Seasonal patterns of heavy metal deposition to the snow on Lambert Glacier basin, East Antarctica

Soon Do Hur[a], Xiao Cunde[b], Sungmin Hong[a],[*], Carlo Barbante[c,d], Paolo Gabrielli[c], Khanghyun Lee[a], Claude F. Boutron[e,f], Yan Ming[g]

[a]*Korea Polar Research Institute, Songdo Techno Park, 7-50, Songdo-dong, Yeonsu-gu, Incheon 406-840, Korea*
[b]*Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Science, Lanzhou 730000, China*
[c]*Department of Environmental Sciences, University of Venice, Ca' Foscari, 30123 Venice, Italy*
[d]*Centre for Studies on Environmental Chemistry and Technology-CNR, University of Venice, Ca' Foscari, 30123 Venice, Italy*
[e]*Laboratoire de Glaciologie et Géophysique de l'Environnement, UMR CNRS 5183, B.P. 96, 38402, Saint Martin d'Hères Cedex, France*
[f]*Observatoire des Sciences de l'Univers et Unité de Formation et de Recherche de Physique, Université Joseph Fourier de Grenoble (Institut Universitaire de France), B.P. 68, 38041 Grenoble, France*
[g]*Polar Research Institute of China, 200128 Shanghai, China*

Abstract

Al, V, Mn, Fe, Cu, As, Cd, Ba, Pb, Bi and U were determined in a continuous series of 46 snow samples from a 2.3-m snow pit, covering the time period from austral spring 1998 to summer 2002, at a site on the east side of the Lambert Glacier basin in East Antarctica. Concentrations are very low for all metals and differ by orders of magnitude from one metal to another, with the mean concentrations ranging from $0.028 \, pg \, g^{-1}$ for Bi to $165 \, pg \, g^{-1}$ for Al. It is estimated that anthropogenic contributions are dominant for Cu, Pb and probably As, in the snow in our study area while the natural contributions from rock and soil dust, sea-salt spray and volcanic emissions account for most of the measured concentrations of the other metals. Our snow profiles show pronounced seasonal variations for Mn, As, Ba, Pb and Bi throughout the year, but a very different situation is observed between different metals. These observations suggest that heavy metals determined in our samples are controlled by different transport and deposition mechanisms related to physical and chemical alterations in the properties and sources of aerosol.
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1. Introduction

Antarctic snow and ice contain very valuable records for characterizing environmental changes in the atmosphere over time. Today, human activity is considered as a major parameter affecting the chemical composition in aerosol and its atmospheric cycles. Of particular concern is how to unravel man-induced changes in the atmospheric cycles of heavy metals entering the Antarctic atmosphere to improve our understanding of the impact of human activity in the Antarctic atmosphere.

*Corresponding author. Tel.: +82 32 2606140; fax: +82 32 2606109.

E-mail address: smhong@kopri.re.kr (S. Hong).

Recently, a reliable comprehensive time series was obtained to provide evidence of changing occurrences of various heavy metals from snow layers from Coats Land in the Atlantic Sector of Antarctica (Wolff and Suttie, 1994; Wolff et al., 1999; Planchon et al., 2002a), and from Victoria Land and the Law Dome in the Indian Ocean Sector (Vallelonga et al., 2002; Van de Velde et al., 2005). Such studies identified that large-scale pollution started in the most remote areas in the Southern Hemisphere for Pb as early as the 1880s and for other metals such as Cr, Cu, Ag, Bi and U since the beginning of the 20th century, with a rapid rise during recent decades.

Apart from full time trends at the decade to century level, it is necessary to investigate detailed aspects of the occurrence of heavy metals in Antarctic snow and ice for a better understanding of the behaviors of atmospheric heavy metals. This is because each heavy metal has different source(s) and transport pathways and thus, the deposition mechanisms are assumed to be different between various heavy metals.

Until now, however, there have been only a very few studies regarding short-term variations (inter- and intra-annual) of heavy metals in Antarctic snow and ice. Moreover, previous studies only followed a few metals covered in a sequence of snow pit samples over a shorter time period (for example, Suttie and Wolff, 1992; Hong et al., 2000b, 2002; Van de Velde et al., 2005), or for selected depth intervals from a sequence of snow blocks with relatively lower seasonal resolutions of each sub-sample throughout the year (Planchon et al., 2002b).

We present here the first complete data set on high-resolution intra-annual variations of 11 different elements in successive snow pit samples covering 3 full years of accumulation at a site with high snow accumulation in the Lambert Glacier basin (LGB), East Antarctica.

