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A climatic control on the accretion of meteoric and super-chondritic iridium–platinum to the Antarctic ice cap ☆

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Abstract

Meteoric smoke particles (MSPs) form through the vaporization of meteoroids and the subsequent re-condensation of metallic species in the mesosphere. Recently, iridium and platinum enrichments have been identified in Greenland ice layers and attributed to the fallout of MSPs supplying polar latitudes with cosmic matter during the Holocene. However, the MSP fallout to Antarctica during the Earth's climatic history remains essentially unknown.

We have determined iridium and platinum in deep Antarctic ice from Dome C and Vostok dated back to 240 kyrs BP. We find high super-chondritic fluxes during warm periods and low meteoric accretion during glacial times, a pattern that is opposite to any known climatic variation in dust fallout to polar regions. The proposed explanation of this accretion regime is a weaker polar vortex during warm periods, allowing peripheral air masses enriched in volcanic iridium and platinum to penetrate inland to Antarctica. The MSP signal emerges only during cold phases and is four times lower than in the Greenland ice cap where more snow accumulates. This suggests that wet deposition is an important route of cosmic material to the Earth's surface.

Keywords: iridium; platinum; meteoric smoke; ice; Antarctica; climate

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1. Introduction

Platinum Group Elements (PGEs) are depleted in the upper terrestrial crust [1] but are enriched by up to a factor of 10,000 in chondritic meteorites [2]. Consequently PGEs, such as Ir and Pt, are often employed as excellent tracers of extraterrestrial material. Recently, some Ir anomalies in sediment cores from the Eastern Congo craton have been interpreted to be a relic of Neoproterozoic global "Snowball" glaciations. At that time it is widely believed that Earth was completely ice covered, so cosmic material enriched in Ir would have accumulated on and within the ice and precipitated during rapid melting at the base of the cap carbonates at the end of the glaciation [3].

A cosmic enrichment in Ir and Pt, likely corresponding to that presumably present in the ice sheets of the Snowball Earth, has been effectively identified in the Greenland ice layers dated at the more recent Holocene epoch and was attributed to the fallout of meteoric smoke particles (MSPs) [4]. These particles form through the vaporization of meteoroids and subsequent re-condensation of metallic species and silica in the mesosphere [5,6]. This fallout of meteoric Ir and Pt provided the first evidence of the importance of MSP as an additional carrier of cosmic PGEs to the Earth's surface, compared to the micrometeorite flux and to the rare large extraterrestrial bodies striking the Earth. It also supported the current understanding that most of the mass of interplanetary dust particles (IDPs) entering the Earth's system ablates in the upper atmosphere.

There is growing interest in the historical record of the accretion rate of IDPs, motivated by the suggestion that variations in the IDP flux triggered the 100 kyrs climatic cycle [7]. This hypothesis has been strongly debated, and recent extraterrestrial helium isotope data from marine sediments appears to refute it [8]. The MSP record provides another test of this hypothesis. In addition, MSPs may have several important roles in the atmosphere, several of which could be linked to climate. For instance, the particles could act as condensation nuclei for noctilucent clouds in the upper mesosphere [9], and for sulphuric acid (Junge layer) aerosols [10] and polar stratospheric clouds [11] in the lower stratosphere. In addition, metallic particles are alkaline, and have been implicated in both the production of nitric acid (HNO_3) from nitrogen pentoxide (N_2O_5) in the upper stratosphere [12] and the removal of HNO_3 from the lower stratosphere [13], thereby affecting O_3 chemistry.

Polar ice sheets are well suited to study the past accretion rates of MSPs because they preserve the unaltered physico-chemical properties of their constituent metals, such as Ir and Pt [4]. In addition, ice cores assure excellent MSP counting statistics [4], resulting in the accurate dating of deposition and fairly precise flux estimates via a rather well known past accumulation rate. Most importantly, polar regions are a key location to study MSP transport pathways through the Earth's atmosphere. This is because, once formed, these particles are thought not to grow large enough (radius >2 nm) to sediment rapidly out of the mesosphere and are therefore transported by the meridional mesospheric circulation into the polar vortex of the winter hemisphere, before descending into the lower stratosphere [4]. Thus, MSPs and consequently Ir and Pt can also provide a tracer of transport from the lower polar vortex to the polar boundary layer.

As a counterpart to the Greenland record [4], here we report the first Southern hemisphere records of Ir and Pt fluxes, determined in two deep ice cores from Dome C (75°06′S; 123°21′E, 3233 m, $t=-54$ °C) [14] and Vostok (78°28′S, 106°48′E, 3488 m, $t=-55$ °C) [15]. These two sites, located on the East Antarctic plateau $\sim$600 km apart, have provided the two oldest ice records ever retrieved [14,15]. This record allows knowledge of important processes involved in the geochemical cycles of Ir and Pt to be extended much further back in time.

2. Experimental procedures

We have analysed 41 samples from the first 2193 m of the Dome C ice core (EDC), and 23 samples from the first 2751 m of the Vostok ice core (VK), spanning from $\sim$5 up to $\sim$60 years each and covering a period from the Holocene back to the next-to-last interglacial period ($\sim$240 kyrs BP). Determination of Ir and Pt total concentrations in Antarctic ice was conducted by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) [4,16]. Traditional methods for quantifying minor fractions of Ir [17] and Pt in micrometric particulate matter filtered from ice samples would fail to include the potentially significant contribution from the much smaller sized MSPs [4,18]. This can only be taken into account by measuring the total Ir and Pt concentration relative to the wet mass of the sample.

