**Atmospheric
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Interactive comment on "Air-snow transfer of nitrate on the East Antarctic Plateau – Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium" *by* J. Erbland et al.

Anonymous Referee #1

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The phenomena surrounding nitrate and NOx on the East Antarctic plateau have been one of the most surprising and interesting discoveries in atmospheric chemistry in the last decade. On the one hand, the photochemistry of nitrate in snow drives intense changes in atmospheric chemistry in the atmospheric boundary layer, dominating the oxidant chemistry for example. On the other hand, the loss of nitrate from surface snow seems to control the concentrations of nitrate seen in ice cores, making it hard to use those concentrations for other interesting purposes. While some of the effects of the processes that occur are well-documented, there remains a lack of data to allow a full understanding (and therefore modelling) of those effects. This paper is an excellent attempt to fill that data gap. Although I think some of the conclusions are overstated,

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Discussion Paper

the data are a very fine resource for future work, and place the phenomena on a sound quantitative footing. For that reason, the paper will make a good addition to ACP, although some moderate changes may be needed. I note in passing that this is part 1 of 2, with a companion modelling paper apparently planned: however, that companion paper is not yet online, so I will treat this paper as freestanding.

The heart of this paper is the data shown in Figs 2 and 3 (and again in the supplement). This is a great dataset and I congratulate the authors on producing it. It really clarifies the extent of the phenomena being described. While I have detailed comments on various aspects of the paper, the major issue I have with the paper concerns the "laboratory" nitrate evaporation experiments and the conclusion from them that the evaporation fractionation is -8.5 permil. This result drives the conclusion that photochemistry dominates the loss process. While I think the conclusion may well be correct, I don't think this number is sound, and the authors should treat it very cautiously. I will therefore start by discussing section 3.2, Figure 8, and section 4.1.1.

It is first necessary to comment on their preconception (based on Frey et al 2009) that the fractionation constant for evaporation would be positive. It is not for this review to comment critically on an earlier paper, but this is a very surprising conclusion. One would naturally assume that the heavier isotope would have a lower vapour pressure and that the fractionation constant for evaporation would be negative. That this was not the conclusion in Frey et al (2009) arose from their decision that calculating the fractionation from the evaporation step was beyond their scope, so that they concentrated only on the fractionation arising from an ionisation step. However that ionisation step arises only if most of the nitric acid is dissociated. In practice, at a typical summer temperature of -30 degrees, and assuming HNO3 as the only impurity in the liquid, the equilibrium concentration in any liquid or liquid-like layer will be around 5 molar (and higher at lower temperatures), implying that a substantial percentage (I estimate of order 10%) of nitric acid is undissociated, and making it probable that the crucial step is the evaporation and not the ionisation. In any case, whether they agree that this is the

reason or not, the present authors need to comment on why the constant they derive from their experiments is of opposite sign to their colleagues' earlier deduction – at present this discrepancy is just ignored.

In the current evaporation experiments, there are a number of issues. The experiments though interesting, are really not very similar to the real field situation, because they are done at a constant temperature (no vertical temperature gradient). In real life, the system is being driven by very strong temperature gradients. This difference is probably why no effect could be seen at the lower temperatures – precisely the relevant temperatures in the field. I am also not clear whether the experiment is in a closed system or whether the air above the snow is (as in real life) being replenished constantly. The authors then state that they have corrected for snow sublimation (page 28566, line 17). The paper needs to explain what they mean by this. I am assuming the authors mean that they "diluted" the concentrations according to the water loss, but we need to have the details of this calculation explained as it is not at all obvious to me how a water sublimation, likely arising mainly from the top layers, is correctly allowed for in a bulk subsample. It is clearly important as my interpretation is that the nitrate concentration was actually higher at the end of the -30 experiment (more water mass loss than nitrate) than at the start, which makes the whole basis for the calculation very uncertain. Clearly this is not mimicking the field, where the nitrate concentration reduces with time. This is probably again down to the temperature: at -10 degrees there is substantial loss of water which will not be the case at field temperatures, and nitrate is likely to be lost as successive layers of water rapidly escape. At lower temperatures more representative of the field, the water loss is much reduced, while the nitrate loss may even be enhanced due to the higher concentrations in the remaining liquid at low temperature and the consequent reduced dissociation. My concern is therefore that we are left with a single experiment that is not really treating the field situation and mechanism, that is being calculated in an approximate way, and in which the slope can be calculated essentially from only a single data point (the one top left of Figure 8).

