

Interactive comment on “Spatial and temporal variability of sea-salts in ice cores and snow pits from Fimbul Ice Shelf, Antarctica” by Carmen Paulina Vega et al.

Anonymous Referee #2

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Comments to the paper: C.P. Vega et al., Spatial and temporal variability of sea-salts in ice cores and snow pits from Fimbul Ice Shelf, Antarctica.

General Comments

The paper is concerning the study of sea-salt components in snow, firn and ice samples collected in a coastal area of East Antarctica. There is a lack of knowledge on environmental and climatic data from firn/ice core stratigraphies in Coastal Regions of Antarctica; therefore, the paper is interesting for the Antarctic Glaciology Community. The paper is well written and sufficiently concise (see Comments to address toward more synthetic sections). However, in my opinion, the manuscript contains

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some weak points that should be addressed before to be accepted for publication on The Cryosphere journal. These weak points are discussed in the Specific and Minor Comments section, but can be here listed:

1. some experimental procedures should be clarified;
2. ss- and nss- fractions of most of the analyzed components (especially Na and Ca) should be calculated as more reliable markers of sea spray (ssNa) and crustal (nssCa) contributions;
3. seasonal characterization of the sub-samples should be made taking into account the d18O profiles, instead of using an interpolation procedure;
4. the evaluation of the spatial variability by snow pit data appears to be not significant, because of the short record (lower than 1-year deposition),
5. the evaluation of ss-sulfate depletion from negative nss-sulfate values has to be completely revised;
6. I'm not convinced about the explanation of abrupt changes in sea salt deposition since 1950 in the S100 ice core (see, Specific Comments);

For these reasons, in my opinion, the manuscript needs major revisions before to be published on the The Cryosphere journal.

Specific and Minor Comments

Title: I'd suggest adding the Antarctic Region where Fimbul Ice Shelf is located (I think DML – Dronning Maud Land). Besides, since three shallow firn cores were analyzed, I'd suggest changing “ice cores” in “ice/firn cores”.

Abstract. Authors should add some basic information about the sampling area.

Line 22, page 1. Please, change “three firn cores” in “three shallow firn cores (about 20 m deep)”

Lines 22-23, page 1. Please, add “(Dronning Maud Land – DML) to “Fimbul Ice Shelf (FIS)” location.

Line 24, page 1. Please, change “five snow pits” in “five snow pits (60-90 cm deep)”

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Line 27, page 1. Please, change “elevation and distance to the sea” in “elevation (50-400 m a.s.l.) and distance (3-117 km) to the sea.

Lines 28-29, page 1. As the same Authors say at Lines 6-7, page 13, latitude and distance from the sea are related one to the other. I'd suggest referring just to the distance from the sea, as the most significant parameter (other than altitude) for the site characterization.

Lines 7-9 page 2. See Specific Comments for the interpretation of the S100 changes in sea salt deposition.

Line 9, page 2. Please change “ice rises cores” in “firn rises cores”.

Introduction. This section seems to be too long and contains several information well known to the Glaciology Community. I'd suggest to summarize such information (especially those related to sea salt sources, specifically discussed in Section 4) focusing on the specific features of low altitude coastal sites, located in areas characterized by the presence of ice rises and ice rumples.

Lines 2-3, page 4. I'd suggest changing “This evidence values) in “This hypothesis is supported by the experimental evidence that the original seawater SO₄/Na ratio cannot be used in nss-SO₄ calculation, leading to negative values . . .”.

Lines 7-8, page 4. I'd suggest changing this sentence in: “These negative values indicate that a lower SO₄/Na ratio has to be used in nss-SO₄ calculation; i.e., a depletion of SO₄, with respect to seawater composition, occurred in wet and dry depositions.”

Lines 9, page 4 – Line 15, page 5. In my opinion, the discussion about the formation of brine, frost flower and other possible sources of fractionated sea-salt aerosol, although interesting, is too long in the introduction. This part should be summarized, eventually moving some key sentences in the Discussion Section.

Line 14, page 4. I think that frost flower, due their fragile structure, cannot cover the fractionated brine, but constitute an alternative processes leading the sulfate fraction-

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ation (as successively well explained by the Authors). I would suggest deleting “frost flower” in this sentence.

Line 6, page 6. Authors should give some basic information on the ranges of altitude and distance from the sea of the FIS ice rises (even if specific data are reported in Table 1). For instance: “Several ice rises (250-400 m a.s.l.; 10-50 km from the sea) are found at FIS”.

Line 30, page 6. Please, add “about 20 m deep” after “Three shallow firn cores”.

Lines 8-9, page 7. I think 4-8 cm is the sample resolution for firn cores. Authors should clarify that.

Lines 11-13, page 7. Information on the sample resolution for the S100 ice core should be reported.

Line 14, page 7. Please, change “five snow pits . . .” in “five snow pits (60-90 cm deep). . .”.

