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Climate of the Past Discussions

Interactive comment on "Sea ice-related halogen enrichment at Law Dome, coastal East Antarctica" *by* Paul Vallelonga et al.

Anonymous Referee #2

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Comments to the paper: Sea ice –related halogen enrichment at Law Dome, coastal East Antarctica P. Vallelonga et al.

General Comments

The paper is concerning the possibility that Br-enr and I-enr can be used as proxy markers for sea-ice extension and/or persistence in Antarctica. The topic is interesting, especially for paleo-climate studies concerning the reconstruction of sea-ice dynamics from chemical stratigraphies of ice cores. Besides, every new information of the chemistry of halogen compounds on snow and sea-ice surface is interesting in order to understand their relationship with marine biological activity, tropospheric ozone and photochemical processes at the sea/atmosphere interface. However, in my opinion, the majority of the information about concentration in the snow (and firn and ice) and

seasonal trends of Br and I was already reported in previous papers and, especially, the relationship between Br-enr and I-enr with sea-ice dynamics (the main goal of the paper) seems to be not sufficiently strong as the Authors assessed. Some interpretations of the temporal trends, especially those concerning the comparison with first year sea ice (FYSI) data, are, in my opinion, not fully corresponding to the profiles shown by the plots (see specific comments). Besides, some improvement should be made in the methodological sections and in the data discussion. In conclusion, I think that the manuscript is not ready, in this form, to be accepted for publication on Climate of the Past journal. However, since the topic is very interesting and a huge analytical work was made to analyze snow, firn and ice samples, I'd like to encourage the Authors to submit an improved manuscript, possibly taking into account my criticisms and suggestions.

Specific and minor comments

Lines 5-8, page 2. Authors should give some summarized information on the chemical processes involved in the "photochemical recycling above salt-rich snow and ice surfaces", even if a reference is correctly cited.

Line 23, page 2.Authors are requested to indicate the DL for bromate and iodide in order to have an idea about their possible (maximum) concentration levels in the Talos Dome samples.

Lines 28-29, page 3. Are the snowfalls really so "regular" to provide very detailed (month-by-month?) stratigraphies? For the time covered by the DSS1213 firn core, some basic information about the snowfalls frequency could be given in the Section 2.

Lines 18-19, page 4. DSS0506 sub-samples were melted and refrozen in 2006 and analyzed in 2014. Have the Authors some evidences about possible effects of melting/refreezing cycle and long-time storing on the determination of Br and I?

Section 2.2 – Analytical measurements. Even if sufficient references were cited, some

analytical methods performances should be here summarized (reproducibility, accuracy, DL, blank values). Was an inter-calibration exercise made between Australian and Italian laboratories?

Line 30, page 5 and line 3, page 6. Mass resolution (m/dm) is dimensionless. Please, delete “amu”.

Lines 4-5, page 6. Please, summarize the method performances in terms of accuracy and difference between blanks and samples values.

Line 9, page 6. The term “core” has to be referred to DSS0505 and not to DSS1516. Where the DSS1516 snow pit were analyzed? At lines 18-19, page 5, Authors report that DSS1516 snow pit samples were analyzed for Br in Australia. Maybe, in Italy the same samples (or samples from a parallel column in the snow pit) were analyzed even for I and Na, other than Br. In this case, were the Br values compared?

Section 2.3. Which samples were analyzed for IC? Were the Na values reported in the manuscript analyzed by IC (soluble fraction) or by ICP-MS (probably total content)? The analyzed Na fraction could play a not-negligible role in evaluating the Br-enr and I-enr fractions, if Na, and not ssNa, is used as sea spray marker. Also for IC measurements, the methods performances (at least for Na and MSA) should be here summarized.

Lines 2-3, page 7. Please, reword the sentence.

Lines 7-8, page 8. I think that median is more suitable than geometric mean in evaluating the asymmetry of the data sets, by comparison with the mean values.

