4] are eight times greater than for the cation method described here, although the detection limits are only

2–3 times lower. However, it is preferable to compare detection limits in terms of concentrations rather than amounts since we are comparing the application of the methods, and often volume restrictions can apply due to limited sample volumes and system capabilities.

3.2. Anions

A sample loop was initially trialed for trace anion ($CH_3SO_3^-$, Cl^-, NO_3^- and SO_4^{2-}) determinations, however, two separate runs were required. $CH_3SO_3^-$ and Cl^- were analysed using a 0.20 ml loop and 2.0 mM $Na_2B_4O_7$ eluent with a total run time of 14 min. The more strongly retained ions, NO_3^- and SO_4^{2-}, were eluted within 9 min using a 0.25 ml loop and 10 mM $Na_2B_4O_7$ eluent. While detection limits were good and comparable to reported limits (Table 4), a single run for all anions was preferred to minimise

Table 3
Comparison of cation detection limits

Cation column type	Detection limit (μM)				Ref.
	Na^+	K^+	Mg^{2+}	Ca^{2+}	
Ionpac Fast Cation I and II[a]	0.004	0.003	0.004	0.002	[2]
Ionpac CS10[b]	0.01	0.01	0.01	0.01	[3]
Ionpac CS12[c]	0.004	0.005	0.004	0.005	[4]
Universal Cation[d]	0.02	0.03	0.02	0.03	[5]
Ionpac CS12A[e]	0.01	0.01	0.02	0.01	This study

[a] Eluent (injection volume): 19 mM HCl/0.3 mM DL-2,3-diaminopropionic acid monohydrochloride (DAP) (0.5 ml).
[b] Eluent (injection volume): 50 mM HCl/5.1 mM DAP (0.5 ml).
[c] Eluent (injection volume): 6.5 mM CH_3SO_3H (2.0 ml).
[d] Eluent (injection volume): 2.5 mM CH_3SO_3H (0.8 ml).
[e] Eluent (injection volume): 11 mM H_2SO_4 (0.25 ml).

Table 4
Comparison of anion detection limits

Anion column type	Detection limit (μM)				Ref.
	$CH_3SO_3^-$	Cl^-	NO_3^-	SO_4^{2-}	
Ionpac AS4A[a]	–	0.014	0.08	0.05	[2]
AS5A[b] or Pax-500[c]	0.003	0.014	0.024	0.01	[3]
Separon HEMA S[d]	–	0.5	0.6	0.4	[6]
Separon HEMA S[e]	–	0.2	0.4	0.1	[7]
Ionpac AG9-HC[f]	0.003[§]	0.008	0.01	0.01	[5]
Ionpac AS14[g]	0.03	0.02	0.08*	0.02*	Loop, this study
Ionpac AS14[h]	0.001	0.006	0.005	0.004	Preconcentrate, this study

[a] Eluent (injection volume): 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ (0.5 ml).
[b] Eluent (injection volume): gradient NaOH (5 ml).
[c] Eluent (injection volume): gradient NaOH/MeOH (5 ml).
[d] Eluent (injection volume): 2 mM potassium hydrogenphtalate (1 ml).
[e] Eluent (injection volume): 2 mM potassium hydrogenphtalate (0.14 ml).
[f] Eluent (injection volume): 12.5 mM Na_2CO_3 (0.3 ml); [§]12 mM $NaHCO_3$ (0.8 ml).
[g] Eluent (injection volume): 2 mM $Na_2B_4O_7$ (0.20 ml); *10 mM $Na_2B_4O_7$ (0.25 ml).
[h] Eluent (injection volume): gradient $Na_2B_4O_7$ (5.0 ml).

sample preparation. The main advantage of the loop method for anions is the reduced sample volume (total of 1.5 ml for two runs), allowing finer resolution ice core sampling.

