

CPD Law Dome Halogens  
Responses to reviewers

Anonymous Referee #1

We thank the reviewer for their interest in the article and their detailed comments. We would like to point out that since the initial manuscript submission, we have identified a bug in the code used to generate the sea ice areas (FYSI was overestimated), which has led to some changes in Figure 3 and some of the correlations in Table 2. Also, revision of the data has identified gaps in the ESMR 1973-1977 satellite dataset, so some years have been removed from the FYSI dataset as a result. The essential findings of the manuscript have not been changed by this new data.

Vallelonga et al. present new halogen (Br and I) data from ice and snow samples at Law Dome, Antarctica. The manuscript is well-structured, clear and concise with nearly all the appropriate information provided. As in previous studies by several of the authors, the enrichment of Br (Brenr), relative to the Br/Na ratio of seawater is suggested as a proxy for first year sea ice. Although the concentration of Br itself shows no seasonality, Brenr is shown to peak in the spring-summer months and this is attributed the 'bromine explosion', a series of self-catalytic photochemical reactions understood to occur over sea ice in the springtime. Two ice cores extend the Brenr data set back to the early 20th century, and a gradual decline is seen, broadly similar to that observed for MSA (a relatively well-understood sea ice proxy) at Law Dome. A correlation between first year sea ice (FYSI) and Brenr is found, suggesting that Brenr could be a potential sea ice proxy. A set of surface snow samples from a traverse provide a first opportunity to consider spatial variability in the Br/Na relationship around Law Dome.

As outlined by the authors, Law Dome is an obvious site for Antarctic sea ice proxy development. Its high accumulation rate, minimal multi-year sea ice and relatively simple meteorological conditions mean that the influence of complicating factors are reduced, plus the Curran et al. (2003) paper solidly established MSA as a proxy for local sea ice conditions. In this respect, this study is a timely and logical next step in the exploration of halogens as potential sea ice proxies. The study presents useful data that allow seasonal, inter-annual and century-long trends to be examined, greatly adding to the halogens data for this site. Some careful consideration of the interpretations and claims made is required, as I will detail below. In addition, the interesting surface snow traverse samples should be investigated further. This study should be suitable for publication in CP, providing the introduction and discussion are expanded to consider the complexities of halogen atmospheric chemistry and their potential impacts on the utility of Br and I as sea ice proxies.

Major comments

The Introduction (3rd paragraph) needs expanding to set this study into context of previous halogens work on snow and ice samples. Br is not a “well-established” sea ice proxy and halogen atmospheric chemistry is highly complex. This needs to be made clear from the outset. It would also help to justify the need for sea ice proxy development at Law Dome, particularly the sample transect which is barely discussed at the moment. The questions surrounding halogen recycling, transport and deposition, aerosol vs. gas phase species are skipped over here but they need to be addressed. For example, in the early study quoted, Spolaor et al. (2013b) describe a mechanism by which Br is depleted relative to Na in glacial periods. They propose that Br is enriched over the sea ice but depleted inland (at Talos Dome) because the sea ice is further away in glacials and all the gaseous-phase HBr is deposited en-route. However, in a later paper, in the Arctic this time, Spolaor et al. (2016, Cryosphere) show good correlations between sea ice area and Br - the sign of correlation has changed to positive. The transect samples could be used to directly address the issue of whether Br is transport/deposited as gaseous HBr or sea salt aerosol (see Simpson et al. 2005, GRL).

We have expanded the introduction to provide additional information regarding halogen chemical processes relevant to polar ice sheets. Changes have been made to the first paragraph of the introduction noting the complexity of halogen chemistry, and elaborating on the key uncertainties and processes relevant to this work. Additionally, examples of insitu observations and combined observations-model exercises have been cited.

Due to the quite different temporal scales involved, we consider it inappropriate to directly compare the findings of the 200 kyr Talos Dome record (2013, ACP) with those from the 50 yr Severnaya Zemlya record (2016, Cryosphere). Firstly we note that in the Severnaya Zemlya record, similar to Law Dome, we are dealing with a period of relatively well-constrained FYSI variability.

