Atmos. Chem. Phys. Discuss., 3, S1024–S1033, 2003
www.atmos-chem-phys.org/acpd/3/S1024/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Trace elements in South America aerosol during 20th 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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Received and published: 11 July 2003

We thank Anonymous Referee #1 for the important comments on our paper. Each of the issues raised by Referee #1 will be addressed below:

1. "In discussing the results the authors attempt to address a rather extensive variety of geo-chemical issues ranging from ENSO driven impact, dry/wet season contrasts, multi-year cycle (connected to stable water isotope patterns) to long term changes of anthropogenically derived elements and the characterisation of (so called) "local soil dust aerosol". However, based on the presented material it is rather difficult to assess the significance of the findings. I generally suggest to reduce the number of addressed issues (concentrating on the significant ones) and to re-organise the paper to make the

findings clearly supported by the data presentation."

This work focused on the characterization of the background aerosol trapped in Illimani ice core, by using a new methodology never reported previously. Seasonal variations and multi-year cycles are important features present in the ice core record, which are related to local precipitation and climatology. ENSO induces large precipitation anomalies on the Western Andes, it is important to assess its impact on the Eastern Andes as well. These issues are key to understand the temporal evolution of aerosol concentration levels. We present the original results of our measurements and interpretations of climate-related changes. These findings do not seek to cover all possible aspects and consequences of this broad research field. Additional papers are planned for exploring more details of the different topics addressed by this study.

Note that we will change "local" soil dust aerosol to "regional". This expression is indeed more appropriate to describe the origin of the particulate matter present in the ice core.

2. "There is a lack in the description of the glaciological drill site feature. Give details of, at least, firn temperature, occurrence of melt layer, sublimation effects, depth of firn (ice transition, see also below) and the drill site position relative to the surface topography (i.e. map with contour lines)."

The description of glaciological features at the drilling site is important for the full characterization of Illimani ice core. These details will be given elsewhere by Simões et al. (2003), and we will emphasize this point in the revised text.

3. "Dating deserves closer attention: what is the typical uncertainty in different sections of the analysed core, is there a systematic change in the annual layer thickness (ice or water equivalent) not explained by vertical strain?"

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We considered the discussion of glaciological features (previous item) and dating methodology to be a little too technical for the scope of Atmospheric Chemistry and Physics. These subjects are fully addressed by Simões et al. (2003). Nonetheless we can extend further this discussion in the revised text.

4. "It remains unclear how the sample handling blanks are obtained (note that firn core decontamination cannot be simulated by a refrozen blank water sample). Blank variability and minimum concentration are missed in Table 2 to assess the deployed method."

It is true that firn core decontamination cannot be fully simulated in the laboratory. Our blank tests cover the majority (but not 100%) of the decontamination process with samples of ultrapure frozen milli-Q water. These samples were submitted to the very same analytical conditions that real samples would face, and 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. By following this methodology, the reproducibility of our elemental concentration measurements was better than 13% for most chemical species.

We will add the standard deviation of blank measurements in Table 2. The minimum concentrations are of little help to assess the quality of the deployed methodology, since most average concentrations of blanks are already under the instrumental detection limits, as stated in the text.

5. "The reasoning that Li is local derived is not conclusive. Similar deviations from Bowens soil ratios are seen for other crustal elements like Ca, K, Ba and Ta. It re-

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mains unclear why the authors put so much emphasis on Li in presenting their data (a less commonly measured species in mineral aerosol). The ENSO-Li link argument is blurred and should be skipped."

It is true that other elements besides Li deviate from Bowen's soil ratios. However, these elements may have multiple aerosol sources, so it is not possible to ascribe them to regional soil dust. Lithium, on the other hand, has no other strong evident regional source than the ubiquitous salars (Risacher, 1992). Bolivian salars are the most important resource of this metal on the global scale. The emphasis on Li measurements arise from the fact that this is the first time, to our best knowledge, that ice core measurements of this light element are reported; it represents the impact of regional aerosol, which is the main focus of this work. Nonetheless, our results are not restricted to Li, we present as well a wide range of other elements measured in Illimani ice core, and we compare these measurements with results obtained by other authors.

ENSO has large impacts as precipitation anomalies over the Western Andes. Assessing its influence over Eastern Andes is an important issue. Our results show that there is no clear relationship between concentration levels and ENSO phases. Although it is a negative result, it is a legitimate conclusion of our research work, and it is in accordance with a recent paper by Hoffmann et al. (2003).

6. "The procedure to dissect dry and wet seasons is not clearly described. What kind of parameters are used, how did the authors cope with the systematic decrease of temporal resolution with depth? What I would expect to see here first are average seasonal cycles presented for some key trace elements."

The compression of layers with depth does not represent a problem for dating the Illimani ice core up to 50 m depth. Although bottom layers are thinner than upper ones, it is possible to apply layer counting up to this depth (and even a few meters below it), and to identify dry and wet seasons with no need for any parameterization.

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The seasonal averages for all 45 elements are in Table 3. Besides that, we also show these seasonal averages for the beginning of the 20th century in the same Table, as explained in the text.

7. "It is unclear how the 2-5 year periodicity in the dry season impurity levels are obtained. The link to meteorological parameters is suggestive and should be skipped (glaciological impacts are possible reasons as well)."

The periodicity of 2-5 years in Figure 3 is a feature of measured concentration levels. The dots simply represent each measurement we performed, the lines connect consecutive dots. The link to meteorological parameters calls the reader attention to this feature, that may be further explored in the future, indicating a possible connection between aerosol concentration levels and quasi-biennial atmospheric oscillations, ENSO in the beginning of 20th century, or even solar variability for longer time periods.