Line 11, page 8 and following. The calculation of nssBr, nssI, Br-enr and I-enr have to be made by using ssNa, and not total Na, as sea spray marker. I’m aware that, in a coastal site, the majority of the Na content in the snow is originated by sea spray, but also local or long-range dust could give not negligible contributions, at least in particular transport events. As well known, the nssNa fraction (and then ssNa by difference)

can be easily evaluated by using Al (if Na is measured by ICP-MS) or nssCa (if Na is measured by IC) as crustal markers and knowing the Al/Na or Ca/Na ratios in the uppermost Earth crust.

Line 12, page 8. Please, change “sodium” in “ssNa”.

Line 15, page 8. Authors are requested adding a short description of meaning and seasonal occurrence of the “bromine explosion” events.

Lines 17-18, page 8. The calculation of the enrichment factors of different snow and aerosol components with respect to seawater composition is well established and cannot be attributed to some of the Authors.

Line 18, page 8. Please, change “Na” in “ssNa”.

Line 22, page 8 and following. In my opinion, the tentative explanation of the different variability of Na and Br in the two records (DSS0506 and DSS1213 firn cores) appears to be not convincing. Table 1 and Figure 4 show that DSS1213 Na profile has higher mean values and much higher variability with respect to the DSS0506 record. On the contrary, the DSS1213 Br profile shows a very sharp smoothing of the 3-yr running mean and lower mean values, with respect to the DSS0506 record. A so large Na and Br opposite variability cannot be attributed, in my opinion, to selective (Br, with respect Na) “memory effects” or to a different depth resolution of the analytical methods (melter vs discrete samples). Memory effects are usually related to the matrix and not to single components; besides they could play a smoothing effect (but not as large as for the Br) and cannot increase the variability (as shown by the Na profile). Differences in measurements resolution (continuous melting vs discrete samples) are fully able to change the data variability, but not in opposite sign for the two components; besides, the different resolution (if not too much large with respect to accumulation rate) should be not able to change the 3-yr mean profiles. Authors are requested to report the estimated depth resolution for the continuous melter system. Finally, snow pit data show very higher Na values and similar Br concentrations (it is difficult to evaluate little

differences in a logarithmic scale; Authors are requested to add the snow pit mean values in Table 1), with respect to DSS1213 firn core. How the Authors can explain these patterns? Could the different profiles be caused by different analytical methods in the different laboratories?

Line 6, page 9. I cannot understand how the variability in the Br-enr data "may act to artificially increase the correlation". Usually, higher variability could cause a loss of correlation or make more difficult the evaluation of a possible correlation between two parameters. Authors are requested to explain their thought.

Line 17, page 9. The Br-enr – FYSI correlation is poor (max R2 value: 0.32) for the 90-110 °E sector and null for the 110-130 °E sector. This sector selectivity seems to be too large (see, also, I-enr, that shows a completely opposite pattern) and could imply that the correlation between the two parameters (Br-enr or I-enr with FYSI) is weak and possibly covered by other factors, such as atmospheric circulation modes (with an opposite effect for Br-enr and I-enr?). Indeed, a 0.32 R2 value, even if significant at the 99% level, means that just 1/3 of the Br-enr variance can be attributed to changes in FYSI. In my opinion, the R2 values are not sufficient to support the Authors hypothesis (see also my below comments to the Figures 5 and 6).

Line 20, page 9. The MSA-FYSI correlation in the 80-140 °E sector cannot support the Br-enr – FYSI correlation because the last correlation is highly sector selective and the 80-140 °E sector covers a sector (110-130 °E) in which the Br-enr – FYSI correlation is completely absent.

Lines 24-30, page 9. As before discussed (my comments to line 17, page 9), Authors attribute to several possible "noise effects" the Br-enr – FYSI correlation variability as a function of summer-summer or winter-winter intervals. In my opinion, the correlation is always poor and R2 values depend on too much factors to be confident. The last sentence (lines 29-30) is not supported by the data.

Lines 14-15, page 10. These limitations in the comparison of MSA and Br-enr temporal

trends are correct, but we have to consider that we are comparing 11-yr mean profiles. Therefore, some limiting factors, especially the different seasonal pattern, surely play a minor or null role.

Line 21 and line 23, page 10. I cannot see in Figure 5 a significant increase, with respect to the noisy baseline along the multi-decadal trend, of MSA during the periods 1920-30 and 1975-85. For instance, the MSA profile in the period 1955-67 could show similar positive anomalies. The only significant increase is related to the period 1940-55.

