We are very grateful to reviewer #2 for his/her detailed comments and very useful suggestions. The manuscript has been substantially modified and reformatted based on these comments/suggestions. Below, we give a point-by-point response to the comments and suggestions of the reviewer, in the order of (1) comments from Referees, (2) author’s response, and (3) author’s changes in manuscript. Reviewer comments are in black, and the responses are in blue.

(1) comments from Referees

This manuscript reports on nitrate in samples collected in the frame of an intensive program of snow sampling made along a traverse from the coast to Dome A (East Antarctica). The samplings include 120 surface snow samples (upper 3 cm), 20 snowpits (down to 1.5-3.0 m depth), and a few crystal ice samples. From the coast to the inner plateau, an increasing trend of nitrate present in surface snow is observed whereas the content of deeper snow pit layers are lower at inland sites than at the coast. Extremely high concentrations are found in crystal ice (reaching almost 1 ppmw). Data are discussed with respect to occurrence of post-depositional remobilization of nitrate, wet and dry deposition, and possible role of other ions (sodium and sulfate).

Overall evaluation:

First, the authors have to be congratulated for having successfully conducted such a very large snow-sampling program, likely sometimes done under harsh weather conditions. The data certainly contain valuable information in view to better understand incorporation, remobilisation and partial preservation of nitrate atmospheric signal in cold archives. This topic is clearly relevant for the Cryosphere journal.

(1) author’s response

We thank the reviewer very much for reviewing our manuscript and the positive comments. As the reviewer mentioned, the snowpit sampling is usually made under the very harsh weather conditions, e.g., extremely low temperature and heavy blowing snow. We appreciate the Chinese inland Antarctic expedition team members for providing help during sampling.

(1) author’s changes in manuscript

We will revise the manuscript following the reviewer’s comments and suggestions, see below.
(2) comments from Referees

As it stands the manuscript however requires major revisions and a reevaluation prior to publication. Indeed, at several places in the manuscript data discussions are incorrect, and generally do not enough consider atmospheric information available for the Antarctic atmosphere. Given the scarcity of data presented in this work, I strongly encourage the authors to reformulate the manuscript and in the following I try to identify what would be addressed in an in depth reformulated version of this manuscript.

(2) author's response

We thank the reviewer for pointing out the shortcomings of the manuscript. We agree that the atmospheric information was not considered enough. We will improve the work following the reviewer’s suggestions/comments.

(2) author's changes in manuscript

The manuscript was modified according to the comments from the reviewer, see below and section 4 in the revised manuscript.

(3) comments from Referees

Introduction.

This paragraph has to be reworded on several aspects:

Lines 54-86: You missed here several important papers that have discussed in details the origins of nitrate in Antarctica. For instance, Legrand and Kirchner (1990) extensively discussed (1) the absence of link between solar activity and nitrate in snow, (2) what are the main possible sources of nitrate for Antarctica (stratospheric reservoir and long-range transport in the upper troposphere of lightning production, etc). Also model simulations from Legrand et al. (1989) discussed the source of nitrate for Antarctic regions.


(3) author's response
We agree with the reviewer and are sorry for missing the two important references concerning Antarctic NO$_3^-$ budget. In terms of the Antarctic NO$_3^-$ budget, lightning and NO$_x$ produced in the lower stratosphere were thought to play a major role (Legrand et al., 1989; Legrand and Kirchner, 1990). Also, it is suggested that there is not necessarily a connection between solar variability and NO$_3^-$ concentrations (Legrand and Kirchner, 1990).

(3) author's changes in manuscript

The two references were included. The major contribution by lightning and by NO$_x$ produced in the lower stratosphere to Antarctic NO$_3^-$ budget was clarified. In addition, the investigation made by Legrand and Kirchner (1990) suggesting no correlation between solar activity (11-year solar cycle, low solar activity time periods, and solar proton events) and the NO$_3^-$ content of south polar snow was added to the manuscript. Please see the revision-tracked version of manuscript.

(4) comments from Referees

Lines 80-83: You missed here to report two recent papers from Wolf et al. that strongly question the assumption that solar flares and SPE are recorded in ice. Also model simulations do not support at all such an assumption (Legrand et al., 1989; Duderstadt et al., 2014).


