

Interactive comment on “Potential genesis and implications of calcium nitrate in Antarctic snow” **by K. Mahalinganathan and M. Thamban**

Anonymous Referee #2

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Comments to the paper: K. Mahalinganathan and M. Thamban Potential genesis and implications of calcium nitrate in Antarctic snow.

General Comments

The paper is concerning the study of the Ca/nitrate relationship along two coastal-inner transects in Princess Elisabeth Land and Dronning Maud Land, East Antarctica. The topic is surely interesting in order to understand the atmospheric processes involved in the dry deposition on the snow surface of nitrate and mineral dust carried by long-range transport from continental source areas (especially Southern South America). In particular, the formation of nitrate salts is relevant in the persistence of nitrate, since it is not irreversibly fixed in the snowpack, due to post-depositional re-emission into the atmosphere of HNO₃ in low-accumulation sites. However, the manuscript contains

C2436

some weak points that, in my opinion, should be overcome before to be published on The Cryosphere journal. 1. The formation of Ca nitrate and the relevance of CaCO₃ particles in preserving nitrate record are well known, at least in the ice-core community. I agree that the manuscript reports an interesting data set (41 sites along two transects) in coastal-inner areas of East Antarctica, but Authors say that a complete ion analysis was carried out on the samples. However, just Ca and nitrate were in deep discussed, with a very short discussion on δ¹⁸O and Na records. I think that a more comprehensive data discussion on other relevant components of Antarctic snow should be addressed, especially about the coastal-inner profiles of sea spray (here just mentioned) and biogenic compounds (mainly nss-sulfate and MSA). Indeed, ionic balances (in Eq/L) of the snow samples are useful in understanding the changes in the different source contributions (and so, of the snow composition) along the transects. Besides, from the ionic balances, a quantitative evaluation of the relationship between nssCa and nitrate and possible residual acidity can be carried out. 2. Calcium species in the discussion and in the figures. The reaction between CaCO₃ and HNO₃ (including that involving N₂O₅, which give HNO₃ by hydrolysis) is an acid-base reaction that can involve only basic compounds of Ca (such as CaCO₃) and the acidic species of nitrate (i.e., HNO₃). In this way, all non-basic Ca compounds, such as sea-spray Ca and crustal CaSO₄ cannot be considered in the Ca-nitrate relationships. Authors rightly say that just nssCa has to be considered in the reaction with nitrate, but all the discussion and figures report Ca and not nssCa concentrations. At least figure 3 and (necessarily) figure 4 have to be re-plotted by using nssCa and not Ca concentrations. For instance, the evaluation of averaged w/w (or mole/mole) ratios between Ca and nitrate in Ca(NO₃)₂ by the slope of the linear regressions of the Ca-nitrate plots (figure 4) can be carried out only if nssCa is used. The Authors just report in Figure 3 the mean percentage of nssCa in coastal and inner areas, but this information is not sufficient because the sea spray contribution (and so, the nssCa fraction) changes very quickly as the distance from the sea and, especially, altitude change. This process can lead to very different nss-Ca contributions sample by sample. 3. The third criticism

C2437

concerns the necessity to carry out a more reliable discussion on the acidic or neutralized species in which nitrate is present in the snow along the transects, and how much nitrate is fixed as calcium salt. Besides, the evaluation of the possible residual acidity of the snow is relevant, in order to understand if the formation of volatile HNO₃ is possible, even after the formation of Ca(NO₃)₂, by acid-base exchange with H₂SO₄ (especially in summer samples, generally characterized by high H₂SO₄ content from marine biogenic emissions). Again, such information could be given by the ionic balance carried out on every sample, from which acidity content (calculated by anions excess) and nssCa/nitrate ratios can be easily evaluated.

For these reasons, I suggest that the manuscript can be accepted for publication in The Cryosphere journal only after major revisions.

Specific comments.

Abstract.

Line 4, page 2. NssCa, and not Ca, can be used as crustal marker.

Lines 13-14, page 2. The reaction is between CaCO₃ and HNO₃ and not with “nitrogen oxides”. A reaction of N₂O₅ and CaCO₃ is also possible, but after hydrolysis (even in heterogeneous phase on CaCO₃ particles) of N₂O₅ to form HNO₃ (N₂O₅ + H₂O = 2 HNO₃).

Lines 24-25, page 2. The nitrate fraction bound to nssCa, with respect to the total nitrate content, is not evaluated in the manuscript.

Introduction.

Lines 1-2, page 3. This sentence is obvious and should be deleted.

Line 3, page 3. Please, change “teleconnect” with “teleconnected”.

Lines 6-7, page 3. There is certain confusion between gas-phase and aerosol components. Besides, nitrate and HNO₃ cannot be named “oxides” (eventually, N-oxidized

C2438

species).

Sampling and methods.

Lines 15-16, page 5. In order to better evaluate the detection limits, the volume of the IC injection loop should be reported. Besides, the detection limit for Ca does not seem to be “excellent”. Indeed, several DML samples show Ca concentrations lower than 5 ug/L, while the DL is 3 ug/L.

Authors are requested to report how ssNa (and so, nssCa) was evaluated.

Results.

In all the discussions about the Ca-nitrate relationships, nssCa (and not total Ca) concentrations have to be used. This is especially relevant in the more coastal sites, where the ssCa fraction could be relevant.

A discussion on sample ionic balances has to be addressed in order to evaluate the different nssCa/nitrate ratios, the possible excess of nitrate or nssCa, and the sample residual acidity. Ionic balances should contain the ss and nss fractions at least of Ca and sulfate.

Discussion.

Lines 18-22, page 7. The atmospheric oxidation of NO_x, together with the stratosphere-troposphere transport of HNO₃, is the most relevant sources of nitrate in the Antarctic PBL.

Line 10, page 8. The “small” ss-Ca fraction could be very relevant in the sites nearest the sea and has to be evaluated.

Lines 9-11, page 9. Could this statement to be demonstrated by the high contribution of larger (> 10 um) dust particles?

Mineral dust reactivity.

C2439

Lines 21-22, page 9. The first part of this sentence is not necessary true, and the second part is obvious. The sentence should be removed.

Line 1-17, page 10. The mechanism for the acid-base reaction between carbonate species and HNO₃ is well known. This part should be summarized and reduced. Back-and Forward-Trajectory analysis. The percentage of trajectories coming from the different dust potential source areas should be reported for the two seasons.

Formation of Ca nitrate.

The diagram shown in figure 6 depicts well known and elementary processes. Besides, the figure does not show any relevant news on the atmospheric processes leading to the formation of Ca-nitrate salt. Besides, no experimental evidence was given on the fact that the CaCO₃ – HNO₃ reaction can be carried out in the atmosphere, during the transport of dust particles, or on the snow surface, after their deposition. I'd suggest deleting the figure.

Figure 2. Ca could be replaced by nssCa.

Figures 3 and 4. Ca has to be replaced by nssCa.

Interactive comment on The Cryosphere Discuss., 9, 6125, 2015.