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 de- velopment. 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 explo- ration 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 meterological/transport-related modification of the sea salt loading (IPO, Vance et al., 2015, 2016) as speculated, nssBr should look different to Brenr (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_{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_{enr} and nssBr are essentially the same measure, represented in different ways. The only difference between Br_{enr} and nssBr is that one (Br_{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_{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).

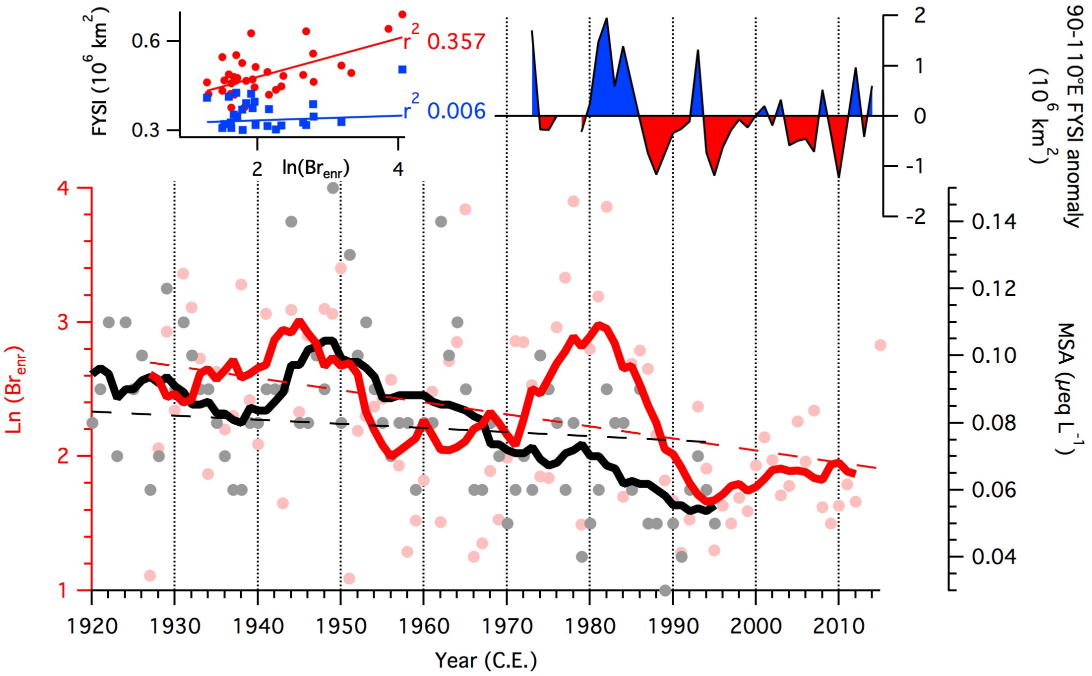
Regarding the possible influence of IPO, it is important to recognize that IPO is not significant at daily timescales relevant to meteorological/transport processes. IPO is a low frequency (multi-decadal) mode of variability related to ENSO and indeed resembles smoothed (low frequency) ENSO variability. 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 Brenr 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_{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 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 $\ln(Br_{enr})$ and FYSI for sectors 90-110ºE and 110-130ºE.



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.

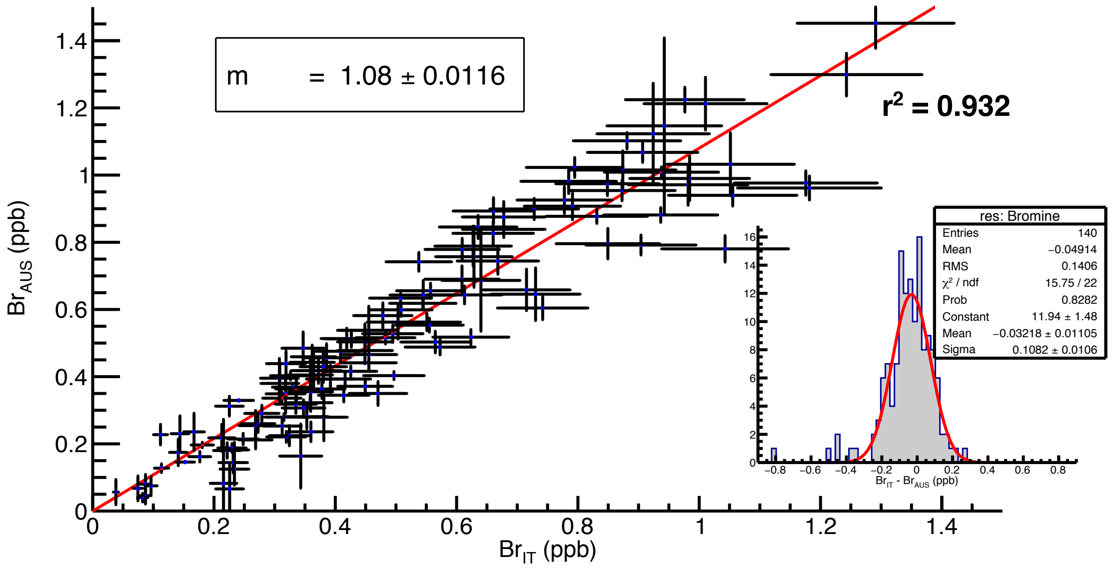
The reference has been removed

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?

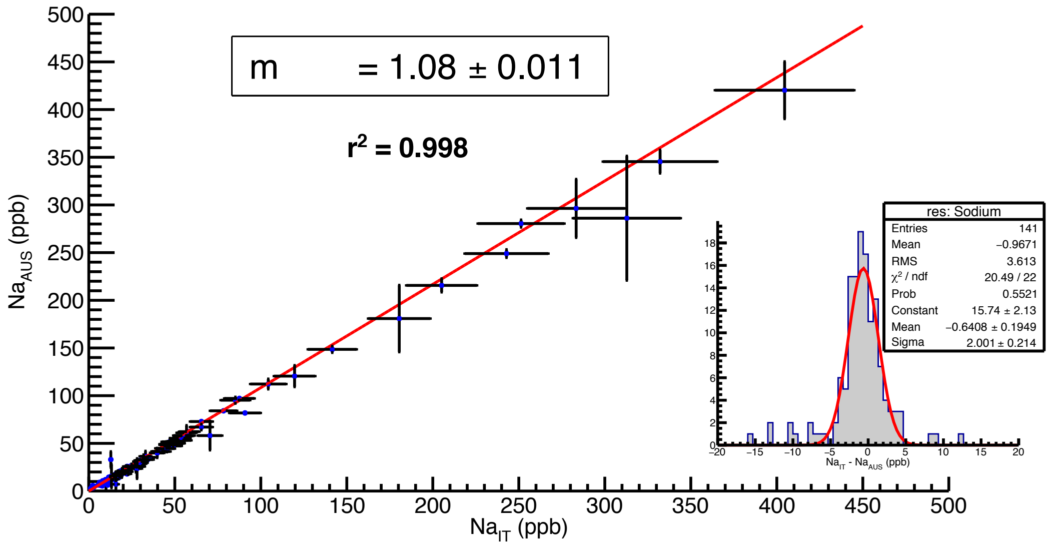
The relevant data quality information for the Italian and Australian ICP-MS laboratories have been added. Figure 8 has been revised to include measurement and accumulation uncertainties. For the other figures, uncertainty bars are too small to be added (Figs 5, 6) or the resolution of the data shown 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 ± 0.19 ppb (sodium, RSD=2.0 ± 0.2 ppb) and -0.03 ± 0.01 ppb (bromine, RSD=0.11 ± 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.

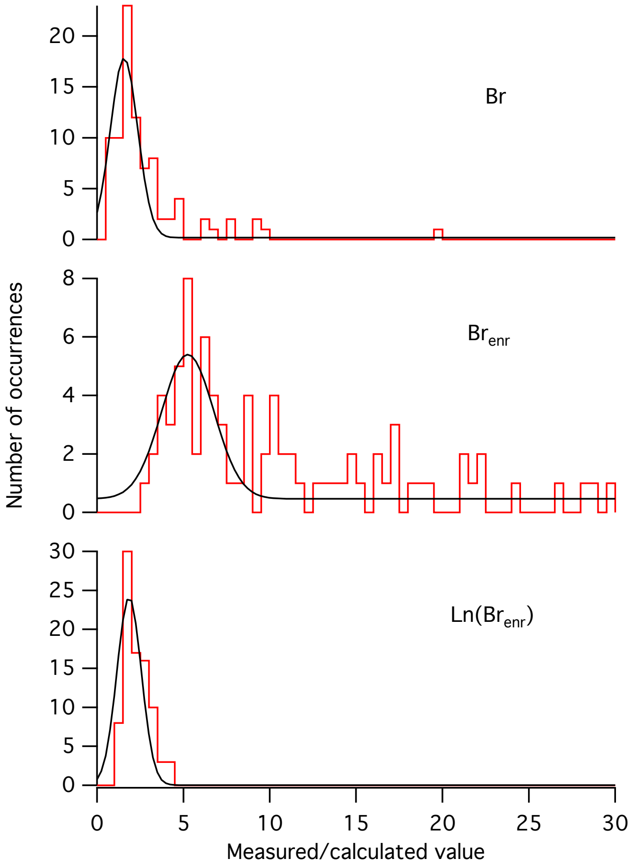
Added to the introduction

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 Brenr 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, 2nd paragraph) refers to Br_{enr}, not I_{enr}. The text has been amended.

