Evidence of Global-Scale As, Mo, Sb, and Tl Atmospheric Pollution in the Antarctic Snow

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ⓢ Supporting Information

ABSTRACT: We report the first comprehensive and reliable time series for As, Mo, Sb, and Tl in the snowpack from Dome Fuji in the central East Antarctic Plateau. Our results show significant enrichment of these elements due to either anthropogenic activities or large volcanic eruptions during the past 50 years. With respect to the values reported from 1960 to 1964, we observed the maximum increases in crustal enrichment factors (EFs) for As (a factor of ~15), Mo (~4), Sb (~4), and Tl (~2) during the period between the 1970s and 1990s, reflecting the global dispersion of anthropogenic pollutants of these elements, even to the most remote areas on Earth. Such enrichments are likely related to emissions of trace elements from nonferrous metal smelting and fossil fuel combustion processes in South America, especially in Chile. A drastic decrease in the As concentration and its EF values was observed after the year 2000 in response to the introduction of environmental regulations in the 1990s to reduce As emissions from the copper industry, primarily in Chile. The observed decrease suggests that governmental regulations for pollution control are effective in reducing air pollution at both the regional and global level.
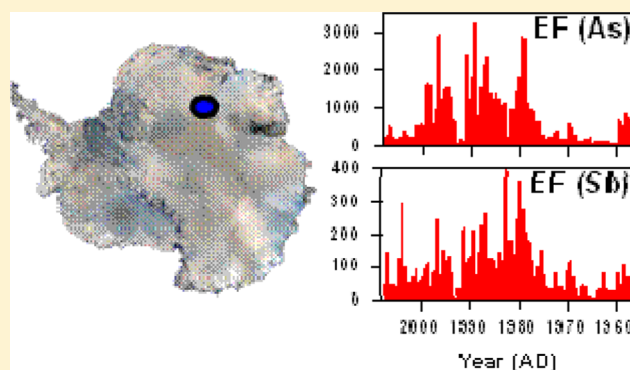
INTRODUCTION

The quantities of As, Mo, Sb, and Tl released into the atmosphere by human activities are comparable to the amounts released from natural sources.[1,2] The dispersion of these elements throughout the atmosphere has significantly affected the natural geochemical cycles in many regions of the Earth's surface. These alteration are preserved in snow and ice cores that can be utilized to examine past changes in the composition of the atmosphere.[2−10] A few reliable snow and ice records, especially from the Canadian Arctic[7,8] and Greenland,[2] have well documented definite enrichments of As, Sb, and Tl in recent decades. These results reflect the hemispheric scale of human interference in the environmental mobilization of these elements in the Northern Hemisphere. For Mo, there exist no long-term snow and ice records from the Canadian Arctic or Greenland, but it is probable that similar trends apply, because Mo was observed to be significantly enriched in recent snow layers from 1991 to 1995 in central Greenland.[11]

