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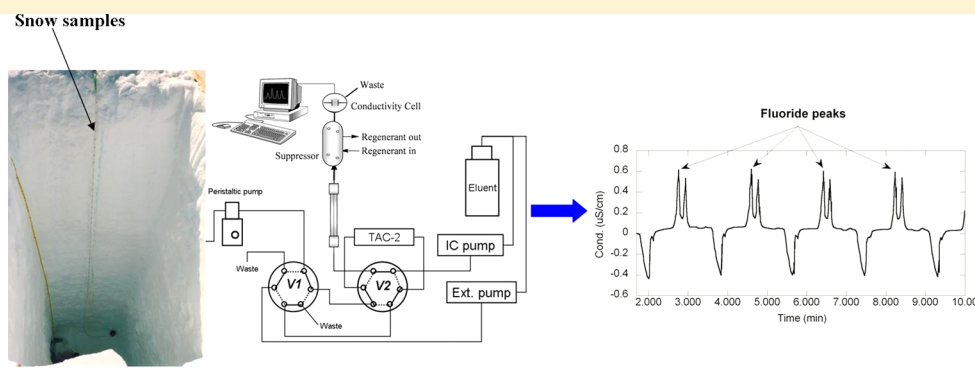
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A Novel Fast Ion Chromatographic Method for the Analysis of Fluoride in Antarctic Snow and Ice

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ABSTRACT: Ice cores are widely used to reconstruct past changes of the climate system. For instance, the ice core record of numerous water-soluble and insoluble chemical species that are trapped in snow and ice offer the possibility to investigate past changes of various key compounds present in the atmosphere (i.e., aerosol, reactive gases). We developed a new method for the quantitative determination of fluoride in ice cores at sub- $\mu\text{g L}^{-1}$ levels by coupling a flow injection analysis technique with a fast ion chromatography separation based on the “heart cut” column switching technology. Sensitivity, linear range (up to $60 \mu\text{g L}^{-1}$), reproducibility, and detection limit ($0.02 \mu\text{g L}^{-1}$) were evaluated for the new method. This method was successfully applied to the analysis of fluoride at trace levels in more than 450 recent snow samples collected during the 1998–1999 International Trans-Antarctica Scientific Expedition traverse in East Antarctica at sites located between 170 and 850 km from the coastline.

1. INTRODUCTION

A wealth of information on past environmental conditions can be inferred from chemical records extracted from ice cores¹ that sometimes cover time periods back as far as 800 kyr.^{2,3} Various soluble and insoluble impurities that can be used as markers or proxies of past environmental conditions are wet and/or dry deposited on ice sheets. The study of their records in the ice cores may provide information on changes over the past in relation to change of source intensity, atmospheric transport pattern to the site, and sometime the chemical evolution of certain species during transport. This concerns the species present in the atmosphere as aerosols or water-soluble gases the change of which over the past inferred from Antarctica ice cores has been already discussed in numerous recent works^{4–7} following the pioneer study conducted over the entire last climatic cycle at Vostok.⁸ Over the past years, many analytical systems were developed in order to obtain high-resolution chemical stratigraphies by coupling a continuous melting system⁹ with continuous or semicontinuous analytical techniques, such as continuous flow analysis (CFA),^{10,11} inductively coupled plasma-mass spectrometry (ICP-MS),¹² and fast ion chromatography (FIC).^{13,14} Ice cores contain detailed records of past volcanism spanning time periods up to tens of thousand years.^{15–19} During volcanic eruptions, large amounts of dust, ash, tephra particles, and SO_2 are emitted into the atmosphere; the released sulfur dioxide is then rapidly

oxidized to sulfuric acid (H_2SO_4) and transported over long distances. Volcanic stratigraphies recorded in ice cores can be reconstructed using different methods with different degrees of specificity. The identification of acidic snow layers by electric conductivity measurement (ECM) and dielectric profiling (DEP) is a simple and nondestructive method that can be carried out directly on the surface of ice core sections.²⁰ However, the interpretation of these measurements is not always straightforward and univocal, especially if acidity-neutralizing substances (such as dust or sea spray) are contemporaneously deposited by dry and wet depositions. Sulfate ice-core stratigraphies^{19–21} represent a more specific method of identifying volcanic signatures, although the ion chromatographic determination of sulfate, which requires a prior tedious decontamination of ice, is more time-consuming than electrical measurements of protons. While the attribution to a volcanic signature is an easy task when a sharp sulfate spike is observed, minor volcanic depositions are unlikely distinguished from the sulfate background profile. Indeed, sulfate in Antarctic snow has several sources, such as sea salt, continental dust, and, especially, biogenic emissions. In particular, non-sea-

