

# Determination of Ir and Pt down to the sub-femtogram per gram level in polar ice by ICP-SFMS using preconcentration and a desolvation system†

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A new analytical methodology, based on inductively coupled plasma sector field mass spectrometry (ICP-SFMS) coupled with a micro-flow nebulizer and desolvation system, has been set up for the quantification of Ir and Pt down to the sub-ppq level ( $1 \text{ ppq} = 1 \text{ fg g}^{-1} = 10^{-15} \text{ g g}^{-1}$ ) in polar ice samples. Ultra-clean procedures were adopted during the pre-treatment phases in our laboratories in order to avoid possible contamination problems and a preconcentration step by evaporation at sub-boiling temperatures was necessary. A procedural detection limit of 0.02 ppq and 0.08 ppq for Ir and Pt, respectively, was obtained. The reproducibility of the analytical procedure at the ppq level was about 50% for Ir and 30% for Pt and the recoveries were 75% and 93% for Ir and Pt, respectively. Spectral interferences, which affect the determination of Ir and Pt, were reduced by using a desolvation system for sample introduction. The contribution of the interfering species was determined and subtracted. This new method allowed us to analyse Ir and Pt in remote uncontaminated ice samples from Antarctica and Greenland down to the sub-ppq level. The concentration ranges were from 0.1 up to 5 ppq for Ir and from 0.2 up to 7 ppq for Pt. These measurements represent the first data of Ir concentrations in unfiltered melted ice samples and the lowest concentrations ever recorded for Pt in environmental samples.

## Introduction

The discovery of the anomalous enrichments of platinum-group elements (PGEs) in the globally extended clay layer signifying the Cretaceous–Tertiary (K–T) boundary provided the first evidence of a large extraterrestrial body impacting the Earth 65 million years ago.<sup>1</sup> This study produced an enormous increase in the interest of the geochemistry of PGEs, and many multidisciplinary studies were conducted in the following years.<sup>2</sup>

Successively dated snow and ice layers deposited in permanent glaciers in polar regions have proved to be valuable archives for reconstructing biogeochemical cycles of heavy metals on Earth.<sup>3–7</sup> Nevertheless, studies on PGEs in polar archives have not previously progressed very far because of the ultra-low concentrations (down to sub-ppq levels,  $1 \text{ ppq} = 1 \text{ fg g}^{-1} = 10^{-15} \text{ g g}^{-1}$ ) of these elements in ice and the very low volume of ice available for study.

Only a few studies, assessing iridium levels in particulate

matter trapped in polar ice, have been reported until now.<sup>8–13</sup> The analytical methods were, however, only suitable for determining the Ir concentrations in the filtered particles ( $> 0.45 \mu\text{m}$ , except in the work by Koeberl,<sup>10</sup> which measured the decanted particulate fraction obtained after melting) by instrumental neutron activation analysis (INAA), missing the fine and soluble fractions. Total concentrations of iridium have only been determined in natural waters (river, ocean and estuarine water) by negative thermal ionisation mass spectrometry (NTIMS) for instance,<sup>14,15</sup> but no analytical procedure has ever been reported, until now, to determine the total concentration of Ir in ice.

Until recently there were no studies on Pt in ice and snow archives. However, thanks to the sensitivity of inductively coupled plasma sector field mass spectrometry (ICP-SFMS), and the use of strict contamination control throughout the analytical procedure, much progress has been made in the determination of Pt, Pd and Rh in polar and alpine archives from the beginning of the industrial period.<sup>16–18</sup> These studies have revealed a global contamination of these heavy metals originating mainly from the exhaust gases of vehicles fitted with catalytic converters.

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Nevertheless, where anthropogenic enrichment has not occurred, the determination of the total concentration of PGEs in uncontaminated polar ice samples remains an analytical challenge. Concentrations of Ir and Pt in remote ancient ice are extremely low (down in the sub-ppq range), and their concentrations in polar archives offer the fascinating possibility of studying the flux of cosmic material. Ir and Pt are relatively abundant in cosmic material (average concentrations in chondrites, the most common meteorites, are 481 ppb for Ir and 990 ppb for Pt)<sup>19</sup> but are rare in the terrestrial crust (average concentrations are 0.05 ppb for Ir and 0.4 ppb for Pt).<sup>20</sup> When inputs of terrestrial dust to polar ice were low, the cosmic fraction of Ir and Pt could be distinguishable from the terrestrial background. Thus, the concentrations of Ir and Pt in ancient polar ice could allow the reconstruction of the input of cosmic material entering the Earth's atmosphere during the last climatic cycles.

In this work we present the development of a method for the determination of the total concentrations of Ir and Pt at sub ppq levels using only about 60 ml of melted ice from Greenland and Antarctica. Samples have been measured after sub-boiling evaporation under ultra-clean condition by ICP-SFMS coupled with a micro-flow nebulisation/desolvation system.

## Experimental

### Clean conditions

The analytical procedures were performed at the Laboratory of Glaciology and Geophysics of the Environment (LGGE) in Grenoble and at the Department of Environmental Sciences (DES) in Venice. Both laboratories have developed special areas where ultra-clean procedures can be adopted to control contamination problems.<sup>21–24</sup> At the LGGE, the cleaning of the low density polyethylene (LDPE) bottles, Teflon (PFA) beakers (both from Nalgene Corporation, Rochester, USA) and the stainless steel items for the decontamination procedure were carried out in a class 100 clean bench located in a class 10000 clean room.<sup>21</sup>

The ultra pure water used was obtained from a mixed bed of ion-exchange resins (maximum flow rate was 2 l h<sup>-1</sup>) from Maxy (La Garde, France).<sup>21</sup> Chloroform (Merck, Darmstadt, Germany) and Suprapur grade HNO<sub>3</sub> (65% Merck) were used for the initial steps of the cleaning procedure. Ultra pure double distilled HNO<sub>3</sub>, supplied by the Department of Applied Physics of Curtin University of Technology (CUT) in Perth, Australia (Prof. K. Rosman), was used for the final steps of the cleaning procedure and for sample acidification and standard addition.