Despite great concern of exposure to As, Mo, Sb, and Tl in terms of human and environmental health, very little is known about the anthropogenic impact on the geochemical cycles of these elements in the Southern Hemisphere.[6,10] Moreover, there is at present no indication as to whether the large-scale pollution of As, Mo, Sb, and Tl observed in the Northern Hemisphere is indeed a global phenomenon. This is mainly because of insufficient long-term snow and ice records from Antarctica, the most remote area on Earth. Detailed long-term data for As, Mo, Sb, and Tl in Antarctic snow and ice is lacking because of the extremely low concentrations of these elements and measurements of these elements require ultraclean protocols throughout the field sampling and experiments in the laboratory as well as highly efficient analytical methods for the direct determination of elemental concentrations down to the subpicogram per gram (1 pg g^{-1} = 10^{-12} g g^{-1}) level.[12,13]
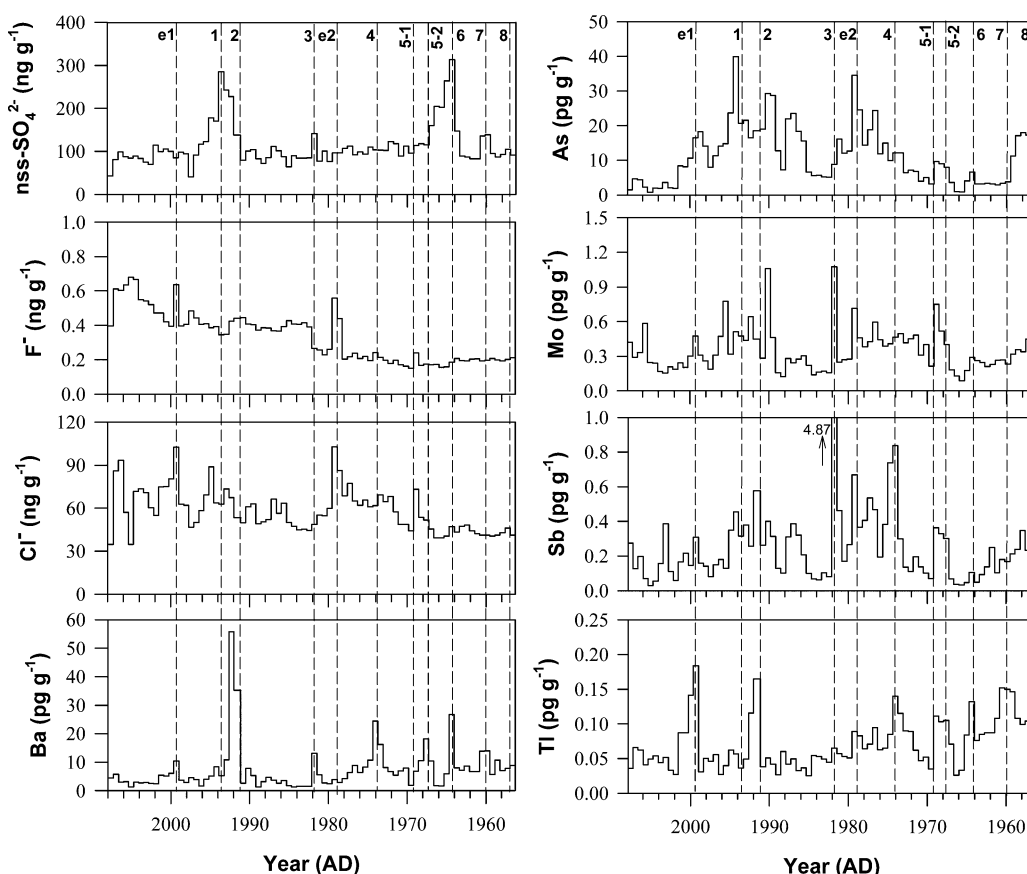
Here, we present the first comprehensive data on the changing levels of As, Mo, Sb, and Tl in successive snow layers over the past 50 years, at Dome Fuji, East Antarctica. The results provide unambiguous evidence of the global atmospheric spread of anthropogenic As, Mo, Sb, and most likely Tl as far as the central Antarctic Plateau.

Figure 1. Concentrations of nss-SO$_4^{2-}$, F$^-$, Cl$^-$, Ba, As, Mo, Sb, and Tl measured in snow pit samples from Dome Fuji in East Antarctica. Vertical dashed lines indicate volcanic layers corresponding to prominent volcanic events: Pinatubo (1), Cerro Hudson (2), El Chichon (3), Ngauruhoe (4), Deception Island (5-1 and 5-2), Agung (6), Cordon Caulle (7), Carrán-Los Venados (8), and Erebus (e1 and e2).

■ MATERIALS AND METHODS

Snow Pit Sample Collection. The samples were collected at a site near Dome Fuji, the second highest dome in Antarctica, located at the summit of Dronning Maud Land, East Antarctica (77°18′ S, 39°47′ E, 3785 m a.s.l.), on December 10, 2007, during the Japanese–Swedish IPY Antarctic expedition (Supporting Information, Figure S1). Great precautions were taken during the collection of samples in the field to prevent the possibility of contaminating the snow. A more detailed description of the methodology has been reported previously.[13,14] A continuous series of 80 snow samples were collected at 5 cm intervals from a 4 m deep snow pit and then poured into an ultraclean 500 mL low-density polyethylene (LDPE) bottle. All equipment used for field sampling was extensively acid-cleaned using rigorous cleaning procedures before use.[15]

Dating of the Snow Pit. The chronology of the snow pit with respect to the depth was deduced from well-identified nonsea-salt SO$_4^{2-}$ (nss-SO$_4^{2-}$) peaks, corresponding to layers of significant volcanic depositions from Mt. Pinatubo (1993–1994), Mt. Cerro Hudson (1991–1992), and Mt. Agung (1964–1965).[14,16] Based on such known volcanic signals, we estimated the age of the snow pit to span approximately 50 years from 1956 to 2007/2008. The estimated mean annual accumulation rate for the depth interval between the Mt. Pinatubo/Mt. Cerro Hudson and Mt. Agung peaks was ∼8 cm yr^{-1} (25 mm water equivalent per year, w.e.y^{-1}). Our estimates

were comparable to previous measurements conducted at the site,[16,17] supporting our assignment of the dates.