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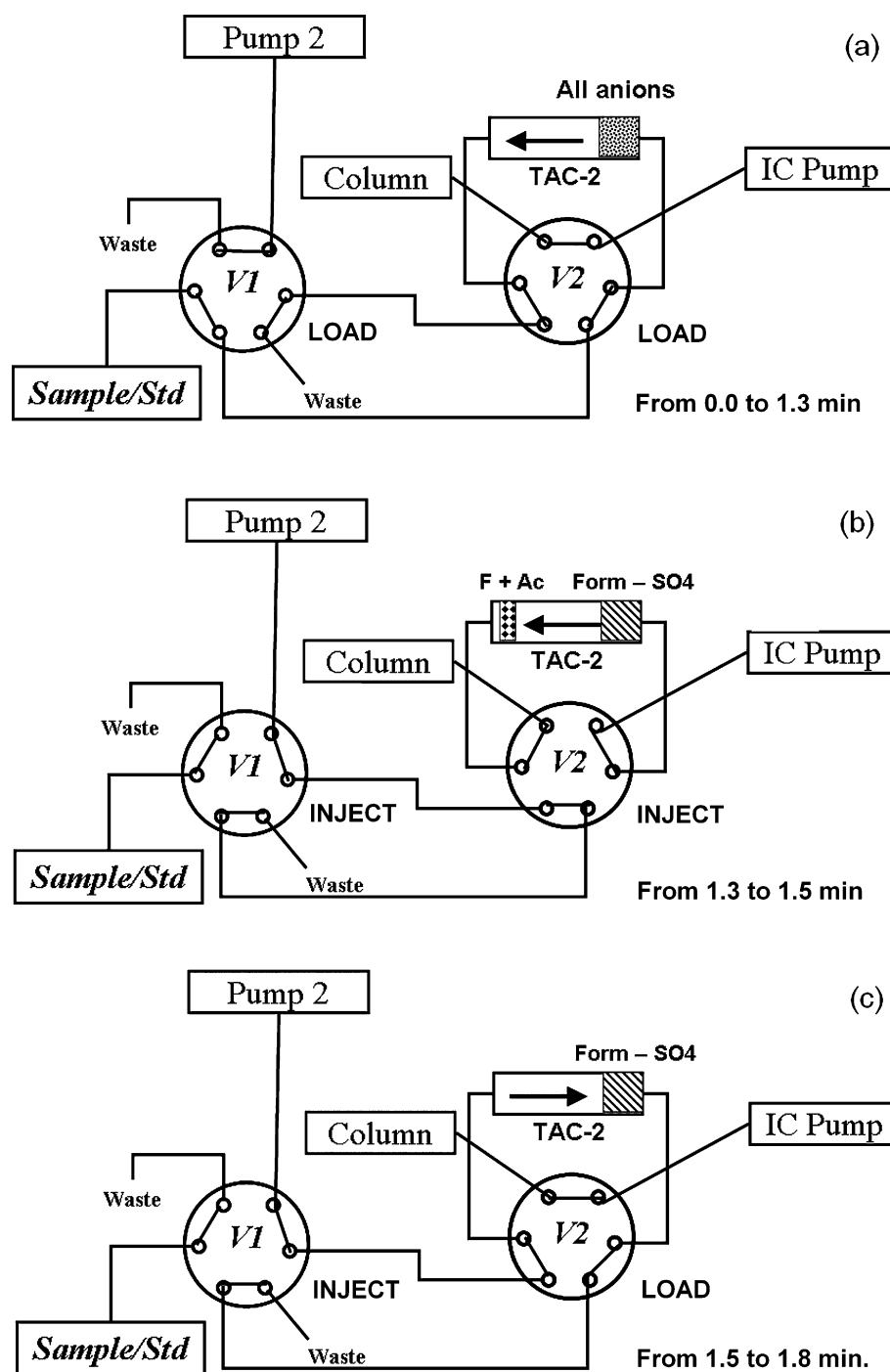


