

## Climate-related variations in atmospheric Sb and Tl in the EPICA Dome C ice (East Antarctica) during the past 800,000 years

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[1] A record of antimony (Sb) and thallium (Tl) from the European Project for Ice Coring in Antarctica (EPICA) Dome C Antarctic ice core provides the characteristics of climate-related natural changes in concentrations and fluxes of these toxic elements over the time period back to Marine Isotope Stage 20.2, ~800 kyr B.P. A strong variability in concentrations and fluxes are observed for both elements, with considerably higher values during glacial maxima and lower values during intermediate and warm periods. Rock and soil dust accounts for, on average, 58% of Sb and 76% of Tl in ice during glacial maxima. This contribution remains significant during warm periods, accounting for 21% for Sb and 27% for Tl. The contribution from volcanoes appears to be very important particularly for Tl when climatic conditions become warmer, with an estimated volcanic contribution of 72% for Tl during interglacials. The sea-salt contribution is significant for Sb, particularly during intermediate climatic periods, with an average contribution of 17%. This sea-salt contribution is most likely caused by greater production of sea salt from highly saline frost flowers and relatively more efficient transport of Sb-enriched sea-ice salt from source areas on the East Antarctic Plateau. Our ice core data, along with snow data recently reported from the Antarctic snow layers at Dome Fuji, shows that the present-day Sb flux (6.6 ng/m<sup>2</sup>/yr) is approximately double the highest natural level (2.8 ng/m<sup>2</sup>/yr) during glacial maxima throughout the last successive eight glacial/interglacial cycles. This result indicates that human activity has induced the greatest perturbation of the atmospheric cycle of Sb ever experienced over a period of ~800 kyr in the most remote area on Earth.

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### 1. Introduction

[2] Sb and Tl are naturally rare in the Earth's crust with an average abundance of 310 ng/g for Sb and 750 ng/g for Tl in the upper continental crust [Wedepohl, 1995]. Because both elements are highly toxic and potentially pose a health risk to human and biota [Peter and Viraraghavan, 2005;

Shtangeeva et al., 2011] and because transfer through the atmosphere is a major part of the biogeochemical cycle of these elements, their distribution and behavior in the atmosphere are of great concern.

[3] During recent decades, various studies on Sb and Tl have led to a growing understanding of temporal changes in the biogeochemical cycling of these elements. These studies have used different environmental archives such as lake sediments [Gélinas et al., 2000; Grahn et al., 2006], peat bogs [Shotyky et al., 1996; Shotyky and Krachler, 2004; Cloy et al., 2009], and snow and ice caps [Van de Velde et al., 1999; Barbante et al., 2004; McConnell and Edwards, 2008; Krachler et al., 2008a, 2008b; Hong et al., 2009, 2012]. These studies aimed primarily at reconstructing anthropogenic Sb and Tl inputs to various sites over timescales of several tens of years to millennia. The findings in these studies showed a noticeable increase in atmospheric depositions of both Sb and Tl, particularly since the Industrial Period, caused by the massive release of these pollutants into the atmosphere from human activities such as non-ferrous-metal production, fossil fuel combustion, and other industrial processes. It is also well documented in polar snow and ice records that atmospheric pollution of Sb and Tl is not confined to local or regional areas but is now

Additional supporting information may be found in the online version of this article.

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wide spread and found in very remote regions, giving rise to global pollution [McConnell and Edwards, 2008; Krachler et al., 2008a, 2008b; Hong et al., 2012].

[4] Although our understanding of the perturbation of atmospheric Sb and Tl cycles linked to human activities has improved, the natural biogeochemical cycles of these two elements in the atmosphere remain uncertain, mainly due to the lack of comprehensive data on their natural sources, transport, and global cycling over sufficiently longer periods. A unique way to obtain such information is to assess the changing occurrence of natural trace elements in the atmosphere and to identify their sources and transport pathways by using deep polar ice cores. Until now, great efforts have been made to retrieve a detailed record of changes in atmospheric trace elements over the past tens of thousands or hundreds of thousands of years in deep ice cores from Greenland and Antarctica [Hong et al., 1996, 2003, 2004, 2005; Gabrielli et al., 2004, 2005a, 2005b, 2006; Marteel et al., 2008, 2009]. One of the most interesting features in these records is that natural factors affecting changes in the natural biogeochemical cycles of atmospheric trace elements vary largely with different climatic conditions. This natural variation with climate indicates that a record long enough to unveil climate-related changes needs to be reconstructed to critically assess the current global cycles of Sb and Tl under recent climate change.

[5] These ice core records, however, are very difficult to obtain because Sb and Tl concentrations in polar snow and ice are extremely low, as low as the sub-picogram-per-gram ( $1 \text{ pg/g} = 10^{-12} \text{ g/g}$ ) level [Krachler et al., 2008a, 2008b; Hong et al., 2012]. In the case of Antarctica, the first reliable high-resolution time series of Sb and Tl in a successive snow deposit from Dome Fuji in the central East Antarctic Plateau were presented very recently by using the ultrasensitive inductively coupled plasma sector field mass spectrometry (ICP-SFMS) technique and ultraclean procedures in clean room conditions [Hong et al., 2012].

[6] In this study, we present the first comprehensive record of past natural changes in the occurrence of Sb and Tl in Antarctic ice over the last successive eight climatic cycles back to Marine Isotope Stage (MIS) 20.2,  $\sim 800$  kyr B.P. Our record demonstrates a large variability in the concentrations and fluxes of Sb and Tl in response to different climatic conditions in this remote area of the Earth.

## 2. Materials and Methods

### 2.1. Ice Core Samples

[7] We analyzed 134 samples (depths from 59.4 to 3189.45 m) from the 3260 m deep EPICA (European Project for Ice Coring in Antarctica) ice core drilled at Dome C (hereafter EDC) on the central East Antarctic Plateau ( $75^{\circ}60'S$ ,  $123^{\circ}21'E$ , altitude 3233 m above sea level). According to the new EPICA EDC3 age scale obtained by combining an ice flow model and a set of independent age markers [Parrenin et al., 2007], the EDC ice core extends the climate record back to  $\sim 810$  kyr before present (B.P.). Among the samples used for this study, 92 samples were chosen from the aliquots of inner core samples available after previous studies used the core samples to determine different trace elements [Gabrielli et al., 2005a, 2006, Marteel et al., 2008, 2009]. The depth of these samples ranged from 59.4

to 3040.13 m, which corresponds to the age of  $\sim 1200$  years B.P. and  $\sim 632,590$  years B.P., respectively. The newly added 42 samples were derived from 30 core sections whose depth ranged from 2973.9 to 3189.45 m. The ice at 2973.9 m is dated at 572,380 years B.P., which corresponds to MIS 15.1, and the ice at 3189.45 m is dated at 801,660 years B.P., which corresponds to MIS 20.2. Further information is given in Table S1 in the supporting information.

