General comments

The manuscript by Shi et al. reports snow pit results of nitrate and its isotopic composition along a traverse from coastal East Antarctic to the interior of the plateau and evaluates the effects of post-depositional processing on snow nitrate. The dataset covers an extensive area and appears to be valuable. However, much of the work (mainly the interpretation) in this manuscript repeats, at a less comprehensive level, what have been done in previous publications (e.g., [*Erbland et al.*, 2013; *Frey et al.*, 2009]) in the same journal. The perhaps only new content compared with the previous work is that the snowpits in this study cover a greater depth. However, the interpretation/discussion on this part is fraud. In particular, the authors state in the abstract that "Predicting the impact of post-depositional loss, and therefore changes in the isotopes with depth, is highly sensitive to the depth interval over which an exponential decrease is assumed". This statement/conclusion comes from the practice that the authors break down the entire snowpit to several depth intervals, use the Rayleigh fractionation model to calculate the fractionation constant, and apply the approach in Erbland et al. [2013] (i.e., using an exponential regression to calculate the asymptotic values of nitrate concentration and isotopes at depth below the photic zone) to a greater depth than the photic zone (up to 300 cm deep). This practice is particularly problematic for several reasons:

First, the Rayleigh Fractionation model calculates the "apparent fractionation constant" [*Erbland et al.*, 2013], which is influenced by the degree of post-depositional processing. The degree of the post-depositional processing is in turn influenced by surface UV intensity, snow accumulation rate and snow light-absorbing impurities (e.g., [*Zatko et al.*, 2013]). When use this model to calculate the fractionation constant at different depth intervals, e.g., 0-25 cm, 25 -100 cm, and 100 cm to bottom, difference is expected on the result, as well as the logarithmic

relationships between the isotope values and concentrations (or mass fraction of nitrate called in this study). This is because that at 25-100 cm, UV intensity is less than in the shallower layer, therefore the degree of post-depositional processing is smaller, which leads to a smaller "apparent fractionation constant" and a weaker relationship between the isotope values and concentrations. This is similar to the observations on snowpits from sites with different snow accumulation rates, i.e., at site with a lower snow accumulation rate the apparent fractionation constant is greater [*Erbland et al.*, 2013] and the calculated logarithmic relationship is stronger (Table 2 of this manuscript) due to the higher degree of post-depositional processing.

Second, it does not make sense to use the Rayleigh model to calculate the fractionation constant at depth below the photic zone. The authors perform this at the depth intervals of 25-100 cm and 100-bottom (200 or 300 cm deep). The e-folding depth of UV radiation in the plateau is 10-20 cm based on observation [*France et al.*, 2011], and 18-22 cm based on model [*Zatko et al.*, 2013] which was recently suggested to be overestimated by ~20% [*Libois et al.*, 2013]. But in any case, most (95%) of UV radiation disappears below the photic zone (in general 3 times of the e-folding depth, which is ~60 cm the maximum), where photolysis of snow nitrate is inhibited. Therefore, what is the point do use the Rayleigh model for the depth interval of 100-200(300) cm?

Third, the authors apply the approach of the exponential regression to different depth intervals and to a depth well below the photic zone, and claim that the "asymptotic values and thus the prediction of nitrate concentration and isotopic values in ice cores depend on which depth interval the exponential regression is done". This also does not make sense. The exponential decrease is expected from the effect of post-depositional loss. Underneath the photic zone, nothing will change any more in theory. So what's the point to do this regression to a depth

well below the photic zone? The basic idea of doing such a regression in Erbland et al. [2013] is, given the condition that the degree of post-depositional processing is constant during the period that a certain layer of snow stays in the photic zone, nitrate concentration and its isotopic composition in that layer will approach constant values and can be predicted (i.e., the asymptotic values in Erbland et al. [2013]) once that layer is buried below the photic zone. However, this is not saying that at every snow layer below the photic zone, nitrate concentration and its isotopic composition should be the same. Because the concentration and isotopic composition below the photic zone are also influenced by that in the originally deposited snow. In addition, the degree of post-depositional processing could also vary with time, given the possible changes in UV radiation, accumulation rate and snow impurities. This alone can lead to difference in nitrate concentration and its isotopic composition in different snow layers below the photic zone. For example, snow layer at 100 cm vs. that at 300 cm in Dome A, snow at the layer of 300 cm deep deposited probably ~ 40 to 50 years ago, while the layer at 100 cm deposited slightly over a decade ago. During this time period, the degree of post-depositional processing certainly varies (e.g., at least stratospheric ozone layer change a lot since the 1980s), thus even the originally deposited values were the same, their asymptotic values (after post-depositional processing) should be different. Therefore, the values of concentrations and isotopic below the photic zone differing from the predictions of exponential regression, as observed by the authors, doesn't mean necessary that other processes occur in deeper layers below the photic zone. This makes their major conclusion, which is "Predicting the impact of post-depositional loss, and therefore changes in the isotopes with depth, is highly sensitive to the depth interval over which an exponential decrease is assumed", fraud.

