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Heavy metals in ancient tropical ice: initial results

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Abstract

Although a wealth of fascinating data have been obtained through the investigation of heavy metals in Greenland, Antarctic and Alpine snow and ice cores, heavy metals have until now never been measured in tropical snow and ice cores despite the great interest of such low latitude cores. We present here preliminary data on the occurrence of Al, Na, Ti, V, Cr, Mn, Co, Cu, Zn, Mo, Pd, Ag, Cd, Sb, Ba, Pt, Au, Pb, Bi and U in a dated ice core drilled at an altitude of 6542 m on the top of Sajama in Bolivia. These data were obtained by analysing four core sections dated 22,000 BP (Last Glacial Maximum, LGM), 8000 BP (early Holocene, EH), AD1650 and AD 1897, using ultrasensitive ICP-SF-MS. Concentrations observed in LGM ice are similar to those measured in EH ice. Al, Na, Ti, V, Cr, Mn, Co, Ba and U are found to derive mainly from rock and soil dust. For the other metals, additional contributions from other sources are needed to explain the observed concentrations.

Keywords: Heavy metals; Tropical ice; Bolivia; Last glacial maximum; Holocene

1. Introduction

Since the pioneering work of Murozumi et al. (1969), a wealth of fascinating data have been obtained through the investigation of the changing occurrence of heavy metals in Greenland and Antarctic ice or snow dated from the last glacial cycle and the recent centuries. Amongst the most interesting results obtained so far are the evidence of climate related changes in the natural occurrence of metals such as Pb, Cd, Zn, Hg and Bi (see, e.g., Boutron and Patterson, 1986; Boutron et al., 1990, 1993; Hong et al., 1996a; Ferrari et al., 2000), the revelation of early pollution of the atmosphere of the Northern Hemisphere for Pb and Cu two millennia ago during Greek and Roman civilizations (Hong et al., 1994, 1996b) and the detailed assessment of post-industrial revolution changes for various metals (see, e.g., Murozumi et al., 1969; Wolff and Suttie, 1994; Candelone et al., 1995; Wolff et al., 1999). More recently, interesting data were also published on post-industrial revolution changes in the occurrence of various heavy metals in high altitude snow and ice obtained at a mid-latitude site near the summit of Mont Blanc in the French–Italian Alps, see, e.g., Van de Velde et al. (1999) and Rosman et al. (2000).

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On the other hand, there are presently no published data on heavy metals in tropical snow and ice cores. This is surprising since such low latitude cores could provide with very interesting time series from the last ice age to present which could prove to be unique links between the time series already obtained for high or mid latitude ice fields in the Northern and Southern Hemispheres. This is largely due to the fact that most tropical ice cores obtained so far were not brought back frozen to the laboratories. Instead, they were often cut and melted while in the field to make the different aliquots required for the determination of oxygen or hydrogen isotopes, dust or major anions or cations (see, e.g., Thompson et al., 1984, 1985, 1988, 1994). It prevented any accurate determinations of heavy metals being made: such determinations are indeed possible only if the investigators can decontaminate the core sections by mechanically chiselling veneer layers of ice or snow from the contaminated outside to the inside of the initial unmelted core sections using complicated and time consuming ultraclean procedures (Candelone et al., 1994) which cannot be carried out in the field.

The recent recovery of several snow/ice cores from the Sajama ice cap (18°06′S, 68°53′W, altitude 6542 m a.s.l.) in Bolivia (Thompson et al., 1998) offered a unique opportunity to obtain the first data on heavy metals in a tropical snow/ice core covering a period of ~25,000 years. The cores were indeed kept frozen below −5°C from the time of drilling to final storage in the laboratory (Thompson et al., 1998).

We present here initial results on the occurrence of Ti, V, Cr, Mn, Co, Cu, Zn, Mo, Pd, Ag, Cd, Sb, Ba, Pt, Au, Pb, Bi and U in one of these Sajama cores. We have determined these metals by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SF-MS) in four sections dated from 22,000 BP (Last Glacial Maximum, LGM), 8000 BP (early Holocene), AD 1650 and AD 1897. The different possible sources of these metals are discussed and the potential of these Sajama cores for further studies is assessed.

