



## Changes in atmospheric heavy metals and metalloids in Dome C (East Antarctica) ice back to 672.0 kyr BP (Marine Isotopic Stages 16.2)

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### ABSTRACT

Cu, Zn, As, Cd, Pb and Bi were determined by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) in seventy-seven sections of the 3270 m deep ice core drilled at Dome C at an altitude of 3233 m on the East Antarctic plateau as part of the European Program for Ice Coring in Antarctica (EPICA). The depth of the section ranged from 2368.85 m (263.6 kyr BP) to 3062.13 m (672.0 kyr BP). When combined with data previously obtained for the upper part of the core, it gives a detailed record of past natural variations in the concentrations of these heavy metals during the last eight climatic cycles from the Holocene back to Marine Isotopic Stage (MIS) 16.2. Concentrations of all metals are found to have strongly varied. For Cu, Pb, Bi and possibly Zn concentrations appear to be closely linked with climate conditions, with high values during glacial maxima and much lower values during interglacials. The situation is less clear for As and Cd, for which variations are less clearly linked with climate conditions. Rock and soil dust appears to be the main source of Cu, Zn, Bi and Pb during glacial maxima, and a significant source for these metals during interglacials, while As, Cd and Bi present a more complex inputs from several sources, with a particularly significant impact of volcanism.

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### 1. Introduction

For the past decades, considerable attention has been given to the study of various heavy metals such as Pb, Cd, Pt and Hg in the environment. This is because human activities are emitting large amounts of these toxic metals to the atmosphere and other compartments of the environment (see e.g. Nriagu and Pacyna, 1988; Nriagu, 1990; Pacyna and Pacyna, 2001; Von Storch et al., 2003; Wilson et al., 2006). Since the dawn of the Industrial Revolution, the emissions have grown considerably to the extent that today the impacts of the long-term accumulated toxic metals have become global in scope. The most fascinating example is Pb. For this metal, contamination of the Northern Hemisphere started as early as Roman times (Hong et al., 1994; Zheng

et al., 2007) while contamination of the Antarctic continent was only significant at the end of nineteenth century (Planchon et al., 2003). The amplitude of the contamination by this metal is extremely pronounced especially because of the huge emissions linked with the widespread use of organolead compounds as anti-knock additives in gasoline from the 1920s onwards (Nriagu, 1990; Von Storch et al., 2003).

Any proper assessment of these man induced changes requires a good knowledge of past natural geochemical cycles of these metals and their variations with different climatic conditions, against which recent trends can be evaluated. Such information can only be obtained from archives such as deep Antarctic ice cores (Petit et al., 1999; EPICA Community members, 2004). As an example, average lead concentrations in deep ice core from the Holocene are of ~0.4 pg/g, while mean concentrations found in recent Antarctic snow (early 20th century, are ~2.0 pg/g (Planchon et al., 2003)), therefore putting modern concentrations into the context of natural variability. Deciphering the ice core archives has unfortunately proved to be extremely difficult because heavy metal concentrations in polar ice are extremely low

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and drilling operations strongly contaminate the outside of deep ice cores. The impetus in the field came from the pioneering work of Patterson, Boutron and co-workers who developed sophisticated methods to decontaminate deep polar ice cores drilled in fluid-filled holes, which allowed for reliable data for heavy metals in these cores to be obtained (Ng and Patterson, 1981; Boutron et al., 1987).

Presently available reliable data for heavy metals and metalloids in deep Antarctic ice cores are only for two locations (Dome C and Vostok) and cover limited time periods. For Dome C, available data cover only the past 217 kyr, which corresponds to the last two climatic cycles (Gabrielli et al., 2005a; Vallelonga et al., 2005). For Vostok, available data cover the past 420 kyr, which corresponds to the last four climatic cycles (Hong et al., 2003, 2004, 2005; Gabrielli et al., 2005b). A drawback of the Vostok data is however that they do not allow a comprehensive view of the entire Marine Isotopic Stage (MIS) 11, considered as a key interglacial period from about 390 to 420 kyr BP, and probably the best analogue of the present Holocene interglacial (Berger and Loutre, 2003; Droxler et al., 2003). MIS 11 is an unusual and perhaps unique interglacial interval. It exhibited warm interglacial climatic conditions for an interval of at least 30 ky, a duration twice as long as the most recent interglacial periods, with orbital parameters (low eccentricity and consequently weak precessional forcing) similar to those of the present. Moreover, there are no data for the period between the Mid-Pleistocene Revolution (MPR) (often dated at about 900 kyr BP) (Raymo et al., 1997) and the Mid-Brunhes Event (MBE) (which roughly corresponds to the transition between MIS 12 and MIS 11 about 430 kyr BP) (Berger and Wefer, 2003).

We present here comprehensive data on past changes in the occurrence of Cu, Zn, As, Cd, Pb and Bi in Antarctic ice during the period from 263.6 kyr BP (MIS 8.2) to 672.0 kyr BP (MIS 16.2). The data

were obtained by analysing various sections of the 3270 m deep ice core recently obtained at Dome C as part of the European EPICA program, using ultra-clean decontamination procedures and the highly sensitive Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) technique. The sections which were analysed include various sections dated from MIS 11, together with sections dated from before and after the Mid-Brunhes Event.

## 2. Experimental

### 2.1. Description of the samples

The 3270 m EPICA/Dome C ice core was drilled at Dome C (75°06'S, 123°21'E, altitude of 3233 m above sea level, mean annual temperature  $-54^{\circ}\text{C}$ ) on the East Antarctic plateau within the framework of the European Project for Ice Coring in Antarctica (EPICA) (EPICA community members, 2004). The core was electro-mechanically drilled in a fluid-filled hole during several successive summer seasons from 1999 to 2005. It reached the depth of 3270 m, about 5 m, above bedrock in January 2005 (EPICA community members, 2004; Parrenin et al., 2007).

The 77 ice samples, considered in this study, derive from 39 core sections from the part of the core whose depth ranges from 2368.85 m to 3062.13 m (see Table 1 in Appendix A). The detailed deuterium variations profile (EPICA Community members, 2004), was used to select sections representing both interglacial and glacial maxima periods.

Age dating of the ice is based on the EDC3Beta6 timescale (Parrenin et al., 2007). The ice at 2368.85 m is dated at about 263.6 kyr BP, which corresponds to the MIS 8.2 glacial maximum. The ice at 3062.13 m is dated at 672.0 kyr BP, which corresponds to the MIS 16.2 glacial

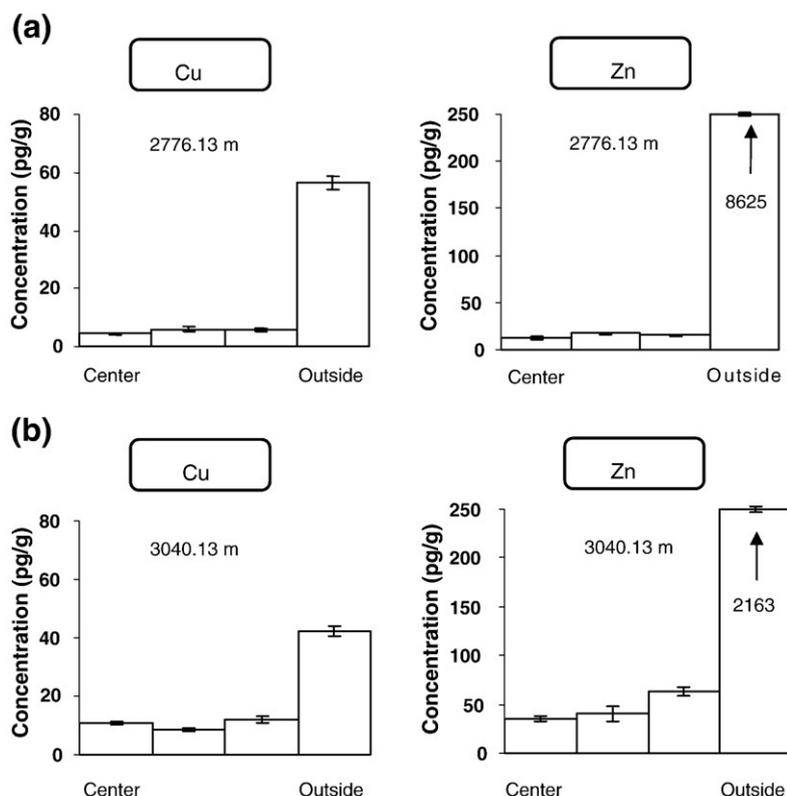


Fig. 1. EPICA/Dome C Antarctic ice core: measured concentrations of Cu and Zn as a function of radius in two sections: (a): depth of 2776.13 m (425.2 kyr BP), MIS 11.3 interglacial; (b) depth of 3040.13 m (632.6 kyr), MIS 16.2 glacial maximum. Concentrations are expressed in pg/g.

