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Field investigation of major and minor ions along Summit (Central Greenland) ice cores by ion chromatography

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ABSTRACT

As a part of the European EUROCORE and GRIP (Greenland Ice Core Project) operations aimed at recovering deep ice cores at Summit (Central Greenland), we have for the first time successfully performed ion chromatography measurements in the field and investigated in detail the soluble impurities, including Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, CH_3COO^-, CH_2OHCOO^-, $HCOO^-$, $CH_3SO_3^-$, Cl^-, NO_2^-, SO_4^{2-} and $C_2O_4^{2-}$, trapped in ice deposited over some 200 000 years in Greenland.

INTRODUCTION

Over the last decades, scientific studies have increasingly focused on the chemical composition of the Earth's atmosphere. The major objective of such studies is to understand the preindustrial environmental system and to anticipate its future evolution (chemical composition of the atmosphere and climate) in response to human activities. Owing to the lack of data for the past, most of these studies are limited to our present atmosphere. However, polar ice cores provide precipitation samples in which the atmospheric chemical composition at the time of deposition is recorded, offering a unique possibility of reconstructing the chemical composition of the atmosphere back to the preindustrial time period.

Among a wide variety of chemical species trapped in snow layers (insoluble particles, trace metals and ionic species), the ionic species appear to be the most useful in tracing major natural and anthropogenic sources of impurities which lead to the final composition of our atmosphere [1–6]. Such studies of the composition of soluble species trapped in snow deposits have clearly opened up an important new scientific field. As discussed by Legrand [7], it is very important in such work to perform a comprehensive study of the soluble species present in the ice in order to check the equilibrium between anions and cations. It is then possible to reconstruct the initial association between the ions and discuss such data in terms of origins and sources. Ion chromatography (IC) is a multispecies technique, as opposed to others such as neutron activation, atomic absorption spectrometry and ionometric and colorimetric methods, and it is well suited to such comprehensive studies of all soluble impurities in ice, except for H^+, which can be measured using an acid titration method such as the one developed by Legrand *et al.* [8].

Nevertheless, such studies have been relatively slow to come into use because of technical difficulties linked with the required low detection limit and with contamination control, both of which are important when working with the low levels of impurities characterizing polar precipitations. Studies were initially dedicated to major anions and cations [9, 10], namely Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}, and more recently have been extended to include some minor anions, such as fluoride [11] and some light carboxylates [12,13].

In this paper, we describe an ion chromatography method for determining mineral as well as some or-

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ganic ions (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, F^-, CH_3COO^-, CH_2OHCOO^-, $HCOO^-$, $CH_3SO_3^-$, Cl^-, NO_2^-, NO_3^-, SO_4^{2-} and $C_2O_4^{2-}$) that we have successfully applied in the field over the four successive summer seasons, 1989–1992, in Central Greenland as a part of the European EUROCORE and GRIP projects. Excellent sensitivity is achieved for all species, and with a 5-ml sample volume it is possible to measure down to a few tenths of an nanogram per gram. We will discuss numerous advantages provided by such field measurements compared with the tedious sample preparation methods used in laboratories to avoid contamination of the samples.

EXPERIMENTAL

A heated laboratory equipped with two IC set-ups on the Greenland ice cap

At the beginning of the 1989 summer season (EUROCORE operation) at Summit, Central Greenland (72° 34′ N, 37° 38′ W, elevation 3240 m above sea level, mean annual temperature −32.5°C), a shelter was equipped to conduct ion chromatography measurements. The equipment in this heated laboratory included a Milli-Q ultrapure water production unit (Millipore), an uninterruptible power system (416 Leroy-Somer), a class 100 horizontal laminar flow clean hood (Flufrance) and a data capture system (Epson PC AX2) connected to two integrators (4270 Spectra-Physics and Chromjet) and to two Dionex Series (4000i and 4500i) ion chromatographs.

A production of 30–90 l per day of ultrapure water is required to prepare eluents and regenerants, to clean sample containers and to process all equipment that comes into contact with ice samples (see section *Sample preparation*). This ultrapure water is obtained by melting snow collected outside the camp and pumping the meltwater through four Milli-Q cartridges (one Super-C, two Ion-ex and one Organex-Q) and a final filter (0.4 μm).

Owing to rather frequent failures of the main power supply of the camp, we used a battery back-up system (1 kW) to supply the PC and the two ion chromatographs (total consumption of 250 W), allowing us to continue running measurements for almost 45 min in the event of a power problem.