2. Experimental

2.1. Field sampling

In January 2002, a continuous series of 46 snow samples from a 2.3-m deep shallow pit was collected at a site (70°50′07″S, 77°04′29″E, elevation 1850 m, 160 km from the coast) on the east side of LGB (Princess Elizabeth Land) in East Antarctica during the 2001/2002 Chinese Antarctic Research

Expedition (Fig. 1). Great precautions were taken in the field to prevent the possibility of snow contamination. A snow pit was sited 100 m upwind of the traverse track and hand-dug by operators wearing full clean room garments and polyethylene gloves with acid-cleaned plastic shovels. About 10 cm of snow were then shaved away from the upwind wall using acid-cleaned ultraclean low-density polyethylene (LDPE) scrapers. The snow samples were collected at a 5-cm interval by horizontally pushing an ultraclean cylindrical Teflon container (5 cm in diameter, 35 cm in length) and then pouring the snow into an ultraclean 500 mL LDPE bottle. All items used for the sampling were extensively cleaned as described in detail in Hong et al. (2000a). The bottles were packed in double-sealed acid-cleaned LDPE bags and kept frozen until analysis.

2.2. Analytical procedures

V, Mn, Fe, Cu, As, Cd, Ba, Pb, Bi and U were determined at the Department of Environmental Sciences in Venice by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) using an Element 2 instrument from Thermo Electron Corporation (Bremen, Germany) using a micro-flow ($<100\,\mu l\,min^{-1}$) PFA nebulization system. Working conditions and measurement parameters are described in detail elsewhere (Planchon et al.,
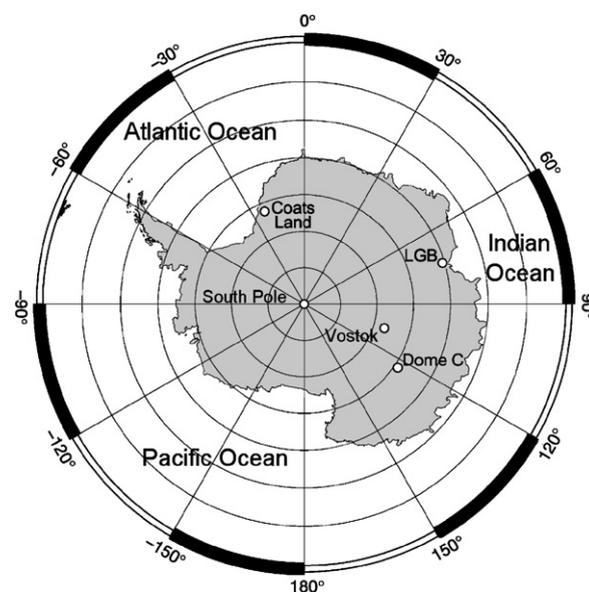

Fig. 1. Schematic map of Antarctica showing the location of the snow sampling on Lambert Glacier basin (LGB), East Antarctica and other sampling sites discussed in the text.

2001; Gaspari et al., 2006). The overall precision of the data was found to range from 5% for Pb to 20% for As at the lowest levels of sample concentrations (Planchon et al., 2001).

Al, Na, Cl, methane sulfonic acid (MSA), SO_4^{2-} and NO_3^- were determined at the Korea Polar Research Institute. For Al, the samples were preconcentrated (by a factor of ~40) by non-boiling evaporation (Görlach and Boutron, 1990) and then measured by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) using a Perkin Elmer 4110ZL instrument equipped with a Zeeman background corrector (Hong et al., 2000a). The precision is estimated to be better than 5% for the highest concentrations (Hong et al., 2000a). Na, Cl, MSA, SO_4^{2-} and NO_3^- were measured by ion chromatography (IC) with Dionex column AS 11 for anions and CS 14 for cations. Analytical precision is in the range between 5% and 10%.

2.3. Dating of the samples

The snow samples were dated by vertical profiles of oxygen isotopes ($\delta^{18}O$), MSA and NO_3^- which all showed very strong seasonal changes in concentration. The value of $\delta^{18}O$ is primarily dependent on the mean air temperature at the deposition site with less negative values in summer. MSA apparently peaks in the Antarctic aerosol and snow in the summer period with relation to dimethylsulfide

(DMS) emission from the marine biota and its oxidation (Mulvaney et al., 1992; Minikin et al., 1998). For NO_3^-, its maximum is observed in the Antarctic aerosol between spring and mid-summer (Wagenbach et al., 1998b), and despite the possibility of post-depositional alteration, a similar seasonal signal remains in snow deposited in the central plateau (Mayewski and Legrand, 1990) and at the coastal sites of Antarctica (Mulvaney et al., 1998).

In our snow samples, the maxima of $\delta^{18}O$ values are found at 0–5, 35–40, 90–100 and 175–180 cm and the minima at 25–30, 55–60 and 130–135 cm depth intervals, respectively (Fig. 2). The well-defined MSA peaks coincide well with the $\delta^{18}O$ maxima at 90–100 and 175–180 cm. The coincident summer peaks for both species support that depth intervals at 90–100 and 165–180 cm correspond to summer snow layers. However, at 0–5 and 35–40 cm depth intervals, MSA does not show a pronounced peak. However, a relatively weak but distinct peak at 10–20 cm and a large peak at 35–45 cm for NO_3^- are observed and both $\delta^{18}O$ and NO_3^- peaks are clearly in-phase (Fig. 2), indicating that these depth intervals can be assigned to distinctive spring and summer layers, respectively.

