

Review of the manuscript “Spatial and temporal variations in snow chemistry along a traverse from coastal East Antarctica to the ice sheet summit (Dome A)” by *Shi and co-workers*.

This manuscript reports on analysis of inorganic ions in snow samples collected in the frame of intensive program of snow sampling made along several successive traverses achieved from the coast (Zhongshan Station) to Dome A (East Antarctica). The samplings include 594 surface snow samples (upper 3 cm), and 3 snow-pits (down to 1-2 m depth). It is shown that  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  concentrations are high within the narrow coastal region, dropping further inland, while  $\text{NO}_3^-$  exhibits an opposite trend. No clear spatial trends were found for  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{Ca}^{2+}$ . Data are discussed with respect to potential origin of ions including for minor ones like calcium, ammonium and potassium.

Overall evaluation: First, the authors have to be congratulated for having successfully conducted such a very large inter-annual snow-sampling program, likely sometimes done under harsh weather conditions.

Whereas these data certainly contain interesting information that would be relevant for the Cryosphere journal, inherent to the poor representativeness of 3 cm snow sampling, an in depth interpretation of data is often very difficult and I find that, in the present version of the manuscript, the authors over-interpret them. The manuscript also reveals several misleading presentations and discussions of data. Finally some key previous works are not adequately referenced in the manuscript.

In conclusion I recommend major revisions and in the following I try to identify what can be removed from the manuscript and reversely what can be developed, in particular (and if possible) taking advantage of more information derived from the snow pit data.

**Overall comments:**

1. It would be far more logic to first present and discuss the snow pit data showing how large is the seasonal variation of all species including ammonium, nitrate, magnesium, calcium and potassium and discuss the basic causes of that. In the present version, only the well-known species (sodium and sulfate) data in the snow-pit are shown in the main text, whereas ammonium is only seen in the SI. Reporting first (and for all species including ammonium, potassium, calcium, nitrate) on the snow-pit data would permit the readers to appreciate the seasonal variability related to surface snow variability.
2. Instead of using enrichment factors (EFs), more illustrative is the calculation of concentration in excess with respect to the seawater composition done with calculation of error propagation (specially for minor species like potassium, magnesium, and calcium). These data would certainly be more useful than EF values to discuss snow pit data (levels, seasonality, etc).
3. Section 4.4: The value of this discussion is very weak since based on samples of poor seasonal representativeness. Please remove it (see also my comment below for section 4.4).

**Comments:**

**Title:** please specify “surface snow” chemistry

**Abstract:** Please remove the last sentence since, in no way, your data can demonstrate something (statistically thought) on this topic: «The interannual variations in ion concentrations in surface snow on the traverse are likely linked to the changes in the Southern Indian Ocean low (SIOL) from year to year, and the deepening of the SIOL in summer tends to promote the transport of marine aerosols to Princess Elizabeth Land. »

Also your statement « Snow  $\text{NH}_4^+$  is mainly associated with marine biological activities » is not really demonstrated (at least as the manuscript stands, see more comments below).

Finally please reword the confusing sentence: «the negative  $\text{SO}_4^{2-}$  signal in winter snow resulted from inputs of sea salts being completely **swamped** by the contribution of marine biogenic emissions. I don't understand what you mean here: do you mean that you have never pure winter snow because of wind mixing after deposition ???

**Introduction:** Several times the choices of your references are strange:

Line 61-65: You miss to cite here Legrand and Delmas (1985) here for a traverse in Adelie Land. This reference is particularly important since it is one the unique traverse for which acidity had been measured (not calculated), see my comment below.

Line 78: I don't think that Saltzman (1995) for the statement "that sulfate in the snow is mainly from marine biogenic sulphur species » is the adequate reference. Please here cite the review from Legrand (1995) or Legrand (1997).

Line 79-80: The two cited references are fine but there are numerous previous works done on that and I would suggest mentioning the article in Nature 1987 (Legrand and Delmas, 1987) for instance.

Line 82-85 : I don't think there is something on the Keene paper on calcium in snow. I suggest citing the study of the Vostok ice core in which the origin (and calculation) of excess potassium, magnesium and calcium were discussed (Legrand et al., 1988).

Line 92: Please cite the first study of ammonium and discussion of its marine origin in Antarctica by Legrand et al. (2000).

Lines 100-105: Please cite Weller et al. (2011) (see my comment on section 4.4).

Legrand M., Sulphur-derived species in polar ice: A review, In *NATO ASI Ser. "Ice cores studies of Global biogeochemical cycles"*, R. Delmas ed., 91-119, 1995.

Legrand, M., Ice-core records of atmospheric sulphur, *Phil. Trans. R. Soc. Lond. B*, 352, 241-250, 1997.

Legrand M., and R.J. Delmas, A 220-year continuous record of volcanic  $\text{H}_2\text{SO}_4$  in the Antarctic ice sheet, *Nature*, 327, 671-676, 1987.

Legrand M., C. Lorius, N.I. Barkov, and V.N. Petrov, Vostok (Antarctica) ice core: Atmospheric chemistry changes over the last climatic cycle (160,000 years), *Atmos. Environ.*, 22, 317-331, 1988.

Legrand M., and C. Saigne, Formate, acetate and methanesulfonate measurements in antarctic ice: Some geochemical implications, *Atmos. Environ.*, 22, 1011-17, 1988.