Chemical Analysis. All samples were thawed, acidified to 1% with Fisher "Optima" grade ultrapure HNO$_3$, and directly analyzed for As, Mo, Sb, Tl, and Ba 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). The analytical instrumentation and ultraclean working conditions were conducted as previously described.[9,18] Special attention was given to daily optimization of the instrumental parameters to obtain high intensities and minimize possible interference. Detection limits, defined as three times the standard deviation of 10 measurements of the blank (1% "Optima" grade HNO$_3$ solution), are (in pg g^{-1}) as follows: 0.1 for As; 0.05 for Mo; 0.01 for Sb and Tl; and 0.2 for Ba. Analysis of dilute solutions of certified riverine water reference materials, SLRS-4 for Mo and Tl and SLRS-5 for As and Sb (National Research Council, Canada), exhibited very good recovery versus certified or compiled values[19] (in pg g^{-1}): 464 ± 15 versus 413 ± 39 for As; 220 ± 2 versus 210 for Mo; 297 ± 2 versus 300 for Sb; 6.1 ± 0.3 versus 6.5 for Tl; and 13 702 ± 226 versus 14 000 ± 500 for Ba.

The ionic species (Na$^+$, SO$_4^{2-}$, F$^-$, and Cl$^-$) were simultaneously analyzed by a two-channel ion chromatography (IC) system that combined two Dionex 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%.

Table 1. Concentration Ranges and Mean Values (in Parentheses) of As, Mo, Sb, Tl, and Ba in Our Snow Pit Samples and Comparison with the Previous Data Reported from Other Sites

location	altitude (m)	time period covered	conc (pg g^{-1})					ref
			As	Mo	Sb	Tl	Ba	
Dome Fuji, Antarctica (77°18′ S, 39°47′ E)	3785	1956–2008	0.79–40 (11)	0.09–1.1 (0.35)	0.03–4.9 (0.29)	0.03–0.18 (0.07)	1.3–56 (7.3)	this work
Lambert Glacier Basin, Antarctica (70°50′ S, 77°04′ E)	1850	1998–2001/ 2002	1.4–24 (10)				0.52–7.6 (2.4)	13
Terra Nova, Antarctica[a] (70° ~ 76° S, 160° ~ 164° E)	>700	1988/89– 1990/91[a]				0.18–0.45 (0.35)		20
Mt. Everest, central Asia (28°03′ N, 86°96′ E)	6518	1960–2002	3.5–195 (41)	0.38–21 (2.9)	0.29–9.4 (2.3)		22–1680 (313)[d]	6
Tien Shan, central Asia (43°03′ N, 94°19′ E)	4512	1953–2004	12–2516 (420)	1.4–151 (33)	4.2–208 (41)	0.9–144 (13)	311–48,668 (5,622)	21
Mont Blanc, central Europe (45°50′ N, 6°51′ E)	4250	1960–2002		0.4–121 (17)	0.2–109 (23)			4
Devon Island, Canadian Arctic (75° N, 82° W)	1860	1994–2004			0.13–3.71 (1.03)[b]	0.35–1.12 (0.50)[b]		7 and 8
ACT2, Greenland (66.0° N, 45.2° W)	2410	1982–2003				(0.1)[c]		2
Summit, Greenland (72°20′ N, 38°45′ W)	3270	1991–1995		0.10–7.0 (1.6)	0.20–4.4 (0.86)			11

[a]Fresh snow. [b]Median value. [c]Mean value only. [d]Unpublished data.

RESULTS AND DISCUSSION

Concentrations of As, Mo, Sb, and Tl. Figure 1 shows the first comprehensive data obtained on the occurrence of As, Mo, Sb, and Tl in Antarctic snow layers during the last several decades. Extremely low concentrations of Mo, Sb, and Tl below the pictogram per gram level are encountered in the majority of samples, with mean concentrations of 0.07 pg g^{-1} (Tl), 0.29 pg g^{-1} (Sb), and 0.35 pg g^{-1} (Mo), respectively (Table 1). Concentrations of As also remain at very low levels, ranging from ~1 pg g^{-1} to tenths of pg g^{-1}, with an average of 11 pg g^{-1}.