Taking into account that snow samples were collected in January 2002, we thus assign the $\delta^{18}O$ peaks at around 0–5, 35–40, 90–100 and 175–180 cm to 2002/2001, 2001/2000, 2000/1999 and 1999/1998

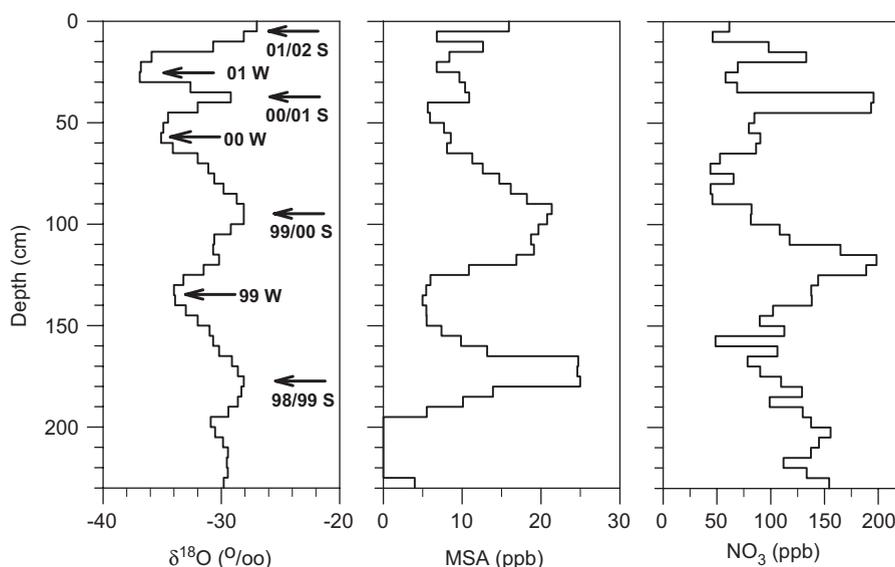Fig. 2. Depth profiles of $\delta^{18}O$, MSA and NO_3^- concentrations measured in snow pit samples from LGB in East Antarctica. S indicates the maxima of $\delta^{18}O$ values in summer and W indicates the minima of $\delta^{18}O$ in winter in the snow pit samples during the time period 1998−2002.

austral mid-summer layers, respectively. The stake measurement made between January 1999 and 2002 clearly supports our assignment of the dating (Xiao et al., 2005).

3. Results and discussion

3.1. Presentation and characteristics of the data

The concentrations of 11 metals measured in each depth interval are listed in the table and given as electronic supplementary information. Fig. 3 shows that the concentration levels are found to be very low for all metals as expected from previous data obtained in recent snow deposits in Antarctica (Planchon et al., 2002a, b). The lowest concentration is as low as $0.007\,\text{pg}\,\text{g}^{-1}$ for Bi. For each metal, however, the concentration levels are highly variable with depth and differ by orders of magnitude