Figure 1. Eluent pathways for the three different configurations of the ion chromatographic system: (a) sample loading (preconcentration), (b) elution of unresolved band containing fluoride and acetate (Ac) from preconcentration column to the analytical column, and (c) separation of F⁻ and Ac in the column and elution of the other anions from the preconcentration column to the waste. The time duration of each configuration is shown in the figures. The “IC pump” and “Pump 2” are two single-reciprocating piston pumps manufactured by Dionex.

salt sulfate (nss-SO₄²⁻), originated by the oxidation of phytoplanktonic dimethyl sulfide emissions, constitutes the highest contribution to the annual budget of sulfate in coastal and inner regions of Antarctica.²² Other compounds can be used in identifying volcanic depositions; in fact, minor components of volcanic emissions include halogenidric acids, such as HF, HCl, and HBr. In particular, HF can identify the emissions from specific volcanic districts. For instance, the eruption and degassing events of the Mount Erebus volcano,

located in the Ross Ice Shelf–McMurdo Sound, are characterized by relatively high concentration of HF.²³ One of the most intriguing topics in the reconstruction of Antarctic volcanic stratigraphies is the study of the so-called “main event”. This event is recorded in ice layers about 17 500 ± 500 years old as a large (about 170 years²⁴) fluoride deposition, not associated with high sulfate spikes. This event could be attributed to a series of eruptions from a subglacial volcano located in West Antarctica.²⁴

Data on the budget of HF and fluoride species present in the atmosphere and precipitation are rather limited. Potential natural sources include sea salt, soil-dust particles, and HF volcanic emissions.^{25,26} In addition, it is expected that the atmosphere of populated regions is affected by anthropogenic sources, such as coal burning, cement and phosphate industrial processes, and aluminum smelters.²⁷ Nevertheless, the lack of available data renders it difficult to evaluate the relative contribution of natural versus anthropogenic sources on the budget of fluoride in the free troposphere. The study of an ice core drilled at Summit (central Greenland) revealed that the atmospheric budget of natural fluoride is dominated there by long-range transported soil-dust aerosols.²⁸ In addition, this Greenland atmosphere was frequently disturbed by volcanic emissions from high-northern latitude regions (Iceland and Kamchatka). This study also revealed that the Greenland fluoride budget has been significantly disturbed by man-made activities (mainly coal burning) from 1960 to the present day. The fluoride record extracted from an ice core drilled nearby the Mont Blanc summit (4250 m elevation, French Alps) was used to investigate the fluoride budget over Europe.²⁹ At the beginning of the 20th century, the major natural source of fluoride is soil-dust emission. Fluoride emissions from aluminum smelters represented a major contribution (up to 80% in 1970) of the total fluoride deposition between 1950 and 1970, whereas the contribution of coal burning remained below 20% over the course of the 20th century. Over the last two decades, in spite of the strong decrease of aluminum smelter emissions, the total fluoride level remains well above its natural level, likely due to a present day strong contribution of other anthropogenic sources, like cement and phosphate industrial processes. So far, no similar fluoride snow and ice studies were yet conducted in Antarctica.

The first measurements of fluoride, present at low levels in Antarctic snow and ice, were carried out by Saigne et al.³⁰ using ion chromatography; later fluoride was routinely determined with a gradient pump system both in Greenland³¹ and Antarctic³² ice core projects. In this work, we present the setup of a new FIC method obtained by coupling a FIA technique with a fast IC separation. One of the greatest advantages of the FIA techniques is the capability to provide a continuous flow of meltwater to the analytical devices, minimizing the sample handling as well as the contact between the sample and the laboratory atmosphere.^{9,10,33} The method here presented is suitable for fast analysis of fluoride at sub-ppb level in firn and ice core samples thanks to its high sensitivity, high reproducibility, and low detection limit. The method was tested on firn samples collected in East Antarctica. The first results of the spatial and temporal distribution of fluoride along an Antarctic traverse (Northern Victoria Land–Dome C transect) are here presented and shortly discussed.