### Sample treatment

To sample the deep ice layers in polar glaciers, electromechanical drills were used to obtain ice cores, with a diameter of about 10 cm. The ice cores were collected in Greenland at Summit (72°34' N, 37°37' W, 3238 m, mean annual temperature -32 °C) within the framework of the European Greenland Ice Core Project (GRIP) and in Antarctica at Dome C (75°06' S, 123°21' E, 3233 m, mean annual temperature -54 °C) within the framework of the European Project for Ice Coring in Antarctica (EPICA). In these international programmes, a given core section (typically 55 cm long) is cut longitudinally into several parts which are used for different kinds of measurements. Thus, only part of the cross section (about 30%), for both the GRIP and EPICA ice cores, was available.

A major problem is that the ice cores are always contaminated on their outside by several heavy metals. The contamination is from the wall retaining fluid, which is used to prevent the closing of the drilling hole at great depths in the glaciers. The possible contamination, derived from the drilling

fluid and the core handling, was carefully evaluated. A special decontamination procedure<sup>25</sup> was performed in a cold laboratory (*t* = -15 °C) at the LGGE in a class 100 clean bench under laminar flow conditions. A preliminary removal of the outermost layer with a special stainless steel knife had to be performed outside the clean bench to prevent the heavily contaminated superficial layer of the ice core from entering the clean area. Then, at least three annular concentric layers were chiselled off inside the clean bench with acid cleaned stainless steel knives before reaching and recovering the uncontaminated inner part of the core which was stored in an ultra-clean 1 l LDPE bottle. With regards to the GRIP samples a single core was recovered from each section, whereas two successive cores were obtained for each EPICA sample. The samples were then melted at room temperature in a class 100 clean bench and an aliquot of about 60 ml was transferred to a 60 ml ultra-clean LDPE bottle and kept frozen until the succeeding analytical step. The typical sample volume required (60 ml) is about 65 times smaller than that previously used for assessing total Ir concentrations in natural water (4 l).<sup>15</sup> This volume represents about 20% of the decontaminated part of the inner core.

Preconcentration<sup>26</sup> was performed by evaporation at sub-boiling temperatures in order to increase the concentration of Ir and Pt by a factor of approximately 60. A metal hot plate, covered by a Teflon film, was used to preconcentrate 11 samples and an ultra pure water aliquot as a reference. PFA ultra-clean beakers were used to contain the samples during evaporation. The beakers had been immersed in a heated 0.1% (v/v) HNO<sub>3</sub> solution in a class 100 clean bench, and were then carefully rinsed and preconditioned for 1 h on the hot plate with ultra-pure water before use. The samples had a typical initial volume of ~60 ml and were reduced to ~1 ml with an evaporation rate of approximately 10 ml h<sup>-1</sup>. The preconcentrated solution was then spiked with HNO<sub>3</sub> up to a final HNO<sub>3</sub> concentration of 1% (v/v), by using a 10 µl precleaned tip (Eppendorf, Germany), before the subsequent transfer into an ultra clean 15 ml LDPE bottle. Preconcentrated samples were then kept frozen until analysis by ICP-SFMS.

### Instrumentation and measurement parameters

The analytical measurements by ICP-SFMS (Element2, Thermo Finnigan MAT, Bremen, Germany) were carried out in a clean laboratory at DES under a class 100 clean bench adopted as a clean sample introduction area for the instrument. The instrumental conditions and measurement parameters are reported in Table 1.

**Table 1** Instrumental conditions and measurement parameters for the ICP-SFMS and the desolvation unit

Forward power/W	1150
Gas flow rates	
Cool/l min <sup>-1</sup>	11.00
Auxiliary/l min <sup>-1</sup>	1.29
Sample/l min <sup>-1</sup>	0.886
Sweep gas/l min <sup>-1</sup>	3.59
Nitrogen flow rate/ml min <sup>-1</sup>	15
Membrane temperature/°C	175
Spray chamber temperature/°C	95
Sample uptake/µl min <sup>-1</sup>	100
Acquisition mode	E-scan; over small mass range
Selected isotopes	<sup>193</sup> Ir, <sup>195</sup> Pt
Resolution adopted	Low ( <i>m</i> Δ <i>m</i> <sup>-1</sup> ) = 300
No. of scan	100
Dwell time per acquisition points/ms	10
No. of acquisition points per mass segment (sample per peak)	40
Acquisition window (%)	100
Search window (%)	100
Integration window (%)	50

The low resolution mode (LRM) with a resolution setting of  $m/\Delta m = 300$  was used to measure Ir and Pt in order to maximise ion transmission at low concentrations. The samples were melted in the sample introduction area of the instrument and were handled by operators wearing LDPE gloves and clean room clothing.

A micro-flow nebulisation/desolvation sample introduction system<sup>27</sup> (Aridus, Cetac Technologies, Omaha, NE, USA) was used to reduce the spectral interferences. The instrument consists of a micro-flow ( $< 100 \mu\text{l min}^{-1}$ ) PFA nebuliser, a heated PFA spray chamber and a heated microporous PTFE tubular membrane. The solvent vapour passes through the membrane and is removed by an exterior flow of Ar gas (sweep gas). In this way the solvent based interferences can be reduced while the signal to background ratio can be increased.

