

Direct Determination of Heavy Metals at Picogram per Gram Levels in Greenland and Antarctic Snow by Double Focusing Inductively Coupled Plasma Mass Spectrometry †

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The potential of a double focusing ICP-MS instrument in terms of high sensitivity, sample throughput and low volume of sample consumed was investigated for the direct, simultaneous determination of Co, Cu, Zn, Mo, Pd, Ag, Cd, Sb, Pt, Pb, Bi and U at the low and sub-pg g⁻¹ level in polar snow. The entire analytical procedure, including cleaning of material, field sampling, sample handling, determination of the blanks and instrumental analysis, is described. The mean concentrations detected in snow samples collected in Central Greenland (2.7 m deep pit) are (in pg g⁻¹): Co 5.8, Cu 4.6, Zn 47, Mo 1.6, Pd 1.1, Ag 0.60, Sb 0.86, Pt 0.61, Bi 2.5 and U 1.8. The Cd, Pb and U concentrations in a snow core section collected in East Antarctica are: Cd 0.39, Pb 5.0, U 0.04 pg g⁻¹. Repeatability of measurements ranges between 8 and 25% depending on the element considered. For some of the elements investigated these results constitute the first available for polar snow. The results of direct analysis by double focusing ICP-MS on Cd and Pb in the Antarctic snow samples and on Zn and Cu in Greenland samples are consistent with those obtained by differential pulse anodic stripping voltammetry (DPASV) and graphite furnace atomic absorption spectrometry (GFAAS), respectively.

Keywords: Double focusing inductively coupled plasma mass spectrometry; trace elements; snow; Greenland; Antarctica

The Greenland and Antarctic snow and ice caps are among the best preserved and most detailed archives for the reconstruction of past and recent variations in the chemical composition of the earth's atmosphere.¹⁻³ These archives consist of successive, datable snow layers accumulated during the past hundreds of thousands of years up to the present. They are depositories of hemispheric-scale events that happened in the atmospheres of the past.

Heavy metals occur in polar snow and ice in such a minute amount that their detection poses real problems for analytical chemists in terms of very high instrumental sensitivity and risk

of sample contamination during collection, storage, treatment and analysis. As an example, the very few reliable data sets available for Cd, Pb, Zn and Cu show that their concentrations range from tenths of pg g⁻¹ (10⁻¹² g g⁻¹) in Antarctic Holocene ice^{4,5} up to tens-hundreds of pg g⁻¹ for present-day Greenland surface snow.⁶

The ideal analytical technique to be used in the challenging task of heavy metal determination in polar snow should present extremely low detection limits, multi-element capability and low sample consumption and should avoid, as far as possible, any preconcentration step which is time consuming and could be the source of contamination.

Various instrumental methods have been used in the past, *i.e.*, laser excited atomic fluorescence spectrometry (LEAFS),⁷⁻¹¹ thermal ionisation mass spectrometry (TIMS),^{5,12-15} instrumental neutron activation analysis (INAA),^{16,17} graphite furnace atomic absorption spectrometry (GFAAS),^{4,18-20} differential pulse anodic stripping voltammetry (DPASV),²¹⁻²⁵ atomic fluorescence spectrometry (AFS)^{26,27} and inductively coupled plasma mass spectrometry (ICP-MS).²⁸⁻³⁰ Of these only LEAFS and DPASV have demonstrated enough sensitivity for a direct determination at the required levels.^{7-11,21-25} However, skilful operators and time consuming procedures are required in both cases and DPASV requires a large amount of sample, which is not always available. The other techniques are less sensitive and require different preconcentration or extraction methods,^{5,31,32} which in addition to slowness, require fairly large volumes of samples and need very great care to avoid contamination.

As regards ICP techniques, a quadrupole ICP-MS instrument, after preconcentration of samples by non-boiling evaporation, has already been used for the determination of trace elements in snowfall of the remote Scottish Highlands at the ng g⁻¹ level.^{28,29} By coupling a quadrupole ICP-MS instrument with an electrothermal vapourisation system (ETV-ICP-MS) trace elements in Arctic snow (Ellesmere Island) have been determined.³⁰ In spite of the considerable improvement in terms of sensitivity achieved through the use of ETV sample introduction, the detection limits of this technique could be too high for direct determination of trace elements in the snow and ice of remote polar regions.

