

Persistent Pb Pollution in Central East Antarctic Snow: A Retrospective Assessment of Sources and Control Policy Implications

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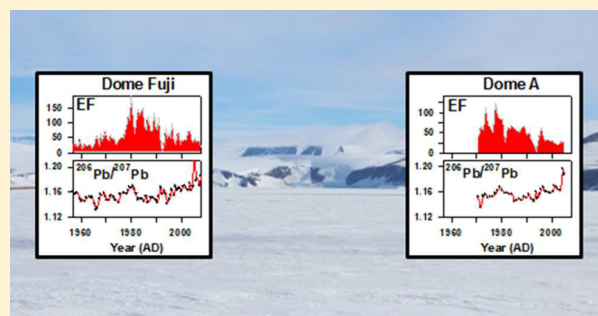
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S Supporting Information

ABSTRACT: Well-defined variations in the enrichments and isotopic compositions of Pb have been observed in snow from Dome Fuji and Dome A in the central East Antarctic Plateau (EAP) over the past few decades. The Pb isotopic fingerprints indicate that the rapid increase in Pb enrichments from the mid-1970s, reaching a peak in ~1980, is due to the massive use of leaded gasoline in northern South America, especially Brazil. Since then, they show a continuous decline, mostly due to the significant removal of the Pb additives from gasoline in Brazil in the 1980s and, subsequently, in Argentina and Chile in the 1990s. After the phase-out of Pb in gasoline, Cu smelting in Chile has become the major source of Pb, contributing ~90% to the total Pb emissions in northern South America in 2005. Nevertheless, Pb pollution in the central EAP declined substantially until recently as a result of the regulatory efforts to curb toxic trace metal emissions from the Cu industry in Chile. However, more than 90% of the Pb in the most remote places on Earth are still of anthropogenic origin, highlighting the need for the continuation of environmental regulations for the further reduction of Pb emissions.



1. INTRODUCTION

Lead (Pb), a highly toxic metal, has become widely distributed and mobilized in the environment, and exposure to and uptake of this nonessential element remain a global concern because of a public health issue of continuing importance.¹ Greenland snow and ice records have clearly demonstrated that the most prominent hemispheric-scale atmospheric Pb pollution in the Northern Hemisphere is undoubtedly due to the massive consumption of leaded gasoline in the second half of the 20th century.^{2–6} These records showed a remarkably similar trend, consisting of a dramatic increase in atmospheric Pb deposition in the late 1960s and a subsequent decline following the phase-out of leaded gasoline in North America and Europe. Recent Pb concentrations in central Greenland snow are observed to be more than 2 times the preindustrial level, due to the significant and lasting contribution from anthropogenic sources, such as coal combustion and smelting processes, especially in China.^{6,7}

In comparison, the timings of the Pb maxima linked to the rise and fall in the use of leaded gasoline in the Southern Hemisphere are observed to differ between sites: the late 1970s to 1980s at the near coastal Antarctic site (Coats Land) of the Atlantic sector,^{8–10} the late 1980s at the coastal sites of the Pacific sector (Victoria Land), and possibly of the Indian sector

(Law Dome).^{11–13} Very recently, a composite Pb record from an extensive array of 16 ice cores across Antarctica was reported, which showed a rapid increase in Pb concentrations up to 1975 and a sustained increase until the mid-1990s.¹⁴ On the other hand, substantial changes in the relative contributions from two source regions, South America and Australia, were proposed to be linked to the sampling locations close to each source region affecting the transport pathways of pollutants to the site on the basis of Pb isotopic signatures.^{12,13,15} However, recent work suggested that Australia was consistently responsible for the anthropogenic Pb deposited over the whole of Antarctica during the past 130 years.¹⁴

The lack of well-established time-dependent features in the deposition and sources of anthropogenic Pb reaching Antarctica over time has made it difficult to establish a quantitative baseline in relation to the environmental regulations designed to reduce the emissions of Pb into the atmosphere since the introduction of alkyl-lead additives in

