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Siderophile metal fallout to Greenland from the 1991 winter eruption of Hekla (Iceland) and during the global atmospheric perturbation of Pinatubo

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ABSTRACT

Ir and Pt are siderophile elements that are considered proxies of meteoric material of cosmic origin entrapped within polar ice layers. However, volcanic and anthropogenic fallouts have the potential to perturb their characteristic extraterrestrial signature even in remote polar areas. Here we show a record of Ir and Pt concentrations in snow samples collected from a 2.7 m pit, which was dug at Summit (Central Greenland), and covered five years from winter 1991 to summer 1995.

A well-defined peak of Pt, and a spike of Ir, were found at the base of the snow pit record. These maxima occur in close concurrence with large concentration peaks in Al, Ag, Cd and Hg. Dating of the snow layers together with some geochemical evidence suggests that these peaks originated from the fallout to Greenland of volcanic ash emitted by the nearby Hekla volcano (Iceland), during the eruption of January–March 1991. Interestingly, an anomalous peak of methane sulfonic acid (MSA) in Greenland snow also corresponds to the Hekla ash fallout. This might point to an early biomass production in the North Atlantic Ocean during the first half of 1991, which was possibly stimulated by the fertilizing action of the Hekla ash fallout to seawater.

During the following years (1992–1995) the global atmosphere was under the influence of the large perturbation produced by the eruption of Mt. Pinatubo (Philippines) in June 1991. Relatively high Ir and Pt concentrations with super-chondritic ratios are recorded especially during summer 1993. We discuss if this can be interpreted as the possible stratospheric input of Pinatubo's aerosol or fallout of extraterrestrial origin. During the same period the snow pit record was also influenced by the advection of air masses enriched in Pt with respect to Ir. One possibility is that this additional Pt contribution originated from widespread emissions into the troposphere produced by vehicles equipped with catalytic converters. In any case, Pt concentration levels found in recent Greenland snow are about two orders of magnitude lower than previously thought, pointing to a much lower anthropogenic contamination of the Arctic regions from Pt. This challenges the concept of an important hemispheric contamination of Pt from vehicles equipped with catalytic converters.

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1. Introduction

Ir and Pt are siderophile elements, which are extremely depleted in the terrestrial upper crust (Wedepohl, 1995) but are enriched up to 10,000 times in chondritic meteorites (Anders and Grevesse, 1989), and to a lesser and more variable extent in volcanic materials and in mafic and ultramafic rocks originating from the terrestrial mantle (McDonough and Sun, 1995; Wasson and Kallemeyn, 1988). Siderophile elements have been extensively studied in sediments and in geological formations, mainly with the aim of determining anomalous enrichments of cosmic origin (e.g., Alvarez et al., 1980; Bodiselitsch et al., 2005) or for estimating past sediment accumulation rates (e.g., Barker and Anders, 1968; Dalai and Ravizza, 2006). In contrast, the Ir and Pt occurrence in natural waters (Anbar et al., 1996; Fenner and Presley, 1984; Hodge et al., 1985) and in the atmosphere (Tuncel and

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Zoller, 1987; Zoller et al., 1983) have been only rarely explored. Therefore the global geochemical cycles of these siderophile elements remain largely unknown.

Polar ice caps constitute an excellent archive of the past atmospheric content of ultra trace elements. Recent studies have focused on the occurrence of Ir and Pt in ancient ice from Greenland and Antarctica (Gabrielli et al., 2004a, 2006). It has been shown that the natural occurrence of Ir and Pt in the past atmosphere was often linked to the cosmogenic input. Meteoroids entering the Earth's atmosphere vaporize and re-condense in the upper mesosphere, producing nano-particles which have been termed meteoric smoke particles (MSP) (Hunten et al., 1980; Plane, 2003). Due to the seasonal mesospheric circulation from the summer pole to the winter pole, MSP are thought to be concentrated in polar regions where they may be deposited by dry and/or wet mechanisms (Gabrielli et al., 2004a, 2006; Lanci and Kent, 2006; Lanci et al., 2007), enriching the ice caps of Antarctica and Greenland with cosmic Ir and Pt.

Studies of Greenland ice have revealed that past atmospheric concentrations of Ir and Pt were strongly influenced also by the high continental load of terrestrial dust occurring during the last glacial age (Gabrielli et al., 2004a). Unexpectedly, ancient Antarctic ice showed, super-chondritic and relatively high fluxes of Ir and Pt during warm climatic periods. This has been speculated as due to a systematic glacial–interglacial change in the Antarctic atmospheric circulation that caused the transport of volcanic aerosol from coastal areas into the inner part of East Antarctica, mainly during mild climatic stages (Gabrielli et al., 2006).

Sporadic perturbations of the atmospheric content of Platinum Group Elements (PGEs) are caused also by volcanic eruptions, as recorded in polar glacial archives (Koeberl, 1989). From January to March 1991, an eruption occurred in the sub-Arctic area at the Hekla volcano (63° N, 19° W, South Iceland). The plume related to this event had its largest extension on the 17th of January 1991, when it attained 11.5 km in height for a few hours (Gudmundsson et al., 1992). Images from the Meteosat geostationary satellite show that this plume spread in a north–northeast direction with a speed of 60–70 km h^{-1} and approached the north coast of Iceland. No long-range ash transport and fallout to the snow in the Arctic area have ever been reported for the emission products of this Hekla eruption, but the scarce information that is available would be consistent with a possible perturbation of the atmospheric chemical content of Greenland shortly after the most intensive phase of the eruption.

Later, from June 1991 to at least the year 1994, the global stratosphere was affected by the largest aerosol perturbation of the last century, namely the emission of volcanic products from the eruption of Pinatubo (15° N, 120° E, Philippines) (McCormick et al., 1995). In June 1991, Pinatubo emitted an estimated peak aerosol mass loading of 30 Tg (McCormick et al., 1995), a large part of which originated from SO_2 oxidation (Bluth et al., 1993). Two months later, another significant eruption from Cerro Hudson (45° S, 72° W) occurred in the Southern Hemisphere. The estimated aerosol loading was about one order of magnitude lower than that from Pinatubo (McCormick et al., 1995), affecting mostly the Southern Hemisphere atmosphere (Cole-Dai et al., 1997; Legrand and Wagenbach, 1999) and the Northern Hemisphere probably only to a negligible extent. Evidence of the fallout of the Pinatubo and Cerro Hudson's emission products to Antarctica was found by studying the sulphate content in several Antarctic snow pits (Cole-Dai and Thompson, 1999; Cole-Dai et al., 1997; Legrand and Wagenbach, 1999). In contrast, until now no evidence of Pinatubo fallout to Greenland, and in general to Northern hemisphere snow and ice, has been reported.