A valuable improvement for the direct determination of a wide range of trace elements in polar snow is potentially offered by double focusing ICP-MS which, thanks to the very low background signal and the high ion transmission, offers extreme sensitivity at and below the pg g⁻¹ level. The high purity of the matrix to be analysed is very attractive for direct

† Presented at the 1997 European Winter Conference on Plasma Spectrochemistry, Gent, Belgium, January 12-17, 1997.

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trace metal determination by double focusing ICP-MS, although spectral interferences should be carefully considered.

This paper presents the first results of a new approach to the simultaneous direct determination of several trace elements in Greenland and Antarctic snow by double focusing ICP-MS, which shows the great potential of the technique in terms of high sensitivity, sample throughput and low volume of sample required. For comparison purposes additional measurements were carried out using GFAAS and DPASV, and results are presented.

EXPERIMENTAL

Laboratories and Chemicals

The clean chemistry laboratory used at Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) of the CNRS (Grenoble, France) is a non laminar flow class 10000 clean room, inside which two class 100 laminar flow clean benches were installed for the cleaning of bottles, handling and acidification of Greenland samples.³³

Clean chemistry laboratories with class 100 vertical laminar flow areas were available at the Dipartimento di Scienze Ambientali (DSA) of the University of Venice (Italy) for the cleaning of plastic items used in the decontamination of an Antarctic snow core section and for acidification of the standards. A cold room (-20°C) equipped with a laminar flow bench (class 100) was used for the storage of samples and for the decontamination of frozen core sections. Researchers followed strictly the clean room procedures in these clean environments.

Ultrapure water was obtained by coupling a reverse osmosis system, Milli-RO, with a four column ion-exchange system, Milli-Q (both from Millipore, Bedford, MA, USA) or by passing tap water through a succession of activated charcoal and mixed bed ion-exchange resins from Maxy (St Remy les Chevreuses, France).

Ultrapure concentrated HNO_3 (70%) doubly distilled at the National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA³⁴ was used for the acidification of samples (1+200) and for the final steps of the cleaning procedures of plastic items (see below). Chloroform (Merck, Darmstadt, Germany) and Suprapur grade HNO_3 (65%, Merck) were used during the first steps of the cleaning procedures.

Acidified (NIST HNO_3 , 1+200) multi-element synthetic standard solutions were prepared through successive dilutions [with ultrapure Maxy water, in *ad hoc* used low density polyethylene (LDPE) bottles (11 and 250 ml)] of ICP-MS stock solutions (1000 mg l^{-1} , Merck, and 1000 mg l^{-1} , Spex Certiprep, Metuchen, NY, USA). These standards contained 14 elements according to the typical elemental concentrations expected in recent Greenland and Antarctic snows. Whenever not used the standard solutions were stored frozen.

Acidified (NIST HNO_3 , 1+200) blank solutions were prepared using Milli-Q and Maxy ultrapure waters.

Cleaning of Materials

LDPE bottles for storage of samples and plastic tools were acid cleaned in the class 100 environment of the LGGE clean chemistry laboratory, following a five-step procedure previously described in detail.³³

Briefly, items were cleaned as follows: rough rinse with tap water to remove dust; degrease with chloroform and rinsing with ultrapure water; immersion in a first acid bath (Merck 'Suprapur' HNO_3 in ultrapure water, 1+3, 50°C , 2 weeks) and rinsing with ultrapure water; immersion in a second acid bath (NIST HNO_3 diluted in ultrapure water, 1+1000, 50°C , 2 weeks) and rinsing with ultrapure water; immersion in a

third acid bath (NIST HNO_3 diluted in ultrapure water, 1+1000, 50°C , 2 weeks); finally, bottles are rinsed several times with ultrapure water, filled with a diluted ultrapure HNO_3 fresh solution (1+1000) and stored inside double polyethylene acid clean bags, while other tools remain in the last bath until use.

A slightly modified multi-step procedure²³ was used for the cleaning of LDPE hammers and LDPE home made scrubbers, used to decontaminate the pit walls and snow core section at the DSA in Venice.

Sampling and Datation

Shallow snow samples were collected in June 1995 at a remote site located a few kilometres East South East of the US-European ATM sampling site ($72^{\circ}20'\text{N}$; $38^{\circ}45'\text{W}$; elevation 3270 m ; mean snow accumulation rate $23\text{ g H}_2\text{O cm}^{-2}\text{ y}^{-1}$) in central Greenland.³⁵ During sampling, operators wore clean room garments, masks, polyethylene gloves and boot covers to prevent contamination.