(4) author's response

Thanks for pointing this out. The observations and modeling works by (Legrand et al., 1989; Legrand and Kirchner, 1990; Wolff et al., 2008; Wolff et al., 2012; Duderstadt et al., 2014;
Duderstadt et al., 2016; Wolff et al., 2016) were included. Indeed, most of observations and recent modeling studies have established that there is not a clear connection between solar variability and NO$_3^-$ concentrations (Legrand et al., 1989; Legrand and Kirchner, 1990; Wolff et al., 2008; Wolff et al., 2012; Duderstadt et al., 2014; Duderstadt et al., 2016; Wolff et al., 2016).

(4) author's changes in manuscript

The works made by Wolff et al., Legrand et al., and Duderstadt et al., are included in the revised manuscript. Please see the revised version of the manuscript.

(5) comments from Referees

A few sentences on the physical form of nitrate (partitioning between the gas phase, and particulate phase) would be welcome (see my next comment) to better introduce the data discussion with respect to deposition, remobilization, etc.

(5) author's response

A good point, thanks. A summary of the observations on partitioning of NO$_3^-$ between the gaseous phase and particulate phase will be helpful to a better understanding of the deposition and re-emission of NO$_3^-$. At Dome C on the East Antarctic plateau, observations on the atmospheric NO$_3^-$ have been carried out during the years from 2006 to 2016 (Traversi et al., 2014; Legrand et al., 2016; Legrand et al., 2017b; Traversi et al., 2017), which are important works towards a quantitative understanding of NO$_3^-$ partitioning in the atmosphere.

(5) author's changes in manuscript

Following the reviewer’s suggestion, a paragraph summarizing the partitioning between the gas phase, and particulate phase on NO$_3^-$ was included in the revised manuscript, as follows,

In the atmosphere in Antarctica, particularly during spring and summer, NO$_3^-$ is found to be mainly in the form of gas phase HNO$_3$, with NO$_3^-$ concentration several times higher in gas phase than in the particulate phase (Piel et al., 2006; Legrand et al., 2017b; Traversi et al., 2017). During the post-depositional processes, the uptake of gaseous HNO$_3$ is thought to be important in NO$_3^-$ concentrations in surface snow layers (Udisti et al., 2004; Traversi et al., 2014; Traversi et al., 2017). Due to the high concentration in summer, HNO$_3$ appears to play an important role in acidifying sea-salt particles, possibly accounting for the presence of NO$_3^-$ in the particulate phase in summer (Jourdain and Legrand, 2002; Legrand et al., 2017b; Traversi et al., 2017). It is noted that the significant increase of NO$_3^-$ during the cold periods (e.g., Last Glacial Maximum) could be associated with its attachment to dust aerosol, instead of the gas phase HNO$_3$ (Legrand et al., 1999; Wolff et al., 2010).
Please see the revised version of the manuscript, section 1 Introduction.

(6) comments from Referees

Data discussion (Section 3): Please reconsider your data in the light of recent papers dealing with nitric acid gas phase and nitrate in the aerosol phase and their changes over the year in Antarctica.

For instance, check the following recent paper and references therein:


(6) author's response

We thank the reviewer for the very constructive suggestion. The partitioning of NO$_3^-$ between gas-phase and particulate phase will be of importance to NO$_3^-$ levels in the snowpack, especially the topmost crystal ice layers. The observed high levels of gas phase HNO$_3$ in central Antarctica during summer support the importance of the re-emission from snow through the photolysis of NO$_3^-$ in affecting atmospheric NO$_3$/NO$_3^-$ budget (e.g., Erbland et al., 2013). The atmospheric gaseous HNO$_3$ likely co-condenses with water vapor (Bock et al., 2016), especially on the extensively developed crystal ice layers on Antarctic plateaus (discussed in the main text), leading to an enrichment of NO$_3^-$ in surface snow. In addition, a large concentration of HNO$_3$ would enhance its reaction with sea-salt, leading to elevated particulate NO$_3^-$ concentrations (Legrand et al., 2017b). The significant correlation between NO$_3^-$ and H$^+$ ($R^2=0.65$, $p<0.01$) and lack of correlation between NO$_3^-$ and sea salt Na$^+$ in inland Antarctic surface snow seems to suggest the importance of atmospheric gas phase HNO$_3$ in affecting surface snow NO$_3^-$ concentrations, in particular NO$_3^-$ levels in the crystal ice samples (correlation between NO$_3^-$ and H$^+$, $R^2=0.99$, $p<0.01$).