When considering glacial-interglacial changes such as those investigated at Talos Dome, changes in MYSI and FYSI areas are of substantially greater magnitudes and hence it is possible for the sampling site (ice core site) to change from a location of bromine enrichment to one of bromine depletion. In this light, the findings from Talos Dome are much more consistent with a recently published article reporting 120 kyr Br record from the NEEM ice core (2016, Scientific Reports) - both sites demonstrate substantial changes in  $Br_{enr}$  linked to corresponding changes in sea ice extent in glacial and interglacial climates.

In the Spolaor et al. (2016) paper Br enrichment and Br excess (which is nssBr as I understand it) are plotted (Fig. 6). Could the same be done here? This would rule out a scenario in which the sea salt input (of Na and Br) changed but the speculated Br explosion component stayed constant, in which case Br enrichment would change but nssBr would remain the same. Along the same lines, if the similar multi-decadal variability in Br and I enrichment results from meteorological/transport-related modification of the sea salt loading (IPO, Vance et al., 2015, 2016) as speculated, nssBr should look different to  $Br_{enr}$  (maybe no change?).

The reviewer is correct that Br excess is identical to nssBr and in future we will consistently use nssBr. We have expanded Figure 4 to include both  $Br_{\text{enr}}$  and nssBr. Overall, there is good agreement between the two measures, as was also the case in the 2016 paper cited by the reviewer. This is because  $Br_{\text{enr}}$  and nssBr are essentially the same measure, represented in different ways. The only difference between  $Br_{\text{enr}}$  and nssBr is that one ( $Br_{\text{enr}}$ ) determines the relative difference while the other (nssBr) determines the absolute difference between Br found in the sample and Br expected from sea salt. Otherwise they are calculated from the same measurements of Br and Na and assume the same Br/Na seawater ratio. As a result,  $Br_{\text{enr}}$  is never less than zero, with values greater than 1 indicated enrichment of Br above sea salt levels and values less than 1 indicating depletion of Br with respect to sea salt levels (as was found for glacial Talos Dome samples).

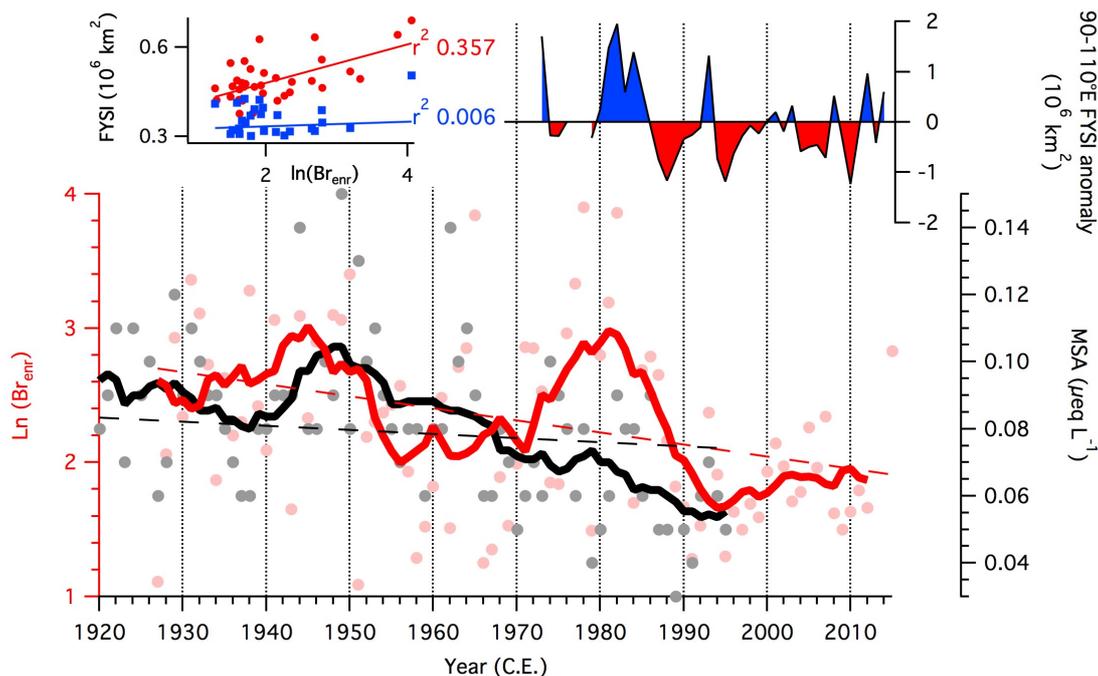
Regarding the possible influence of IPO, it is important to recognize that IPO is not significant at daily timescales relevant to meteorological/transport processes. IPO is a low frequency (multi-decadal) mode of variability related to ENSO and indeed resembles smoothed (low frequency) ENSO variability. Both the IPO and ENSO have a low frequency impact on multidecadal variability across and beyond the Pacific Basin. Therefore while IPO is likely to influence sea salt levels in Law Dome (among many other locations), we do not expect IPO to influence the processes underlying Bromine explosion events. A more detailed investigation of IPO influences to Law Dome is presented by Vance et al. (GRL, 2015).