Table 1 compares our data for As, Mo, Sb, Tl, and Ba with the few other reliable data points obtained from snow and ice in Antarctica and other regions. Despite large differences between the geographical characteristics of the sites, the concentration ranges appear to be comparable for As and Tl in the Antarctic snow. Comparing Antarctica and Greenland, the concentration levels in Greenland snow are of similar magnitudes to ours for Mo, Sb, and Tl. Interestingly, the Sb and Tl concentrations observed in the Canadian Arctic snow are comparable to or slightly greater than those in the Antarctic snow, although the Canadian Arctic would be expected to receive more pollution. The situation is very different for the levels determined in central Asia and Europe. The comparison demonstrates that the concentrations in these regions are one or two orders of magnitude higher than those in our samples. Such strong enrichment of atmospheric As, Mo, Sb, and Tl in the mid latitudes of the Northern Hemisphere can be attributed with certainty to the proximity to natural and anthropogenic sources of trace element emissions.

We have averaged the individual data points over five years, in order to compensate for short-term changes in concentrations (Supporting Information, Table S1). The five year averaged concentrations of As display a pronounced enhancement up to 20 pg g^{-1} in the period 1975–1979, reaching a maximum of 24 pg g^{-1} from 1990 to 1994. The concentrations are respectively ~5 and ~7 times higher during those periods in comparison with the earlier period of 1960–1964, in which there was a relatively low mean concentration. The highest

value (0.76 pg g^{-1}) for Sb is observed for the period 1980–1984, with an increase factor of ~5 relative to 1960–1964. In comparison, no large variations in the concentrations of Mo and Tl are observed. The highest concentration levels are seen for Mo (0.52 pg g^{-1}) from 1990 to 1994 and for Tl (0.11 pg g^{-1}) from 1956 to 1964.

Natural Contributions to the Input Levels of As, Mo, Sb, and Tl. The contributions from primary natural sources of trace elements in each snow sample were evaluated using the following indicators: nss-SO$_4^{2-}$ for volcanic emissions; Ba for rock and soil dust; and sea-salt Na (ss-Na) from sea-salt spray.

Volcanic emissions from both quiescent degassing and explosive eruptions could contribute significantly to the natural atmospheric cycles of trace elements.[22,23] First, the contribution from quiescent degassing of volcanoes in each sample was estimated using the concentration of nss-SO$_4^{2-}$ and the mean values of the element/S ratios in volcanic emissions given by data published in the literature,[23−27] assuming that ~13% of nss-SO$_4^{2-}$ in Antarctic snow and ice originated from volcanoes.[28] For As and Sb, the contribution from the quiescent degassing of volcanoes appears to be insignificant, accounting on average for ~5% (As) and ~9% (Sb) of the measured concentrations. This contribution increases slightly to ~15% for Mo. In contrast, our estimate gives a volcanic contribution that accounts for most of the Tl in the snow samples, suggesting that volcanic emissions could be the largest contributor to its deposition in the central Antarctic plateau. However, it should be noted that the estimated contributions from volcanoes are very tentative, because of the orders-of-magnitude differences between the element/S ratios of individual volcanoes as well as uncertainties in characterizing trace element behavior in volcanic plumes and during transport.[27]