(6) author's changes in manuscript

The physical form of NO$_3^-$ affecting NO$_3^-$ concentrations in snow was discussed and included in the revised manuscript, as follows,

In inland Antarctica, the dominant NO$_3^-$ species in the atmosphere is gaseous HNO$_3$ during summertime, while particulate NO$_3^-$ is more important in winter (Legrand et al., 2017b; Traversi et al., 2017). The high levels of gas phase HNO$_3$ in summer support the importance of the re-emission from snow through the photolysis of NO$_3^-$ in affecting the atmospheric NO$_3$/NO$_3^-$ budget (Erbland et al., 2013). On the one hand, the gaseous HNO$_3$ can be efficiently co-condensed with water vapour onto the extensively developed crystal ice layers on Antarctic plateaus.
(discussed above), leading to an enrichment of NO$_3^-$ in surface snow (Bock et al., 2016). On the other hand, a large concentration of HNO$_3$ would enhance its reaction with sea-salt, leading to elevated particulate NO$_3^-$ concentrations (Legrand et al., 2017b). The significant correlation between NO$_3^-$ and H$^+$ in inland Antarctic surface snow ($R^2 =0.65, p<0.01$) seems to support the importance of atmospheric gas phase HNO$_3$ in affecting surface snow NO$_3^-$ concentrations, in particular NO$_3^-$ levels in the crystal ice samples (Fig. 1).

Please see the revised version of the manuscript, section 4.1.2 NO$_3^-$ in inland snowpack.

(7) comments from Referees

Two overall comments:

The idea that nitrate is trapped on coarse sea-salt particles is incorrect (or not enough precise): Atmospheric data show that nitrate stays on the intermediate size particles (1-2 micron range) and not on the coarse ones like sea-salt (even at the coast): Jourdain and Legrand (2002); Teilina et al. (2000), Rankin et al. (2003), and Legrand et al. (2017).


(7) author's response

Atmospheric NO$_3^-$ in Antarctica is mainly in the gas phase (HNO$_3$), while the particulate phase represents less, particularly in inland Antarctica. As for the particulate phase (also called “aerosol” in previous observations), most of the NO$_3^-$ is found on the intermediate size particles (1 – 2 μm) (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2017b). As the reviewer mentioned, the NO$_3^-$ is not trapped on the coarse sea-salt particles. But the presence of sea salt aerosol can influence atmospheric NO$_3^-$ in two ways. Firstly, higher atmospheric sea salt aerosol concentrations are expected to promote the conversion of gaseous HNO$_3$ to particulate phase, allowing for the efficient deposition of NO$_3^-$ via the aerosol mechanisms. On the other hand, the saline ice in the atmosphere favors the direct uptake of gaseous HNO$_3$ on ice surface. Thus, sea salt aerosols play an important role in the scavenging of gaseous HNO$_3$ from the atmosphere (Hara et al., 2005), and elevated NO$_3^-$ concentrations are usually accompanied by Na$^+$ spikes in
snowpack (e.g., at Halley station, a coastal location; Wolff et al., 2008).

(7) author’s changes in manuscript

Following the reviewer’s comments, the relationship between NO$_3^-$ and sea salt in the snowpack was re-discussed, as follows,