2. EXPERIMENTAL SECTION

The complete separation and quantitation of specific analytes can be difficult in samples that contain many compounds. In such complex matrices, a heart-cut system using two columns with different separation characteristics can be employed to efficiently separate and quantify specific compounds. The setup of a fast ion chromatographic (FIC) method for the analysis of fluoride in ice core samples can be difficult due to the simultaneous presence of anions with retention times much higher than fluoride, which have to be eluted from the column before the injection of the following sample. This problem can

be solved in two different ways: (1) using an eluent concentration gradient in order to elute more quickly the anions with high retention times after the elution of the fluoride peak and (2) preventing the injection in the column of these anions with retention times much higher than fluoride. Owing to the long stabilization time requested by the first solution, we decided to follow the second one, which represents the best way to obtain a higher sampling rate.

The method proposed in this paper is based on the “heart-cut” column switching techniques,^{34–36} which consists of separating a pair (or more) of unresolved analytes from other compounds with higher retention time possibly present in the sample matrix using a preseparation step. After this preliminary separation, the selected analytes are sent to an analytical column that does resolve the target compounds, while the remaining substances are eluted off into the waste. The analytical setup of the method consists of three phases: (1) preconcentration of the analytes coming from the device where ice core sections are continuously melted, (2) preseparation between analytes (short retention time) and compounds with higher retention times by selective elution from the preconcentration column, and (3) separation of the analyte group in the analytical column, while the elution to the waste of the anions still in the preconcentration column occurs. The general setup of the ion chromatographic system is shown in Figure 1a–c. A Dionex DX-120 ion chromatograph was coupled with a flow-analysis device. The system includes a peristaltic pump for sample loading, two six-port valves (V1 and V2), a Dionex TAC-2 (4 mm) preconcentration column, a Dionex AS17 (4 mm, 250 mm) separation column, a Dionex ASRS suppressor (run at 100 mA), and a Dionex CDM-3 conductivity detector. The sample loading was carried out using a peristaltic pump (Minipulse 3, Gilson, Middleton, WI) with a flow rate of 1.0 mL min⁻¹ for a pre-established running time (1.3 min, corresponding to a sample volume of 1.3 mL). Standard solutions for calibrations were daily prepared in precleaned polyethylene vials by diluting a stock standard solution (1000 mg L⁻¹) purchased from Merck (Darmstadt, Germany) with ultrahigh purity water (UHP-H₂O) of resistivity >18 MΩ cm (Milli-Q system by Millipore, Billerica, MA). UHP-H₂O was also used for the preparation of the eluent and for the regenerant solution for the ASRS suppressor. NaOH (0.4 mM), used as eluent, was daily prepared by dilution of a stock solution obtained from a 0.1 N DILUT-IT analytical concentrate (J. T. Baker). The ultrapure water used for the eluent preparation was previously degassed by helium purging to avoid the carbonation of NaOH with a resulting increase in the strength of the eluent.

2.1. The Preseparation. The sample was loaded into the preconcentration column TAC-2 setting the V1 and V2 valves in the “load” positions (Figure 1a). After the sample loading (1.3 min), both V1 and V2 valves were switched into the “inject” position (Figure 1b); in this way, the eluent flows into the TAC-2 preconcentration column in the same direction as the loading phase. The eluent strength and the elution time were chosen in order to elute only the anions with retention times similar to fluoride. In this way, we obtained the separation of fluoride (together with a few analytes with similar retention times) from the residual anionic content (not eluted from the preconcentration column). The target analytes were thus injected in the separation column (see section 2.2). During the separation step, valve V2 was switched into the “load” position so that the TAC-2 preconcentration column was back-

flushed with another eluent line and the trapped anions were sent to the waste (see section 2.3).

The efficiency of the preconcentration column in retaining the total amount of the analyte in the loading phase was already tested in the method applied to the high-resolution analysis of other inorganic anions (chloride, nitrate, and sulfate) on deep Antarctic ice cores.¹³ Various eluents at different concentrations and flows have been tested with 0.4 mM NaOH at a flow rate of 3.0 mL/min eluting the target analyte efficiently. By using an elution time of 0.2 min, the total amount of fluoride, about 80% of acetate, and less than 5% of formate and propionate were eluted from the preconcentration column to the separation one.