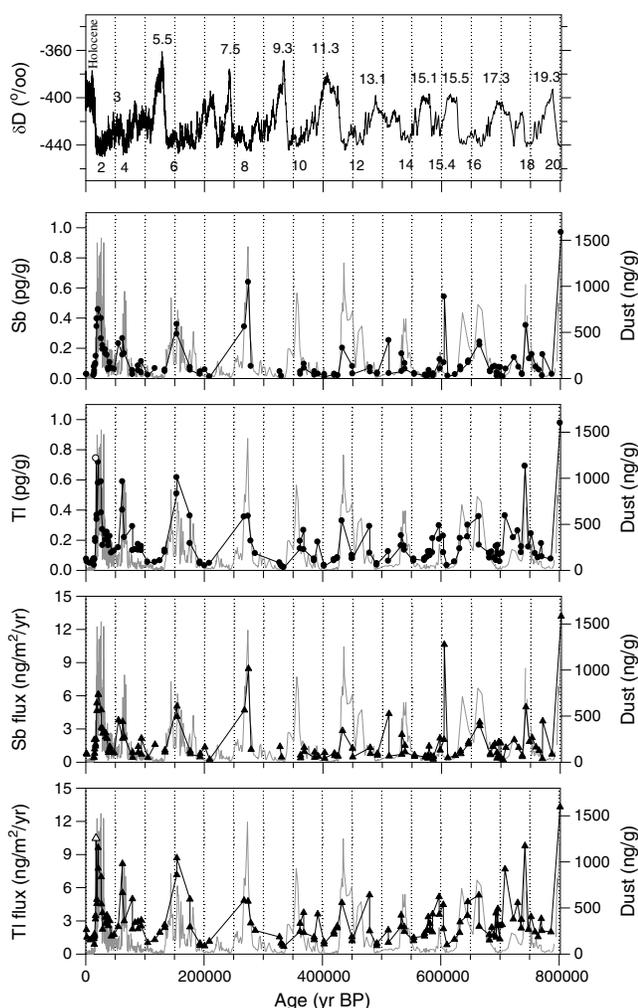
### 2.2. Ice Core Decontamination

[8] Each of the new 30 ice core sections (length of 55 cm) was mechanically decontaminated to remove the outside of the core using ultraclean procedures described in details elsewhere [Candelone et al., 1994; Hong et al., 2005]. Briefly, these procedures involve the chiseling of successive veneer layers of ice in progression from the contaminated outside toward the pristine center. This chiseling was performed inside a laminar flow class 100 clean bench at  $-15^{\circ}\text{C}$  using an acid-cleaned polyethylene lathe and ultraclean working procedures. All the equipment used during the entire operation was extensively acid cleaned prior to use. When the whole inner core ( $\sim 45$  cm in length) was available after the completion of the decontamination procedure, the innermost part of each core section was then divided into three consecutive parts as described in previous studies [Gabrielli et al., 2005a, 2006, Marteel et al., 2008, 2009]: (1) two consecutive 20 cm long parts, which were used for this study, giving the 42 depth intervals listed in Appendix A and (2) a 5 cm long part at the bottom of the section for the subsequent determination of Hg. The efficiency of the decontamination was assessed by determining the concentrations of Sb and Tl in the profiles as a function of radius, which showed a plateau in the innermost layers, representing a pristine inner core [Candelone et al., 1994; Hong et al., 2005].

### 2.3. Chemical Analysis

[9] Sb and Tl were directly measured by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) (Element2, Thermo Fisher Scientific, Bremen, Germany), coupled with an APEX micronebulization desolvation system (APEX, HF, ESA, USA) in a class 10 clean booth located in a class 1000 clean room at the Korea Polar Research Institute (KOPRI). For this study, Ba was also measured in the newly added 42 samples. The analytical instrumentation and ultraclean working conditions are described in detail elsewhere [Hong et al., 2009; Soyol-Erdene et al., 2011]. Special attention was given to daily optimization of the instrumental parameters to obtain high intensities and minimize possible interference. Detection limits were calculated as three times the standard deviation of 10 measurements of the blank (1% "Optima" grade  $\text{HNO}_3$  solution). Detection limits of 0.01 pg/g for both Sb and Tl and 0.2 pg/g for Ba were obtained. The results from the dilute solutions of certified riverine water reference materials, SLRS-5 for Sb and SLRS-4 for Tl (National Research Council, Canada), showed good agreement with the certified or compiled values [Rodushkin et al., 2005] (in pg/g):  $297 \pm 2$  versus 300 for Sb,  $6.1 \pm 0.3$  versus 6.5 for Tl, and  $13,702 \pm 226$  versus  $14,000 \pm 500$  for Ba.

[10] The ionic species ( $\text{Na}^+$  and  $\text{SO}_4^{2-}$ ) in the newly added samples were simultaneously analyzed by using a two-channel ion chromatography (IC) system that combined two Dionex



**Figure 1.** Changes in the Sb and Tl concentrations and fluxes over the past 800 kyr. Also shown at the top of the figure is deuterium (Antarctic temperature proxy) [Jouzel *et al.*, 2007] with Marine Isotope Stage (MIS) numbers [Lisiecki and Raymo, 2005]. Changes in dust concentrations (gray solid lines) [Lambert *et al.*, 2008] are shown with the concentration and flux records for comparison. The open circle and the triangle in the figures for Tl concentrations and fluxes represent data at a 471.2 m depth dated 17,320 years B.P. (see text).

IC sets: Dionex ICS 2000 with IonPac AG 15 and AS 15 columns for anions and IC 25 with IonPac CG 12A and CS12A columns for cations, with an analytical precision of less than 10% [Hong *et al.*, 2012].

### 3. Results and Discussion

#### 3.1. Variations in Concentrations and Fluxes During the Past 800 kyr

[11] Figure 1 shows the concentration records of Sb and Tl measured in the 134 innermost portions of the ice core over the last successive eight climatic cycles (the past ~800 kyr). Deuterium, an Antarctic temperature proxy [Jouzel *et al.*, 2007], dust concentration [Lambert *et al.*, 2008], and MIS numbers [Lisiecki and Raymo, 2005] are also given in Figure 1, facilitating a comparison of our data along with

different climatic stages. All data are listed in Table S1 of the supporting information. They are the first data of their kind ever obtained for ice dated back to ~800 kyr B.P. (MIS 20.2).