2. Experimental

2.1. Core drilling and dating

The Sajama ice cap covers the summit of an extinct Andean volcano that sits on the Northern edge of the Altiplano plateau in Bolivia (Fig. 1) (Thompson et al., 1998). It reaches 6542 m a.s.l. at its highest point. The data obtained by a satellite linked weather station installed on the ice cap shows that air temperature ranges from −25°C to −5°C, with a mean annual temperature of −12°C. The mean annual snow accumulation rate is ~40 cm H_2O/year. The close-off depth (firn–ice transition) is 25 m.

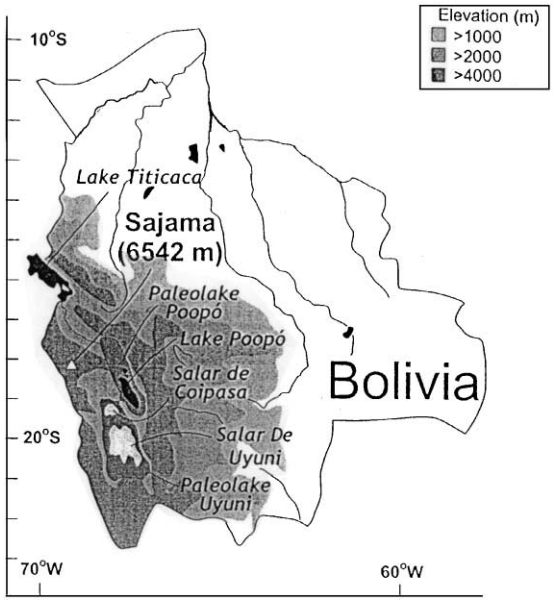

Fig. 1. Sketch map of Bolivia. The location of Sajama is shown with an open triangle. Adapted from Thompson et al. (1998).

In this study, we have analysed four sections of a 132.4 m snow/ice core which was drilled from the surface down to the bedrock in 1997 close to the top of the ice cap. The core was recovered from a dry hole with a solar-powered electromechanical drill. The core sections were packed in polyethylene bags and returned frozen to Ohio State University (OSU).

The methods used for the dating of the core are described in detail in Thompson et al. (1998). They especially included C^{14} age dating by accelerator mass spectrometry of organic material found in the core, measurements of the O^{18}/O^{16} ratio of paleoatmospheric O_2, H_3 calibrated annual layer counts of the most recent 100 years, and the ash horizon from the eruption of Huaynaputina in AD 1600. The results show that the core extends to ~25,000 years BP, back to the LGM.

2.2. Selection and decontamination of the core sections

Four ice sections have been selected for this initial work: (a) one section dated from 22,000 years BP (LGM), depth of 124.45–124.80 m; (b) one section dated at 8000 years BP (early Holocene), depth of 101.57–101.92 m; (c) two sections dated from the recent centuries: AD 1650 (60.0–60.35 m) and AD 1897 (40.07–40.43 m). The diameter was 10 cm. About 80% of the initial cross section was available for heavy metal analyses, Fig. 2. The time intervals integrated by the sections ranged from several years for the AD 1897 section up to several hundred years for the LGM section. It allowed to compensate for possible short term

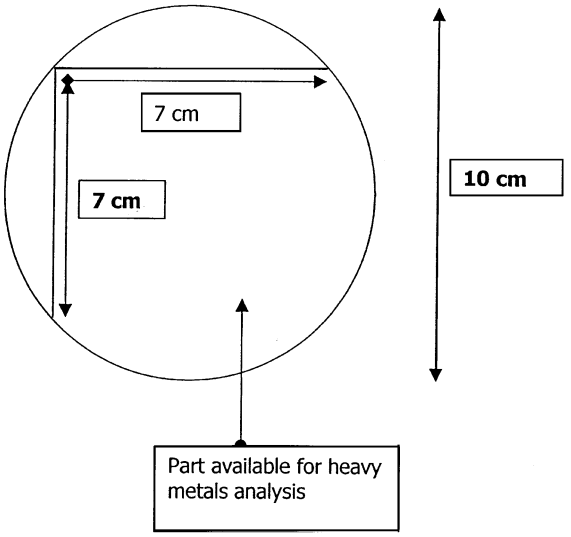

Fig. 2. Cross section of the sections (length: 35 cm) of the Sajama ice core analysed for heavy metals in this work. Two shallow chord cuttings had previously been made for other analyses, leaving ~80% of the initial full cross section for heavy metal analysis.

variability in the concentrations such as seasonal variations. These core sections had been transported frozen from OSU to the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) in Grenoble.