Legrand, M., and P. Mayewski, Glaciochemistry of polar ice cores: A review, *Reviews of Geophysics*, 35, 219-243, 1997.

Legrand, M., E. Wolff, and D. Wagenbach, Antarctic aerosol and snowfall chemistry: Implications for deep Antarctic ice core chemistry, *Ann. Glaciol.*, 29, 66-72, 2000.

## **Section 2.2:**

Line 197-189: This statement "In Antarctic snow, concentrations of  $\text{H}^+$  are usually not measured directly, but deduced from the ion-balance disequilibrium in the snow » is wrong and very misleading. In fact more than 1000 Antarctic snow and ice samples covering various time periods (present-climate, last glacial age) and collected at various places were measured for  $\text{H}^+$  (Legrand, 1987; Legrand and Delmas 1984) including along a traverse in Adelie Land (Legrand and Delmas, 1985). From that is was shown that the measurement of chloride, nitrate, sulfate, proton, sodium, ammonium, potassium, magnesium and calcium permit to verify the good balance between measured anions and measured cations. And from these studies that it was

postulated that if not available the H<sup>+</sup> concentration can be derived from the equation  $H^+ = [SO_4^{2-}] + [NO_3^-] + [Cl^-] - [Na^+] - [NH_4^+] - [K^+] - [Mg^{2+}] - [Ca^{2+}]$ .  
So please modify this section accordingly.

Legrand M., and R. Delmas, The ionic balance of antarctic snow: A 10-year detailed record, *Atmos. Environ.*, 18, 1867-1874, 1984.

Legrand M., and R. Delmas, Spatial and temporal variations of snow chemistry in Terre Adélie (East Antarctica), *Ann. Glaciol.*, 7, 20-25, 1985.

Legrand M., Chemistry of Antarctic snow and ice, *J. de Phys.*, 48, 77-86, 1987.

### **Section 2.3:**

Why do you play with EF instead of the amount of species present in excess with respect to the seawater composition. The calculations of excess are far more useful to discuss data (see further comments). In any case, calculations of error propagation are clearly needed here, especially for potassium, calcium, and magnesium.

### **Sections 2.4:**

In your case (and it is often the case) the PCA approach does not give more information than those that can be simply derived by checking your plots. Checking your Figure 2, it immediately appears that (as expected) you have more sea-salt at the coast than inland (leading to your PC1). Outside of that, other information derived from the PCA analysis are not very powerful (see my further comments).

### **Section 3.1:**

Line 234-245: It is for a very short time that melted snow is under saturated with respect to CO<sub>2</sub>. In fact after 10 min or so the equilibrium is reached but don't forget that another important factor is the temperature (colder is water more CO<sub>2</sub> is dissolved). Another source of uncertainty here is the PCO<sub>2</sub> in the lab of analysis (related for instance to the number of people). Please report the temperature at which your pH measurements were done.

Would be good here to compare your calculated H<sup>+</sup> not only with previous similar estimates but also with previous actual measurements (Legrand and Delmas, 1985, for instance).

### **Section 3.2:**

Line 274: I feel that after having calculated nssSO<sub>4</sub> (excess sulfate) you will identify an increasing trend of excess-sulfate from the coast to inland due to dry deposition (the sulfate one being obscured by the large amount of sea salt at the coast).

### **Section 3.3:**

This section needs to be significantly developed. First please show all species, second calculate excesses and corresponding error bars.

### **Section 4.1:**

Please present excess here.

Line 371-373: I disagree with that since only a very small amount of potassium from dust is leachable (and measured with your IC) but it is not at all true for calcium (see Legrand et al., 1988, for instance). Therefore you cannot compare your snow data with the mean crust composition from Bowen that refers to total potassium (insoluble and soluble). Please check in Legrand et al. (1988) or Legrand (1987) information on excess potassium versus excess calcium.

I find also that your calcium data (Fig 2) are often above 4 ppb (that is also higher than seen in numerous ice cores under present-day climate. Please comment.

Line 445-454: I disagree with this discussion. Whereas I agree nitrate is clearly related to atmospheric oxidant, the link to sulfate (its similar presence in PC3) is due to the fact that you concentrate  $\text{nssSO}_4$  due to dry deposition at sites with low accumulation rate while nitrate is enhanced for a totally different reason (photochemistry).

**Section 4.2:**

Line 430: Your argument of an absence of correlation between ammonium and organic tracers (Shi et al., 2019) is not correct since the authors invoked a decrease of levoglucosan from the coast to inland due to its photochemical degradation.

Line 433: Checking your Fig S1 in fact you have an outstanding value (17 ppb). Discarding this value I have difficulty to identify a seasonal cycle. Also your mean value (removing the outlier) is close to 2 ppb (it is slightly but significantly higher than what was seen in previous ice core studies). Please comment.

**Section 4.4:** Given the poor representativeness of snow samples, it is clear that examination with respect to SOI is very difficult. For your information, based on a continuous record of 25 year of aerosol, Weller et al. (2011) examine the inter-annual variability with respect to climate-related indices (SAM, SOI, SIE) and nothing very significance had appear.

Weller, R., D. Wagenbach, M. Legrand, C. Elsässer, X. Tian-Kunze, and G. König-Langlo, Continuous 25-years aerosol records at coastal Antarctica: I. Inter-annual variability of ionic compounds and links to climate indices, *Tellus*, 63B, 901-919, DOI:10.1111/j.1600-0889.2011.00542.x, 2011.

End of the review.