

Heavy metals in South America aerosol during 20th century from Illimani ice-core, Eastern Bolivian Andes

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Abstract. A 137 m ice-core drilled from Eastern Bolivian Andes at Nevado Illimani (16°37' S, 67°46' W, 6350 m asl) allows studying historical concentrations of heavy metals in South America aerosol along the 20th century. About 50 m of this ice-core were dated by multi-proxy analysis, providing a record of environmental variations of about 80 years from 1919 to 1999. Elemental concentrations for 45 chemical species (Li to U) in 744 samples along the upper 50 m ice-core section were determined by Inductively Coupled Plasma-Mass Spectrometry. This work focuses on heavy metal concentrations along the ice-core profile. Further discussion on other trace elements is given elsewhere [1]. Most elements like Al, Fe, La, Th and U show a pattern for concentration averages and standard deviations with little variation along 20th century, evidencing their natural origin. Other heavy metals like: Pb, Mo, Zn, Cd, Ni, Co and Cu show increases in average concentrations and standard deviations from the beginning of 20th century to recent years. For example, Cu average concentration values change from 0.604±0.440 ng g⁻¹ to 3.46±3.02 ng g⁻¹ along 20th century. Time evolution of these elements concentrations may be related to local economic growth and human activities in South America.

1. INTRODUCTION

Ice-cores from several polar sites have been used for decades to understand past chemical and physical conditions of the atmosphere. Recently, with the beginning of research at high-altitude tropical ice-cores new features and challenges have arisen [2]. Tropical ice-cores have in general more moisture available during precipitation than their polar counterparts. As a consequence of that, one can study the characteristics of tropical ice-cores at higher temporal resolutions. Particularly in the case of heavy metals, previous works of either polar or tropical ice-cores show results covering typically a few elements, in a limited number of samples [3]. This work addresses this lack of continuous measurements of several heavy metal concentrations, for a tropical ice-core during 20th century.

A 137 m ice-core was drilled in 1999 from Eastern Bolivian Andes at the summit of Nevado Illimani (16°37' S, 67°46' W, 6350 m asl, about 40 Km SE from La Paz). Ice-core sections measuring about one meter in length and eight centimeters in diameter were transported to La Paz and then to cold chambers in European laboratories, being kept frozen at all times. The upper 50 m were sub-sampled at the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) in Grenoble, France, and samples were analyzed at the Laboratoire des Mécanismes et Transfert en Géologie (LMTG) in Toulouse, France. The analyses resulted in a panoply of elements measured continuously during most of 20th century [1]. This work explores the results found for heavy metal concentration profiles.

2. SUB-SAMPLING AND ANALYSIS BY ICP-MS

The top 50 meters of Illimani ice-core were cut in 744 sub-samples with 6-10cm in length inside a cold chamber. These sub-samples were decontaminated by removing their external layer with a stainless steel

plane under a laminar-flow clean bench. They were taken to a class 100 clean room in double-sealed pre-cleaned plastic vessels and allowed to melt at about 25°C in a laminar-flow bench, then split in aliquots for several analyses. Simões et al. [4] discuss details concerning dating and analyses of insoluble particles. De Angelis et al. [5] cover the results of major ionic content in the ice-core.

The aliquots for ICP-MS analyses were wrapped in moisture-proof tape (Parafilm M, Structure Probe), and frozen in cold chambers in double-sealed plastic bags. These sub-samples were transported frozen between the laboratories in Grenoble and Toulouse. They were allowed to melt and acid-digested to assure complete dissolution of insoluble aerosol particles. Before analysis a solution containing In and Re was added to each sample for calibration and elemental concentration determination by the internal standard with external calibration method [6, 7]. In the ICP-MS system (Elan 6000, Perkin Elmer), the sample introduction system is composed of a cyclonic spray chamber, a Meinhard nebulizer and a Knauer desolvation unit. This system increases the sensitivity for analyses of low concentration natural waters by a factor of 5–10 relative to simple cross-flow nebulizers [8].

Quality assurance of sample handling and decontamination procedures was controlled with laboratory blanks. For the ICP-MS analyses, specific batches of instrument blanks were used to assess analytical quality. Several blank concentration values are under the average detection limits for the analyses performed. Typical sample elemental concentrations lie in the range of hundreds to thousands of lab blank concentration levels and instrumental detection limits. Correia et al. [1] show further details about sample handling and analysis by ICP-MS for this ice-core.