It was likely that significant heavy metals contamination had been introduced onto the outside of the core during drilling operations and core handling. Each core section was therefore mechanically decontaminated by chiselling three successive veneer layers of ice from the outside toward the center using ultraclean procedures which have been described in detail in Candelone et al. (1994). This yielded the uncontaminated cylindrical inner part (diameter: ~4 cm) of each of the four core sections.

To make sure that the inner part of the core was free from contamination, we analysed separately each veneer layer and inner core and monitored changes in the concentrations of each metal from the outside to the center of each core section. Significant contamination was found on the first veneer layer for some of the metals, but the outside–inside radial concentration profiles show that concentrations always level off to well established plateau values from the second veneer layer inward. These plateau values then represent the original concentrations in the snow or ice.

2.3. Analysis

Each veneer layer or inner core were melted separately at room temperature in a clean laboratory (Boutron, 1990). 5 ml aliquots were then taken in 15 ml low density polyethylene (LDPE) bottles which had been extensively cleaned with ultrapure water and acids (Boutron, 1990). They were immediately acidified with ultrapure twice distilled nitric acid to make 0.5% solutions, frozen, and transported frozen to the Department of Environmental Sciences of the University Ca Foscari of Venice (UCFV) for analysis by ICP-SF-MS.

Ti, V, Cr, Mn, Co, Cu, Zn, Mo, Pd, Ag, Cd, Sb, Ba, Pt, Au, Pb, Bi and U were determined at UCFV by ICP-SF-MS with microconcentric nebulization, using a Finnigan MAT "Element" sector field mass spectrometer. Detailed working conditions are given in Barbante et al. (1999a, b). Possible interferences coming from isobaric atomic ions, multiply charged ions or polyatomic ions were carefully considered, and a correction was made for these interferences when necessary. The blanks and instrumental repeatability of the data were also carefully determined, as explained in detail in Barbante et al. (1999a, b). We also measured certified reference riverine water (SLRS 3, Riverine Reference Material for Trace Metals, National Research Council of Canada, Ottawa, Canada): our values were found to be in good agreement with the certified values for the metals for which certified values are available (Barbante et al., 1999a).

In addition, Al and Na were measured at LGGE by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) using a Perkin-Elmer AAnalyst 100 instrument equipped with a HGA 800 graphite furnace.

The precision of the concentration data so obtained depended on the metals and the concentration levels. It was typically ±10%.

3. Results and discussion

3.1. Presentation of the data

Concentrations measured in the four core sections are presented in Table 1. To our knowledge, they are the first heavy metals data published for tropical ice cores. For Ti, V, Cr, Co, Mo, Pd, Ag, Sb, Pt, Au and U, they are even the first data ever published for glacial ice since no reliable data have been published so far for these metals for Antarctic or Greenland ice dating from the last ice age.

Measured concentrations are found to differ by orders of magnitude from one metal to another, Table 1. The highest concentrations fall in the μg/g range: they are observed for Al and Na which are major constituents of crustal material (Wedepohl, 1995). The lowest concentrations fall in the sub-pg/g range: they are observed for elements such as Pt, Pd or Au which are present at very low concentrations in crustal material (Wedepohl, 1995).

Table 1
Concentrations of 20 metals measured in four sections of an ice core obtained at Sajama, Bolivia. All concentrations are expressed in pg/g ($1\,pg = 10^{-12}\,g$)

Metal[a]	Depth and age of the core section			
	124 m[b] (22,000 BP)	101 m[c] (8000 BP)	60 m[d] (AD 1650)	40 m[e] (AD 1897)
Al	205,000	240,000	540,000	373,000
Na	63,000	74,000	165,000	118,000
Ti	1400	1630	380	960
V	56	150	71	105
Cr	34	45	10	24
Mn	2460	3525	5160	3620
Co	61	35	56	43
Cu	90	240	58	147
Zn	266	224	205	380
Mo	5.5	14.4	8.3	10.5
Pd	0.32	0.42	0.28	0.32
Ag	0.54	0.66	0.58	1.71
Cd	1.8	4.0	6.0	7.9
Sb	1.6	2.5	5.1	111
Ba	1780	1910	1300	1290
Pt	0.09	0.10	0.12	0.14
Au	0.08	0.08	0.08	0.08
Pb	30	90	57	356
Bi	0.30	1.7	0.37	7.1
U	4.4	8.1	2.7	5.3