2.2. The Separation. It is important to note that we have to use the same eluent in the preseparation, separation, and washing steps in order to avoid long re-equilibration (or reconditioning) periods for the preconcentration and separation columns. For this reason, the eluent choice is very critical, because such eluent must be sufficiently weak for the separation of analytes poorly retained in the separation column (such as fluoride and acetate) and, at the same time, must allow the complete elution of highly retained components (such as sulfate) from the preconcentration column in a very short time. With a separation column suitable for the separation of low-retained ions (Dionex AS17 4-mm), 0.4 mM NaOH was chosen as the best compromise for the different needs: (1) promoting the complete elution of fluoride from the preconcentration column, (2) eluting fluoride and acetate (and lactate, if present; see later in this section) into the analytical column, (3) obtaining a sufficient resolution between their peaks, and (4) completely eluting from the preconcentration column species with high retention times (i.e., chloride, nitrate, and sulfate).

Figure 2 shows five consecutive separations of standard solutions at increasing concentrations of fluoride with an eluent

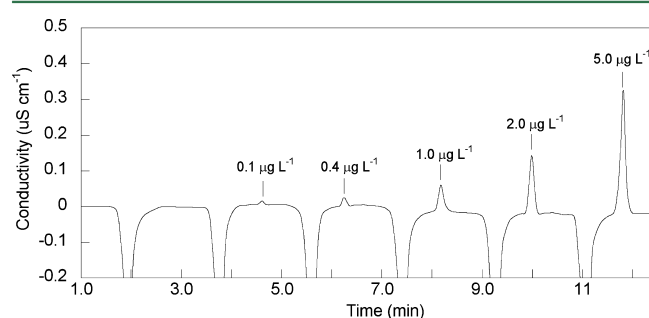


Figure 2. Example of five consecutive injections of F^- (between 0.1 and $5.0 \mu g L^{-1}$) preceded by the injection of a blank (UHQ- H_2O). Every injection is recognizable by the negative peak, called “water dip”, due to the lower ionic conductivity of the sample with respect to the suppressed eluent one. The sample volume used for the analysis is 1.3 mL.

flow rate of 3.0 mL/min. The presence of lactate, which shows an intermediate retention time with respect to fluoride and acetate, represents a drawback to the measurement of these two compounds, because of the partial overlap of the peaks. Our measurements point out that lactate is not usually present in Antarctic snow and ice samples and its presence in these samples is always due to contamination during the sampling, melting, and analysis procedures. In fact, sweat contains lactic acid and relatively high concentrations of lactate can be released by human skin into the samples. Due to its large interference in

the fluoride determination, every precaution has to be taken in the sample manipulation, such as the use of gloves and the treatment of samples under laminar flow hoods. For this purpose, the minimal sample manipulation allowed by using a flow-analysis system for melting and loading the samples in the IC in an automatic way eliminates the lactate interference from the determination of fluoride and acetate in ice- and firn-core samples.^{6,32}

In any case, the eluent here used allows one to obtain a sufficient, even if not complete, separation between fluoride and lactate. We have to note that the sensitivity for fluoride is about 12 times higher than for lactate; therefore, only relatively high lactate concentrations are able to heavily affect the detection of fluoride peaks. A small percentage of propionate and formate that eluted from the preconcentration column together with fluoride, acetate, and, possibly, lactate does not represent at all an interference on fluoride signal, because their chromatographic peaks are completely resolved.

2.3. The Washing Step. After the elution of fluoride and acetate from the preconcentration column (0.2 min), valve V2 is switched to the “load” position (Figure 1c), separating the target analyte with a “heart-cut” column switching. Anions with higher retention times are back-flushed from the preconcentration column using the second eluent line (pump 2), as shown in Figure 1c. The time required to completely elute the remaining anions out of the preconcentration column using the eluent at $5.0 mL min^{-1}$ flow rate is 0.3 min. Back-flushing the preconcentration column efficiently cleans the column and reduces the total run time per analysis. The total analysis time of a sample is 1.8 min. With the sample analyzed and the preconcentration column flushed, the analytical sequence is ready to be repeated. Valve V1 is switched back to the “load” position and the next sample is started. Details about the switching times of valves V1 and V2 are summarized in Figure 1a–c.

