

This paper presents some previously unpublished data on the isotopic values in nitrate in air samples from Summit, Greenland. It also compiles previous data on isotopes in nitrate in air, surface snow and “archived” snow at the same site. The paper then focusses on a discussion of the role of snow photolysis of nitrate in influencing the observed isotope values, their seasonality, and the differences between air and snow.

There are a few general comments to make about the paper. Firstly, the new data are potentially very useful and deserve to be published, even if I have a few questions about them. The authors have also done a nice job of compiling previous data, shown in Figure 2, which serves as an excellent starting point for a discussion.

The discussion is quite a tough read, even for someone who is quite well-versed in the issues but this probably reflects the difficulty of making clear statements in the light of sparse data, and a definite divergence in opinion between the major groups working on this topic. My main concern with the paper is that some statements are made, sounding quite definite, that are based on differences that are highly marginal. I realise it is disappointing when the conclusion of a study is “we’re not sure if this is real”, but in some cases this would have been a fairer conclusion. I think the overall structure of the paper and the way it tries to use the different datasets is good, so my comments mainly focus on particular statements that seem too definite or not to be well-supported by the data shown. For that reason, I just go through the paper in order, with both minor and major comments mixed in.

Title: the word “reality” seems a bit misplaced here. Of course one can read in the text an undercurrent that the message of the paper is directed at a competing group and that this paper is saying “there really is an effect”. But I think for the neutral reader it would be less provocative and more accurate to write “evidence for the postdepositional effect”.

Abstract: line 24: since you argue that you have collected aerosol and gas-phase nitrate, the word “aerosol” should be removed here.

Abstract: line 28: you should review the wording “no apparent seasonality”. I will discuss this later, at line 248.

Abstract: please review what you have written in the light of edits elsewhere in the paper. I am particularly concerned that lines 37-43 are stronger than the data really allow (see later).

Line 51: Wolff 2008 is not in the reference list, whereas Wolff 1995 is, but is not cited in the paper.

Line 148, 156 and surrounds. Obviously a lot hangs on the quality of the atmospheric data. I have two issues I’d like clarified. The first concerns the use of GF filters. I agree they have often been assumed to collect gas phase nitrate as well as aerosol but the evidence is quite minimal for polar sites; the mechanism is assumed to be through attachment to sea salt loads on the filters (see eg Wagenbach et al, JGR, 103, 11007-11020, 1998 for a discussion of this, albeit related to cellulose filters). Given this I propose that Fig 2 (or a supplementary figure) should show a comparison of the concentrations of nitrate in this study compared to those found in previous studies (including Fibiger and Jarvis) that used mist chambers. This would allow a more informed discussion of whether this study is reporting a similar fraction of total nitrate to earlier studies.

In addition, I am a bit alarmed by the observation that nearly half the collected samples were discarded because they were too close to the blank (for nitrate concentration, I assume). This might imply that there remains a significant blank component in many of the filters that were not discarded and this could then affect the isotopic ratios measured if the blank is contributing

significantly. Please comment on this (I would assume you have some isotopic measurements on blank filters?).

Figure 1: I find it a bit strange that you choose not to plot the data chronologically but instead that you have Jan to Jul 2002 followed by Jul-Dec 2001. I would propose plotting the data chronologically (Jul-Jul) in Fig 1, and from Jan-Jan in Fig 2.

Line 208-209. I don't request a change but I note that this is a bit circular. You use the similarity in seasonality to support your seasonal assignments in snowpack, and then later you use the same alignment as evidence that $\delta^{17}\text{O}$ in particular is unaffected by photochemistry.

Line 243. You attribute spikes to Arctic Haze events. Could it also be that it reflects more efficient scavenging during inputs of high sea salt (you would be able to support or deny this by looking at seasalt in the aerosol data)?