Received: June 28, 2016

Revised: October 12, 2016

Accepted: October 13, 2016

Published: October 14, 2016

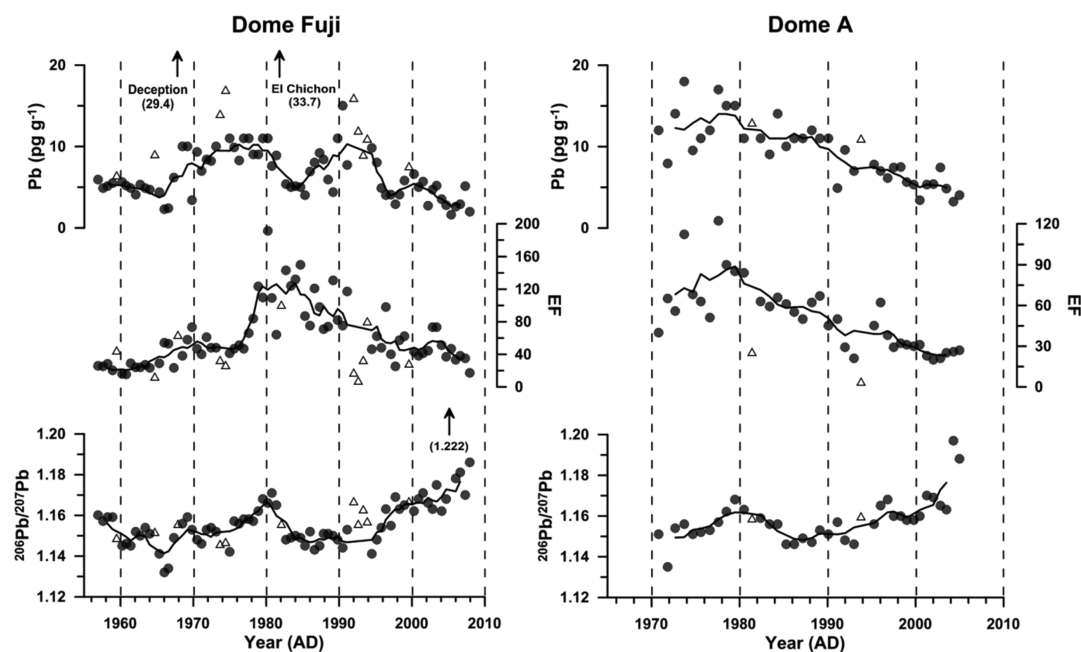


Figure 1. Changes in Pb concentrations, crustal EFs, and $^{206}\text{Pb}/^{207}\text{Pb}$ in the snow from Dome Fuji and Dome A in the central East Antarctic Plateau. Open triangles represent the values determined in volcanic layers possibly related to prominent volcanic events (see text and [Supporting Information](#), Tables S1 and S2). Solid lines represent the five-running average after excluding individual values that are likely associated with the possible volcanic layers.

gasoline in the Southern Hemisphere. Herein, we present detailed temporal records of the atmospheric fallout of Pb and its isotopic signatures in two inland sites, Dome Fuji and Dome Argus, in East Antarctica over the past few decades, during which time the consumption of leaded gasoline has become the major contributor to anthropogenic Pb released into the atmosphere in the Southern Hemisphere. The main objective is to identify the main sources of Pb reaching the central East Antarctic Plateau (EAP) during the period investigated, which to some extent reflect the effectiveness of national regulations in reducing the atmospheric Pb level throughout the Southern Hemisphere.

MATERIALS AND METHODS

Sample Description. The samples were collected at Dome Fuji ($77^{\circ}18' \text{ S}$, $39^{\circ}47' \text{ E}$; elevation: 3785) and Dome Argus (hereafter referred to as Dome A; $80^{\circ}22' \text{ S}$, $77^{\circ}21' \text{ E}$; elevation: 4093) in the central EAP ([Supporting Information](#), Figure S1). The sampling site at Dome Fuji, the second highest dome in Antarctica, was ~ 1000 km from the coast, and that at Dome A, the highest summit of East Antarctica, was ~ 1200 km away from the nearest coast. At Dome Fuji, a continuous series of 80 samples was obtained at a 5 cm interval from a 4-m-deep pit by horizontally pushing an ultraclean cylindrical Teflon container (5 cm in diameter, 35 cm in length) in December 2007 during the Japanese–Swedish IPY Antarctic expedition. At Dome A, a total of 40 snow samples at Dome A were collected from the surface to a depth of 2 m in a snow pit when a Chinese team first stepped onto the summit of Dome A in January 2005 during the 2004/05 Chinese Antarctic Research Expedition. Great precautions were taken during the collection, handling, and storage of the samples, according to the methodology previously reported, in order to minimize the possibility of the snow becoming contaminated.^{15,16}