The beginning of the 1990s is of particular interest also for studying the possible presence of anthropogenic PGEs dispersed into the polar atmosphere. In general there are a lack of studies aimed at evaluating the occurrence of anthropogenic Pt and Ir in the atmosphere during the current Anthropocene (Crutzen and Stoermer, 2000). Pollution of the Northern Hemisphere by Pt has been ascertained in some cases and attributed to the emission from vehicles equipped with catalytic converters (Barbante et al., 2001; Moldovan et al., 2007; Rauch et al., 2005a; Rauch et al., 2005b; Van de Velde et al., 1998, 2000). There are even less studies on anthropogenic Ir. This heavy metal is widely used by the chemical and electrochemical industries, in electronics and in automobile catalysts (although to a lesser extent than Pt), but it is still not clear to what extent these human activities might have affected its natural budget. A few studies have reported Ir concentrations in sediments and roadside environments (Ely et al., 2001; Muller and Heumann, 2000; Rauch et al., 2004, 2006) but none address remote areas of the globe.

This paper is aimed at understanding the extent to which the Ir and Pt atmospheric budget was perturbed by the volcanic eruptions of Hekla and Pinatubo in 1991, and from the growing anthropogenic use of these metals in recent years. For this purpose, we have determined the Ir and Pt concentrations in Summit (Central Greenland) snow pit samples, spanning a period from winter 1991 to summer 1995. The snow accumulation (260 cm in four years) and the sampling resolution (60 samples) allow for the first time a seasonal study of the variations in Ir and Pt concentrations in polar snow.

2. Method

The snow pit samples were collected in June 1995 at a remote site in the Summit area in central Greenland (72° 20′ N; 38° 45′ W; elevation 3270 m; mean snow accumulation rate 23 g cm^{-2} y^{-1} of water equivalent). The sampling site was far away from drilling sites such as Eurocore/GRIP (30 km SW) and GISP2 (20 km S), in order to prevent contamination (Barbante et al., 2003). The snow pit was hand-dug by operators wearing full clean room clothing and shoulder-long polyethylene (PE) gloves, using acid cleaned PE shovels. A continuous series of 60 samples was collected from the surface down to a depth of 2.6 m, using a cylindrical low-density polyethylene (LDPE) coring tube (4.5 cm in diameter and 30 cm long), which was hammered horizontally into the wall of the pit using an LDPE hammer. The content of the tube was then transferred directly into an ultra-clean LDPE wide mouth 1 l bottle. The bottles were packed in double acid cleaned PE bags and kept frozen until processing in the laboratory.

Samples were melted at room temperature in the original 1 l LDPE bottle, inside an all-plastic laminar flow clean bench in a clean laboratory (Boutron, 1990). An aliquot of 60 ml was transferred in a Perfluoroalkoxy (PFA) beaker (Nalgene), pre-concentrated by sub boiling evaporation to 1–2 ml and finally spiked with 1% v/v of ultra pure HNO_3. The pre-concentrated solution was transferred in an ultra-cleaned 15 ml LDPE bottle and kept frozen until analysis. Ir and Pt were determined by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) (Thermo Scientific, Element*2*), coupled to a desolvation system (CETAC-Aridus) for sample introduction, allowing elimination of spectroscopic interferences. Precision, accuracy, and blanks as well as a full presentation of the analytical method are extensively described elsewhere (Gabrielli et al., 2004b).

In a previous study (Barbante et al., 2003), Pt was measured directly (without pre-concentration) by ICP-SFMS in the same samples considered in this work. A comparison of median values shows that results obtained at that time (350 fg g^{-1}) were higher by about two orders of magnitude with respect to Pt concentrations reported in this work (5.6 fg g^{-1}). After a careful data re-evaluation, we found out that in the earlier work, a lower instrumental sensitivity, together with an underestimation of the instrumental background, resulted in higher Pt concentrations. To resolve this large discrepancy, a direct determination (without any pre-concentration) of Pt in some of these snow samples, was attempted again by using the current ICP-SFMS configuration. In these analyses Pt concentrations were found to be below the limit of detection of this direct method (~5 fg g^{-1}).

Additional confidence in our results comes from a study presenting a completely new procedure developed for PGEs determination in snow and ice based on pre-concentration by using an alumina column and ICP-SFMS analysis, (De Boni et al., in preparation). This shows Pt concentrations ranging from the sub-femtogram per gram up to few femtograms per gram in recent Greenland snow. These levels are just slightly lower than Pt results presented in this work (possibly because alumina micro columns pre-concentrate only the acid leachable fraction of Pt). However, it should be noted that all these most recent studies always obtained Pt concentrations at the femtogram per gram level in Greenland snow. This supports the reliability of the Pt concentration data reported in this work and suggests that a pre-concentration step is always necessary to quantify Pt in polar snow and ice by ICP-SFMS.

Samples from a parallel series collected at the same time from the same snow pit were also analyzed for ionic species directly after melting at room temperature down to a depth of 260 cm (Jaffrezo et al., 1998) and for stable isotopes ($\delta^{18}O$) down to a depth of 209 cm using the method already described in a published manuscript (Stenni et al., 2002).

3. Results

3.1. Dating the snow pit

The chronology of the different seasons in the snow pit was deduced from the $\delta^{18}O$ values and the concentration profiles of Na^+. $\delta^{18}O$ is a proxy of the site atmospheric temperature and shows more negative values during winters and less negative values during summers (Stenni et al., 2000). The Na^+ profile generally provides a good definition of winters, characterized by high Na^+ concentrations. Strong marine Na^+ inputs are in fact associated with increased cyclogenesis in the Northern Atlantic (Barlow et al., 1997; Whitlow et al., 1992).

The strong seasonal pattern of $\delta^{18}O$ and Na^+ was recorded and allows a proper definition of winters 1991, 1992, 1993 and 1994 (Fig. 1). Although it was not possible to determine $\delta^{18}O$ from 208 cm down to 260 cm because of the lack of samples, we assign winter 1991 to the snow layers characterized from the previous and deepest Na^+ peak (Fig. 1). This definition is consistent with the snow accumulation observed between this deepest Na^+ peak and winter 1992 (~60 cm), which is in line with the snow accumulation observed during the four following years and with the average snow accumulation rate recorded at Summit (Kuhns et al., 1997). The five years in our record are defined with an estimated maximum temporal uncertainty of three months.

3.2. Ir and Pt concentrations

The Ir and Pt concentrations determined in the recent Greenland snow samples are illustrated in Fig. 1 and Table 1 and show a complex profile. Variations of concentrations for both Ir and Pt are large, with values ranging from the sub-femtogram per gram level up to several tenths of femtogram per gram.