We have set up an analytical methodology, based on ICP-SFMS coupled with a micro-flow nebulizer and desolvation system, for the quantification of Ir and Pt down to the sub-femtogram per gram level (1 fg $g^{-1}=10^{-15}$ g g^{-1}) in polar ice samples (for a full description of the method see reference [16] and the supplementary online information in reference [4] http://www.nature.com/nature/journal/v432/n7020/suppinfo/nature03137.html). Ultra-clean procedures were adopted during the pre-treatment phases in our laboratories in order to avoid possible contamination problems and a pre-concentration step by evaporation at sub-boiling temperatures was necessary. Using a

desolvation system for sample introduction reduced spectral interferences, which affect the determination of Ir and Pt. The contribution of the interfering species was determined and subtracted whenever necessary. This method benefited from an ultra-clean chemical processing of the sample based on the simple addition of ultrapure HNO_3 to the melted and pre-concentrated ice samples. The complete ionization of the MSPs in the plasma (at ~7000 K) of the ICP-SFMS was assured by the already quasi-molecular size of these particles, without the need to add any supplemental chemical reagent.

A procedural detection limit of 0.02 fg g^{-1} and 0.08 fg g^{-1} for Ir and Pt, respectively was obtained. The recoveries were 75% and 93% for Ir and Pt, respectively and the reproducibility of the concentrations at the femtogram per gram level was ~50% for Ir and ~30% for Pt.

Overall reproducibility (R_o) of Ir/Pt mass ratio was ~15%. This was estimated as the relative standard deviation of three mass ratios obtained by pre-concentrating and analysing three aliquots of 60 ml taken from a single sample (with Ir and Pt concentrations values at the sub-femtogram per gram level). Interestingly, this estimation (~15%) is similar to the average random instrumental uncertainty of the Ir/Pt mass ratios (U_m), determined in Antarctic samples (~15%). U_m is calculated as the mean of U_i, which is the square root of the sum of the powers of the relative instrumental standard deviations of the Ir and Pt concentrations determined by ICP-SFMS in a single EDC or VK sample (i).

This similarity suggests that R_o is mainly affected by U_i and thus by the random uncertainty due to the instrumental determination by ICP-SFMS and only to a lesser extent by the previous pre-concentration step by sub-boiling evaporation (see Ref. [16] and the supplementary online information in Ref. [4]). This latter is on the other hand most likely responsible of the relatively low reproducibility of the single Ir and Pt concentrations values (~50% for Ir and ~30% for Pt).

The better reproducibility of the Ir/Pt mass ratios (~15%) with respect to that of the Ir and Pt concentration values (~50% for Ir and ~30% for Pt) is probably due to the fact that minor quantities of Ir and Pt lost by volatilization during the pre-concentration procedure are equivalent for the two metals. In other words, this means that the pre-concentration procedure does not significantly fractionate Ir and Pt, likely because the isotopes determined, ^{193}Ir and ^{195}Pt, have a high and very similar atomic mass. The absence of a significant and systematic fractionation is further supported by the experimental observation that Ir/Pt mass ratios are clearly correlated to a completely independent parameter such as δD‰ (see below).

As mentioned, R_o and U_m are of the order of ~15% but for few Ir/Pt mass ratios derived from the lowest Ir and Pt concentration values, U_i can be much higher, up to 80%. As a consequence of this, we have chosen to adopt as uncertainty for every single Ir/Pt mass ratio, U_i, allowing a better evaluation of the robustness of every single data point (as it will be reported in Fig. 2, Table 1 and Table 2).

3. Results and discussion

3.1. Ir and Pt concentrations and fluxes

Concentrations of Ir and Pt appear to be quite variable in EDC, and less so in VK (Tables 1 and 2) during the last climatic cycles. The median values at both sites are comparable (Ir=1.9 fg g^{-1}, Pt=2.3 fg g^{-1} in EDC; Ir=1.1 fg g^{-1}, Pt=1.8 fg g^{-1} in VK). Minimum concentrations are at the sub-femtogram per gram level also at both sites. In EDC, maxima of 18 and 12 fg g^{-1} for Ir and Pt were found at 1 and 22 kyrs BP whereas in VK significantly smaller maxima of 2.1 and 5.2 fg g^{-1} of Ir and Pt were determined at 119 and 143 kyrs BP.

Interestingly, the median concentrations found in the Greenland Summit ice core (GRIP) (0.3 and 0.7 ppq for Ir and Pt) [4] are lower than in EDC and VK. This is likely due to the low snow accumulation rate on the East Antarctic plateau (2.5 g cm^{-2} y^{-1} of water equivalent in Dome C), smaller by about one order of magnitude than in Central Greenland (23 g cm^{-2} y^{-1} of water equivalent in Summit). When concentrations are combined with snow accumulation rates (from Ref. [15] and Parrenin F., personal communication) to calculate the fluxes, Ir and Pt fallouts to the East Antarctic plateau are in fact lower than to the Greenland ice cap [4].

Also fluxes of Ir and Pt appear to be quite variable in EDC, and less so in VK (Fig. 1). In EDC, maxima of 58 and 17 fg cm^{-2} y^{-1} for Ir and Pt are recorded at 1 and 22 kyrs BP whereas in VK significantly smaller maxima of 5 and 8 fg cm^{-2} y^{-1} of Ir and Pt are observed at 119 and 143 kyrs BP. However, the median values at both sites are in close agreement (3 and 4 fg cm^{-2} y^{-1} for Ir and Pt in EDC; 2 and 4 fg cm^{-2} y^{-1} for Ir and Pt in VK), since medians are essentially not affected by the three large concomitant spikes of Ir and Pt recorded in the upper part of EDC only and dated at 1, 7 and 15 kyrs BP.