In comparison with nssSO$_4^{2-}$ aerosols, the sea-salt aerosols (Na$^+$) are coarser and can be removed preferentially from the atmosphere due to a larger dry deposition velocity. High atmospheric sea salt aerosol concentrations are expected to promote the conversion of gaseous HNO$_3$ to particulate phase, considering that most of the NO$_3^-$ in the atmosphere is in the gas phase (HNO$_3$). In this case, particulate NO$_3^-$ can be efficiently lost via aerosol mechanisms. In addition, the saline ice also favors the direct uptake of gaseous HNO$_3$ to the ice surface. Changes in partitioning between gas phase (HNO$_3$) and particulate phase will affect NO$_3^-$ levels due to the different wet and dry deposition rates of the two species (Aw and Kleeman, 2003). Thus, sea salt aerosols play an important role in the scavenging of gaseous HNO$_3$ from the atmosphere (Hara et al., 2005), and elevated NO$_3^-$ concentrations are usually accompanied by Na$^+$ spikes in snowpack (e.g., at Halley station, a coastal site; Wolff et al., 2008). Here, no significant correlation was found between Na$^+$ and NO$_3^-$ in coastal snow (Fig. 7b). The concentration profiles of NO$_3^-$ and Na$^+$ in coastal surface snow are shown in Fig. 8, and NO$_3^-$ roughly corresponds to Na$^+$ in some areas, e.g., 50-150 km and 300-450 km distance inland, although in general they are not very coherent. It is noted that amongst the 4 snow samples with Na$^+ > 1.5$ μeq L$^{-1}$ (open circles in Fig. 8), only one sample co-exhibits a NO$_3^-$ spike. This is different from observations at Halley station, where Na$^+$ peaks usually led to elevated NO$_3^-$ levels in surface snow in summer (Wolff et al., 2008). Of the 4 largest Na$^+$ spikes, one is a fresh snowfall sample (dashed ellipse in Fig. 8), and this sample shows the highest Na$^+$ concentration (2.8 μeq L$^{-1}$) and low NO$_3^-$ (0.75 μeq L$^{-1}$). It is noted that NO$_3^-$ concentration in this fresh snowfall is close to the model predictions (0.7±0.07 μeq L$^{-1}$; section 4.1.1), validating that the simple linear deposition model (i.e., the Eq. 6) can well depict the deposition and preservation of NO$_3^-$ in coastal snowpack. At inland sites, no correlation was found between NO$_3^-$ and Na$^+$ (Fig. 7e), likely explained by the alteration of NO$_3^-$ concentration by post-depositional processing (discussed above).

Please see the revised version of the manuscript, section 4.2 Effects of coexisting ions on NO$_3^-$. 

(8) comments from Referees

The relationship between NssSO4 and nitrate: The interpretation of the correlation between nitrate and sulphuric acid referring to Brown et al. (2006) is misleading. Indeed this study discussed of the reaction of N2O5 on acidic sulphate promoting the formation of HNO3 in a polluted atmosphere at night. Whatever the Antarctic site, the acidic sulphate is maximum in summer whereas, if present, N2O5 can only exit in the Antarctic atmosphere in winter (due to photolysis of the NO3 radical in summer, N2O5 does not exist in summer). So the correlation seen in snow
cannot be explained like that.

(8) author's response

We agree with the referee that the conversion of \( \text{N}_2\text{O}_3 \) to HNO\(_3\) during austral summer could be rather negligible due to the photolysis of NO\(_3\) radical in summertime (NO\(_3\) + NO\(_2\) + M → N\(_2\)O\(_3\) + M). This point was clarified in the revised manuscript. Following previous investigations, the high concentrations of nssSO\(_4^{2-}\) aerosols could provide nucleation centers forming the multi-ion complexes with HNO\(_3\) in the atmosphere, possibly leading to elevated NO\(_3\)\(^-\) concentrations in the snow (Laluraj et al., 2010). On the other hand, the presence of fine nssSO\(_4^{2-}\) aerosol may also enhance the direct uptake of gas phase HNO\(_3\) onto the surface, resulting in NO\(_3\)\(^-\) deposition via aerosol mechanisms. It is acknowledged that these are the plausible explanation of the association between the two anions, and it cannot be ruled out that other processes and/or chemistry would influence the relationship of the parameters. Further works are needed to characterize the formation of SO\(_4^{2-}\) and NO\(_3\)\(^-\) and their potential association in Antarctic atmosphere.