The gas flow rate was optimised daily to obtain the maximum signal intensity.<sup>24</sup> The maximum sensitivities at the optimum flow rate in LRM were  $2\text{--}3 \times 10^6$  counts  $\text{s}^{-1}$  (cps) for 1 ppb of In, depending on the tuning conditions. The good signal stability meant that internal standards could be eliminated, avoiding the possible introduction of contamination into the samples.

Mass calibration using a 1 ppb multi-element standard solution was carried out weekly in LRM.

## Results and discussion

### Calibration

External calibration curves were used for the quantification of the analytes. Standards were prepared weekly from a  $10 \text{ mg l}^{-1}$  in 10% HCl, PGE multi-element ICP-MS stock solution (CPI International, The Netherlands) in 1% (v/v)  $\text{HNO}_3$  acidified ultra-pure water. Standard solutions were stored at about  $4^\circ\text{C}$  to minimise ion exchange with the walls of the LDPE bottle. The concentrations in the final standard solutions, used to quantify the preconcentrated samples, were 10, 20, 50 and 200 ppq. In this range, linear calibration curves were obtained for  $^{193}\text{Ir}$  ( $y = 2.379x + 3.7$ ;  $R^2 = 0.9998$ ) as well as for  $^{195}\text{Pt}$  ( $y = 0.750x + 6.2$ ;  $R^2 = 1$ ) (where  $y$  is expressed in cps and  $x$  in ppq). Calibration standard solutions were analysed at the beginning and at the end of the measurement session. Whenever differences in the slope of the calibration curves were higher than 10%, they were taken into account during the quantification.

### Interference study

Because of the high purity of ancient ice samples from Antarctica and Greenland, they could be characterised as an ideal matrix for the determination of ultra trace elements. Nevertheless, the relatively high input of dust to polar regions, especially during glacial periods, and the adopted preconcentration step of the samples, could produce a relatively complex matrix possibly interfering with the determination of the analytes.

Table 2 shows a list of the most abundant isotopes<sup>28</sup> of Ir and Pt, together with the most important interfering species.  $^{193}\text{Ir}$  and  $^{195}\text{Pt}$  were chosen because they are the naturally most abundant and should have fewer interferences than other isotopes. The most important interferences for  $^{193}\text{Ir}$  and  $^{195}\text{Pt}$  are  $^{177}\text{Hf}^{16}\text{O}$  and  $^{179}\text{Hf}^{16}\text{O}$ , with an abundance of 18.51% and 13.6%, respectively. Hf is a trace element in the continental crust (4.9 ppm), but is much more abundant than Ir (0.05 ppb) and Pt (0.4 ppb).<sup>20</sup> Even very low concentrations of Hf (present at a sub-ppt level in our samples;  $1 \text{ ppt} = 1 \text{ pg g}^{-1} = 10^{-12} \text{ g g}^{-1}$ ) could therefore interfere with the determination of Ir and Pt.

Working in LRM, the spectroscopic resolution of the interfering species from the analyte peaks is not feasible. Therefore,

**Table 2** Potential spectral interferences that could affect the determination of ultra trace levels of Ir and Pt in polar ice

Analyte	Potential interference		Resolution ( $m/\Delta m$ )	
	Isotope	Abundance (%)		
$^{191}\text{Ir}$	37.30	$^{175}\text{Lu}^{16}\text{O}$	97.17	7667
		$^{173}\text{Y}^{18}\text{O}$	0.03	8222
		$^{174}\text{Y}^{17}\text{O}$	0.01	8449
$^{193}\text{Ir}$	62.70	$^{177}\text{Hf}^{16}\text{O}$	18.51	7782
		$^{177}\text{Lu}^{16}\text{O}$	0.19	8389
$^{194}\text{Pt}$	32.90	$^{178}\text{Hf}^{16}\text{O}$	27.17	8100
		$^{177}\text{Hf}^{17}\text{O}$	0.007	9600
		$^{176}\text{Hf}^{18}\text{O}$	0.01	8800
		$^{176}\text{Yb}^{18}\text{O}$	0.02	9200
		$^{176}\text{Lu}^{18}\text{O}$	0.005	9200
		$^{179}\text{Hf}^{16}\text{O}$	13.6	8200
$^{195}\text{Pt}$	33.80	$^{178}\text{Hf}^{17}\text{O}$	0.01	6900
		$^{177}\text{Hf}^{18}\text{O}$	0.04	8800
		$^{180}\text{Hf}^{16}\text{O}$	35.00	8348
$^{196}\text{Pt}$	25.20	$^{180}\text{W}^{16}\text{O}$	0.13	8408
		$^{180}\text{Ta}^{16}\text{O}$	0.01	8692
		$^{178}\text{Hf}^{18}\text{O}$	0.05	8875
		$^{179}\text{Hf}^{17}\text{O}$	0.005	9803
		$^{196}\text{Hg}$	0.14	226550

<sup>a</sup> For polyatomic species calculated as the product of the natural abundances of each isotope divided by 100.

it was necessary to reduce the interfering species by using a desolvation system, and contemporaneously quantifying the residual interference of Hf and applying a mathematical correction.