[12] Table 1 gives a summary of the statistics for the observed concentrations overall, as well as for those separated into different climatic conditions. During the entire 800 kyr period, the concentrations of Sb and Tl range from 0.01 to 0.97 pg/g and 0.02 to 0.98 pg/g, with mean concentrations of 0.11 pg/g and 0.18 pg/g, respectively, representing ultralow concentration levels of these elements in Antarctic ice. Both the Sb and Tl concentration records show strong variability, with lower levels found during warm periods and much higher levels found during the coldest stages (glacial maxima), particularly MIS 2, 6, 8, 18, and 20 (Figures 1, 2a, and 2b). The ratios between the maximum and minimum concentrations are 97 for Sb and 49 for Tl. The mean concentrations of Sb and Tl during glacial maxima with  $\delta D$  values below  $-430\text{‰}$  are observed to be approximately five to seven times higher than those during warm periods with  $\delta D$  values above  $-400\text{‰}$  (Table 1). During intermediate climatic stages, the mean Sb and Tl concentrations are approximately three times lower than those observed during glacial maxima. A subsequent decrease in the Sb and Tl concentrations by a factor of 2 appears in warm climatic conditions. The high correlation between the changes in the Sb and Tl concentrations and the climatic conditions ( $\delta D$ ) is illustrated in Figures 2a and 2b. Figure 2a shows that the Sb concentrations rapidly drop when the  $\delta D$  values increase during colder glacial periods and remain relatively low when the  $\delta D$  values are above  $\sim -430\text{‰}$ . The Tl concentrations sharply decrease between  $\sim -450\text{‰}$  and  $\sim -430\text{‰}$  and then show a continuous decrease when the climate becomes warmer (Figure 2b).

[13] Figure 3 shows the typical record over the last 50 kyr back to MIS 3.3. Very high Sb and Tl concentrations, higher than 0.4 pg/g during the coldest period (Last Glacial Maximum; LGM), are observed when dust concentrations also peak, whereas Sb and Tl concentrations remain either very low during the Holocene or slightly enhanced during more mild glacial stages (MIS 3.1–3.3). The most striking feature of this 50 kyr record is the significant correlation between the elements Sb and Tl and the dust profiles during both the coldest and less cold periods (Figure 3). This correlation suggests that the changes in the Sb and Tl concentrations during these different climatic periods are primarily dependent on the dust concentrations that, in turn, are linked to the Antarctic temperature, as discussed later in this paper. This association between the trace elements and the Antarctic temperature and dust was previously found for other trace elements in the EDC and Vostok Antarctic ice cores [Hong *et al.*, 2003, 2004, 2005; Gabrielli *et al.*, 2005a, 2005b; Siggaard-Andersen *et al.*, 2007; Marteel *et al.*, 2008, 2009].

[14] Because dry deposition at low-accumulation sites likely dominates the atmospheric aerosol concentration [Fischer *et al.*, 2007], the concentrations of trace elements in ice at our site may vary with the accumulation rate, which varied by a factor of  $\sim 2$  between glacial maxima ( $\sim 13 \text{ kg/m}^2/\text{yr}$ ) and interglacials ( $\sim 27 \text{ kg/m}^2/\text{yr}$ ) [Parrenin *et al.*, 2007]. We therefore calculated the deposition fluxes of Sb and Tl by multiplying the concentrations measured in the ice at each depth with snow accumulation rates derived from deuterium values, based on the EDC3 age scale [Parrenin *et al.*, 2007].

**Table 1.** A Statistical Summary of Concentrations, Fluxes, and Crustal Enrichment Factors (EFs) During Different Climatic Periods in the EPICA Dome C Ice Core and Present-Day Data Obtained From a Snow Pit at Dome Fuji in East Antarctica

Period		Concentration (pg/g)			Flux (ng/m <sup>2</sup> /yr)			EF	
		Sb	Tl	Ba	Sb	Tl	Ba	Sb	Tl
All periods	Mean	0.11	0.18	99	1.7	3.0	1500	4.6	3.5
	Min–max	0.01–0.97	0.02–0.98	5.0–961	0.2–13	0.7–13	130–15,860	0.3–39	0.1–17
	Max/min	97	49	192	65	19	122	130	170
Cold periods (< –430‰)	Mean	0.20	0.32	211	2.8	4.5	2930	2.2	1.6
	Min–max	0.03–0.97	0.12–0.98	41–657	0.4–13	1.6–13	630–8840	0.7–8.6	0.5–5.0
	Max/min	32	8	16	32	8	14	12	10
Intermediate periods (–430‰ ~ –400‰)	Mean	0.06	0.12	45	1.2	2.3	810	5.9	4.4
	Min–max	0.01–0.54	0.03–0.36	5.7–961	0.2–11	0.7–7.7	130–15,860	0.3–39	0.1–17
	Max/min	54	12	169	55	11	122	130	170
Warm periods (> –400‰)	Mean	0.03	0.06	12	0.8	1.7	350	6.1	5.1
	Min–max	0.01–0.05	0.02–0.12	5.0–26	0.4–1.4	0.7–3.4	160–620	2.8–19	1.2–9.4
	Max/min	53	6	5	4	5	4	7	8
Modern period (1970–1995) <sup>a</sup>	Mean	0.26	0.06	5.2	6.6	1.4	130	128	13

<sup>a</sup>From *Hong et al.* [2012].

The pattern of both the concentration and flux records of Sb and Tl appears to be fairly parallel to each other (Figure 1), with smaller ratios between the highest and the lowest fluxes of each element (Table 1) because of the lower accumulation rates during glacial maxima. The calculated fluxes of Sb and Tl are listed in Table S1 of the supporting information.

### 3.2. Relative Contributions From Different Natural Sources

[15] The primary natural sources of Sb and Tl in the atmosphere are rock and soil dust, sea-salt spray, and volcanic emissions [*Nriagu*, 1989; *Krachler et al.*, 2008a, 2008b; *Kellerhals et al.*, 2010]. We evaluated the relative magnitudes of the contributions from these natural sources, which varied with climatic conditions over the entire 800 kyr record.

[16] The contribution from the rock and soil dust was calculated using the Ba (a conservative crustal reference element) concentrations measured in each sample and the mean Sb/Ba and Tl/Ba ratios in the upper continental crust [*Wedepohl*, 1995].

