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# ***Interactive comment on “Spatial-temporal dynamics of chemical composition of surface snow in East Antarctic along the transect Station Progress-Station Vostok” by T. V. Khodzher et al.***

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Reviewer 1: The comparison of the same depth ranges in sites characterised by very different accumulation rates is not right. The same depth range surely covers very different time periods, especially when comparing coastal and plateau stations. A dating (or just a coarse estimation of dating) is an essential request for a reliable discussion on the temporal trends in every site. Authors: Thank you for your useful comments and suggestions. We agree with this comment. In corrected manuscript we will include data of snow dating (as separate paragraph).

R1: Every seasonal characterization of the snow layers is missing. Both wet (snowfalls)

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and dry (deposition of aerosol particles or adsorption of gaseous species on the snow cover) deposition processes have a clear seasonal pattern. For instance, the deposition of sea-salt components and biogenic compounds (nss-sulfate and Methanesulfonic acid – MSA) has opposite seasonal occurrence (winter and summer, respectively). In this sense, the observation of the entire (but without relevant components such as chloride, nitrate and ammonium) ionic load of the snow samples does not seem a useful tool. I strongly suggest that some seasonal markers (surely MSA, if measured, and nss-sulfate in summer; possibly Na in winter) are used in order to seasonally characterize the snow layers (of course, at least in the sites where a sufficient accumulation rate allows that single seasonal layers are present in the 10 cm sample resolution);

A: In corrected manuscript we will include data on seasonality test (for sodium and sulphate ions) as a separate paragraph. Unfortunately, low (10 cm) sampling resolution does not allow the define clear seasonal differences in ion concentrations even in highest accumulation site.

R1: A very relevant component, the nss-sulfate emitted from marine biogenic processes (by atmospheric oxidative processes of dimethylsulfide – DMS – emitted by phytoplanktonic activity) is completely neglected in the data discussion. On the contrary, minor sources are supposed to have a major contribution. A: We agree. In corrected manuscript we will discuss all possible sulphate sources, including marine biogenic processes.

R1: No study was carried out on the transport processes of air masses over the studied area. The discussion is limited to a qualitative synoptic description of the dominant cyclonic circulation in the neighboring marine regions. Without a statistical study of the frequency (possibly annual trends) of the air-masses back trajectories, it is very difficult to interpret in a reliable way the depositional anomalies of dust components along the traverse route. A: In corrected paper we will include (in Discussion) statistical analysis of 5-day back trajectories for three sites along the traverse.

R1: Line 5, page 2008. What “cores” means? In the “Material and Methods” section,

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the sampling method has to be clarified (by snow pits or firn corer or a simple tube vertically inserted into the snow). See also below. A: In new version we will clarify sampling technique. No cores were used here but snow pits.

R1: Line 8, page 2008. I think that “snow cover chemical composition” is better than “snow cover formation”, because snow cover formation is affected by several factors: wet and dry deposition, wind redistribution, photochemical reactions, post-depositional effects, snow accumulation rate etc. See also below. A: We agree.

R1: Line 10, page 2008. “Marine derived components”. Authors have to distinguish between primary sea spray (or sea salt) contribution and secondary aerosol by marine biogenic emissions (completely neglected in this paper, see also below). A: We agree and will take into consideration this comment.

R1: Line 12, page 2008. Authors should clarify the meaning of “continental origin”. Does the term refer just to dust or also to volcanic emissions, anthropogenic sources etc.? Besides, the major sulfate source in Antarctica is constituted by marine biogenic emissions, while the continental sources are very scarce (with the exception of deposition of explosive volcanic eruptions, very intense but not frequent – see also below). A: We will clarify the meaning of “continental origin”. The term refers to dust of terrigenous origin, volcanic emissions, and anthropogenic sources.

R1: Line 14, page 2008. The Pinatubo signature in the sampled snow layers is very hard to demonstrate because no snow-layer dating was carried out. A: The presence of the Pinatubo signature (1991) was traced in elevated concentrations of non-sea salt sulphates (nss-SO<sub>4</sub><sup>2-</sup>) at 1276 km within the depth interval of 120-130 cm. The details will be given in text.

R1: Lines 16-22, page 2008. Authors report some sentences apparently inconsistent one with each other. In the first sentence, the snow is indicated as a marker of the status of the environment and is supposed to include traces of “technogenic sources”. In the second sentence, Antarctica is considered “not subject to global transfer of im-

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purities due its remoteness : : :”. Authors are requested to clarify their thought. A: We agree and will remove it.

R1: Line 22, page 2008. Sea salt is a dominant snow component just in coastal areas and for winter-spring snowfalls. In summer-fall, biogenic compounds (especially nss-sulfate) prevail. A: We agree with this comment.