Line 20, page 7. I'd suggest adding: “, therefore snow pits samples cover the last year deposition”.

Line 22, page 7. There is a reason why ammonium was not determined together with the other cations?

Line 4, page 8. Here, a resolution of 2 cm is indicated, while Lines 17-18 report a resolution of 4 cm. Authors are requested to clarify the resolution of G4a and G5a snow pits.

Lines 14-16, page 8. I'm aware that Na probably originates mainly from sea salt in this coastal area. However, Authors should use ss-Na as specific sea salt marker or justify the choice of using total Na by demonstrating that nss-Na is a negligible (for instance, lower than 5%) fraction of total Na. This could be especially relevant for KC site, where PCA shows a significant crustal contribution.

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Line 4 and Line 8, page 9. How the Authors identified the previous summer layers, if 18dO measurements were not performed? By ice lens, different density, or other physical features? Authors should clarify their procedure, even if a reference is cited.

Section 3.1. Firn cores and snow pits values are reported as median. This is correct but it was not possible to evaluate the data variability, in order to compare the different sea salt contributes in the different sampling site. If median is used, then 25th and 75th percentile have to be shown, at least. I'd suggest plotting box plots with median, percentiles and outlier for each data set and reporting mean, minimum, maximum, and standard deviation in Table 2. In this way, it will be easier to appreciate the significance of the inter-site comparison.

Line 4, page 10 and following. PCA analysis. Usually, PCA analysis is carried out on raw data. Authors should clarify why They used normalized values as input for PCA data matrices. Indeed, PCA analysis on raw data is able to give results independent site-by-site and comparable among them. I do not know if this can be a result of the normalization, but the factor loading in every PCx factor seems to be quite low (lower than 0.5 in the majority of the loadings). In every way, I agree with the PCA results: the factors are surely related to sea salt, biogenic emission (mixed to nitrate) and crustal (for the site farthest from the sea) sources.

Lines 26-27, page 10. As a marker of the crustal source, the nss-Ca fraction has to be calculated at least for the KC site (but it could be useful to evaluate the ss- and nss-fractions for all the components in every data record).

Line 29-30, page 10. A further explanation could be common transport processes or pathways from marine areas at lower latitude. I do not think that nitrate, as a major nutrient, is a limiting factor for phytoplanktonic bloom in the Antarctic marine regions.

Line 8, page 11. The common sea-salt source between Cl and Na has to be confirmed (other than from PCA analysis) by calculating the Cl/ssNa ratios and comparing them with seawater composition. In this way, also a possible chloride depletion (for instance,

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by wet or dry deposition of aged sea spray aerosol) could be observed. In particular, it has to be noted and discussed that Na and Cl have quite different temporal profiles in the KC firn core (constant or light increase for Cl; quite sharp decrease for Na).

Section 3.3. Seasonal pattern. I have some doubts about the linear interpolation procedure. Indeed, a simulated resolution of about 3 days has not a physical meaning, especially considering the variability of composition and temporal occurrence and frequency of snowfall events and dry deposition. Have the Authors information about the seasonal pattern of snowfalls in the studied area? I strongly suggest attributing the sample seasonality by using the raw data and the d18O profiles, identifying the four seasons by high, low or intermediate d18O values or, simply, classifying the samples as “summer” or “winter” samples, by assuming a threshold for summer/winter d18O values. If the results of this seasonal attribution are different from those reported in figure 3, all the section should be revised accordingly.

Section 3.4. Spatial variability. As the same Authors say (Line 6-7, page 13), differences in latitude reflect differences in distance from the coast. Besides, longitude variations are too little (at least for snow pits) to constitute a significant parameter for ion composition (as demonstrated by the not significant relationships, see Line 8-9, page 13). In the studied area, I think the only significant parameter is the distance from the sea and, possibly, the altitude (at least for the firn cores). Therefore, I suggest to discuss only the effect of the distance from the sea (and altitude and position with respect to the glacier tongue, if firn cores are included in the discussion) in this section.

Line 5, page 13. Probably, all these ions are mainly (or completely) coming from sea spray. It could be interesting to calculate their ss- and nss- fractions (at least for Na, Ca and Mg).

Section 3.6. Authors have to be aware that the evaluation of sulfate depletion from the observation of negative values of nss-sulfate is a difficult and controversial task. In coastal areas, the contribution of nss-SO₄ from phytoplanktonic emissions (marked by

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relatively high MSA concentrations) could be very relevant in spring/summer period. The nss-SO₄ originated by the biogenic source can “cover” the ss-sulfate depletion by adding nss-SO₄ to the sulfate budget. Therefore, a ss-sulfate depletion can occur even if no negative nss-SO₄ values were found. The correction for biogenic nss-sulfate can be made by considering aerosol size distribution, aerosol seasonality and the nssSO₄/MSA ratio from DMS atmospheric oxidation. No discussion on this relevant topic is given in this manuscript.