maximum. The samples analysed in this work then cover a ~400 kyr time period from MIS 16.2 to MIS 8.2. A given core section (length of 55 cm) is found to integrate about 200 yr at 2369 m and about 1000 yr at 3062 m.

## 2.2. Ice core section decontamination

Each core section was mechanically decontaminated in order to remove the outside of the core which was heavily contaminated during drilling operations, especially because of the wall-retaining fluid (kerosene densified with 141b freon substitute) which was used to counterbalance the huge pressure encountered at great depth. It involved chiselling concentric veneer layers of ice in progression from the contaminated outside towards the pristine central part of each section, inside a laminar flow clean bench at  $-15^{\circ}\text{C}$ , using ultra-clean procedures which have been described by Candelone et al., 1994 and Hong et al., 2005. Each decontaminated section was then divided into three consecutive parts: (1) a 5 cm long part at the bottom of the section for the subsequent determination of Hg; (2) two consecutive 20 cm long parts, which were used for the present study giving the 77 depth intervals listed in Table 1, Appendix A. The weight of the sample was ~400 g before the decontamination and it is reduced to less than ~80 g after the decontamination.

In order to check the efficiency of the decontamination, changes in the concentration of each metal from the outside to the inside of the sections were investigated. Good plateaus of concentration were observed in the central part of the cores in all cases, as illustrated in Fig. 1 for Cu and Zn in the 2776.13 m section (dated at 425.2 kyr BP, which corresponds to the MIS 11.3 interglacial period) and the

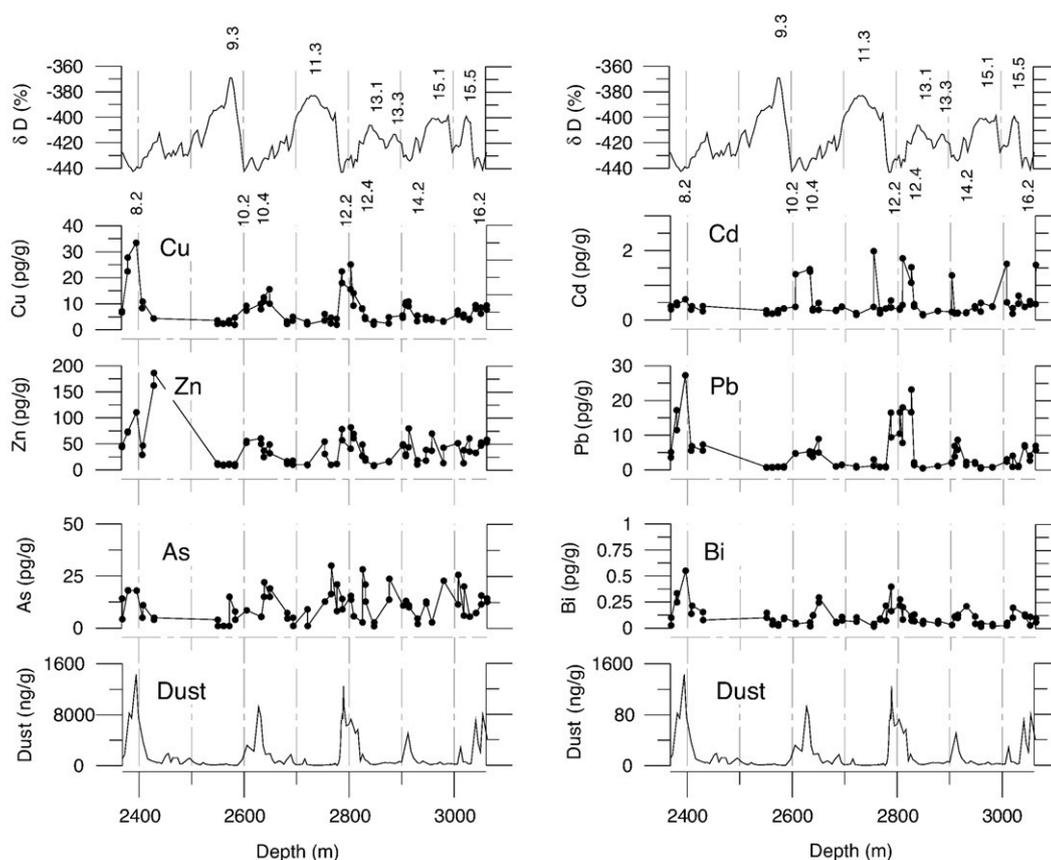
3040.13 m section (dated at 632.6 kyr, which corresponds to the MIS 16.2 glacial maximum). It indicates that external contamination has not penetrated to the central part of the cores and that the plateau concentrations represent the original concentrations in the ice.

Decontaminated samples were melted at room temperature in ultra-clean wide mouth low-density polyethylene (LDPE) 1 L bottles inside a clean laboratory (Boutron, 1990; Ferrari et al., 2000). 10 mL aliquots were then taken inside ultra-clean 15 mL LDPE bottles, acidified with ultrapure nitric acid prepared by sub-boiling distillation (Burton et al., 2007) to make 1% solutions and kept frozen until analysis.

## 2.3. Analysis by ICP-SFMS

Cu, Zn, As, Cd, Pb and Bi were determined by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) using an Element2 instrument from Thermo Fisher (Bremen, Germany) equipped with a micro-flow ( $<100\ \mu\text{L}\ \text{min}^{-1}$ ) PFA nebulisation system (Planchon et al., 2001). The instrument can be used with three different resolution modes (low resolution mode LR:  $m/\Delta m=400$ ; medium resolution mode MR:  $m/\Delta m=4000$ ; high resolution mode HR:  $m/\Delta m=10,000$ ). The LR mode was used for the determination of Cd, Pb and Bi, while the MR mode was preferred for Cu and Zn and the HR mode was selected for As.

Detection limits (calculated as 3 times the standard deviation of the response of the instrument to a solution of ultra pure water spiked with 1% (v/v) of  $\text{HNO}_3$ ) ranged from 0.04 pg/g for Bi to 2.2 pg/g for Zn. Overall procedural blanks were determined by processing an artificial ice core prepared by freezing ultrapure water in which the concentrations of the different metals was known beforehand (Vallelonga et al., 2002). The corresponding contribution was found



**Fig. 2.** EPICA/Dome C Antarctic ice core: changes in concentrations of Cu, Zn, As, Cd, Pb and Bi as a function of depth from 2368.85 m to 3062.13 m (263.6 to 672.0 kyr BP). Also shown at the top of the figure are the variations in deuterium concentrations (expressed in delta per mil) (EPICA Community members, 2004), Marine Isotope Stages (MIS) numbers (Bassiot et al., 1994), and at the bottom of the figure changes in dust concentrations (expressed in ng/g) (EPICA Community members, 2004).

to be extremely small (during interglacial times, from 2% for As to 7% for Bi; during glacial times, from 1% for Pb to 3% for Zn). Typical precisions in terms of relative standard deviations were found to range from 8% for Zn and Pb to 26% for As.