While the Ir and Pt fluxes determined in the Greenland deep ice core exhibit a classical climatic profile for heavy metals and in general for dust fluxes, with higher values during the last ice age (median values of 26 and 34 fg $cm^{-2}y^{-1}$ for Ir and Pt) and lower values

Table 1
Ir and Pt concentrations, fluxes, mass ratios and enrichment factors (EF_c) relatively to Mn concentrations in the Dome C ice core

Depth (m)	Age (kyrs BP)	Ir (fg g^{-1})	Pt (fg g^{-1})	Ir flux (fg cm^{-2} y^{-1})	Pt flux (fg cm^{-2} y^{-1})	Ir/Pt	Ir/Pt uncertainty	Mn (pg g^{-1})	EF_c Ir	EF_c Pt
32.5	0.6	3.3	3.1	8.9	8.4	1.1	0.1	7	5100	600
59.1	1	19	9	58	27	2.2	0.2	9	22000	1300
86.6	2	2.7	3.2	7.2	8.3	0.9	0.1	12	2300	340
152.1	4	2.3	1.5	5.9	4.0	1.5	0.2	8	3000	250
229.1	7	5	2.7	14.8	7.8	1.9	0.3	14.5	3800	250
316.0	10	3.3	2.3	11.6	7.8	1.5	0.2	12	2800	240
379.2	13	2.3	2.3	5.0	5.0	1.0	0.2	14	1700	210
405.6	14	3.0	2.3	6.3	4.8	1.3	0.2	39	800	80
419.4	15	10.0	5.5	28	15	1.8	0.1	20	5300	370
432.6	16	3.7	2.1	9.4	5.4	1.7	0.2	40	1000	70
461.2	17	2.3	2.3	4.0	4.0	1.0	0.1	170	140	20
471.1	18	1.0	2.8	1.6	4.3	0.4	0.1	341	30	10
488.7	20	3.1	3.8	4.5	5.6	0.8	0.1	529	60	10
515.6	22	2	12	3.3	17.0	0.2	0.1	760	30	20
573.9	27	1.5	5.1	2.1	7.2	0.3	0.1	394	40	20
598.1	29	3.7	2.7	6.0	4.3	1.4	0.2	319	120	10
653.1	34	1.3	2.3	2.1	3.6	0.6	0.1	176	80	20
653.7	34	0.4	1.4	0.6	2.1	0.3	0.1	236	20	10
680.9	36	1.6	1.8	2.5	2.7	0.9	0.2	201	80	10
708.7	38	1.7	1.7	3.0	3.1	1.0	0.2	103	180	20
735.6	40	2.2	3.5	3.2	5.2	0.6	0.1	229	100	20
763.1	43	6.1	4.5	10.0	7.4	1.4	0.1	127	500	50
818.1	47	1.8	2.3	2.7	3.6	0.8	0.1	163	110	20
900.6	54	1.3	1.7	2.2	2.9	0.8	0.1	223	60	10
983.1	61	1.0	2.5	1.6	3.7	0.4	0.1	340	30	10
1010.6	63	0.8	2.6	1.2	3.8	0.3	0.1	396	20	10
1093.1	72	1.7	2.0	3.1	3.7	0.8	0.1	40	450	70
1148.1	77	2.5	2.3	4.2	3.9	1.1	0.2	96	280	30
1203.1	81	0.7	1.3	1.5	2.8	0.5	0.1	50	150	30
1258.1	86	1.3	1.8	2.3	3.2	0.7	0.1	107	130	20
1313.1	91	1.5	2.2	2.8	4.2	0.7	0.1	27	570	110
1423.1	102	1.6	2.2	2.9	4.1	0.7	0.1	59	280	50
1533.1	114	2.7	2.2	7.1	5.8	1.2	0.2	11	2500	250
1643.1	123	2.7	2.1	8.4	6.7	1.3	0.2	21	1400	130
1753.1	132	1.1	0.4	2.4	0.8	3.3	1.4	64	190	10
1863.1	152	0.5	0.2	0.7	0.2	3.3	1.3	480	10	1
1973.1	174	0.6	2.0	1.0	3.1	0.3	0.1	296	20	10
2050.1	191	0.8	1.5	1.4	2.4	0.6	0.1	174	50	10
2094.1	199	4.1	1.9	10.0	4.6	2.2	0.3	12	3700	210
2138.1	207	1.9	2.0	4.7	4.9	1.0	0.1	16	1200	160
2193.1	217	1.3	1.9	2.7	4.0	0.7	0.1	76	180	30

Ages are derived from Ref. [14].

during the Holocene (10 and 21 fg $cm^{-2}y^{-1}$) [4], the response of Ir and Pt to different climatic conditions in East Antarctica is different from any known variation in past terrestrial trace element and dust fallout recorded in polar ice. The highest fluxes of Ir and Pt (median values of 7 and 5 fg $cm^{-2}y^{-1}$ in EDC; 3 and 4 fg $cm^{-2}y^{-1}$ in VK for Ir and Pt) occur during warm periods (defined by $\delta D > -420‰$ in EDC (data from Jouzel, J., in preparation) and $\delta D > -445‰$ in VK [15]) with several pronounced spikes in EDC during the Holocene whereas, apart from Pt in VK, cold periods are characterized by lower fluxes (median values of 3 and 4 fg $cm^{-2}y^{-1}$ in EDC; 2 and 4 fg $cm^{-2}y^{-1}$ in VK for Ir and Pt) (Fig. 1).