When compared to ancient Holocene Greenland ice samples (Gabrielli et al., 2004a), higher concentrations are observed for Ir and Pt in these samples from the 1990s. Median concentration values in recent Greenland snow are 1.6 fg g^{-1} for Ir and 5.6 fg g^{-1} for Pt. These median concentrations are higher by a factor of 5 for Ir, and by a factor of 8 for Pt, than the corresponding values found in pre-industrial ice over the Holocene (Gabrielli et al., 2004a). Minimum values are 0.4 fg g^{-1} for Ir and 2.5 fg g^{-1} for Pt, whereas maximum values are 30 fg g^{-1} for Ir and 90 fg g^{-1} for Pt. Minimum concentration values found in recent Greenland snow are higher by a factor of 4 and of 6 than those found for Ir and Pt in Holocene Greenland ice, whereas the corresponding maximum concentration values are higher by a factor of 5 for Ir, and by a factor of 13 for Pt. It is also worth noting that instrumental standard deviations of Ir and Pt concentrations (see Table 1) were always low suggesting that no large particle (e.g. micrometer sized extraterrestrial particle) influenced our Ir and Pt concentrations by causing occasional spikes in the spectra.

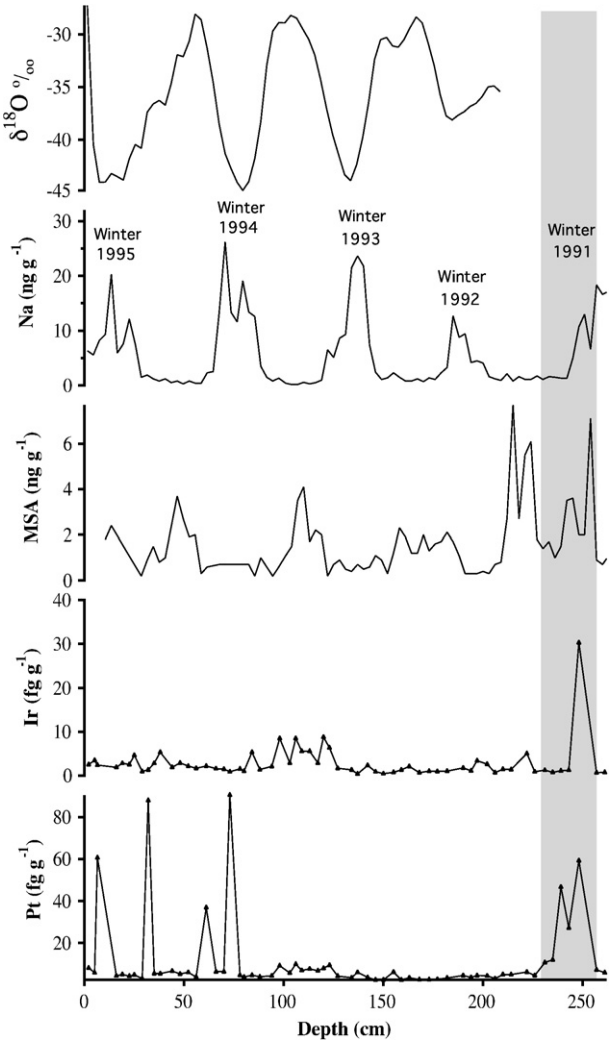

Fig. 1. $\delta^{18}O$ and concentrations, Na^+, Methane Sulphonic Acid (MSA), Ir and Pt. $\delta^{18}O$ is a proxy of the site atmospheric temperature and shows more negative values during winters and less negative values during summers. High Na^+ concentrations are typical of winter, whereas high MSA concentrations occur normally during spring and summer. Note that the year 1991 is atypical since a double peak of MSA is present, the first during late winter/early spring and the second, longer and more pronounced, during summer (see discussion in the text).

4. Discussion

Three main features emerge from our data set. First, a well-structured Pt peak and large spike of Ir can be observed during approximately the first half of 1991 (Figs. 1 and 2). Second, we note four large isolated spikes of Pt occurring during the years 1994 and 1995 (Figs. 1 and 2). Third, it is remarkable to note the highly variable, but significantly-correlated ($r=0.70$; $n=51$), background concentrations of Ir and Pt, including relatively high levels (up to 10 fg g^{-1}), recorded mainly during summer periods and in particular during summer 1993 (Fig. 3).

In order to evaluate the crustal terrestrial contribution to the Ir and Pt budgets in snow, we have calculated the crustal enrichment factor (EF_c), which is defined as:

$$EF_c = \{[Metal]_{snow}/[Al]_{snow}\}/\{[Metal]_{crust}/[Al]_{crust}\}$$

Table 1
Ir, Pt and Hg concentrations, Ir/Pt mass ratio and crustal enrichment factors (EF_c) of Ir, Pt and Hg calculated with respect to Al, taken as a proxy of continental dust