Second, we traced the possible contributions from large volcanic eruptions by combining various chemical indicators of these signals such as nss-SO$_4^{2-}$ (volcanic SO$_2$), Ba (volcanic ash), and Pt (volcanogenic element) peaks.[14] Strongly to moderately enhanced peaks of either nss-SO$_4^{2-}$ or Ba are indicated by the dashed lines 1−7 in Figure 1, and they can be assigned to prominent volcanic events: Pinatubo (15° N) and
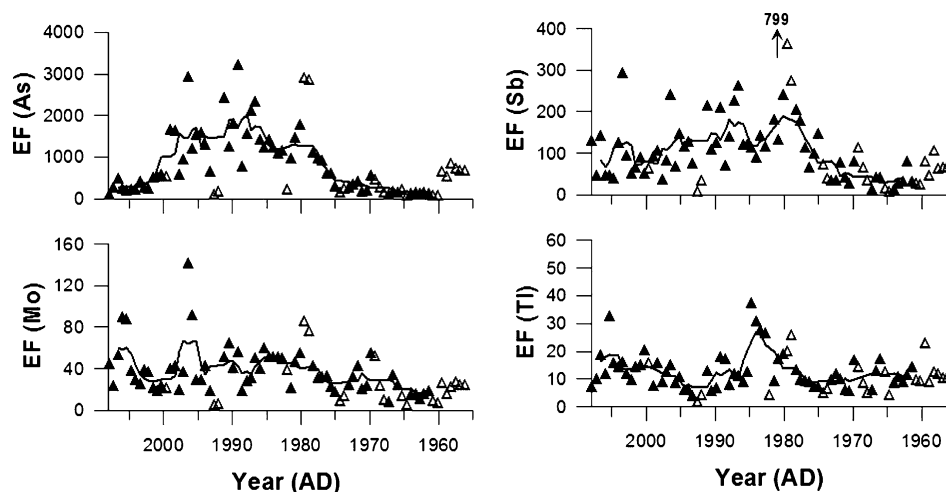
Figure 2. Changes in crustal EFs of As, Mo, Sb, and Tl in the snow from Dome Fuji, East Antarctica, over the past 50 years. Open triangles represent the EFs determined in volcanic layers related to prominent volcanic events (see text). The arrow on the panel for the EF of Sb indicates an abnormally high EF value (799) in a volcanic layer corresponding to the El Chichon eruption. Solid lines represent the five-point running average after excluding individual EF values (open triangles) that are likely associated with large volcanic eruptions.

Cerro Hudson (45.5° S) in 1991 (lines 1 and 2), El Chichon (17° N) in 1982 (line 3), Ngauruhoe (37° S) in 1974 (line 4), Deception Island (62.5° S) in 1967−1970 (line 5-1 to 5-2), Agung (8° S) in 1963 (line 6), and Cordon Caulle (40.5° S) in 1960 (line 7) (Supporting Information, Figure S2). From the Pt peak observed in a previous study, it is surmised that line 8 corresponds to the eruption of Carrán-Los Venados (40° S) in 1955.[14] Interestingly, the F⁻ and Cl⁻ peaks (the main halogen components enriched in volcanic plumes[23]) are observed at the depth intervals of 65−70 cm (line e1) and 220−230 cm (line e2) without well-identified nss-SO_4^{2-} or Ba signals, though these halogens suffer postdepositional loss in snow at sites linked to very low accumulation rates.[29] The most likely candidate for such peaks is Mt. Erebus (77.55° S, 167.17° E), the world's southernmost active volcano, located on Ross Island, Antarctica, because F⁻ and Cl⁻ in Antarctic snow layers could be the potential tracer of the volcanic gas plume of Mt. Erebus.[30] As for the F⁻ and Cl⁻ peaks at the 300−305 cm depth interval dated to ~1969, it is difficult to attribute this signal to the impact of Mt. Erebus, because multiple eruptions of the Deception Island volcano between 1967 and 1970 are superimposed on this snow layer.[31] For convenience, we have assigned it to the multiple eruptions of the Deception Island volcano.

In Figure 1, moderately enhanced or pronounced concentration peaks can be identified for all four elements at lines e1 and e2, reflecting a potential contribution from Mt. Erebus as previously proposed for different trace elements as well as platinum group elements in East Antarctica.[14,30] Our data show no synchronous increase in the concentrations of all four elements at line 1 corresponding to the Pinatubo eruption, while remarkable increases in Sb and Tl concentrations are detected at line 2, which are related to the eruption of Cerro Hudson. A volcanic layer linked to the El Chichon eruption is characterized by greatly enhanced concentrations of Mo and Sb, which are as much as 3 times (Mo) and 11 times (Sb) larger than the mean values. Both Sb and Tl show a remarkable increase due to the eruption of the Ngauruhoe volcano (line 4). During the multiple eruptions of the Deception Island volcano between lines 5-1 and 5-, moderate concentration increases are observed for Mo, Sb, Tl, and probably As. The situation is