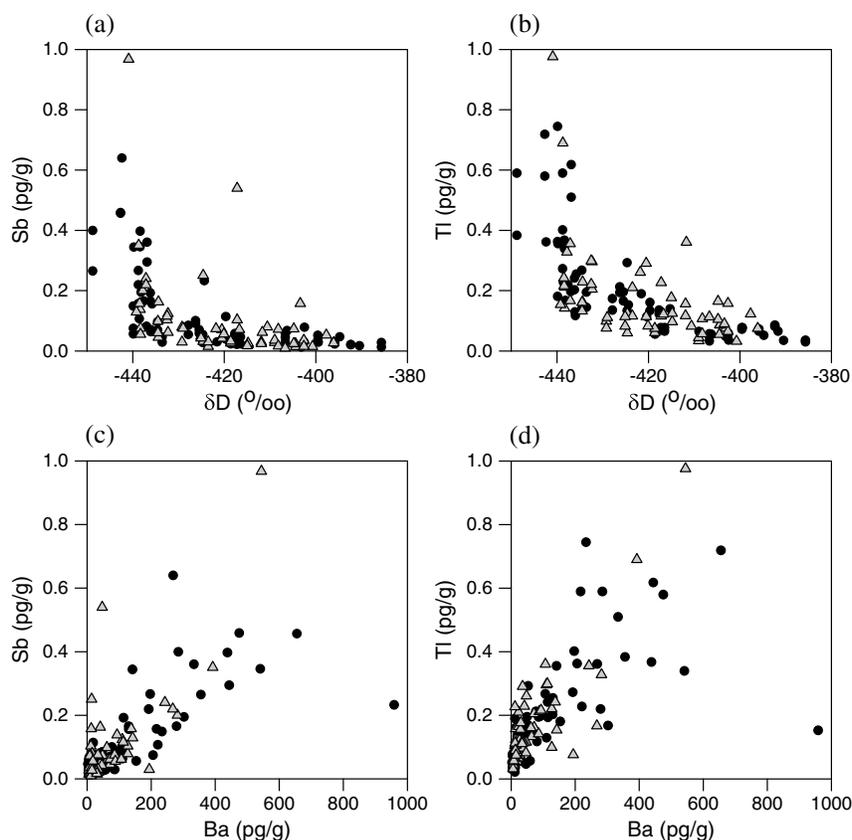
[17] The contribution from the sea-salt spray was estimated using the Na concentration measured in each sample after subtracting the Na contribution from crustal dust using the Ba concentrations and then applying the average sea-salt elemental ratios in seawater [*Li*, 1991]. The possible elemental enrichment in sea-derived aerosols relative to seawater was not taken into account in the sea-salt elemental ratios because previous studies have raised some doubt about a potential contamination problem concerning these enrichments [*Hunter*, 1997].

[18] A rough estimate of the contribution from volcanic emissions was made based on the concentration of non-sea-salt sulfate (nss-SO<sub>4</sub><sup>2-</sup>) in each sample by assuming that ~6% of nss-SO<sub>4</sub><sup>2-</sup> in the ice at Dome C originated from volcanoes [*Castellano et al.*, 2005]. The fraction of nss-SO<sub>4</sub><sup>2-</sup> of volcanic origin in each sample was combined with the mean values of the Sb/S and Tl/S ratios in the volcanic emissions given by published sets of data obtained from individual volcanoes in low-latitude regions [*Olmez et al.*, 1986; *Patterson and Settle*, 1987; *Nriagu*, 1989; *Elias et al.*,

1998; *Hinkley et al.*, 1999; *Mather et al.*, 2012]. It must, however, be emphasized that these estimates are very tentative, particularly because of the large dispersion in the published element/S ratios in volcanic emissions and because of the uncertainty in assuming volcanic background sulfate levels in Antarctic snow and ice [*Boutron and Patterson*, 1986; *Castellano et al.*, 2005].

[19] Table 2 gives the mean estimated contributions from the three different natural sources of Sb and Tl during glacial maxima and intermediate and warm climatic stages. Rock and soil dust is the most important source for both elements during glacial maxima, accounting for an average of 58% and 76% of the measured Sb and Tl concentrations, respectively. This contribution becomes 26%–41% smaller during the intermediate climatic stages but remains substantial for the Sb and Tl concentrations. During warm periods, the crustal contribution accounts for 21%–27% of the measured concentrations of Sb and Tl, suggesting that crustal dust still remains a significant contributor to both Sb and Tl. In Figure 3, we show the highly resolved correlation of elemental concentration changes with dust concentration changes during the last 50 kyr. The estimated crustal fractions of the measured Sb and Tl concentrations explain the feature of a synchronous peak of elements and dust during the LGM (Figure 3), emphasizing the importance of the crustal dust contribution to the deposition of Sb and particularly Tl in the ice at Dome C during very cold periods. As illustrated in Figures 2c and 2d, the general pattern of changes in the Sb and Tl concentrations versus the Ba concentrations supports crustal dust as a significant contributor to the Sb and Tl concentrations, regardless of the climatic period.

[20] A different scenario is observed concerning the estimated contribution from volcanoes to Sb and Tl concentrations. For Tl, an average volcanic contribution appears to increase from 24% during glacial maxima to 72% during warm stages, which is the opposite trend observed for crustal contribution during the corresponding climatic stages (Table 2). Our rough estimates indicate that volcanic emissions could have contributed a significant portion of the Tl concentration in ice in central Antarctica when the crustal contribution was reduced during warm periods and, to a



**Figure 2.** Changes in (a and b) the concentrations of Sb and Tl as a function of the deuterium content and (c and d) Ba concentrations. Data before the Mid-Brunhes Event (MBE) are shown as gray triangles and after the MBE as solid circles.

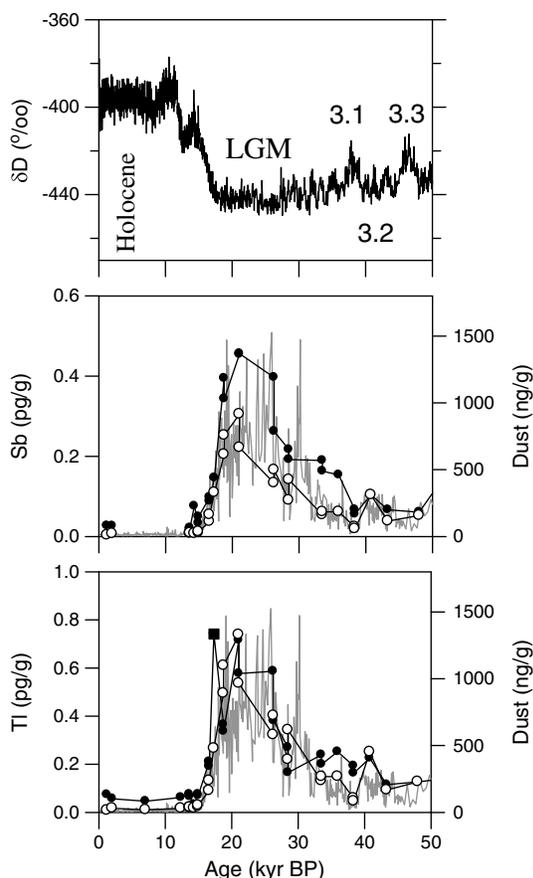
lesser extent, during less cold glacial periods. This trend of the volcanic contributions associated with climatic conditions might be caused by a weaker Antarctic Polar Vortex during warmer periods, which renders more efficient transport of volcanic aerosols to inland Antarctica, as previously observed for different trace elements of volcanic origin [Gabrielli *et al.*, 2006]. Volcanic emissions were a significant source of Sb during intermediate and warm periods as well, contributing to more than 20% of the measured Sb concentrations (Table 2). However, the magnitudes of the volcanic contributions to the Sb concentrations appear to be smaller for the respective climatic stages compared to the volcanic contributions to the Tl concentrations. This different volcanic contributions means that the atmospheric Sb reaching central Antarctica is less influenced by the volcanic emissions compared with Tl, regardless of the climatic period (Table 2). This pattern is expected based on an estimate of worldwide volcanic emissions showing Tl values that are approximately an order of magnitude higher than Sb values in volcanic emissions [Hinkley *et al.*, 1999].