Depth (cm)	Ir (fg g^{-1})	Ir SD (fg g^{-1})	Pt (fg g^{-1})	Pt SD (fg g^{-1})	Hg (pg g^{-1})	Hg SD (pg g^{-1})	EFc Ir	EFc Pt	EFc Hg	Ir/Pt
2	2.5	0.2	8.1	0.2	2	1	134	44	6	0.31
5	3.5	0.2	6.0	0.1	1.4	0.4	192	33	5	0.57
6.5	2.3	0.1	61	1	–	–	2416	6273	–	0.04
16	1.8	0.1	4.4	0.1	1.5	0.4	2015	482	101	0.42
19	2.8	0.2	5.1	0.1	1.1	0.3	2101	386	54	0.54
22.5	2.5	0.1	4.3	0.1	6	2	9039	1567	1372	0.58
25	4.6	0.2	4.8	0.1	1.6	0.5	10801	1133	232	0.95
29	0.9	0.1	3.1	0.1	5	1	1766	590	539	0.30
32	1.3	0.1	88	1	4	1	1350	9080	246	0.01
35	2.8	0.1	5.5	0.2	1.0	0.3	3337	664	72	0.50
38	5.3	0.2	5.5	0.1	2	1	5462	574	147	0.95
44	1.8	0.2	6.6	0.1	<LOD	–	1571	568	–	0.28
48	2.9	0.2	5.3	0.3	3	1	4213	777	240	0.54
52	2.2	0.2	6.0	0.2	1.5	0.4	–	–	–	0.36
56	1.6	0.1	3.8	0.1	2	1	1534	363	129	0.42
61	2.2	0.1	37	1	4	1	335	577	40	0.06
66	1.6	0.1	6.3	0.1	3	1	117	47	12	0.25
70	1.4	0.1	6.4	0.1	7	2	132	59	40	0.22
73	0.9	0.1	90	2	4	1	235	2416	66	0.01
78	1.5	0.2	4.8	0.3	5	1	590	184	119	0.32
80	1.0	0.1	3.8	0.1	0.8	0.3	342	129	18	0.27
84	5.3	0.3	4.8	0.2	3	1	3584	325	109	1.10
88	1.4	0.1	4.1	0.1	3	1	468	140	56	0.33
94	2.1	0.1	4.4	0.1	5	2	1172	248	181	0.47
98	8	1	9.2	0.2	5	1	10696	1162	397	0.92
103	2.8	0.1	5.8	0.2	1.0	0.3	1426	292	32	0.49
106	8.5	0.4	10.0	0.2	5	1	6582	774	241	0.85
109	6	1	7.1	0.3	2	1	41923	5363	995	0.78
113	5.5	0.2	7.8	0.1	4	1	6482	919	281	0.71
117	2.8	0.2	6.8	0.3	5	2	2437	582	282	0.42
120	8.7	0.3	8.0	0.2	5	1	7403	681	254	1.09
123	6.3	0.3	9.5	0.2	3	1	4489	677	150	0.66
127	1.6	0.1	4.3	0.2	2	1	435	116	34	0.37
134	1.3	0.2	3.6	0.1	5	1	390	109	88	0.36
137	0.4	0.1	6.1	0.2	2	1	92	143	26	0.06
142	2.3	0.2	3.7	0.1	0.6	0.2	1366	221	24	0.62
146	0.9	0.1	2.5	0.1	2	1	362	106	45	0.34
150	0.4	0.1	2.6	0.1	6	2	115	66	98	0.18
155	0.7	0.1	6.2	0.1	2	1	43	36	8	0.12
159	1.3	0.1	2.6	0.1	5	1	2695	535	642	0.50
163	2.1	0.2	3.5	0.1	4	1	1777	304	205	0.58
168	0.7	0.1	2.7	0.1	2	1	455	182	78	0.25
173	1.0	0.1	2.6	0.1	4	1	228	61	51	0.37
177	0.9	0.1	2.9	0.1	4	1	177	54	48	0.33
182	1.0	0.1	3.4	0.1	4	1	90	31	22	0.29
190	1.7	0.1	4.6	0.1	1.3	0.4	699	188	33	0.37
194	1.1	0.1	3.7	0.1	2	1	637	213	73	0.30
197	3.4	0.3	4.7	0.1	4	1	1388	192	111	0.72
202	2.6	0.2	4.4	0.2	3	1	1430	247	89	0.58
206	0.6	0.1	3.1	0.1	3	1	753	382	249	0.20
210	1.4	0.1	5.1	0.1	9	3	516	181	195	0.29
214	1.3	0.2	5.1	0.2	3	1	429	163	53	0.26
222	5.0	0.3	6.2	0.1	4	1	6572	816	297	0.81
226	0.9	0.1	4.6	0.1	6	2	722	379	306	0.19
231	1.2	0.1	10.8	0.2	9	3	664	578	289	0.11
235	0.7	0.1	12.2	0.1	11	3	82	133	77	0.06
239	1.1	0.1	47	1	730	70	227	968	9573	0.02
243	1.3	0.1	27	1	490	50	31	68	774	0.05
248	30	1	59	1	23	7	2030	397	95	0.51
257	0.7	0.1	7.4	0.2	8	2	210	234	157	0.09
261	0.7	0.1	5.9	0.1	3	1	190	158	56	0.12

with $\{[Ir]_{crust}/[Al]_{crust}\}=6.28\times10^{-10}$, and $\{[Pt]_{crust}/[Al]_{crust}\}=5.03\times10^{-9}$ taken from (Wedepohl, 1995) and $[Al]_{snow}$ taken from (Barbante et al., 2003). It is assumed that Al is a good indicator of continental dust in Greenland snow (Gabrielli et al., 2004a). The respective median EF_c values obtained for Ir and Pt with this calculation are strikingly high, at 737 and 298, respectively. Because the EF_c values always greatly exceed the value of 1 (Table 1) even during elevated continental dust fallout, it is suggested that the fluxes of Ir and Pt cannot be explained by the crustal contribution. Therefore, in the following sections we will examine and discuss the three main observed features in the light of other potential sources.

4.1. The volcanic peak in 1991

As can be seen in Fig. 2, a peak in Pt concentrations defined by 5 data points in the range of 11–59 fg g^{-1} was found at a depth interval 231–248 cm, during approximately the first half of 1991. This