Sample Preparation and Analysis. All sample handling and ultraclean procedures were performed under a Class 10 laminar airflow bench or booth in clean laboratories (Class 1000) at the Korea Polar Research Institute (KOPRI) as described in detail elsewhere.¹⁶ Briefly, ~ 10 g of the sample was evaporated to dryness with a mixture of 10 μL of 65% HNO_3 (Fisher “Optima” ultrapure grade), 20 μL of 48% HF (Merck “Ultrapur” grade), 4 μL of dilute H_3PO_4 (Merck “Suprapur” grade; $\sim 5\%$ by weight), and 10 μL of a ^{205}Pb tracer on a Teflon-coated hot plate at ~ 80 $^{\circ}\text{C}$. A drop of PL-7 silica-gel activator was then dropped into the evaporated residue, and the sample and silica-gel mixture were transferred to a degassed (4 A, 30 min), zone-refined rhenium filament (99.999% Re, 0.7 mm wide, 0.04 mm thick, H. Cross Company). The samples were then analyzed using a thermal ionization mass spectrometer (TIMS; TRITON, Thermo Scientific) fitted with a 23 cm radius, 90° magnetic sector containing a 21-sample carousel at KOPRI. The addition of the ^{205}Pb enriched tracer to the sample enabled both the Pb concentration (by isotope dilution mass spectrometry, IDMS) and Pb isotopic composition to be determined in the same aliquot. Our ultraclean analytical procedures ensured an accuracy of less than 10% (95% confidence interval) for the concentrations and a precision of $\sim 0.28\%$ and $\sim 0.20\%$ for the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios, respectively, for a few tens of picograms of Pb, allowing for the reliable and simultaneous determination of the concentrations and isotopic ratios of Pb at the extremely low concentrations encountered in Antarctic snow and ice samples.¹⁶

The Ba concentrations were measured by an inductively coupled plasma sector field mass spectrometer (ICP-SFMS; Element2, Thermo Scientific), coupled with an APEX micro-nebulization desolvation system (APEX IR, HF, ESA, USA).¹⁷ The detection limit, defined as 3 times the standard deviation of the blank, was 0.2 pg g^{-1} , and the analysis of a certified riverine

Table 1. Summary of Pb Concentrations (pg g^{-1}), Crustal Enrichment Factors, $^{206}\text{Pb}/^{207}\text{Pb}$ Ratios, and Mean Values (in Parentheses) in Our Snow Pit Samples and Comparison with the Previous Data Obtained at Various Locations^a

location	period	elevation (m)	accumulation rate ($\text{g cm}^{-2} \text{ yr}^{-1}$)	Pb	EF	$^{206}\text{Pb}/^{207}\text{Pb}$	ref
Dome Fuji (77°18' S, 39°47' E)	1956–2007	3785	2.5	1.6–34 (7.6)	8–191(59)	1.132–1.223 (1.157)	this work
				<i>1.6–15 (6.4)</i>	<i>15–191 (61)</i>	<i>1.132–1.223 (1.157)</i>	
Dome A (80°22' S, 77°21' E)	1969–2004	4093	2.3	3.2–18 (9.4)	4–122 (49)	1.135–1.197 (1.158)	this work
				<i>3.2–18 (9.3)</i>	<i>20–121 (52)</i>	<i>1.135–1.197 (1.158)</i>	
NUS07–5 (78°39' S, 35°38' E)	1956–1988	3619	2.7	2.4–22.9 (6.6)	12–110(35)		14
NUS07–7 (82°4' S, 54°53' E)	1969–2007	3725	2.9	5.8–19.2 (10.3)	23–110(63)		14
South Pole (90° S, 0°0' E)	1956–1994	2800	6.4	3.3–19.4 (9.0)	15–138(47)	1.133–1.228 (1.183)	14
NUS08–4 (82°49' S, 18°54' E)	1956–2008	2552	3.7	2.9–18.7 (7.7)	16–199 (62)	1.054–1.489 (1.187)	14
NUS08–5 (82°38' S, 17°52' E)	1956–1999	2554	3.7	4.2–19.8 (7.5)	18–186 (66)	1.054–1.695 (1.214)	14
B40 (75°12' S, 0°4' E)	1956–2010	2892	6.2	1.1–24.1 (6.5)	9–169 (39)	1.053–1.322 (1.168)	14
Law Dome (66°46' S, 112°21' E)	1956–1989	1370	16	0.88–7.0 (2.4)	13–59(33)	1.100–1.168 (1.150)	12
Coats Land (77°34' S, 25°22' W)	1958–1990	1420	5.6	0.1–9.3 (3.5)	2–164 (51)	1.101–1.165 (1.139)	10
Victoria Land (73°52' S, 163°42' E)	1957–1994	1700	16	1.5–21.2 (6.6)	4–92 (32)	1.104–1.193 (1.161)	13

^aFor Dome Fuji and Dome A, the values excluding those measured in the possible volcanic layers are shown in italic type (see text).

water reference material (SLRS-5 by the National Research Council of Canada, Ottawa) agreed very well with the certified value (13.7 ± 0.2 versus $14.0 \pm 0.5 \text{ ng g}^{-1}$). The ionic species (Na^+ , F^- , Cl^- and SO_4^{2-}) were simultaneously analyzed using 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%.¹⁷