8. "I feel the delta-D insertion is out of scope (to be skipped as long as the issue is not really substantiated)."

The Delta-D profiles are in principle related to major temperature changes during the 20th century, they are important to understand climatological modifications occurring in South America. Referee 2 indeed asks for more discussion on the isotopic variations, even if it is not the primary focus of our work.

9. "Following Fig. 4, I cannot recognise a significant link between delta-D and crustal (Ti) level minima as indicated. There are other events with a vice versa feature."

The link between Delta-D and Ti refers to multi-year time scales. We will add lines in Figure 4 to highlight this relationship and make it clearer to the reader.

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10. "Comparison with Antarctic ice core data are of little help due to the totally different spatial source distribution."

It is really difficult to make comparisons with other results, due to the scarcity of data available, as well as due to differences in methodologies and analyses performed. In Table 3 we compare differences and possibly similarities in elemental concentrations between different locations. We do not seek to infer a direct relationship between aerosols in Antarctica and in South America, but although the Antarctic continent is located far from the Illimani site, there are evidences of atmospheric transport of South America aerosols to Antarctica, particularly in glacial conditions (Lunt and Valdes, 2002).

11. "The overview of concentration levels in Table 3 lacks any indication of the Illimani data variability, whereas the number of samples is relatively unimportant. Best give the resp.log and/or linear SD values to make the means useful, possibly include the data ranges as well."

The number of samples is very important. Statistically, in a normally distributed population, there is more than 60% probability of underestimating standard deviations if one takes less than 5 samples from that population, a condition not uncommon in ice core studies.

Illimani data variability is shown in the last 4 columns of Table 3. There is one column for dry season averages for the whole record (D), one column for wet season averages for the whole record (W), one column for the dry season in the beginning of the 20th century (Db) and one last column for the wet season in the beginning of the 20th century (Wb), as explained in the text. These columns are representative of elemental concentration variability in Illimani, dry season averages correspond to higher end val-

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ues and wet season averages to the lower end values. The columns for the beginning of the 20th century represent the elemental concentration ranges in Illimani before the onset of the vigorous economic development occurred in South America during the second half of last century.

12. "Within the above chapter, also long therm changes are addressed though to a minor extent and without respective data presentations. Having an ice core data set on hand covering so many elements I would expect that evaluation of net temporal changes of anomalously enriched elements would be a primary focus. I wonder why there is no parametrisation given on the significant temporal changes seen in the data set."

This work shows a new methodology for the full chemical characterization of background regional aerosol in South America from the Illimani ice core. It does not intend to cover completely all issues related to environmental pollution of anthropic origin, which will be addressed elsewhere.

13. "The discussion in these chapters is somewhat redundant in view of the EF feature under high and low (i.e. dry and wet) conditions. It is obvious that any non-crustal excess (no matter what the reason is) becomes eventually diluted (up to non-detectable levels) if the crustal impurity is increased over several orders of magnitude. Expecting a more or less log-normal frequency distribution of the Al-(reference) values presented here it is no surprise that EF-values are driven by the crustal impurity content. The related material in chapter 3.4 and 3.5 may be strongly condensed, therefore."

Several factors may affect the enrichment factors of aerosol particles. During their formation, fractionation may change the elemental concentration ratios during aerosol mobilization and transport between natural reservoirs. Specifically in the Amazon Basin,

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there are enormous emissions of biomass burning plumes every year during the dry austral winter, covering a large fraction of the South America continent. Among several other works, Echalar et al. (1995) showed that biomass burning aerosol emissions during the dry season in the Amazon Basin are highly enriched compared to natural background conditions. In addition, Vuille (1999) showed that the prevailing wind pattern in the Amazon Basin conveys moisture to the Eastern Andes, so there could also be an impact from biomass burning plumes, bringing enriched aerosol particles to the Andes Mountains. Contrary to this expectation, our work shows that aerosol enrichment factors in the dry season attain their minimum values, and are highest during wet austral summer, a non-obvious result.

Section 3.5 describes a new methodology for obtaining the chemical characterization of the regional soil dust aerosol measured in ice cores, which has never been reported elsewhere to our best knowledge. For this reason it requests the full explanation showed in the text.

14. "Change anthropic into anthropogenic, throughout."

We used the words "anthropic" and "anthropogenic" very carefully, according to their definitions in the Merriam-Webster dictionary. "Anthropic" is used as "related to human activities", while "anthropogenic" is used as "originated from human activities", a slightly different meaning. Thus we might have used expressions like "anthropogenic aerosol source" or "aerosol source of anthropic origin". We understand that an expression like "aerosol source of anthropogenic origin" would be less appropriate.

15. "Plots of temporal records (either for trace elements of delta-D) should be strictly revised: give data as a histogram (as they are analyses), not individual points connected by a line - show original data, if necessary together with some smoothing (actually the

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delta-D lines in Figs. 3 and 4 cannot be ascribed to the data)."

Following Referee #1's indication, we performed several tests to determine the best way to plot our graphs, i.e., the best way to convey information to the readers. Histograms are the best choice when one has a variable oscillating about a mean value. In our case, we have more than 700 sequential samples corresponding to variable time steps, with varying trends that would not be conveniently highlighted in histogram plots. We determined that plotting our data as line-connected dots expresses best the temporal evolution of our measurements, and represents the best way to convey this information to the ACP audience.

The Delta-D lines in Figures 3 and 4 were obtained by from measurements performed at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE, Gif-sur-Yvette, France). These Delta-D measurements were averaged over the same depth interval corresponding to each one of our samples, so their values correspond to the best Delta-D estimates that can be compared with our measured elemental concentration profiles.

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