

ION CHROMATOGRAPHIC DETERMINATION OF MAJOR ANIONS AND CATIONS IN ANTARCTIC ICE

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Abstract. The ionic content of polar ice sheet is useful in tracing the sources of impurities, which lead to the final composition of the atmosphere. Ion chromatography is a suitable tool for analysing the ionic content of polar ice, provided precautions are taken to avoid ice contamination during sampling and analyses. In the present study a method for handling and analysing ice core samples was developed. The knowledge obtained was then applied for the determination of major ions in Dome B (East Antarctica) ice core to analyse the potential of extracted information for understanding the past atmospheric changes.

Key words: ion chromatography, polar ice.

INTRODUCTION

Archives of numerous environmental parameters are recorded in polar ice sheets [1]. Snow accumulating in polar areas buries atmospheric impurities, which are then preserved for millennia in the ice layers. These impurities are incorporated in snowflakes when precipitation is formed in clouds. Significant amounts of atmospheric trace substances may also deposit directly on the snow surface. Ionic species appear to be useful in tracing sources of impurities that lead to the final composition of the atmosphere. Ion chromatography is a multispecies technique and is well suited for the analysis of ice ionic content. However, such studies are affected by several technical problems connected with

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the needed low detection limit and with contamination control, both of which are important when analysing low levels of impurities characterizing polar precipitation [2, 3].

In the present study a method for contamination free handling and analysis of an ice core from Dome B (East Antarctica) was developed. The method was applied for the determination of concentrations of chloride, nitrate, sulphate, sodium, ammonium, potassium, calcium, and magnesium ions in ice core sections in the depth interval 346–606 m. These sections include the climate change period between the last ice age and the present Holocene interglacial period [1]. The ionic data were then compared with those obtained using isotope analyses to study whether they can be interpreted in terms of processes that have affected the atmosphere in the past.

EXPERIMENTAL

Sample preparation

Radial distribution of contamination in the ice core (diameter 8 cm) was studied by shaving off the fractions of the selected core sections using a special lathe designed in our laboratory (similar to [3]). The successive shaving fractions were collected and analysed applying the methods described in a previous paper [4]. Based on these results the remainder of the ice core was decontaminated by shaving off the outer 2–2.5 cm parts of the core with a stainless steel knife previously rinsed with ultrapure water (conductivity 0.06 $\mu\text{S}/\text{cm}$). Water was produced using the Millipore Milli-Q water system. The lathe and the knife blade were cleaned by repeatedly cutting ice, prepared from Milli-Q water. All sampling procedures were performed in the cold room of the Estonian Biocentre at -20°C under a clean air hood. Face masks and polyethylene gloves were used during the entire sample preparation step. To monitor the chemical contamination level of the sample storing and handling procedure, a portion of Milli-Q water was frozen in a polyethylene measuring cylinder to make a Milli-Q ice core, which was then handled in the same way as the sample cores. The decontaminated samples were put in air-tight bottles and kept frozen until the injection into the chromatograph.

Ion chromatography

The apparatus used was an IAK-12 analytical chromatograph with a conductivity detector (INKROM Ltd., Estonia). The separation columns used were ion chromatography cation and anion columns 3×150 mm, packed with resins synthesized in our laboratory. The resin matrix used for syntheses was Separon HEMA S 1000 with particle size 10 μm (Tessek Ltd., Czech Rep.). The chromatographic experiment was performed at a flow rate of 1.0 mL/min. The sample volume used was 1.0 mL. The column, loop injector, and the cell of the conductivity detector were maintained at 35°C . Cation separation was performed

with 7.5 mM tartaric acid + 0.8 mM pyridine-2,6-dicarboxic acid eluent and anion separation with 2.0 mM potassium hydrogen phthalate eluent (pH = 4.01).

All the reagents used were of analytical grade (Merck KGaA, Germany). Standard solutions were prepared by dilution of individual stock solutions at 1000 ppm ($\mu\text{g/g}$) with concentration ratios chosen to be similar to those in ice samples. Standard solutions for calibration were prepared a few minutes before use and their concentrations were checked with ion reference solution (Alltech, US).

RESULTS AND DISCUSSION

Dome B is a very cold and relatively low accumulation site located on the high East Antarctic plateau. Because of the remoteness of Central Antarctica from anthropogenic and biological influences, the composition of the atmosphere in this area reflects generally the background levels of different constituents. A deep ice core from this area is therefore well suited for studying global atmospheric processes including aerosol transfer of ionic species. A thermal drilling was conducted during the 1987–88 Austral season by the 33rd Soviet Antarctic Expedition. A series of samples (1 m ice increments cut after every 10 m) was transported to Tallinn and stored in a cold store at -20°C .

The outer part of the ice cores is generally significantly contaminated during the drilling and packing, transportation, and storing procedures. Our results confirmed that the outer layer of the core was significantly contaminated. As shown in Fig. 1, the contamination remains in the outer 2 cm layer of the core and the inner 4 cm section corresponds to the part of the core representing the original ion content of the ice.

However, this procedure is too time consuming for the decontamination of the whole ice core. Therefore, the major part of the core was decontaminated by shaving off its outer 2–2.5 cm section with a special stainless steel knife. Blank analyses from Milli-Q ice core indicated contamination free sample handling and analysing procedures as all the ion peaks found on the chromatograms remained below the detection limits.