Dating of the Samples. On the basis of the well-identified large volcanic depositions from Mt. Pinatubo (1993–1994), Mt. Cerro Hudson (1991–1992), Mt. El Chichón (1982–1983), and Mt. Agung (1964–1965), the chronology for the samples at Dome Fuji was previously estimated to cover ~51 years (1957–2007), with a mean annual accumulation rate of $\sim 8 \text{ cm year}^{-1}$ (~ 8 months per depth interval and 2.5 cm water equivalent per year, w.e.y.⁻¹).^{17–19} For Dome A, the chronology from the snow surface to the depth of 80 cm was deduced from the strong non-sea-salt SO_4^{2-} (nss- SO_4^{2-}) and Ba peaks, which acted as volcanic SO_2 and ash indicators at depth intervals of 75–80 cm and 135–140 cm, corresponding to the Pinatubo/Cerro Hudson and El Chichon volcanic signals, respectively (Supporting Information, Figure S2). Below a depth of 80 cm, the dating was made using the β activity peak observed at a depth of 220–240 cm in the snow blocks, which were coincidentally collected at the same site on Dome A during our snow pit sampling.²⁰ This β activity peak corresponds to the snow layer of 1964 and 1965 A.D.²¹ Combining the well-defined volcanic signals and β activity peak, the dating from the surface down to a depth of 2 m was estimated to span a 36 year time period from 1969 to 2004. Together with the density-depth profile, the estimated mean accumulation rate is $\sim 5.5 \text{ cm year}^{-1}$, corresponding to ~ 1 year

per depth interval and 2.3 cm w.e.y.⁻¹, a value virtually comparable to those at the other Antarctic inland sites.²⁰

RESULTS AND DISCUSSION

Overview of Pb Concentrations. Figure 1 shows the Pb concentrations and Pb isotopic ratios determined from the two snow pits at Dome Fuji (1957–2007) and Dome A (1969–2004). The concentrations of Pb are in the ranges of 1.6–34 and 3.2–18 pg g^{-1} at Dome Fuji and Dome A, respectively, with a slightly higher mean value at the latter (9.4 pg g^{-1}) than at the former (7.6 pg g^{-1} ; Table 1). The ratios of the maximum to minimum Pb concentrations are ~ 21 and ~ 6 for Dome Fuji and Dome A, respectively. The strong variability at Dome Fuji may be partly due to the short-term (intra-annual) variations resulting from the relatively higher sampling frequency (less than a year per depth interval) at Dome Fuji than that (\sim a year per depth interval) at Dome A, as previously observed in Antarctic snow (Supporting Information, Tables S1 and S2).^{22,23}

The significant depositions of Pb might originate from known volcanic eruptions during the time period investigated.²⁴ Previous studies identified volcanic signals from large volcanic eruptions by combining various volcanic peaks such as nss- SO_4^{2-} , Ba, and volcanogenic Pt in the snow pit at Dome Fuji.^{17,18} As shown in Figure S2 of the Supporting Information, these peaks correspond to the volcanic layers of the Pinatubo (15° N, 1993–1994) and Cerro Hudson (45.5° S, 1991–1992), El Chichon (17° N, 1982–1983), Ngauruhoe (37° S, 1974), Deception Island (62.5° S, 1967–1970), Agung (8° S, 1964–1965), and Cordon Caulle (40.5° S, 1960). Besides these volcanic events, possible volcanic depositions from Mt. Erebus (77.55° S, 167.17° E), the world's southernmost active volcano, located on Ross Island, Antarctica, were also assigned in the Dome Fuji snow pit according to the peaks in the main halogen

components (F^- and Cl^-) enriched in volcanic plumes (Supporting Information, Figure S2).^{17,18,25} By comparison, no volcanic fallout from events in Ngauruhoe (1974) and Deception Island (1967–1970) were observed for Dome A, while the signals from eruptions in Pinatubo/Cerro Hudson and El Chichon are preserved in the snow pit (Supporting Information, Figure S2). The discrepancy between these two sites could be due to the different atmospheric circulation patterns prevailing in different locations of the Antarctic Plateau and/or postdepositional processes such as wind erosion.^{26,27} We did not estimate the contribution of volcanic eruptions to Pb deposition in the central EAP, because it is beyond the scope of our study.

After excluding the individual data points of the possible volcanic layers (Supporting Information, Tables S1 and S2), the five-point running average shows the well-established temporal changes in the Pb concentrations as a function of the age of the snow (Figure 1). At Dome Fuji, an increase in their concentrations started in the mid-1960s, and they remained high during the 1970s, reaching a maximum of $\sim 11 \text{ pg g}^{-1}$ in the late 1970s. The Pb concentrations show a dip to $\sim 6 \text{ pg g}^{-1}$ in the early 1980s and a second maximum with a mean concentration of $\sim 11 \text{ pg g}^{-1}$ comparable to the previous maximum level. Since then, a clear decrease in Pb concentrations is observed from the mid-1990s, with the lowest mean value of $\sim 4 \text{ pg g}^{-1}$ being observed in the 2000s, which is lower than those in the mid-1950s to early 1960s (Supporting Information, Table S1). By comparison, the Pb profile at Dome A displays a pronounced concentration peak with a significantly higher value of up to $\sim 18 \text{ pg g}^{-1}$ (mean value of 13 pg g^{-1}) in the 1970s and then a continuous decline from the early 1980s onward, approaching a mean of $\sim 5 \text{ pg g}^{-1}$ in the 2000s (Figure 1 and Supporting Information, Table S2).