3. RESULTS AND DISCUSSION

3.1. Method Performances. The method performances were evaluated in terms of sensitivity, reproducibility, linear range, and detection limit. The linear range was calculated following the iterative procedure of Morganti et al.³² with a 15-point regression curve (Figure 3a) and yields a limit of linearity that extends to $60 \mu g L^{-1}$.

Reproducibility, calculated as percentage standard deviation (%RSD) of 10 replicates of a $0.55 \mu g L^{-1}$ standard solution is <3% and comparable to the earlier work of Legrand et al.³¹ using a larger sample volume of 5 mL. The sensitivity was calculated as the slope of the linear regression of five standard solutions shown in Figure 3b and it was $79.4 nS \mu g^{-1} L$. Blanks obtained by injection of ultrapure water did not show any measurable peak in the chromatograms. The background noise of the baseline was evaluated for 10 replicate injections of a blank solution and the resulting detection limit, calculated as the mean plus 3SD of the signal of these 10 replicate injections divided by the sensitivity, was $0.02 \mu g L^{-1}$.

3.2. Analysis of ITASE Snow Pits. In the framework of the ITASE (International Trans-Antarctic Scientific Expedition) program, several sites were sampled during scientific traverses across Northern Victoria Land (East Antarctica), in order to investigate the spatial and temporal variability of snow depositions along coastal to inland transects. The location of sampling sites for fluoride determinations along the Northern Victoria Land–Dome C route are reported in Table 1. At each

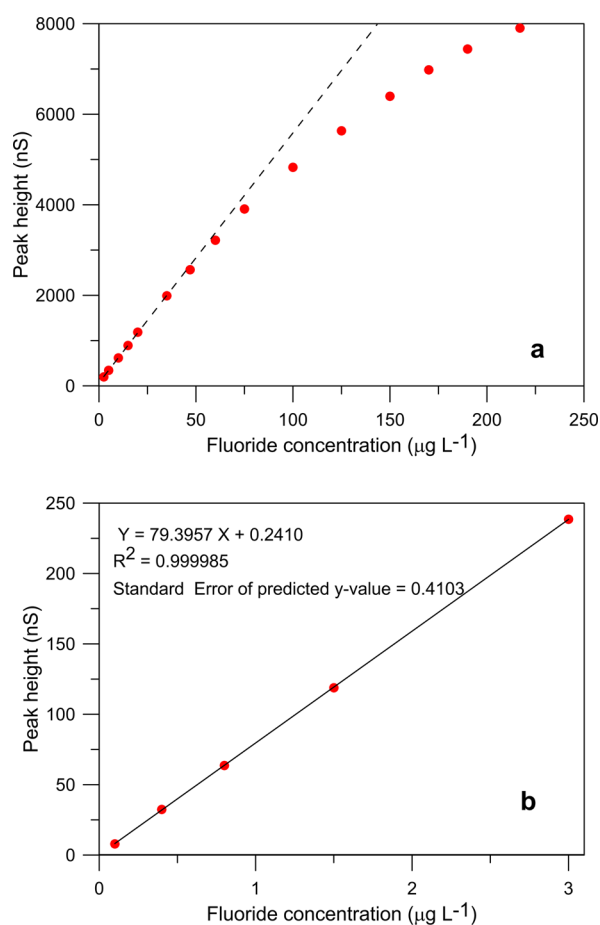


Figure 3. (a) Evaluation of the linear range of the method through calculation of the slope variation. (b) Example of a calibration curve in the concentration range between 0.1 and 3.0 $\mu\text{g L}^{-1}$. The sample volume used is 1.3 mL for both calibration curves.

of the seven sites, a snow pit is dug. Pit walls are cleaned by removing a 5–10 cm thick snow layer with a stainless-steel scraper immediately before sampling.³⁸ Cleaned polypropylene vials are used to sample the vertical snow walls; after removal, each vial is closed, labeled, sealed in a double polyethylene bag, and stored at $-20\text{ }^{\circ}\text{C}$. Samples at each site were collected at 2.5–3.0 cm resolution.