The attraction of Law Dome for this study is the MSA-sea ice relationship established by Curran et al. 2000. Unfortunately, the similarity between MSA and  $Br_{\text{enr}}$  ends at them both showing a slight decrease over time. Statements on pg 10 3rd paragraph and in the conclusion should be scaled back. It seems at least equally likely that the multi-decadal variability in Br enrichment is related to meteorology (as pg, 11, line 10) and not sea ice.

We reduced have scaled back the statements regarding similarities between the MSA and  $Br_{\text{enr}}$  records and added a consideration of the potential influence of IPO on the records. Accordingly changes have been made to pg 10 (paragraph 3) and in the conclusions.

The significant, but rather weak, correlation between  $\ln(Br_{\text{enr}})$  and FYSI then becomes central to the study and the relationship is not obvious from Fig.5. This deserves a separate figure or sub-figure.

An inset figure has been added to figure 5 showing the correlation between  $\ln(Br_{\text{enr}})$  and FYSI for sectors 90-110°E and 110-130°E.



Updated Figure 5.

All data (including raw Br, I and Na) should be made available in supplement or online database as indicated.

We have prepared the data files and these have been sent to the NOAA and PANGAEA paleoclimate databases for archiving.

Minor comments

O'Dwyer et al., 2000 study Pg. 3 line7 is focused on the Arctic, not an Antarctic MSA record.

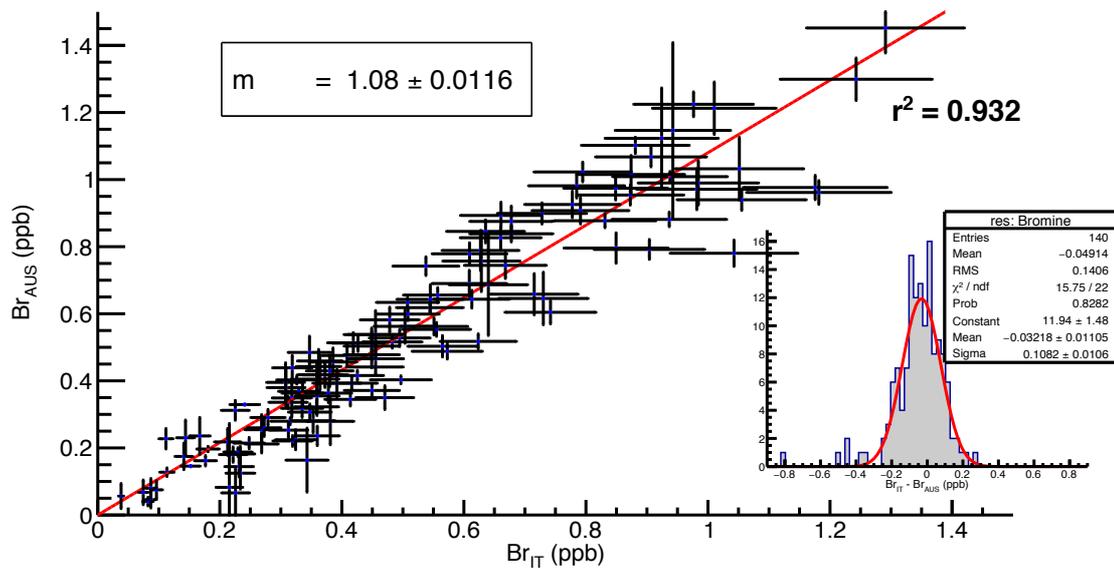
The reference has been removed

Sect 2.2, pg. 6 line 4: All data presented should be accompanied by data quality information (blanks, precision, accuracy). Representative 2-sigma uncertainty bars should ideally be included on figures (if they are large enough to see!). Please add this information to the supplement and include some discussion if it helps to resolve the differences between the two cores (Fig. 4). Were replicate samples measured in both labs?