[21] A possible local volcanic source within Antarctica could be Mount Erebus (77.55° S, 167.17° E), the world's southernmost active volcano, located on Ross Island, Antarctica. A recent study reported that Mount Erebus has sporadically contributed to substantial increases in the atmospheric deposition of Sb and Tl to the snow in central Antarctica [Hong *et al.*, 2012]. In our samples, an example of this possible contribution is shown in the ice at a

471.1 m depth, dated 17,320 years B.P., in which the Tl concentration and its flux are 0.74 pg/g and 11 ng/m<sup>2</sup>/yr, respectively. This concentration and flux are relatively high compared with those in the nearby samples (Figures 1 and 3). At the same sample depth, a previous study reported extremely high concentrations of Cd and Bi, which are elements sensitive to volcanic emissions and are attributed primarily to the fallout of local volcanic emissions on a centennial timescale near or within Antarctica [Gabrielli *et al.*, 2005a]. In contrast to the Tl concentration and flux, the concentration and flux of Sb in the 471.2 m section do not show any elevated levels with respect to the neighboring values (Figures 1 and 3). This example clearly indicates that volcanic input has a more significant impact on Tl than on Sb.

[22] Finally, the contribution from sea-salt spray is found to be negligible for Tl, regardless of the climatic period. In contrast, the sea-salt contribution to Sb concentrations is found to account for 9% of the Sb concentrations during glacial maxima and may be significant during intermediate climatic conditions, with an average contribution of 17% to the measured Sb concentrations. This contribution slightly decreases during warm periods, but more than 10% of Sb remains attributed to the sea-salt contribution (Table 2).

[23] The sum of the three different natural contributions explains virtually ~100% of the Tl concentrations measured in ice over the last successive eight climatic cycles in our record (Table 2). In contrast, the total natural contributions for Sb range from 59% during warm stages to 82% during



**Figure 3.** Changes in Sb and Tl concentrations (solid circles) and the estimated crustal contributions (open circles) for each measured concentration over the last 50 kyr. Also shown at the top of the figure is the deuterium record [Jouzel *et al.*, 2007] with MIS numbers [Lisiecki and Raymo, 2005]. Changes in dust concentrations (gray solid lines) [Lambert *et al.*, 2008] are shown with concentration profiles for comparison. The solid square at the bottom of the figure represents data measured at a 471.2 m depth dated 17,320 years B.P. (see text).

intermediate stages. These Sb contribution levels may indicate either an underestimation of contributions from the three different natural sources or other possible contributions from sources such as wild forest fires and continental and marine biogenic sources [Nriagu, 1989]. Our data do not allow for any estimate of the contributions from these other possible sources. However, it is unlikely that these contributions are significant to the Sb measured in our samples because these other possible sources hold insignificant contributions to atmospheric Sb [Nriagu, 1989; Krachler *et al.*, 2008b].

[24] An underestimation of the contributions from volcanoes could be a possible explanation for the underestimation of Sb sources. In our study, we assumed that ~6% of  $\text{nss-SO}_4^{2-}$  in the ice at Dome C was attributed to volcanic origin [Castellano *et al.*, 2005]. This background volcanic  $\text{nss-SO}_4^{2-}$  value is approximately two times lower than the value (~10%–15%) given for Antarctic ice by Boutron and Patterson [1986] that has been widely used in previous studies. Such a difference in the assumed  $\text{nss-SO}_4^{2-}$  fraction of volcanic origin may be partly responsible for the substantial

underestimation of the volcanic contribution. In addition, the large dispersions in the published Sb/S and Tl/S ratios in volcanic emissions could be another factor adding uncertainty to the estimation of the volcanic contribution.

[25] Alternatively, recent studies indicate that frost flowers (referred to as sea-ice salt) produced on the sea-ice surface are an important source of sea salt to central Antarctica during glacial periods with very large sea-ice extent. These frost flowers result in higher sea-salt Na (ssNa) fluxes in the glacial periods than in the interglacial periods by a factor of ~2 [Rankin *et al.*, 2002; Rankin and Wolff, 2003; Wolff *et al.*, 2010]. Because frost flowers contain high bulk salinity and fractionated sea-salt ions (sulfate depletion and bromide enrichment with respect to seawater), the chemical composition of the sea salt derived from frost flowers differs from that of the seawater [Rankin *et al.*, 2002; Alvarez-Aviles *et al.*, 2008]. There is potential evidence that the formation of frost flowers yields an enrichment of mercury in the Arctic [Douglas *et al.*, 2008]. Despite the lack of data concerning the enrichment of Sb and Tl in frost flowers, we speculate that the contribution from the sea-salt spray, which was calculated by combining ssNa concentrations in ice and the average sea-salt elemental ratios in seawater, may be a lower limit of the estimated sea-salt contribution, as discussed later in this paper.

### 3.3. Crustal Enrichment Factors

[26] We calculated the crustal enrichment factor (EF) to evaluate the degree to which Sb and Tl are attributed to crustal inputs during different climatic conditions. The EF is defined as the concentration ratio of a given element to Ba in ice, normalized to the same concentration ratio in the upper continental crust. For example, the calculation of EF for Sb is as follows:  $\text{EF (Sb)} = (\text{Sb/Ba})_{\text{ice}} / (\text{Sb/Ba})_{\text{crust}}$ . Here we used the data for the upper continental crust given by Wedepohl [1995]. EF values close to unity indicate that rock and soil dust is the dominant source for the element. Conversely, EF values larger than unity indicate a significant contribution from other natural sources.

[27] As shown in Figure 4, the EF records for Sb and Tl show a general pattern of glacial–interglacial contrast by a factor of ~3, with values close to unity during glacial maxima when dust concentrations peaked and elevated values during warmer climatic conditions ( $\delta\text{D} > -430\text{‰}$ ). This record is in good agreement with the fact that crustal dust was the main contributor to both elements during cold periods and that contributions from natural sources other than crustal dust were significant during warmer periods. The relation between the EF values and the climatic conditions ( $\delta\text{D}$ ) is also well defined in Figure 5, showing lower EFs associated with cold periods (higher Ba concentrations) and higher EFs associated with warm periods (lower Ba concentrations).