A 4 mm TAC anion concentration column (Dionex, California) and a two-stage gradient method was developed to elute all anions of interest in a single run over 24 min (Fig. 1b). The changes in eluent concentration during analysis are given in Table 5. The first stage was a gentle eluent ramp from 1.25 to 3.8 mM $Na_2B_4O_7$, which separated $CH_3SO_3^-$ and Cl^-, and eluted NO_3^-. The second stronger ramp increased the $Na_2B_4O_7$ concentration from 3.8 to 10.2 mM and eluted SO_4^{2-}, before being reduced to 1.25 mM prior to the next sample injection. The concentration ramps affect the baseline (Fig. 1b), particularly for SO_4^{2-} detection, however the effects were reproducible from run to run. The solid line below the SO_4^{2-} peak gives the base of the peak above which the peak area was

integrated, and again this was reproducible. This high reproducibility is reflected in the low errors of estimation and high correlation coefficients observed (Table 2). The calibration ranges and associated regression equations are also given in Table 2. The precision of anion analysis was adequate and ranged between 0.6 and 4% for 20 replicates of a low standard (Table 2). The detection limits of anion analysis significantly improved with the addition of the concentrator column using a 5 ml sample, and these limits are believed to be the lowest so far reported (Table 4). This method resulted in successful separation and determination of very low levels of $CH_3SO_3^-$ in the presence of relatively high levels of Cl^- in winter ice samples, while separating NO_3^- and SO_4^{2-} in a single run.

3.3. Data quality

The concentration of ions in Q-water and Q-ice

Table 5
Concentration changes of $Na_2B_4O_7$ eluent during the anion gradient method

Time (min)	Q-water (%)	2.5 mM $Na_2B_4O_7$ (%)	20 mM $Na_2B_4O_7$ (%)	$Na_2B_4O_7$ (mM)
0	0.50	0.50	0.0	1.25
13	0.54	0.31	0.15	3.80
18	0.35	0.16	0.49	10.20
24	0.50	0.50	0.0	1.25

samples were monitored at all times for differences. Q-ice samples were treated the same as real ice samples with the same cutting, decontamination, thawing and pipette transfer stages of sample processing. In the case of $CH_3SO_3^-$, the levels in Q-water and Q-ice were below detection limits. In the case of the other ions, there was a small background concentration, however there was no evidence of a difference between the levels in Q-water and Q-ice samples ($P > 0.1$ for all ions (see Table 2); Student's t-test). This indicates there was no significant contamination of ice samples during sample processing and is evidence of the effectiveness of the clean sample preparation procedures used.

A series of ice cores was sampled in duplicate and processed in our laboratory and at the Glacier Research Group (S. Whitlow), University of New Hampshire (UNH), USA, using a method slightly modified from Buck et al. [2]. There was excellent agreement for all ions between the two sets of samples, and a Ca^{2+} record is given as an example (Fig. 2). Despite two very different analytical procedures and that ice core samples are easily contaminated for Ca^{2+}, these results highlight good agreement between the two laboratories.

3.4. Ice core data
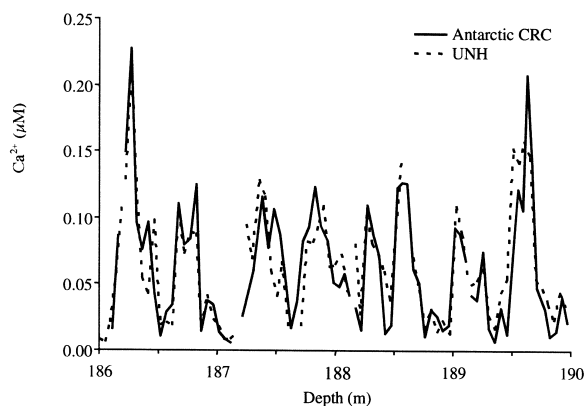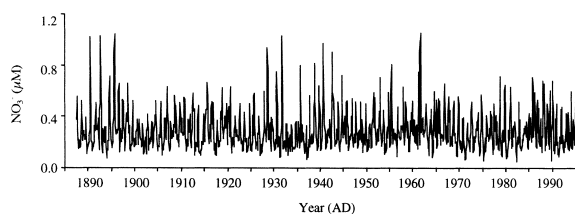
The methods presented here for anion and cation

Fig. 3. NO_3^- timeseries from Dome Summit South, Law Dome, East Antarctica.

analysis have been used to produce trace ion timeseries data from a number of Antarctic ice cores, which can be interpreted as environmental and climate records. A full record of trace ion species covering the last 110 years with approximate monthly resolution was produced from a Law Dome ice core (dated using annual layer counting). The NO_3^- record is shown as an example (Fig. 3). The spikes in this record are due to the seasonal increase in NO_3^- during summer. This record was used to provide the first statistical evidence for a solar source of atmospheric NO_3^- [14]. The $CH_3SO_3^-$ record from the same Law Dome ice core was used to show a relationship between $CH_3SO_3^-$ and Antarctic sea-ice extent [Curran, unpublished], and the SO_4^{2-} record has been used to estimate the lag time of volcanic fallout reaching Antarctica [Palmer, unpublished].