(8) author's changes in manuscript

Following the comments from reviewer#2 and Prof. Savarino, the correlation between SO\(_4^{2-}\) and NO\(_3\)\(^-\) was re-discussed in the revised manuscript, as follows,

In surface snow, the non-sea salt fraction of SO\(_4^{2-}\) accounts for 75 - 99 % of its total budget, with a mean of 95 %. The percentages are relatively higher in inland regions than at coastal sites. On the coast, a positive relationship was found between nssSO\(_4^{2-}\) and NO\(_3\)\(^-\) (\(R^2 = 0.32, p < 0.01\); Fig. 7a). Previous observations suggest that NO\(_3\)\(^-\) and nssSO\(_4^{2-}\) peaks in the atmosphere and snow are usually present in summer (Jourdain and Legrand, 2002; Wolff et al., 2008; Sigl et al., 2016; Legrand et al., 2017a; Legrand et al., 2017b). However, the similar seasonal pattern of the two species is associated with distinct sources, i.e., SO\(_4^{2-}\) is mainly derived from marine biogenic emissions while NO\(_3\) is influenced by photolysis and tropospheric transport (Savarino et al., 2007; Lee et al., 2014; Zatko et al., 2016). In the atmosphere, most of SO\(_4^{2-}\) is on the submicron particles, while most of NO\(_3\)\(^-\) is gaseous HNO\(_3\) and the particulate NO\(_3\)\(^-\) is mainly on the intermediate size particles (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2017a; Legrand et al., 2017b). Thus, the correlation between NO\(_3\)\(^-\) and SO\(_4^{2-}\) is unlikely explained by the sources or their occurrence state in the atmosphere (i.e., gaseous and particulate phases). Laluraj et al. (2010) proposed that the correlation between nssSO\(_4^{2-}\) vs. NO\(_3\)\(^-\) in ice (\(R^2 = 0.31, p<0.01\)) could be associated with the fine nssSO\(_4^{2-}\) aerosols, which could provide nucleation centers forming the multi-ion complexes with HNO\(_3\) in the atmosphere. This assertion, however, should be examined further, considering that the complex chemistry of SO\(_4^{2-}\) and NO\(_3\)\(^-\) in the atmosphere is far from understood (e.g., Wolff, 1995; Brown et al., 2006). Thus far, the mechanism of nssSO\(_4^{2-}\) influencing NO\(_3\)\(^-\) in the snowpack, however, is still debated, and it cannot be ruled out that nssSO\(_4^{2-}\) further affects mobilization of NO\(_3\)\(^-\) during and/or after crystallization (Legrand and Kirchner, 1990; Wolff, 1995; Röthlisberger et al., 2000). It is noted that no relationship was found between nssSO\(_4^{2-}\) and NO\(_3\)\(^-\) in inland snow (Fig. 7d), possibly due to the strong alteration of NO\(_3\)\(^-\)
during post-depositional processes, as discussed in section 4.1.2.

Please see the revised version of the manuscript, section 4.2 Effects of coexisting ions on NO$_3$.

(9) comments from Referees

Other comments:

Information on the chemistry of ice crystal are rather rare, so may important to develop this aspect in the revised manuscript (showing the full chemical composition and its comparison with snow).

Did you have measured MSA?

I think you can say that nssCl is HCl and it can be interesting to compare with gas phase HNO3.

End of the review.

(9) author's response

Thanks to the reviewer for this suggestion. As the reviewer mentioned, the information on the crystal ice samples on Antarctic plateaus remain limited. So, showing the full chemical composition of the crystal ice can provide important information on snow chemistry in Antarctica. In addition, a comparison of chemical ion concentrations between surface snow and crystal ice was made in the revised manuscript.

Unfortunately, we did not measure the concentrations of MSA now. But we will measure the MSA concentrations in the samples of surface snow/snowpits. Possibly it will be another paper focusing on the biogenic sulfur (nssSO$_4^{2-}$ and MSA).

Yes, the nssCl can be taken as HCl. This point was re-discussed in the manuscript.

(9) author's changes in manuscript

Following the reviewer’s comment, a figure was included in the supporting information, as follows,
Figure S2 Major chemical ions in surface snow and crystal ice samples on the traverse from coast to the ice sheet summit (Dome A) in East Antarctica. Contribution percentages of each ion to total ion concentrations are shown in (a) and (b), respectively. Concentrations of ions in surface snow and crystal ice are shown in (c), with error bars of one standard deviation (1σ). The concentration of H+ is calculated from the difference between sum anions and sum cations. Note that a base-10 log scale is used for ion concentrations in (c).