[28] Despite this general pattern of changes in EFs with changing climatic conditions, the phasing between the EF values and the climatic conditions is less evident for an individual climatic period. Moderately, elevated EF values are observed at MIS 5, 9, 11, and 17, whereas much higher values are found during intermediate climatic conditions. These higher values can be observed for Sb, for example, in the periods dated 511,270 years B.P. ( $\delta\text{D} = -424\text{‰}$ ,  $\text{EF} = 39$ ), 604,460 years B.P. ( $\delta\text{D} = -417\text{‰}$ ,  $\text{EF} = 25$ ), and 769,830 years B.P. ( $\delta\text{D} = -415\text{‰}$ ,  $\text{EF} = 27$ ) and for Tl in

**Table 2.** Mean Contributions From Rock and Soil Dust, Sea-Salt Spray, and Volcanoes for Different Climatic Periods, Expressed Both in Concentrations (pg/g) and Percentages

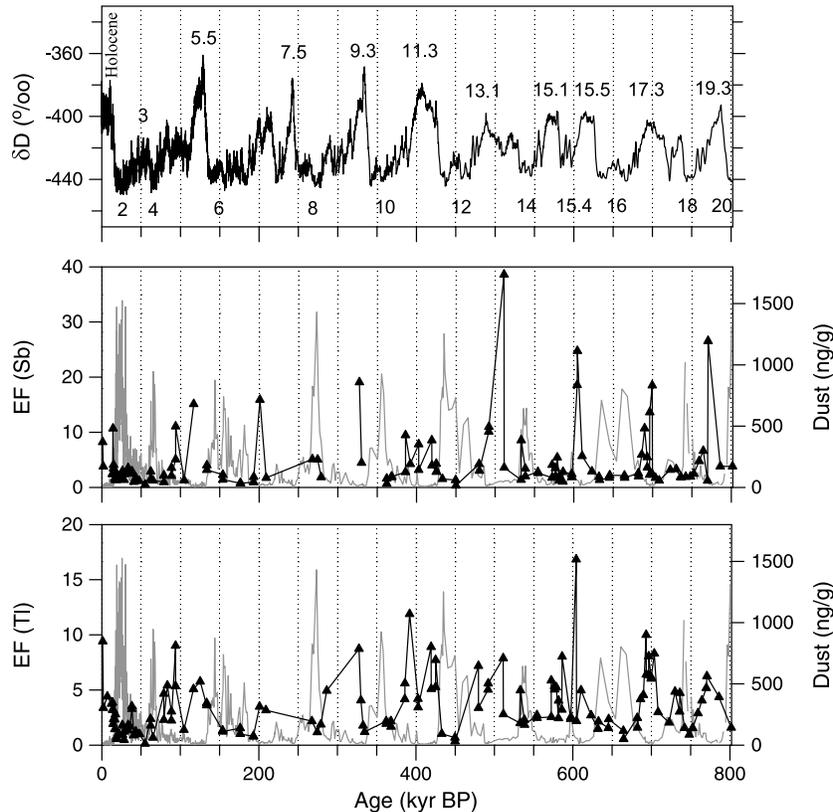
Period	Rock and soil dust contribution				Volcanic contribution				Sea-salt contribution				Sum (%)		
	Sb	%	Tl	%	Sb	%	Tl	%	Sb	%	Tl	%	Sb	Tl	<i>n</i> <sup>a</sup>
Cold periods (< -430‰)	0.098	58	580.237	76	0.010	8	0.058	24	0.010	9	0.0010	0.4	75	101	47
Intermediate periods (-430‰ ~ -400‰)	0.021	43	0.050	45	0.007	22	0.043	49	0.006	17	0.0005	0.6	82	95	71
Warm periods (> -400‰)	0.006	21	0.013	27	0.006	25	0.035	72	0.003	13	0.0003	0.5	59	100	16

<sup>a</sup>Number of samples analyzed.

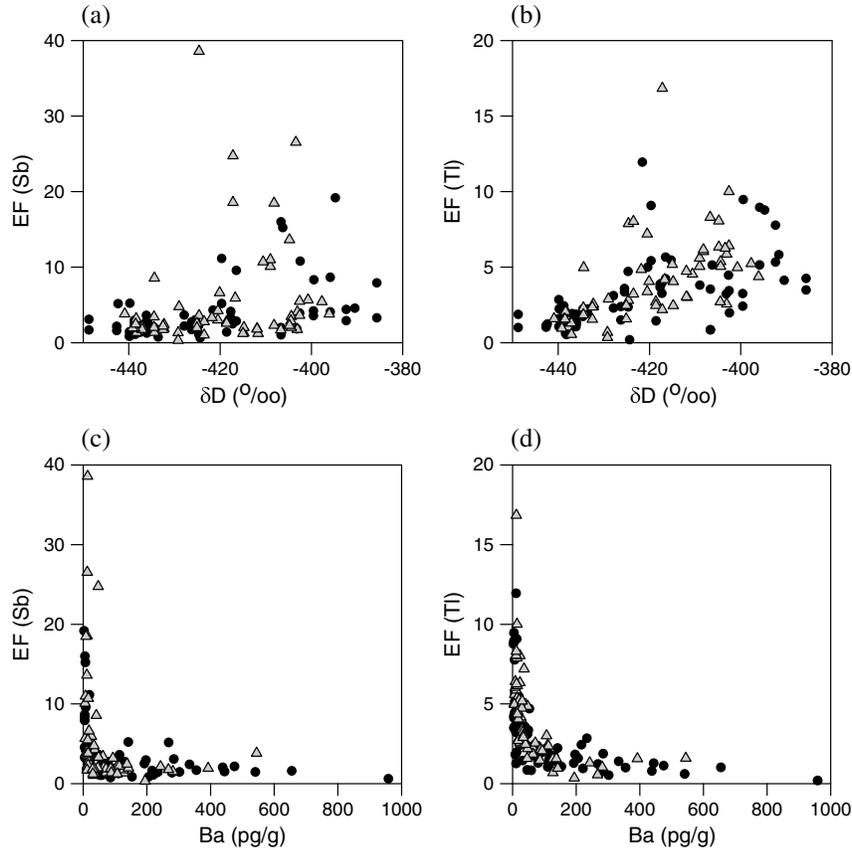
the periods dated 392,070 years B.P. ( $\delta D = -421\text{‰}$ ,  $EF = 12$ ) and 604,150 years B.P. ( $\delta D = -417\text{‰}$ ,  $EF = 17$ ) (Figure 4). This pattern is well illustrated in Figures 5a and 5b. The relationship between the elements Sb and Tl and  $\delta D$  appears to be slightly different between the two elements. The EF values for Sb remain relatively low when the  $\delta D$  values are below  $\sim -420\text{‰}$ , and highly enhanced EFs are found between  $\sim -420\text{‰}$  and  $\sim -400\text{‰}$ , with a ratio of maximum/minimum EF values of 130. The EFs then decrease to generally lower values during warm periods ( $\delta D > -400\text{‰}$ ), with a maximum/minimum ratio of  $\sim 7$ . The average EF value between  $-420\text{‰}$  and  $-400\text{‰}$  is slightly higher (6.4) than that (6.1) during warm periods. For Tl, the EF values tend to continuously increase when the  $\delta D$  values increase (Figures 5a and 5b). Several particularly high EFs are observed between  $-430\text{‰}$  and  $-400\text{‰}$ , with a very high maximum/minimum ratio (170). During warm periods, a decreasing pattern of the

EF values is not evident, but the maximum/minimum ratio is lower ( $\sim 8$ ) than that during colder periods (Table 1). It should be noted that the data points corresponding to the warm stages are small in number. Sufficient time resolution at all periods is needed to resolve a more detailed pattern showing a decrease in the EF values in warm climatic conditions.