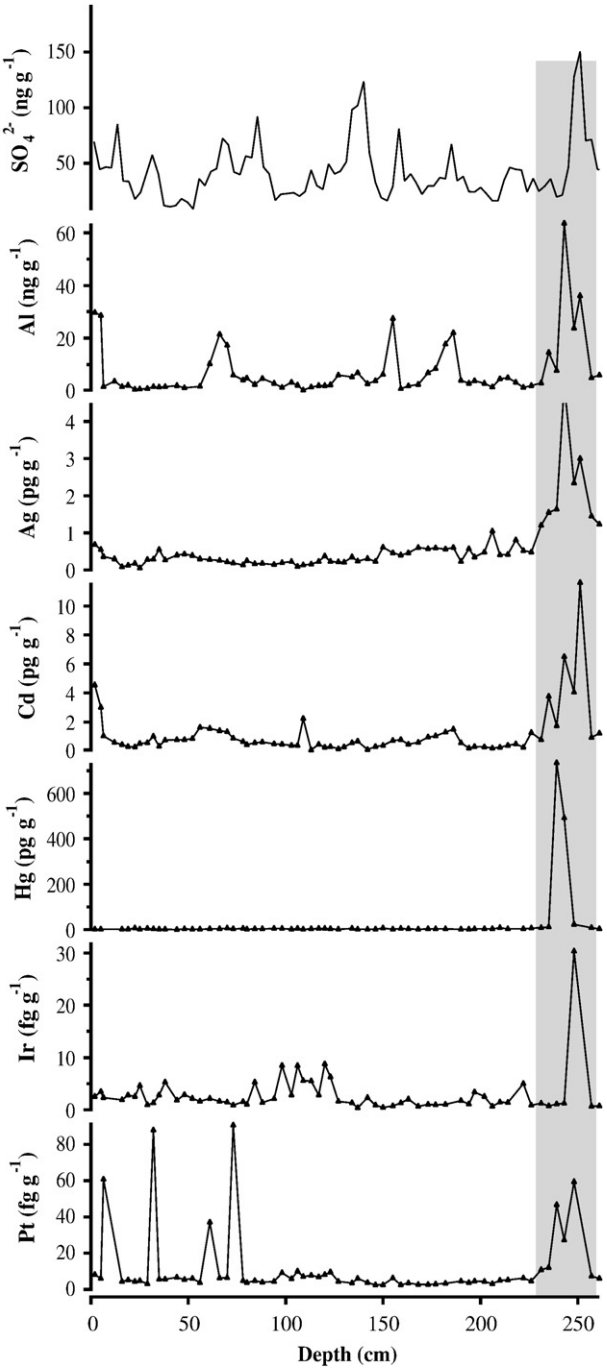

Fig. 2. Concentrations of Pt, Ir, Hg, Cd, Ag, Al and sulphate. Note that a large peak of Pt and the only large spike of Ir occur in close concurrence with large peaks of dust enriched in typical volcanic elements such as Cd, Ag and Hg during the first half of 1991, concomitantly with the Hekla (Iceland) eruption that occurred in January–March 1991 but too in advance to be interpreted as the fallout of ash from the Mt. Pinatubo (Philippines) eruption (June 1991) that may have occurred not before than September 1991. Note also that the sulphate peak in 1991 is not particularly unusual.

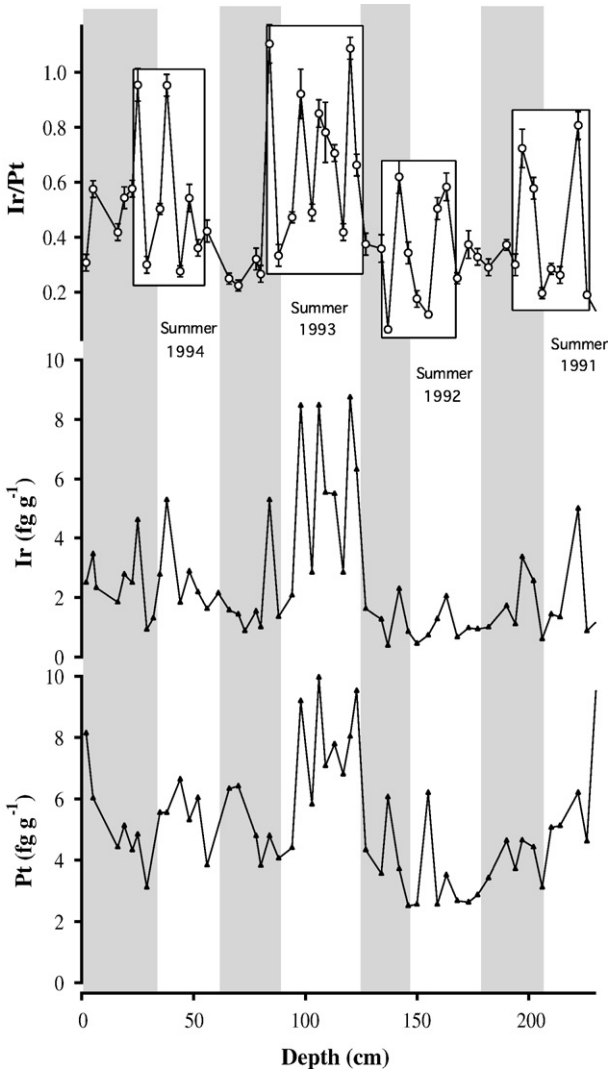

Fig. 3. Background concentration values of Pt, Ir and the Ir/Pt mass ratio in the upper part of the snow pit. The four large Pt spikes are excluded from the figure. Note that high concentrations of Ir and Pt and super-chondritic Ir/Pt ratios occurred mainly during summer periods and in particular during summer 1993.

coincides with a large Ir spike (30 fg g^{-1}) occurring at a depth of 248 cm. In a previous study conducted on aliquots from the same snow pit samples, well-structured peaks of Al, Ag and Cd (Fig. 2) (and less clearly of Zn and Mo, not shown) were reported over the same depth interval (Barbante et al., 2003). In the present study we also report a profile of Hg concentrations determined on the same samples by ICP-SFMS with a method described elsewhere (Planchon et al., 2004). This Hg profile shows a huge peak up to 730 pg g^{-1} at this same depth interval (Fig. 2 and Table 1). These peaks can be interpreted to be due to a substantial fallout of dust enriched in Ag, Cd and Hg with respect to the crust composition (EF_c of Ag ranges between ~100 and ~600, EF_c of Cd between ~130 and ~200, EF_c of Hg between ~80 and ~9600, calculated with respect to the mean Al terrestrial upper crust content (Wedepohl, 1995). A corollary is that the high EF_c values shown for heavy and siderophile metals at this snow depth should be considered only as lower limits because, as we will report below, the Al concentrations, which were used as the crustal reference, were most likely influenced by an additional input of volcanic Al at this depth.

Because Al, Cd, Ag, Ir, Pt and Hg peaks approximately coincide with the Na^+ peak, which was found exactly at a depth where winter snow was expected to accumulate (Fig. 1), we conclude that the strong enrichment of these heavy metals recorded in Summit snow during the first half of 1991 originated most probably from the fallout originating from the January–March 1991 eruption of Hekla in South Iceland. This conclusion is supported by several pieces of evidence:

(i) Cd, Ag, Hg and Ir are often found to be enriched in volcanic emissions (Hinkley et al., 1999; Nriagu, 1989; Pyle and Mather, 2003; Zoller et al., 1983).
(ii) In particular Cd, Ir and Hg have also been found to be enriched in volcanic ash layers trapped in glacial archives (Gabrielli et al., 2005; Hong et al., 1996; Koeberl, 1989; Schuster et al., 2002).
(iii) The absence of any exceptional peak of sulphate concentrations at the base of the snow pit (Barbante et al., 2003) supports the idea of volcanic fallout from an eruption close to Greenland so that SO_2 has not had enough time to be oxidized as it takes up to 15 days to SO_2 to be converted into sulphate in the upper troposphere (Laj et al., 1990).
(iv) Unusually high Al concentrations were determined at the base of the snow pit and unexpectedly high Al concentrations were found also to be released from metal salts adsorbed onto volcanic ash from the 2000 eruption of Hekla (Frogner et al., 2006) (which produced a magma indistinguishable in composition from that of the 1991 eruption of Hekla (Moune et al., 2006)).
(v) The Cd/Al mass ratio of $3.9 \pm 2.6 \times 10^{-4}$ (with Al corrected for crustal background average concentration) found at the base of the snow pit, and the ratio of $9.6 \pm 5.9 \times 10^{-4}$ in tephra scavenged from a snow storm in Iceland during the 2000 eruption of Hekla (Moune et al., 2006), are mutually consistent within their environmental variability (at the 1σ level).
(vi) The initial trajectory of the major plume from the 1991 eruption of Hekla observed by satellite on January the 17th, and the forward trajectories calculated at different heights (2000–5000 m) with the NOAA Hysplit model (Fig. 4), are consistent with the fast transport of the ash plume towards northern latitudes and a subsequent rapid eastward circulation. Therefore, Hekla ash could have reached Greenland from the west after being transported towards the Arctic circumpolar regions.
(vii) The Pinatubo fallout originating from the eruption of June 1991 was first detected in the Arctic stratosphere in September 1991 (Di Girolamo et al., 1994), and therefore the heavy metal peaks found at the base of the snow pit occurred too early to be attributed to the fallout from this volcanic event.