The two chromatographic systems were carefully rinsed with methanol prior to packing and transport to Greenland.

All chromatographic columns were handled with care in the field by workers, taking special precautions to avoid damage by the low temperature. In spite of this, during the first operation (1989), the cation micromembrane suppressor (CMMS) was damaged before arriving at Summit and the tetrabutylammonium hydroxide (TBAOH) solution (40%) used to prepare the regenerant for cation measurements reached Greenland completely frozen.

During the winters of 1989–1990, 1990–1991 and 1991–1992 the laminar flow hood, the battery back-up system and the Millipore system stayed in Greenland and survived in spite of very low temperatures (−65°C). Other equipment (ion chromatographs, PC and chromatographic columns) was sent back to France at the end of each summer.

Sample preparation

The outer part of firn and ice cores extracted from ice caps were generally significantly contaminated during the drilling procedure. When the entire core was available, the outer part of the core was removed using an ice core lathe designed in our Grenoble laboratory (Fig. 1). The efficiency of such a procedure was tested with an ice core section from a depth of 159 m at Dome C (Antarctica), on which successive shaving fractions were recovered and measured (Fig. 2). The results clearly show that there was very significant superficial contamination of the ice, except for $CH_3SO_3^-$. Then concentrations decrease rapidly from the outside to the inside of the ice core, the inner part exhibiting a plateau corresponding to the part of the core that is free of contamination. Fig. 2 also suggests that the contamination remains restricted mainly to the first outer centimetre of the core. Such a procedure was used along the upper 70 m of the Eurocore core for which the entire core was available.

Along the GRIP core, numerous experiments have been carried out by various workers, and only small lamella (2.5 × 3.5 cm section) were available to perform our study of soluble species. The use of the lathe was therefore not possible. However, considering the limited penetration of the contamination inside a piece of ice (Fig . 2), we proceeded in the field with mechanical decontamination by shav-

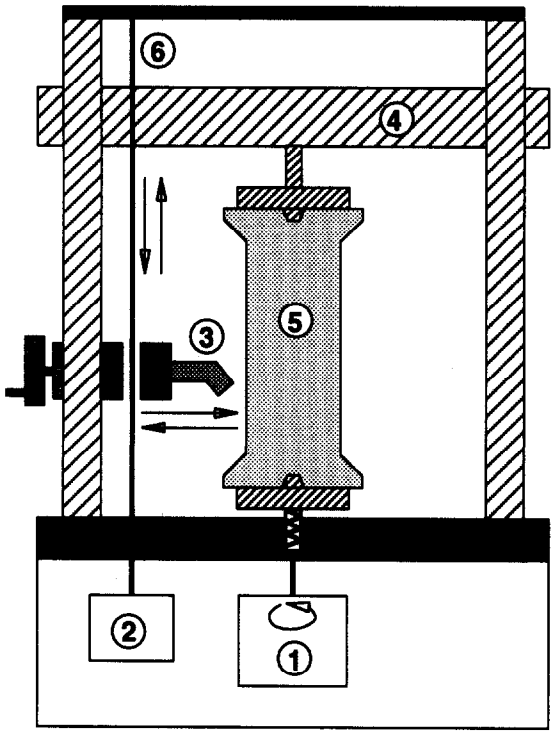

Fig. 1. Ice core lathe equipped with a stainless-steel knife (3) used to remove the outer part of ice core sections. 1 = Motor; 2 = reducer; 4 = mobile plateau; 5 = ice core section; 6 = threaded rod.

ing off approximately 50% of the ice lamella with scalpels previously rinsed with ultrapure water. Such a procedure performed in the field presents two major advantages. First, performed immediately after core recovery, such a procedure does not require ice sections to be stored in sealed plastic bags, a process that leads to organic acid contamination [11]. Second, such field work prevents us from breaking these small and fragile pieces of ice during the transport.

Because the species we are concerned with may be present in the atmosphere of the heated laboratory as aerosols or in the gas phase, special precautions have to be taken during the melting step. A clean air hood prevents our samples from contamination by aerosols but not from contamination by trace gases such as nitric acid or ammonia and some volatile organic acids.