R1: Lines 25-26, page 2008. The sentence “spatial variations : : : .. sea-salt snow” should be clarified. A: We will clarify this sentence.

R1: Line 4, page 2009. What “snow width” means? It will be deleted.

R1: Line 5, page 2009 and References: please change “Bertle et al. 2005” in “Bertler et al. 2005”. A: It will be corrected.

R1: Line 7, page 2009. What “fine aerosol fraction” means? PM<sub>2.5</sub>? Sub-micrometric fraction? Where “fine aerosol fraction” contributes 86% of the ionic budget? Please, cite references. A: We changed “fine” for “submicron”.

R1: Lines 9-11, page 2009. The most relevant sources for sulfate are sea spray (ss-sulfate), in coastal areas and in winter, and especially biogenic emission (nss-sulfate, produced by oxidation of the gas-phase precursor DMS) in summer in coastal and inner Antarctica. Besides, the sulfate stratospheric source is just related to the emissions of explosive volcanic eruptions, which are able to inject large quantities of SO<sub>2</sub> (later oxidized to nss-sulfate). Such contribution could be very high (sharp sulfate spikes) in concomitance of the deposition of the volcanic emissions, but they contribute very little to the sulfate budget at medium-long period because explosive eruptions are infrequent. A: We agree with the Reviewer. The will indicate that the most probable sources of sulphate (SO<sub>4</sub><sup>2-</sup>) are sea spray (ss-sulphate), biogenic emission (nss-sulphate), volcanoes, mineral dust and secondary aerosols.

R1: Line 14, page 2009. Authors should clarify that the formation of HCl occurs via exchange reaction between NaCl and H<sub>2</sub>SO<sub>4</sub> and that this reaction is common in all

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the Antarctica regions (not only in the James Ross Island). A: We agree with this comment. The Na/Cl ratio that is higher than 1.8 and that is characteristic of sea water is evidence of frequent formation of hydrochloric acid in the acidic atmosphere (Aristarain and Delmas, 2002, Legrand et al., 1988).

R1: Lines 16-19, page 2009. The relationship between nitrate and solar activity is a controversial topic and presently under discussion. Anyway, Authors have to cite other sources for nitrate, such as mid-latitude lightning, NO<sub>x</sub> emissions by anthropic and natural combustion processes, sedimentation of Polar Stratospheric Clouds (PSCs) etc. A: We agree that this is a controversial topic, it will be deleted.

R1: Lines 20-23, page 2009. This sentence has to be clarified. Besides, the expression “formation of snow cover” has to be explained. Indeed, many processes contribute to that: wet and dry deposition relative contribution, reactivity of chemical species in the snow layers, photochemistry, snowdrift by wind, transformation or re-emission into the atmosphere by post-depositional processes, accumulation rate, superficial snow melting or sublimation, adsorption of gas-phase compounds on the uppermost snow layers etc. A: We will try to clarify it in corrected manuscript.

#### Materials and Methods

R1: A map of the Antarctic sector Ingrid Christensen Coast –Vostok Station, with the indication of the sampling stations, should be shown. A: This map will be done.

R1: Lines 2-5, page 2010. Every information on sampling and, eventually, sub-sampling is missing. How were the samples collected? Authors used a firn corer? Or have they used a simple tube vertically inserted into the snow? Or sub-samples were directly obtained by inserting the containers into the snow wall of snow pits? If the samples were collected by a tube or a firn core, some disturbance of the snow layers could have occurred, due to the compression of the most superficial (less dense) snow layers. Besides, in this case, how were the sub-samples obtained? A: The information on sampling methods will be added.

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R1: Line 21, page 2010. Please, invert the order of IonPac columns CS12A (cations) and AS19 (anions). A: It will be done.

R1: Line 25, page 2010. Maybe the term “trends” is more suitable than “dynamics”. What “... and one order of magnitude measured” means? A: We agree with this. We will correct this sentence.

R1: Lines 26-28, page 2010. The description of the analytical differences is confused. Which is the mean discrepancy between the samples analyzed in the two laboratories? Anyway, 30 % discrepancy is a very high value for IC measurements of sulfate at 100 ppb level. Some samples show differences very higher than 30% (see Figure 1). A: We can explain the high discrepancy between the samples, as these are natural samples with very low concentrations. The mean discrepancy between the samples analysed in the two laboratories was 13% and 24% for ions of sulphate and sodium, respectively. According to the documents of WMO and EMEP, the permissible discrepancy range is 30% at the concentration of less than 0.05 meq L<sup>-1</sup> (EMEP, 1996). Taking into account low concentrations of the components determined (on average, 0.002 meq L<sup>-1</sup> for SO<sub>4</sub><sup>2-</sup> and 0.001 meq L<sup>-1</sup> for Na<sup>+</sup>), one can conclude that the analysis results of the same samples carried out by two independent laboratories were consistent.