The peak of volcanic Al (Fig. 2) suggests that the fallout occurred in the form of volcanic ash to the Greenland snow (however no visible ash layer was observed at the base of the snow pit), and therefore that Cd, Ag, Ir, Pt and Hg were also present in particulate form, possibly as metal salts. It has been suggested that volcanic aerosol, consisting of acids and water-soluble metal salts, adsorb onto the surface of volcanic ash and form deliquescent metal salt encrustations and crystalline salts (Oskarsson, 1980, 1981).

However, a point-by-point closer inspection suggests that Al, Cd, Ag, Hg, Ir and Pt might have been not necessarily deposited exactly at the same time, possibly as a consequence of their different refractory (Al, Ir, Pt) or volatile (Ag, Cd, Hg) behavior. We also cannot exclude that selective post-depositional processes might have affected the concentration of some particularly reactive trace elements (e.g. Hg) or that snow layers might have been reworked to some extent.

In any case, we report indications that Ir and Pt can be transported over medium distances with small volcanic ash particles. Interestingly, only a single large Ir spike is recorded during this volcanic fallout. The Ir/Pt mass ratio in this particular sample (0.51) is very close to the chondritic ratio of 0.49 (Anders and Grevesse, 1989). In general however, the Ir/Pt ratios <1 measured in the snow layers influenced by

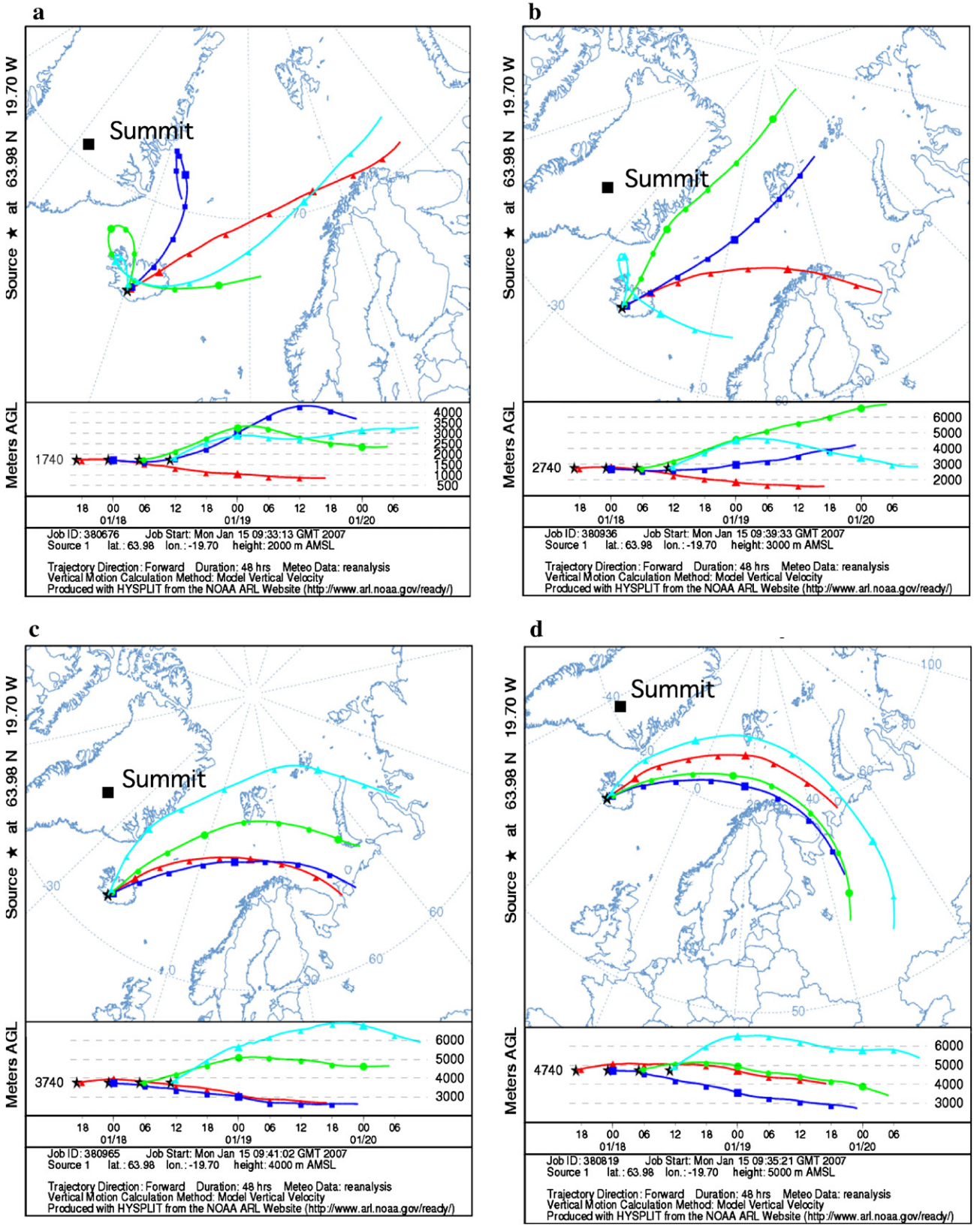

Fig. 4. Forward trajectories starting from the troposphere above the Hekla volcano calculated for different heights of the ash plume (2000 m (a), 3000 m (b), 4000 m (c) and 5000 m (d)) with the Hysplit model of NOAA after the main explosive event of the 1991 eruption (17 UTC on January the 17th 1991). Trajectories higher than 5000 m (not shown) depart more markedly eastward from the Greenland continent. Trajectories between 2000 and 5000 m are consistent with the rapid transport of the ash plume towards northern latitudes departing from the Greenland continent and with a rapid eastward circulation towards the Arctic circumpolar regions suggesting that the Hekla ash approached Greenland from the west.

the Hekla fallout are consistent with sub-chondritic ratios in most volcanic lavas (e.g. Greenough and Fryer, 1990).