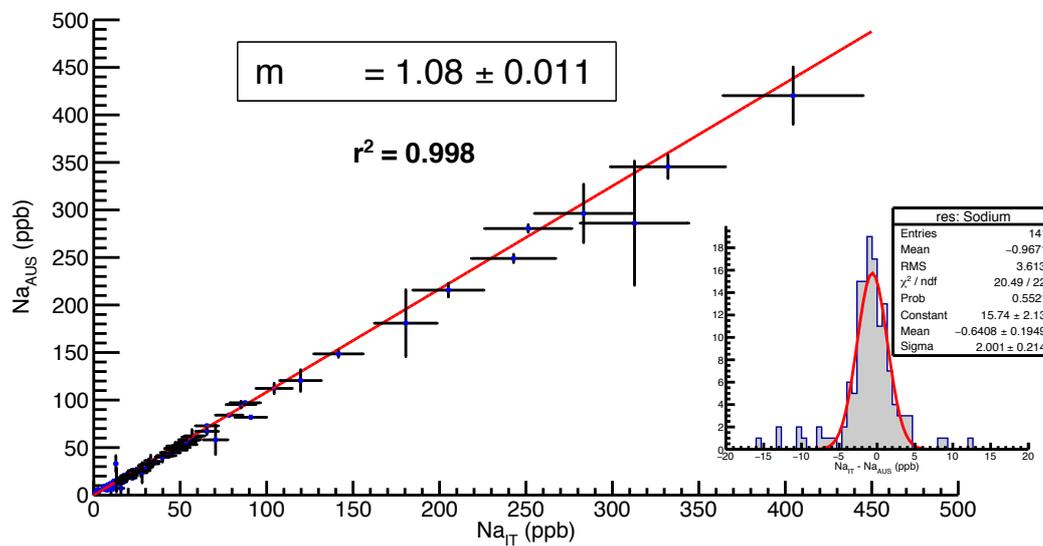
The relevant data quality information for the Italian and Australian ICP-MS laboratories have been added. Figure 8 has been revised to include measurement and accumulation uncertainties. For the other figures, uncertainty bars are too small to be added (Figs 5, 6) or the resolution of the data shown precludes the addition of error bars (Figs 4, 7). Finally, a paragraph has been added to section 2.2.2 describing interlaboratory reproducibility measurements:

The reproducibility of measurements between the two laboratories was tested by analyzing 140 Greenland snow pit samples in both laboratories. Compatibility of the measurements (Supplementary Figures S1 and S2) showed a regression line with  $R^2 > 0.9$  ( $n=140$ ,  $p < 0.05$ ) for both analytes. Distributions of residuals show an average measurement offset of  $-0.64 \pm 0.19$  ppb (sodium,  $RSD=2.0 \pm 0.2$  ppb) and  $-0.03 \pm 0.01$  ppb (bromine,  $RSD=0.11 \pm 0.01$  ppb).

And two supplementary figures have also been added.



Supplementary Figure S1



Supplementary Figure S2

Sect. 3.1, pg. 8 line ~15: If the introduction is improved, it may not be necessary, but it should be made clear here that both Na and Br come from the sea salts

(from open ocean and sea ice surface), but that Br levels in atmosphere can be “enriched” through the Br explosion.

### Added to the introduction

Sect 3.1 pg. 8, line ~25: This section is confusing. Clearly Br is less variable in the latter part of the record (DSS1213) and this is attributed to smoothing in melter system, which I can understand. However, the Na record shows greater variability or may even show a step-wise increase (?). Why is the Na record not smoothed like Br? What does that suggest about the annual cycles of the two species and the seasonal  $Br_{enr}$  calculated from them?