from one metal to another (Fig. 3). Table 1 gives a summary of the statistics for the observed concentrations. From the ratios between maximum and minimum concentrations for each metal, we can see that for most of the metals there is a strong variability in concentration. This is especially the case for V, Mn and Fe, for which the highest concentrations are approximately 20–50 times higher than the lowest concentrations. Meanwhile, mean concentrations range from $0.028\,\text{pg}\,\text{g}^{-1}$ for Bi to $165\,\text{pg}\,\text{g}^{-1}$ for Al (Table 3), indicating that a large difference in concentration from one element to another occurs. Our data confirm that the transport and subsequent deposition processes of each different metal to LGB Antarctic snow is more complex than what was previously found elsewhere in Antarctica (Suttie and Wolff, 1992; Hong et al., 2000b, 2002; Planchon et al., 2002b; Van de Velde et al., 2005).
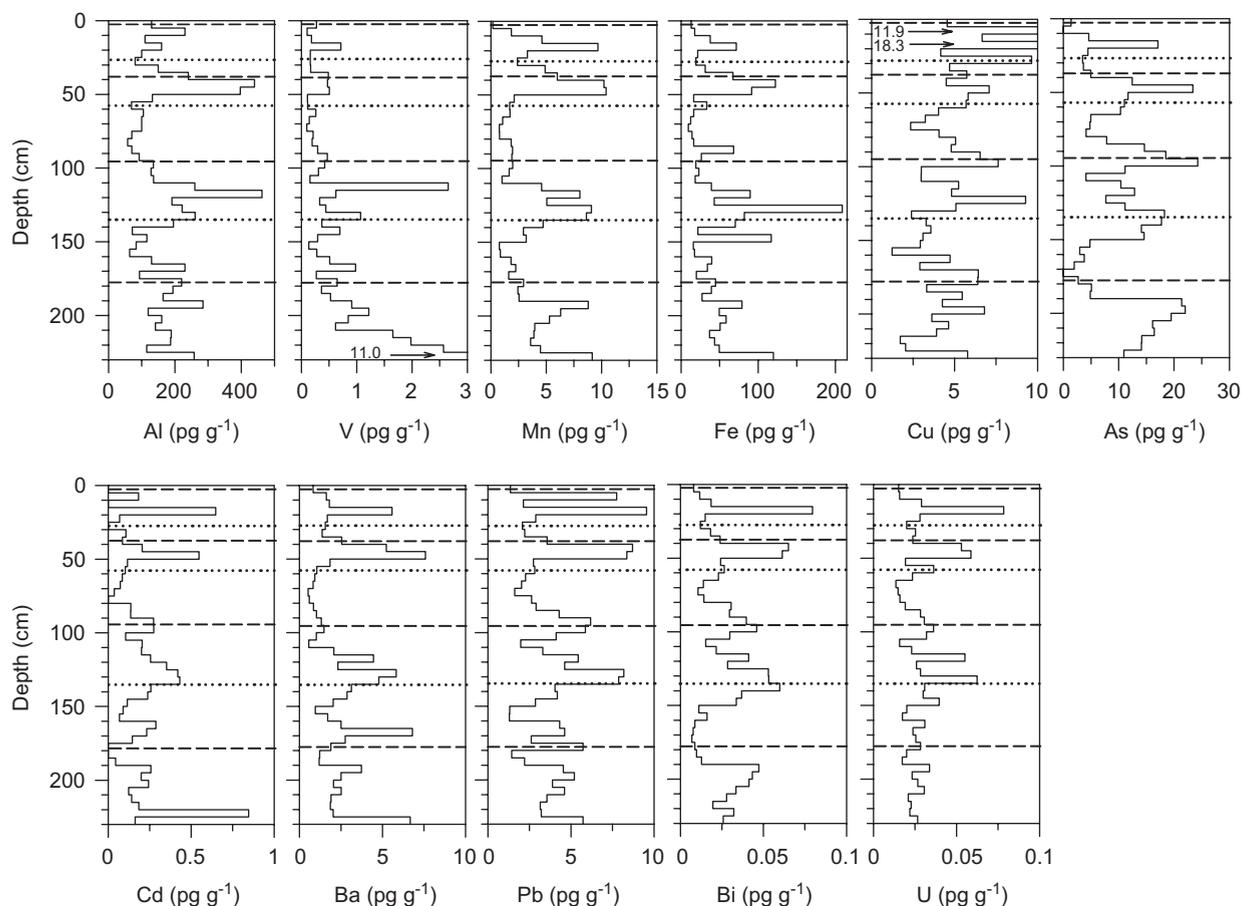

Fig. 3. Depth profiles of Al, V, Mn, Fe, Cu, As, Cd, Ba, Pb, Bi and U measured in our snow pit samples from LGB in East Antarctica. Thick dotted lines represent the maxima of $\delta^{18}\text{O}$ values in summer in the snow pit samples, while thin dotted lines represent the minima of $\delta^{18}\text{O}$ in winter as indicated in Fig. 2.

3.2. Comparison with concentration level observed from previous studies

The only reliable data set for multi-element measurements is the snow record given from the analysis of a series of the snow blocks and snow cores dated from the early 1830s to 1986, which was collected at a site in Coats Land (Planchon et al., 2002a). We thus compared our mean concentration values with the average values covering a relatively recent time period (1965–1986) from this only previous reliable data (Table 2). It should be noted that this comparison must be tentative, because of large differences in geographic properties between the two different sampling sites, time periods investigated and inter- and intra-annual variations in concentrations possibly observed in both data sets.

As shown in Table 2, the mean concentration values between the two sites are in good agreement

for V, Cu, Cd, Ba, Pb and to a lesser extent for U, despite differences in various factors mentioned above. For Al, Mn and Bi, on the other hand, our values are more than two-fold lower than those of the Coats Land data. This difference is probably due in part to snow accumulation rate, since the snow accumulation rate at our site is much higher than that at Coats Land. Concerning the As concentration level, we cannot assess whether its concentration level in our samples is comparable to those in other parts of Antarctica because there is no previous data on As from recent Antarctic snows. Holocene As levels obtained from the Vostok and Dome C ice cores range from 2 to $4 \, pg \, g^{-1}$ (Gabrielli et al., 2005a, b). The present-day snow accumulation rates ($\sim 2.5 \, g \, cm^{-2} \, yr^{-1}$) at Vostok and Dome C on the East Antarctic plateau are much lower than those at our site. Since the heavy metal concentrations at sites with higher snow accumulation rates are expected to be lower, our As concentration level, as expected, is much higher compared to the natural As level throughout Antarctica.

3.3. Estimates of natural and anthropogenic contributions

In order to differentiate the relative magnitudes of natural and anthropogenic contributions for our snow samples, we first investigated the possible magnitude of contributions from different natural sources including rock and soil dust, sea-salt spray, volcanic emissions, wild forest fires, and continental and marine biogenic activities (Nriagu, 1989).

The contributions from rock and soil dust were calculated from Al concentrations measured in each sample and the mean metal/Al ratios in the upper crust (Wedepohl, 1995).

