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Changes in the occurrence of heavy metals in the tropical atmosphere during the past 22,000 years as recorded in Bolivian ice core

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Abstract. Nine sections from the Sajama ice core recovered from the summit of an extinct Andean volcano in Bolivia were analysed for various heavy metals to assess anthropogenic changes in the tropical upper troposphere over South America. These samples include two sections dating from 14,100 to 19,200 years BP, corresponding to the Last Glacial Stage (LGS), one section dating from 2800 years BP (the late Holocene), and six sections dating from AD 790 to 1988. Our preliminary data, combined with data reported elsewhere, demonstrate that the heavy metal concentrations since the late Holocene are higher than in the period from the LGS to the early Holocene. The enrichment factors calculated by normalizing for crustal abundance using the metal/Al ratio in the mean upper continental crust indicate that a significant input of heavy metals attributed to anthropogenic contributions has occurred since the beginning of the 19th century for Pb and from the last century for Cd, Cu, and Zn.

1. INTRODUCTION

In the past two decades, polar snow and ice cores have provided a wealth of information on temporal changes in the atmospheric cycles of various heavy metals of interest that are related to climate conditions over full climatic cycles and, in particular, to human activities from prehistoric times to the present [1-6]. Although the ice records available from Greenland and Antarctic ice cores are still limited, they indicate that marked variation in past natural heavy metal concentrations occurred in both hemispheres over the course of climatic cycles, with much higher levels during cold glacial periods. They have also clearly documented that human activities have caused large-scale atmospheric pollution by various heavy metals over different historic periods including Greek, Roman, and Medieval times, the post Industrial Revolution period, and the past few decades.

Despite the insight obtained from these ice records, our knowledge of past large-scale atmospheric heavy metal variation is sparse. Detailed evidences from ice records of both polar and mid- and low-latitude snow and ice cores are essential for a full understanding of the evolution of global atmospheric cycles of heavy metals. Only recently have comprehensive data on these changes been produced over time scales ranging from several decades to centuries in well-dated alpine snow and ice, especially from the French-Italian Alps [7-9]. Ferrari et al. [10] recently presented the only published data obtained from a low-latitude snow and ice core from the Sajama ice cap in Bolivia. Considering the primary importance of the low-latitude ice record for investigating the link between the two hemispheres, it is unfortunate that reliable ice-core records of the variation in the occurrence of heavy metals at low latitude are scarce. In this context, we present further data obtained from nine more sections from the Sajama ice core to complete the earlier work [10].

2. MATERIALS AND METHOD

In 1997, two ice cores (diameter 10 cm) to bedrock (depths of 132.4 m, core C-1, and 132.8 m, core C-2) were recovered from dry holes using solar-powered electromechanical drills on the summit of the Sajama ice cap (18°06'S, 68°53'W, elevation of 6542 m a.s.l., mean annual temperature -12°C, mean annual snow accumulation rate ~40 cm H_2O yr^{-1}) in Bolivia [11]. The cores were dated using various methods, as described in detail in [11]. The glaciological timescale dates the bottoms of the C-1 and C-2 cores to about 25,000 years BP, back to the Last Glacial Maximum (LGM).

Thirteen core sections from a 132.4-m-long core (C-1) were transported frozen from the Ohio State University (OSU) to the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), France, where four sections were decontaminated to determine trace metals by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SF-MS) [10]. In this study, we analyzed the remaining nine sections at our laboratory at the Korea Ocean Research and Development Institute (KORDI). The depths and ages of the samples, including the four previously analyzed sections, are presented in Table 1.

After the highly contaminated outermost ~1-mm layer was removed, all the samples were decontaminated by mechanically chiselling successive veneers of ice from the outside toward the center, as described in detail elsewhere [12]. All the analytical procedures were carried out in class 100 clean conditions [13]. We measured the Pb, Cd, Cu, Zn, Mn, Fe, and Al concentrations by GFAAS, using a Perkin Elmer 4110ZL instrument equipped with a Zeeman background corrector. The direct injection method was used for Pb, Cu, Zn, Mn, Fe, and Al. Cd was determined by GFAAS after preconcentration (by a factor of 30) by non-boiling evaporation [14]. The precision of the data was estimated to be better than 5% for the highest concentrations and to decrease to about 20% for lower concentrations [13]. Na^+, NH_4^+, and SO_4^{2-} were analyzed in un-acidified samples by ion chromatography and total organic carbon (TOC) was determined using a Shimadzu 5000A TOC analyzer.