A total of 68 shallow snow samples were collected in a 2.7 m deep hand-dug pit, inserting cylindrical LDPE containers (id 4 cm, length 40 cm) horizontally in the carefully decontaminated upwind pit wall and then transferring the contents to clean, wide-mouth LDPE 11 bottles (Nalgene, Nalge Company, Rochester, NY, USA). After collection the containers were sealed inside double polyethylene bags and transported frozen to LGGE, where they were stored at -20°C .

Inside the clean laboratory, samples were allowed to melt at room temperature and sub-aliquots of 15 ml were transferred to 15 ml LDPE clean bottles and 75 μl of ultrapure NIST HNO_3 was added. These sub-aliquots were then transported frozen to the DSA in Venice.

Snow core samples were collected in January 1994 in the Hercules Névé, Victoria Land, East Antarctica ($73^{\circ}06'\text{S}$; $165^{\circ}28'\text{E}$; elevation 2960 m , mean snow accumulation rate $16\text{ g cm}^{-2}\text{ y}^{-1}$).³⁶ A stainless steel auger (id 10.4 cm) was used to collect samples down to a depth of 10 m. After collection, snow core sections were sealed in double polyethylene bags and transported frozen to the DSA in Venice. In this work a 37 cm length core section (depth at the middle 956 cm, estimated year of deposition, 1968³⁶) was used.

Despite the great care taken in the field to avoid contamination, the external layers of the snow core collected in Antarctica were more or less susceptible to contamination by metal impurities due to the auger tube and the long storage period. For this reason a special decontamination procedure³⁷ was carried out in the laminar flow area of the cold room. This method allows four concentric layers of snow (radius 0–1.5, 1.5–2.5, 2.5–3.5, 3.5–5.0 cm) to be separated and stored for analysis. Melted snow samples were then acidified (NIST HNO_3 , 1+200) and the trace element concentrations measured from the outside to the centre in order to obtain a radial concentration profile.

The age of the Greenland pit samples was estimated from the Na and Al concentration profiles obtained by GFAAS in different sub-aliquots of the same samples. As usual the Na and Al late winter/spring concentration maxima were used to reconstruct the age of snow layers.

The age of the Antarctic snow core was roughly estimated from the hydrogen peroxide and $\delta^{18}\text{O}$ vertical profiles measured in cores drilled at the same sites in the 1991–92 season.³⁶

Analytical Instrumentation

Measurements were carried out with a Finnigan MAT Element (Finnigan MAT, Bremen, Germany) High Resolution Inductively Coupled Plasma Mass Spectrometer (double focusing ICP-MS).^{38–40} The instrument is equipped with a fast scan,

laminated magnetic sector field analyser and an electrostatic analyser (ESA) in reverse Nier–Johnson geometry. This particular geometry, with the magnet in front of the ESA, make it possible to reduce the background signal intensity and simultaneously increase the abundance sensitivity. Furthermore the sampling interface, operating at the ground potential, is easily accessible, thus facilitating the coupling with several sample introduction systems and hyphenation. Moreover the pre definite resolution settings available of 300, 3000 and 7500 $M/\Delta M$ allow most spectral interferences caused by polyatomic species to be separated.

The ion detection unit consisted of a conversion dynode in front of a secondary electron multiplier (SEM). Because of the low concentrations expected for the analysed elements, the counting mode was chosen instead of the analog mode.

The sample introduction system consisted of a Spetec (Erding, Germany) peristaltic pump, a Meinhard nebulizer Type A (Meinhard, Santa Ana, CA, USA) and a home made, quartz, double-pass spray chamber, cooled at 5 °C by a closed circuit refrigerating system. The same quartz Fassel torch was used throughout the experiment. The tube of the peristaltic pump was cleaned by allowing a solution of ultrapure acid (NIST HNO_3 , 1+100) to flow for at least two hours before each measurement session. Sampling and skimmer cones, with an orifice diameter of 1.0 and 0.75 mm, respectively, were made of nickel.

Instrumental Parameters

The instrumental conditions used throughout the work are reported in Table 1.

The ion intensities recorded by the detection system are a function of several parameters, the most important of which are sampling distance, lens voltage, nebulizer gas flow rate and the radio-frequency generator power.