The peaks observed at both sites are generally similar to the pattern of the composite Pb record from an extensive array of 16 ice cores in Antarctica, showing a peak in the 1970s and a sustained increase until the mid-1990s.¹⁴ However, differences in the peaks are observed from site to site. For example, a peak in the Pb concentrations is observed in the late 1970s to early 1980s in Coats Land and in the mid-1980s to late 1980s in Victoria Land.^{8–11,13} This difference was attributed to the different contributions of anthropogenic Pb from either South America or Australia at different locations in Antarctica.

When compared to the few reliable natural Pb concentration values (0.15–0.47 pg/g) previously obtained from Dome C Holocene ice (~ 2010 to 7600 years BP) in the East Antarctic Plateau, for which the mean snow accumulation rate is similar to those at our sites,^{28,29} the lowest Pb concentration levels observed at both sites in recent years are still an order of magnitude above the natural Holocene level.

Changes in Crustal Enrichment Factors. The changes in the crustal enrichment factors (EF) of Pb as a function of the age of the snow are shown in Figure 1. The EF is defined as $EF = [Pb/Ba]_{\text{snow}}/[Pb/Ba]_{\text{crust}}$, where $[Pb/Ba]_{\text{snow}}$ and $[Pb/Ba]_{\text{crust}}$ refer to the concentration ratios of Pb to Ba in the snow and in the mean upper continental crust,³⁰ respectively. EF values close to unity indicate that the Pb in the snow is derived primarily from the continental crust, while values larger than unity indicate that there are significant contributions from other natural or anthropogenic sources.

The EF values at Dome Fuji range from 15 to 191 with an average of 61 after excluding any individual EF values that are likely associated with known large volcanic eruptions (Table 1).

The profile is characterized by a very well-defined change during the past 50 years (Figure 1). Following the continuously increasing pattern from ~ 25 to ~ 45 between the mid-1950s and mid-1970s, the EF values show a dramatic increase, rising up to 191 at ~ 1980 . Very high EF values (mean value of 127) are observed from the late 1970s to the early 1980s. A pronounced and continuous decline is then observed from the mid-1980s onward. The mean EF value (44) in the 2000s is observed to be still 2 times higher than the lowest mean EF value (23) observed between 1956 and the mid-1960s. At Dome A, the EF values vary from 20 to 121 with a mean value of 49 without including the values in volcanic layers (Table 1). The EFs at Dome A are slightly lower than those at Dome Fuji during the corresponding time interval. The EF profile reveals a pronounced increase in the mid-1970s, reaching a peak with an average value of ~ 95 in the late 1970s. The EF values subsequently declined and dropped down to ~ 25 in the 2000s (Figure 1). Our EF values are generally comparable to those previously published from different sites for the last several decades (Table 1). Considering the few reliable natural Holocene EF values (~ 1),^{28,29} it is thought that only a small amount (~ 2 –4%) of the Pb deposited in the central EAP in the 2000s is of crustal origin.

The EF peaks in ~ 1980 at Dome Fuji and Dome A are in good agreement with that observed at Coats Land,^{9,15} while they are observed in the late 1980s in Victoria Land¹³ and at the sites NUS07–5 and NUS07–7 in the central EAP¹⁴ (Supporting Information, Figure S1).

Despite this difference, it can be concluded that the dramatic increase in the EFs in the second half of 20th century was undoubtedly due to the very large rise in the use of leaded gasoline in the Southern Hemisphere as reported in previous studies.^{8–15} However, the relative contributions from two major source regions, South America and Australia, for anthropogenic Pb aerosols reaching Antarctica were proposed to be linked to the locations close to each source region.^{8–15} A crucial clue to the identification of potential contributors to anthropogenic Pb deposited in the central EAP will now be discussed in the following sections.

Changes in $^{206}\text{Pb}/^{207}\text{Pb}$ Ratios. The changes in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios over time are displayed in Figure 1. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios vary from 1.132 to 1.186 (excluding an abnormally high value of 1.223 observed at the 20–25 cm depth interval, Supporting Information, Table S2) at Dome Fuji and from 1.135 to 1.197 at Dome A with very similar average values of 1.156 and 1.158, respectively (Table 1). These $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are apparently less radiogenic in comparison to the natural Holocene values of ~ 1.2 in central Antarctic ice.²⁹ The relatively low radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and high EF values observed in our records suggest that Pb deposited in the central EAP during the time period investigated is mostly of anthropogenic origin.