To investigate this problem, several vials filled with 10 ml of ultrapure water were left open over increasing time periods within a clean air bench located in our Grenoble laboratory. As reported in Table I, rapid contamination occurs for NH_4^+, $HCOO^-$ and CH_3COO^-, as previously pointed out by Legrand *et al.* [9] and Saigne *et al.* [11], corresponding to the dissolution of ammonia and carboxylic acid traces present in the atmosphere:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Furthermore, the observation of NO_2^- contamination (Table I) is probably due to the presence of nitric acid in the atmosphere of our laboratory following:

$$HNO_2 + H_2O \rightleftharpoons NO_2^- + H_3O^+$$

To prevent our samples from such rapid contamination during the melting step, we put the decontaminated pieces of ice in air-tight bottles kept frozen until the analyses.

TABLE I

CONCENTRATIONS OF VARIOUS IONS IN VIALS FILLED WITH 10 ml OF ULTRAPURE WATER AND LEFT OPEN OVER INCREASING TIME PERIODS WITHIN A CLEAN AIR HOOD IN OUR GRENOBLE LABORATORY

Species	Concentration after 90 min (ng g^{-1})	Mean rate (ng g^{-1} h^{-1}) of contamination over 8 h
NH_4^+	12	9
$HCOO^-$	7	5
CH_3COO^-	22	18
NO_2^-	2	2.5

Ion chromatography

For the anion chromatographic system, we used AS5A and Pax-500 separator columns with AG5 and CG10 guard columns, respectively. Two anion trap columns (ATC1) were placed in series before the injection valve. A Dionex anion micromembrane suppressor (AMMS1 and later on AMMS2)

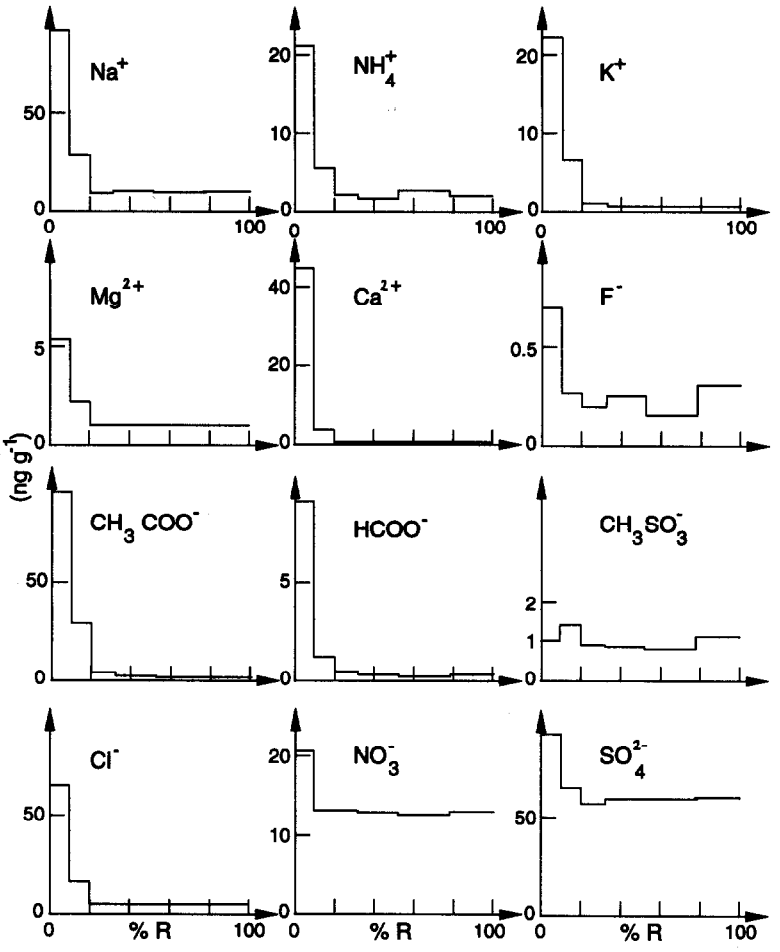

Fig. 2. Decontamination of a piece of ice from a depth of 159 m at Dome C (Antarctica) using the lathe. Concentrations (in ng g^{-1}) are given as a function of the shaved fraction of the ice core section (percentage of the initial radius, *R*).