Table 1
A statistical summary of heavy metal concentrations determined in 46 snow samples from a 2.3-m pit on Lambert Glacier basin in East Antarctica

Metal	Concentration (pg g-1)		
	Min	Max	Max/Min
Al	58	462	8
V	0.10	11	27
Mn	0.17	10	52
Fe	9.3	209	23
Cu	1.23	18	15
As	1.41	24	17
Cd	0.04	0.85	16
Ba	0.52	7.6	15
Pb	1.29	9.6	7
Bi	0.007	0.080	11
U	0.014	0.078	6

Table 2
Comparison of heavy metal concentration values in recent Antarctic snow

Location	Distance from the coast (km)	Altitude (m)	Accumulation rate ($g \, H_2O \, cm^{-2} \, yr^{-1}$)	Concentration ($pg \, g^{-1}$)										
				Al	V	Mn	Fe	Cu	As	Cd	Ba	Pb	Bi	U
This study (70°50′S, 77°04′E)	160	1850	29[a]	165	0.46	3.7	45	5.3	10.0	0.21	2.4	4.0	0.028	0.029
Coats land (1965–1986)[b] (77°34′S, 25°22′W)	200	1420	5.6	460	0.56	8.8	–	4.0	–	0.25	2.7	4.7	0.071	0.047

[a]Mean snow accumulation rate estimated by combining mean snow density of $0.38 \, g \, cm^{-3}$ from the surface down to 1 m depth, which was measured in situ during the sampling, with a 2.3-m snow depth covering full 3 years' accumulation.
[b]Averaged concentration values in snow dated from 1965 to 1986 from Coats Land given by Planchon et al. (2002a).

The contribution from sea-salt spray was evaluated from Na concentration measured in each sample (after correction for Na contributed from rock and soil dust) and the metal/Na ratios in surface ocean waters. When such data were available, we used mean metal concentrations observed in the Indian sector of the Antarctic Ocean (Bordin et al., 1987) or in the Southern Ocean (Westerlund and Öhman, 1991; Flegal et al., 1993; Löscher et al., 1997). When such data were not available, we used the lowest metal/Na ratios in bulk surface ocean waters (Chan et al., 1976; Chen et al., 1986; Donat and Bruland, 1995). In previous studies, these ratios were often combined with tentative enrichments for metals in sea-derived aerosols relative to seawater when the marine aerosol is formed by bubble bursting through the sea-surface microlayer. However, recent studies have raised some doubt about these possible enrichment mechanisms ranging from one to three orders of magnitude for individual metals, on account of feasible contamination problems (Hunter, 1997). We have thus estimated sea-salt spray contribution both without and with such an enrichment using tentative enrichment factors (10 for Mn, 50 for V, 100 for Fe and Pb, 200 for Cu, As and Cd), for which enrichment data have been documented (Weisel et al., 1984; Arimoto et al., 1987; Nriagu, 1989).

The contribution from volcanic emissions was estimated from the concentration of non-sea-salt sulfate (nss-SO_4^{2-}) in each sample and mean values of metal/S ratios in volcanic emissions given by published sets of data obtained from individual volcanoes of the low-latitude region (Olmez et al., 1986; Patterson and Settle, 1987; Nriagu, 1989; Nho et al., 1996; Elias et al., 1998; Hinkley et al., 1999). We assumed that ∼10–15% of nss-SO_4^{2-} originated from volcanoes (Boutron and Patterson, 1986). It must be emphasized that such estimates are very tentative, especially because of the large dispersion in the published metal/S ratios in volcanic emissions. In addition, this approach for estimating volcanic inputs is likely to be overestimated for our samples as the sampling site is located in a coastal region where the marine biogenic source dominates the atmospheric sulfur content (Minikin et al., 1998).

The averaged calculated contributions from natural sources are listed in Table 3. It appears that rock and soil dust is a dominant source for Fe and Ba and an important source for V and Mn. The contribution from sea-salt spray calculated without

Table 3
Estimated contributions from rock and soil dust, sea-salt spray and volcanoes and their mean percentage relative to the mean measured concentrations

	Concentration (pg g⁻¹)																			
	V	%	Mn	%	Fe	%	Cu	%	As	%	Cd	%	Ba	%	Pb	%	Bi	%	U	%
Mean measured concentration	0.80		3.9		47		5.1		10.7		0.22		2.4		4.0		0.028		0.029	
Mean natural contribution																				
Rock and soil dust	0.11	32	1.13	48	66	185	0.03	0.72	0.004	0.06	0.0002	0.14	1.43	74	0.036	1.02	0.0003	1.27	0.005	20
Seasalt spray																				
Without enrichment	0.004	1.2	3×10⁻⁴	<1ᵃ	7×10⁻⁵	2×10⁻⁴	4×10⁻⁴	≪1	0.005	≪1	4.3×10⁻⁵	≪1	0.05	<1	3.2×10⁻⁵	≪1	1.4×10⁻⁷	≪1	0.01	40
With enrichment	0.190	59	0.003	<1	0.007	<1	0.08	1.97	0.96	13.9	0.009	6.20	–	–	0.003	<1	–	–	–	–
Volcanoesᵇ	0.10	33	0.77	42	1.36	4.6	0.30	6.80	1.58	0.10	0.067	45	0.026	1.63	0.15	4.6	0.25	1299	–	–