In particular the effect of the nebulizer gas flow rate on the signal intensity was carefully investigated on the snow matrix. Considering the purity of the polar snows, which can be considered as among the purest natural materials in the earth's surface, an acidified (NIST HNO_3 , 1+200) synthetic snow sample was prepared by successive dilution in ultrapure water of Co, In and Pb ICP stock solutions. The concentration of the elements in the tuning solution was 10 pg g^{-1} . Cobalt, In and Pb were selected because they represent a wide range of relative masses, which encompasses masses of several of the analytes investigated. This solution was measured at different gas flow rates and signal behaviour plots (signal intensity *versus* nebulizer gas flow rate) were recorded. A nebulizer gas flow rate corresponding to the peak maximum was selected for the analysis (see Fig. 1).

The ion transmission at low resolution (300 $M/\Delta M$) was 50 000–100 000 counts s^{-1} per ng g^{-1} of In, depending on tuning conditions. Optimisation of instrumental parameters was carried out daily in order to maximise the performance of the instrument in terms of sensitivity and signal stability. The acquisition parameters selected for all measurements are briefly summarised in Table 2.

Low resolution ($M/\Delta M = 300$) was used for all the isotopes

Table 1 Instrumental conditions for the Finnigan MAT Element

Forward power	1300 W
Gas flow rates	
Plasma	14.5 l min^{-1}
Intermediate	0.7 l min^{-1}
Nebulizer	Optimised to obtain maximum signal intensity
Sample uptake rate	0.8 ml min^{-1}
Ion sampling depth	Optimised to obtain maximum signal intensity
Ion lens settings	Optimised to obtain maximum signal intensity

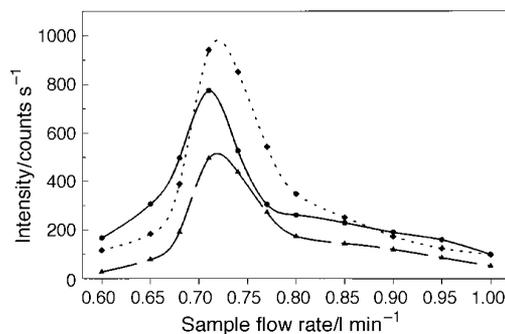


Fig. 1 Optimisation of aerosol carrier gas flow rate with a radio-frequency generator power of 1.3 kW. A 10 pg g^{-1} solution of Co (\blacktriangle), In (\bullet) and Pb (\blacklozenge) was used.

Table 2 Measurement parameters for the Finnigan MAT Element

Acquisition mode	E-scan; electric scanning over small mass range
No. of scans	25
Dwell time per acquisition point	10 ms
No. of acquisition points per mass segment	50
Total acquisition time	0.5 s per mass segment and per scan
Washing time	3 min
Resolution required	
^{59}Co , ^{64}Zn , ^{63}Cu	$M/\Delta M = 3000$
^{98}Mo , ^{106}Pd , ^{107}Ag , ^{109}Ag , ^{112}Cd , ^{114}Cd , ^{195}Pt , ^{208}Pb , ^{209}Bi , ^{238}U	$M/\Delta M = 300$

except ^{59}Co , ^{63}Cu and ^{64}Zn , for which severe interference mainly due to $^{40}\text{Ar}^{18}\text{OH}$, $^{43}\text{Ca}^{16}\text{O}$, $^{40}\text{Ar}^{19}\text{F}$, $^{23}\text{Na}^{40}\text{Ar}$, $^{24}\text{Mg}^{40}\text{Ar}$, $^{32}\text{S}^{16}\text{O}_2$, $^{48}\text{Ca}^{16}\text{O}$ and $^{38}\text{Ar}^{12}\text{C}^{14}\text{N}$ could affect the accuracy of analytical determinations.

Calibration Curves and Quantification

Considering that the more direct the analytical procedure is, the more appropriate it will be for contamination control, an external calibration curve was used for the quantification of concentrations in the real samples, avoiding the use of internal standards. Owing to this procedure, to avoid problems due to the drift of the signal intensity with time, a special sequence of standards and samples was adopted. A blank (acidified Maxy water), 4 standards and 6–8 samples were analysed during each session of measurement and the results immediately evaluated before proceeding with another session.

For each isotope the intensity of the blank was then subtracted from the intensities of the standard solutions and the signal increment plotted against the nominal concentrations of the standards. The linear calibration curves so obtained were used for trace element quantification in the real samples measured in the same session.

A total of nine sessions was used for the whole analysis.