The correction was calculated with the following eqns. ((1)–(2)):

$$I_{\text{Ir}} = I_{\text{Ir},s} - (I_{(177)\text{Hf},s} \times R_{(177)\text{Hf}(16)\text{O}, (177)\text{Hf}}) \quad (1)$$

$$I_{\text{Pt}} = I_{\text{Pt},s} - (I_{(179)\text{Hf},s} \times R_{(179)\text{Hf}(16)\text{O}, (179)\text{Hf}}) \quad (2)$$

where  $I_{\text{Ir}}$  and  $I_{\text{Pt}}$  are the corrected intensity of the element to be determined,  $I_{\text{Ir},s}$  and  $I_{\text{Pt},s}$  the apparent intensity of the interfered element in the sample,  $I_{(177)\text{Hf},s}$  and  $I_{(179)\text{Hf},s}$  the intensity of the interfering element in the sample and  $R_{(177)\text{Hf}(16)\text{O}, (177)\text{Hf}}$  and  $R_{(179)\text{Hf}(16)\text{O}, (179)\text{Hf}}$  the ratio between the interfering species and the interfering element.<sup>29</sup>  $I_{(177)\text{Hf},s}$  was quantified indirectly from the  $I_{(180)\text{Hf},s}$  signal because the former isotope could be affected by an interference caused by  $^{40}\text{Ar}^{137}\text{Ba}$  (abundance 11.27%).

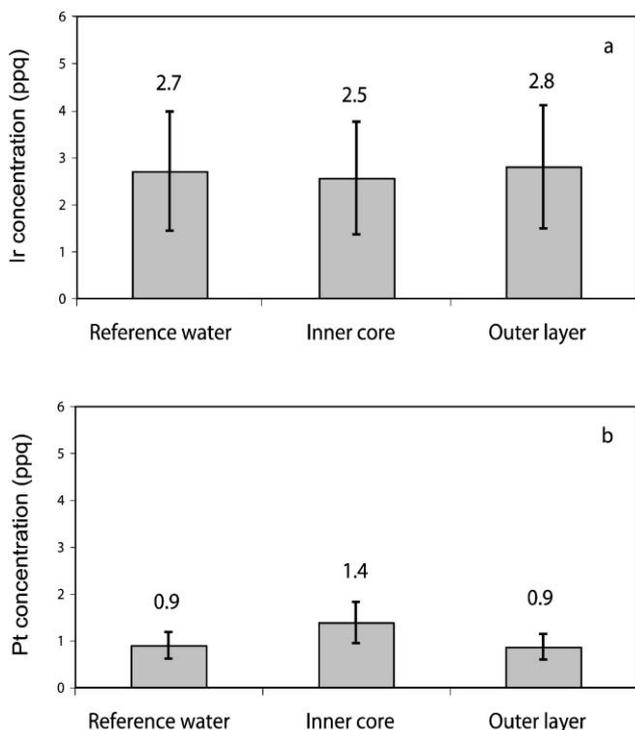
The ratios between the interfering species and the interfering elements were determined daily using four acidified (1% v/v  $\text{HNO}_3$ ) ultra-pure water solutions spiked to 0, 1.7, 4.8 and 9.2 ppt of Hf, respectively. During the analysis the intensities of  $^{193}\text{Ir}$ ,  $^{195}\text{Pt}$ , as well as  $^{179}\text{Hf}$  and  $^{180}\text{Hf}$ , were measured. From the experimental data in Table 3 it can be established that in both cases the effect of oxide formation exceeded the blank signal at Hf concentrations above  $\sim 5$  ppt.

Applying eqns. (1) and (2), the contributions of  $^{177}\text{Hf}^{16}\text{O}$  and  $^{179}\text{Hf}^{16}\text{O}$  on the signal of  $^{193}\text{Ir}$  and  $^{195}\text{Pt}$  can be determined. For example, analysing Ir and Pt in a sample dated at 941 BP from

**Table 3** Intensity values (cps) of blank solutions spiked with different amounts of Hf

Isotope	Interference	Concentration of Hf (ppt) <sup>a</sup>			
		0	1.7	4.8	9.2
$^{177}\text{Hf}$		7 (27)	538 (5)	1423 (6)	3137 (22)
$^{193}\text{Ir}$	$^{177}\text{Hf}^{16}\text{O}$	4 (56)	5 (29)	6 (28)	13 (25)
$^{179}\text{Hf}$		5 (45)	380 (9)	1060 (6)	2308 (21)
$^{195}\text{Pt}$	$^{179}\text{Hf}^{16}\text{O}$	7 (24)	8 (38)	9 (34)	15 (20)

<sup>a</sup> In parentheses, are relative standard deviation in % (RSD)



**Fig. 1** Outer layer and inner core concentrations of Ir (a) and Pt (b) in an artificial ice core prepared at CUT (Curtin University of Technology, Perth) and a comparison with the reference water produced in the same laboratory and used to prepare the artificial ice core. Error bars refers to the reproducibility at 1 ppq level.

Summit (Greenland), using the conventional sample introduction system, the contributions of the interfering species were 93% of the Ir signal and 69% of the Pt signal. As the ratios of the interference signal to the corrected signal were very high in both cases, the determination was considered unacceptable.<sup>30</sup> These contributions were reduced to 3% for both Ir and Pt by using the desolvation system, making the application of mathematical correction to the determination of Ir and Pt concentrations in ancient ice samples feasible. However in many cases the correction was negligible, because the concentration of Hf in the samples was often below 5 ppt even after preconcentration.

### Blanks

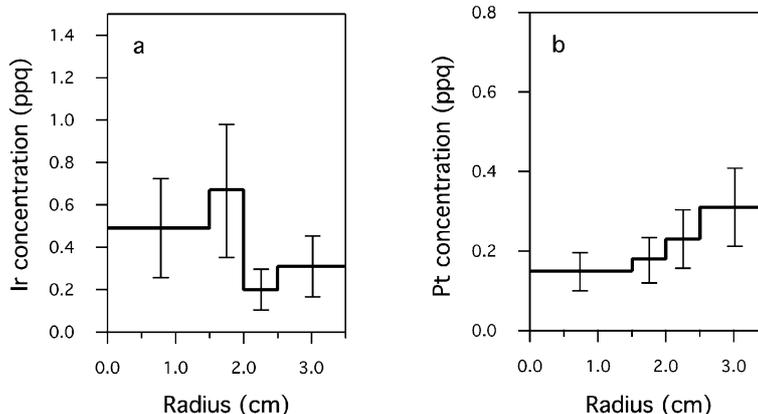
Considering the extremely low concentrations of Ir and Pt in the samples, special care was taken to evaluate the procedural blanks in each step of sample preparation and in particular during the decontamination and preconcentration procedures.