ᵃ<1 refers to percentage which is only slightly lower than 1, while ≪1 refers to percentage which are much lower than 1.
ᵇMean values of metal/S ratios in volcanic emissions given by published data from individual volcanoes in the world (see the text).

enrichment factors was found to be negligible for most of trace metals measured, except for U for which sea-salt contribution is important. A recent study reported that sea-salt aerosols are a major source of U in Antarctic snow and ice, based on U isotope ratios (^{234}U/^{238}U) in glacial melt waters in the McMurdo Dry Valleys of Antarctica (Henderson et al., 2006). This finding suggests that the calculated marine contribution based on Na concentrations without proper enrichment factors may lead to an underestimation of the true magnitude of the marine component of total U present in Antarctic snow and ice. Sea-salt contribution combined with tentative enrichment factors seems to be important for V, accounting for ~60% of measured concentrations. This contribution is also shown to be possibly important for As with an average of ~15% of measured concentrations.

The estimates of the contribution from volcanoes show that, bearing in mind the large uncertainty, volcanic emissions might be the main contributor for Bi, accounting for the total Bi found in our snow samples. For V, Mn and Cd, this contribution is found to account for ~30–45% of measured concentrations, indicating that volcanoes could also be an important contributor to these metals.

Other possible contributions from sources such as wild forest fires and continental and marine biogenic sources cannot be estimated from our data. However, contribution from marine biogenic emissions might be significant for at least part of the trace metals determined, since some studies have documented the production of methylated metals by polar marine bacteria (Heumann, 2001).

We shall now consider possible anthropogenic contributions affecting the concentrations of trace metals observed in our snow samples. For this tentative evaluation, we have combined the mean contributions from rock and soil dust, sea-salt spray and volcanic emissions and then investigated the magnitude of natural metal inputs to the snow. Based on the fact that the calculation of sea-salt spray contribution without possible enrichment factors is likely to cause an underestimation of values, we excluded this contribution in combining different natural contributions.

As shown in Table 3, natural contributions seem to explain most of the measured concentrations of V, Mn, Fe, Ba and Bi. For Cu, As and Pb, whereas natural inputs appear to account for only a small part of the measured concentrations, suggesting that a significant part of the measured concentrations for

these metals can be attributed to a contribution from anthropogenic sources. Recent studies have observed an increasing trend of anthropogenic influences on the deposition of trace metals such as Cr, Cu, Ag, Pb, Bi and U to the snow in Coats Land, West Antarctica (Wolff and Suttie, 1994; Wolff et al., 1999; Planchon et al., 2002a). This supports our observation that trace metals of anthropogenic origin are definitely affecting the inputs of Cu, Pb and probably As in recent accumulated snow in LGB, East Antarctica. Regarding As, we currently note that the supplementary information on the occurrence of As in Antarctic snow for at least several decades must be acquired to precisely characterize different contributions from natural and anthropogenic sources for this metal. For Cd and U, we cannot draw any conclusions on whether part of the measured concentrations of these metals could be anthropogenic in origin. It is, however, assumed that most inputs of U present in our snow samples are likely to be attributed to natural accumulation. This is because the marine contribution could account for the total U measured in the samples when we calculate its contribution by using the least possible enrichment factor in sea-derived aerosols relative to seawater.

3.4. Seasonal changes in the input of trace metals to snow

As shown in Fig. 3, a strong variability of concentrations is observed for all the metals through the depth profiles. This observation reflects seasonal variations and a complexity of transport and deposition of heavy metals to Antarctic snow as found in previous studies (Suttie and Wolff, 1992; Planchon et al., 2002b; Van de Velde et al., 2005).

The occurrence patterns of the seasonal variations in concentrations vary between different metals. They are now compared among groups of metals dominantly contributed from crustal, volcanic, marine and anthropogenic sources, respectively.

First, the seasonal patterns of crustal metals such as Al and Fe tend to be less well defined. The Al profile exhibits pronounced peaks during spring/summer 2000/2001 (at 40–50 cm depth interval) and spring 1999 (at 115–120 cm) (Fig. 3). For different depth intervals, no clear annual cycle in Al concentration was observed. As shown in Fig. 3, Fe displays a conspicuous enhancement at the 125–130 cm depth interval, corresponding to winter

1999. Some less clear but elevated Fe levels are also observed in the spring/summer snow layers (for instance at 15–20 and 40–50 cm depth intervals). For Ba, rather well-defined concentration peaks are observed in the spring/summer snow layers (at 15–20, 40–50, 165–170 and 225–230 cm depth intervals), with occasionally enhanced inputs in winter 1999 (at 125–135 cm depth interval) (Fig. 3). Maximum concentrations at each peak appear to be more or less at a similar level. The variations of Mn, for which rock and soil contributions are also important, are found to closely parallel Ba variations. Previous studies reported similar seasonal patterns of crustal components in aerosol and snow at different Antarctic sites with higher values during spring/summer (Wagenbach et al., 1988; Suttie and Wolff, 1992; Planchon et al., 2002b; Mishra et al., 2004). The case of a winter maximum was also observed in snow collected at a site on the east coast of the Antarctic Peninsula (Suttie and Wolff, 1992). Although the seasonal patterns of Al and Fe are less clear, it may thus be reasonable to infer that the input of crustal components to the snow over Antarctica seems to be enhanced during spring/summer with an occasional peak in winter.