different for lines 6 and 7. Significant changes in the elemental concentration in these volcanic layers corresponding to the eruptions of Agung and Cordon Caulle are seen only for Tl. Finally, volcanic signals for As, Mo Sb, and Tl can be seen in the depth interval below 380 cm (~1956 to ~1959), and are probably linked to the eruption of Carrán-Los Venados (line 8). Our data conclusively show that volcanic eruptions at the mid to low latitudes as well as Mt. Erebus within Antarctica have sporadically contributed to significant increases in the atmospheric fluxes of the measured elements in the central Antarctic Plateau. However, the situation is different for each element. This reflects the complexity of atmospheric transport processes of trace elements derived from large volcanic eruptions prior to deposition, which could vary depending on factors associated with the individual volcanoes such as volcano latitude and distance from the site, the altitude at which emissions are injected (troposphere to stratosphere), and the volume and composition of ejected materials and their chemical and physical properties.[14,32,33]

The contributions from rock and soil dust were calculated from Ba concentrations (a crustal reference element) in each sample and the mean element/Ba ratios in the upper crust.[34] After excluding the estimates in the volcanic layers that are likely associated with large volcanic eruptions with strongly enhanced Ba peaks (Figure 1), the average contribution from rock and soil dust appears to be negligible for As and Sb (less than 1%) and insignificant for Mo (~4%). This contribution is shown to be important for Tl, accounting for ~11% of the measured concentration.

The contribution from sea-salt spray was evaluated from ss-Na (after a correction for Na contributed from rock and soil dust) and the average sea salt elemental ratios in seawater.[35] The tentative enrichments of elements in sea-derived aerosols relative to seawater were not combined with the sea-salt elemental ratios, because such enrichments are in doubt due to potential contamination problems.[36] This contribution was estimated to be negligible for As, Sb, and Tl, with the average values ranging from less than 1% of the measured concentrations for As and Tl to ~2% for Sb. In comparison, this contribution appears to be significant for Mo in some

samples, accounting for more than 10% of the measured concentrations.

When combined, the estimated contributions of various natural sources to As and Sb concentrations appear on average to account for only ~6% and ~12%, respectively, of the measured concentrations, whereas a significant proportion (~25%) of the measured Mo concentration seems to be of natural origin. Our estimates indicate that most Tl in the snow can be attributed primarily to volcanic emissions and partially to rock and soil dust.

Anthropogenic Enrichment of As, Mo, Sb, and Tl. Figure 2 shows changes in the crustal enrichment factors (EF) of As, Mo, Sb, and Tl in snow dated from 1956 to 2007/2008. We calculated the EFs for each element using the following equation: $\mathrm{EF} = [X/\mathrm{Ba}]_{\mathrm{snow}}/[X/\mathrm{Ba}]_{\mathrm{crust}}$, where X is the element of interest and $[X/\mathrm{Ba}]_{\mathrm{snow}}$ and $[X/\mathrm{Ba}]_{\mathrm{crust}}$ refer to the concentration ratios of element X to Ba in the snow and in the mean upper continental crust, respectively.[34] Elemental EF values larger than unity indicate that the contributions from other natural or anthropogenic sources are important, while EFs close to unity suggest that the elements in the snow are derived primarily from the continental crust.[6,9] In Figure 2, the EF values are highly variable between elements with the lowest mean value for Tl (12) and the highest for As (822) (Supporting Information, Table S1). Significantly enhanced EFs for As, Mo, and Sb most likely indicate input from anthropogenic sources. This is also the case for Tl, for which higher EFs than the mean value are seen in some of the samples.

To help emphasize the main features of anthropogenic inputs, five-point running-averaged EFs for As, Mo, Sb, and Tl are plotted in Figure 2, and mean concentration and EF values during specific time periods are presented in the Supporting Information, Table S2, after excluding individual data points that are likely linked to large volcanic eruptions. A very well-defined change in the EFs is indeed observed for As during the past 50 years (Figure 2). The temporal trend of the EF values of As is characterized by a significant increase in the EF from the mid-1970s onward and a peak around 1990 (Supporting Information, Table S2 and Figure 2). From the mid-1980s to the late 1990s, the EF level remains more than 10 times (with a maximum of 15) higher than that recorded between 1960 and 1964 (Supporting Information, Table S2). The profile then shows a rapid decline in the EF since the 1990s, with values in the 2000s slightly higher than those in the late 1960s. Similar to the As EF record, the Sb EF is observed to markedly increase from the mid-1970s and maintain significantly enhanced values until the mid-1990s. The maximum increase (a factor of ~4) for Sb is smaller than that for As. Rather significant decreases in the EF are also observed for Sb between the mid-1990s and 2000s (Supporting Information, Table S2 and Figure 2). In contrast to As and Sb, the EF values for Mo reveal no distinct temporal trends. The EF for this element has exhibited increased levels since the mid-1960s with the maximum increase (a factor of ~4) during the period 1995−1999. Interestingly, the EF for Mo remained elevated in the 2000s. Finally, the EF for Tl appears to maintain levels roughly similar to those reported between 1960 and 1964 for the entire time period, except for 1980−1984, during which the average EF was enhanced by a factor of more than two (Supporting Information, Table S2). This is consistent with the suggestion that Tl in the snow samples originates primarily from natural inputs, as described earlier.