**Blank of the decontamination procedure.** In order to assess whether any Ir and Pt contamination occurs when chiselling the outer layer with stainless steel knives, an artificial ice core was prepared at CUT by freezing ultra-pure water<sup>31</sup> and was then processed at the LGGE using the ice core decontamination procedure.<sup>25</sup> Ir and Pt concentrations were determined in the external layer and compared with the inner core values as well as with an ultra-pure water aliquot used to prepare the artificial ice core. Figs. 1(a) and (b) show that the concentrations measured in the external layer, in the inner core and in the reference ultra-pure water, show negligible differences both for Ir and for Pt, indicating that there is no detectable contribution due to the decontamination procedure.

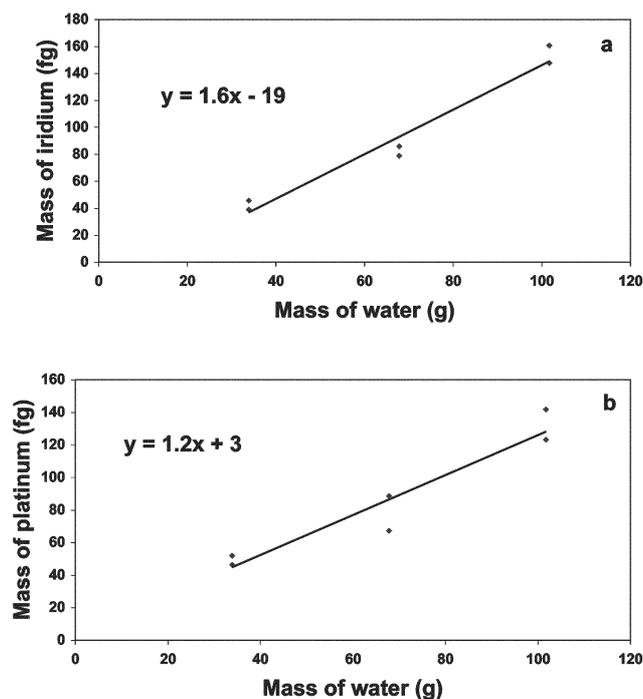
The outermost layer of real ice cores is heavily contaminated for several heavy metals because of the extensive use of drill fluid during the sampling operations in Greenland and Antarctica. Therefore it was necessary to check if contamination by Ir and Pt had occurred and to what extent. For this purpose, concentrations were determined in three successive outer layers and in the inner core of real ice core sections. A real example is the radial profile of Ir and Pt in an Antarctic ice core section drilled at Dome C at a depth of 1863.1 m, which is reported in Fig. 2. It can be observed that the concentration of Ir and Pt in the external layers and in the inner core shows only an insignificant variation, probably due more to the inhomogeneity of the test sample solutions and/or (as discussed later) to the measurement uncertainty than to a possible contamination originating from the external layer. In general, Ir and Pt concentrations are extremely low even in the outermost layers of both the GRIP and EPICA ice core sections. Therefore it can be stated that, thanks to the careful precautions taken, any additional Ir or Pt deriving from the drilling fluid does not affect the innermost parts of the core sections.

**Blank of the preconcentration procedure.** The blank of the preconcentration procedure was assessed by preconcentrating three aliquots of different volumes (30–100 ml) of ultrapure water to about 1 ml. These preconcentration factors (32, 62 and 99, respectively) covered the range of factors used for the real samples (typically about 60 but varying between 30 and 100). For every aliquot two repeat measurements of Ir and Pt concentrations were performed.

Plotting the calculated mass of Ir and Pt as a function of the initial mass of the ultra-pure water (Fig. 3(a) and (b)) we have calculated a regression line for which the intercept represents an interpolation of the mass of Ir and Pt eventually released (positive masses) or adsorbed (negative masses) by the walls of the Teflon beakers during preconcentration. The intercepts are close to zero for both Ir ( $-19 \pm 32$  fg) and Pt ( $3 \pm 38$  fg) (uncertainty is given with a confidence interval of 0.95), suggesting a small exchange for both metals with the beakers



**Fig. 2** Radial concentration profile of Ir (a) and Pt (b) for an Antarctic EPICA ice core section (Dome C, depth of 1863.1 m). Error bars refers to the reproducibility at 1 ppq level.



**Fig. 3** Measurements of the mass (in fg) of Ir (a) and Pt (b) released/adsorbed by the walls of the beakers during the pre-concentration procedure as the intercept of the regression line of the mass of Ir and Pt recovered *versus* different quantities of ultra-pure water pre-concentrated.

during the sample pre-concentration procedure. The contribution from acidification of the sample was also checked and was always found to be below the detection limit of the instrument.

**Concentration of Ir and Pt in the ultra-pure water.** The slope of the previously calculated regression line (Fig. 3(a) and (b)) represents an estimation of the concentration of Ir ( $1.6 \pm 0.4$  ppq) and Pt ( $1.2 \pm 0.5$  ppq) in the ultra-pure water. These concentration values could be directly related to the water production rate: a longer ion exchange of the tap water with the resin columns (corresponding to a low production rate of about  $0.5 \text{ l h}^{-1}$ ) resulted in the concentration dropping down to 0.3 and 0.4 ppq for Ir and Pt, respectively. These results are consistently lower than the lowest concentrations found in the real pre-concentrated samples (Ir = 5 ppq and Pt = 15 ppq; before application of the pre-concentration factor). This means that any contribution from small ultra-pure water drops left on the instruments after rinsing is negligible when added to the much larger sample volume.