Because of these problems, I unfortunately can't recommend this manuscript for publication.

In addition to the above, they are many other concerns as follows:

1. Section 2.2.: sample analysis: the authors claim that only 5 nmol nitrate in sample is required to do the isotopic analysis. I am concerning in practice, how the authors ensure that their samples in each run exactly contain the same amount of nitrate as the standards. In other words, how close is their sample peak area to the peak area of all standards? This is critical, because that it is know the influence of background/blank is larger at smaller quantity of sample nitrate, thus a decay of the measured isotope ratios along with sample nitrate quantity is observed [*Costa et al.*, 2011]. It is okay if the standards are exactly at the same size as the samples, as all the background is equally corrected. However, at such a small 5 nmol level, a slight size difference between the standards and the samples will lead to probably significant over-correction or under-correction. So if the data are going to published, I suggest the authors add information on the sample peak area vs. standard peak area in a particular run to valid the quality of the data.

2. Section 4.1.2.: in this part, the authors completely ignore the what likely occurs in the gas phase. Re-oxidation in the overlying air (i.e., the equilibrium in the air snow interface [*Erbland et al.*, 2013; *Frey et al.*, 2009]) and in the interstitial air of snowpack also occurs. Although the re-oxidation in the condensed phase is likely dominated, the authors should at least discuss other processes.

 3. Section 4.1.3.: Why "the importance of this process (volatilization) is unclear"? Hasn't the relative importance of this physical release to photolysis been evaluated extensively in [*Erbland et al.*, 2013; *Frey et al.*, 2009] and concluded clearly that photolysis dominates in the post-depositional processing? These two references are cited in this same section and the authors pretty much rely on the results of these two previous publications here to make the discussion. In addition, the field experiments in [*Erbland et al.*, 2013]) suggested a fractionation constant

with respect to the physical release of close to or below zero. Doesn't this imply that the assumption and model result on the isotopic effects of physical release in [*Frey et al.*, 2009] are less reliable?

4. Section 4.2.: This is by far the part with the largest issue. Much of them have been discussed above in the general comments, but there are additional concerns. In page 31959, the last paragraph, the authors suggest the d18O continued to change below the photic zone is due to re-formation of nitrate in the gas phase through O_3 oxidation. There are several problems with this. First, d18O increases from the depth of ~10 cm continued to a depth of 200 cm. At depth below the photic zone (i.e, < 60 cm), how NO_x is produced and how much oxidants (O3) are available in the interstitial air? Second, why this phenomenon is not observed in Pit 6? which should be expected if the authors are correct. Third, [*Meusinger et al.*, 2014] suggests that nitrate in snow grains can be categorized into two domains: photolabile nitrate and buried nitrate. Photolabile nitrate is nitrate in the surface of snow grain which is easily photolyzed and the photoproduct mainly escapes into the air; while the buried nitrate are in the snow grains, the photolysis of this nitrate leads to re-formation of nitrate in the condensed phase and depletion of oxygen isotopes due to exchange with water oxygen. The experiments in [*Meusinger et al.*, 2014] then suggest that the photolabile nitrate is quickly removed under UV radiation, and buried nitrate started to be photolyzed after photolabile nitrate is almost gone. Therefore, in the field, at surface, the photoproducts mainly escapes to the air (because nitrate are in the surface of snow grains) without significant re-oxidation in the condensed phase; but at depth, re-oxidation in the condensed phase becomes more important as where it is "buried nitrate" photolysis and the products stay in the condensed phase longer before escaping to the interstitial air. This means, as going deeper, NO_x is more difficult to escape (more re-oxidation in the condensed phase). This

offsets the effect of re-oxidation of NO_x by O_3 on d18O of snow nitrate at greater depths, even the later indeed occurs.

By the way, in the second paragraph in Page 31960, the authors are pretty much against themselves.

5. Section 4.3.: as discussed in the general comments, this section makes no sense. It is meaningless to apply this approach for depth below the photic zone, and give the time period the snowpit covers (300 cm, approximately 50 years), other factors have to be considered.