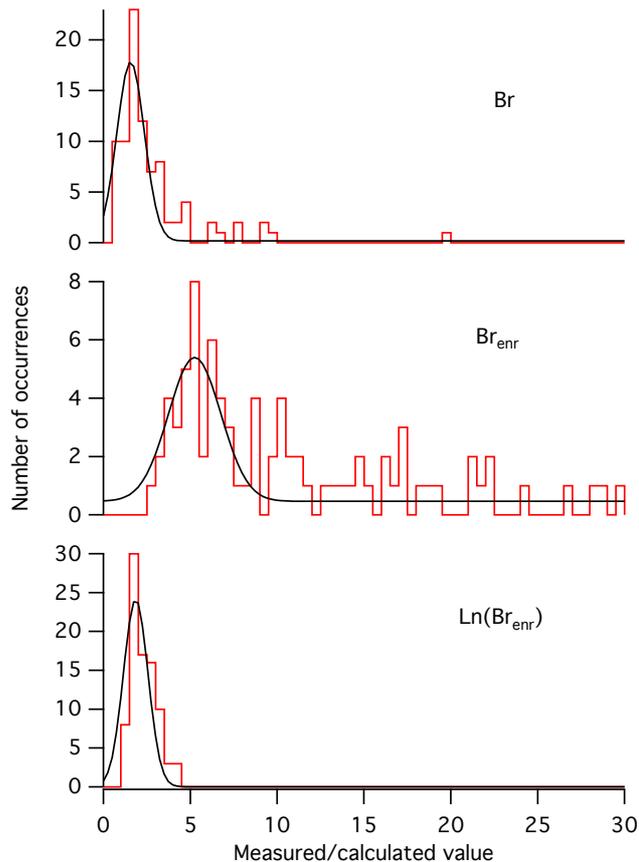
The text has been rewritten. The text was not clear in explaining the smoothing of the Br signal is not attributed to the melter, but instead to the ICP-MS sample introduction system used during the continuous melting analysis. Bromine is commonly known to be a “sticky” element for ICP-MS measurements and therefore the instrument requires a specialised cleaning method (with  $NH_4OH$ , as described in the text). The DSS0506 samples were sampled and measured discretely, hence the sample introduction system could be thoroughly cleaned between each analysis. The DSS1213 core was analysed continuously in a long melting sequence, hence there was limited opportunity to thoroughly clean the sample introduction system. This is the reason why a comparable smoothing is absent in the sodium record.

Regarding the seasonality of the species, we note that the data shown in figure 7 are consistent with previous measurements of bromine and sodium seasonality in Law Dome (Spolaor et al., ACP, 2014; Curran et al., Annals of Glaciology, 1998). The aliasing induced by the continuous measurement technique would be expected to reduce the amplitude of any seasonality in bromine concentration. As the reviewer has noted previously, there does not appear to be a strong seasonality in bromine, unlike sodium.

Sect. 3.2 Pg. 6 line 5: I’m not sure I understand the justification for using natural log, as it relates to Br chemistry. Br enrichment is a ratio, not a concentration. Please clarify.

The reviewer alludes to the log-normal distribution of concentrations of many ionic species dry-deposited in polar snow. In the case of bromine, the log-normal distribution of bromine excess is based upon the exponential nature of the ‘bromine explosion’. As described in the text, one reactive bromine species (HOBr) leads to the liberation of  $Br_2$  which is the precursor to two bromine explosion multiphase reactions.

We have further added a figure to the supplementary material (Fig S3) showing the distributions of Br concentration,  $Br_{enr}$  and  $\ln(Br_{enr})$  and fitted gaussian distributions.



Supplementary Figure S3

Sect 3.2, pg. 9 line 26: Levine et al. (2014) do not discuss post-depositional remobilization, please add another citation here.

The term 'post-depositional remobilisation' has been removed.

line 27: do you mean "seasonality" of sea salt deposition?

Changed to 'regularity of seasonal sea salt deposition'

line 30: How is the correlation "consistent", with what?

'Consistent' has been removed

Sect 3.4, pg 10, line 30: Do you mean iodine enrichment in snow, not sea ice?

In that sentence we are discussing emission and recycling mechanisms over sea ice, not iodine enrichment over snow pack.

Sect 3.4, pg 10, line 31: Do heterogeneous reactions really "release" particulate species?

'release' has been changed to 'emission'

Sect. 3.4 Why is the seasonality of iodine not shown on Fig. 7? Does the correlation stated refer the results from this study or previous one? Later in sect.4 the text says that "iodine enrichment displays broad summer peak" but that is not shown anywhere is it?