#### Detection limits

The instrumental limit of detection (LOD) was calculated as 3 times the standard deviation of the 1% v/v  $\text{HNO}_3$  ultra-pure water response: the LODs were 1 and 5 ppq for Ir and Pt, respectively. Nevertheless, to know what is the minimum measurable Ir and Pt concentration, it is necessary to calculate the procedural detection limit because the pre-concentration step can decrease it by a factor corresponding to the pre-concentration factor. So, dividing the instrumental detection limit by the typical pre-concentration factor ( $\sim 60$ ) we obtain procedural detection limits of 0.02 ppq for Ir and 0.08 ppq for Pt. These are 5 and 3 times less than the minimum concentrations detected in polar ice samples for Ir and Pt, respectively.

#### Reproducibility

An estimation of the instrumental repeatability of the data was obtained from 3 repeat analyses (on a 1.2 ml sample) of a

polar pre-concentrated ice sample (Greenland, Summit, depth 1394.3 m, age 8723 BP). The mean values and the relative standard deviations (in parentheses) were the following: 0.3 ppq (4%) for Ir and 0.5 ppq (3%) for Pt. A more realistic estimation of the repeatability of the measurements is given by taking into account the uncertainty produced by the pre-concentration step so we can estimate the overall reproducibility. This was done by simultaneously pre-concentrating 6 aliquots of ultra-pure water, thus obtaining the following mean values and the relative standard deviations (in parentheses): 0.5 ppq (47%) for Ir and 1.1 ppq (32%) for Pt. These high relative standard deviations are due to the extraordinarily low concentrations in the ultra-pure water samples (comparable with the lowest concentrations in our samples) and can be considered as an upper limit of the method reproducibility.

#### Recovery

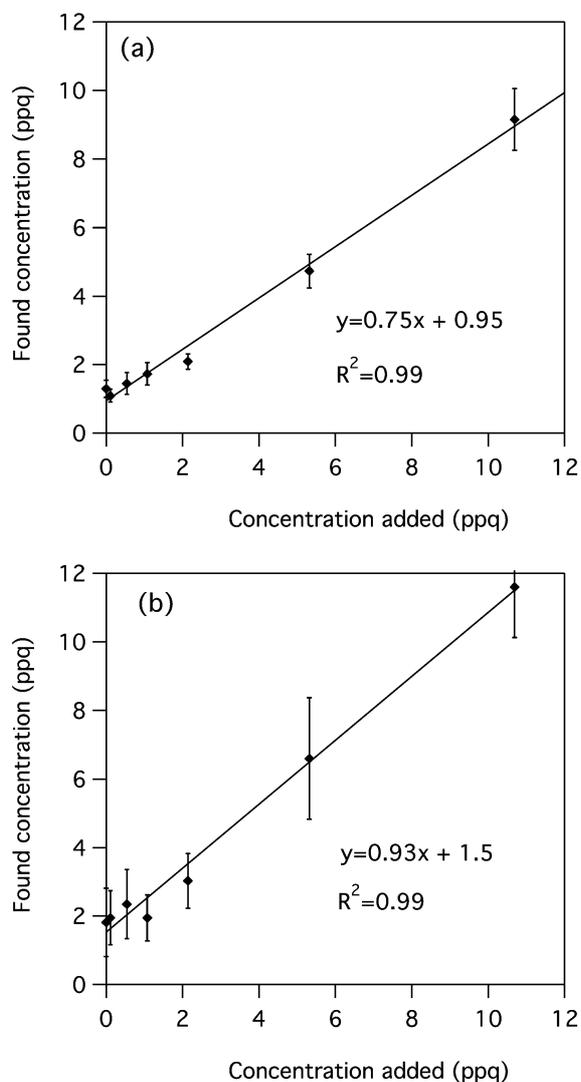
Estimating the accuracy for ultra-trace determinations down to the sub-ppq level is very difficult due to the numerous sources of error and especially because of the lack of an adequate reference material. The most critical step affecting the procedural accuracy of the measurements is probably the pre-concentration step, a delicate and not completely conservative analytical procedure that could produce analyte losses by evaporation.

To estimate the accuracy of the method, a recovery test, by pre-concentrating a series of standards with Ir and Pt concentrations similar to the sample concentrations with the same initial volume ( $\sim 60$  ml) and with the same pre-concentration factor ( $\sim 60$ ), was performed. The final concentrations of the standards were 0, 0.1, 0.5, 1.1, 2.1, 5.3 and 11.0 ppq. Fig. 4(a) and (b) show the found concentration as a function of the added concentration for Ir and Pt. The slope given by the linear regression represents the fraction of the analyte conserved in the final solution. The recovery for Ir was 75% while for Pt it was 93%. These values are in good agreement with other heavy metals treated in a similar manner (but with concentrations at least 3 orders of magnitude higher) published in previous work.<sup>26</sup> It is likely that the chemical form of Ir and Pt in the standards has different behaviour from the species present in real samples. For this reason the accuracy estimated with this recovery test can only be indicative and does not allow a systematic correction of analyte losses from real samples during pre-concentration.