### 3. Results and discussion

#### 3.1. Changes in concentrations during the last eight climatic cycles

Heavy metals and metalloid concentrations measured in the innermost part of the 77 samples are listed in Table 1, Appendix A. They range from 0.01 pg/g for Bi in ice dated at 566 kyr BP to 186 pg/g for Zn in ice dated at 286 kyr BP. They are the first data ever obtained for ice dated back to 672.0 kyr BP.

Fig. 2 shows that concentrations of all metals and metalloids have strongly varied during the ~400 kyr period covered by our samples. For Cu, Pb, Bi and possibly Zn, concentrations appear to be closely linked with climate conditions with high values during the coldest periods such as MIS 8.2, 10.4 and 12.2, and low values during interglacial periods such as MIS 9.3, 11.3 and 15.1 (Fig. 2). The situation appears to be less clear for As and Cd, with observed variations which are less clearly linked with deuterium changes. The highest maximum/minimum concentration ratios are observed for Cu, Zn and Pb (~40) while lower ratios are observed for As, Cd and Bi (~20). These are ratios which are lower than the maximum/minimum ratios observed for dust (~100, EPICA Community members, 2004) and for elements such Al, Mn and Ba which mainly derived from crustal dust (Marteel et al., in press; V. Gaspari personal communication).

For Cu, As, Cd, Pb and Bi, our data can be combined with the data previously obtained by Gabrielli et al. (2005a) and Vallelonga et al. (2005) for the upper 2193 m of the EPICA Dome C ice core (ice dated from 0.5 to 217 kyr BP), giving comprehensive time series for these five elements over a ~672.0 kyr period from the Holocene to the end of MIS 16.2, Fig. 3. It is the first time that past natural variations in heavy metals have been observed during such a long time period with high sampling frequency (about 159 depth intervals in total). During this 672.0 kyr period, variations in concentrations of Cu, Pb and Bi are found to fairly well parallel changes in climate with high concentrations during glacial maxima and a low concentrations during interglacials. The amplitude of the variations appears however to be larger during the most recent climatic cycles than during the oldest ones, especially before the Mid-Brunhes Event (Fig. 3). The situation is less clear for As and Cd. For these two metals indeed, elevated concentrations are observed for the most recent glacial maxima (MIS 2.2 and 4.2) but not for earlier maxima such as MIS 12.2.

#### 3.2. Fallout fluxes for heavy metals and metalloids during the past 672.0 kyr bp

Fallout fluxes were calculated for each metal by combining concentrations measured in the ice for each depth interval with the estimated yearly ice accumulation rate at that depth (expressed in  $\text{g H}_2\text{O cm}^{-2} \text{y}^{-1}$ ). The accumulation rate at Dome C has varied by a factor ~2 between glacial maxima (~1.3  $\text{g H}_2\text{O cm}^{-2} \text{y}^{-1}$ ) and interglacial periods (~2.7  $\text{g H}_2\text{O cm}^{-2} \text{y}^{-1}$ ) (F. Parrenin, personal communication).

