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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Trace elements in South America aerosol during 20^{th} century inferred from a Nevado Illimani ice core, Eastern Bolivian Andes (6350 m a.s.l.)" *by* A. Correia et al.

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We thank Anonymous Referee #2 for the valuable suggestions and comments on our paper. The recommendations given by Referee #2 are related to discussions on the analytical methodology. Most of these discussions were intentionally left out of the original manuscript in order to focus on the discussion of the results. The full analytical methodology will be the subject of a more technical publication, but we will extend its discussion on the revised version of the paper, according to the issues raised by Referee #2:

1. "(...) It is important to sample the center of the ice core (...) Additionally, it might have been better to remove the external layer of the sample using a Teflon scraper (...)".

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We indeed used only the center of each sample for the analyses. This issue will be made clearer in the text. The use of a stainless steel plane for decontamination showed to be acceptable considering the extensive blank tests we performed and the typical elemental concentration ranges in our samples.

2. "Although many blanks were analyzed and found to be uncontaminated, it is not clear to me how sample handling and decontamination methods were tested by these blanks."

We used samples of ultrapure frozen milli-Q water submitted to the very same analytical conditions that real samples would meet, including full sample handling and decontamination procedures. In all cases elemental concentration levels were comparable to fresh milli-Q water, about hundreds of times below typical real sample values. Besides that we used 2 blanks per batch of 20-25 samples for the entire ICP-MS analysis of the 744 samples, as stated in the text. The average elemental concentration of these 2 blanks was subtracted from the corresponding samples in each batch.

3. "I also am concerned about the fact that sub-samples of a larger sample were used for different analyses. I realize that this might be considered to provide a more uniform sample, but I would be very concerned that pouring off an aliquot would cause fractionation of particles. Furthermore, it is mentioned that some samples were refrozen after sub-sampling, and this is not ideal because of chemical changes that can take place while samples sit out on a counter even for short periods."

In order to prevent particle fractionation during aliquot separation, each sample was first submitted to gentle circular shaking and then immediately split. The whole splitting process took about 2 seconds per sample.

The occurrence of chemical reactions and modifications during sample handling is re-

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ally an important issue. However, in this work we do not seek to analyze these chemical species, we focus only on the chemistry of insoluble particulate matter present in the samples. Accordingly, volatile chemical components are allowed to be lost during sample handling, as well as during the sample acidic digestion described in the text, and are not addressed in this work.

4. "It might be useful to provide a few more details about the ICP-MS analysis in Table 1, such as typical sensitivity per ppb of a tuning solution and total scan time per sample."

We will add further details about the ICP-MS setup in Table 1:

Element	Tuning solution sensitivity (counts per second)
Mg	94000
Rh	560000
Pb	700000
Acquisition time	1m57s
Wash delay	1m
Flush delay	1m40s
Total scan time per sample	4m37s

5. "Is there any assessment of long-term reproducibility of data through the repeated use of specific standards?"

We can add this information also in Table 1:

Reproducibility of results using SLRS-4 Riverine water standard, 51 determinations in

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11 months:

For Li, Na, Mg, Al, P, K, V, Cr, Co, Ni, Zn, Ga, As, Zr, Mo, Cd, Sb, Th and U, reproducibility was 7-13%

For Ti, Mn, Fe, Rb, Sr, Y, Ba, La, Ce, Pr, Nd, Sm, Yb, Lu and Pb, reproducibility was 3-6%

6. "The large number of elements being analyzed makes accurate quantification especially challenging. The use of In and Re as internal standards probably only works best for elements that have similar atomic weights. Since a number of lighter elements are analyzed, precision might be improved by quantifying the lighter elements differently. Sc is an element that might work, although there is a small amount of Sc in the ice core."

It is true that using light elements as internal standards may improve their determination. But this represents a rather difficult choice, since the concentration of light elements is non-negligible in snow and ice samples, or in natural waters in general. Nonetheless, one can assess the accuracy of light element measurements in our methodology (i.e. using In and Re as internal standards) by comparing the average determination of Na, Mg and Al in SLRS-4 certified standard:

Element	SLRS-4 Concent, ng/g (std dev)	Average ICP-MS, ng/g (std dev)
Na	2400(200)	2250(300)
Mg	1600(100)	1590(140)
Al	54(4)	53.0(3.8)

7. "One additional comment: Although isotopes are not the subject of this paper, it

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might be useful to show the oxygen isotope record, or a portion of the record to show the dating and seasonality."

We will extend further the discussion of the stable isotopic record and the dating methodology. These issues are extensively covered elsewhere in papers by Ramirez et al. (2003) and Simões et al. (2003).

References

Ramirez, E. Hofmann, G., Taupin, J.-D., Francou, B., Ribstein, P., Caillon, N., Ferron, F. A., Landais, A., Petit, J.-R., Pouyaud, B., Schotterer, U., Simões, J. C., Stievenard, M. A new Andean deep ice core from Nevado Illimani (6350 m), Bolivia. Earth. Plan. Sci. Let. 6674, 1-14, 2003 (in press).

Simões, J. C., Taupin, J.-D., Ribstein, P., Petit, J.-R., De Angelis, M., Ramirez, E., Hofmann, G., Correia, A., Delmas, R. J., Dupré, B., Ginot, P., and Francou, B. Forty years of environmental record from the Nevado Illimani ice core, Central-Eastern Andes. J. Geophys. Res., (in preparation), 2003.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 2143, 2003.