In Figure 1, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios at both sites show a significant increase from the mid-1970s to ~ 1980 , before subsequently decreasing. During the period between the mid-1980s and the mid-1990s, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios remained relatively low (average ~ 1.15). A pronounced increase in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios is then observed from the mid-1990s to recent years, in parallel with the steady decrease in the anthropogenic Pb inputs, as reflected by the Pb concentrations and EFs during the corresponding time period (Figure 1). The substantial variations in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios observed during

the whole period clearly indicate that there are changes in the major sources of anthropogenic Pb and/or the relative strengths of the natural and anthropogenic contributions to the Pb inputs in the central EAP, as discussed in the next section.

Provenance of Anthropogenic Pb in Central East Antarctica. Figure 2 shows the isotopic characteristics of a

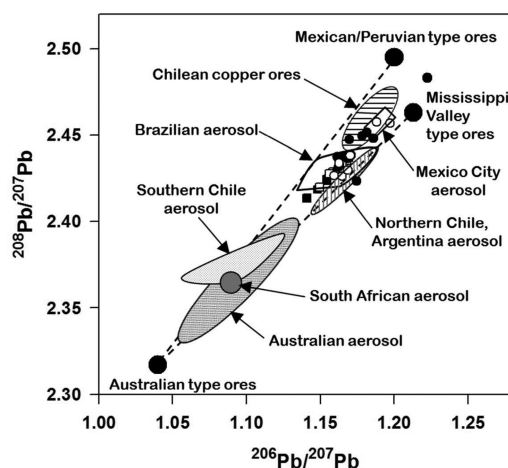


Figure 2. Pb isotopic compositions in snow from Dome Fuji (■) and Dome A (□) in 1994–1999 and Dome Fuji (●) and Dome A (○) in the 2000s. Also shown are various Pb ores,^{35–37} Chilean copper ores (shaded area),⁵¹ and aerosols from Brazil, Chile, Argentina, Mexico, South Africa, and Australia available for the period between 1994 and 1999.^{31–33}

three-isotope plot ($^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$) of the distinctive Pb isotopic fingerprint of airborne particles available for the period between 1994 and 1999 in the Southern Hemisphere.^{31–33} The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ values in aerosols are significantly lower in the southern region of the Southern Hemisphere (Australia, South Africa, and Southern Chile), while the ratios are relatively higher in the northern parts of South America (Brazil, Chile, and Argentina) and significantly higher in central America (Mexico). In South America, there is an increasing pattern of the isotopic ratios in the aerosols from south to north. This is especially the case in Chile. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are characterized by a distinct increase northward from Punta Arenas (1.063–1.081) via Villa Rica (1.069) and Concepción (1.103) to Santiago (1.150–

1.182). This pattern is probably due to either a relative increase in the industrial Pb emissions or different isotopic compositions of alkyl-lead additives used in different cities of the individual countries.³²

In order to trace the source region responsible for the anthropogenic Pb inputs to the central EAP, we compared the isotopic data of the Dome Fuji and Dome A snow samples spanning the period 1994–1999 with those in the aerosols. As shown in Figure 2, the isotopic compositions in the snow samples at both sites are distinguishable from those for the southern region of the Southern Hemisphere and Central America, while they are closer to those derived from the aerosol Pb isotopes from northern South America, especially Brazil. This indicates that the most important source of anthropogenic Pb reaching the central EAP is the anthropogenic emissions in northern South America. Because Brazil was a major contributor to anthropogenic Pb emissions to the atmosphere in the early 1980s, accounting for about half of the total Pb emissions from South America,³⁴ the sharp increase in the EFs in the snow from the mid-1970s to the early 1980s is presumed to be due to the large emission of Pb from leaded gasoline in Brazil. This hypothesis is supported by the changes observed in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in our samples during this period.