[29] We deduce that the interesting feature of highly elevated EFs observed during intermediate climatic stages could be related to the enriched Sb and possibly Tl in the sea salt generated from the frost flowers on the sea-ice surface that prevailed under these climatic conditions. Possible sources of sea-salt aerosols in the polar regions include sea spray, blowing snow containing sea salts on sea ice, and frost flowers [Domine *et al.*, 2004]. Among these sources, frost flowers have recently been recognized as the dominant source of sea-salt aerosols, particularly in Antarctic coastal regions close to areas of sea-ice formation during winter



**Figure 4.** Changes in the crustal enrichment factors (EF) of Sb and Tl over the past 800 kyr. Also shown at the top of the figure is the deuterium record [Jouzel *et al.*, 2007] with MIS numbers [Lisiecki and Raymo, 2005]. Changes in dust concentrations (gray solid lines) [Lambert *et al.*, 2008] are shown with concentration profiles for comparison.



**Figure 5.** Changes in (a and b) crustal enrichment factors (EF) of Sb and Tl as a function of the deuterium content and (c and d) Ba concentrations. Data before the Mid-Brunhes Event (MBE) are shown as gray triangles and after the MBE as solid circles.

and spring [Rankin *et al.*, 2002; Rankin and Wolff, 2003; Wolff *et al.*, 2006, 2010]. Frost flowers may also be a potentially significant source of sea salt reaching the ice sheet on the Antarctic Plateau [Wolff *et al.*, 2003]. Because of the formation of the frost flowers on newly formed sea ice, the factor controlling the amount of the sea salt transported inland is primarily winter sea-ice extent in modern conditions as well as in glacial conditions [Wolff *et al.*, 2006; Fischer *et al.*, 2007], yielding a general pattern of ssNa concentrations in Antarctic ice cores peaking seasonally in winter today and during glacial periods on glacial–interglacial timescales [Kaspari *et al.*, 2005; Wolff *et al.*, 2006, 2010].

[30] As described previously, frost flowers have an elevated salinity of about three times that of bulk seawater [Alvarez-Aviles *et al.*, 2008]. The significance of sea-salt fluxes from frost flowers leads to the possibility that Sb and possibly Tl in sea-ice salt arriving on the ice sheet in central Antarctica could be enriched in comparison to the average sea-salt elemental ratios in seawater used for calculating marine contributions in our samples. To properly evaluate this possibility, substantial studies on the enrichment of trace elements in frost flowers are required. Moreover, the relative contributions of sea-salt aerosols from the open ocean and from sea ice during different climatic conditions have not yet been established for the East Antarctic Plateau [Fischer *et al.*, 2007], which makes a quantitative estimate of the contribution of sea-ice salt to the Sb and Tl fluxes difficult to calculate.

[31] Despite the current lack of such knowledge, it is reasonable to assume that highly elevated EF values for Sb during intermediate climatic stages might have resulted from greater production of sea salt from frost flowers, which were related to greater sea-ice extent. In fact, the estimated contributions from sea-salt spray appear to be somewhat greater during intermediate periods (Table 2), supporting the likelihood of this assumption. During extreme glacial conditions when sea ice was at its maximum, it is difficult to evaluate the contribution from the sea-ice salt because of high crustal dust fluxes that mask any pattern created by this contribution. The high Sb EFs observed particularly between  $\sim -420$ ‰ and  $\sim -400$ ‰ are likely attributed to different sensitivities to the changes in the glacial/interglacial sea salt and crustal dust fluxes, with a factor of  $\sim 2$  change for the sea-salt flux and a factor of  $\sim 25$  change for the crustal dust flux [Lambert *et al.*, 2008; Wolff *et al.*, 2006]. A slightly decreasing pattern of EFs with no significantly enhanced EF values during warm periods may be caused by a lower production of sea-ice salt because the sea-ice extent was reduced during the corresponding warm periods. Seasonally resolved further study will allow us to verify our assumption of the significant contribution of the sea salt from the frost flowers to the deposition of Sb in central Antarctica.

[32] Meanwhile, the less extreme features in the Tl record are likely caused by natural phenomena in view of the fact that the estimated contribution from sea salt appears to be negligible for this element, regardless of the climatic period

(Table 2). However, there are several points of noticeably elevated EF values (above 6) at  $\sim -420\%$ , which deviate largely from the general increasing trend (Figure 5b). For these data points, the sum of the crustal and volcanic contributions accounts for less than 50% of the Tl concentration. This finding suggests that sea-ice salt might be an important source for atmospheric Tl entering inland Antarctica, particularly during specific climatic conditions with both sufficiently large sea-ice extent and more effective transport distance from the source area to the Antarctic Plateau.

### 3.4. Concentrations and EFs Before and After the Mid-Brunhes Event (MBE)

[33] The deuterium temperature record of the EPICA Dome C ice core during the past 800 kyr is characterized by less warm interglacials than those of the past four climatic cycles and by warmer glacial maxima than MIS 2, with smaller amplitudes of glacial/interglacial climatic variations before the Mid-Brunhes Event (MBE) at  $\sim 430$  kyr B.P. [EPICA community members, 2004; Jouzel *et al.*, 2007]. With respect to the concentrations and fluxes of Sb and Tl before and after the MBE, the pattern appears to be different for each element. The Sb concentrations and fluxes during MIS 2 (LGM) are shown to be lower compared to MIS 8, 15.4, and 20.2, although MIS 2 is the coldest period in the past 800 kyr (Figure 1). Less elevated concentrations are also exhibited during glacial maxima MIS 4, 6, 16, and 18. During interglacials, there is no visible difference in the concentration levels before or after the MBE. Generally, no difference in the Sb concentrations associated with climatic conditions (variations in  $\delta D$  and crustal dust) between the pre-MBE and post-MBE record is observed, as shown in Figures 2a and 2c.

[34] By comparison, the Tl concentrations and fluxes during post-MBE glacial maxima show a gradual increase from MIS 11.3 to MIS 2 (Figure 1). The Tl concentrations and fluxes are relatively low during glacial maxima before the MBE, with the exception of MIS 18 and 20.2, during which concentration and flux levels are comparable to or higher than those during MIS 2, 4, and 6. The concentrations and fluxes of Tl during glacial maxima are remarkably related to the dust concentrations over the last successive eight glacial periods (Figures 1 and 2), as expected by the fact that crustal dust was a dominant source for this element during glacial maxima. Lower Tl levels during MIS 8, 10, and 12 may result partly from a lack of available samples corresponding to the peaks of these glacial maxima. During interglacials ( $\delta D > -410\%$ ), the Tl concentrations and fluxes are greater before the MBE than after the MBE (Figures 1 and 2b) with mean values of  $0.09 \text{ pg/g}$  ( $2.1 \text{ ng/m}^2/\text{yr}$ ) before the MBE and  $0.05 \text{ pg/g}$  ( $1.4 \text{ ng/m}^2/\text{yr}$ ) after the MBE. The  $\delta D$  value of  $-410\%$  was chosen to delineate interglacial periods because of the scarcity of data points above  $-400\%$  caused by less pronounced warmth before the MBE (Figure 1).