TABLE II

WORKING GRADIENT CONDITIONS USED FOR ANION DETERMINATIONS WITH THE AS5 SEPARATOR COLUMN

Time (min)	Eluent 1, 200 m*M* sodium hydroxide (%)	Eluent 2, water (%)	Eluent 3, 1 m*M* sodium hydroxide (%)	Injection valve	Flow-rate (ml/min)	Eluent (m*M* sodium hydroxide)
0.1	0	50	50	Inject	1.8	0.5
2.5	0	50	50	Inject	1.8	0.5
11.5	15	35	50	Inject	1.8	30.5
12.0	15	35	50	Inject	1.8	30.5
12.2	0	50	50	Inject	1.8	0.5
14.2	0	50	50	Load	1.8	0.5

TABLE III

WORKING GRADIENT CONDITIONS USED FOR ANION DETERMINATIONS WITH THE PAX-500 SEPARATOR COLUMN

Time (min)	Eluent 1, 200 m*M* sodium hydroxide (%)	Eluent 2, water (%)	Eluent 3, 4 m*M* sodium hydroxide (5% methanol) (%)	Injection valve	Flow-rate (ml/min)	Eluent (m*M* sodium hydroxide) (1.25% methanol)
0.1	0	75	25	Inject	1.0	1.0
0.5	0	75	25	Inject	1.0	1.0
8.0	14	61	25	Inject	1.0	29.0
14.0	14	61	25	Inject	1.0	29.0
14.1	0	75	25	Inject	1.0	1.0
18.5	0	75	25	Load	1.0	1.0

was used with a mobile phase (0.025 *M* sulfuric acid) at a flow-rate of 1.6 ml/min. A 5-ml sample volume was preconcentrated on an TAC1 column. Using the gradient pump system, the mobile phase is a mixture of three different liquids (water, sodium hydroxide solutions at two different concentrations and methanol continuously degassed by flowing helium; see Tables II and III) at a flow-rate of 1.8 and 1.0 ml/min for the AS5 and Pax-500, respectively. With the AS5 column and using the working gradient conditions reported in Table II, we obtained a background conductivity of approximately 1.8–2.5 μS and 0.8–1.3 μS with the AMMS1 and AMMS2, respectively, for the weak eluent. Using an AMMS2 and the working conditions reported in Table II and Table III, we observed an increase in the background conductivity of 0.3 and 0.5 μS for AS5 and Pax-500, respectively, along the run.

For the cation chromatographic system, we first used Fast Cation I and Cation II to perform two runs, one for monovalent cations, the other for divalent cations. Later on, a CS10 separator column, which allows a separation of mono- and divalent cations in a single isocratic run, was used. Rejecting the use of TBAOH, we first prepared regenerant using a 25% tetramethylammoniumhydroxide (TMAOH) solution, but later on we preferred the use of TMAOH pentahydrate at 97% (Janssen), which provides more stable and lower background conductivity (3–5 μS). The mobile phase was 50 m*M* hydrochloric acid–5.1 m*M* 2,3-diaminopropionic acid monohydrochloride (DAP), and the regenerant was 70 m*M* tetramethylammonium hydroxide (TMAOH), with flow-rates of 1.0 and 4–5 ml/min, respectively. The background conductivity of the cation system ranges between 3 and 4.5 μS with a new CMMS but then increases slowly. We found that this increase in the background conductivity with time was highly dependent on the quality of the TMAOH.

RESULTS AND DISCUSSION

The ion chromatographic procedures were calibrated with artificial samples of various concentrations using a pipette to dilute the required volume of the parent solutions in ultrapure water. Parent solutions were prepared by dilution of individual standard solutions at 1000 mg l^{-1} with concentration ratios chosen to be similar to those in Greenland ice. Because of the observed decrease (up to 50% after 2 weeks) in the formic and acetic contents in these parent solutions with time (probably due to biological activity), it was necessary to make new parent solutions for anions at regular intervals (once a week). The different standard solutions used for calibration were prepared just a few min before they were needed.

Calculated regression lines, estimated errors, correlation coefficients and detection limits are given in Table IV and Table V. Significant (twice the detection limit) positive *y*-intercepts are observed for CH_3COO^- (*ca.* 1 ng g^{-1}) and NH_4^+ (*ca.* 1 ng g^{-1}). Such blank values probably reflect weak contam-

TABLE IV

CALIBRATION PARAMETERS FOR ANION (USING AN AS5 SEPARATOR COLUMN) AND CATION DETERMINATIONS

c represents the concentration (in ng g^{-1}) and S the peak area expressed in relative units. DL denotes the detection limit defined as the amount of solute producing a signal to noise ratio of 5. r is the correlation coefficient.