R1: Lines 1-3, page 2011. By observing figure 1, the discrepancy between ICP and IC measurements for Na seem to be very high, especially for 5-9 and 77-89 samples. Besides, sometimes, IC (soluble) Na is higher than ICP (total) Na. Authors should comment this result with more details. A: Inter-comparison of snow samples from East Antarctica was performed at two laboratories using only ion chromatography. Yes, there is significant discrepancy between the samples, especially for 5-9 and 77-89 samples. We stress again that these are natural samples, they were not fixed.

R1: The “total” ionic concentration does not seem a relevant and significant parameter for the spatial and temporal trends in the chemical composition of the snow. The snow concentration of ions in coastal and inner regions of Antarctica strongly depends

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on seasonality and accumulation rate, the latter heavily changing along coast-inland transects. Similar total ionic concentrations could reflect a completely different composition. Usually, the large ionic load of sea salt in winter (with a little contribution of nss-sulfate) is counterbalanced by large deposition of marine biogenic sulfate (and low sea-salt content) in summer. Besides, especially inland Antarctica, most of the ion load is due to dry deposition, so that the ion concentration is inversely dependent on accumulation rate. The alternating trend observed by the Authors along the transect could be explained in this way: in the first part of the traverse, a decreasing trend is observed (especially in the first 2 stations) because of the progressive increase of the distance from the source areas (especially primary and secondary marine aerosol) and the main contribution of the wet deposition. In the inner stations, the slight increase of the concentration is probably caused by the decreasing accumulation rate and the predominance of the dry deposition. In addition, the concentration of substances in the superficial snow layers is highly affected by wind distribution phenomena, such as snowdrift and sastrugi fields. Finally, the term “total” is not fully correct, because at least three relevant components were not measured: chloride, ammonium and nitrate. A: We agree with this comment and in corrected manuscript we are planning to compare mean concentrations and fluxes of sub-surface snow layers (with similar age) along the traverse.

R1: The comparison among snow layers located at the same depth in the different sites is not significant and misinterpreting. In fact, Authors compare snow layers that, although related to the same depth range, cover very different time periods. In coastal sites, the first 100 cm could represent 2-3 years of snowfall. When we move inland, the temporal range encompassing the same depth range almost progressively increases. For instance, at Vostok Station, the accumulation rate is about 2.2 cm water equivalent (w.e.) per year, corresponding to about 7 cm of snow (considering a density of about 0.3 – 0.35 g/ml). In this approximation, a layer of 100 cm of snow covers about 14 years. It is evident that the information given by a similar depth range is completely different from that obtained by comparing similar time intervals. Authors should make

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every effort in evaluating a snow layer dating, eventually by observing the depth trends of seasonal markers (high values of biogenic nss-sulfate and d18O in summer, probably high Na values in winter). Only a stratigraphic dating (even grossly obtained) could allow a significant comparison of snow layers belonging to the same temporal range. The problem is the sample resolution. Maybe 10 cm resolution is sufficient to appreciate a seasonal signal in the site nearest to the coast, but is surely insufficient for the inner stations. I wonder if the Authors have a more depth-resolved data set. A: Yes, we will add a section about snow dating and we will compare even-aged snow layers. As for seasonal signal, we can not see it because of too low sampling resolution.

R1: The Authors rightly distinguish between ss-sulfate and nss-sulfate. Since the two components have very different sources, with an opposite seasonal trend, I think it is incorrect to report the total sulfate spatial and temporal trends. The discussion should be addressed on ss-sulfate and nss-sulfate separate trends (as shown in figure 4). Even in this case, the discussion about the concentration trend of a component in the same depth range is misinterpreting (see above). We have to note that, in calculating the ss-sulfate fraction, Authors use the 0.06 values as sulfate/Na ratio in seawater. This value is related to the Mole/Mole ratio and not to the Eq/Eq ratio (= 0.12), as the Authors say (line 2, page 2015). Finally, the highest sulfate values in the innermost stations, in particular at Vostok, are surely driven by the changes in the accumulation rate, considering that the dry deposition of nss-sulfate dominates. In fact, at Vostok, where the lowest accumulation rate is measured, sulfate concentrations are higher than in the neighboring stations. A: We agree with the comments of the Reviewer. The section was rewritten.