3.2. The crustal enrichment factor and the Ir/Pt mass ratio

To evaluate the crustal terrestrial contribution to the Ir and Pt budgets in ice, we have calculated the crustal enrichment factor (EF_c), which is defined as $EF_c = \{[Metal]_{ice}/[Mn]_{ice}\}/\{[Metal]_{crust}/[Mn]_{crust}\}$; $\{[Ir]_{crust}/[Mn]_{crust}\} = 9.5 \times 10^{-8}$ and $\{[Pt]_{crust}/[Mn]_{crust}\} =$

Table 2
Ir and Pt concentrations, fluxes, mass ratios and enrichment factors (EF_c) relatively to Mn concentrations in the Vostok ice core

Depth (m)	Age (kyrs BP)	Ir (fg g^{-1})	Pt (fg g^{-1})	Ir flux (fg cm^{-2} y^{-1})	Pt flux (fg cm^{-2} y^{-1})	Ir/Pt	Ir/Pt uncertainty	Mn (pg g^{-1})	EF_c Ir	EF_c Pt
126.7	5	1.2	1.1	2.6	2.4	1.1	0.2	14	950	110
150.5	6	2.0	2.0	4.2	4.2	1.0	0.1	18	1200	150
193.9	8	2.0	2.2	4.0	4.5	0.9	0.2	28	730	100
513.0	30	0.9	1.6	1.3	2.2	0.6	0.1	250	40	10
938.1	65	1.1	4.2	1.5	5.8	0.26	0.03	552	20	10
948.0	66	1.6	4.2	2.2	5.6	0.39	0.04	883	20	10
1050.0	75	0.7	1.1	1.2	1.7	0.7	0.1	77	100	20
1205.7	87	1.5	2.5	2.7	4.5	0.6	0.1	57	280	60
1353.5	97	1.0	1.2	1.8	2.2	0.8	0.1	42	250	40
1514.5	108	0.3	0.7	0.4	1.1	0.4	0.3	201	10	5
1651.4	119	2.1	2.1	4.9	5.1	1.0	0.1	17	1300	160
1815.5	128	1.1	1.6	3.3	5.0	0.7	0.1	37	312	60
1879.8	131	0.8	1.4	2.2	3.6	0.6	0.1	14	310	130
1917.5	134	0.6	1.3	1.2	2.4	0.5	0.1	116	60	15
1999.0	143	1.9	5.2	2.8	7.6	0.37	0.05	638	30	10
2199.4	165	1.6	4.1	2.5	6.3	0.39	0.03	387	40	15
2252.4	172	0.6	1.5	1.1	2.7	0.41	0.04	407	20	5
2378.4	188	0.8	3.0	1.4	4.9	0.28	0.03	294	30	15
2504.5	203	1.0	1.8	2.5	4.4	0.6	0.1	30	370	80
2534.0	207	1.2	2.2	2.5	4.5	0.6	0.1	95	140	30
2616.0	216	0.8	1.8	2.0	4.5	0.4	0.1	63	140	40
2682.4	226	1.4	2.1	2.7	4.2	0.6	0.1	119	120	20
2751.0	237	0.5	1.2	1.4	3.6	0.4	0.2	60	80	30

Ages are derived from Ref. [15].

7.6×10^{-7} from Ref. [1]; $[Mn]_{ice}$ from ref. [19,20]), where Mn is a good indicator of continental dust in Antarctic ice [19]. Since previously calculated EF_c in EDC and VK ice are very close to the value of 1 for typical crustal atmospheric trace elements [19,20], we believe that the bulk elemental crustal ratios used to calculate the EF_c for Ir and Pt are also likely to be roughly representative of terrestrial dust transported to East Antarctica.

The respective median EF_c values for Ir and Pt are remarkably high: 182 and 32 in EDC, and 121 and 27 in VK. Because the EF_c values most often greatly exceed the value of 1 (Tables 1 and 2), even during the intense glacial continental dust fallout, the Ir and Pt fluxes cannot in general be explained by the crustal contribution. Only a careful inspection of the individual data points shows that among the VK samples (see Table 2), the three highest values of Pt and of Mn occur simultaneously; thus, despite an EF_c higher than 1 (between 6 and 11), an occasional important crustal contribution of Pt may have occurred during glacial periods. Nevertheless, the very high EF_c and the general lack of correlation of Ir and Pt with Mn indicate that non-crustal sources dominated not only in warm times but in contrast with the Greenland ice record [4], also in glacial periods.

The Ir and Pt elemental mass ratio (Ir/Pt) can also assist in identifying their origin. When Ir/Pt is compared with δD (data from Jouzel J., in preparation and Ref. [15]), taken as a proxy of the past local atmospheric temperature, it emerges that these two parameters are significantly correlated both in EDC ($r=0.73$) and in VK ($r=0.58$) (Fig. 2). In both ice cores the more negative δD values (low temperatures) are in fact associated with Ir/Pt ≈ 0.5, whereas less negative δD values (higher temperatures) are linked with Ir/Pt close to or greater than 1. The similar response in both the Dome C and Vostok records provide evidence that Ir/Pt in East Antarctica is essentially chondritic (~ 0.49, from Ref. [2]) during cold periods, whereas in warmer times it is neither chondritic nor crustal (~ 0.2, from Ref. [1]), but exhibits a rather puzzling super-chondritic mass ratio (~ 1). In the following two paragraphs we will discuss in detail the super-chondritic ratios found during warm periods (Section 3.3) and the chondritic ratios found during cold periods (Section 3.4).