4.2. The possible fertilization of the North Atlantic from the Hekla ash fallout

Methane Sulphonic Acid (MSA) is known to be of biogenic origin as its precursor, the dimethyl sulphide (DMS), is mostly of oceanic origin. Maxima in the MSA concentrations in the snow pit series at Summit are generally linked with the late spring/summer season (Jaffrezo et al., 1994; Li et al., 1993; Whitlow et al., 1992). In our series, the observed substantial MSA peaks are coherently associated with increased biological production in the North Atlantic during summer, and alternate with the Na^+ winter peaks except during the first half 1991 (see Fig. 1). In the interval of time considered, the year 1991 is atypical since a double peak of MSA is present, the first during late winter/early spring (coincident with the Na^+ winter peak) and the second, longer and more pronounced, during summer. Interestingly, the first early peak of MSA coincides with the volcanic ash fallout from Hekla.

The North Atlantic Ocean is a large net sink for atmospheric CO_2 because of the biological drawdown occurring during summer. However, the availability of phosphate in the North Atlantic Ocean may limit primary production (Takahashi et al., 1993) and thus phosphate provided by the ash fallout to this ocean may act as fertilizers. The fertilization potential of ash from the 2000 eruption of Hekla was measured extensively during several tests conducted by Paul Frogner and co-workers (Frogner et al., 2001). They found that this volcanic ash exposed to seawater initially released large amounts of adsorbed phosphate, Fe, Si and Mn. They concluded that macro-nutrients and bioactive trace metals are released fast enough to become available to support primary production.

The early MSA peak found in the Summit snow pit concomitantly with volcanic ash fallout from the 1991 eruption of Hekla is thus a hint that early biological production due to fertilization of the North Atlantic might have occurred following the dissolution in Arctic seawater of the volcanic ash emitted by Hekla in 1991.

4.3. The Pt spikes in 1994 and 1995

As observed in Fig. 1, four isolated large Pt spikes, ranging from 37 fg g^{-1} to 90 fg g^{-1}, were recorded during the years 1994 and 1995, whereas the corresponding concentrations of Ir remain always at extremely low values. This suggests for these cases a different origin for these two siderophile elements. By comparing Pt concentrations with the previously reported Sb, Zn, and Pb profiles in the same snow pit (Barbante et al., 2003), we observe that the four Pt spikes occur close to the peaks of Sb, Zn and Pb (Fig. 5). High EF_c for Sb (13–240), Zn (6–65) and Pb (16–109), together with the current large excess of anthropogenic vs. natural emissions of these metals (Nriagu, 1989; Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2001) suggests the advection to Greenland of anthropogenically-enriched air masses in Sb, Zn and Pb during these periods.

One possible anthropogenic source of Pt in recent Greenland snow is emissions of vehicles equipped with catalytic converters (Barbante et al., 2001). However, the concentrations of these Pt spikes are lower by about one order of magnitude when compared to the Pt concentrations determined previously (Barbante et al., 2003), suggesting that the load of anthropogenic Pt to northern Arctic latitudes is much lower than previously thought. Concomitant low concentrations of Ir with these Pt spikes may reflect the fact that only traces of Ir are present in the majority of catalytic converters and hence they do not strongly perturb its natural atmospheric budget.

A study of the source regions of air masses reaching the top of the Greenland Ice Sheet, was performed using a 44-year series of daily air mass back trajectories (Kahl et al., 1997). This study showed that during the winter period about 67% of the 10-day trajectories extended westward as far back as the heavily industrialized regions of Eastern Asia and Eastern Europe, whereas trajectories tended to be shorter in summer, with the majority of the trajectories reaching back to North America. As three out of the four Pt spikes observed occurs at the major seasonal transitions (Fig. 1), it is difficult for the moment to constrain the geographical origin of the Pt measured in the ice and snow.

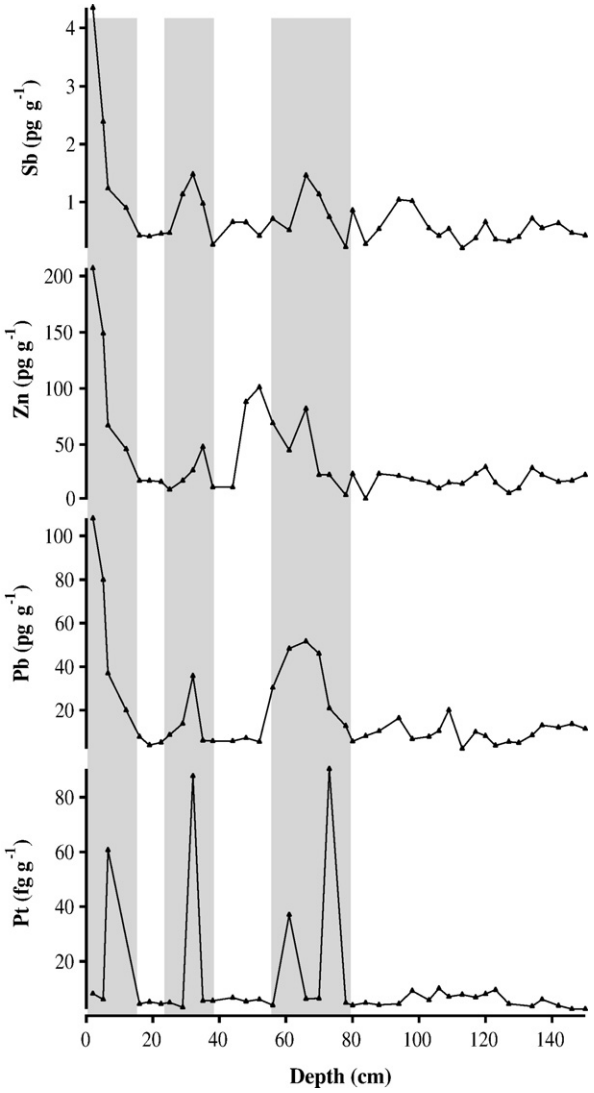

Fig. 5. Concentrations of Pt, Pb, Zn and Sb (the latter three from Barbante et al., 2003). Note that the four large Pt spikes are approximately concomitant with the deposition of typically anthropogenic metals such as Pb, Zn and Sb occurring in the upper part of the record.