	F^-	CH_3COO^-	CH_2OHCOO^-	$HCOO^-$	$CH_3SO_3^-$
Range	0.1–1.8	1.2–22.5	0.25–4.5	1.0–16.0	0.5–9.0
Regression line	$S = -0.03 + 2.76c$	$S = 0.42 + 0.35c$	$S = -0.03 + 0.4c$[a]	$S = 0.26 + 0.958c$	$S = 0.03 + 0.565c$
Error	± 0.03	± 0.5[a]	See text	± 0.15	± 0.1
r	0.9997	0.9988	0.9955	0.9998	0.9997
DL	0.05	0.6	0.25	0.2	0.25
	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$
Range	2.5–45.0	0.5–9.0	7.5–135.0	10–180	0.5–4.5
Regression line	$S = 0.003+0.135c$	$S = -0.02+0.113c$	$S = -0.01+0.082c$	$S = -0.26+0.108c$	$S = -0.02+0.1c$[a]
Error	± 0.3	± 0.2	± 1.0	± 3.0	see text
r	0.9999	0.9997	0.9999	0.9998	0.998
DL	0.5	0.5	1.5	1.5	0.5
	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Range	0.5–40	0.5–40	0.125–10	0.25–20	0.5–40
Regression line	$S = 0.03+0.282c$	$S = 0.22+0.198c$	$S = -0.03+0.221c$	$S = -0.1+0.538c$	$S = -0.1 + 0.34c$
Error	± 0.6	± 0.6	± 0.4	± 0.3	± 0.8
r	0.9997	0.993	0.998	0.9996	0.9995
DL	0.2	0.3	0.25	0.2	0.5

[a] See text.

ination during the preparation of the standard solutions in relation to the above-mentioned rapid contamination by trace gases present in the atmosphere of the laboratory, especially for NH_4^+ and CH_3COO^- (Table I).

In two cases we calculated a negative y-intercept, one for SO_4^{2-} when using an AS5 column (Table IV), the other for NO_3^- when using a Pax-500 column (Table V). Such negative blank values (2.5 and 3 ng g^{-1} for SO_4^{2-} and NO_3^-, respectively) appear when the peak (sulphate with AS5 and nitrate with Pax-500) overlaps the wide hydrogencarbonate peak (Fig. 3) that corresponds to the carbon dioxide dissolution in our sample. Areas calculated using a linear baseline on the tail of the bicarbonate peak are slightly underestimated, leading to errors for nitrate and sulphate when present at low levels.

Determinations of CH_2OHCOO^- and $C_2O_4^{2-}$ using an AS5 column can lead to major errors because of a large overlapping of their peaks with acetate and sulphate peaks respectively (see Fig. 3a). Indeed, depending on the ratios CH_3COO^-/CH_2OHCOO^- and $SO_4^{2-}/C_2O_4^{2-}$, the peak areas have to be calculated in different ways (baseline at valley or resolved rider peak on the tail of the preceding peak). More accurate determinations of these two organic acids were obtained using a Pax-500 separator column, even using a minimal amount of methanol (1.25%), which significantly increases the separation between these species and acetate and sulphate species.

For all species, excellent sensitivity was achieved with detection limits sometimes one order of magnitude lower than the mean content of Greenland precipitation (see Table VI).

The IC method described has been used for investigation in various glaciochemical studies. Among the results, the discovery of the important