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

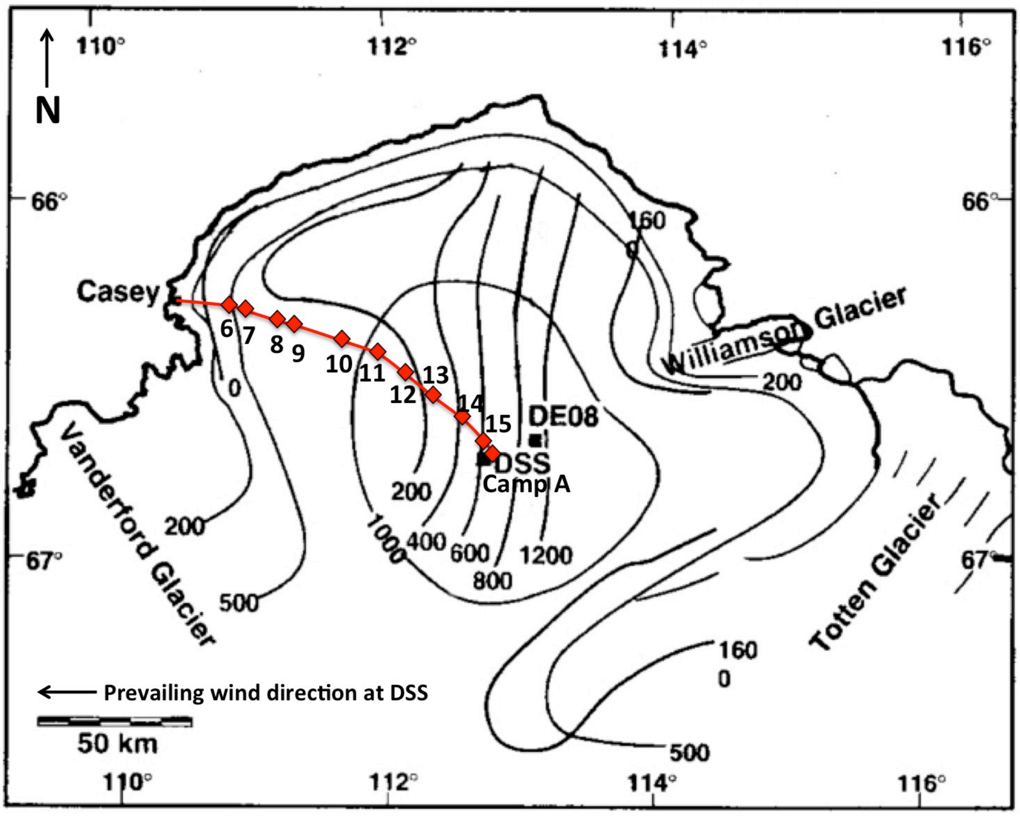
Concentration changed to 'values'

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.

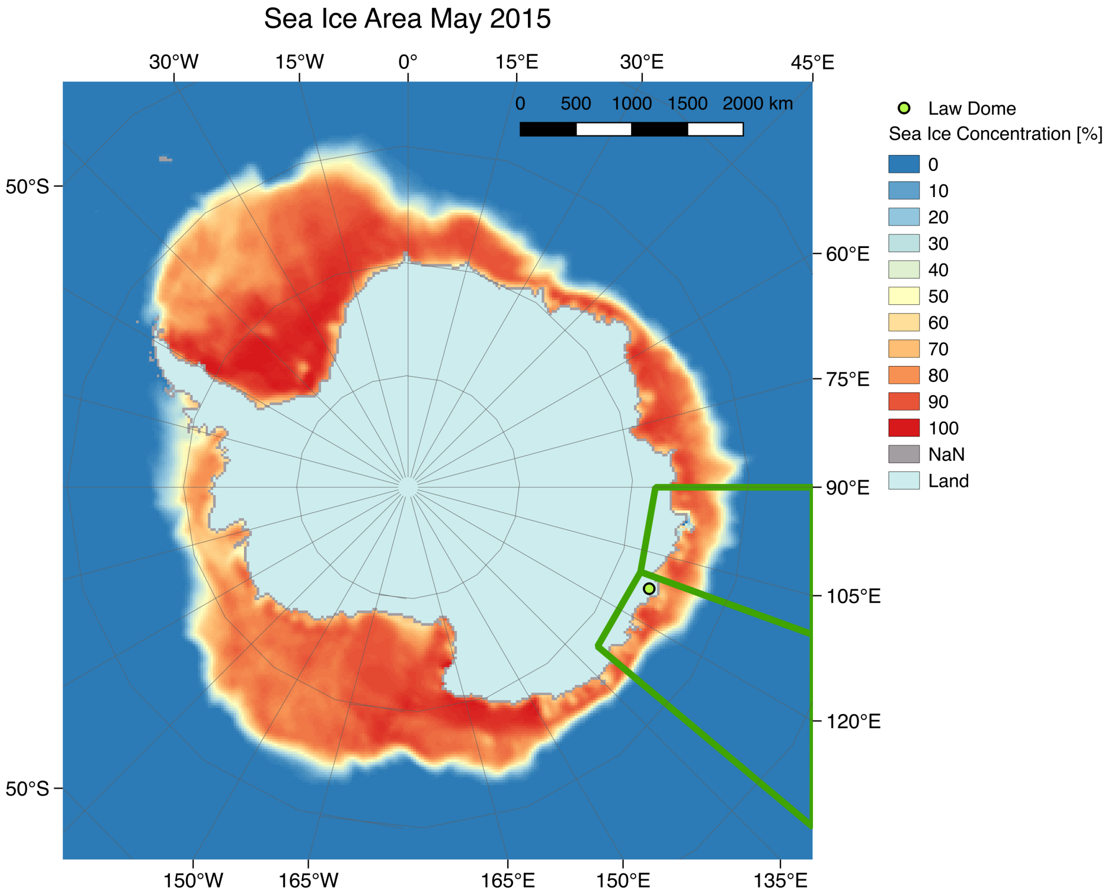
A north arrow and an arrow indicating prevailing wind direction at DSS have been added. The ice movement arrows have been removed.



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

Responses to reviewers

Anonymous Referee #2

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.

We thank the reviewer for their detailed comments and suggestions and hope that the revised manuscript is found to be suitable for publication. We would like to point out that the manuscript does present new information, especially with regard to Law Dome, where previously only a 4-year sequence of Br and I concentrations have been published. Additionally, we include measurements along a surface traverse from Casey station to Law Dome which, to our knowledge, are the first data regarding spatial distribution of halogens in snowpack. Many of the reviewer comments have already been addressed by our responses to reviewer 1.

We would also 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.

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.

Additional information regarding photochemical recycling has been added:

Photochemical recycling of bromine primarily involves heterogeneous reactions of halide salts (such as HOBr and $BrONO_2$) in sea ice and snowpack leading to the emission of Br_2 molecules. Br_2 is then photodissociated into two Br^- radicals that are available for further heterogeneous chemical recycling. Bromine explosion events primarily occur in early spring and summer, although winter sources of organohalide emissions have also been observed in coastal polar regions although the relative influence of such sources is still a topic of investigation (Impey et al., 1997; Nerentorp Mastromonaco et al., 2016; Simpson et al., 2007).

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.

The DLs have been added (38 pg BrO_3^- g^{-1}, 7 pg IO_3^- g^{-1}).

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.

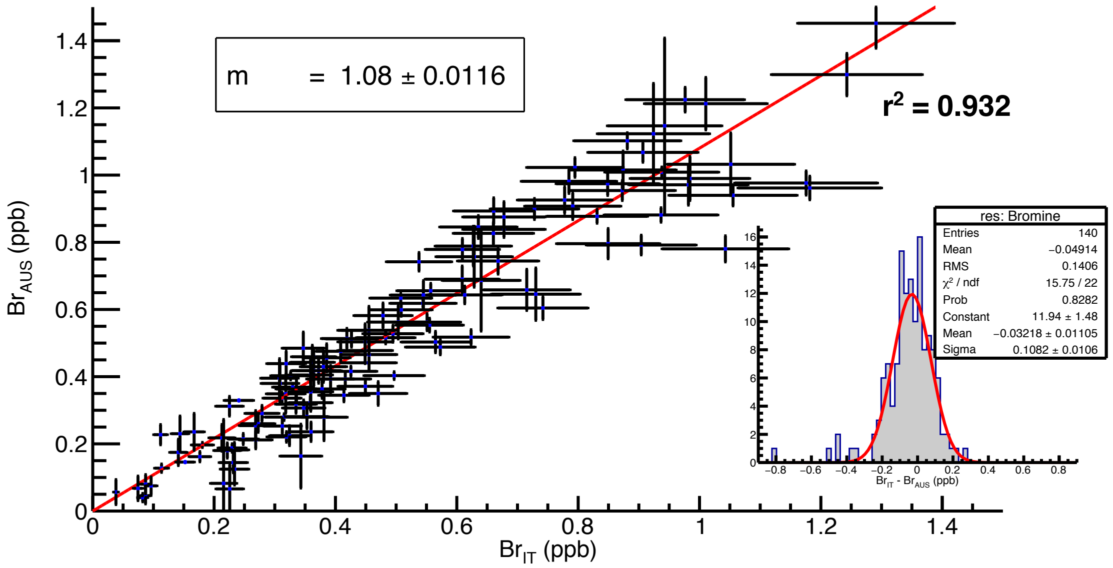
The Law Dome site is well known for its relatively plentiful and regular snowfall, as well as benign deposition conditions. A number of studies have investigated snowfall regularity and seasonality at the site (eg Morgan et al., 1997, J. Glacio.; McMorrow et al., 2004, Ann. Glacio.). These references are included in 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?