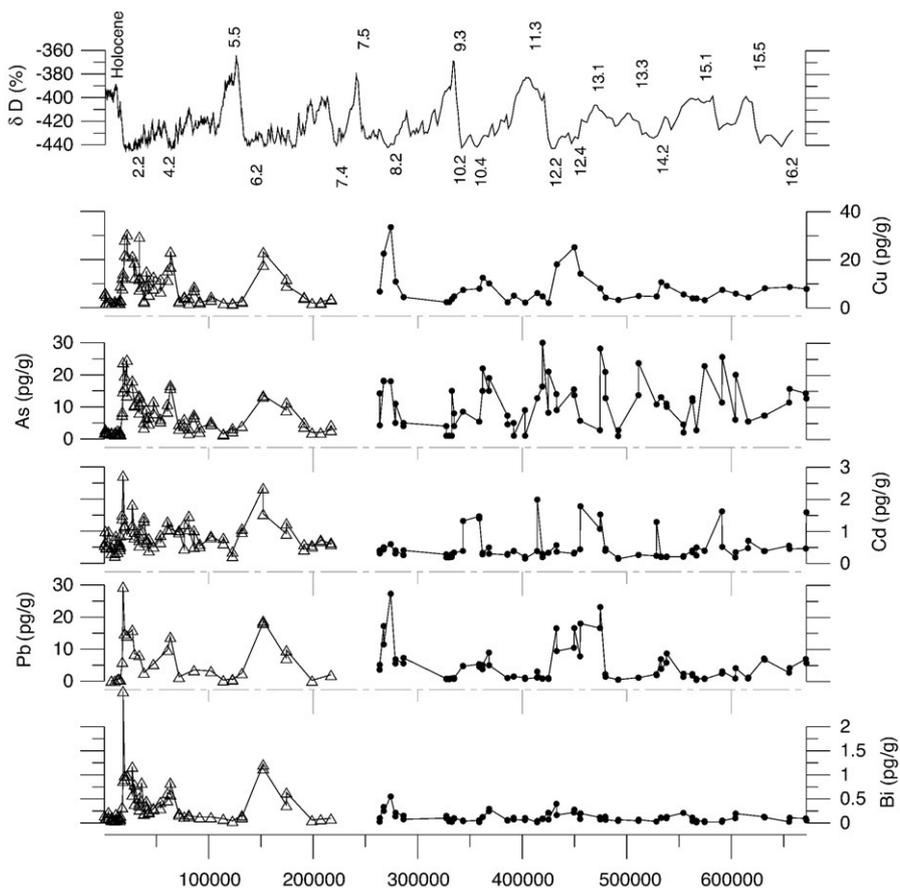


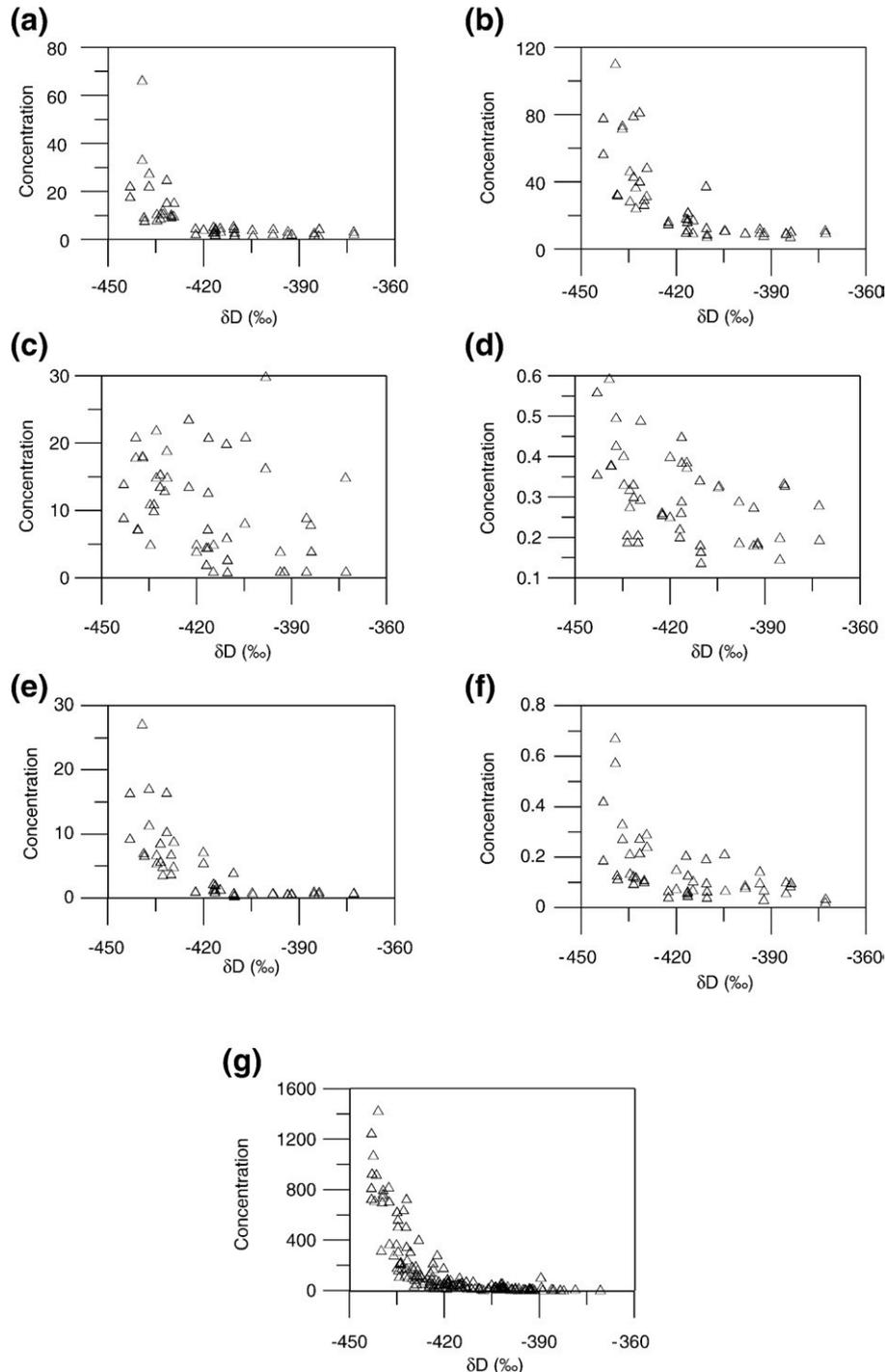
Fig. 3. EPICA/Dome C Antarctic ice core: changes in concentrations of Cu, As, Cd, Pb and Bi during the past 672.0 kyr (EDC3Beta6 timescale from Parrenin et al., 2007). Open triangles are used for ice samples dated from 0.5 to 217 kyr BP (data from Gabrielli et al., 2005a) while full circles are used for ice samples dated from 263.6 to 672.0 kyr BP. Also shown at the top of the figure is the deuterium profile and MIS numbers (EPICA Community members, 2004). Concentrations are expressed in pg/g, except for deuterium (delta per mil).

Changes in fallout fluxes are found to parallel fairly well changes in concentrations during the past 672.0 kyr. The ratio between the highest and the lowest fluxes is however about half of the corresponding ratio for concentrations since the accumulation rate is lower during glacial maxima when concentrations are maximum.

### 3.3. Heavy metals and metalloids concentrations versus deuterium

Concentrations of Cu, Zn, Pb, Bi and dust in Dome C ice during the past 672.0 kyr are found to remain very low for  $\delta D$  values between  $\sim -380\%$

and  $\sim -420\%$  as illustrated in Fig. 4 for Cu, Zn, Pb, Bi and dust but increase strongly when  $\delta D$  values fall below  $\sim -420\%$ . It suggests that there is a critical point in the climate mechanism, beyond which fallout of heavy metals to the high East Antarctic Plateau increases considerably. A possibility is that when a critical temperature gradient between low and high latitude was reached, it induced changes in wind strength, then allowing larger amounts of heavy metals to be transported to the Antarctic ice cap (Gabrielli et al., 2005b). Another possibility could be rapid changes in local conditions in the different source areas such as Patagonia or Australia from



**Fig. 4.** EPICA/Dome C Antarctic ice core: changes in concentrations of Cu (a), Zn (b), As (c), Cd (d), Pb (e), Bi (f) (expressed in pg/g) and dust (g) (expressed in ng/g) as a function of the deuterium content of the ice (expressed in delta per mil) from 263.6 to 672.0 kyr BP.

**Table 1**  
Dome C, East Antarctica: mean, minimum and maximum concentrations (expressed in pg/g) and mean, minimum and maximum crustal enrichment factors (EF<sub>c</sub>) (using Ba as crustal reference element) of various metals and metalloids for the successive glacial maxima back to MIS 16.2

			Glacial maxima									
			MIS 2.2 (6)	MIS 4.2 (4)	MIS 6.6 (4)	MIS 8.2 (10)	MIS 10.2 (4)	MIS 10.4 (6)	MIS 12.2 (4)	MIS 12.4 (4)	MIS 14.2 (4)	MIS 16.2 (6)
Cu	Concentration	Average	34 <sup>a</sup>	20 <sup>a</sup>	21 <sup>a</sup>	28	11	9	20	20	10	8
		Min–Max	13–107	17–23	18–23	22–33	7–15	8–10	18–22	16–25	9–11	6–10
	EF <sub>c</sub>	Average	4.7 <sup>a</sup>	2.8 <sup>a</sup>	2.5 <sup>a</sup>	5.6	3.5	3.4	4.9	5.9	7.4	4.8
		Min–Max	2.1–17.0	2.8–2.9	2.4–2.5	4.3–9.0	3.4–3.6	3.1–3.7	3.7–6.0	5.7–6.0	6.6–8.2	4.2–5.1
Zn	Concentration	Average	–	–	–	86	46	55	68	61	62	41
		Min–Max	–	–	–	72–110	25–60	50–60	57–78	40–82	43–80	32–53
	EF <sub>c</sub>	Average	–	–	–	6.2	6.3	5.8	4.4	4.8	12.5	6.9
		Min–Max	–	–	–	5.2–7.8	5.5–7.0	5.4–6.2	4.1–5.2	4.1–5.4	9.0–15.9	4.9–9.6
As	Concentration	Average	16 <sup>a</sup>	16 <sup>a</sup>	13 <sup>a</sup>	18	9	5	12	15	11	10
		Min–Max	11–25	16–17	13–14	18.0–18.2	5–15	4–6	9–14	14–15	10–11	7–16
	EF <sub>c</sub>	Average	14 <sup>a</sup>	17 <sup>a</sup>	12 <sup>a</sup>	34	23	15	19	32	56	45
		Min–Max	10–21	14–19	11–13	19–65	20–26	14–15	17–21	23–41	52–59	27–65
Cd	Concentration	Average	1.1 <sup>a</sup>	1.1 <sup>a</sup>	1.9 <sup>a</sup>	0.5	0.9	1.4	0.5	0.3	0.2	0.4
		Min–Max	0.8–1.8	0.9–1.2	1.5–2.4	0.4–0.6	0.3–1.5	1.4–1.5	0.4–0.6	0.2–0.4	0.1–0.3	0.4–0.5
	EF <sub>c</sub>	Average	21 <sup>a</sup>	21 <sup>a</sup>	34 <sup>a</sup>	25	53	77	15	13	21	38
		Min–Max	9–33	18–25	23–46	14–36	21–85	76–77	13–17	11–16	20–21	28–57
Pb	Concentration	Average	14 <sup>b</sup>	12 <sup>b</sup>	19 <sup>b</sup>	19	5	5	13	14	7	5
		Min–Max	14–15	10–14	18–19	11–27	4–9	4–5	9–16	10–17	6–9	3–7
	EF <sub>c</sub>	Average	1.4 <sup>b</sup>	1.6 <sup>b</sup>	1.8 <sup>b</sup>	3.0	1.7	1.6	2.5	3.3	4.5	2.5
		Min–Max	1.1–1.7	1.3–1.9	1.3–2.1	1.9–3.9	1.7–1.8	1.5–1.7	2.3–2.6	3.2–3.4	3.7–5.3	1.7–3.2
Bi	Concentration	Average	0.85 <sup>a</sup>	0.72 <sup>a</sup>	1.18 <sup>a</sup>	0.38	0.10	0.04	0.28	0.25	0.11	0.09
		Min–Max	0.40–1.18	0.60–0.84	1.14–1.22	0.25–0.55	0.02–0.24	0.02–0.05	0.16–0.40	0.22–0.28	0.10–0.13	0.02–0.13
	EF <sub>c</sub>	Average	12 <sup>a</sup>	12 <sup>a</sup>	17 <sup>a</sup>	9	2.1	1.6	7	9	10	6
		Min–Max	8–18	10–11	14–20	2–13	2.0–2.4	0.8–2.4	6–8	8–9	9–11	2–8

Numbers of samples studied for each period are expressed in brackets at the top of the table.