3. RESULTS AND DISCUSSIONS

The ICP-MS analyses resulted in continuous concentration profiles for 45 chemical elements ranging from Li to U in the 744 samples. This work focuses on results obtained for heavy metal elements. Further discussion on other trace elements is given by Correia et al. [1]. As an example of the results obtained, Figure 1 shows the Lanthanum elemental concentration profile measured at Illimani along 80 years from 1919 to 1999. La is a rare-earth element originated from soil dust, with an average detection limit of $0.57 \times 10^{-12} \text{ g g}^{-1}$ (i.e. parts per trillion of La per gram of sample solution) for the ICP-MS setup used in the analyses [1].

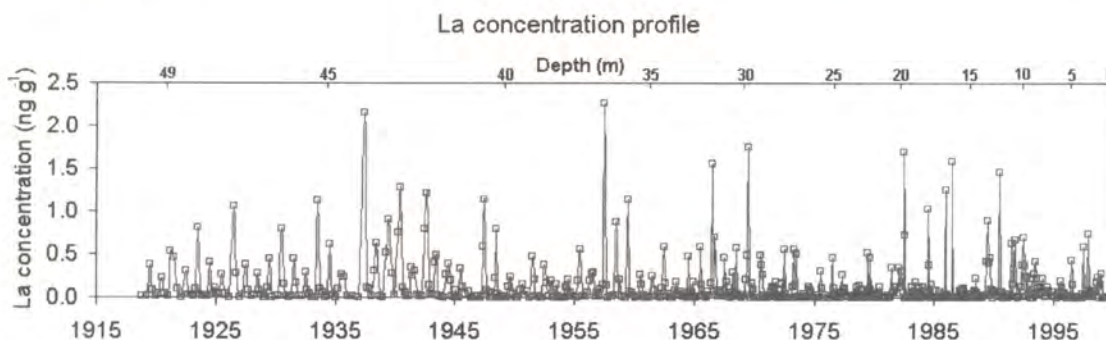


Figure 1. La concentration profile at Illimani from 1919 to 1999.

There is a strong seasonality evidenced in the La profile, a common feature for most elemental concentrations measured, which can be assessed only because of the high number of samples analyzed. This seasonality is attributed to yearly precipitation regimes at the site, with low concentrations during the wet season (austral summer) and high concentrations during dry season (austral winter). During winter snow sublimation is increased due to availability of solar radiation, and also soil dryness increases due to lower levels of precipitation [5]. Table 1 shows the average concentrations and standard deviations for selected elements for two time periods: from the beginning of the century (ca. 1919) up to 1950 and from

1950 to 1999. N is the number of samples used for the averages and standard deviation calculations. The last column shows the ratio between 1950-1999 averages to 1919-1950 averages. Table 1 is sorted by ascending values of the last column. All values are reported with three significant figures.

In Table 1, there are more samples for the period 1950-1999 than for the period 1919-1950. This is due to the weight of consecutive snow precipitation: as depth (i.e. age before present) increases the thinning of snow layers causes less samples per unit length. The upper horizontal depth scale in Figure 1 illustrates this effect. The standard deviations in Table 1 represent the variability of concentration values measured.

Table 1. Averages and sample standard deviations of elemental concentrations at Illimani for the two halves of 20th century.