DPASV and GFAAS Measurements

Since no reference materials exist for polar snow and ice, we measured Cd and Pb in the Antarctic snow core sample and Zn and Cu in the Greenland snowpit samples by independent techniques in order to check the analytical quality of the data.

DPASV had already been used with success for the direct simultaneous determination of Cd and Pb in Antarctic snow.²³ The principle of the technique is based on electrolytic

deposition of analytes on a thin mercury film electrode (TMFE) and subsequent stripping by means of a differential pulse potential scan with measurement of the diffusion current involved in the process. The concentrations of metals in the sample are then determined through the heights of the current peaks developed during the stripping phase, using the standard additions method. Because of the very high sensitivity of the technique, samples are analysed directly after melting, without any preconcentration step.²³

GFAAS was used for the determination of Zn and Cu in the Greenland samples. The relatively high Zn concentration allowed the metal to be determined, with a precision of $\pm 10\%$, directly without any preconcentration.³¹ Multiple injections (up to 10) of a 50 μl sample in the graphite furnace were used. The Cu concentration in Greenland snow often falls below the detection limit of the technique; in this case a volume (about 30 ml) of the sample was preconcentrated to about 1 ml by non-boiling evaporation inside FEP Teflon beakers, according to a procedure already reported,³¹ and then analysed by GFAAS. For Cu the repeatability of measurements is about 30% (RSD). External calibration curves were used for the quantification of Zn and Cu concentrations.

RESULTS AND DISCUSSION

Blank Determinations

Considering the high purity of the analysed matrix, particular care was taken in the choice of reagents, storage bottles, plastic items used for sampling and decontamination of snow cores and in the evaluation of the blanks.

Possible, although low, contributions to the trace element concentrations could come from several sources: snowpit sampling, melting of samples in LDPE bottles, handling, sub-aliquots preparation, decontamination procedure for the Antarctic snow core samples and introduction of samples in the sampling injection interface of the instrument. Particular care has been devoted to the estimation of the possible blank coming from the acidification of the samples and from the use of ultrapure waters. The contribution of the acid was evaluated by measuring ultrapure Maxy water solutions with increasing content of HNO_3 NIST (from 1+1000 to 1+50). No signal intensity variations were observed that were significantly different from the blank standard deviations (see below) for all the measured elements, except for Zn. For this element the contribution due to acidification was estimated to be 0.4 pg g^{-1} in the final (1+200 acidified) sample.

The amount of metal impurities introduced with the acidifications was also calculated from literature data,³⁴ considering the 1+200 dilution of samples. The obtained concentration increments due to acidification were: Co 1, Cu 15, Mo 3.5, Pd 4, Cd 25, Sb 5, Pt 40, Pb 20 and U 1 fg g^{-1} ($10^{-15} \text{ g g}^{-1}$), while it was 0.31 pg g^{-1} for Zn. It is to be noted that concentrations are always below the detection limit of the technique (see below). In most cases the calculated contribution of acidification (with respect to both samples and ultrapure waters) can be considered negligible except for Zn and Pt. However, while the Zn contribution has been detected in approximately the same amount in the acid used in this work, no signal for Pt has been observed, which shows that the present acid batch is of better quality than the one analysed at NIST in the past.³⁴ For these reasons only the measured Zn contribution has been subtracted from the results of measurements carried out in samples and ultrapure water.

The concentrations of trace elements in the ultrapure Milli-Q and Maxy waters were determined from the four-point calibration curves used as in the standard additions method. In Table 3 the concentration values for the two ultrapure waters are reported together with previously published data for the

Table 3 Trace elements concentration of ultrapure Milli-Q and Maxy waters

	Element concentration/ pg g^{-1}			Detection limit*/ pg g^{-1}
	Milli-Q water	Maxy water		
		This work	Literature data	
Co	1.55 (0.04)†	1.47(0.03)†		0.09
Cu	0.9 (0.3)	0.6 (0.2)	<0.1‡	0.6
Zn	2.1 (0.3)	1.8 (0.3)	0.3‡	0.9
Mo	0.32 (0.09)	0.64 (0.07)		0.21
Pd	0.20(0.02)	0.24 (0.03)		0.09
Ag	0.07 (0.01)	0.06 (0.01)		0.03
Cd	0.8 (0.2)	0.6 (0.1)	<0.05§	0.3
Sb	0.15 (0.05)	0.15 (0.02)		0.06
Pt	0.05 (0.01)	0.043 (0.003)		0.009
Pb	1.2 (0.2)	1.04 (0.03)	0.27 ; 0.28	0.09
Bi	0.03 (0.04)	0.02 (0.01)		0.03
U	0.12(0.03)	0.06 (0.03)		0.09

* From Maxy water data, according to the 3s criterion (see text).⁴¹

† In brackets, standard deviations, $n=5$.