The fast ion chromatographic system for high-resolution analysis of fluoride was used to measure the fluoride concentration on 467 snow-pit samples, and the obtained data set represent the most extensive and detailed time resolution profiles of fluoride in Antarctica.

Fluoride concentrations in the seven different sites are shown in Figure 4 as stacked columns containing the contributions of the three identified sources of fluoride. A few spikes in fluoride concentration are visible for the seven different sites over the stable background concentrations. This pattern is particularly evident at 31DPT and GPS2 sites. Background fluoride values, calculated as the median, ranged from 0.13 to 0.33 $\mu\text{g L}^{-1}$ and are consistent with the fluoride background value of 0.19 $\mu\text{g L}^{-1}$ estimated for the Antarctic ice sheet.³⁰

Sea spray and crustal inputs represent significant sources of fluoride to accumulating snow in Antarctica. The contribution of these two sources to the total fluoride content for each sample is considered. The fluoride fraction arising from sea spray was calculated using the $\text{F}^{-}/\text{Na}^{+}$ mean ratio in seawater ($1.20 \times 10^{-4} \text{ w/w}^{39}$), whereas the fraction related to dust delivery was estimated using the average F/Ca ratio in the upper crust ($1.21 \times 10^{-2} \text{ w/w}^{39}$). These different contributions to the total fluoride budget are plotted in Figure 4, where the fraction of fluoride originated by sea spray is shown in red, the crustal one is in brown, and the remaining fraction is in gray.

We have to notice that the assessment of the crustal fluoride is likely biased; the calculated value is underestimated since the measured calcium in ion chromatography, which is only the soluble fraction of calcium, is probably lower than the total calcium amount derived from mineral dust so that multiplying it for the crustal ratio yields a lower value of crustal fluoride. The remaining fluoride fraction is related both to a background of volcanic inputs in the studied area and long-range transport inputs. The volcanic background inputs represent both eruptions and pure gaseous emissions from the different volcanic districts in this area of Antarctica, and the long-range transport represents all those processes delivering fluoride likely produced by anthropogenic activity in the midlatitude area and transported to the Antarctic continent via free troposphere or via injection into the stratosphere. In general, we can observe that this non-sea-salt and noncrustal contribution accounts for the greatest part of the measured fluoride (between 66% and 92% for the different snow pits), whereas the crustal and the sea-spray fractions of fluoride account only for 7–30% and 1–3%, respectively. Figure 4 does not show any clear volcanic peak in the seven snow pits and in order to check for the possible presence of volcanic signatures, the corresponding nssSO_4^{2-} records were examined. As expected, due to the short time periods covered by these records and to the relatively high accumulation rate and closeness to the coast of 31DPT and GPS2 sites (preventing the detection of volcanic signals), no major and/or known signature of volcanic eruption was spotted, even in the nssSO_4^{2-} profile. Despite that some of

Table 1. Details on the Sampling Sites of the Snow Pits Analysed in This Work^a

site name	latitude	longitude	elev (m asl) ^b	dist from sea (km)	time period ^c (years)	mean time resolution (samples/year)	mean Na^{+} concn ($\mu\text{g L}^{-1}$)	mean Ca^{2+} concn ($\mu\text{g L}^{-1}$)
GPS2	74.645°S	157.502°E	1776	167	5	15.0	44.3	4.7
31DPT	74.025°S	155.960°E	2065	238	5	12.4	52.7	2.8
M2	74.805°S	151.269°E	2308	327	≈ 14	4.9	16.9	2.6
MDP	75.536°S	145.857°E	2454	460	≈ 27	2.4	21.0	3.6
D2	75.622°S	140.631°E	2611	587	≈ 22	2.8	20.0	3.6
D4	75.598°S	135.832°E	2792	692	≈ 40	1.8	24.7	1.3
D6	75.448°S	129.809°E	3024	851	≈ 40	2.0	23.0	2.1

^aThe time period covered by each record was estimated on the basis of the mean accumulation rate from Frezzotti et al.³⁷ ^bMeters above sea level.