In addition, the major chemical ion concentrations and a comparison between surface snow and crystal ice was included in the updated version of the manuscript (3.1 NO₃⁻ concentration in surface snow), as follows,

In the crystal ice, the means (ranges) of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺ and H⁺ concentrations are 0.98 (0.62 – 1.27), 10.40 (8.35 – 16.06), 1.29 (0.87 – 2.13), 0.27 (0.21 – 0.33), 0.24 (0.03 – 0.56), 0.05 (0.03 – 0.08), 0.18 (0.15 – 0.22), 0.18 (0.05 – 0.57) and 11.75 (9.56 – 18.12) μeq L⁻¹, respectively. H⁺ and NO₃⁻ are the most abundant species, accounting for 46.4 and 41.0 % of the total ions, followed by SO₄²⁻ (5.1 %) and Cl⁻ (3.9 %). The other 5 cations, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺, only represent 3.6 % of the total ion budget. A significant linear relationship was found between NO₃⁻ and the total ionic strength (R² = 0.99, p < 0.01), possibly suggesting that NO₃⁻ is the species controlling ion abundance by influencing acidity of the crystal ice (i.e., H⁺ levels). In comparison with surface snow, concentrations of H⁺ and NO₃⁻ are significantly higher in crystal ice (Independent Samples T Test, p<0.01), while concentrations of Cl⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ are comparable in the two types of snow samples (Fig. S2 in supporting
information). To date, the information on the chemistry of ice crystal is rather limited but data from the so-called skin layer at Dome C, where NO$_3^-$ concentrations in the top 0.4 cm snow layer are in the range of 9 – 22 μeq L$^{-1}$ in summertime (Erbland et al., 2013), generally comparable to our observations.

In addition, the association between NO$_3^-$ and the major chemical ions in crystal ice was re-discussed (4.2 Effects of coexisting ions on NO$_3^-$), as follows,

With regard to the crystal ice, no significant correlation was found between NO$_3^-$ and the coexisting ions (e.g., Cl$^-$, Na$^+$ and SO$_4^{2-}$), possibly suggesting that these ions are generally less influential on NO$_3^-$ in this uppermost thin layer, compared to the strong air-snow transfer process of NO$_3^-$ (Erbland et al., 2013). It is noted that NO$_3^-$ accounts for most of the calculated H$^+$ concentrations (81 - 97 %, mean = 89 %), and a strong linear relationship was found between them ($R^2$ = 0.96), suggesting that NO$_3^-$ is mainly deposited as acid, HNO$_3$, rather than in particulate form as salts (e.g., NaNO$_3$ and Ca(NO$_3$)$_2$). This deduction is in line with the observations at Dome C, where atmospheric NO$_3^-$ was found to be mainly in gaseous phase (HNO$_3$) in summer (Legrand et al., 2017b). On average, the deposition of HNO$_3$ contribute >91% of NO$_3^-$ in the crystal ice (the lower limit, 91 %, calculated simply by assuming all of the alkaline species (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$) neutralized by HNO$_3$ in the atmosphere), suggesting a dominant role of HNO$_3$ deposition in snow NO$_3^-$ levels. The elevated high atmospheric NO$_3^-$ concentrations observed at Dome A (>100 ng m$^{-3}$; 77.12°E, 80.42°S; Table S1 in supporting information) possibly indicate oxidation of gaseous NO$_3^-$ to HNO$_3$, suggesting that NO$_3^-$ recycling driven by photolysis plays an important role in its abundance in snowpack on East Antarctic plateaus.

The relationship between nssCl$^-$ (i.e., the HCl) and NO$_3^-$ in snow was re-discussed in the revised manuscript, please see the revised manuscript, 4.2 Effects of coexisting ions on NO$_3^-$

End of responses to Referee #2.
References


Shi, G., Li, Y., Jiang, S., An, C., Ma, H., Sun, B., and Wang, Y.: Large-scale spatial variability of major ions in the atmospheric wet deposition along the China Antarctica transect (31° N– 69° S), Tellus B, 64, 17134, doi:10.3402/tellusb.v64i0.17134, 2012.


End of the responses.