Taken together, our data indicate that the enrichment of As, Mo, Sb, and most likely Tl in the snow at Dome Fuji has occurred due to anthropogenic contributions during the last 50 years, providing clear evidence for the global dispersion of anthropogenic pollutants of these elements even as far as the central Antarctic Plateau, the most remote area of our planet.

Potential Anthropogenic Sources and Source Regions. Nonferrous metal production, especially Cu smelting processes, is the most important contributor to As emissions, while anthropogenic Mo and Tl are exclusively emitted from fossil fuel combustion.[1,37] Sb emissions can be traced to both fossil fuel combustion and nonferrous metal production.[1,37] In order to apportion the sources and source regions affecting the inputs of the measured elements, we used differences resulting from historical variations in nonferrous metal production and fossil fuel consumption in different regions (South America, Southern Africa, and Australia) as a surrogate for the changing emission rates of each element from these sources. This is because emission factors for calculating emission rates could vary due to differences in industrial development and technology from country to country, as well as varying with time.[1]

In Figure S3 of the Supporting Information, the Cu smelting production rates exhibit different patterns in different regions. Since the largest portion of anthropogenic As is emitted from Cu smelting processes,[1,37] the temporal pattern of the EF for As in our samples is reasonably expected to provide a fingerprint to identify a possible source region. Cu smelting production in Southern Africa rapidly increased by a factor of ~3, from ~34 000 tons in the early 1960s to ~100 000 tons in 1965, reaching a peak of ~160 000 tons in 1970. High Cu production rates up until the mid-1980s began to gradually decrease and showed a prompt decline down to ~50 000 tons in 1993. Considering that emission factors were estimated to have diminished by a factor of more than two from the mid-1980s to the mid-1990s,[1,37] a vast decrease in As emissions from Cu production in Southern Africa is thought to have occurred in the 1990s. However, these considerations for Cu production and other relevant As emissions in Southern Africa do not match the changes in the EF of As observed in our samples, suggesting that Southern Africa does not represent an important source region. Similarly, Cu production in Australia is relatively small, and its temporal trend is not compatible with the EF pattern, confirming that Australia is not a dominant contributor. On the other hand, Cu smelting production in South America shows a rapid rise after the mid-1970s with substantial growth of production rates until the present. Such changes from the mid-1970s to 1990s are likely to match with the temporal trend of the As EF in our samples during the corresponding time period (Figure 2 and Supporting Information, Figure S3). However, there is a very distinct difference between the trends of Cu production and of the EF after the mid-1990s, showing a continuous increase in Cu production and a substantial decrease in the EF (Supporting Information, Table S2 and Figure S3). Such disagreement seems to be plausibly linked to the introduction of environmental regulations in 1991 to reduce trace element emissions (especially As) from the copper industry in Chile,[38] which is the largest Cu producer in South America, accounting for approximately 75% of total Cu production. Stronger environmental regulation of As emissions was then introduced in 1999, which led to a further reduction in As emissions from the copper industry.[38,39] For instance, airborne As concentrations in Santiago, Chile, showed a sharp