This work is the first direct comparison between long-term stored samples and freshly recovered core samples. We have two lines of information indicating that remelting does not influence the Br concentration as long as the sample is otherwise stored frozen in dark conditions:

Firstly, we note in section 3.1 (and Fig 4) the good agreement of Br concentrations in overlapping sections of DSS0506 (long-term storage and remelting) and DSS1213 (freshly sampled by continuous melting). Unfortunately I was not measured in the DSS1213 core so a similar comparison cannot be made at this time.

Secondly, we note that there is excellent agreement between Br measurements of Greenland snow pit samples (Supplementary Figure S1) measured in the two laboratories. Note that these samples were melted and refrozen three times (during sampling in Copenhagen, during analysis in Venice Italy, and during analysis in Perth Australia). The same samples in the same vials were melted three times and measured twice, futher indicating that Br is preserved as long as samples are kept frozen and stored in darkness.



Supplementary Figure S1

Section 2.2 – Analytical measurements. Even if sufficient references were cited, some analytical methods performances should be here summarized (reproducibility, accu- racy, DL, blank values). Was an inter-calibration exercise made between Australian and Italian laboratories?

Reviewer 1 had an identical comment and we copy here the response:

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, for which two supplementary figures have also been added.

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

Done

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

As per the previous comment, this information has been added. To summarise here:

A 10 times repetition of the same samples obtain a standard deviation in average of 5% (from 2% to 8% maximum). The blank value is in the order of 40 cps while a samples is in the range of 150 cps using the medium resolution mode. This is an average value since the sensibility of the instrument can change (quite common for the ICP-SFMS) modifying the blank value and the response of the instrument to the sample concentration. During the analysis and external calibration were run every 20 samples to correct the instrument oscillation. Detection limits, calculated as three times the standard deviation of the blank, were 5 and 50 pgg for I and Br, respectively. Reproducibility was evaluated by repeating measurements of selected samples characterized by different concentration values (between 20 pg g and 400 pg g for I and between 400 and 600 pg g for Br). The residual standard deviation (RSD) was low for both halogens and ranged between 1–2 % and 2–10 % for Br and I, respectively. Detail information can be found in Spolaor et al 2013 (The Cryosphere, 7, 1645–1658 , 2013)

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?

The description of DSS1516 as a core was a mistake and has been removed.

We note in section 2.1.4 "All samples collected during the Casey-Law Dome traverse and from the DSS1516 snowpit were sent to the TRACE laboratory at Curtin University of Technology for bromine analysis." and in section 2.2.1 "Law Dome traverse and DSS1516 snowpit samples were analysed discretely using a Seafast-II autosampler with syringe pump connected to the abovementioned analytical system."

As we have noted above, a laboratory intercomparison has been performed using Greenland snow pit samples and the results are discussed in section 2.2.2 and shown in figures S1 and S2.

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.

The reviewer is correct that IC typically determines soluble sodium whereas ICP-MS typically determines total Na. The partitioning of sea-salt and mineral dust inputs to Law Dome have been studied in detail by Vallelonga et al. 2004 (Ann. Glac.) as well as Curran et al. (Ann. Glac., 1998). Vallelonga et al., found that sea salts accounted for 98% of impurities in Law Dome snow by mass (average 205 ng/g) whereas mineral dust was just 2% (2.8 ng/g). Therefore, there is little difference between total Na and ssNa for Holocene samples from Law Dome.

Sodium has been determined by ICP-MS in all samples. Additionally, Na has been determined in DSS0506 samples by IC. In fact, comparison of Na concentrations determined by IC and ICP-MS in the DSS0506 samples was the method used to evaluate contamination of the samples (due to cracking of the sample vials) and discard contaminated results. This information has been added to the text.

The IC performance statistics have been added.

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

Done

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.
Medians have been added

Sample designation	Time interval	# years	Sodium (ppb)			Bromine (ppb)			Ln(Br)		Ln (Br_{enr})	
			mean	median	variance	mean	median	variance	mean	variance	mean	variance
DSS1516 snowpit	2015-2016	0.8	241	179	91078	1.4	0.8	3.5	-0.34	1.5	0.1	4.6
DSS1213 core	1987-2012	25	115	106	4355	2	1.9	0.2	0.67	0.06	1.8	0.1
DSS0506 core	1927-1986	59	77	74	571	3.3	2.3	9.7	0.88	0.57	2.5	0.6

Table 1 revised

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.
As discussed in a previous response, the influence of mineral dust on sodium concentrations at Law Dome is negligible.
Line 12, page 8. Please, change "sodium" in "ssNa".
For the reasons mentioned above, we prefer not to change sodium to 'ssNa' in this case.
Line 15, page 8. Authors are requested adding a short description of meaning and seasonal occurrence of the "bromine explosion" events.
This information has been provided in the text added to the introduction.
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.
We do not imply that this method should be attributed to the authors, rather to indicate previous applications of this calculation with respect to bromine. The text has been amended.
Line 18, page 8. Please, change "Na" in "ssNa".
For the reasons mentioned above, we prefer not to change 'Na' to 'ssNa' in this case.
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

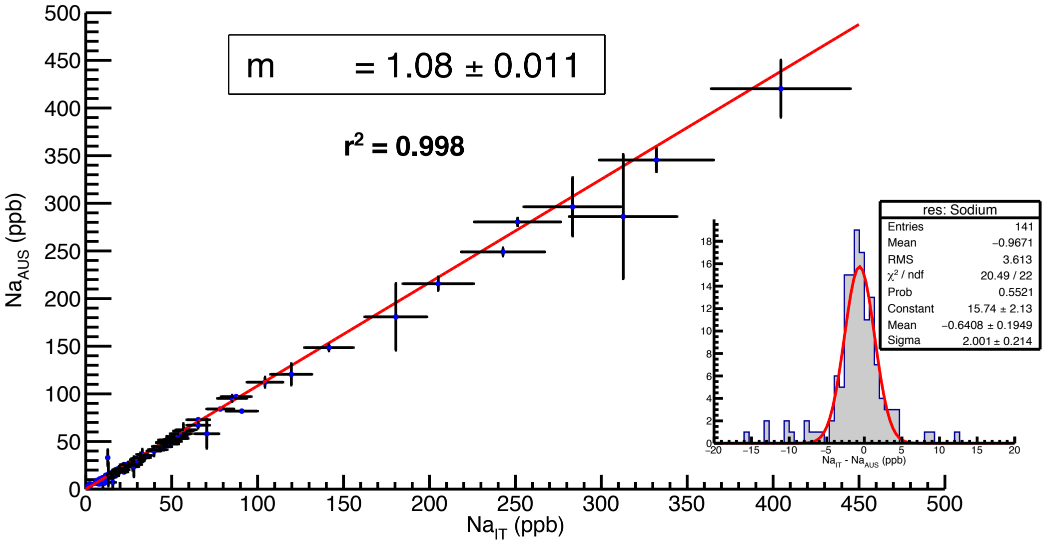
to change the data variability, but not in opposite sign for the two components; besides, the different resolution (if not too much large with respect to accumulation rate) should be not able to change the 3-yr mean profiles. Authors are requested to report the estimated depth resolution for the continuous 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?

Reviewer 1 also expressed similar concerns and the text has been altered to better explain the sources of apparent discrepancy between DSS0506 and DSS1213 records. Following the previous comment of the reviewer, we have added medians and DSS1516 snowpit data to table 1.

As mentioned in our response to reviewer1, 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.

The depth resolution of the melter system (less than 1 mm) is standard for contemporary CFA systems, and has been added to the text.

Regarding the accuracy of the two instruments used for measurements, these have also been described in our response to reviewer 1 and are treated in section 2.2.2 and supplementary figures S1 and S2.