<sup>a</sup> Gabrielli et al. (2005a).

<sup>b</sup> Vallelonga et al. (2005).

which the crustal contribution to heavy metals originate (Delmonte et al., 2002, 2004; Revel-Rolland et al., 2006, Lambert et al., 2008).

The situation appears to be different for Cd and As. For these two metals indeed, concentrations in the ice does not depend clearly upon  $\delta D$ , as illustrated in Fig. 4c for As and Fig. 4d for Cd. These are metals and metalloids for which crustal dust is not the dominant source, as discussed later.

### 3.4. Crustal enrichment factor

Rock and soil dust is an important source of heavy metals and metalloids in the natural atmosphere (Nriagu, 1989). In order to assess the importance of rock and soil dust contribution in Dome C ice for the metals and metalloids studied in this work, we have calculated Crustal Enrichment Factors (EF<sub>c</sub>) for each element and depth. EF<sub>c</sub> is defined as

**Table 2**  
Dome C, East Antarctica mean, minimum and maximum concentrations (expressed in pg/g) and mean, minimum and maximum crustal enrichment factors (EF<sub>c</sub>) (using Ba as crustal reference element) of various metals and metalloids for the successive interglacial periods back to MIS 15.5

			Interglacials							
			MIS 1 (14)	MIS 5.5 (4)	MIS 9.3 (8)	MIS 11.3 (12)	MIS 13.1 (6)	MIS 13.3 (4)	MIS 15.1(8)	MIS 15.5 (6)
Cu	Concentration	Average	2.8 <sup>a</sup>	1.7 <sup>a</sup>	2.5	3.8	2.6	6.3	3.6	4.0
		Min–Max	2.0–6.0	1.6–1.8	1.9–3.6	2.1–6.1	2.0–3.2	2.5–10.6	3.1–4.2	3.8–4.3
	EF <sub>c</sub>	Average	27 <sup>a</sup>	8 <sup>a</sup>	17	22	18	8	29	21
		Min–Max	9–56	7–8	14–22	9–46	15–21	5–12	15–46	20–22
Zn	Concentration	Average	–	–	10	19	8	31	41	48
		Min–Max	–	–	8–12	9–54	8–9	15–49	13–70	35–60
	EF <sub>c</sub>	Average	–	–	17	41	16	12	100	69
		Min–Max	–	–	10–26	25–192	15–16	5–16	16–228	50–87
As	Concentration	Average	2.0 <sup>a</sup>	2.9 <sup>a</sup>	1.0	3.4	1.8	15	13	5.4
		Min–Max	1.5–3.0	2.5–3.4	0.9–1.1	1.0–9.0	0.9–2.7	10.8–23.6	2.7–22.7	5.2–5.6
	EF <sub>c</sub>	Average	151 <sup>a</sup>	97 <sup>a</sup>	167	405	87	200	510	203
		Min–Max	55–293	77–117	42–467	223–886	48–127	60–413	183–836	201–204
Cd	Concentration	Average	0.6 <sup>a</sup>	0.3 <sup>a</sup>	0.2	0.3	0.1	0.4	0.4	0.6
		Min–Max	0.2–1.0	0.2–0.4	0.2–0.3	0.2–0.4	0.1–0.2	0.2–1.3	0.2–0.5	0.5–0.7
	EF <sub>c</sub>	Average	990 <sup>a</sup>	190 <sup>a</sup>	202	406	150	85	415	426
		Min–Max	204–1810	154–226	152–337	131–685	126–171	19–211	250–820	345–506
Pb	Concentration	Average	0.4 <sup>b</sup>	0.5 <sup>b</sup>	0.7	1.3	0.5	2.8	0.7	1.00
		Min–Max	0.3–0.5	0.4–0.6	0.6–0.9	0.7–3.0	0.4–0.5	1.1–6.9	0.4–0.8	0.8–1.1
	EF <sub>c</sub>	Average	1.5 <sup>b</sup>	1.5 <sup>b</sup>	3.9	6.5	2.8	2.8	4.1	4.4
		Min–Max	1.3–1.7	1.3–1.7	2.8–5.3	3.1–13.8	2.7–2.9	1.9–3.7	3.0–7.1	3.7–5.0
Bi	Concentration	Average	0.11 <sup>a</sup>	0.05 <sup>a</sup>	0.06	0.07	0.05	0.06	0.03	–
		Min–Max	0.06–0.23	0.04–0.05	0.02–0.14	0.01–0.11	0.04–0.07	0.03–0.11	0.01–0.04	–
	EF <sub>c</sub>	Average	158 <sup>a</sup>	24 <sup>a</sup>	57	44	44	10	27	–
		Min–Max	37–377	22–27	12–164	23–76	36–51	4–19	12–62	–

Numbers of samples studied for each period are expressed in brackets at the top of the table.

<sup>a</sup> Gabrielli et al. (2005a).

<sup>b</sup> Vallelonga et al. (2005).

the concentration ratio of a given element to that of Ba (which is a good proxy of crustal dust) (Patterson and Settle, 1976) in the ice, normalized to the same concentration ratio characteristic of the upper continental crust (Wedepohl, 1995). For example, the  $EF_c$  for Cu is thus:

$$EF_c(\text{Cu}) = \frac{[\text{Cu}]_{\text{ice}}/[\text{Ba}]_{\text{ice}}}{[\text{Cu}]_{\text{crust}}/[\text{Ba}]_{\text{crust}}}$$

It should however be emphasised by the choice of other crustal compositions, for instance that given by Bowen (1979), Gaiero et al. (2002, 2003), would not make any significant differences in the interpretation.

Since the composition of rock and soil dust reaching Dome C might significantly differ from the composition of the mean upper continental crust,  $EF_c$  values up to ~5 will indicate that the corresponding element mainly originated from rock and soil dust. Conversely,  $EF_c$  values much larger than unity will indicate a significant contribution from other natural sources such as sea-salt spray and volcanoes.

Table 1 shows the mean  $EF_c$  values obtained for the different metals and metalloids during the successive glacial maxima from MIS 2.2 to MIS 16.2, while Table 2 shows the mean  $EF_c$  values calculated for the successive interglacials from the Holocene to MIS 15.5.

When looking at the values listed in Tables 1 and 2 and Fig. 5, the metals and metalloids can be separated into three groups. The first group consists of only one element: Pb. It seems that Pb has a low and invariant  $EF_c$ . So, this behaviour points it out the crustal origin of Pb whatever the climatic period. It confirms the results obtained by Vallelonga et al. (2005) which demonstrated that dust usually accounts for ~70% of Pb in Dome C ice whatever the climatic period over the last 220 kyr. For the second group consisting of three metals (Zn, Cu and Bi), low  $EF_c$  values are observed during glacial maxima, while moderately elevated values are observed for Zn and Cu during interglacials and very high values for Bi during interglacials (Tables 1 and 2). This is also illustrated in Fig. 5, which shows changes in  $EF_c$  values for these metals during the past 672.0 kyr. It would suggest that Zn and Cu mainly derived from rock and soil dust during glacial maxima, while contributions from other sources were significant during interglacials. Bi shows a climatic-dust behaviour but shows also a volcanic contribution as discussed in the next section, which is most important during interglacials. The difference observed between Pb and Zn, Cu and Bi could indicate changes in continental dust source areas or transport processes between glacial and interglacial periods and also between each climatic periods (Marteel et al., in press).