6. Section 4.4.: First, beside the discussion on stratospheric sources, it is unclear throughout this part which sources and how they shift. **Last paragraph in page 31965:** why the more stratospheric nitrate in the most recent winter in P1 is relate to the smaller ozone hole in the spring of 2012? Theoretically, chemical ozone loss in the stratospheric requires the growth of PSCs and which favors at lower temperature in polar winter (e.g., [*Manney et al.*, 2011]). Only severe cold promotes the growth of PSCs, when it grows big enough it starts to descend, leading to surface enhancement of nitrate. Lower ozone loss indicates probably less abundance / growth of PSCs in polar winter, and should be consistent with less stratospheric nitrate input. So the argument in this paragraph does not make sense. **First paragraph in page 31966:** the authors claim that the high d15N values (31 per mil) in clod seasons indicate that stratospheric nitrate should be higher than [*Savarino et al.*, 2007] calculated. In Figure 7, in the season with the largest stratospheric nitrate contribution (the most recent one, as indicated by the largest d18O and D17O values), d15N is the lowest. Therefore, it is not reasonable to attribute the high d15N values in the cold seasons to stratospheric influence alone, as if so d15N in the most recent cold season should be the highest. In addition, [*Savarino et al.*, 2007] measured seasonal atmospheric nitrate in a coast regions of East Antarctica, which should be more directly influenced by

stratospheric signals. The fact, that the snow nitrate in P1 possesses much higher d15N in all season compared to the atmospheric measurements [*Savarino et al.*, 2007] (though not in the same location, but if consider stratospheric signal, the spatial variability should be small), should not imply other process (e.g., post-depositional processing) in the air-snow interface plays a role? As a reminder, the stratospheric signals [*Savarino et al.*, 2007] measured in the boundary layer is less than 10 per mil for d15N, while in the snow in this study is 31 per mil.

There are some other points:

1) P31964, line 16: the oxygen-17 anomaly reflects oxidants involved in nitrate production, not oxygen isotopes. NOx itself and water vapor in the atmosphere also influence oxygen isotope in nitrate.

2) P31967, line 8-10: what are the problems?

3) P31949, line 15-16: The sentence starts with "secondly..." is confusing. Does it mean that one sample was replicated 38 times?

4) P31949, line 23 to the end of this paragraph: when correct for oxygen isotope exchange with water, it seems only water in the sample matrix is considered. How about water in the bacterial media? or it is dry bacteria added to the liquid samples?

5) P31951, line 11-15: It must to make it clear that the 2.5 per mil underestimate without step 2 correction when using pre-concentration is only true for samples with nitrate at 35 nmol around; if there are 350 nmol nitrate in each sample, this effect will be much reduced to minor.

6) P31956, line 8: it is "sect. 4.1.3", not 4.1.2;

7) P31958, line 14: this is true at only low snow accumulation sites. Please make it clear.

8) P31958, line 25-26: This statement is not true according to table 2, as where it shows the

relationship between d15N and nitrate concentration shifts from negative to positive, opposite to that between d18O and concentration.

Reference:

Costa, A. W., G. Michalski, et al. (2011), Analysis of atmospheric inputs of nitrate to a temperate forest ecosystem from $\Delta17O$ isotope ratio measurements, *Geophys. Res. Lett.*, *38*(15), L15805, doi: 10.1029/2011gl047539.

Erbland, J., W. C. Vicars, et al. (2013), Air-snow transfer of nitrate on the East Antarctic Plateau - Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium, *Atmos. Chem. Phys.*, *13*, 6403-6419, doi: 10.5194/acp-13-6403-2013.

France, J. L., M. D. King, et al. (2011), Snow optical properties at Dome C (Concordia), Antarctica; implications for snow emissions and snow chemistry of reactive nitrogen, *Atmos. Chem. Phys.*, *11*(18), 9787-9801, doi: 10.5194/acp-11-9787-2011.

Frey, M. M., J. Savarino, S. Morin, J. Erbland, and J. M. F. Martins (2009), Photolysis imprint in the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling, *Atmos. Chem. Phys.*, *9*(22), 8681-8696, doi: 10.5194/acp-9-8681-2009.

Libois, Q., G. Picard, et al. (2013), Influence of grain shape on light penetration in snow, *The Cryosphere*, *7*(6), 1803-1818, doi: 10.5194/tc-7-1803-2013.

Manney, G. L., M. L. Santee, et al. (2011), Unprecedented Arctic ozone loss in 2011, *Nature*, *478*(7370), 469-475, doi: http://www.nature.com/nature/journal/v478/n7370/abs/nature10556.html#supplementary-information.

Meusinger, C., T. A. Berhanu, J. Erbland, J. Savarino, and M. S. Johnson (2014), Laboratory study of nitrate photolysis in Antarctic snow. I. Observed quantum yield, domain of photolysis, and secondary chemistry, *The Journal of Chemical Physics*, *140*(24), -, doi: doi:http://dx.doi.org/10.1063/1.4882898.

Savarino, J., J. Kaiser, S. Morin, D. M. Sigman, and M. H. Thiemens (2007), Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica, *Atmos. Chem. Phys.*, *7*(8), 1925-1945, doi: 10.5194/acpd-6-8817-2006.

Zatko, M. C., T. C. Grenfell, et al. (2013), The influence of snow grain size and impurities on the vertical profiles of actinic flux and associated NOx emissions on the Antarctic and Greenland ice sheets, *Atmos. Chem. Phys.*, *13*(7), 3547-3567, doi: 10.5194/acp-13-3547-2013.