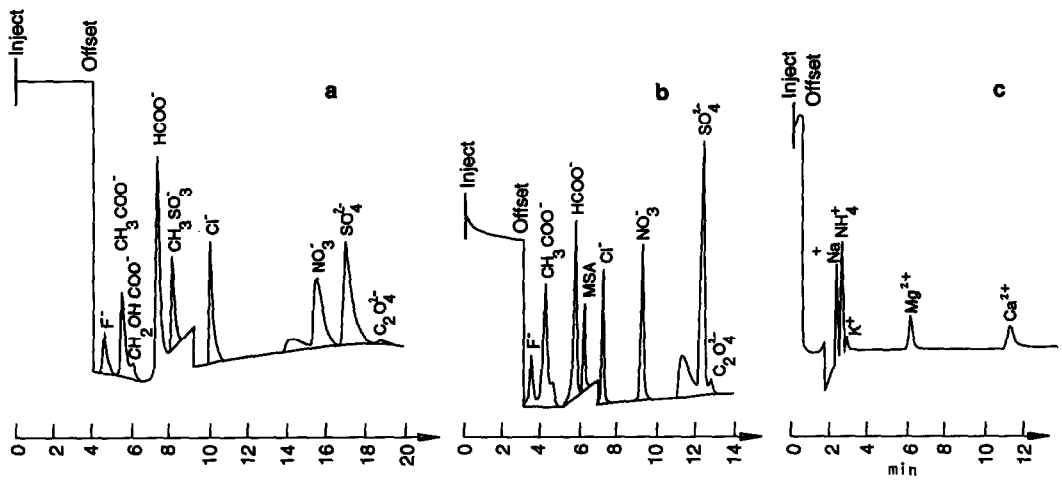

Fig. 3. (a) Anion Pax-500 chromatogram: F^- (0.4 ng g^{-1}), CH_3COO^- (5 ng g^{-1}), CH_2OHCOO^- (1 ng g^{-1}), $HCOO^-$ (5 ng g^{-1}), $CH_3SO_3^-$ (4 ng g^{-1}), Cl^- (20 ng g^{-1}), NO_3^- (40 ng g^{-1}), SO_4^{2-} (60 ng g^{-1}), $C_2O_4^{2-}$ (4 ng g^{-1}). (b) Anion AS5 chromatogram: F^- (0.8 ng g^{-1}), CH_3COO^- (10 ng g^{-1}), CH_2OHCOO^- (2 ng g^{-1}), $HCOO^-$ (6 ng g^{-1}), $CH_3SO_3^-$ (4 ng g^{-1}), Cl^- (20 ng g^{-1}), NO_3^- (60 ng g^{-1}), SO_4^{2-} (80 ng g^{-1}), $C_2O_4^{2-}$ (2 ng g^{-1}). (c) Cation CS10 chromatogram: Na^+ (4 ng g^{-1}), NH_4^+ (4 ng g^{-1}), K^+ (1 ng g^{-1}), Mg^{2+} (2 ng g^{-1}), Ca^{2+} (4 ng g^{-1}). The sample volume was 5 ml. The detector sensitivity was 3 μS at the beginning of the run and 30 μS later on (change between the $CH_3SO_3^-$ and the Cl^- peaks) for anions (a and b), and is unchanged (c) for cations (10 μS).

role played by organic acids in the chemical composition of the past atmosphere has been discussed by Legrand *et al.* [6]. This study of organic species, which are particularly sensitive to severe contamination, has shown the great advantage of performing IC measurements in the field.

TABLE V

CALIBRATION PARAMETERS FOR ANION DETERMINATIONS USING A PAX-500 SEPARATOR COLUMN

	F^-	CH_3COO^-	CH_2OHCOO^-	$HCOO^-$	$CH_3SO_3^-$
Range	0.1–1.8	1.2–22.5	0.25–4.5	1.0–18.0	0.5–9.0
Regression line	$S = 0.03 + 4.77c$	$S = 0.59 + 0.543c$	$S = -0.03 + 1.071c$	$S = -1.1 + 1.9c$	$S = 0.01 + 0.9995c$
Error	± 0.02	± 0.5	± 0.2	± 0.3	± 0.2
r	0.9998	0.998	0.998	0.993	0.9995
DL	0.02	0.6	0.2	0.2	0.25
	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$
Range	2.5–45.0	0.5–9.0	7.5–135.0	10–180	0.5–4.5
Regression line	$S = -0.05 + 0.267c$	$S = -0.004 + 0.157c$	$S = -0.44 + 0.145c$	$S = -0.27 + 0.201c$	$S = -0.025 + 0.146c$
Error	± 0.3	± 0.25	± 2	± 0.2	± 0.15
r	0.9998	0.998	0.9996	0.9998	0.997
DL	0.5	0.5	1.5	1.5	0.5

TABLE VI

MEAN IONIC COMPOSITION OF GREENLAND PRECIPITATION OBSERVED BY LEGRAND *et al.* [9]

Values followed by asterisks denote large disturbances of the background level of NH_4^+ and of some organic species in relation to inputs from forest fires, as discussed in ref. 9.

	Ionic composition (ng g^{-1})				
	F^-	CH_3COO^-	CH_2OHCOO^-	$HCOO^-$	$CH_3SO_3^-$
Range	0.05–0.3	10–35*	0.5–15*	10–1000*	0.5–5.0
Mean	0.15	13	1	12	3
	Cl^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$	Na^+
Range	2–30	25–100	10–40	0.5–20.0*	1–20
Mean	15	80	30	1	8
	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
Range	3–400*	0.5–3	0.5–4.0	0.5–10	
Mean	5	1.0	2.0	8	

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