Figure 7 shows the results from the DSS1213 core, which was melted in Australia and therefore analysed with fine spatial/temporal resolution. Iodine was not measured during the DSS1213 melting campaign, and therefore is not included in the figure.

The sentence mentioning correlation has been re-written to clarify that we are referring to the temporal trends between  $Br_{enr}$  and  $I_{enr}$  (Fig 6).

The “broad summer peak” (Conclusions, 2<sup>nd</sup> paragraph) refers to  $Br_{enr}$ , not  $I_{enr}$ . The text has been amended.

Sect 3.5, pg11 line 31:  $Brenr$  is not a concentration.

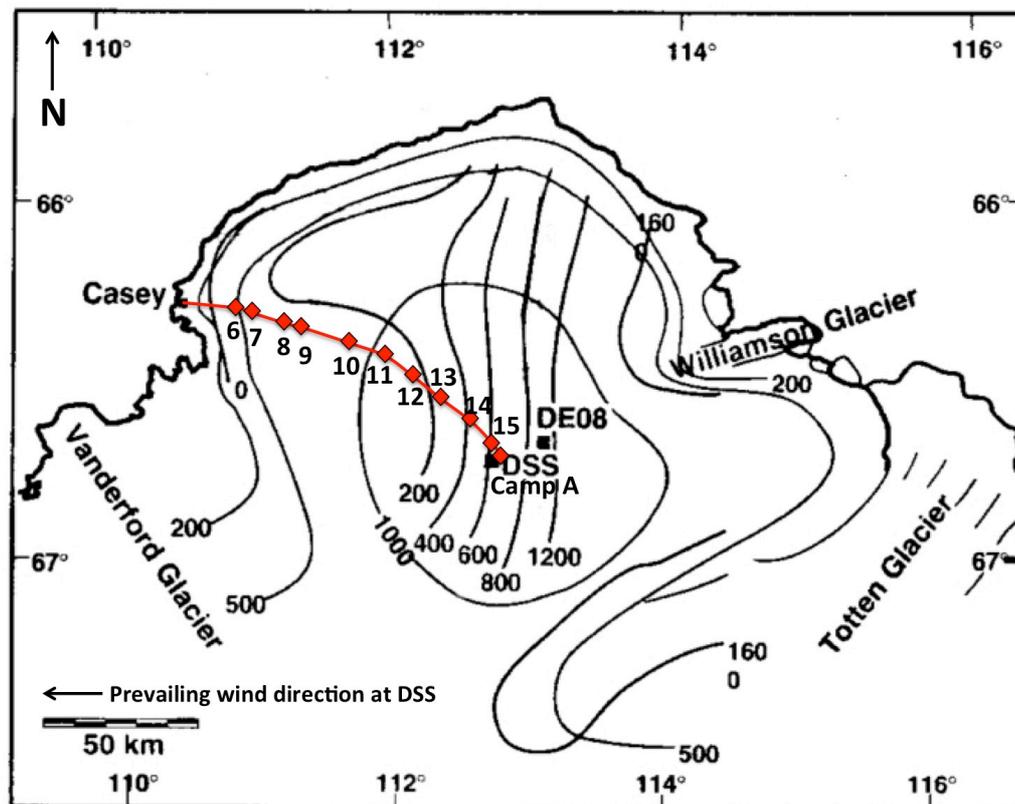
Concentration changed to ‘values’

Sect 4, pg. 13. paragraph 2: this paragraph makes little sense because no iodine seasonality data is presented. I also struggle to see how iodine can experience greater “meteorological disturbance” compared to Br. Differences in chemical reactions in snowpack and atmosphere seem more likely.

As per the previous comment, comments on iodine seasonality have been removed.

Figure 1: Could an arrow be added to show direction of cyclone movement across site? Also a north arrow? Please add explanation of ice movement arrows to caption, or remove them.