^cAccording to Frezzotti et al.³⁷

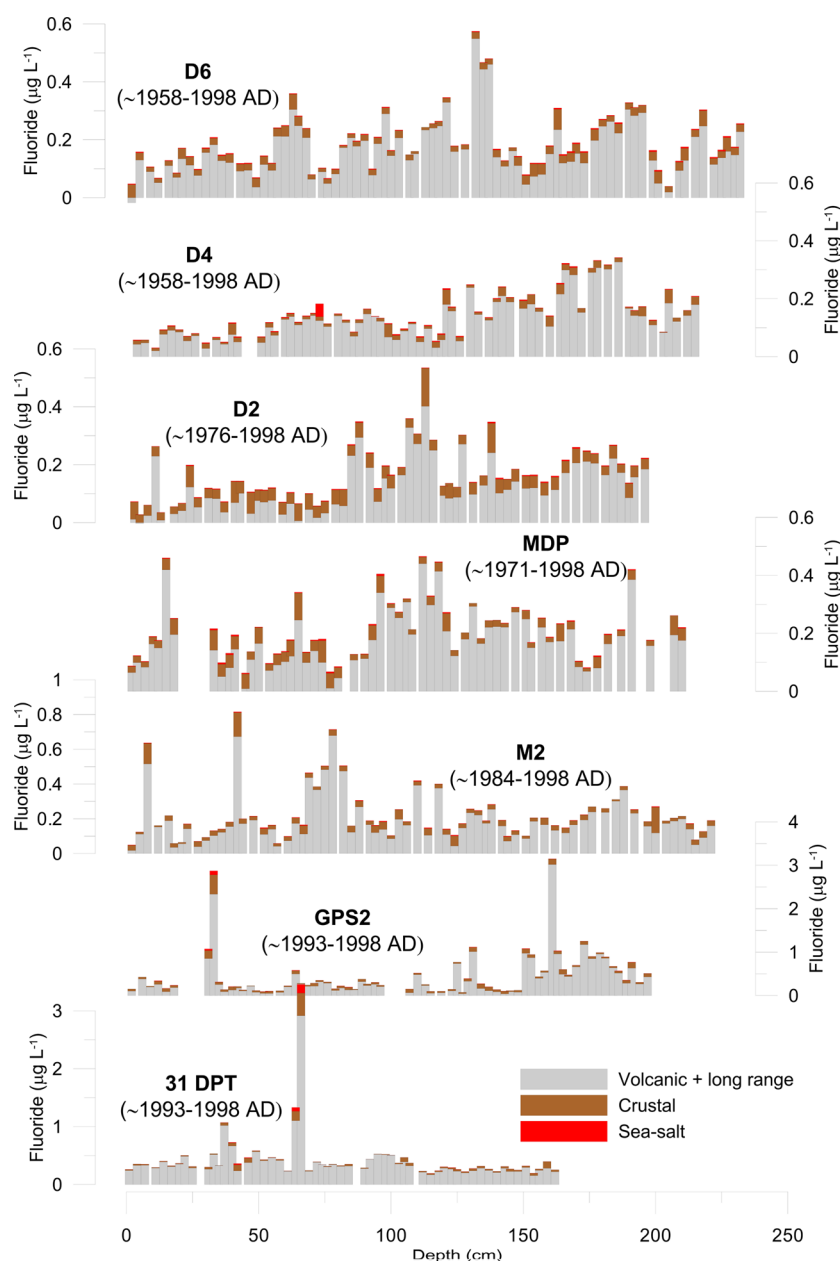


Figure 4. Fluoride concentration profiles for the seven snow pits analyzed in this work. The total measured fluoride is shown for each snow pit as the sum of the three different contributions: sea salt fluoride (in red), crustal fluoride (in brown), and fluoride originated by volcanic emissions or long-range transported (in gray). An estimate of the covered time period is given for each snow pit.

these snow pits are expected to record historically known eruptions, such as Pinatubo (1991 AD) and/or Agung (1964), the reworking of the snow by strong winds at these sites represents a huge drawback for an undisturbed accumulation of the snow layers.

The results obtained show that our novel FIC method is a reliable technique for measuring fluoride concentration in snow pits and represents a useful tool for interpreting the volcanic records found in polar archives, including deep ice cores.

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Notes

The authors declare no competing financial interest.

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