The alkyl-lead additives in gasoline determine the isotopic composition of Pb emitted by the combustion of leaded gasoline. Broken Hill (Australia) type Pb ores and Mississippi Valley (U.S.) type ores were the main Pb ores used by the world's two largest alkyl-lead suppliers, Associated Octel (U.K.) and Ethyl Corp. (U.S.).³² Australian type Pb ores have relatively low radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{208}\text{Pb}/^{207}\text{Pb}$) ratios of ~ 1.05 (~ 2.33),^{33,35,36} while Mississippi Valley type ores are marked by highly radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{208}\text{Pb}/^{207}\text{Pb}$) ratios of 1.281–1.396 (2.51–2.61) (Figure 2).³⁷ The alkyl-lead additives produced by Associated Octel were usually characterized by relatively low ratios (1.06–1.10 of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio) in the 1980s and 1990s, because Associated Octel used about 50–80% Australian Pb ores.³⁸ In comparison, the isotopic signature of the alkyl-lead additives provided by Ethyl Corp. comprised a relatively high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, because of the use of more radiogenic Mississippi Valley type Pb.⁵ The Pb isotopic variations in the air at the specific sites, which are strongly influenced by the Pb emissions from leaded gasoline, will therefore be determined by the market-share of the different alkyl-lead retailers.^{32,33} As shown in Figure 1, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios at Dome Fuji and Dome A show a similar trend moving

Table 2. Annual Emission Estimates of Pb from the Two Major Anthropogenic Sources (Leaded Gasoline Consumption and Cu Smelting Production) in Brazil, Argentina, and Chile (in tons year⁻¹)

year	leaded gasoline			Cu smelting ^d			national total			regional total
	Brazil ^a	Argentina ^c	Chile ^c	Brazil	Argentina	Chile	Brazil	Argentina	Chile	
1977	8211	1927	953	0	0	1732	8211	1927	2685	12 823
1980	5160 ^b	1256	1,054	0	0	1859	5160	1256	2913	9329
1985	2000	1029	976	183	0	2123	2183	1029	3099	6311
1990	858 ^b	1049	1,337	306	0	2591	1164	1049	3928	6141
1995	0	826	833	165	0	1666	165	826	2499	3490
2000	0	0	710	184	0	1460	184	0	2170	2354
2005	0	0	0	199	0	1558	199	0	1558	1757

^aFrom Paoliello and De Capitani.⁴² ^bThe values for 1980 and 1990 are the 1979 and 1988 data presented in ref 42, respectively. ^cEmission estimates were based on the consumption of gasoline (data from www.nationmaster.com: Sector-Transportation; Road Sector Gasoline Fuel Consumption) and lead contents in gasoline.⁵² ^dEmission estimates were based on the Cu production rates from British Geological Survey's World Mineral Statistics and Mineral Yearbook (U.S. Bureau of Mines) and the emission factors.^{53,54}

toward more radiogenic values when the EFs peaked between the mid-1970s and the early 1980s. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of gasoline used in Brazil was a relatively radiogenic value of ~ 1.2 , indicating the predominant use of alkyl-lead additives manufactured from the highly radiogenic Mississippi Valley type Pb in Brazil.³⁹ In contrast, leaded gasoline in Argentina and Chile was characterized by a relatively low $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (~ 1.06), because of the primary use of alkyl-lead supplied by Associated Octel, despite the fact that different alkyl-lead mixtures were supplied to different cities.^{32,40,41} Consequently, the increasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios from the mid-1970s to the early 1980s could be considered to support the hypothesis that the large increase in the EFs in the snow during the corresponding period is primarily due to the large emissions of Pb originating from the combustion of leaded gasoline in Brazil.

From the early 1980s, on the other hand, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios showed a prominent decrease and remained relatively low between the mid-1980s and the mid-1990s (Figure 1). The phase-out of lead from gasoline in Brazil started in 1975 as a consequence of the National Anhydrous Ethanol Program, promoting the use of anhydrous ethanol as automotive fuel.⁴² However, the amount of lead in gasoline began to substantially decrease in the 1980s, due to the elimination of tetraethyl lead, which was replaced by up to 22% of its volume by ethanol for ordinary gasoline after a regulatory disposition (Resolution 14/79) was issued in 1979. The total amount of alkyl-lead added to gasoline in Brazil decreased from 5160 tons to 1044 tons between 1979 and 1987.⁴² This reduction in the use of leaded gasoline resulted in a rapid drop of up to 72 to 82% in the atmospheric Pb levels in the residential areas of Brazil during that period.⁴² As shown in Table 2, the Pb emissions from the combustion of leaded gasoline in Brazil fell significantly by a factor of more than 4 from 1980 to 1990, while those in Argentina and Chile remained on the same order of magnitude during this period. In Argentina and Chile, the use of Pb additives in gasoline was completely phased out in 1997 and 2001, respectively.^{43,44} When considering that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the Pb additives added to gasoline in Argentina and Chile were relatively low, due to the primary use of alkyl-lead supplied by Associated Octel as described above, the less radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ signatures observed in our snow samples from the mid-1980s to the mid-1990s appear to be a consequence of the continuous increase in the relative contribution of Pb emissions from the combustion of gasoline in Argentina and Chile.