Supplementary Figure S2

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.
The sentence was not clear. We are referring to autocorrelation induced by a non-gaussian distribution of the data. The sentence has been rephrased as "With the intention of reducing data autocorrelation, we transform the Br_{enr} data to a gaussian-like distribution using the natural logarithm of Br_{enr} for correlation to FYSI data." and we have plotted data histograms in supplementary figure S3.
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).
Please note our opening comment that Br_{enr} and I_{enr} correlations to FYSI have changed as a result of a calculation error in the sea ice algorithm used for the initial submission.
We agree that the Br_{enr}-FYSI correlation is not strong but it is comparable to correlation statistics used for sea ice reconstructions at Law Dome based on MSA ($r^2=0.36$, $p<0.002$) using sea ice extent between 80ºE and 140ºE. Note also that we base our regression calculation on FYSI area rather than maximum or minimum sea ice extent (SIE), which we hypothesize to be most directly representative of the bromine enrichment due to bromine photochemical recycling.
Regarding iodine we note that there are clear indications of summertime re-emission (at both Law Dome and Neumayer station) and hence we are more tentative with our conclusions. We have written:
"Correlation significance levels for I_{enr} are consistently below the 95% level and correlation coefficients are generally low. The strongest correlation of I_{enr} is between the summer-summer (calendar year) averaged signal and the 110-130° E FYSI sector, but this is still below the 95% significance level."
In response to similar concerns of reviewer1, we have "scaled back" the conclusions regarding the use of bromine for reconstruction of sea ice at Law Dome.

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.
We have amended the text accordingly

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.

The last sentence has been removed.

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.

The text has been changed accordingly:.

Due to the 11-year smoothing applied to the data, influences of seasonal patterns, factors influencing biological growth, relations to sea ice and transport efficacy should be minimised for the comparison of bromine enrichment and MSA trends at Law Dome

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.

We agree and have changed the text accordingly.

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.

We agree with the reviewer (and also with respect to the comments of reviewer1) that there is not a constant agreement between the MSA and Br records shown in Figure 5. As we have noted in the text, both data indicate a peak in the 1940's and a small decreasing trend over the 20th century, but diverge after 1955. Given that the data are smoothed by 11-year running means, we are not necessarily concerned by a 4-year difference in the peaks of the two data sets in the 1940's [1949 MSA, 1945 ln(Br_{enr})].

As the reviewer has noted, only a third of the variance of Br can be attributed to FYSI, so it is clear that there may be influences that are not related to sea ice variability. With regard to the divergence between 1955 and 1970, we have written:

"Bromine and MSA both point toward greater sea ice area during the period from 1945 to 1950 but diverge between 1955 and 1970. The cause for this divergence is not yet known, but before speculating on a possible cause, these trends should be confirmed by measurements of other snow and ice samples from Law Dome as well as other sectors of the East Antarctic coast. The possible influence of multidecadal-scale climate variability, such as the Interdecadal Pacific Oscillation (IPO), on the bromine record is discussed in detail in section 3.4, but will briefly be considered here. IPO forcing of Antarctic sea ice area has been demonstrated at decadal timescales (Meehl et al., 2016), with the negative IPO phase triggering SLP and near surface wind changes that can influence sea ice expansion, storm tracks and potentially nutrient supply to DMS-producing algal communities."

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.

We respect the reviewers clear interest in the applicability of Br to reconstructing FYSI, but we are hesitatant to expect a perfect year-by-year agreement between Br_{enr} and FYSI area. We have observed a similar correlation coefficient for Br and FYSI as Curran et al. found for MSA and SIE (Sea Ice Extent), which may suggest that other factors, such as meteorological noise, deposition variability and ice core representability may account for the other 70% of signal variability.
In line with this and other comments from both reviewers, we have made a more conservative evaluation of Br_{enr} as a proxy of Law Dome sea ice variability.

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.

Please note our opening comment that Br_{enr} and I_{enr} correlations to FYSI have changed as a result of a calculation error in the sea ice algorithm used for the initial submission.
As we note in the text (and following suggestions by reviewer1) halogen chemistry is complex and there are many chemical processes that are still to be understood, especially with regard to iodine. Considering that it has been observed that iodine is reemitted from the snow surface, and is retained in snowpack only in the winter, we also find it surprising that there is any

correlation between FYSI and I_{enr} at all. Using our corrected sea ice area calculations, we find that some years (1973, 1975) of the FYSI record should have been excluded, as full year-round observations were not available. Consequently, we do not find a significant correlation with I_{enr} for any sea ice sector or I_{enr} seasonal pattern. As we have written in the text, halogen chemistry is a topic of ongoing research and an accurate interpretation of the data is best served by building up an array of records from along the East Antarctic coast.

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 1 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.

We agree with the reviewer that the correlation between I_{enr} and Br_{enr} is statistically weak but visually distracting. We have expanded our consideration of possible co-incident causes leading to such similar variability between the two measures, while being cautious that the correlation is poor.

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?

We have expanded our description of links between IPO and Antarctic atmosphere-ocean-sea ice variability and relevance to coastal East Antarctica:

"The IPO is a low frequency climate mode related to the El Niño-Southern Oscillation which operates on multidecadal timescales. It affects climate variability at the multidecadal scale across and beyond the Pacific Basin (Power et al., 1999; Vance et al., 2015). Impurities deposited at Law Dome have been demonstrated to faithfully reflect IPO variability (Vance et al., 2015) and reanalysis data indicates a strong IPO signal in the Indian Ocean (Vance et al., 2016). Furthermore, recent work has demonstrated an IPO forcing of Antarctic sea ice area at decadal timescales, with the late 1990's shift to a negative IPO phase triggering SLP and near surface wind changes that are conducive and consistent with an expansion in sea ice in all seasons across multiple regions of the Antarctic seasonal ice zone (Meehl et al., 2016). Thus the overall correlation between iodine and bromine enrichment may be linked to decadal-scale states of the atmosphere-ocean-sea ice system in the Indian sector of the Southern Ocean. It must be noted that, in addition to larger-scale influences of atmospheric transport and ocean-related sea ice variability, both Ienr and Brenr are calculated using Na as an indicator of sea salt content in the samples. The possibility of an IPO-related signal, transmitted through Na concentrations, cannot be discounted from contributing to the apparent correlation of Ienr and Brenr in DSS0506 core samples."

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).

We prefer to keep the discussion of seasonality as a stand-alone section, mostly because the "previous results on shorter data series" that the reviewer refers to is just a four-year period from 1910 to 1914. Furthermore, those data were measured from discrete samples of the DSS0506 core and in this way we are able to present an independent seasonality study, from a different core sampled and measured independently, with better temporal control and better statistics.
Regarding the lag between spring bromine explosion and summer Br_{enr} peak, we write the following:
"Satellite observations of atmospheric BrO in polar regions suggest an early spring peak in bromine activity in Antarctica (Spolaor et al., 2014), thereby implying that additional processes may be occurring in the snowpack during the summer after the peak atmospheric bromine explosion has occurred. While snowpack remobilisation at Law Dome is minimal, it might be the case that photochemically-driven heterogenous recycling of bromine occurs in the snowpack after the springtime occurrence of the bromine explosion. This effect requires further investigation, from satellite and ground-based observations to weekly surface snow sampling, in order to be fully characterised and understood."

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.
The text has been changed accordingly.

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.

We appreciate that the reviewer finds this novel spatial-transect study of interest. As we note in the text, the samples were collected during a traverse from Casey station to Law Dome summit, and hence have been collected on the down-wind (or lee-side) of Law Dome. For a thorough evaluation of deposition characteristics of Na and Br at Law Dome it is important to sample further east, on the up-wind side of Law Dome.

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

Sea ice-related halogen enrichment at Law Dome, coastal East Antarctica

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Abstract. The Law Dome site is ideal for the evaluation of sea ice proxies due to its location near to the Antarctic coast, regular and high accumulation throughout the year, an absence of surface melting or remobilization, and minimal multiyear sea ice. We present records of bromine and iodine concentrations and their enrichment beyond seawater compositions and compare these to satellite observations of first year sea ice area in the 90-130° E sector of the Wilkes coast. Our findings support the results of previous studies of sea ice variability from Law Dome, indicating that Wilkes coast sea ice area is currently at its lowest level since the start of the 20th century. From the Law Dome DSS1213 firn core, 26 years of monthly deposition data indicate that the period of peak bromine enrichment is during Austral spring-summer, from November to February. Results from a traverse along the lee (Western) side of Law Dome show low levels of sodium and bromine deposition, with the greatest fluxes in the vicinity of the Law Dome summit. Finally, multidecadal variability in iodine enrichment appears well correlated to bromine enrichment, suggesting a common source of variability that may be related to the Interdecadal Pacific Oscillation (IPO).