3.3. The super-chondritic signature as possible evidence for volcanic fallout

As far as we know, this is the first time that a super-chondritic Ir/Pt signature has been observed in the field of PGE atmospheric chemistry. However, it is not unknown in geochemistry: super-chondritic Ir/Pt is

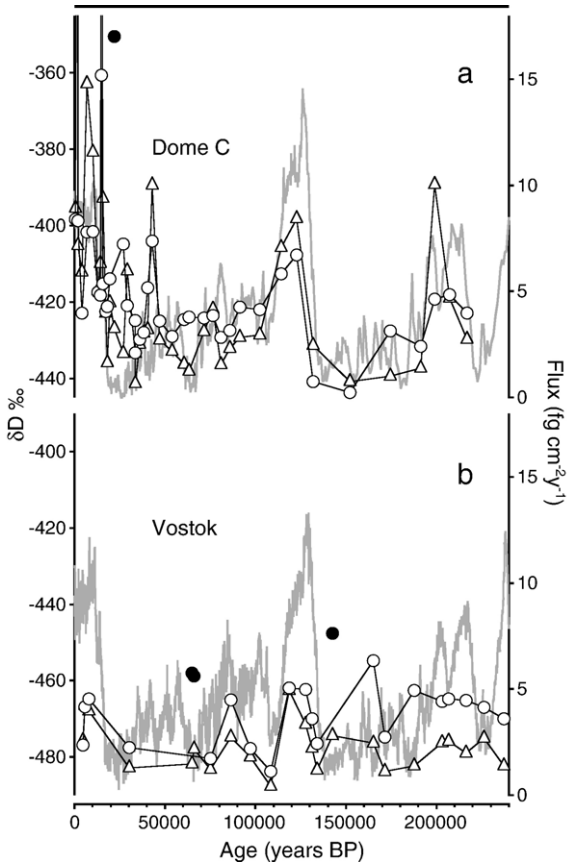

Fig. 1. Fluxes of Ir (open triangles, solid line) and Pt (open circles, solid line) in (a), the EPICA Dome C ice core (EDC), and (b), in the Vostok ice core (VK), during the last two climatic cycles. Climate changes are indicated by variations in the δ*D*‰ (grey solid line) [14,15], taken as a proxy of past local atmospheric temperature. Ir and Pt fluxes are related to climate variations, with generally higher fluxes during warm periods and lower during cold periods. The only clear exceptions are four relatively high values of Pt in VK and one in EDC (the latter characterized by a ~50% of instrumental standard deviation) during cold phases. But at least three of these VK Pt values and the EDC one, indicated with full circles, are most likely caused by significant crustal contributions. These particular samples are in fact characterized by the highest concomitant concentrations in Mn (>550 pg g^{-1}) (taken as a crustal indicator; not shown, see Table 2), along the records. Note also that the large spikes of Ir and Pt in EDC during the current interglacial are not recorded in VK. Estimated Ir flux uncertainty is ~52% whereas Pt flux uncertainty is ~34% (see text).

observed in the sulphides of rocks from the mantle [21], for instance.

Interestingly, in the Holocenic upper sections of EDC, mass ratios calculated from the three concomitant Ir and Pt spikes values are in reasonable agreement with the super-chondritic mass ratios obtained from the lower fluxes in EDC during the same period (see upper enlarged panel in Fig. 2). Thus, the Holocenic EDC spikes, of up to several tens of fg cm^{-2} y^{-1}, cannot be explained by rare events such as asteroid impacts or fallouts from explosive volcanism, but appear to be caused by fluctuations in the influence of a common and continuous source of Ir and Pt.

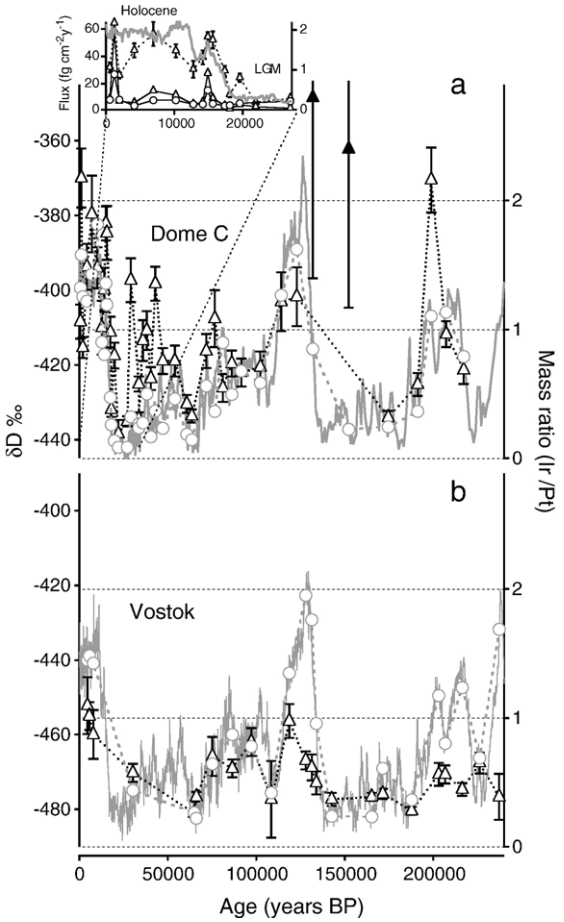

Fig. 2. Mass ratios (open triangles, dotted line) of Ir and Pt (Ir/Pt) in (a), the EPICA Dome C ice core and (b), in the Vostok ice core, during the last two climatic cycles. Climate changes are indicated by variation in δ*D*‰ (grey solid line) [14,15], taken as a proxy of local atmospheric temperature. Open grey circles indicate the δ*D*‰ measured at the same depth as the samples analysed in this study (from Jouzel J. in preparation and Ref. [15]). The Ir/Pt co-varies with temperature; chondritic values (~0.49) are seen during cold periods, and non-chondritic values, close to or higher than 1, during warm periods. Two outliers from Dome C at ~132 kyrs BP and ~152 kyrs BP are indicated with full triangles and are caused by large errors affecting the two linked lowest Pt concentration values. Excluding these two values, the correlation coefficient between Ir/Pt and δ*D*‰ is higher (0.73 instead of 0.56). Slightly lower values in VK Ir/Pt can be interpreted as a result of a minor contribution of Pt from terrestrial continental dust especially in three samples as evidenced also in Fig. 1. In the upper panel, the Holocenic EDC Ir/Pt and Ir–Pt fluxes (open triangles–solid line and open circles–solid line respectively) are expanded. Firstly note the co-variation between δ*D*‰ and Ir/Pt and secondly that those Ir/Pt mass ratios calculated from the concomitant Ir and Pt high values (spikes) in the flux are in reasonable agreement with those non-chondritic mass ratios obtained from the other lower flux values in EDC during the Holocene.