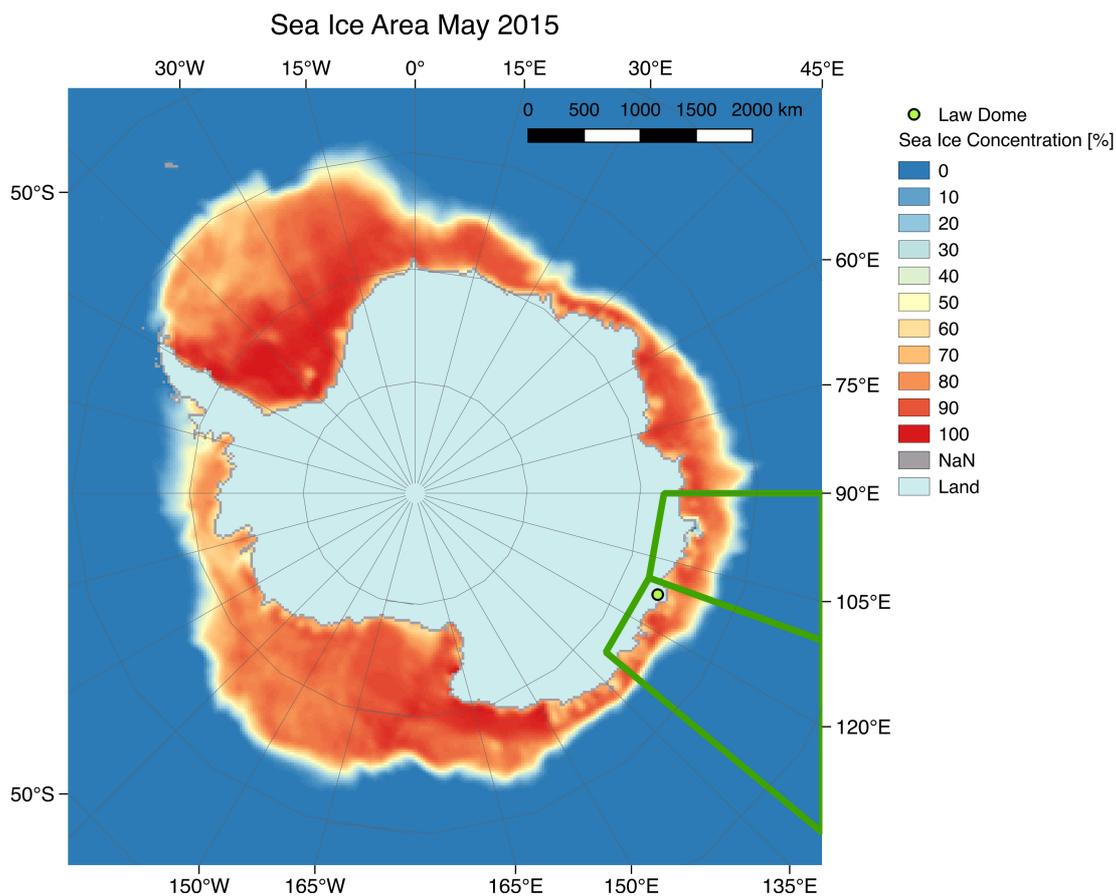
A north arrow and an arrow indicating prevailing wind direction at DSS have been added. The ice movement arrows have been removed.



Revised Figure 1

Figure 2: This would be easier to interpret quickly if axes were de- grees, rather than arbitrary grid. Is the blue color meaningful, probably outlining the two regions is enough?

The figure has been revised accordingly.



Revised Figure 2

Not sure that I see the worth of Figure 3 – seems like a technical detail. Suggest moving to the supplement. Some of the technical detail in Sect. 2.4 could also be moved to the supplement.

Figure 3 is important in that it demonstrates the correspondance between the measures of sea ice area used in this work and that of Curran et al (1998). The Sea Ice Edge measure calculated by Jo Jacka and used by Curran et al. is shown to be in agreement and “calibrated” against the more commonly-used metric of sea ice area available from NSIDC. As the halogen records require FYSI observations for calibration, such material should be considered more than just technical detail. We consider the text regarding these sea ice metric calibrations to be similarly important.

Figure 4: Why are I concentration data from DSS1213 not plotted on Fig. 4 or enrichment on Fig. 6)? Methods indicate that iodine was measured.

Iodine was not measured on the DSS1213 core. The text has been modified to make this more explicit.

Technical notes

abstract, line 23. Change “particularly” to specifically – correlation only found for the one sector.

done

line 23: Iodate should be iodate

done