Element	Time period						Ratio between averages 1950-1999 / 1919-1950
	1919-1950			1950-1999			
	N	Average concentration (ng g ⁻¹)	Sample standard deviation (ng g ⁻¹)	N	Average concentration (ng g ⁻¹)	Sample standard deviation (ng g ⁻¹)	
As	150	1.10	1.71	422	0.557	0.704	0.506
Nb	130	0.0847	0.119	261	0.0446	0.0889	0.527
Yb	123	0.0112	0.0150	413	0.00668	0.0124	0.596
Al	150	325	497	495	194	432	0.597
Ga	141	0.102	0.152	451	0.0610	0.129	0.598
La	149	0.188	0.318	480	0.113	0.248	0.601
Ce	149	0.382	0.645	481	0.234	0.504	0.613
Pr	149	0.0426	0.0719	480	0.0262	0.0566	0.615
Zr	147	0.536	0.826	461	0.332	0.745	0.619
Sm	131	0.0331	0.0510	421	0.0206	0.0403	0.622
Nd	143	0.165	0.270	453	0.103	0.215	0.624
Cs	148	0.0768	0.111	458	0.0482	0.0986	0.628
Y	149	0.0950	0.143	491	0.0600	0.122	0.632
Hf	123	0.0298	0.0373	300	0.0189	0.0370	0.634
Rb	150	0.605	0.925	497	0.384	0.808	0.635
U	139	0.0163	0.0245	427	0.0105	0.0206	0.644
Pd	56	0.00341	0.00229	133	0.00220	0.00279	0.645
Fe	149	154	239	498	101	212	0.656
Lu	110	0.00187	0.00228	314	0.00126	0.00204	0.674
Sr	149	1.57	2.43	471	1.11	2.12	0.707
Ba	149	3.53	5.36	476	2.52	4.84	0.714
Sb	141	0.0736	0.0919	470	0.0529	0.0709	0.719
Th	148	0.0532	0.0895	403	0.0402	0.0822	0.756
Ta	118	0.00874	0.00957	194	0.00675	0.0111	0.772
Tl	131	0.00508	0.00654	264	0.00463	0.00666	0.911
Ag	70	0.00474	0.00329	120	0.00465	0.00429	0.981
Ge	90	0.0136	0.0150	204	0.0135	0.0184	0.993
Pb	149	0.333	0.431	498	0.345	0.514	1.04
Mo	120	0.0189	0.0260	411	0.0347	0.0421	1.84
Zn	113	1.69	1.82	459	3.82	6.10	2.26
Cd	95	0.00604	0.00498	458	0.0157	0.0207	2.60
Ni	94	0.205	0.397	454	0.791	1.45	3.86
Co	143	0.0718	0.100	488	0.298	0.766	4.15
Cu	123	0.604	0.440	456	3.46	3.02	5.73

Most elemental concentrations in the second half of 20th century have lower averages than during the first half of the century. A number of explanations can be put forward to explain this effect, among which a greater number of wet season (i.e. low-concentration) samples for the upper part of the ice-core due to an increase in precipitation, shifting averages down. Elements with low crustal enrichment factors [1] have average ratios (last column, Table 1) ranging roughly between 0.5 and 0.8, and are associated in

general with a single local soil dust source. The variability (i.e. standard deviations) of most elements shows also a similar pattern when comparing both periods. These are indications that sources for the elements in this situation had little change during 20th century, and this is in agreement with the advocated soil dust origin for several of these elements [1]. As and Sb are exceptions, with average ratios of 0.506 and 0.719, yet presenting high enrichment factors [1] (not shown), which tie these elements to anthropogenic activities. This is due to the averaging out of temporal variations along the 20th century for the selected time periods.

Some elements in Table 1 show more pronounced changes in the average concentrations and standard deviations along the 20th century, like Pb, Mo, Zn, Cd, Ni, Co and Cu. Incidentally, these elements show moderate to high crustal enrichment factors [1]. For these elements the existing sources in the beginning of the century were impacted by other sources in the second half of the century, especially anthropogenic ones like metal mining/production, where heavy metals may be released to the atmosphere as rejects or as a consequence of inefficient production practices. Especially in the case of Cu, concentration values change from $0.604 \pm 0.440 \text{ ng g}^{-1}$ in the period 1919-1950 to $3.46 \pm 3.02 \text{ ng g}^{-1}$ in the second half of 20th century. This may be due to Cu mining/production in Chile (S of Illimani), as this country is today the largest Cu producer in the world [9], but also from mining activity in Peru (N of Illimani) and Bolivia itself.

4. CONCLUSIONS

Concentration profiles for 45 elements and heavy metals were determined by ICP-MS in 744 ice and firn samples from Illimani, Eastern Bolivian Andes, encompassing about 80 years continuously during 20th century. Most profiles show a strong seasonality attributed to yearly precipitation regimes at the site.

Several heavy metal concentrations show a similar pattern for averages and sample standard deviations comparing the beginning of 20th century (1919-1950) and more recent years (1950-1999). This indicates in general little impact over the sources for these heavy metals during the century. As and Sb are exceptions, with anthropic sources (i.e. high crustal enrichments [1]) varying in strength along 20th century, yet showing little change in average and standard deviation of concentration values. Heavy metals from anthropic sources (e.g. metal mining/production) show a distinct pattern, with higher average concentration values and standard deviations for the second half of 20th century: Pb, Mo, Zn, Cd, Ni, Co and Cu. For these elements the existing sources in the beginning of the century (either natural or not) were impacted by other sources related to economic activities in the second half of the century.

Acknowledgments

A. Correia thanks CNPq for grant 142.683/98-1 and CAPES for grant BEX 0458/99-6.

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