This statement is further supported by the high Ir and Pt flux correlations, which are observed not only in EDC ($r=0.97$) but also in VK ($r=0.66$) during warm periods (the higher correlation in EDC compared with VK is essentially due to the three EDC upper spikes occurring during the Holocene).

Since the continuous super-chondritic Ir/Pt does not support the hypothesis of either a prevalent extraterrestrial or a crustal source during warm periods, other terrestrial atmospheric sources need to be considered. Ir has in fact been documented to be highly enriched in volcanic quiescent emissions, probably as Ir hexafluoride [22]. Nevertheless, the lifetime of this atmospheric species is thought to be rather short because of its likely fast oxidation and deposition. Until now, the only volcanic Ir enrichment recorded in ice was found by analysing large particles decanted after melting an Antarctic tephra ice layer sample; these particles most likely originated from the eruption of a nearby volcano [23]. Unfortunately, there are no published equivalent data for Pt that document its concentrations in volcanic emissions (or in tephra ice layers) and more generally in the atmosphere.

Pb isotope mass ratios [24] and some trace elements (e.g., Cd and Bi) [19,20,25], determined in the same samples as this study, do not show significant correlations with Ir and Pt but indicate in general that Dome C and Vostok have been subjected to frequent volcanic heavy metal fallout, originating from both quiescent and explosive activity. This could be due to Mt. Erebus [26], a currently active volcano situated at Ross Island, which is about 1000 km from Dome C and 1100 km from Vostok. In addition, EDC volcanic ash fallouts are documented from other Antarctic volcanoes such as the Melbourne (Victoria Land) and Marie Byrd Land (West Antarctica) volcanoes, whereas volcanic sources in VK could include the Bransfield Strait (Antarctic Peninsula) and Marie Byrd Land [27–29].

In the light of i) the strong fluctuations of Ir and Pt super-chondritic fluxes in EDC, ii) the general continuity of this super-chondritic mass ratio, and iii) the frequent fallout of volcanic heavy metals determined in the same samples, we tentatively suggest that the super-chondritic mass ratio found in Antarctic ice was produced by fluctuations in the fallout of an aerosol enriched in Ir and Pt. This might have been continuously and quiescently emitted [30] by a close source such as the coastal/western Antarctic volcanoes.

In addition, the gradients between Dome C and Vostok of the Ir and Pt median fluxes, and of the median super-chondritic mass ratios (1.3 in EDC and 0.9 in VK), are respectively consistent i) with the stronger influence on Dome C of a close-by PGE source enriched in Ir, and ii) with the emitted aerosol becoming more depleted in this metal along the longer trajectory taken by the peripheral air masses to reach Vostok with respect to Dome C [31]. Thus, although not conclusive, the data appears consistent with the scenario of volcanic super-chondritic Ir and Pt being able to reach the East Antarctic plateau without being deposited earlier, because of the relatively short tropospheric trajectory and the dry Antarctic air minimising washout. Of course, new data of atmospheric Ir and Pt concentrations determined at the possible volcanic sources of quiescent emission and along the trajectories are warranted in order to better constrain this hypothesis.

Although a more intense volcanic activity during warm periods, due to isostatic adjustments to ice cap loading [32], might be invoked to explain the occurrence of volcanic PGEs fallout, we rather believe that the weaker action of the polar vortex during warm times [33] is sufficient to explain the transport of volcanic PGEs to inland Antarctica due to the facilitated advection of peripheral tropospheric air masses during these periods [34]. A substantial increase in the transport strength toward the Antarctic continent during warm periods is supported by the observation of increased continental dust sizes recorded in EDC during the Holocene [35]. In contrast, during glacial times, a more persistent polar vortex [33] and the linked thermal anticyclone might have generated a more frequent transport from the interior to the coasts, preventing the advection of volcanic PGEs. Thus, the switch from chondritic to super-chondritic Ir/Pt in our data set may reflect a major glacial–interglacial change in the Antarctic atmospheric circulation during the past climatic cycles.

Our suggestion of a more efficient transport into inner Antarctica during warm periods is actually opposite to the common view of the glacial–interglacial variation in the Southern hemisphere circulation. This view requires a substantial increase in the winds strength during glacial ages in order to justify the much larger occurrence of sea salt and continental dust recorded in Antarctic ice over cold times [36]. However, recent findings support our explanation since they point out that the recorded increases in dust and sea salt fallouts were not due to a substantially increased meridional transport efficiency, but to higher Aeolian dust production in Patagonia and to a larger sea ice extent around Antarctica during cold periods [37].