The third group consists of As and Cd. For these elements, elevated  $EF_c$  values are observed both during glacial maxima and interglacials.

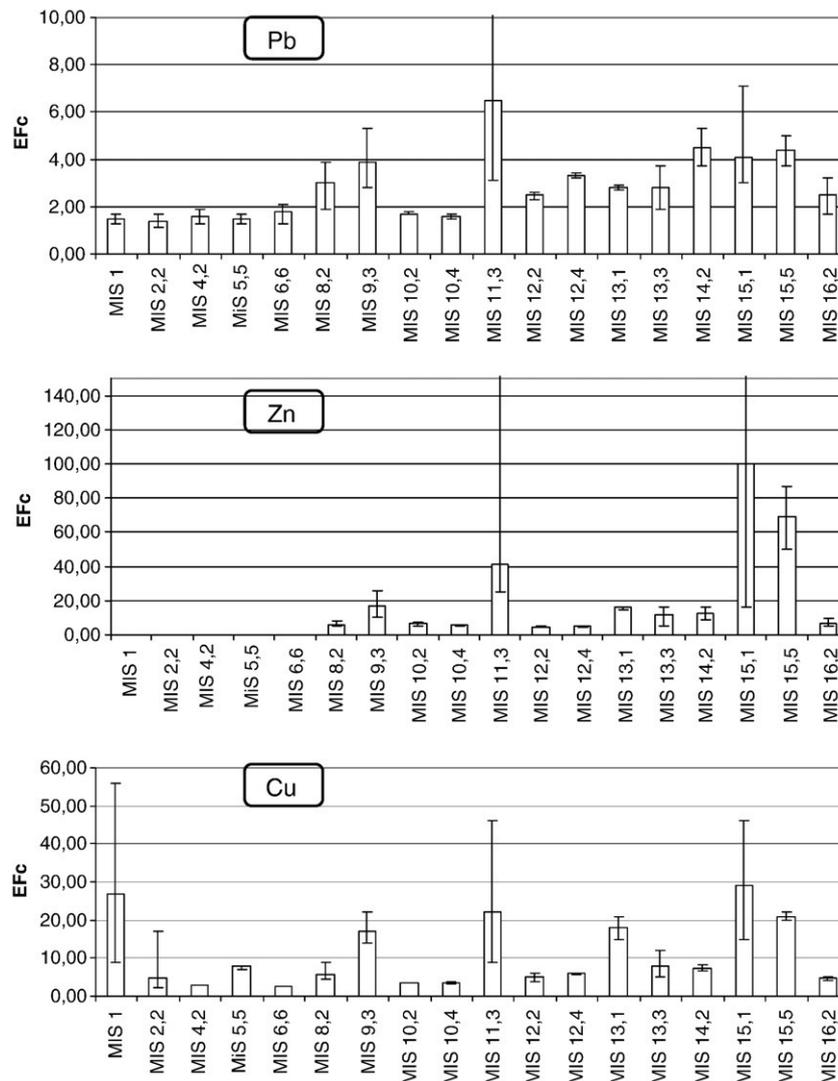


Fig. 5. EPICA/Dome C Antarctic ice core: average over the entire MIS in crustal enrichment factors ( $EF_c$ ) for Pb, Zn, Cu and Bi, As and Cd during the past 672 kyr.

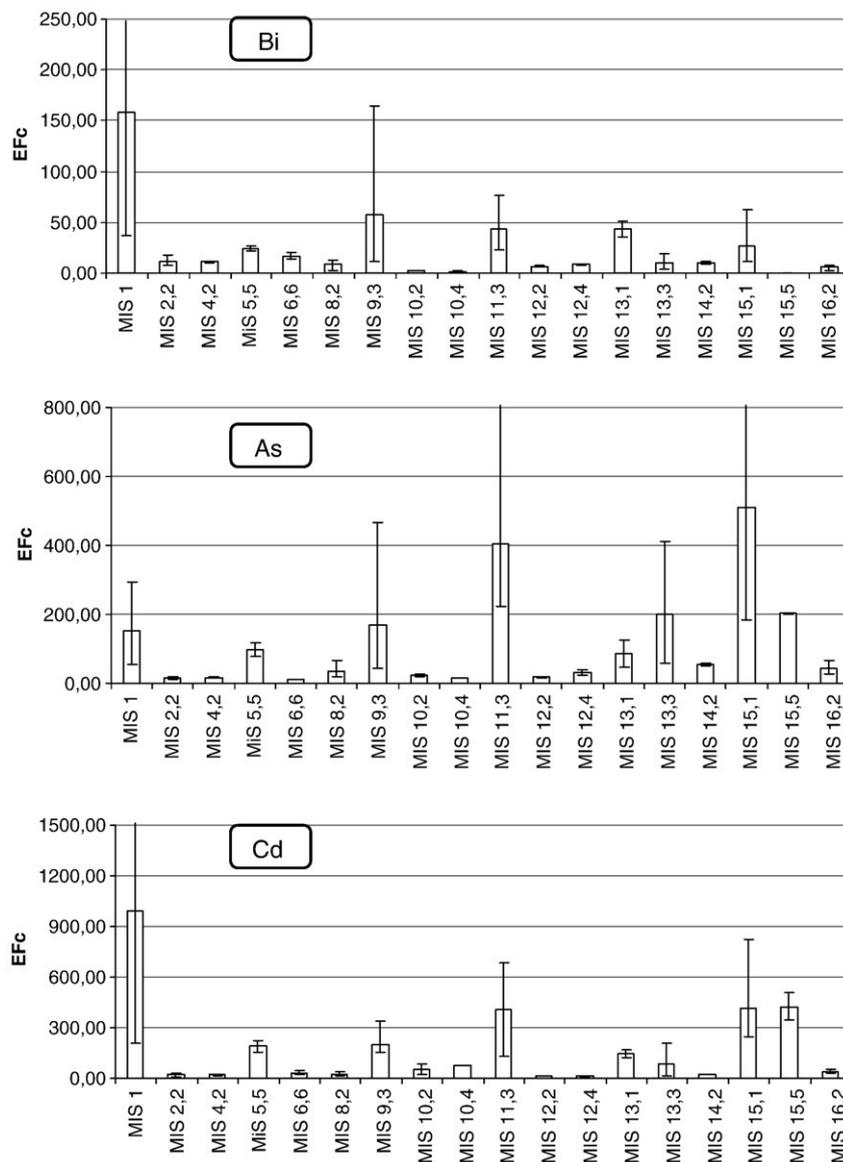


Fig. 5 (continued).

The values observed during interglacials are however higher than the values for glacial maxima. This is illustrated in Fig. 5, which shows changes in EF<sub>c</sub> values for these metals during the past 672.0 kyr. Tables 1, 2 and Fig. 5 indicate that rock and soil dust was a minor source of As and Cd during the past 672.0 kyr whatever the period and that they mainly derived from other sources.

### 3.5. Contributions from rock and soil dust, sea-salt spray and volcanoes

The main natural sources of atmospheric heavy metals are rock and soil dust, sea-salt spray, volcanic emissions and continental and marine biogenic emissions (Nriagu, 1989).

The contribution from rock and soil dust was evaluated from Ba concentration measured in the ice (Marteel et al., in press) and the mean metal/Ba concentration ratios in the upper continental crust (Wedepohl, 1995).