4. Conclusion

The methods developed were successfully applied to the analysis of both anions and cations in ice cores where sample volumes were limited to less than 10 ml. Best results for trace anions were obtained by combining sample preconcentration with gradient elution analysis, which achieved the lowest reported detection limits. Low concentrations of $CH_3SO_3^-$ in winter snow were detected in the presence of high concentrations of Cl^-, without interference, and all anions were analysed in a single run. Direct injection of a small volume produced acceptable results for cations. The ice core chemistry data produced have demonstrated important links between ice core records and environmental signals such as solar activity, volcanic activity and sea ice extent.

Fig. 2. Comparison of Ca^{2+} records from core sections analysed at the Antarctic CRC and at the University of New Hampshire (UNH).

Acknowledgements

References

[1] J.P. Steffensen, Analysis of the seasonal variation in dust, Cl^-, NO_3^-, and SO_4^{2-}, in two Central Greenland firn cores, Ann. Glaciol. 10 (1988) 171.

[2] C.F. Buck, P.A. Mayewski, M.J. Spencer, S. Whitlow, M.S. Twickler, D. Barrett, Determination of major ions in snow and ice cores by ion chromatography, J. Chromatogr. 594 (1992) 225.

[3] M. Legrand, M. De Angelis, F. Maupetit, Field investigation of major and minor ions along Summit (Central Greenland) ice cores by ion chromatography, J. Chromatogr. 640 (1993) 251.

[4] A. Doscher, M. Schwikowski, H.W. Gaggeler, Cation trace analysis of snow and firn samples from high alpine sites by ion chromatography, J. Chromatogr. A 706 (1995) 249.

[5] T. Jauhianinen, J. Moore, P. Peramaki, J. Derome, K. Derome, Simple procedure for ion chromatographic determination of anions and cations at trace levels in ice core samples, Anal. Chim. Acta 389 (1999) 21.

[6] J. Ivask, J. Pentchuk, Analysis of ions in polar ice core samples by use of large injection volumes in ion chromatography, J. Chromatogr. A 770 (1997) 125.

[7] J. Ivask, M. Kaljurand, Reduction of the detection limits of anions in polar ice core analysis using correlation ion chromatography with detector signal processing, J. Chromatogr. A 844 (1999) 419.

[8] Y. Yang, J. Kang, H. Lu, Q. Ou, F. Liu, Determination of trace level anions in snow samples by capillary electrophoresis with sample stacking, J. Chromatogr. A 834 (1999) 387.

[9] J.P. Ivey, D.M. Davies, V. Morgan, G.P. Ayers, Methansulphonate in Antarctic Ice, Tellus 38B (1986) 375.

[10] C. Saigne, M. Legrand, Measurements of methansulphonic acid in Antarctic Ice, Nature 330 (1987) 240.

[11] R. Mulvaney, D.A. Peel, Anions and cations in ice cores from Dolleman Island and the Palmer Land Plateau, Antarctic Peninsula, Ann. Glaciol. 10 (1988) 121.

[12] A. Sigg, K. Fuhrer, M. Anklin, T. Staffelbach, D. Zurmuhle, A continuous analysis technique for trace species in ice cores, Environ. Sci. Technol. 28 (1994) 204.

[13] M.A.J. Curran, T.D. van Ommen, V. Morgan, Seasonal characteristics of the major ions in the high-accumulation Dome Summit South ice core, Law Dome, Antarctica, Ann. Glaciol. 27 (1998) 385.

[14] A.S. Palmer, T.D. van Ommen, M.A.J. Curran, V. Morgan. Ice-core evidence for a small solar-source of atmospheric nitrate. Geophys. Res. Lett. 28 (2001) 1953.