[35] Under these climatic conditions, crustal contributions explain 19% of the measured Tl concentrations before the MBE and 37% after the MBE. Volcanic emissions are considered to be a more important source for Tl after the MBE, accounting for 78% of the measured Tl concentrations, whereas volcanic emissions explain 58% of the Tl concentrations before the MBE. This difference in the volcanic contribution suggests that at least  $\sim 20\%$  of Tl during warm periods before the MBE originated from a source other than crustal

and volcanic sources. In a previous section, sea-ice salt was proposed as a potentially important source for Sb and possibly Tl during cold stages when the sea-ice extent was large. Although the sea-salt spray contribution remains negligible (less than 1%) for all warm periods over the past 800 kyr, higher Tl concentrations and fluxes observed during warm periods before the MBE are most likely related in part to greater winter sea-ice extent caused by less warmth during the corresponding climatic period, leading to a greater input of Tl derived from frost flowers to central Antarctica.

[36] In summary, the apparent relationships between elemental concentrations and fluxes and climatic conditions, as well as between EFs and Ba concentrations, suggest that the atmospheric cycles of Sb and Tl in central Antarctica may be sensitive to changes in the relative strength of contributions from different natural sources that are strongly linked to climatic conditions over the past 800 kyr.

### 3.5. Comparison of Natural Sb and Tl Data With Present-Day Levels

[37] Recently, the first reliable data on modern atmospheric Sb and Tl deposition were obtained from snow layers deposited over the past 50 years at Dome Fuji on the central East Antarctic Plateau [Hong *et al.*, 2012]. For a better understanding of the extent of anthropogenic perturbation, we compare these present-day Sb and Tl data with those of the past eight climatic cycles, which shows very large glacial–interglacial changes. Although present-day snow accumulation rates at Dome C and Dome Fuji are very similar ( $\sim 25 \text{ kg/m}^2/\text{yr}$ ) [Parrenin *et al.*, 2007; Hong *et al.*, 2012], the accumulation rates have varied by a factor of  $\sim 2$  between glacial maxima and interglacials [Parrenin *et al.*, 2007]. We therefore compare only the deposition fluxes and EFs between the two different sites, because the concentration levels vary with accumulation rates.

[38] As shown in Table 1, the mean present-day Sb flux ( $6.6 \text{ ng/m}^2/\text{yr}$ ) between 1970 and 1995, a period during which this element was most enriched during recent decades [Hong *et al.*, 2012], appears to exceed by a factor of more than 8 the lowest mean level ( $0.8 \text{ ng/m}^2/\text{yr}$ ) observed during warm interglacials. Surprisingly, the present-day Sb flux is approximately double the glacial maxima value, exhibiting the highest mean level ( $2.8 \text{ ng/m}^2/\text{yr}$ ) observed over the last successive eight climatic cycles (Table 1). This anthropogenic perturbation of the natural Sb cycle in the Antarctic atmosphere becomes more prominent when the mean enrichment factors are compared. The mean EF value (128) during the recent decades is approximately 21 times the levels ( $\sim 6$ ) observed during intermediate and warm periods, during which the natural contributions from crustal dust, volcanoes, and sea salt to the Sb deposition were significant. Therefore, taking into account the mean modern natural background EF value of  $\sim 6$  for Sb, it is estimated that  $\sim 95\%$  of Sb deposited on the central East Antarctic Plateau during the recent decades was of anthropogenic origin. Our comparison between the ice core Sb values and their present-day levels documents that human activity has drastically changed the atmospheric cycle of Sb, resulting in the present-day Sb flux being the greatest Sb flux observed over the past 800 kyr, similar to the case of atmospheric  $\text{CO}_2$  [Lüthi *et al.*, 2008]. Unlike  $\text{CO}_2$ , however, there is evidence that the Sb flux in central Antarctica has been decreasing

since the 2000s because much effort has been made to reduce atmospheric pollution in major source regions in South America [Hong *et al.*, 2012].

[39] As for Tl, the mean present-day flux ( $1.4 \text{ ng/m}^2/\text{yr}$ ) is observed to be comparable to the lowest mean level ( $1.7 \text{ ng/m}^2/\text{yr}$ ) during warm periods, whereas the Tl flux appears to be lower by a factor of  $\sim 3$  than that ( $4.5 \text{ ng/m}^2/\text{yr}$ ) during glacial maxima (Table 1). This result indicates that the factor causing the highest input of Tl to Antarctica was not human activity but terrestrial mineral dust. In contrast to the Tl fluxes, the highest mean EF value (13) is observed during recent decades (Table 1). Based on the natural EF value of  $\sim 5$  during warm periods, it is estimated that anthropogenic inputs account for  $\sim 60\%$  of Tl in snow deposited between 1970 and 1995 in central Antarctica, despite the fact that the present-day Tl flux is the lowest flux observed over the past 800 kyr.

#### 4. Conclusions

[40] The results demonstrate a large natural variability of Sb and Tl in Antarctic ice dated from 1215 to 801,660 years B.P. This variability is strongly linked to climatic conditions over the last successive eight climatic cycles. Highly elevated concentrations and fluxes of both Sb and Tl are observed during glacial maxima, whereas lower levels of Sb and Tl persist during intermediate and warm periods. Rock and soil dust was a major contributor to Sb and Tl concentrations during glacial maxima, leading to noticeably enhanced concentrations and fluxes with much lower EF values during these climatic periods. The contribution from volcanoes was increasingly important for Sb and particularly Tl when climatic conditions became warmer.

[41] A number of highly elevated EF values observed for Sb and Tl during intermediate climatic periods between  $\sim -420\%$  and  $\sim -400\%$  may be the result of greater production of sea salt from highly saline frost flowers when the sea-ice extent was relatively large. Future studies are now needed to verify a potential contribution of sea salt from frost flowers to the atmospheric cycles of trace elements both in coastal and inland areas and in the present-day and glacial conditions in Antarctica.

[42] A comparison between the Antarctic ice core record presented in this study and the present-day Sb and Tl values from snow layers at Dome Fuji in East Antarctica shows that the Sb flux during recent decades is at the highest level (an approximately twofold increase above the highest natural level during glacial maxima) observed over the last  $\sim 800$  kyr, indicating that human activity has greatly perturbed the atmospheric behavior of this element.

[43] Finally, it will be interesting to extend previously available EDC ice core records of various trace elements, as well as Pb isotopes (a good tracer of dust origin), back to MIS 20.2,  $\sim 800$  kyr B.P.

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