4.4. The Ir and Pt background values

By excluding the four upper samples with large Pt spikes of possible anthropogenic origin discussed above, and the five samples influenced by the volcanic emissions from Hekla, we may observe subtler features emerging from the background values (n=51). In this case Ir and Pt concentrations are relatively high (up to ~10 fg g^{-1}) and well correlated (r=0.70), while the Ir/Pt mass ratios span an interval from 0.1 up to 1.1 with an arithmetic mean of 0.46 (σ=0.26) and a median of 0.37, very close to the chondritic ratio (0.49). The high median EF_c values for Ir and Pt are 1172 and 247, respectively. This would seem to suggest a MSP contribution (Gabrielli et al., 2004a).

However, given that meteoric Ir and Pt concentrations in Greenland ice were constantly lower during pre-industrial times (Gabrielli et al., 2004a), the relatively high values might be explained differently. In a plot of Pt vs. Ir background concentrations (Fig. 6), we observe a significant positive end member for Pt (3.6±0.6 fg g^{-1}, 95% of confidence), which is evidence of an additional input of Pt with respect to Ir. We suggest that, similar to the large Pt enrichment spikes discussed in the previous section, this minor but emerging additional input of Pt might be also of anthropogenic origin. This may explain the median ~10-fold Pt enrichment with respect to the corresponding pre-industrial levels.

Interestingly, this enrichment of Pt with respect to Ir does not hold always true during summer. In particular, relatively high Ir and Pt concentration values (up to ~10 fg g^{-1}) and super-chondritic Ir/Pt mass ratios (~1) can be observed during summer 1993 (Fig. 3), meaning that an additional input of Ir occurred during this period. Interestingly, although on a very different climatic timescale, concomitant higher concentrations, Ir/Pt super-chondritic ratios and higher air temperatures were found also in ancient interglacial Antarctic ice and were tentatively attributed to the advection of a volcanic aerosol (Gabrielli et al., 2006).

It is well documented that the atmospheric global load of aerosol was perturbed for at least three years after the 1991 Pinatubo eruption (McCormick et al., 1995). We speculate that the relatively high Ir and Pt concentrations and the Ir/Pt super-chondritic mass ratios observed during the summers 1992–1995 might be explained in the light of this event. If Pinatubo emissions were introduced into the stratosphere in June 1991, they might have been confined there for several years. The super-chondritic ratios and relatively high Ir and Pt concentrations might then be linked to the delayed fallout of this stratospheric material to Greenland during summer.

Clearly further research is needed to test this hypothesis as, to our knowledge, no Ir/Pt mass ratios determined in the Pinatubo emissions or indeed any other volcanic emissions are currently available in the literature. We note also that, the fact that Ir/Pt ratios are super-chondritic does not necessarily rule out a MSP contribution, as even extremely similar PGEs such as Ir and Os deviate from the canonical chondritic ratio of ~1 in individual micrometeorites (0.4 to 1.7) (Kurat et al., 1994). Atmospheric processing may lead to larger deviations from the chondritic ratio in the case of Ir and Pt that are chemically less similar than Ir and Os and so we cannot exclude the possibility that short term processes may affect the chemical composition and the fallout of MSP.

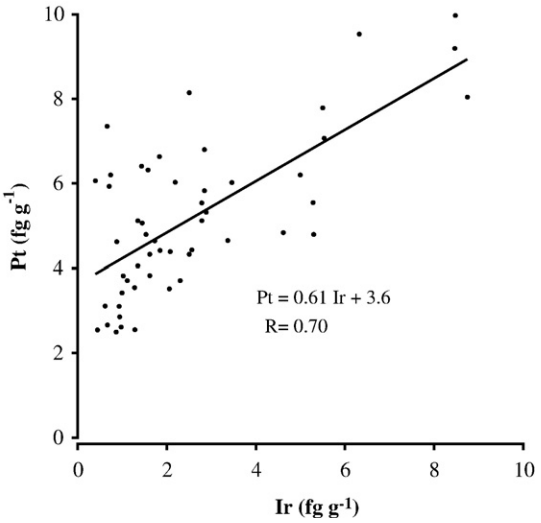

Fig. 6. Background Pt concentrations vs. background Ir concentrations. The regression line obtained shows a significant positive intercept of 3.6 fg g^{-1} for Pt, which is evidence of a general additional input of this metal with respect to Ir.

In any event, to explain an Ir and Pt summer fallout from the stratosphere one should consider the atmospheric stability over Central Greenland during the winter months, and thus the associated limited vertical mixing that transport atmospheric particles from the high troposphere to the surface. In contrast, when the winter polar vortex breaks down at the end of the cold season, there is an outflow of air to lower latitudes, followed by exchange from the stratosphere into the troposphere through tropopause folding events at mid- to high-latitudes (Hsu and Prather, 2005). Thus, a stratospheric source of Ir and Pt would not tend to be deposited in Greenland until spring and early summer. This is consistent with the higher activity ^{7}Be of stratospheric origin found in Summit aerosol during summer (Dibb, 2007).

5. Summary and conclusions

High concentrations of Ir and Pt were recorded in Greenland snow layers during the first half of 1991. We attribute this enrichment to the fallout of ash from the January–March 1991 volcanic eruption of Hekla (Iceland). The ash fallout from the 1991 eruption of Hekla might also have been responsible for the fertilization of the North Atlantic Ocean, producing earlier than expected biomass production and thus explaining an anomalous peak of MSA observed in Greenland snow at the time of the Hekla ash fallout. In the future it would be interesting to determine phosphorus species in these same samples in order to better constrain this working hypothesis.

Although to a much lesser extent than previously reported (Barbante et al., 2003), the observation of large Pt spikes and a general enrichment of Pt with respect to Ir in the period 1992–1995 suggest an anthropogenic contribution of Pt to the Northern latitudes. This may derive from the emissions of vehicles equipped with catalytic converters. However, the much lower Pt data reported in this work challenges the concept of an important hemispheric contamination of Pt from catalytic converters. We note also that the Ir atmospheric budget does not appear clearly perturbed by catalytic converters and more in general by anthropogenic activities.

Relatively high background concentrations of Ir and Pt and super-chondritic ratios were mainly observed during the summer. This could be linked to a stratospheric input from the volcanic aerosol load emitted into the stratosphere from the 1991 Pinatubo eruption or from MSP deviating from the canonical Ir/Pt chondritic mass ratio. In conclusion, Ir and Pt concentrations in recent Greenland snow layers spanning the 1991–1995 period do not reflect only the cosmic signal caused by the fallout of MSP, as is the case during pre-industrial periods of the Holocene (Gabrielli et al., 2004a). This observation challenges the potential for using Ir and Pt as markers of MSP over recent periods, at least in the Northern Hemisphere.

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