Table 1. Depth intervals, the corresponding ages, and the measured Pb, Cd, Zn, Cu, Mn, Al, and Fe concentrations in the thirteen sections from the Sajama ice core. Data from earlier work [10] are also included.

Depth interval[a]	Age	Pb	Cd	Zn	Cu	Mn	Al	Fe
			(pg/g)[b]				(ng/g)	
10.15-10.35	AD 1988	780	20.9	1493	1901	7.14	808	86
20.55-20.90	AD 1972	75	<3.01	<207	<208	0.17	14	15
30.15-30.50	AD 1954	292	5.68	1234	481	4.15	229	38
40.07-40.43*	AD 1905	356	3.50	380	147	3.62	373	118
50.18-50.53	AD 1825	711	9.27	1225	575	13.6	1425	223
60.00-60.35*	AD 1700	57	4.29	205	58	5.16	540	165
70.27-70.45	AD 1410	643	5.49	<2282	3880	12.2	2004	355
80.70-81.05	AD 790	490	13.2	1438	1366	13.5	1930	368
90.70-91.05	2800 BP	3950	31.0	12,670	9203	61.5	21,630	5031
101.57-101.92*	8400 BP	90	2.43	224	240	3.53	240	74
111.72-111.90	14,160 BP	46	0.61	172	92	1.87	189	37
120.61-120.81	19,200 BP	66	1.00	339	149	2.80	339	86
124.45-124.80*	22,000 BP	30	0.74	266	90	2.46	205	63

[a] The previously analysed sections (marked as a symbol *) from [10], for which the ages are given as the best available for the Sajama ice core (L.G. Thompson, personal communication). For these sections, the Pb, Zn, Cu, Mn, and Al concentrations are given in [10], while the Cd and Fe concentrations were determined by GFAAS at our laboratory.

[b] Symbol < indicates the concentration values given as upper limits, because continuous decreases in the Cd, Zn, and Cu concentrations were observed from the outside toward the very center in these sections; see text.

3. RESULTS AND DISCUSSION

3.1 Characteristics of the data

To check whether the concentrations measured in the central parts of the core represent true values, full outside-inside profiles of concentrations were obtained for each core section, as described previously [1-8]. Although the outermost ~1-mm layer was removed before the decontamination operation, the first layer of the core sections investigated contained up to ~1000 pg Pb/g and 30 pg Cd/g, and extremely high concentrations of Zn and Cu (~9,000 pg Zn/g and 5,000 pg Cu/g, respectively). Despite this high outside contamination, we found good concentration plateaus for the measured heavy metals in all but two sections. A continuous decrease in concentration as a function of radius was observed for Cd, Zn, and Cu in the 20.55-20.90 m section, and for Cu in the 70.27-70.45 m section. In these cases, outside contamination had penetrated to the very center of the core so that the concentrations measured in the inner core must be regarded as upper limits of the original concentrations in the snow and ice.

Table 1 lists the concentrations of each metal measured in the thirteen core sections, including the four sections from [10]. Note that the two upper sections (10.15-10.35 m and 20.55-20.90 m) integrate less than 1 year of accumulation because of the high accumulation (~440 mm of H_2O) over the upper 33 years [11]. The concentrations vary by up to three orders of magnitude from one section to another. The respective mean concentrations and corresponding standard deviations are 584 ± 1048, 7.8 ± 9.0, 1,703 ± 3,365, 1,415 ± 2,581 pg/g for Pb, Cd, Zn, and Cu and 10.1 ± 16.1, 2,302 ± 5,846, and 489 ± 1,194 ng/g for Mn, Al, and Fe. The unexpectedly high concentrations in the 90.70-91.05 m section result in large deviations from the mean concentrations of each metal. Overall, our data demonstrate that the heavy metal concentrations since the late Holocene are higher than those in the period from the Last Glacial Stage (LGS) to the early Holocene. This is consistent with the fact that the accumulation rate decreased and snowlines were elevated during the Holocene, which contributed to increased dust concentrations in the Sajama ice core [11].