The contribution from sea-salt spray was estimated from Na concentrations measured in the ice (Wolff et al., 2006), after subtracting Na contributed from crustal dust, and metal/Na concentration ratios in bulk ocean water ([www.agu.org/eos\\_elec/97025e-refs.html](http://www.agu.org/eos_elec/97025e-refs.html)). It has been debated in the literature, within which range the crustal contribution to Na might be, particularly during glacial times.

On average, more than one third of the entire water-soluble [Na<sup>+</sup>] originates from continental aerosols. Hence [Na<sup>+</sup>] records from the East Antarctic plateau do not represent a pure marine signal during glacial times (Bigler et al., 2006). Moreover, these ratios were not combined with possible enrichments in ocean derived aerosols relative to bulk ocean water, when marine aerosol is formed by bubble bursting through the surface micro-layer, since studies have put doubt on such possible enrichments (Hunter, 1997).

A rough estimate of the contribution from volcanoes was made from the concentrations of non non-sea-salt sulphate (nssSO<sub>4</sub>) in the ice (Wolff et al., 2006) by assuming that ~10–15% of nssSO<sub>4</sub> originates from volcanoes (Boutron and Patterson, 1986). They were combined with available data on metal/S ratios in volcanic emissions (Hinkley et al., 1999). It must however be kept in mind that these estimates are very rough especially because of the wide range of published data for metal/S ratios in volcanic emissions.

Available data do not allow to evaluate possible contributions from continental and marine biogenic activities although such contributions could be significant (Heumann, 1993, 2001).

Table 3 gives the mean estimated contributions from rock and soil dust, sea-salt spray and volcanoes both during glacial maxima and

**Table 3**

Dome C, East Antarctica: evaluation of the mean contributions from rock and soil dust, sea-salt spray and volcanoes for glacial maxima and interglacial periods, expressed both in concentrations (pg/g) and percentages

	Cu		Zn		As		Cd		Pb		Bi	
	conc	%										
Mean measured concentration in ice during glacial maxima (33)	11		49		11.6		0.6		8		0.16	
Mean natural contribution												
Rock and soil dust <sup>a</sup>	11	99	42	86	1.6	14	0.08	14	8	100	0.1	62
Sea-salt spray <sup>b</sup>	$4 \times 10^{-5}$	$\ll 1^c$	$3 \times 10^{-4}$	$\ll 1^c$	$1 \times 10^{-3}$	$< 1^c$	$2 \times 10^{-7}$	$\ll 1^c$	$1 \times 10^{-3}$	$< 1^c$	$4 \times 10^{-5}$	$< 1^c$
Volcanoes <sup>d</sup>	1	12	3	6	4	32	1.1	$> 100^e$	0.4	5	0.8	$> 100^e$
Mean measured concentration in ice during interglacial periods (44)	3.6		22		8.4		0.4		1.1		0.07	
Mean natural contribution												
Rock and soil dust <sup>a</sup>	0.9	23	3.4	60	0.1	1	0.007	2	0.9	87	0.008	11
Sea-salt spray <sup>b</sup>	$1 \times 10^{-6}$	$\ll 1^c$	$2 \times 10^{-5}$	$\ll 1^c$	$1 \times 10^{-4}$	$< 1^c$	$2 \times 10^{-8}$	$\ll 1^c$	$5 \times 10^{-6}$	$\ll 1^c$	$2 \times 10^{-6}$	$< 1^c$
Volcanoes <sup>d</sup>	2	40	3.5	16	10	$> 100^e$	1.4	$> 100^e$	0.5	48	1	$> 100^e$

Numbers of samples can be seen in brackets.

<sup>a</sup>Based on metal concentrations in the upper continental crust (Wedepohl, 1995), see text.

<sup>b</sup>Contribution calculated from ssNa concentrations in the ice (Wolff et al., 2006) and metal/Na ratio in surface sea water (www.agu.org/eos\_elec/97025e-refs.html). We have assumed that there is no enrichment for heavy metals in sea derived aerosols compared with sea water, see text.

<sup>c</sup> $< 1$  refers to a percentage which is only slightly lower than 1 (i.e.  $10^{-3}$ – $10^{-2}$ ),  $\ll 1$  refers to a percentage which is much lower than 1 (i.e.  $10^{-4}$ – $10^{-5}$ ).

<sup>d</sup>Contribution calculated from nssSO<sub>4</sub> concentrations in the ice (Wolff et al., 2006) and metal/S ratio in volcanic emissions (Hinkley et al., 1999), see text.

<sup>e</sup> $> 100$  refers to a percentage which is higher than 100.

interglacials. It should be emphasised that the contributions should be considered as rather tentative, especially for sea-salt spray and volcanoes contribution. This is for instance obvious for the sum of the three different natural contributions does not give 100%, sometimes we get less than 100% and sometimes much more than 100%.

For glacial maxima, it appears clearly that rock and soil dust explains virtually 100% of Cu, Zn and Pb measured in Dome C ice, and part of Bi, while this contribution appears to be smaller for As and Cd than the other elements. Sea-salt spray contribution is always extremely small. Contribution from volcanoes has a considerable importance for Bi and Cd in the ice and could be a significant contributor for As (see Table 3).

During interglacials, rock and soil dust remains a major source of Zn and Pb and minor source of Cu and Bi. Sea-salt spray contribution remains negligible. Volcanoes could be the main source of As, Cd and Bi, and to a lesser extent of Cu (see Table 3).

The conclusion that Bi might derive mainly from volcanoes would be in good agreement with the indication by Patterson and Settle (1987) that volcanic emissions of Bi to the atmosphere are by far the predominant source for Bi in the atmosphere during interglacial periods.

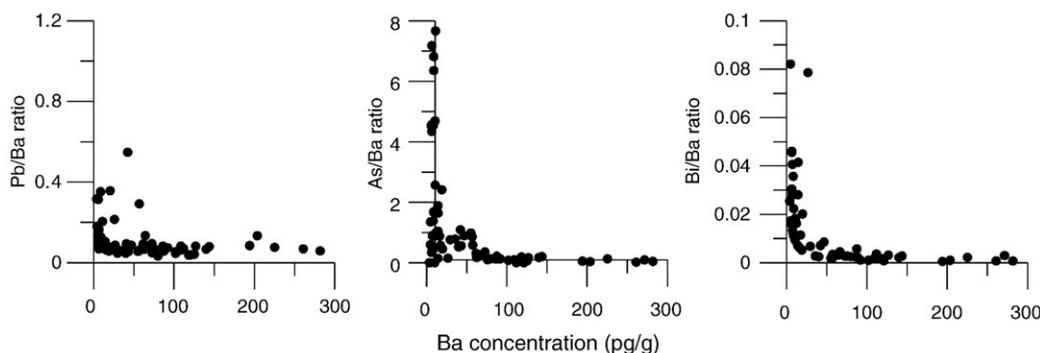
These changing patterns in the origin of the different metals as a function of climate is further confirmed in Fig. 6 which shows, as examples, changes in Pb/Ba, As/Ba and Bi/Ba concentration ratios as a function of Ba concentrations in the ice. The ratios appear to be very different for ice with high Ba concentrations (glacial maxima), and for

ice with low Ba concentrations (interglacials). The changes are however less important for Pb/Ba (the rock and soil dust contribution remains important for Pb even during interglacials) than for As/Ba and Bi/Ba (As and Bi appear to derive mainly from volcanic emissions during interglacials, while a small rock and soil dust contribution can be hypothesized for these metals during glacial maxima). This finding shows that Bi has an important volcanic contribution, which is more evident during interglacial times, but it shows also a non-negligible climatic-dust behaviour.

### 3.6. Contribution from Antarctic volcanoes

A possible volcanic source within East Antarctica could be the Mount Erebus active volcano (77°33' S, 161°10' E, 3794 m above sea level), which is the southernmost active volcano in the world. There have been various studies about emissions of various compound in the persistent volcanic plume which emanates from the summit crater (see e.g. Chuan et al., 1986). Interest in such measurements came not only from volcanologists wishing to better understand the volcano's behaviour but also from atmospheric scientists trying to establish the sources of natural pollution in the clean Antarctic environment.