Keywords. Antarctica, Halogens, Bromine, Iodine, Law Dome, sea ice, sea ice reconstruction, polar halogen chemistry

1 Introduction

Atmospheric halogen chemistry is highly complex and has been a topic of intensive study over the past three decades (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). A major branch of this research involves the occurrence of enhanced concentrations of boundary-layer bromine in coastal Antarctica, which has been linked to the depletion of tropospheric ozone and mercury (Simpson et al., 2015). Tropospheric ozone is critical to solar forcing, ultravioletUV absorption and aerosol formation in the polar regions whereas the concentration of mercury in polar snow is a matter of great concern for Arctic ecosystems in the future (Brooks et al., 2006; Hylander and Goodsite, 2006). Recent studies indicate that boundary layer bromine is driven by photochemical recycling above the salt-rich snow and ice surfaces, with such recycling predominantly occurring in the Austral spring, when the concentration of surface salts and surface area of first-year sea ice are at their greatest (Pratt et al., 2013; Zhao et al., 2016). Photochemical recycling of bromine primarily involves heterogeneous reactions of halide salts (such as HOBr and $BrONO_2$) in sea ice and snowpack leading to the emission of Br_2 molecules. Br_2 is then photodissociated into two Br^- radicals that are available for further heterogeneous chemical recycling. Bromine explosion events primarily occur in early spring and summer, although winter sources of organohalide emissions have also been observed in coastal polar regions although the relative influence of such sources is still a topic of investigation (Impey et al., 1997; Nerentorp Mastromonaco et al., 2016; Simpson et al., 2007).

The processes and physical conditions underlying photochemical bromine recycling events, commonly called ‘bromine explosions’, are subject to investigation through a combination of satellite and insitu observations as well as chemical transport modelling. Bromine and sodium in coastal Antarctic air are predominantly sourced from sea salts, but only bromine is enriched by bromine explosion events. Processes and precursors of halogen recycling in polar regions include: the role of acids in snowpack in enhancing heterogeneous bromine production; the role of organic molecules as sources of radicals – particularly in the Arctic, where formaldehyde and other organic pollutants may be present in significant concentrations; and the partitioning of bromine between gas and particulate phases in snowpack and boundary layer air. The transport of bromine is being understood through a combination of ground and satellite-based measurements combined with simple models that incorporate explicit snowpack chemistry (Spolaor et al., 2016b; Zhao et al., 2016). These models demonstrate the importance of such features as wind velocity and vertical mixing (boundary-layer turbulence) as well as the surface parameters mentioned above (Toyota et al., 2014). Insitu observations of halogens in both gaseous and aerosol forms (Legrand et al., 2016) are essential to understanding halogen deposition and recycling processes in polar regions and improve current atmospheric models.

Reactive iodine has a global influence on ozone depletion and the oxidizing capacity of the polar atmosphere by influencing the repartitioning of HO_x and NO_x (Saiz-Lopez et al., 2012). In particular, large amounts of oxidized iodine detected by a ground-based spectrometer were observed in coastal Antarctica (Saiz-Lopez et al., 2007) highlighting these coastal areas as iodine hotspots. Enhanced sea ice bioproductivity during springtime and winter organic emissions have been suggested as the main sources of iodine in the Antarctic Peninsula (Atkinson et al., 2012; Granfors et al., 2014; Saiz-Lopez et al., 2015). Recent iodine instrumental measurements in the Antarctic coastal sea ice zone showed that I_2 dominates the iodine atom fluxes to the atmosphere (Atkinson et al., 2012). The same study revealed that iodocarbon concentrations above sea ice brines were over ten times greater than those of the sea water below.

The first measurements of bromine and iodine species (bromide Br^- and bromate $Br0_3^-$, Iodide I^- and iodate IO_3^-) in Antarctic ice were reported by Spolaor et al., (2012) indicating relatively stable concentrations of 100-200 pg Br^- g^{-1} and 5-32 pg I^- g^{-1} in Talos Dome ice core from the early Holocene. Bromate and iodate were not present above detection limits (38 pg BrO_3^- g^{-1}, 7 pg IO_3^- g^{-1}) in these samples. Subsequently, total bromine concentrations in the Talos Dome ice core were reported for the past two glacial cycles, observing a depletion of bromine relative to the Br/Na ratio found in seawater during the last two glacial maxima (Spolaor et al., 2013b). The temporal variability of bromine depletion corresponded well with a reconstruction of sea ice duration in the Victoria Land sector (Crosta et al., 2004), opening a basis for the further investigation of links between sea ice extent and bromine in polar ice cores. The seasonal nature of bromine enrichment in Antarctic ice was demonstrated by Spolaor et al. (2014), who reported spring/summer peaks of bromine enrichment and winter peaks of iodine concentration in Law Dome ice dating to 1910-1914 CE.

Reconstruction of Antarctic sea ice from ice core-based proxies is primarily based on fluxes of sodium and/or methanesulphonic acid (MSA, $CH_3SO_3^-$) (e.g., Abram et al., 2013; Curran et al., 2003). In the EPICA Dome C ice core, sodium concentrations were investigated by Rothlisberger et al. (2010) and compared to sea ice reconstructions from Southern Ocean marine sediment cores. For the last two glacial cycles, good correspondence was found between sea salt-derived sodium and the marine record. For reconstruction of sea ice area on decadal or even centennial scales, the influence of meteorological and depositional noise has been shown to be an important factor to consider especially for drill sites located far inland such as Dome C (Levine et al., 2014).

In contrast, the presence of MSA in ice cores has been successfully linked to observed sea ice variability in some Antarctic ice cores (e.g., Abram et al., 2007; Abram et al., 2013). In some cases, the presence of MSA is either positively or negatively correlated with sea ice, depending on such factors as local wind direction, polynya and sea ice seasonality (Abram et al., 2013). The longest reconstruction of sea ice extent using MSA has been reported for Law Dome, East Antarctica (Curran et al., 2003) covering the past 200 years and indicating a steady decrease in sea ice extent to the year 2000 C.E. Recent satellite observations report a slow increase in Antarctic sea ice over the past three decades (Parkinson and Cavalieri, 2012), and other MSA-based sea ice reconstructions support such observations (Thomas and Abram, 2016).

In this work, we report halogen deposition from the Dome Summit South (DSS), Law Dome ice core record covering the 20th century, with an emphasis on high-resolution measurements corresponding to the period since satellite observations of sea ice began. We examine correlations between sea ice area and bromine as well as halogen enrichment in the DSS Law Dome ice cores. The high rate of snow accumulation and regular year-round snowfall at Law Dome makes the site ideal for such a study, as well as the detailed MSA-based sea ice reconstruction already reported for the site. Although MSA originates from a different emission source than bromine, both are related to sea ice area and hence should be expected to produce an overall similar pattern of sea ice variability on a multi-year or decadal scale.

2. Methods

2.1 Sample collection

2.1.1 Dome Summit South (DSS), Law Dome

The DSS ice cores are from Law Dome, East Antarctica. Law Dome is a small ice cap located approximately 120 km inland from the Wilkes Land coast (Fig. 1). The summit of Law Dome experiences relatively high and constant year-round precipitation, providing clear seasonal variability in stable isotopes of water and ionic species (Curran et al., 1998; McMorrow et al., 2004). The summit of Law Dome features a snow accumulation rate of approximately 60 cm ice equivalent per year, with an average annual temperature of -20° C. The precipitation is predominantly due to westerly cyclonic systems which produce a strong accumulation gradient from East (high accumulation) to west (low accumulation). The Law Dome summit is at an altitude of 1310 m asl, above approximately 1200 m of ice dating back to the last glacial (Morgan et al., 1997). The ice core samples were collected from the DSS site that is within a few hundred metres of the Law Dome summit, with the specific co-ordinates and sampling details described in the following sections. In all cases, the samples described here have been dated by identification and counting of annual cycles in stable isotopes of water (Morgan and van Ommen, 1997; Roberts et al., 2015) and ionic species (Curran et al., 1998) as well as synchronisation of well-dated volcanic eruption tie points (Plummer et al., 2012). Impurities in Law Dome snow are dominated by sea salt inputs (98% by mass) with a minor input from mineral dust (2% by mass) (Vallelonga et al., 2004).

2.1.2 DSS0506

A 258 m deep ice core was drilled using a 20 cm diameter thermal drill near to the Law Dome summit (66°46’19.68” S, 112°48’25.60” E) in November 2005 (Burn-Nunes et al., 2011). The core, designated DSS0506, was subsampled in October 2006 in a cold laboratory in a storage freezer in Hobart. For each ~1 metre long section of ice, a 35 mm x 35 mm stick was collected for chemical analysis, and subsequently decontaminated by chiselling with a microtome blade in an HEPA-filtered laminar flow bench in a freezer. All equipment used for the decontamination was repeatedly cleaned and stored in deionised water (Millipore MQ system, 18.2 MW/cm). The decontaminated samples were collected in polystyrene “Coulter counter” accuvettes and then melted for analysis by ion chromatograph. The remaining melted sample, usually 3 to 8 mL, was then refrozen and stored. In 2014 the remaining samples were sent to the University Ca’ Foscari of Venice for bromine determination. The depth range of DSS0506 samples reported here is from 19.7 m (1991 C.E.) to 72.5 m (1929 C.E.). The sampling resolution increased with depth, from 5 cm near the surface to 3 cm at depth, ensuring higher than monthly resolution at approximately 25 and 15 samples per year, respectively.