Line 23, page 13. Please, change: “. . . increase in ion concentrations after 1950s . . . “ in “. . . increase in ion concentrations after 1950s in the S100 ice core. . .”.

Line 30, page 13. Nitrate and sulfate correlation coefficient can be statistically significant, probably thanks to the high number of samples, but their values are so low (-0.04 and -0.10) to exclude every real correlation.

Lines 11-12, page 14. A dominant role of dry deposition should be demonstrated also by a significant negative correlation between snow concentration and accumulation rate. By looking to Table 5, that does not occur for Na ($R_{\text{conc}} = -0.12$). I think that both wet and dry deposition are relevant for a site so near to the sea (3 km) and located at so low altitude (48 m a.s.l.) to be affected from snowfall deposition, as well as from direct sea-spray primary production (i.e., aerosol directly produced by wind action on open sea surface or on frost flowers/brine structures over the sea ice surface).

Line 25, page 14. The value 0.06 is the well-known SO₄/Na molar ratio in seawater (corresponding to the w/w ratio of 0.25) and the reference here cited is not pertinent.

Line 29, page 14. the negative values do not mean that “nssSO₄ is strongly depleted in SO₄ relative to Na”, but that the sea-salt content in the snow is depleted in ss-sulfate with respect to seawater composition, so leading to an under-evaluation of nssSO₄, if the 0.06 SO₄/Na ratio is used. Indeed, if part of the original ss-sulfate is precipitated as mirabilite (in case of frost flower formation), the sea salt aerosol originated from the sea-ice surface is depleted in seawater sulfate.

Line 1, page 15 and following. In order to better understand the meaning of the lower SO_4/Na (k) values here calculated, the Authors are requested to compare these values (k' , k'' , k''') with the SO_4/Na ratio for the frost flowers (0.07 w/w, Wagenbach et al., 1998, corresponding to 0.017 mol/mol). In this way, Authors could evaluate the relative contributions of sea salt from seawater ($k = 0.06$) and from frost flowers ($k = 0.017$).

Section 4. Discussion. The discussion is focused on the interpretation of the temporal trend of sea-salt components in the S100 ice core, showing a dramatic increase from 1950 to 2000. Indeed, this increase is impressive and, in my knowledge, never observed (with this intensity) in coastal and inner area of Antarctica (with the exception, of course, of the interglacial/glacial changes). Authors report a 6-times concentration increase from 1750-1949 to 1950-2000 periods. This difference, however, is calculate on the long-period median values (also in this case, percentile values or mean values with standard deviations could help in evaluating the data variability). If we observe the increasing trend of Na in figure 2, we can note that the concentration increases follows a continuous and quite constant trend, up to values as high as 200 $\mu\text{mol/L}$. In comparison with the quite constant concentrations measured along the 1750-1949 period (around 15 $\mu\text{mol/L}$), the Na concentration increases of a factor higher than 13. Chloride follows a similar trend. These S100 sea-salt values are about 4 to 20 times higher than those measured in the three firn cores. Authors attribute this large variation to changes in extension and persistence of sea ice east of the glacier tongue, after the tongue breaking on 1967. The decrease of the glacial tongue could have been against the preservation of multi-annual sea ice, promoting annual fast sea ice, where the formation of fractionated sea-salt aerosol and of frost flowers is more efficient (Lines 3-6, page 17). This is possible (and probable), but some experimental evidences, in my opinion, make weak this hypothesis. 1. The increase is not related to abrupt changes starting on 1967, but Figure 2 shows a very gradual and progressive trend (at least seeing the “linear trends” plotted in figures 2a and 2c) since 1950, before the glacier tongue breaking. 2. The two firn cores located on the same side of the glacier tongue (KM and KC) show sea-salt concentrations very lower and not characterized by an in-

creasing trend (at least for the years covered by the records). In particular, the nearest firn core (KC) show stable (Cl) or slightly decreasing (Na) concentrations about 10 times lower than those measured in the most recent S100 sections (Figure 2b and 2d). 3. All the firn cores (and, in particular, KC and KM), do not show negative nss-sulfate values (Figure 4c). Authors attribute this different pattern to changes in altitude (lines 25-28, page 16), but KC, for instance, is only 200 m above the S100 site and particles as small as 1 μm (Line 26, page 16) are easily transported to very high altitudes. If the altitude plays a similar dramatic effect, then no contribution of sea salt from frost flowers or salty snow sublimated aerosol should be observed in high-altitude plateau sites. On the contrary, some evidences of ss-sulfate depletion (shown by negative nss-SO₄ values) have been found at the sites where Dome Fuji, EPICA-DML and EPICA-DC ice cores were drilled. In conclusion, in my opinion, the Authors hypothesis seems to be not confirmed by the firn cores data and other mechanisms should be investigated.

Lines 19-20, page 17. I strong suggest adding at least a composite figure showing the most relevant changes of extension and shape of the glacier tongue since 1967.

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