‡ From Boutron.³³

§ From Bolshov *et al.*¹⁰

|| From Bolshov *et al.*¹¹

Maxy water.³³ No considerable differences are noted between the Milli-Q and Maxy ultrapure waters, except for Mo, which is more concentrated in Maxy water, and U, which shows higher concentrations in Milli-Q water.

The discrepancies observed for the results obtained by ICP-MS and other techniques for the Maxy water could be imputed to a possible release from the sampling injection interface. This possible contribution of a procedural blank is presently under investigation.

Repeatability and Detection Limits

Repeatability of measurements was determined on a real Greenland sample collected at the depth of 257 cm, for which the available sample volume was unusually large. Ten distinct consecutive measurements were carried out within 140 min. The trace element concentrations determined in the sample (in pg g^{-1}) and the relative standard deviations (% in brackets) are: Co 5.4 (10), Cu 4.6 (8), Zn 39 (8), Mo 2.6 (16), Pd 1.2 (14), Ag 1.4 (15), Sb 0.7 (25), Pt 0.4 (16), Bi 1.3 (12), U 0.8 (21).

From these findings it is possible to observe that the repeatability of measurements ranges typically between 8 and 25% depending on the element considered.

Detection limits were calculated as three times the standard deviation of the blank.⁴¹ Five aliquots were analysed five times each and the standard deviation calculated from the five averages obtained. The results are reported in Table 3. Considering that the estimated instrumental detection limit was reported as about 8 fg ml^{-1} ,⁴⁰ blanks coming from different steps of the analytical procedure can be considered the real limiting factor for the determination of trace elements at the low and sub pg g^{-1} level.

Antarctic Snow Samples

With the aim of intercalibration between double focusing ICP-MS and DPASV, Cd and Pb concentrations were determined in the four concentric layers of the snow core collected in Antarctica. Uranium concentrations were also determined in these samples by double focusing ICP-MS. Results obtained for Cd and Pb are reported in Table 4 together with comparative data obtained by DPASV. The radial concentration profile for U is reported in Fig. 2.

The radial profiles for the three metals exhibit a clear concentration plateau in the two–three internal layers, showing

Table 4 Comparative determination of Cd and Pb in Antarctic snow by double focusing ICP-MS and DPASV. Analysis of radial layers of a snow core collected in the Hercules Névé, Victoria Land, East Antarctica

Layer (from outside)	Cd concentration/ $\mu\text{g g}^{-1}$		Pb concentration/ $\mu\text{g g}^{-1}$	
	double focusing ICP-MS	DPASV	double focusing ICP-MS	DPASV
1st	8.8*	(9.2, 8.9)*	80*	(77, 65)*
2nd	1.6*	(1.3, 1.9)*	11.0*	(8.8, 12.6)*
3rd	0.43	0.45	5.0	4.9
Central	0.38	0.44	5.0	4.4
Mean	0.40	0.45	5.0	4.6

* Values not considered in the mean calculation.

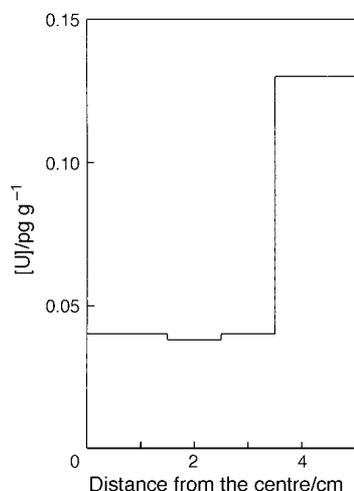


Fig. 2 Uranium radial concentration profile for an Antarctic snow core determined by double focusing ICP-MS (Hercules Névé, Terra Victoria, summer 1993–94, depth 956 cm).

that the external contamination of snow cores did not diffuse to the central part of the section. The plateau concentration values, therefore, represent the real concentrations of the core.

Concentration values for Cd and Pb are in good agreement with reliable data reported for recent Antarctic snows.^{10,20,25,42} Results of the intercomparison show good agreement between the two independent techniques for all the snow layers.