Second, concentrations of Bi, which derives mainly from volcanic emissions, show peaks at the 15–20, 40–45, 95–100 and 190–195 cm depth intervals. These snow layers correspond to the spring to summer periods (Fig. 3). A pronounced peak of Bi is also found in winter 1999 (Fig. 3). Our profile of Bi concentrations then demonstrates that elevated concentrations are generally common during spring to summer throughout the year, with an occasional peak in the winter. Peak concentrations of As are very similar to the seasonality of Bi. The similarities between Bi and As are probably due to the same pathway of their input to the Antarctic atmosphere and/or to the same source of both metals, despite the fact that volcanic contribution is unlikely to explain a large part of As measured in our samples, as described in the previous section.

The third group, U and probably V, estimated to originate dominantly from sea-salt spray shows less well-defined seasonal patterns with sporadic peaks generally occurring in the spring/summer and occasionally in the winter (Fig. 3). At sites in coastal Antarctica, the annual sea-salt cycle in the aerosol and snow is relatively weak with rather episodic peaks either in the winter half-year at the higher latitudes (Wagenbach et al., 1998a) or in the summer half-year at the lower latitudes (Jourdain

and Legrand, 2002; Mishra et al., 2004). This contradicting situation is supposed to be associated with a strong influence of local parameters such as the surface wind regime, the extent of sea-ice cover and topography. Taking these observations into account, it can be deduced that seasonal variability in concentrations of U and probably V in our snow samples is linked mainly to intrusions of marine air masses during spring/summer and also to an occasional intrusion during winter.

Finally, our depth profiles represent that Cu and Pb, which are mainly of anthropogenic origin, show different seasonal patterns. As shown in Fig. 3, Pb variations appear to display rather similar pattern to those of Bi, with noticeable concentration peaks during spring/summer 2001/2002 and 2000/2001 (at 5–10, 15–20 and 40–50 cm depth intervals) and winter 1999 (at 125–135 cm). Less elevated concentrations are also observed for the 90–100 cm depth interval, i.e., summer 1999/2000 and for the 175–180 cm, 1998/1999 summer. Therefore, it is very likely that concentration peaks for Pb occur generally during spring to summer throughout the year, with an occasional peak in the winter. A very different situation is observed for Cu. The seasonal variation in concentration of Cu is less well defined and shows sporadically large inputs of Cu between winter 2001 and summer 2001/2002, with relatively minor enhancements in the spring/summer snow layers from 1998 to 2000 and in the winter deposit in 2000 (Fig. 3).

When comparing our data with the snow profiles at different sites from the limited number of reliable studies, differences exist regarding the seasonal variations of Pb and Cu. Our data revealed that a dominant input of Pb to the snow on the east side of LGB occurred during spring/summer. On the other hand, Pb concentrations peaked during autumn/winter at the site on the Antarctic Peninsula and, in contrast, in the spring/summer period with comparatively high concentrations throughout the winter in Coats Land. Meanwhile, no regular seasonal pattern was observed in the snow pit samples covering the period 1991–1994 in Victoria Land (Van de Velde et al., 2005). In the case of Cu, inconsistent variations were observed throughout the year in the study by Suttie and Wolff (1992), but Cu peaked in spring/summer in the profile of Planchon et al. (2002b). These differences between the different sites may indicate spatial changes in input mechanisms of pollutant Cu and Pb aerosols arriving at the different sites over Antarctica, which

could be due to their different source areas and transport pathways. It must, however, be noted that previous data in comparison with our profiles displayed different time periods for snow accumulation and relatively short and low-resolution snow records, which might have obscured the peak occurrence patterns. To draw any definite conclusion of spatial variations of the inputs of these metals to the snow, other high-resolution seasonal data of Cu and Pb in modern Antarctic snow at various sites would be required.

3.5. Transport pathways and input mechanisms of heavy metals

Heavy metals derived from various sources would have undergone different transport and deposition mechanisms related to the physical and chemical alteration of properties and sources of aerosol. The seasonal patterns in Fig. 3 reflect a complexity of such processes. To investigate the mechanisms affecting snow profiles of heavy metals observed in our study area, we analyzed the relationship among heavy metals including Na and Cl associated with sea-salt aerosol.

As shown in Table 4, Al, a reference metal for rock and soil dust shows strong correlations with respect to other crustal metals (Fe, Ba and, to a less extent, Mn), which indicate similar transport and deposition processes of these metals. Interestingly, a comparatively less-significant correlation associates Al with Fe, probably due to a fractionation of bulk crustal aerosol occurring during transport from the source region to Antarctica. Bi tends to show a

significant correlation with crustal metals. It thus seems probable that Bi aerosol of volcanic origin attached to crustal aerosol particles during their transport to Antarctica, leading it to follow the same pathway of input into the Antarctic atmosphere and deposition in the snow.