Line 22, page 10. I agree that MSA and Br-enr profiles show a common multi-decadal trend (a slight decrease), but the single common feature, around 1940-1955, shows peaks shifted of about 4 years. Besides, the trend in the period 1955-80 is opposite. Even neglecting the large 1970-90 Br-enr peak, which is not evident in MSA profile, the 1955-70 trends of Br-enr (increasing) is opposite to that of MSA (decreasing). I think that the agreement between the two parameters is weak and Authors should try to explain the observed differences in the temporal shift of the 1940-50 peaks and in the 1955-70 opposite trends.

Lines 25-26, page 10. I have some perplexities also concerning the comparison between FYSI and Br-enr. Unfortunately, the period covered by satellite measurements is short and a reliable comparison is difficult. However, I can see two clear evidences that should be explained. By observing the Br-enr large peak around 1970-90, we have to note that while it is correct that the highest value is synchronous with the 1982 large positive anomaly in the FYSI, its temporal evolution does not follow the FYSI dynamics. Indeed, the Br-enr peak show an abrupt increase when FYSI positive anomalies are not marked (unfortunately, FYSI 1977 and 1978 satellite data are missing, but 1976 and 1979-80 data show null or slightly negative anomalies). Besides, after the 1981 peak, Br-enr quickly decreases, while FYSI shows relevant positive anomalies until 1985. Finally, almost continuous FYSI negative anomalies from 1993 to 2010 do not cause negative peaks in the Br-enr profile that, on the contrary, shows a continuous

and clear increase. I think the Authors should reconsider their assessments and better discuss (and, possibly, interpret) the complex FYSI-Br-enr relationship. As the Authors report in the next section, the two Br-enr peaks (around 1945 and 1981) could be related to changes in atmospheric circulation modes (e.g., changes in the IPO) that could include (but not only) changes in sea ice dynamics.

Lines 6-7, page 11. The correlation coefficient between I-enr and FYSI for summer-summer 110-130 °E sector (R2 = 0.42) is higher than that of Br-enr for 90-110 °E (R2 = 0.32), even if the p-value is slightly lower (<0.01, with respect to <0.001, but anyway significant). Authors should discuss why the correlation between I-enr and FYSI is so sector selective, and opposite of that, similarly sector selective, between Br-enr and FYSI.

Line 10, page 11. A correlation with R2 = 0.27, even if the value is statistically significant, is really too poor and cannot demonstrate that the two parameters are correlated (just $\frac{1}{4}$ of the variance of a parameter is explained by the variability of the other). However, by observing figure 6, the two profiles are very similar. Maybe, the correlation is poor because there are temporal shifts between the peaks of the two records. Indeed, the 1945 Br-enr peak leads the I-enr peak and the opposite pattern is visible for the 1980 Br-enr peak. In my opinion, the Br-enr – I-enr relationship deserves an improved discussion.

Lines 13-18, page 11. The relationship of I-enr and Br-enr with IPO is potentially very interesting. Unfortunately, Authors barely touches on the topic. The Authors should improve the discussion and evaluate how the IPO changes can affect the Br and I emissions or transport processes. For instance, why positive-to-negative and negative-to-positive IPO phase changes cause the same effects on I-enr and Br-enr profiles? Which are the relationships between IPO phases and atmospheric circulation around Antarctica or sea-ice dynamics?

Section 3.5. Maybe this section should be moved just after (or inside) section 3.1.

No novelty on the seasonal pattern of Br is here reported, with respect to previous results on shorter data series. The tricky dephasing between spring Br explosion and Br summer maximum in the snow is not explained (and I agree that this pattern has to be in deep studied).

Line 16, page 12. Figure 8 show fluxes and not concentrations. Na fluxes are very higher in the final 25 km, with respect to more coastal sites.

Line 20, page 12. This Na and Br pattern is interesting and should be enlightened. Higher fluxes in higher snow-accumulation sites mean that Na and Br deposition occurs mainly by wet-deposition, while dry deposition could be negligible. This fact can have implications in ice-core studies.

Conclusions. This section should be revised accordingly to the suggested manuscript changes.

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