As regards U, the mean value obtained from data of the central core and the two inner layers is $0.04 \mu\text{g g}^{-1}$. The present data constitute, to the authors' knowledge, the first report for uranium concentration in Antarctic snow. For this reason, in order to test the reliability of our value for U, a possible natural background concentration has been estimated, although with large uncertainty.^{5,20,25} The metal contribution from rock and soil dust is calculated from the Al concentration measured in the same sample (2 ng g^{-1}). Combining this value with the U:Al mass ratio in bulk crustal material (1.1×10^{-5}),⁴³ an average rock and soil dust contribution of $0.022 \mu\text{g g}^{-1}$ of uranium is obtained. This contribution is close to the U concentration in the snow, which indicates that U probably originates from rock and soil dust. The possible excess in the U concentration found in the Antarctic snow sample could be attributed to other natural (e.g., marine, volcanic or biogenic) or unknown anthropogenic origin. However, the use of mean crustal values listed in literature⁴³ could not be correct, since the field site could be under the influence of a particular source. In this respect the calculation of rock and soil dust contribution must be considered as order of magnitude estimations.

Greenland Snow Samples

The 68 Greenland snow samples were analysed directly after melting and acidification (NIST HNO_3 , 1+200), to determine the concentration of Co, Cu, Zn, Mo, Pd, Ag, Sb, Pt, Bi and U.

A few statistics of the results obtained are reported in Table 5. The wide dispersion of concentration values is highly dependent upon variations due to the strong seasonal influence on the mechanism of atmospheric transport from remote continents to the Greenland ice sheet. As an example Zn and Cu depth concentration profiles are reported in Fig. 3(a) and (b), respectively, together with the estimated period of deposition of the snow. Comparative results obtained by GFAAS are also reported.

As regards Zn, the agreement between the two independent techniques used is good: slope, double focusing ICP-MS versus GFAAS = 1.16 ± 0.13 (95% confidence interval), corr 0.916. For Cu the values measured by double focusing ICP-MS are systematically lower than those measured by GFAAS: slope, double focusing ICP-MS versus GFAAS = 0.53 ± 0.08 (95% confidence interval), corr 0.860. The cause of this systematic difference for Cu is presently under investigation by means of further intercalibration exercises on real samples.

However, it is to be observed that, in spite of the differences in the absolute concentrations found for Cu, consistent temporal changes are observed with both techniques for the two metals, which show a similar seasonal pattern. In fact both concentration profiles reveal spring and summer maxima, which can be attributed to the transport and subsequent scavenging of polluted Arctic air masses from lower latitude countries during these periods of the year. The transition from winter to spring is often associated with enhanced vertical mixing correlated to the northward retreat of the polar front, while the summer layers peaks may reflect short, but intense input phenomena closer or within the Arctic circle.⁴⁴

Uranium concentrations in Greenland snow are much higher than those found in the Antarctic and also with respect to calculated values due to rock and soil dust input, but they agree with the value reported for recent Greenland snow (about $3 \mu\text{g g}^{-1}$).⁴⁵ This difference may be imputed to the different extent of pollution of the Greenland snow, which is close to the highly industrialized countries of North America, Europe and Western Asia.

Mean contributions to each metal from rock and soil dust are tentatively estimated, for the present-day climatic conditions, by combining the Al concentration values, measured by GFAAS in each of the 68 samples (mean 7.3 ng g^{-1} , SD 10.7 ng g^{-1}), with the metal:Al mass ratio in bulk crustal material,^{43,46} according to the usual procedure. Results are reported in Table 5. The excess in the metal concentrations found in the Greenland snow samples could be attributed to other natural (e.g., marine, volcanic or biogenic) or unknown anthropogenic origin. A detailed geochemical interpretation of seasonal variations in the concentration of trace elements in

Table 5 Summary statistics for concentration of trace elements in 68 Greenland snow samples covering a four year time period (Winter 1990 to Spring 1995). Crustal contributions are calculated combining Al concentration measured in the samples by GFAAS with the metal:Al mass ratio in bulk crustal material.^{43,46}