2.1.3 DSS1213

In austral summer 2012/2013, a 30 m firn core was drilled at DSS, Law Dome (66°46’21” S, 112°48’40.59” E) using the 4-inch Kovacs Mark VI coring system (Roberts et al., 2015). The firn core was transported to Hobart, Australia, and subsampled in the freezer at the Australian Antarctic Division (AAD)/Antarctic Climate and Ecosystem CRC (ACE CRC). For each 1-metre length of firn, a 35 mm x 35 mm stick was cut and sent to the Trace Research Advanced Clean Environment (TRACE) laboratory at Curtin University of Technology, Perth, Western Australia, for bromine determination. A parallel 35 mm x 35 mm stick was decontaminated and analysed for trace ions at the AAD/ACE CRC in Hobart, with a parallel section analysed for stable isotopes of water. Data covering the full depth range of the firn core are reported here, covering the period from summer 2012/2013 to late 1987 and overlapping with the DSS0506 record.

2.1.4 Law Dome traverse and DSS1516 snowpit

Another sampling expedition was conducted at Law Dome summit in February 2016, with snow surface samples collected during the traverse to the DSS site and from a 1-m snowpit. The DSS1516 snowpit (66°46’23.51” S, 112°48’40.59” E) was collected upwind from the traverse camp (designation: Waypoint A, 66°46’22.12” S, 112°48’28.19” E) and sampling was conducted immediately after the pit was prepared. Samples were collected every 3 cm by plunging pre-cleaned 50 mL polyethylene tubes into the pit wall. Stable isotopes of water ($\delta^{18}O$ and δD) measured in the parallel snow pit wall confirm that the 1 m sequence covers the period from winter (July) 2015 to February 2016.

In addition to the DSS1516 snowpit, surface snow samples were collected during a 1-day traverse from Casey station to the DSS Campsite A. Details of the sampling sites are included in Table S1 (supplementary material). Eleven samples were collected during the 114 km traverse, extending from an altitude of 500m asl to 1320 asl at the DSS1516 site. The samples were collected every 10 to 15 km by moving approximately 15 m upwind of the Hagglunds traverse vehicle and plunging a polyethylene tube into the snow surface. The tubes were immediately sealed after sampling and were kept frozen until analysis. All samples collected during the Casey-Law Dome traverse and from the DSS1516 snowpit were sent to the TRACE laboratory at Curtin University of Technology for bromine analysis.

2.2 Halogen measurements

2.2.1 Australia

The DSS1213 1-metre sticks were cut and prepared in the TRACE laboratory located at Curtin University of Technology, Perth, Australia (Ellis et al., 2015). The 35 mm x 35 mm cross-section sticks were melted on a silicon carbide melter head at a melt rate of 5 cm/minute following the setup of McConnell et al (2002), with a depth resolution of less than 1 mm. The central melt line was directed to a Thermo Element XR ICP-SFMS fitted with cyclonic peltier-cooled spray chamber (2° C) and 400 uL/minute PFA ST nebulizer (both from ESI, Omaha, USA). The sample line was acidified with 2% ultrapure nitric acid and internal standard (4 ppb ^{115}In) immediately before introduction to the plasma. Only bromine and sodium were determined, at medium resolution (~4000), in the DSS1213 firn core.

Law Dome traverse and DSS1516 snowpit samples were analysed discretely using a Seafast-II autosampler with syringe pump connected to the abovementioned analytical system. For these samples, iodine (^{127}I) was determined at low mass resolution (~300) and all other elements at medium resolution (^{23}Na, ^{35}Cl, ^{79}Br). A 4 ppb ^{115}In internal standard was used at both mass resolutions. Analytical blanks and quality control standards were determined after every 10 samples analysed.

Irrespective of the sample delivery method, the analytical performance of the Element XR ICP-SFMS was consistent during the measurement campaigns. Calibration standards were prepared by sequential dilution from primary stock solutions (Bromine, 10 µg/mL in H_2O; Sodium, 1000 µg/mL in 1% HNO_3) from High-Purity Standard (Charleston, USA). Sodium and bromine were calibrated using 7 concentration standards of increasing concentration up to 100 ppb (sodium) and 4 ppb (bromine). All linear calibration regressions showed $R^2 > 0.99$ ($n=8$, $p<0.001$). Detection limits for bromine and sodium were 0.18 and 1.1 ppb respectively (n=80) Repeatability of measurements was systematically tested in each analytical run by measuring replicates of quality controlled standards. The variability was calculated as the standard deviation of the signals and found to be 9% for bromine and 4% for sodium.

2.2.2 Italy

The DSS0506 core samples were measured at the Environmental Analytical Chemistry laboratory of the University Ca'Foscari of Venice. The samples were stored in plastic vials and were kept frozen until analysis. For the DSS0506 samples, some of the polystyrene accuvettes were broken in transport and were found to be contaminated upon comparison of sodium concentrations measured before and after transport. Consequently, data corresponding to the years 1945-6, 1950-1, 1954-5 and 1963-4 are incomplete.

Similar to the Curtin University analysis, samples were measured on a Thermo Element2 ICP-SFMS instrument using a cyclonic peltier-cooled spray chamber (ESI, Omaha, USA). System cleaning and operational parameters have been described previously (Spolaor et al., 2013b) and will be summarized here. Before beginning each analytical session, the sample introduction system was cleaned with alternating washes of 5% NH_4OH, then 2% HNO_3 acid, separated by 30s of MQ water. During the analytical sessions, the sample line was thoroughly cleaned using 2% nitric acid (120 s) and UPW (120 s) between each analysis. Elements were determined in low- (^{127}I) and medium-resolution (^{23}Na, ^{79}Br) with plasma stability evaluated by the continuous monitoring of ^{129}Xe. External standards, ranging from 0.01 to 4 ppb, were prepared by diluting a 1000 ppm stock IC solution (TraceCERT® purity grade, Sigma-Aldrich, MO, USA). Excellent precision was found with calibration correlations of $R^2>0.99$ ($N=6$, $p=0.05$). Calculated detection limits were 0.05 ppb Br, 0.005 ppb I and 0.8 ppb Na.

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 ± 0.19 ppb (sodium, RSD=2.0 ± 0.2 ppb) and -0.03 ± 0.01 ppb (bromine, RSD=0.11 ± 0.01 ppb).

2.3 Ion chromatography measurements

Major and minor ions were determined at the AAD/ACE CRC laboratory in Hobart Australia following the established suppressed ion chromatographic methods (Curran and Palmer, 2001). Samples were stored and prepared in an HEPA-filtered cleanroom and all laboratory apparatus was cleaned using filtered deionized water (Siemens Ultrapure water system, 18.2 MΩ/cm). Detection limits for MSA and Na were 0.095 ppb and 0.23 ppb, with reported precisions of 3.8 ppb and 0.46 ppb and analytical ranges of 0.6-40 ppb and 0.7-500 ppb, respectively. The MSA data covering the period 1920-1995 are those reported by Curran et al. (2003). Sodium data from the DSS main ice core record have been previously discussed by Palmer et al. (2001).

2.4 Sea ice area

Satellite-based observations of sea ice area and concentration have been used to evaluate the suitability of bromine and iodine as proxies for sea ice area reconstructions. We have calculated sea ice area as the product of sea ice concentration and grid cell size for each grid cell in the two sectors considered. Note that sea ice *area* is different to, and slightly less than, sea ice *extent*, as sea ice *extent* is commonly defined as the sum of grid cells containing at least 15% sea ice coverage. The sea ice area has been evaluated in two ocean sectors adjacent to Law Dome and are used for comparison: one to the west of Law Dome (90 to 110° E) and one to the east of Law Dome (110 to 130° E); as shown in Fig. 2. A strong East-to-West accumulation gradient has been observed across Law Dome. Hence it is expected that sea salts carried to Law Dome will predominantly originate from low pressure systems developing from the 90-110° E sector.

A discontinuous record of monthly sea ice area is calculated from a series of satellite-based sensors, covering the period from 1974 to 2015 with missing years for 1975, 1977 and 1978. Sea ice area for the period 1973 to 1977 was determined from daily brightness temperatures monitored by the ESMR instrument mounted on the NIMBUS-5 satellite (Parkinson et al., 2004). For the period January 1979 to May 2015, sea ice observations were obtained from the SMMR and SSM/I and SSMIS instruments mounted on various satellite platforms (Cavalieri et al., 1996, updated yearly). These data are freely available from the US National Snow and Ice Data Centre (NSIDC) website (Cavalieri et al., 1999; Fetterer et al.).

First year sea ice (FYSI) area has been calculated as the difference between the late-summer (February/March) minimum and late-winter (September/October) maximum of sea ice area occurring each year. FYSI data series' calculated for the 90-110° E and 110-130° E sectors are shown in Fig. 3. Also shown in Fig. 3 are two other publicly available datasets reporting sea ice extent (not sea ice area), largely calculated from the same satellite observations. The first dataset, here referred to as 'Jacka SIE', reports monthly observations of the northernmost sea ice edge (SIE) for 10° sectors of longitude around Antarctica over the period 1973-1998. The data are available online (https://data.aad.gov.au/metadata/records/climate_sea_ice) and were employed by Curran et al. (2003) to validate their MSA-based Law Dome sea ice reconstruction. The second dataset is produced by National Snow and Ice Data Centre (NSIDC) and offers near-daily sea ice extent over the period 1978-2013 for Antarctica. The data are divided into 5 Antarctic sectors, of which the "Pacific Ocean" sector encompasses 90-160° E and includes Law Dome. The Jacka SIE and NSIDC datasets are shown to demonstrate their general correspondence with the FYSI data reported here for regression analysis with Law Dome bromine data. In Fig. 3, we also plot the sum of the 90-110° E and 110-130° E FYSI datasets to allow better comparison to Jacka SIE and NSIDC.

