Atmos. Chem. Phys. Discuss., 8, S5804–S5809, 2008
www.atmos-chem-phys-discuss.net/8/S5804/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Reassessment of the factors controlling temporal profiles of nitrate in polar ice cores using evidence from snow and atmospheric measurements" *by* E. W. Wolff et al.

E. W. Wolff et al.

Received and published: 11 August 2008

We thank the reviewers for their comments.

The two reviewers both make comments about the overall balance of the paper between the discussion of SPEs and the wider interpretation of nitrate in ice cores, and about the length. We will therefore firstly address this point for both reviewers in a common section; it is already discussed partially in our initial comment entitled "Nitrate and SPEs: a closed topic?";. We accept the point that most of the topics in this paper are not new, and have separately been discussed before. Our intention was indeed to provide an update of what are the prospects for deriving information of use to atmospheric chemists from nitrate in ice cores. Our feeling was that, apart from a brief section in a

recent review paper (Grannas et al., 2007), such an overall assessment has not been tackled for over a decade (Wolff, 1995), despite it being the stated motivation of many recent studies.

Turning specifically to the issue of SPEs, as already discussed, while ice core scientists may think they have thoroughly dismissed the identification of peaks in nitrate with SPEs, this is definitely not understood in the solar-terrestrial community. I agree with the sentiment that a really good paper from an ice core perspective in a specifically solar-terrestrial journal is overdue; however here we have tackled the issue from a somewhat novel atmospheric chemistry angle. While previous papers have discussed the difficulty of replicating findings of SPE papers in different cores (Legrand and Kirchner, 1990), or of explaining such high concentrations from SPEs, here we concentrated our new work on the opposite problem, of coming up with a good alternative explanation for the spikes reported in earlier work (McCracken et al., 2001). We do this by using the Halley data as an exemplar of how the spikes can be created; we have then used reasoning to extend the findings to explain how similar spikes might be found in the sites investigated in that earlier work.

Thus we feel that the SPE work does need to be aired (as accepted in the last comment by reviewer 2), and that there is a logic to including it in this paper with a more general goal in ACP. As long as it is included, it is not possible to make the very drastic length reduction called for by reviewer 1, although we have removed several paragraphs from our revised text, and thereby shortened an already quite short paper. We do not feel we can go further without damaging the readability that reviewer 2 praised.

Reviewer 1:

In addition to the general point, reviewer 1 makes a more specific point about the relevance of Halley data to the interior of Antarctica. Firstly, for the high-resolution records, Halley is not an untypical site; high sea salt concentrations are characteristic of the coastal regions and the ice shelves, where many ice core records with sub-annual

ACPD

8, S5804–S5809, 2008

resolution have been taken. However, there is certainly no implication that Halley tells us about deposition to the inland plateau; however it is the coupling between the inland (where little nitrate is preserved in ice) and the coast (which appears to be the recipient) that we feel needs further study.

Regarding the use of the term "NOy production";, we were not sufficiently clear in explaining when we mean polar production or otherwise. We have now altered both the introduction and conclusion to clarify what we believe ice cores might be capable of.

Reviewer 2:

In addition to the general point, reviewer 2 makes several specific comments that we have addressed as described below (page and line numbers refer to discussion paper).

Page 11041, line 29: We agree, Mayewski and Legrand, 1990 removed.

P11042, around line 15: "I can only encourage the authors to rephrase that section, clearly stating that nitrate ice core concentration will be interpreted differently from different sites." DONE.

Same page, end of page: Although we think it is true that the recent work on atmospheric nitrogen and ice cores has not been brought together, we have removed the sentence about that.

P11043, L18: "Why describing the denuder collection system when no data are presented." Because we later mention the denuder data (even though not showing it), we leave a reduced description here.

P11044, L20: "I wonder if the first event in figure 1 is a good example to show the discrepancies btw SPE and nitrate peak." We have added a sentence to say what we mean about the discrepancy between SPEs and spikes.