#### Ir and Pt concentrations in polar ice

The samples selected to test the developed method belong to unique ice archives covering past changes in atmospheric conditions. They cover the last and penultimate glacial and the last interglacial periods. The Greenland samples collected at Summit in Central Greenland were four deep ice core sections<sup>7,32</sup> dated 941, 8723, 27151 and 45358 years before present<sup>33</sup> that are part of 35 sections decontaminated for this project. The Antarctic samples collected at Dome C in East Antarctica were two ice core sections taken at a depth of 1753.1 m and 1863.1 m and dated, from an estimated chronology, in the proximity of the penultimate glacial–interglacial transition about 150 000 years before present. These two samples are part of 41 EPICA Dome C sections decontaminated for this project.

Concentrations of Ir and Pt in four ice core sections from central Greenland and the two from East Antarctica are reported in Table 4. The concentrations are within the sub-ppq and ppq levels, both in the samples from Greenland and Antarctica, ranging between 0.1 and 5 ppq for Ir and between 0.2 and 7 ppq for Pt. Among the four samples from Greenland, a large variation could be found: ice core sections from the Holocene (941 and 8723 years BP) show lower concentrations



**Fig. 4** Determination of the recovery of the preconcentration procedure for Ir (a) and Pt (b) using preconcentrated synthetic standards with ultra-low concentrations. Found concentration (ppq) refers to the measured concentration after evaporation divided by the preconcentration factor. Error bars as instrumental SD are also reported.

than from the last glacial age (27151 and 45358 years BP). The explanation, extensively discussed elsewhere,<sup>34</sup> for higher concentrations of Ir and Pt detected in Greenland during the last glacial age, could be mainly related to the extremely high input of continental dust at high latitudes, transferring a relatively large amount of terrestrial Ir and Pt into the ice and covering the much lower Ir and Pt signal of extraterrestrial origin. Conversely, the cosmic signature of Ir and Pt could be recognised in Holocene samples characterised by a much lower terrestrial dust content.

**Table 4** Concentrations of Ir and Pt in four samples from central Greenland (Summit) and two samples from East Antarctica (Dome C)

Site	Depth/m	Age <sup>a</sup> (years BP)	Ir (ppq)	Pt (ppq)
Greenland (Summit)	239.3	941	0.1	0.4
	1394.3	8723	0.3	0.5
	2054.3	27151	3.9	5
	2334.2	45358	5	7
Antarctica (Dome C)	1753.1	~130000	1.1	0.4
	1863.1	~150000	0.5	0.2

<sup>a</sup> Summit (GRIP), time scale is the ss09 sea, from ref. 33; Dome C (EPICA) time scale is extrapolated from the time scale of the Vostok ice core (see ref. 35).

### Comparison with other studies

Few studies have attempted to estimate the concentrations of Ir in ice,<sup>8–13</sup> most using INAA almost exclusively to measure the particulate fraction (>0.45 μm) present, consequently missing the fine and the soluble fractions. The total concentration of Ir in ice has never been measured and therefore a comparison of these studies with our results is not possible.

Ir concentrations that are comparable with our values were measured by Negative Thermal Ionisation Mass Spectrometry (NTIMS) in natural water,<sup>14,15</sup> and total concentrations in the range of 0.1 and 3 ppq are reported. We report values in the ice with a similar range (between 0.1 and 5 ppq). The minimum concentration reported for the hydrosphere corresponds to the lowest value of Ir that we reported for the cryosphere.

Pt total concentration measurements in snow and ice were already attempted in samples from Greenland, Antarctica and the Alps but were mainly devoted to studying the anthropogenic contribution from the last few decades due to the emissions of vehicles fitted with catalytic converters.<sup>16–18</sup> Total concentration values from 8 ppq up to 830 ppq are reported in recent snow at Summit in Greenland and from 540 up to 640 ppq in recent shallow snow in Antarctica, exceeding our measurements by several orders of magnitude.

The only two values that could be comparable with our data are two ice core sections sampled at Summit in Greenland in the framework of the GRIP project, referring to 7260 and 7760 years BP, showing concentration values of 8 and 15 ppq, considerably higher, by a factor of 10, than the values that we report for the same ice core during the Holocene. It must be considered that these data were measured only to have an estimation of the natural background in order to assess the relatively high concentrations in the recent anthropogenically enriched samples and that there was not an accurate procedure developed for measuring Pt at the sub-ppq level.

### Conclusions

We have developed an ultra-clean and simple method in order to measure the total concentration of ultra-low traces of Ir and Pt in polar ice down to the sub-ppq level. An ultra-clean procedure for decontaminating the ice core sections and a suitable ultra-clean preconcentration method by sub-boiling evaporation were fundamental sample preparation steps required to obtain negligible procedural blanks and to increase the concentration by a factor of 60. The volume used was about 65 times smaller than that used for assessing total Ir concentrations in natural water and the addition of reagents was limited to only a 1% (v/v) ultrapure HNO<sub>3</sub> addition to the 1 ml of preconcentrated solution. The extremely high sensitivity of the ICP-SFMS, the very low instrumental background, and the very low sample consumption with the reduction of spectral interferences by the desolvation system were the four most important factors that enabled us to obtain the first results of the total concentration of Ir in the cryosphere and the lowest concentrations ever recorded for Pt in environmental samples.