[a] Metals are ranked according to increasing atomic weights.
[b] Depth interval: 124.45–124.80 m.
[c] Depth interval: 101.57–101.92 m.
[d] Depth interval: 60.0–60.35 m.
[e] Depth interval: 40.07–40.43 m.

3.2. Observed changes in the concentrations as a function of the age of the ice

An interesting feature of the data shown in Table 1 is that for virtually all the 20 elements investigated, concentrations observed in ice from the LGM (22,000 BP) are similar to concentrations measured in ice from the early Holocene (8000 BP). For Cu, Zn, Cd, Pb and Bi, this is different from what has been observed in Antarctic and Greenland ice. Cu, Zn, Cd, Pb and Bi concentrations are indeed much higher in Antarctic and Greenland ice from the LGM than from the early Holocene (see, e.g., Boutron and Patterson, 1986; Boutron et al., 1990, 1993; Hong et al., 1996a; Ferrari et al., 2000). As an example, Pb concentration in Dome C Antarctic ice dated from 22,000 BP is ~ 30 pg/g, which is two orders of magnitude higher than at 8000 BP when it was ~ 0.4 pg/g (Boutron and Patterson, 1986). Our preliminary data suggest that such huge differences are not observed in Sajama ice. It must however be stressed that with only one datapoint for each climatic period, it is not possible to draw any definitive conclusion. Clearly, it will be necessary to assess what heavy metals variability is within the LGM and the early Holocene.

Another distinct feature is that elements such as Pd, Pt and Au show similar concentrations in all samples. Even the other elements show rather small variations, Table 1.

3.3. Crustal enrichment factors

In order to help to evaluate the relative contribution of rock and soil dust versus other sources, it is interesting to express the metals concentrations in the ice in the form of crustal enrichment factors (EF_c). EF_c is defined as the concentration ratio of Al (or any other element which derives principally from rock and soil dust) normalized to the same concentration ratio characteristic of the mean upper continental crust (Wedepohl, 1995). For example, the enrichment factor for Cd is thus

$$EF_c(Cd) = [Cd/Al]_{ice}/[Cd/Al]_{mean\ crust}.$$

The mean composition of the upper crust is used here as a surrogate for the changing composition of regional and/or local rock and soil since we do not know the exact geographical origin of dust found in Sajama ice. Given this uncertainty in the crustal values used for the normalization, it is wise to consider that EF_c values between $\sim \pm 10$ times the mean crustal abundance (i.e. values ranging from ~ 0.1 to 10) can still indicate a dominant input from rock and soil dust. Conversely, EF_c values significantly larger than ~ 10 will strongly suggest a pronounced contribution from other sources. EF_c values for the four sections are listed in Table 2.

It can be seen in Table 2 that for part of the elements, namely Na, Ti, V, Cr, Mn, Co, Cu, Zn, Mo, Ag, Ba, Pb and U, EF_c's between ~ 0.1 and 10 are observed for all the core sections, irrespective of their age. It is therefore likely that these elements derived mainly from rock and soil dust. Conversely, EF_c's larger than ~ 10 are observed for Pd, Pt and possibly Cd and Au in all the sections: it indicates that rock and soil dust contribution was minor for these metals, and that they mainly originated from other sources.

3.4. Contribution from other natural sources

Other possible natural sources mainly include volcanoes, biogenic continental particulates and volatiles, and wild forest fires (Nriagu, 1989). Contribution from seasalt spray and marine biogenic emissions is indeed probably insignificant at this very high altitude (6542 m a.s.l.) site ~ 150 km away from the nearest ocean.