Line 248. You say there is no distinct seasonality in the atmospheric ^{15}N . But I look at Fig 2b, where you also show the snowpack ^{15}N from Geng, which you claim has a clear seasonality. While obviously the aerosol data have large variability within each month, I see just as strong a seasonal dip in the aerosol data as I see a seasonal peak in the snowpack data. In the end this isn't crucial because it's the differences between the air and the snowpack in different months (which is clear) that you focus on, but still please reword more cautiously.

Line 257: "(18O) displayed an almost identical seasonal pattern with $\Delta^{17}\text{O}(\text{NO}_3)$ as expected". I'm sure if I'd read your previous papers I would know why this was expected but it's not obvious, given that the former is a mass dependent fractionation and the latter is a mass independent one that could be quite separate. Please spell out why it's expected.

Figure 2. In part a, please clarify that the curve refers to the actinic dose (not "does") that would have been experienced by the snowpack samples.

Fig 2e: I assume these seasalt data refer to the snowpack data (but then which: Geng et al?). Please clarify this in the caption. Also, I'd be really surprised if the Na are in mg/L, surely they are ppb or $\mu\text{g}/\text{L}$?

Fig 2 caption. "The vertical lines represent the interval of seasons". I don't understand what this means. Are the error bars the differences between years for the same month/period, or are they the variability within a month or season. This is crucial to understanding what values are significantly different to others.

Line 290. This is the first case where I really feel you say things the data don't support. You refer to a progression of ^{15}N from atmosphere to surface to snowpack. However when looking at Figure 2, it would be really stretching it to say that the surface snow data of Fibiger et al are significantly different from the snowpack data, taking into account the error bars shown. I agree there is a difference between the single Jarvis data point but as you later question this data I don't feel it's justified to make a wide-ranging and repeated statement about a progression on the basis of that. To me this is a place where you have to say that there is a clear difference between atmosphere and snow, but the data are insufficient to state with any certainty whether the surface snow and snowpack are different. The same issue is repeated in line 340.

(As an aside if the Jarvis atmospheric data in Fig 2b are right then the variability in the atmosphere between years is also too high to make a clear statement but I think it's Ok just to have noted the discrepancy).

Fig 3: Why do you only show J against SZAs (in the inset) almost entirely smaller than those experienced at Summit in the main figure?

Line 413, Fig 3 and surrounding discussion. I am really mystified by this lengthy section. Of course it's a nice advance that you can find a simple formula to represent the complex output of the model for PIE. However you don't then use it. Apparently PIE is the "difference between surface snow $^{15}\text{N}(\text{NO}_3^-)$ and archived snow $\delta^{15}\text{N}(\text{NO}_3^-)$ ". So why don't you plot the actual data in Fig 3 and see if it agrees with the model and its simplified (eq 3) representation. And of course the answer is that it doesn't. The observed PIE in May-July looks from Fig 2b to be about 3 permil, not the predicted values of about 10. (We can argue about the significance of the single value for spring, which you later suggest you don't believe). In any case my point is that there is no point having this section and figure unless you also show and discuss the data.

Line 423 – "J also varies with depth". This is wrong because J is the surface photolysis rate constant. The exponential term changes the actinic flux seen at depth.

Line 458-9. This is a strange statement in that it's not clear how a data point obtained by another group can be "explored and confirmed".

Line 680, 685 and what follows, plus 715 and following. A quite definite conclusion is based on the assertion that the slope of the snowpack data is significantly different from that of the atmosphere (not aerosol) and surface snow data. Your reported uncertainties on the slopes might indeed suggest that but sometimes it's better just to look at the data – would anyone really say that the yellow data are a significantly different population from the blue and black data? In fact you suggest that what is happening is an enrichment of ^{18}O in the snowpack samples. But again, just look at the data: it's quite obvious that if there is a difference it is that the snowpack data have a subpopulation that is enriched in ^{17}O (I admit I am not sure how that leads to a lower slope and indeed by eye its very hard to see how the yellow points can have a slope of 0.3). Please reconsider this whole discussion; I think you are building a lot on very shaky differences.

Lines 724-736. Yes, I like this paragraph.