For the other metals, the situation is different with respect to each other, leading to difficulties in interpreting the behavior of their transport and deposition. For instance, a rather good correlation associates Pb with crustal metals (Table 4), suggesting that both Pb pollutants and crustal particles are probably transported and deposited to the snow in a similar manner. However, Cu, for which a large part is also estimated to be of anthropogenic origin, tends to show insignificant correlations with crustal metals, while they fairly correlate with respect to Pb (Table 4). Such decoupling may be due to different source areas and/or independent depositional mechanisms related to different properties of their aerosol.

From our data, it is interesting to observe that correlations of metals with sea-salt-derived components, Na and Cl, show a contrasting situation. Some metals such as Cu, Pb and Bi significantly correlate with Cl, but no correlations are observed for Na (Table 4). This is especially the case for U, for which a very significant correlation ($r^2 = 0.82$) with Cl is observed (Table 4). Considering that U in our snow samples is of marine origin, as already mentioned, this observation indicates that sea-salt aerosol is modified when the air mass moves inland and both U and Cl have a similar deposition mechanism. Fractionation of the sea-salt has been

Table 4
Correlation coefficients determined for a continuous series of 46 samples collected in a snow pit

	Al	V	Mn	Fe	Cu	As	Cd	Ba	Pb	Bi	U	Na	Cl
Al	1	0.23	**0.74**	**0.57**	0.08	0.27	0.28	**0.69**	**0.59**	**0.43**	**0.52**	−0.01	0.19
V		1	0.36	0.31	−0.02	0.13	0.11	**0.41**	0.16	0.04	0.01	0.34	−0.03
Mn			1	**0.78**	0.28	**0.51**	**0.53**	**0.80**	**0.72**	**0.75**	**0.70**	0.17	**0.46**
Fe				1	0.05	0.36	0.37	**0.70**	**0.61**	**0.61**	**0.50**	0.06	0.25
Cu					1	0.18	0.33	**0.50**	0.30	0.39	**0.51**	0.12	**0.51**
As						1	**0.44**	0.35	**0.59**	**0.80**	**0.53**	0.35	**0.47**
Cd							1	**0.50**	**0.58**	**0.58**	**0.53**	0.12	**0.48**
Ba								1	**0.72**	**0.56**	**0.64**	0.19	**0.44**
Pb									1	**0.74**	**0.73**	0.18	**0.56**
Bi										1	**0.78**	0.25	**0.68**
U											1	0.28	**0.82**
Na												1	**0.45**
Cl													1

The coefficients that are significant with 99% confidence levels are expressed as the bolder type.

previously reported in aerosols over Antarctica (e.g., Wagenbach et al., 1998a; Jourdain and Legrand, 2002). As the sea-salt moves inland from the coast, sea-salt particles progressively react with H_2SO_4 to produce HCl, causing large Cl loss with respect to bulk seawater (Mulvaney et al., 1993). The sulfate salt particles and gaseous HCl have different transport and deposition behaviors. The mean value (0.89) of the Cl/Na ratio observed in our samples is lower than the value of bulk seawater (1.17), indicating a significant modification in sea-salt during the transport of sea-salt particles from their source areas to our sampling site. The observed features of significant correlations between some metals and Cl instead of Na are, therefore, probably in part due to the chemical interactions of these metals with HCl to form chlorine compounds of the particulate phase and subsequent deposition in the snow. An alternative probable explanation may be the preferential removal of these metals and gaseous HCl by a similar mechanism of deposition.

4. Conclusion

Our study has provided the first complete snow profile for the concentrations of Al, V, Mn, Fe, Cu, As, Cd, Ba, Pb, Bi and U from a snow pit on the east side of LGB in East Antarctica. The pronounced seasonal variations are observed for Mn, As, Ba, Pb and Bi, but the occurrence patterns are different for the different metals. Crustal components such metals as Ba and Mn tend to show similar seasonality patterns. The variations of Bi and As appear to be generally comparable, despite different source contributions for these two metals. Seasonal variability of U, originating dominantly from sea-salt spray, is very likely to be linked with local parameters generating sea-salt aerosol. For anthropogenic Pb and Cu, the variations display different seasonal patterns. Their patterns also show differences between different sites in Antarctica, which may indicate spatial variations of Pb and Cu distributions. The relationships among heavy metals and primary sea-salt aerosols (Na and Cl) illustrate possible mechanisms affecting snow profiles of heavy metals. Our study conclusively supports the idea that transport and subsequent deposition of heavy metals to Antarctic snow is not simple due to different physical and chemical alterations of properties and sources of aerosol. Further investigations at various sites with different geographical parameters such as altitude and distance from the coast are required to expand our understanding on processes and mechanisms controlling the glacial records of heavy metals in Antarctic snow and ice.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2007.07.012.

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