Volcanoes are tempting candidates to explain at least part of the observed excesses above rock and soil dust. There are indeed numerous high altitude active volcanoes all the way along the Andes (see, e.g., Simkin and

Table 2
Crustal enrichment factors for four sections of an ice core obtained at Sajama, Bolivia. See text for explanations

Metal[a]	Depth and age of the core section			
	124 m[b] (22,000 BP)	101 m[c] (8000 BP)	60 m[d] (AD 1650)	40 m[e] (AD 1897)
Al	1	1	1	1
Na	0.93	0.93	0.92	0.95
Ti	0.17	0.17	0.017	0.064
V	0.40	0.91	0.19	0.41
Cr	0.37	0.42	0.041	0.14
Mn	1.8	2.2	1.4	1.4
Co	2.0	0.97	0.69	0.77
Cu	2.4	5.4	0.58	2.1
Zn	1.9	1.4	0.57	1.5
Mo	1.5	3.3	0.85	1.6
Pd	303	340	100	166
Ag	3.7	3.8	1.5	6.5
Cd	6.7	13	8.4	16
Sb	2.0	2.6	2.4	74
Ba	1.0	0.92	0.28	0.40
Pt	85	81	43	73
Au	12	10	4.6	6.7
Pb	0.67	1.7	0.48	4.3
Bi	0.92	4.5	0.43	12
U	0.65	1.03	0.15	0.44

[a] Metals are ranked according to increasing atomic numbers.
[b] Depth interval: 124.45–124.80 m.
[c] Depth interval: 101.57–101.92 m
[d] Depth interval: 60.0–60.35 m.
[e] Depth interval: 40.07–40.43 m.

Siebert, 1977). Moreover, various authors have shown that heavy metals are highly enriched in volcanic plumes and fumaroles (see, for instance, Mroz and Zoller, 1975; Lepel et al., 1978; Zoller et al., 1983; Patterson and Settle, 1987). Our data however do not allow quantitative estimates of this contribution to be made.

Contribution from biogenic continental particulates or volatiles and forest fires could also be significant at Sajama because most air masses giving precipitation at Sajama originate from Amazonia.

Another possible source for metals such as Pd and Pt is extraterrestrial dust. The corresponding input for these two metals can tentatively be evaluated by combining estimates for cosmic dust influx to the whole Earth ($\sim$150,000 tonnes/year, Ceplecha, 1996), Pd and Rh concentrations in cosmic material ($\sim$560 and 990 ng/g, respectively, Anders and Grevesse, 1989) and the snow accumulation rate at Sajama ($\sim$40 cm H_2O/year). If we consider an homogeneous dispersion of cosmic dust over the surface of the Earth, it gives contributions of the order of $0.5–1 \times 10^{-3}$ pg/g, i.e. a minor contribution to Pd and Pt found in Sajama ice.

3.5. Anthropogenic contributions

Even before the twentieth century, anthropogenic emissions of various heavy metals were probably already significant in South America. This is especially because of non ferrous metal production which was already important in countries such as Chile or Peru, with higher emission factors than during recent times (Hong et al., 1996c).

Especially, Ag and Au are metals that have been produced for a long time in South America, see for instance Patterson (1971, 1972). The production became important as early as the mid-16th century when the patio amalgamation process was developed into an industrial scale operation (Nriagu, 1994). Bolivia and Peru dominated world Ag production during the 16th and 17th centuries. As an illustration, Bolivia and Peru produced 36% and 26%, respectively, of world Ag during the 17th century (Nriagu, 1994).

4. Conclusions

The preliminary results presented here show that the Sajama snow/ice core, and more generally other tropical cold snow/ice cores, have the potential of providing very interesting information on natural and man induced changes in the occurrence of heavy metals in low latitude areas.

It will now be necessary to considerably expand the limited data set presented here by analysing a large number of core sections in order to get detailed time series. Especially, it will be particulary rewarding to get comprehensive time series for the Incas and Conquistadores periods, and for the LGM–Holocene transition. In addition, it will be interesting to determine new metals, especially Hg which is a volatile element which was emitted in enormous quantities to the atmosphere in Bolivia and Peru since the 16th century because of the massive production of Ag using Hg amalgamation (Nriagu, 1994). Also, it will be worth analysing these core sections for Pb isotopes in order to help to discriminate between the different natural and anthropogenic contributions for this metal.

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