The sample preparation and analysis method described here was then used to analyse the ion concentrations in Dome B ice core sections in the depth interval of 346–606 m. The mean ionic content and ion concentration ranges observed in the analysed ice core sections are presented in Table 1. The values obtained are similar to those from other Antarctic ice cores [5]. Variations of the analysed ionic species concentrations were compared with those obtained by ^{18}O isotope analyses performed in our laboratory [1]. Figure 2 shows that the start of the climate warming after the last ice age (corresponding increase in $\delta^{18}\text{O}$) correlates with the peak in sulphate and calcium concentration in ice core sections in the depth interval of about 520–580 m. This was caused by the increased mobility of air masses with a corresponding increase in the input of the species of marine

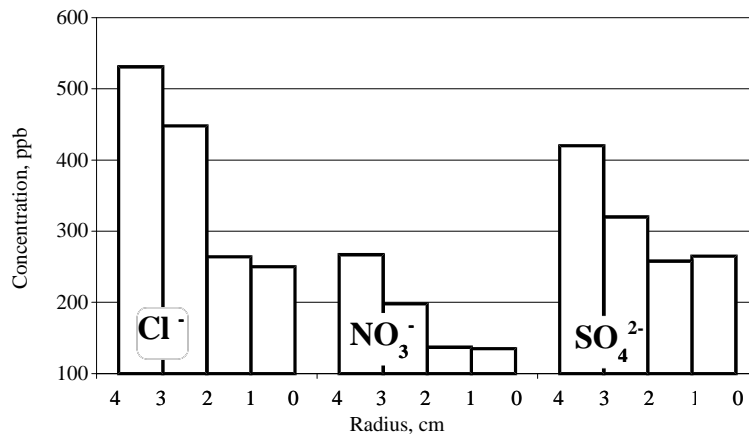


Fig. 1. Radial distribution of the contamination in an ice core section at a depth of 512 m.

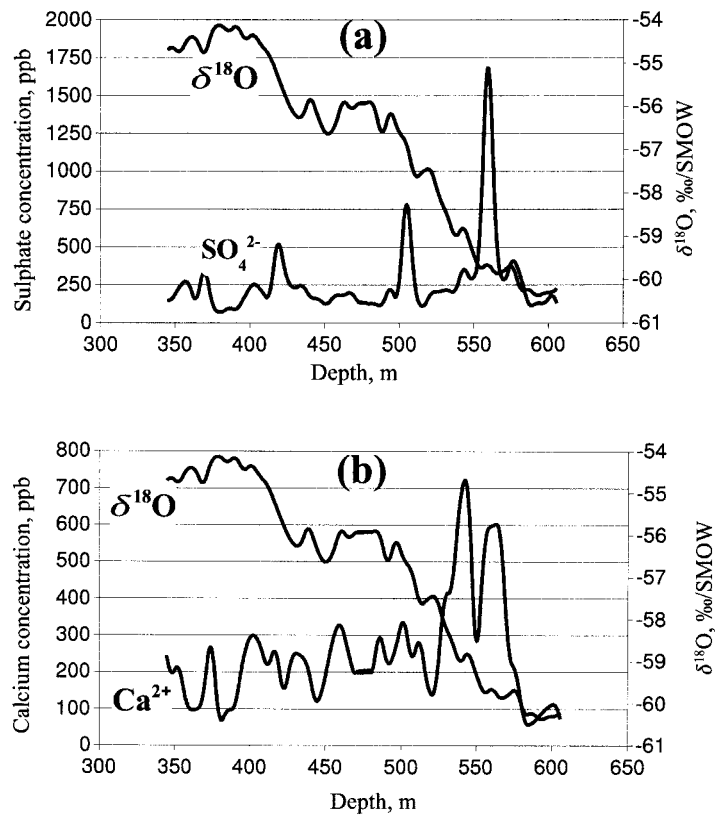


Fig. 2. The Dome B ice core averaged (β -spline) profiles of $\delta^{18}\text{O}$ with sulphate (a) and calcium (b). SMOW= standard mean ocean water.

Table 1. Mean ionic composition and concentration (in ppb) ranges in the analysed Dome B ice core sections

Ion	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Mean	307	72	242	207	93	72	137	411
Range	32–452	38*–82	61–451	51–891	15–267	13*–343	29*–408	61–608

* denotes the detection limit.

(e.g. sulphate) and continental (e.g. calcium) origin [6]. The results demonstrate that ion chromatographic analysis of the ionic content of polar ice can be used to improve the understanding of processes that have affected the atmosphere in the past.

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ANTARKTIKA JÄÄ PEAMISTE ANIOONIDE JA KATIOONIDE IOONKROMATOGRAAFILINE MÄÄRAMINE

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Polaarjää ioonkoostise analüüs annab kasulikku teavet protsesside kohta, mis mõjutasid mineviku kliimat ning atmosfääri koostise kujunemist. Tavaliselt määratakse polaarjää ioonkoostis ioonkromatograafia, kuid sealjuures tuleb arvestada komplikatsioone, mis on seotud ionide väikese sisaldusega polaarjääs ning proovi saastumise võimalusega selle võtmisel, hoidmisel ja töötlemisel. Autorid on välja töötanud meetodika Dome B (Ida-Antarktika) jääpuursüdamiku proovide käsitlemiseks neid saastamata. Pindmise 2–2,5 cm kihi eemaldamisel oli võimalik jõuda saastumata jääkihtideni. Saadud teadmisi rakendati kloriid-, nitraat-, sulfaat-, naatrium-, ammonium-, kaalium-, magneesium- ja kaltsiumioonide kontsentratsiooni määramiseks jääpuursüdamiku sügavuste vahemikus 346–606 m, mis katab ka kliimamuutuse viimase jääaja ning praeguse, holotseeni jäävaheaja vahel. Ioonanalüüsi tulemusi võrreldi isotoopanalüüsi tulemustega eesmärgiga interpreteerida neid minevikus atmosfääri mõjutanud protsessidest lähtudes.