Various studies have shown that the Erebus plume is enriched in various heavy metals (see e.g. Kyrle et al., 1990 and Zreda-Gostynska et al., 1997). Of special interest are the data obtained by Zreda-Gostynska et al. (1997) for the years 1986 to 1991. They collected



**Fig. 6.** EPICA/Dome C Antarctic ice core: changes in Pb/Ba, As/Ba and Bi/Ba concentration ratios as a function of Ba concentrations in the ice for the samples dated from 263.6 to 672.0 kyr BP.

plume samples with filters during December 1986, 1988 and 1989 and January 1991. The filters were then analysed by instrumental neutron activation analysis for various trace elements, including several metals considered in our work (Cu, Zn, As and Cd). From their data, they estimated average yearly emission rates for these various elements. The yearly emission rates they found for the four metals considered in our work were 43 metric tons/year (t/yr) for Cu, 130 t/yr for Zn, 11 t/yr for As and 4 t/yr for Cd. These values must however be considered with great caution, since the sampling periods were short (for instance, only 5 days in 1986), which makes it very difficult to extrapolate the data over longer time periods.

Zreda-Gostynska et al. (1997) suggested that emissions from Mount Erebus could be transported easily inland over the East Antarctic plateau and could be a major contributor to heavy metals such as Cu, Zn, As and Cd in East Antarctic snow and ice, based on the hypothesis of a homogeneous deposition over the East Antarctic plateau. Their data are however only for very recent periods, and it is impossible to know if such contribution was important during the very long time periods cover by our EPICA/Dome C ice samples. Moreover, it would be necessary to use transport models (see e.g. Cosme et al., 2005) to make quantitative estimates of the deposition patterns over the East Antarctic plateau in order to confirm

that emissions from Mount Erebus make a significant contribution to heavy metals in snow and ice in Dome C.

### 3.7. Ternary diagrams for glacial maxima and interglacials before and after the Mid-Brunhes Event (MBE)

Fig. 7a, b shows Cu, Zn and Pb concentrations both for glacial maxima (Fig. 7a) and interglacial periods (Fig. 7b) using ternary diagrams (after normalization using Pb concentrations). Different symbols have been used for ice dated before the Mid-Brunhes Event (MBE, about 430 kyr BP) and after the MBE.

It can be seen that during glacial maxima the data points are very well well-grouped together both before and after the MBE, which is consistent with inputs from a single well-defined source for these three elements, namely rock and soil dust (see Section 3.5). For interglacial periods, the situation appears to be different before and after the MBE: the data points are rather dispersed on the ternary plot before the MBE, but are well-grouped together after the MBE. It points towards a more complex input for Cu, Zn and Pb before the MBE.

Fig. 7c, d shows the ternary diagrams for As, Cd and Bi for glacial maxima (Fig. 7c) and interglacials (Fig. 7d), after normalization using Bi concentrations. The data points are found to be strongly dispersed

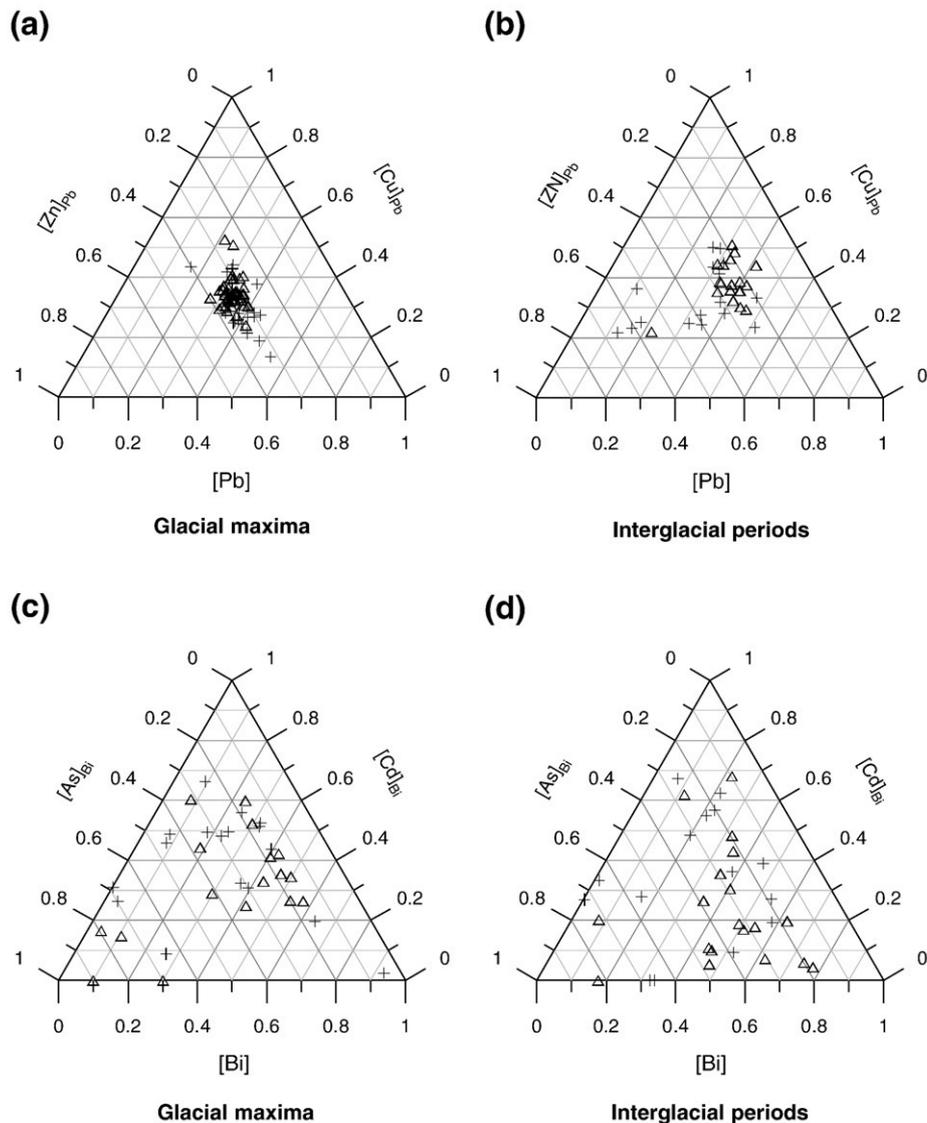


Fig. 7. EPICA/Dome C Antarctic ice core: ternary plots for Pb, Cu, and Zn for glacial maxima (a) and interglacials (b) and for Bi, Cd and As for glacial maxima (c) and interglacials (d) crosses are used for ice samples dated from before the MBE, while open triangles are used for ice dated from after the MBE.

both before and after the MBE, whatever the climatic periods, pointing towards much more complex inputs from several sources.

#### 4. Conclusion

This work has allowed to document large natural variations in heavy metals in Antarctic ice dated back to 672.0 kyr BP (MIS 16.2), with generally elevated concentrations during glacial maxima and much lower values during interglacials. Rock and soil dust appears to be the dominant source for Cu, Bi, Pb and possibly Zn during glacial maxima, while Cd and As appear to derive mainly from volcanoes whatever the period.

It will be interesting in the future to extend this study to the deepest part of the EPICA/Dome C ice core which extends back to MIS 20.2, ~800 kyr ago. It will also be very interesting to investigate changes in other heavy metals such as Hg and Se (including speciation). Finally, it will be also of high interest to analyse other ice cores which have recently been obtained in other areas in Antarctica, especially in Dronning Maud Land (EPICA Community members, 2006) and at Talos Dome (Stenni et al., 2002).

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2008.05.021.

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