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## References

- 1 L. W. Alvarez, W. Alvarez, F. Asaro and H. V. Michel, *Science*, 1980, **208**, 1095–1108.
- 2 N. J. Evans and C. F. Chai, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 1997, **132**, 373–390.
- 3 C. F. Boutron and C. C. Patterson, *Nature*, 1986, **323**, 222–225.
- 4 C. F. Boutron, C. C. Patterson, V. N. Petrov and N. I. Barkov, *Atmos. Environ.*, 1987, **21**, 1197–1202.
- 5 C. F. Boutron, C. C. Patterson and N. I. Barkov, *Earth Planet. Sci. Lett.*, 1990, **101**, 248–259.
- 6 C. F. Boutron, S. N. Rudnev, M. A. Bolshov, V. G. Koloshnikov, C. C. Patterson and N. I. Barkov, *Earth Planet. Sci. Lett.*, 1993, **117**, 431–441.
- 7 S. Hong, J. P. Candelone, C. Turetta and C. F. Boutron, *Earth Planet. Sci. Lett.*, 1996, **143**, 233–244.
- 8 H. Takahashi, Y. Yokoyama, E. L. Fireman and C. Lorius, *Lunar Planet. Sci.*, 1978, **9**, 1131–1133.
- 9 R. Ganapathy, *Science*, 1983, **220**, 1158–1161.
- 10 C. Koeberl, *Earth Planet. Sci. Lett.*, 1989, **92**, 317–322.
- 11 R. Rocchia, P. Bonte, C. Jehanno, E. Robin, M. De Angelis and D. Boclet, *Geol. Soc. Am. Spec. Pap.*, 1990, **247**, 189–193.
- 12 K. Rasmussen, H. B. Clausen and G. W. Kallemeyn, *Meteoritics*, 1995, **30**, 634–638.
- 13 D. B. Kerner, J. Levine, R. A. Muller, F. Asaro, M. Ram and M. R. Stolz, *Geochim. Cosmochim. Acta*, 2003, **67**, 751–763.
- 14 A. D. Anbar, G. J. Wasserburg, D. A. Papanastassiou and P. S. Andersson, *Science*, 1996, **273**, 1524–1528.
- 15 A. D. Anbar, D. A. Papanastassiou and G. J. Wasserburg, *Anal. Chem.*, 1997, **69**, 2444–2450.
- 16 C. Barbante, G. Cozzi, G. Capodaglio, K. Van de Velde, C. Ferrari, A. Veyseyre, C. F. Boutron, G. Scarponi and P. Cescon, *Anal. Chem.*, 1999, **71**, 4125–4133.
- 17 C. Barbante, A. Veyseyre, C. Ferrari, K. Van de Velde, C. Morel, G. Capodaglio, P. Cescon, G. Scarponi and C. F. Boutron, *Environ. Sci. Technol.*, 2001, **35**, 835–839.
- 18 K. Van de Velde, C. Barbante, G. Cozzi, I. Moret, T. Bellomi, C. Ferrari and C. F. Boutron, *Atmos. Environ.*, 2000, **34**, 3117–3127.
- 19 E. Anders and N. Grevesse, *Geochim. Cosmochim. Acta*, 1989, **53**, 197–214.
- 20 K. H. Wedepohl, *Geochim. Cosmochim. Acta*, 1995, **59**, 1217–1232.
- 21 C. F. Boutron, *Fresenius' J. Anal. Chem.*, 1990, **337**, 482–491.
- 22 C. P. Ferrari, A. I. Moreau and C. F. Boutron, *Fresenius' J. Anal. Chem.*, 2000, **366**, 433–437.
- 23 F. A. M. Planchon, C. F. Boutron, C. Barbante, E. W. Wolff, G. Cozzi, V. Gaspari, C. Ferrari and P. Cescon, *Anal. Chim. Acta*, 2001, **450**, 193–205.
- 24 C. Barbante, T. Bellomi, G. Mezzadri, P. Cescon, G. Scarponi, C. Morel, S. Jay, K. Van de Velde, C. Ferrari and C. F. Boutron, *J. Anal. At. Spectrom.*, 1997, **12**, 925–931.
- 25 J. P. Candelone, S. Hong and C. F. Boutron, *Anal. Chim. Acta*, 1994, **299**, 9–16.
- 26 U. Gorlach and C. F. Boutron, *Anal. Chim. Acta*, 1990, **236**, 391–398.
- 27 M. P. Field and R. M. Sherrel, *J. Anal. At. Spectrom.*, 2003, **18**, 254–259.
- 28 K. J. R. Rosman and P. D. P. Taylor, *Pure Appl. Chem.*, 1998, **70**, 217–235.
- 29 A. Varga, C. Barbante, G. Cozzi, I. Mantovan, G. Rampazzo and P. Cescon, *J. Phys. IV*, 2003, **107**, 1337–1340.
- 30 S. Rauch, M. Lu and G. M. Morrison, *Environ. Sci. Technol.*, 2001, **35**, 595–599.
- 31 P. Vallenga, K. Van de Velde, J. P. Candelone, K. J. R. Rosman, C. F. Boutron, V. I. Morgan and D. J. Mackey, *Anal. Chim. Acta*, 2002, **453**, 1–12.
- 32 S. Hong, J. P. Candelone and C. F. Boutron, *Atmos. Environ.*, 1997, **31**, 2235–2242.
- 33 S. Johnsen, D. Dahl-Jensen, N. Gundestrup, J. P. Steffensen, H. B. Clausen, H. Miller, V. Masson-Delmotte, E. A. Sveinbjörnsdóttir and J. White, *J. Quatern. Sci.*, 2001, **16**, 299–307.
- 34 P. Gabrielli, C. Barbante, J. Plane, A. Varga, S. Hong, G. Cozzi, V. Gaspari, F. A. M. Planchon, W. Cairns, P. Cescon, C. Ferrari and C. F. Boutron, in preparation.
- 35 J. R. Petit, J. Jouzel, D. Reynaud, N. I. Barkov, J. M. Barnola, I. Basile, M. Bender, J. Chapellaz, M. Davis, G. Delaygue, M. Delmotte, V. I. Kotlyakov, M. Legrand, V. Y. Lipenkov, C. Lorius, L. Pépin, C. Ritz, E. Saltzman and M. Stievenard, *Nature*, 1999, **399**, 429–436.