3.4. The chondritic signature and the meteoric smoke input

In contrast with warm periods, there are three pieces of evidence for the dominance of MSP fallout during cold periods in East Antarctica: the essentially chondritic

Ir/Pt; the significant correlation in the fluxes of Ir and Pt ($r=0.64$ in EDC (excluding the Pt value at ~22 kyrs BP because of its very large uncertainty) and $r=0.71$ in VK); and the high EF_c [4]. This allows us to calculate MSP input from Ir and Pt concentrations in Antarctic ice (Section 3.4.1), to perform a comparison with MSP input calculated from the Greenland Ir and Pt record (Section 3.4.2), and finally to infer new information about the MSP fallout distribution and its mechanisms of deposition (Section 3.4.3).

3.4.1. Calculation, uncertainty and upper limits of the MSP input

To allow a better comparison with previous cosmic input estimates, the MSP accretion rate can first be calculated by assuming a homogeneous fallout of MSPs over the whole Earth's surface. We use Ir and Pt concentrations that correspond to an approximate chondritic mass ratio ($0.3 \leq Ir/Pt \leq 0.8$), and we scale their fluxes with the relative chondritic abundances [2]. This yields two essentially identical global estimates of ~20 kt y^{-1} in EDC and VK. This fallout is in rough agreement with an estimate of the global meteoric input of ~11 kt y^{-1} derived from the determination of cosmic Ir in the aerosol at the South Pole [38]. In that study Ir was considered as an indicator of the meteoritic component, which is essentially equivalent to MSPs in the aerosol.

Since the snow accumulation rate is combined with the concentration to determine the flux there are two sources of uncertainty linked to the mean MSP flux: i) the uncertainty in the determination of Ir and Pt concentrations in ice, ii) the uncertainty in the estimation of the snow accumulation rates. First, Ir and Pt ultra-low concentrations in polar ice are determined with our method within a reproducibility of ~50% and ~30% respectively [16]. Since the mean MSP flux calculated using Pt concentrations does not differ substantially from the value calculated adopting Ir, the higher reproducibility of Pt makes this metal preferable for a more robust estimate of the MSP flux. Second, the estimated snow accumulation rate is thought to have ~15% (1σ) uncertainty in EDC and in VK during cold periods (Parrenin F., personal communication), whereas this is less than 5% in GRIP during the Holocene [39], for instance. This lower uncertainty is essentially due to the much higher snow accumulation rate occurring in Central Greenland compared with East Antarctica.

In summary, the MSP flux, calculated using the more reproducible Pt is characterized by a total random uncertainty (calculated by combining these uncertainties in quadrature) of ~34% in Antarctica during cold periods and of ~30% in Greenland during the Holocene. It is interesting to note that, in the context of the MSP flux calculation, a higher uncertainty in the estimate of the snow accumulation rate in Antarctica is counterbalanced by a better precision in the determination of the higher Ir and Pt concentrations recorded, compared with Greenland [4].

There is also a natural time variability of the MSP flux. Adopting Pt concentrations for calculations, the relative standard deviation (σ) of the mean MSP flux, representing the natural time variability, is ~40% in EDC and VK over cold periods and ~25% when the Greenland influx is calculated over the Holocene. Depending on the values of the total random uncertainty of the method (in Antarctica ~34% and in Greenland ~30%) and the natural variability of the flux, the highest will be adopted to define the general uncertainty of the mean MSP flux (so in Antarctica 40% (natural variability) and in Greenland ~30% (total random uncertainty)).

By assuming a perfectly homogenous MSP flux to the Earth's surface, and that the uncertainty affecting the Earth's surface value is negligible, we can transfer the upper and lower limits calculated for the MSP flux to the MSP global input. The MSP global input derived from Antarctica during cold periods (calculated with Pt) can thus be given as 20 ± 7 kt y^{-1}, whereas the Greenland counterpart during cold climates as 76 ± 23 kt y^{-1} (the latter essentially replicating the value reported in [4] of 78 ± 30 kt y^{-1}).

Table 3
Meteoric smoke global input and its upper limits derived from the southern (Dome C and Vostok, Antarctica) and northern (Summit, Greenland) hemisphere Ir and Pt determinations during warm and cold climatic periods

	Antarctica		Greenland
	EPICA Dome C (kt y^{-1})	Vostok (kt y^{-1})	GRIP Summit (kt y^{-1})
Cold periods			
Average (calculated from Ir)	**27***	**20**	*<258*
Average (calculated from Pt)	**20****	**21**	*<165*
Warm periods			
Average (calculated from Ir)	*<89****	*<34*	**81**
Average (calculated from Pt)	*<31*	*<21*	**76**

In bold: Global meteoric smoke input derived from periods with dominant Ir and Pt chondritic contributions.
In italic: Upper global meteoric smoke input derived from periods with dominant Ir and Pt terrestrial contributions (continental dust, volcanic aerosol).
* Excluding the highest value dated at 43 kyrs BP.
** Excluding the highly uncertain value dated at 22 kyrs BP.
*** Excluding the highest value dated at 1 kyr BP.

In an analogous way, by using the flux of Pt in VK, which appears to be less influenced by the local super-chondritic PGE source, we can estimate the upper limit to the MSP fallout during warm climates of 21 ± 7 kt y^{-1} (see Table 3).

3.4.2. Hemispheric inter-comparison of MSP fluxes

Unfortunately, a synchronous direct comparison between the MSP accretion rates in the northern and southern hemisphere ice caps is not possible because the MSP fallout in Greenland is dominated in glacial times by inputs of crustal PGEs [4], whereas in Antarctica a similar difficulty arises during warm periods due to the input of the presumed volcanic PGEs. Nevertheless, as calculated in the previous section, the super-chondritic fluxes observed in East Antarctica during warm times provide at least an upper limit to the MSP fallout during these periods, which is 21 ± 7 kt y^{-1} and represents the sum of the MSP fallout and the additional contribution from volcanic PGEs. This limit is lower by a factor of ~ 4 than the input measured in Greenland during the Holocene [4].