I do not have a brilliant solution to this, though I think it would be possible to estimate the fractionation constant for evaporation based on vapour pressures (which may exist in the literature), or from evaporation experiments simply based on bulk cooled solutions in which the water loss could be controlled better. It is also possible to buy $H^{15}NO_3$ as a pure compound on which experiments could be done. These are beyond the scope of this paper, but I nevertheless propose that the calculated fractionation constant needs to be treated with extreme caution, and that conclusions based on it must be heavily annotated with uncertainty.

Beyond this major point, all my other comments are relatively minor and are listed below.

Page 28560, line 15: I think it is misleading to give the fractionation constant for evaporation as having such a small error and the caveats around the experiment need to be mentioned here.

Page 28561, line 2: "relationship. . ..rate on the residence time" should be "rate with" or "rate and".

Page 28563, line 5. Please, for those who don't want to go to Blunier (2005) spell out how epsilon is calculated (ie as $R/R\_0=(f\hat{}epsilon)$, where R is the isotope ratio and f is the fraction of nitrate remaining).

Page 28563, line 25: I would suggest adding caveats about why the estimate of positive epsilon in Frey is dubious (as above). You will need this in order to avoid having to show extreme surprise when you find a negative value in the experiments.

Page 28567, line 4: convert nitrate to N_2O, not "in H_2O".

Page 28568, line 2 (and several other places, eg Fig 8, y-axis): there is a little carelessness about factors of 1000 here, you mean that you plotted 1 +delta/1000 if delta is in permil.

Page 28568, line 5, explicated is not a word, please use explained.

Page 28569, line 11 and 12. N equivalent is a bit confusing as equivalent means something else in chemistry (microequivalents being a concentration unit). Please re-word this "expressed as kg (N) m^-2 a^-1" for example.

Page 28570, line 4, snow not snowe

Page 28570, line 13, displayed not displayer.

Section 3.4 and Fig 11: I am not sure we learn anything from this figure and I'd be inclined to leave it out.

Page 28574: Here is somewhere where more caution is needed about the role of evaporation. You should perhaps also mention that there is also evidence for loss of HCl from snow at Dome C (eg Rothlisberger et al 2003). As there is no obvious photochemical route for this, it suggests that evaporative loss can occur and maybe a scaling calculation (using vapour pressures) would allow an estimate to be made for nitric acid (though one would have to be cautious because of different ionisation fractions). As a matter of interest did you measure chloride profiles in your snowpits?

Page 28579. If you believe that +24.7 is the fractionation constant for deposition to the snow, then doesn't it follow that -24.7 is the constsnat for sublimation from the snow? This might be a more defendible value than the one from the evaporation experiments?

Page 28580. I don't think the explanation for the temporal offset really makes sense. Remember that the snow is the far larger reservoir, so it should be the concentration of nitrate in snow driving the air not the other way round. I have not calculated it but I would have thought a more likely explanation is that the lifetime of nitric acid in air (due to photolysis) decreases in midsummer, so that the atmospheric NOy is transferred much more into NOx rather than HNO3 during the snow peak. Unfortunately the Frey et al 2012 NOx data don't extend early enough to assess this.

Page 28583, line 6. Cage recombination deserves a longer explanation for the reader please.

Interactive
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Interactive Discussion

Discussion Paper

Page 28584. There have been attempts to use the nitrate concentration in snow as a proxy for snow accumulation rate in the past (Wolff et al, 2010, QSR). Would you like to speculate on whether use of 15N might enhance this possible application?

Page 28585, line 14 "well explain" is not quite English, "easily explain" would be better. References: all have the pages on which citations occur, please make sure these are removed from future versions.

Table 1 caption. Explicated -> explained.

Figure 4 and 7. The lower x axis usage is unusual. I'd prefer the more normal "Aˆ-1 / mˆ2 a kgˆ-1"

Fig 9 caption. I don't really understand what you mean by "the date when the data were composited". Please explain what this means.

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