R1: The majority of the information contained in the “introduction” of this section is well known and should be shortened, so giving more relevance to the data discussion. Besides, the relevance of some concepts to this manuscript is not clear. For instance, the Authors rightly cite the mechanism of formation of sea salt particle (production of aerosols with different size) and the ability of the natural surfactants in the enrichment

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of some components (not listed) with respect to the seawater composition, but no discussion is reported on sea salt size distribution or on the enrichment factors of selected components. A: We will rewrite this section.

R1: Line 6, page 2013. What the sentence: “components in the Antarctic snow are emitted with aerosols from the atmosphere : : :..” means? Chemical components are included in or adsorbed on the aerosol particles, which are scavenged from the atmosphere by wet and/or dry deposition; otherwise, if they are in gas-phase, they can be directly adsorbed on the surface of the snow cover. Besides, even the compounds emitted from volcanoes eruptions are subjected to photochemical reactions (e.g., the oxidation of SO<sub>2</sub> to sulfuric acid). The sentence has to be improved. A: This sentence was deleted and Discussion section rewritten.

R1: Line 17, page 2013. I think “deposited” is better than “accumulated”. We agree.

R1: Line 24, page 2013. Please correct “Bertle” in “Bertler”. A: We will correct it.

R1: Lines 3 and 7, page 2014. The pH measurements are very difficult for the Antarctic snow, especially in inner sites, due to the very low ion content and buffer capacity. Besides, even a slight absorption of atmospheric CO<sub>2</sub> during the measurements is able to give wrong results. As a consequence, reproducibility and accuracy are low and the measurements request particular techniques (Gran titration, addition of electrolytes, specific pH probes). In an alternative way, the H<sup>+</sup> contribution can be estimated by the ion balance, if all the most relevant components are measured (but they have to include even chloride, ammonium and nitrate). How the Authors carried out the pH measurements? A: The authors agreed that it is difficult to measure pH, therefore this information will be deleted.

R1: Line 4, page 2014. I think that “The content of Al : : :..equalled analytic zero” has to be changes in “The content of Al : : :..was below the detection limit”. A: It will be corrected.

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R1: Line 9 and followings, page 2014. The discussion about the transport of air masses in the traverse region is too qualitative and not supported by studies on air-masses back trajectory temporal series (e.g., back trajectory cluster analysis). In my opinion, it is very difficult interpreting the increased concentration of Ca at 560 and 618 km and Al at 618 km in this way. Are there local sources? Could the accumulation rate be relevant? A: Back trajectory analysis will be added to new manuscript.

R1: Line 20, page 2014. The Authors should say that the most relevant nss-sulfate source in coastal and inner Antarctica is from the oxidation processes of phytoplanktonic DMS emissions. A: The authors agree with this comment of the Reviewer that the most relevant nss-sulphate source in coastal and inner Antarctica is from the oxidation processes of phytoplanktonic DMS emissions. It will be discussed in new version.

R1: Line 2, page 2015. The sulfate/Na ratio is 0.06 Mole/Mole and 0.12 Eq/Eq. A: The concentration is given in  $\mu\text{mol L}^{-1}$ .

R1: Lines 5 and followings, page 2015. As previously discussed, it is very hard comparing nss-sulfate signatures in the same or different depth ranges if we do not know the snow layer dating in the different stations. Nss-SO<sub>4</sub> spikes in the different sites could be related to different events occurred in different time periods. In my opinion, the only station where the Pinatubo eruption can be recorded is the Vostok station. Snow samples were collected on 2008 and Pinatubo eruption occurred on 1991 and recorded in Antarctic snow in 1991-93 snow layers. Therefore, snow (firn) samples have to cover 15-17 years. That means an accumulation rate of 10 cm snow (about 3 cm water equivalent) per year. This very low accumulation rate seems to be suitable just for Vostok. In fact, the sulfate spike is recorded in this station at 120-130 cm (maximum value of the peak), corresponding to about 17 years ago, considering an accumulation rate of about 7 cm/yr (present accumulation rate = 2.2 cm w.e.; mean density = 0.30-0.35). In my opinion, it very difficult that sites at 560 km and, especially, at 253 km from the coast, have so low accumulation rates (in absence of ablation of some annual snow layers by the wind). Finally, just the Vostok spike has the classical

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shape of a volcanic deposition. However, Authors could be right, but at least a coarse dating is necessary to assess the presence of the Pinatubo signature in the snow layers of the different sites. A: We agree with this comment. We will correct it. The only volcanic spike attributed to Pinatubo eruption (June of 1991) was recorded at 1276 km snow pit. It will be discussed in the manuscript.

R1: This section has to be changed tacking into the account the previous comments.

A: The “Conclusions” section will rewritten according to the comments.

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Interactive comment on The Cryosphere Discuss., 7, 2007, 2013.

TCD

7, C2099–C2109, 2013

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