3. Results and discussion

3.1 Halogen and sodium records

Mean bromine, iodine and sodium glaciochemical concentrations (1927-2012 CE for Br and Na, 1927-1989 CE for I) at DSS were comparable to previously reported values for Law Dome (Curran et al., 1998; Spolaor et al., 2014). Considering annual averages over the period 1927-2012, we find average concentrations of 88±45 (1σ) ng g^{-1} for Na and 2.9±2.7 (1σ) ng g^{-1} for Br. For iodine, the average for the period 1927-1989 is 0.061±0.023 ng g^{-1} (1σ, n=62). As may be expected from the "spiky" nature of the data, both the medians (81.1 ng Na g^{-1}, 2.1 ng Br g^{-1}, 0.056 ng I g^{-1}) and geometric means of the data (81.0 ng Na g^{-1}, 2.3 ng Br g^{-1}, 0.057 ng I g^{-1}) are 5 to 20% lower than the arithmetic means. Annually-averaged non-sea salt Br (nssBr) concentrations average 2.4 ng g^{-1} (geomean 1.6 ng g^{-1}) are comparable to values reported previously for Law Dome (Spolaor et al., 2014). Sodium concentrations are also in good agreement with previously reported values of 3.47±3.03 (1σ) μeq L^{-1} (80±70 ng g^{-1}) (Curran et al., 1998).

The bromine, iodine and sodium time series records determined for DSS firn and ice cores are shown in Fig. 4. No significant trend is present in any of the timeseries. The sodium data are representative of sea salt inputs from the Southern Ocean to the site whereas bromine is known to be subject to enhancement in photochemical 'bromine explosion' events. We quantify the strength of such photochemical enrichment by calculating the bromine enrichment (Br_{enr}) beyond the bromine/sodium abundance ratio found ubiquitously in seawater [Br/Na=0.006; Turekian (1968)]. Following common practice (e.g. Spolaor et al., 2013a; Spolaor et al., 2016a) we calculate $Br_{enr} = Br_{conc}/(Na_{conc}*0.006)$, where Br_{conc} and Na_{conc} respectively describe the concentrations of Br and Na measured in a sample. For iodine enrichment (I_{enr}) we apply the same enrichment calculation but using the iodine/sodium ratio in seawater of 5.93 x 10^{-6} (Turekian, 1968). Iodine and bromine enrichment data and their relation to sea ice variability will be discussed in the following sections.

There appears to be less interannual variability in the DSS1213 Br record, with respect to the DSS0506 record. The average values of Br_{enr} and Br_{conc} are similar for the two cores but the variance of annual averages is much greater for the DSS0506 samples (Table 1). For sodium, there is no substantial difference in average concentration but the opposite trend is found for variance, with greater variance in the DSS1213 data. We attribute this difference in variance to the different sampling and analytical techniques applied to each core – DSS0506 was sampled by discrete chiselling and DSS1213 sampled by continuous melting. The ice core melter system had a flow path ~5 times longer than the discrete sampling system, and there was likely greater memory-effect of bromine coating onto the inside of the ICP-SFMS sample introduction system (peltier-cooled cyclonic spray chamber) used for the continuous melting analysis. Note that the memory effect is much more significant for bromine than for sodium, which is efficiently transported through the ICP-SFMS spray chamber in a HNO_3 acid solution. Sodium does not have a significant memory effect and the higher variance found by the ice core melter is expected due to the higher depth-resolution of the melter system compared to discrete sampling. Despite the apparent aliasing of the DSS1213 Br record, the two records show good agreement in the overlap period from calendar 1988 to 1989 (Fig. 4). A double peak in Br was found with the initial peak in the DSS0506 core leading the DSS1213 record by approximately 2 weeks (from comparison of the time scales), which is well within the sub-annual dating error. Furthermore the seasonality of bromine and sodium measured in the DSS1213 samples (discussed in section 3.5) are in agreement with previous studies conducted on Law Dome samples (Curran et al., 1998; Spolaor et al., 2014).

3.2 Bromine and first year sea ice

Considering the known relationships between emissions of bromine and seasonal sea ice area, we investigated the reliability of bromine, and bromine enrichment, as a proxy for regional seasonal sea ice area adjacent to Law Dome. With the intention of reducing data autocorrelation, we transform the Br_{enr} data to a gaussian-like distribution using the natural logarithm of Br_{enr} for correlation to FYSI data. An additional reason for applying a logarithmic transformation is due to the exponential nature of the “bromine explosion” process occurring above the bromine-rich FYSI surface: in each stage of the explosion, one reactive bromine species (HOBr) is consumed in the process of liberating Br_2 from the sea ice surface. As Br_2 is the reactive precursor to two subsequent bromine explosion multiphase reactions, the process develops exponentially. Histograms of Br concentration, Br_{enr} and $\ln(Br_{enr})$ are shown in Supplementary Figure S3, demonstrating that the distribution of $\ln(Br_{enr})$ values in Law Dome is well represented by a gaussian curve. Correlation tests have been performed using different subsets of the $\ln(Br_{enr})$ data; such as summer-summer (calendar year), winter-winter (July-June) and spring-only (August-October) intervals. The FYSI data used for correlation has been described in Sect. 2.4. Note that the optimal correlation is found when $\ln(Br_{enr})$ is compared to the FYSI value from the previous year. This is due to the timing of formation of sea ice in the Antarctic (from March to September) occurring, by necessity, earlier than the springtime bromine explosion that occurs in the following calendar year.

A summary of the correlation analysis between Law Dome bromine enrichment and FYSI is shown in Table 2. We observe firstly that $\ln(Br_{enr})$ is better correlated with the 90-110°E sector than for the 110-130°E sector. Such a finding is consistent with the westerly circulation around Antarctica, despite the individual cyclonic systems producing an east-to-west deposition gradient across Law Dome. The 80-140° E sector was used for correlation between sea ice extent and MSA concentrations at Law Dome (Curran et al., 2003), with the best correlation found for sea ice in the 110ºE sector. The strongest correlation (r^2

0.357, $p<0.001$) is between $\ln(Br_{enr})$ and 90-110° E sector FYSI for the summer-summer calendar year period. A weaker and less-significant correlation is found between $\ln(Br_{enr})$ and 110-130° E FYSI for the winter-winter interval (r^2 0.20, $p<0.01$). Such a finding is counter-intuitive because the bromine explosion occurs primarily in spring/summer and should be most completely captured in the winter-winter interval. As has been demonstrated thoroughly by Levine et al. (2014), meteorological transport variability and other "noise effects" can have a strong influence on the regularity of seasonal sea salt deposition. Hence it may be that the summer-summer interval produces a marginally stronger correlation with 90-110° E FYSI due to the smoothing effect caused by the averaging of consecutive spring/summer periods.

3.3 Bromine enrichment as a sea ice proxy

On the basis of the significant correlation between bromine enrichment at Law Dome and 90-110° E FYSI, we consider the implications for reconstructing past sea ice area at Law Dome. Figure 5 shows Law Dome $\ln(Br_{enr})$ and MSA (Curran et al., 2003) since 1927 C.E. as well as the 90-110° E FYSI data plotted as an anomaly from the average of the data, to better display FYSI trends. We firstly note that a selection of running-mean smoothing filters has been applied to such data previously, such as 3- and 20- year means (Curran et al., 2003) and 11-year means (Abram et al., 2010). Here we follow the latter and show 11-year means as well as the individual annual data points.

When comparing two proxies purporting to represent the same phenomenon it is vital to consider the different physical processes involved in the proxy generation, transport and deposition. We note that MSA is produced biologically and, for the Law Dome sector, has been quantitatively linked to the opening of sea ice-covered seawater during the summer and autumn seasons. Bromine enrichment occurs primarily in spring/summer and is dependent upon the presence of FYSI (Saiz-Lopez and von Glasow, 2012). Due to the 11-year smoothing applied to the data, influences of seasonal patterns, factors influencing biological growth, relations to sea ice and transport efficacy should be minimised for the comparison of bromine enrichment and MSA trends at Law Dome.