Our assignment of northern South America as the most likely source differs from the very recent conclusion that the main source of the anthropogenic Pb deposited in the central EAP is Australia.¹⁴ However, this previous study identified the possible Pb sources using the semiquantitative ratios of ^{206}Pb and ^{207}Pb determined by the relatively low precision single collector inductively coupled plasma mass spectrometry (ICP-MS), as compared to TIMS which has the capability of measuring ^{204}Pb -based ratios at the low picogram per gram level.⁴⁵ This relatively low precision of the Pb isotopic ratios offered unusually high $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (1.3–1.7) in part of the core samples (Table 1), which are not expected even in the natural radiogenic isotopic ratios available from all Antarctic snow and ice records.²⁴ In addition to their use of a semianalytical approach, it must be noted that anthropogenic sources of Pb are not well characterized when using only two (^{206}Pb and ^{207}Pb) isotopes. Nonetheless, the possibility of a partial input of

Pb from Australia could not be excluded, because Australia was proposed as a potential dust source in East Antarctica.^{46,47} Subseasonal multiple records of changes in isotopic and elemental compositions in recent snow layers from different sites in East Antarctica will enable us to better understand spatially and temporally varying anthropogenic Pb sources and transport.

Shift in the Major Source of Pb. The continuous decrease in the EF values since the mid-1990s appears to be coupled with the trend moving toward more radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ values (Figure 1). Because a continuous decrease in Pb concentrations and EFs indicates a reduction of the anthropogenic inputs to the site, this feature could reflect the increasing influence of more radiogenic natural Pb ($^{206}\text{Pb}/^{207}\text{Pb} = \sim 1.20$).²⁹ As discussed above, however, only a small amount (less than 10%) of Pb in the 2000s is of natural origin, indicating that the contribution of natural Pb to the trend toward more radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ratios appears to be minor. Alternatively, we suggest that the temporal variations in the Pb isotopic ratios could be due to a shift in the major anthropogenic source(s) over time. This speculation is supported by the estimated Pb emissions from Cu production in Chile and changes in the Pb isotopic ratios in the post-1990s. As shown in Table 2, the contribution of Cu production in Chile to the total Pb emissions indeed increased from 20% in 1980 to $\sim 90\%$ in 2005. In Figure 2, most of the data points in the 2000s are characterized by a shift toward the isotopic composition of Chilean Cu ores with their more radiogenic values. The relative increase in the isotope ratios between the mid-1990s and 2000s is thus likely associated with the steady increase in the contribution of Pb emissions from Cu production in Chile, corresponding to the elimination of lead from gasoline in Argentina and Chile.

A few words should be said about possible contribution from Australia. The observed isotopic signatures toward more radiogenic ratios since the mid-1990s eliminate Australia and support northern South America as a potential source of anthropogenic Pb reaching the central EAP, because the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in Australian aerosols remained relatively low (1.044–1.126) between the mid-1990s and 2000s,³³ during which the introduction of unleaded gasoline and the phase out of leaded gasoline from the late 1980s to the beginning of the 2000s resulted in consequent reductions of Pb emissions.⁴⁸

Here, it is worth mentioning that the total Pb emissions in northern South America have significantly decreased since the mid-1990s, due to the significant reduction in Pb emissions from Cu production in Chile caused by the environmental regulations governing trace element emissions (especially As) from the copper industry over the past two decades (Table 2).⁴⁹ It is therefore likely that the substantially decreasing trends of Pb concentrations and EFs in the central EAP since the mid-1990s are a consequence of this decrease in the Pb emissions in northern South America. Similar temporal changes in the EFs for As and Sb, which are emitted largely from the Cu smelting processes, were also observed in Antarctic snow and ice records.^{17,50} Despite the effective regulatory efforts to curb toxic trace metal emissions from the Cu industry in Chile, our data show that more than 90% of the Pb deposited in the central EAP in recent years is still of anthropogenic origin. This highlights the need for the implementation and continuation of national and international regulations in order to further reduce the emissions of highly toxic trace elements resulting from

human activities and return to the preindustrial level of atmospheric Pb in the most remote areas on Earth.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.6b03209](https://doi.org/10.1021/acs.est.6b03209).

Figures showing the locations of Dome Fuji and Dome A and the other sampling locations referred to in the text and changes in concentrations of nss-SO_4^{2-} , F^- , Cl^- , and Ba measured in the two snow pits and tables of the data (PDF)

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Notes

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■ ACKNOWLEDGMENTS

We thank all field personnel for sampling during the 2007/08 Japanese-Swedish IPY Antarctic expedition and the 2004/05 Chinese Antarctic Research Expedition. This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2012R1A1A2001832 and NRF-2014R1A2A1A11050765). This work was also supported by a research grant (PE16010) from the Korea Polar Research Institute (KOPRI) in Korea, the Japan Society for the Promotion of Science (JSPS) research grant ((A) 20241007) in Japan, and the Chinese Academy of Sciences research grant (XDB03030101-4).

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