P11045, L19: "Getting the right concentration of surface snow can be a difficult task

ACPD
8, S5804–S5809, 2008

because of the sharp decrease of concentration in low accumulation sites." This certainly true, but Halley is not a low accumulation site - events tend to be deposited and removed at the several cm scale. We have many years of experience of collecting such samples, and do not feel that sampling problems can explain what we see.

P11047 L2: "Sentence issue." Wording adjusted.

P11047 L7: "Gas phase nitrate can dominate particle phase even a ground level. If high concentration of NaCl is present, the partition btw gas and particle should show this mass transfer even at ground level." While this is true, we are not sure we agree with the sentiment behind this comment, because we were considering the opposite situation (which we have observed (Rankin and Wolff, 2002)), in which NaCl can have low concentrations near the ground, but higher concentrations aloft, leading to the possibility that deposited snow can have high concentrations of nitrate that has attached to sea salt aloft, despite there being no indication at ground level.

Section 3.3: "I wonder if this section cannot be merged with 3.1." We decided to leave this as it was, because we think it imporves the narrative flow.

P11051, L13: "Reference to Blunier experiment. I will advise the author to be cautious about Blunier experiment." We have rephrased this section to make it less definite. However, see the comment regarding page 11052, line 13.

P11052 first lines: "As I said before, in most inner part of Antarctica, nitrate profile may actually become a proxy of meteorological factor more than representing a change in NOy production." Yes, we agree, this is the point we intended to make, that it is not yet obvious which part of the processes is best represented in the ice core record.

P11052, L13: "Again caution should prevail here. Blunier, Anastasio Chu and others abundantly shown that even in the form of a salt, nitrate is photolysed in snow." We agree completely that photolysis could occur in whatever form nitrate is present. However, the fact is that, at the sites (Vostok, Dome C) in which most nitrate is lost

ACPD

8, S5804–S5809, 2008

under present conditions, the concentrations of nitrate are much higher in glacial-age snow. That implies that, for whatever reason, the loss does not occur to anything like the same extent. This is actually a strong argument that it is indeed the re-evaporation that is important in the present, because it is obvious how the increased dust concentrations would fix nitrate in central Antarctica and prevent re-evaporation, analogous to what happens with sea salt at the coast today.

P11053, L5: "mass distribution with depth in central part of Antarctica may be different that the one exposed by the authors." We have deliberately referred to the mass balance of nitrate that is RETAINED in snow. In other words we ant to calculate how much nitrate is buried to a depth where it is stable each year. To do that calculation, one ignores the high concentration surface snow (which is not retained in central Antarctica, but subsequently appears as deposited material somewhere else after recycling). This is why we have used the concentrations recorded at a few metres depth.

Typo: P11053 L22 and in bibliography: "Subscript 3 for nitrate and x or y for NOx and NOy." Sorry - these were introduced during typesetting of the discussion paper and not noticed during proofreading.

Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Dominé, F., Frey, M. M., Guzmán, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H. W., Klán, P., McConnell, J., Plane, J., Sander, R., Savarino, J., Shepson, P. B., Simpson, W. R., Sodeau, J. R., von Glasow, R., Weller, R., Wolff, E. W. and Zhu, T.: An overview of snow photochemistry: Evidence, mechanisms and impacts, Atmos. Chem. Phys., 7, 4329-4373, 2007.

Legrand, M. R. and Kirchner, S.: Origins and variations of nitrate in south polar precipitation, J. Geophys. Res., 95, 3493-3507, 1990.

McCracken, K. G., Dreschhoff, G. A. M., Zeller, E. J., Smart, D. F. and Shea, M. A.: Solar cosmic ray events for the period 1561-1994 1. Identification in polar ice, 1561-

ACPD

8, S5804–S5809, 2008

1950, J. Geophys. Res., 106, 21585-21598, 2001.

Rankin, A. M. and Wolff, E. W.: Aerosol profiling using a tethered balloon in coastal Antarctica, J. Atmos. Oceanic Technol., 19, 1978-1985, 2002.

Wolff, E. W.: Nitrate in Polar Ice, in: Ice core studies of global biogeochemical cycles, edited by: Delmas, R. J., Springer-Verlag, Berlin, 195-224, 1995.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 11039, 2008.