Element	Element concentration/pg g ⁻¹		Crustal contribution/pg g ⁻¹
	Median (min-max)	Mean (SD)	Mean (SD)
Co	5.3 (0.65-17.2)	5.8 (3.6)	2.5 (3.7)
Cu	3.7 (0.78-13.6)	4.6 (3.0)	6.5 (9.6)
Zn	30 (2.0-207)	47 (40)	6.9 (10.1)
Mo	1.6 (0.08-7.0)	1.6 (1.2)	0.09 (0.13)
Pd	0.9 (0.05-4.2)	1.1 (0.81)	0.09 (0.13)
Ag	0.38 (0.08-5.0)	0.60 (0.75)	0.006 (0.009)
Sb	0.72 (0.21-4.3)	0.86 (0.60)	0.02 (0.03)
Pt	0.55 (0.08-1.5)	0.61 (0.34)	0.001 (0.001)
Bi	1.7 (0.29-21.2)	2.5 (3.2)	0.02 (0.03)
U	0.8 (0.21-15.4)	1.8 (2.7)	0.08 (0.12)

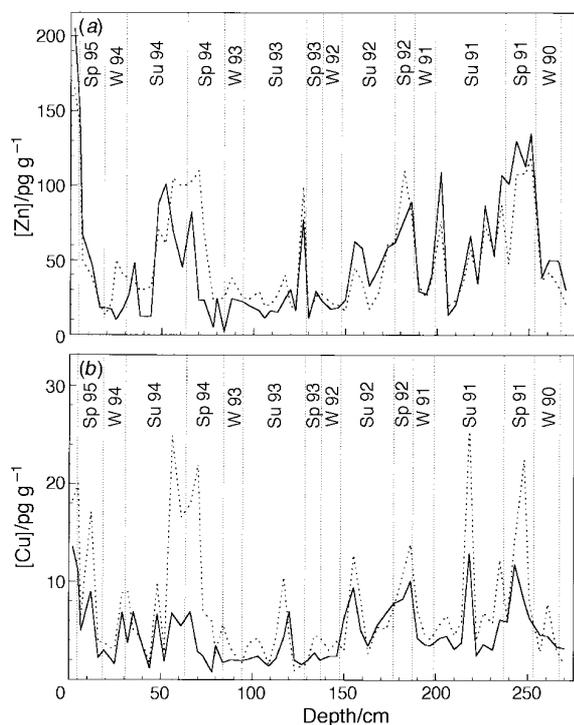


Fig. 3 (a) Zn and (b) Cu depth profiles at Summit (Central Greenland) obtained by double focusing ICP-MS (—). GFAAS results (- - -) are shown for comparison. Datation is also reported: W=Winter; Sp=Spring; Su=Summer.

terms of changing sources and/or associated transport pathways is presently under consideration and will be discussed in a future publication.

CONCLUSIONS

Owing to the low signal background and the high sensitivity, the detection limit obtained by double focusing ICP-MS can be considered adequate for the direct determination of trace elements down to sub pg g⁻¹ level in polar snow. Furthermore the multi-element capability of the technique allows the simultaneous determination of several elements in just a few ml of samples, which is of paramount importance in glacio-chemical investigations, particularly when deep ice cores are to be analysed.

Most of the elements considered here and others which could potentially be determined by double focusing ICP-MS have never been detected in polar snow; indeed they could constitute important tracers of the natural and anthropogenic

origin of airborne deposited material, making it possible to obtain valuable new information on sources and long range transport pathways from mid-latitudes to the polar troposphere.

This study was performed in the framework of projects on 'Environmental Contamination' and 'Glaciology and Paleoclimatology' of the Italian *Programma Nazionale di Ricerche in Antartide* and financially supported by ENEA through co-operation agreements with the Universities of Venice and Milan, respectively. The financial contribution of the European Project for Ice Coring in Antarctica (EPICA) supported by the European Union and coordinated by the European Science Foundation is gratefully acknowledged. The Greenland samples were collected within the European program TAGGSI (EC EV5V-0412) as part of the joint US-European ATM program. We would like to thank the PICO, GISP-2 and GRIP personnel for general support in the field. This work was supported by the French Ministry of the Environment (grant 92095 and 94074), the Institut Universitaire de France, the Institut National des Sciences de l'Univers and the University Joseph Fourier of Grenoble. Special thanks are due to Jean-Luc Jaffrezo and Valérie Hoyau for their valuable work in the collection of the Greenland snowpit samples and to the researchers of the 'Environmental Contamination' group for the skilful sampling activity in Antarctica.

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Paper 7/01686G

Received March 11, 1997

Accepted June 16, 1997