decrease by a factor of ~4, from ~0.2 μg m^{-3} between 1997 and 1999 to ~0.05 μg m^{-3} between 2000 and 2003.[39] Interestingly, this factor of 4 decrease from the late 1990s to the early 2000s is comparable to the value (3.7) observed for As concentrations in the Antarctic snow during the corresponding period (Supporting Information, Table S2). The EF of airborne As in Santiago also decreased sharply by a factor of ~3, as observed for the As EF in the snow. Taken together, the observed As EF profile is likely representative of the changing As emissions from Cu smelting processes, especially in Chile, leading to South America being the most likely source region for the anthropogenic input of As at Dome Fuji. This finding is supported by a previous observation that the air masses reaching Dome Fuji predominantly originate from the Atlantic Ocean with more western curvature of trajectories with increasing altitude, reflecting substantial transport of airborne pollutants from South America.[40] Despite the general similarity between temporal changes in Cu production (i.e., As emissions) in South America and the As EF in the snow, there is a large difference in the magnitude of the increase in Cu production (a factor of 2.3) in South America and the As concentrations (i.e., atmospheric As deposition flux, a factor of ~5) in the snow between 1960−1964 and 1985−1989 (Supporting Information, Table S2). This difference may be attributed in part to anthropogenic As emissions from coal combustion and other nonferrous metal production (Pb and Zn).[1,37] It is worth mentioning that global As emissions from these sources were ~65% of those from global Cu production in the 1990s.[41] Coal consumption and Zn production increased by a factor of ~5 and Pb production by ~2 in South America between the two periods (Supporting Information, Figure S3).

As mentioned previously, it is suggested that the enrichments of Sb, Mo, and probably Tl observed in the snow resulted from emissions of these elements in South America. The primary anthropogenic sources of Sb emissions are nonferrous metal production (especially Cu and Pb smelting) and coal combustion.[1,37] By using previously reported median emission factors for the mid-1980s,[37] the average Sb emissions in South America (mostly from Chile) in the 1980s are estimated at ~200 tons yr^{-1} with the largest contribution from Cu production (~165 tons yr^{-1}). This implies that the common source for both As and Sb was Cu smelting processes and thus transport processes for these two elements were probably similar. A significant correlation coefficient (r^2 = 0.60) is observed for As and Sb concentrations in the snow, excluding the volcanic layers during the entire time period (Figure 3). The correlation coefficient increases to 0.86 when calculated for the time period between 1980 and 1999, during which greater enrichments are observed for both elements (Figure 3). Such a strong relationship and similar temporal changes in the As and Sb EFs support the idea that the transport and deposition behavior of As and Sb were similar due to major emissions of these elements from Cu smelting production in South America.

The consumption of coal and oil, primary sources of Mo emissions, in South America has continuously increased during the last few decades. Specifically, the coal and oil consumption in South America increased by factors of ~5 and ~2, respectively, between 1960−1964 and 1985−1989, respectively (Supporting Information, Figure S3). The observed temporal variation in the Mo EF appears to resemble the trends of coal and oil consumption rates with fairly constant enhancement of the EF during the 2000s. Interestingly, the EF of airborne Mo in Santiago showed no significant decrease (from ~1060 to
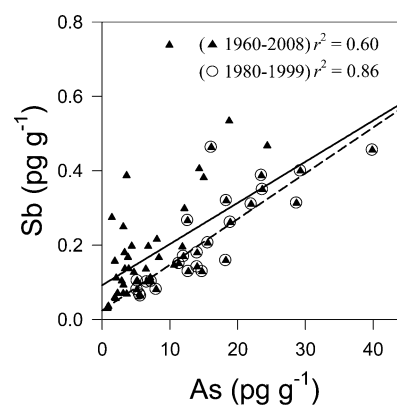
Figure 3. Comparison of correlation coefficients between As and Sb concentrations in the snow samples during the time periods 1960−2008 (full triangles) and 1980−1999 (open circles). Linear regression lines are indicated by a solid line for concentrations from 1960 to 2008 and a dashed line for concentrations from 1980 to 1999.

~940) between 1997−1999 and 2000−2003,[39] reflecting a less-significant reduction in the emissions of Mo from fossil fuel combustion in South America.

Coal combustion is the exclusive source of Tl emissions into the atmosphere, with average Tl emissions of ~1 ton yr^{-1} from South America in the 1990s.[1] Compared to worldwide Tl emissions of ~1800 tons yr^{-1} during the same period,[1] the Tl emissions from South America were quite small. This probably explains the negligible enrichment of Tl in the snow samples in the central Antarctic Plateau. However, a significant increase (a factor of ~2) in the EF of this element between 1980 and 1984 may be related to anthropogenic Tl emitted from coal combustion in South America.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Figures showing the location of sampling sites in Antarctica and volcanoes, and changes in nonferrous metal production and coal and oil consumption rates in different source region, and tables summarizing mean concentration and EF values during specific time periods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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