There are several ways in which MSPs could enter the Antarctic troposphere after descending from the mesosphere in the winter polar vortex to the base of the stratosphere. The first is an outflow from the vortex to lower latitudes, followed by exchange from the stratosphere to the troposphere through mid- to high-latitude tropopause folding [40]. Second is direct subsidence from the stratosphere (since the tropopause defined by a temperature minimum is largely absent), driven by the requirement to resupply the katabatic winds which blow down the slopes of the Antarctic plateau [41]. A global tracer transport model indicates that roughly three times as much vortex mass enters the troposphere through this route compared with cross-vortex transport to lower latitudes [42]. Third, MSPs have been shown to be concentrated into polar stratospheric cloud particles [11], and if these grow large enough they could sediment directly into the troposphere.

Considering that the Antarctic polar vortex has been proposed as a more important route than the Northern polar vortex for stratospheric air to pass into the troposphere [41,42], and that a more persistent polar vortex occurred during glacial times [33], a much higher fallout of MSPs might be expected in Antarctica during cold periods than in Greenland during the Holocene. An intriguing possible explanation for the opposite observation is that, since the snow accumulation rate in Dome C and Vostok is ~ 10 times less than in Summit (Central Greenland), wet deposition might be the major route for MSPs into the Greenland snow pack. MSPs may in fact act as condensation nuclei for ice crystals and thus MSP fallout intensity might be controlled not only by the proximity to the polar vortices [4] but also by the rate of precipitation. So the large observed MSP flux to Greenland would have occurred mainly by wet deposition, whereas in Antarctica the smaller flux would have mainly been due to the less efficient dry deposition of meteoric material attached to aerosol, most likely sulphate particles [43].

3.4.3. Major implications

What is becoming apparent from our data is that the atmospheric transport and deposition of MSPs is complex, leading to climate dependent and quite heterogeneous MSP spatial distributions. This of course raises the question of whether estimates of the global input of cosmic material which are obtained through measuring the MSP flux to the polar regions, are representative. For instance, if the MSP fallout to Earth is mainly by wet deposition, and MSPs are homogeneously distributed in the troposphere as a function of latitude, then this would imply a global fallout that was much larger than calculated from Antarctic (~ 20 kt y^{-1}) and Greenland (~ 78 kt y^{-1}) data, since a much higher precipitation rate than on the Antarctic plateau (~ 2 g $cm^{-2}y^{-1}$) and Central Greenland (~ 25 g $cm^{-2}y^{-1}$) is common over most of Earth (~ 100 g $cm^{-2}y^{-1}$ average). Nevertheless, if most of the material enters the troposphere and is deposited polewards of 55° latitude (which is about one fifth of the global surface area), the measured input from the ice record must be divided by a factor of about 5 (since the meridional flow reverses every 6 months) [4]. Then the estimated MSP global fallout would be much lower and would lie between the upper Greenland (14 kt y^{-1}) and the lower Antarctic (4 kt y^{-1}) corrected estimates. The correction factor used is consistent with transport into the troposphere either being directly thought the base of the polar vortex [41,42], or through tropopause folding at mid- to high-latitudes [40]. However, it is clear that future work should involve using a general circulation model up to at least 80 km altitude, in order to investigate the atmospheric transport of MSPs.

Although it is difficult to infer an absolute global MSP input value, chondritic PGEs recorded in a rather limited geographical area where climatic differences are negligible and wet deposition is a minor process, such as the area between Dome C, Vostok and the South Pole, can provide a direct indication of the relative temporal variations of the MSP accretion rate, and thus indirectly of the IDP flux. If we compare i) our glacial MSP input estimates (20 kt y^{-1}) from Dome C and Vostok, ii) our upper limit to the MSP input during warm times (<21 kt y^{-1}) in Antarctica, and iii) the meteoric input [38] derived from cosmic Ir

measurements determinations in aerosol at South Pole (11 kt y^{-1}), which was considered representative of the MSP fallout during the Holocene, it appears that a substantial glacial–interglacial increase in the IDP influx can probably be ruled out, and also that a significant glacial–interglacial decrease did not occur. Thus, our work supports the previous suggestion derived from extraterrestrial helium isotopes determined in marine sediments [8] that variations in the IDP flux are unlikely to have triggered the 100 kyrs climate cycle [7].

4. Conclusions

Remarkably, the super-chondritic, most likely non-cosmic (volcanic) Ir and Pt flux recorded in East Antarctica during warm periods, together with the intense Ir and Pt crustal fallout reported in Greenland ice during the last ice age [4], indicate that the atmospheric chemistry of PGEs was strongly and systematically influenced by significant terrestrial contributions over large geographic areas during particular climatic periods of the Earth's history. Once deposited, the accumulation of these terrestrial airborne PGEs might have had an important role in the formation of various Ir and Pt anomalies present in different terrestrial climatic archives.

Comparison of chondritic Ir and Pt fluxes to Antarctica and Greenland suggests that wet deposition is an important route of cosmic material to the Earth's surface. In addition, the glacial–interglacial shift from the chondritic to the super-chondritic Ir/Pt mass ratio offers a first hint of the advection of air masses enriched in volcanic iridium and platinum inland to Antarctica, exclusively during mild periods. This would also represent new evidence of a major glacial–interglacial change in the Antarctic atmospheric circulation during past climatic cycles, which is in contrast with the current view of an increased transport towards Antarctica during glacial periods.

We conclude that meteoric and super-chondritic iridium and platinum accretions to Antarctica were likely modulated by atmospheric processes, rather than changes in extraterrestrial input or in volcanic activity during the past climatic cycles.

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