3.2 Contributions from various sources to the heavy metals in the samples

As briefly described in the previous section, rock and soil dust was likely a dominant contributor of the heavy metals in the samples. To evaluate this contribution, the crustal enrichment factors (EF_c) were estimated using the formula $EF_c = (metal/Al)_{ice} / (metal/Al)_{crust}$, using the metal/Al ratio in the mean crustal material [15]. As shown in Fig. 1, the EF_c values are close to unity for Mn and Fe throughout the time period investigated, which indicates that they were dominated by a crustal source. Pb and Zn retain EF_c values close to unity until AD 1700 and AD 1905, respectively, after which the EF_c increases were marked. Conversely, the EF_c values for Cd and Cu are higher than unity until AD 1905, which suggests inputs from other sources; after that time the EF_c values for Cd and Cu are markedly elevated.

Although it is difficult to estimate contributions from other natural sources, such as sea-salt spray, volcanoes, biogenic continental particulates, and forest wildfires [16], it appears that contributions, from these sources, of Pb, Zn, Mn, and Fe are probably insignificant, since the changes in the available sea salt Na^+, excess SO_4^{2-}, TOC, and NH_4^+ concentrations, which are closely related to these sources, were not consistent with the observed variability in the concentrations of these metals in the corresponding samples. For Cd and Cu, however, these natural contributions could account for a large part of the concentration remaining, after excluding the crustal contribution to the samples between 22,000 years BP and the beginning of the 20th century. During this period the measured Cd and Cu concentrations were thought to be natural because the EF_c values are within a similar range above unity [Fig. 1].

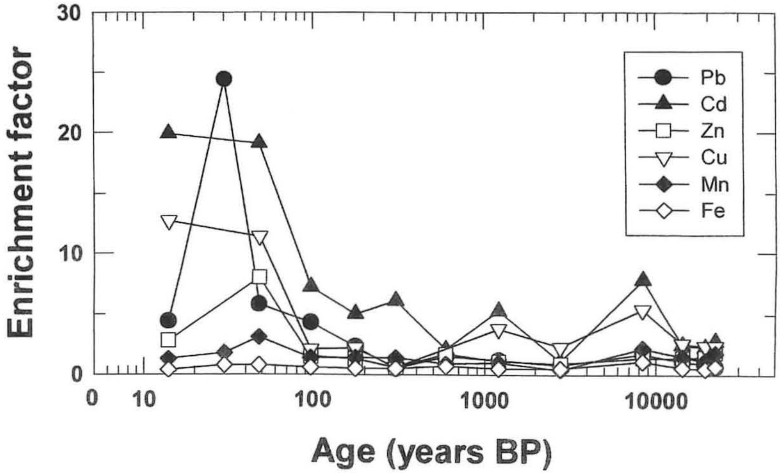

Fig. 1. Changes in the crustal enrichment factors in the Sajama ice from 22,000 years BP to AD 1988. Horizontal axis is expressed as logarithmic scale.

A possible source of the excess Pb concentrations observed in the sample from AD 1825 and those of Cd, Cu, and Zn from AD 1954 is anthropogenic. In South America, significant amounts of Pb, Cd, Cu, and Zn were emitted to the atmosphere from various anthropogenic sources, such as mining, smelting, and the production of metals during the last century [6]. In particular, a vast amount of Pb was released via the use of leaded gasoline after the middle of that century. Since these metals were produced before the 20th century in South America [17], an anthropogenic source probably perturbed the occurrence of certain heavy metals for a long time. Further investigations will provide more detailed information on past changes in atmospheric heavy metal cycling that were influenced by changing natural and anthropogenic source strengths at low latitudes over time.

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