Some differences are seen among the sea ice trends indicated by MSA and bromine at Law Dome over the 20th century (Fig. 5). Both proxies display substantial multidecadal variability, so any long-term trend is here treated with caution. In the cases of both bromine and MSA, simple linear regression indicates small declining trends for both species. Bromine enrichment values are greater during the period 1940-1950 and 1975-1985 while the highest MSA concentrations are observed during the period 1945-1955. Bromine and MSA both point toward greater sea ice area during the period from 1945 to 1950 but diverge between 1955 and 1970. The cause for this divergence is not yet known, but before speculating on a possible cause, these trends should be confirmed by measurements of other snow and ice samples from Law Dome as well as other sectors of the East Antarctic coast. The possible influence of multidecadal-scale climate variability, such as the Interdecadal Pacific

Oscillation (IPO), on the bromine record is discussed in detail in section 3.4, but will briefly be considered here. IPO forcing of Antarctic sea ice area has been demonstrated at decadal timescales (Meehl et al., 2016), with the negative IPO phase triggering SLP and near surface wind changes that can influence sea ice expansion, storm tracks and potentially nutrient supply to DMS-producing algal communities. Smaller magnitudes of change are observed in MSA over the 20th century, compared to Br_{enr}. Despite the short time period available, satellite-based observations of FYSI display positive anomalies before 1985 and negative anomalies in the last decades (Fig. 5) which are consistent with recent trends of both MSA and Br_{enr}.

3.4 Iodine enrichment

Iodine enrichment in sea ice could be explained by complex heterogeneous reactions that take place above seasonal sea ice releasing gas-phase iodine and particulate species. Peak I concentrations have been found in winter snow strata at Law Dome (Spolaor et al., 2014) and Neumayer station (Frieß et al., 2010), suggesting surface re-emission and/or remobilization during the Austral summer.. There is no significant correlation between Br_{enr} and I_{enr} signals on an annual basis (r^2=0.05, p<0.1). This lack of significant correlation might be related to the different iodine emissions and recycling mechanisms over sea ice: i) emission of iodine from sea-ice enhanced bioproductivity and subsequent upwards migration through brine channels (Saiz-Lopez et al., 2015); ii) photochemical reactions over iodate frozen salts (Spolaor et al., 2012) and ii) atmospheric release of gas-phase iodine from triiodide production via iodide oxidation in frozen solution (Kim et al., 2016). Another indicator of the complex ocean-sea ice-atmosphere interrelation arises from the statistical comparison with FYSI records (Table 2). Correlation significance levels for I_{enr} are consistently below the 95% level and correlation coefficients are generally low. The strongest correlation of I_{enr} is between the summer-summer (calendar year) averaged signal and the 110-130° E FYSI sector, but this is still below the 95% significance level.

Correlation between 11-year smoothed I_{enr} and Br_{enr} records (Fig. 6) is significant (r^2=0.269, p<0.001) suggesting a long-term (decadal scale) common driver controlling halogens deposition in coastal Antarctica. The iodine enrichment time series shows a similar pattern to that of bromine enrichment, with higher values particularly during the 1940s and back from negative to positive in the 1970s (Fig. 6). These periods coincide with rapid changes in the Interdecadal Pacific Oscillation (IPO) phase from positive to negative in the 1940s and back from negative to positive in the 1970s. The IPO is a low frequency climate mode related to the El Niño-Southern Oscillation which operates on multidecadal timescales. It affects climate variability at the multidecadal scale across and beyond the Pacific Basin (Power et al., 1999; Vance et al., 2015). Impurities deposited at Law Dome have been demonstrated to faithfully reflect IPO variability (Vance et al., 2015) and reanalysis data indicates a strong IPO signal in the Indian Ocean (Vance et al., 2016). Furthermore, recent work has demonstrated an IPO forcing of Antarctic sea ice area at decadal timescales, with the late 1990's shift to a negative IPO phase triggering SLP and near surface wind changes that are conducive and consistent with an expansion in sea ice in all seasons across multiple regions of the Antarctic seasonal ice zone (Meehl et al., 2016). Thus the overall correlation between iodine and bromine enrichment may be linked to decadal-scale states of the atmosphere-ocean-sea ice system in the Indian sector of the Southern Ocean. It must be noted that, in addition to larger-scale influences of atmospheric transport and ocean-related sea ice variability, both I_{enr} and Br_{enr} are calculated using Na as an indicator of sea salt content in the samples. The possibility of an IPO-related signal, transmitted through Na concentrations, cannot be discounted from contributing to the apparent correlation of I_{enr} and Br_{enr} in DSS0506 core samples.

3.5 Bromine seasonality

Due to the availability of consistent and highly resolved data from the DSS1213 core, it is possible to investigate seasonal distributions of sodium and bromine at Law Dome. The seasonal cycle of major and minor ions has been previously reported for Law Dome (Curran et al., 1998) but for bromine only four years are available (Spolaor et al., 2014). Here we present the DSS1213 record, spanning the period 1987 to 2012. The seasonality of sodium and Br_{enr} are shown in Fig. 7. Sodium shows a broad period of high concentrations from April to September, with lower concentrations during the summer. This pattern broadly agrees with that reported by Curran et al., (1998) although those authors found a sharper sodium peak in late winter, associated with both the local sea ice maximum and the strongest local wind fields. We also note that the highest concentration of sodium is found in March-April and is likely due to one of '*a small number of large storm events which occasionally occur early in the year, lofting higher concentrations of sea-salt aerosol onto the summit of the dome*' (Curran et al., 1998).

The trend observed for Br_{enr} is one of lower values in winter and higher values from November to February. There is high variability in the sodium signal throughout the year, whereas the Br_{enr} signal is most variable during the summer months. The seasonality of Br_{enr} found here confirms that suggested by the four-year data series presented by Spolaor et al. (2014), with a broad summer peak in Br_{enr}. Satellite observations of atmospheric BrO in polar regions suggest an early spring peak in bromine activity in Antarctica (Spolaor et al., 2014), thereby implying that additional processes may be occurring in the snowpack during the summer after the peak atmospheric bromine explosion has occurred. While snowpack remobilisation at Law Dome is minimal, it might be the case that photochemically-driven heterogenous recycling of bromine occurs in the snowpack after the springtime occurrence of the bromine explosion. This effect requires further investigation, from satellite and ground-based observations to weekly surface snow sampling, to be fully characterised and understood.

3.6 Bromine deposition across Law Dome

Variability in sodium and bromine was investigated along the transect line from Casey station to the Law Dome summit. The traverse route is indicated in Fig. 1, where 11 samples were collected over a period of 4 hours on the 10th February 2016. Conditions were clear with low wind and good visibility. Details of the sampling sites are included in Table S1 (supplementary material). The sodium and bromine results for each station are shown in Fig. 8.

Substantial variability can be seen along the traverse, with increasing fluxes of sodium and bromine approaching the Law Dome summit. It should be noted that the sampling was undertaken on the ‘lee side’ of Law Dome, across a region which generally exhibits low annual accumulation on the order of <200 kg m^{-2}. The final 25 km of the traverse sees a threefold-increase in annual accumulation to >600 kg m^{-2}. Higher fluxes of Na and Br in zones of higher accumulation suggest that both Na and Br are wet-deposited over the eastern half of Law Dome. The data presented here represent a first attempt to capture the surface variability of sodium and bromine across Law Dome. Future expeditions to Law Dome should incorporate a procedure for surface sampling along the traverse line and ideally further east toward the origin of the precipitation pathway over Law Dome.

4. Conclusions

The Law Dome site is ideal for studies of sea ice proxies, due to the regular and high level of annual precipitation allowing detailed studies of seasonality as well as the optimal preservation conditions. We find here that bromine enrichment over the past century displays some similarity to that of MSA, which has been previously used for reconstruction of local sea ice extent. The bromine-based reconstruction of the sea ice area in the 90110° E Antarctic sector suggests a reduction of sea ice area over the 20th century and hence is supportive of previous findings based on MSA. In agreement with satellite observations there is some indication of an increase in sea ice area since 1990.

In agreement with a previous study of halogen seasonality at Law Dome, we find that bromine enrichment displays regular seasonality with a broad summer peak. Iodine enrichment appears to be correlated to bromine enrichment on decadal scales but not annual scales, suggesting that despite their different chemical processes of emission and deposition, a multidecadal climate signal such as the Interdecadal Pacific Oscillation may act as a common influence on the enrichment of both halogen elements.

More extensive sampling across Law Dome and further inland should be considered in future field seasons. Samples collected during a traverse from Casey station to Law Dome DSS site display a consistent increase in deposition fluxes from west to east, as expected from the easterly cyclonic systems responsible for the precipitation at Law Dome. Additional traverse data should be collected at the next available opportunity and ideally, the traverse should be extended over the dome summit and onto the eastern side of the dome. The Law Dome halogens record presented here should be extended further back in time and similar studies should be undertaken at other Antarctic locations, to ensure consistency and validation of the sea ice reconstruction presented here.

Data availability

Data will be made publicly available online through the NOAA Paleoclimatology database and PANGAEA data repository.

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Table 1. Statistical summary of time series data presented from Law Dome Dome Summit South (DSS) ice cores.

Sample	Time	No.	Sodium (ppb)			Bromine (ppb)			Ln(Brconc)		Ln (Brenr)	
designation	interval	years	mean	median	variance	mean	median	variance	mean	variance	mean	variance
DSS1516 snowpit	2015-2016	0.8	241	179	91078	1.4	0.8	3.5	-0.34	1.5	0.1	4.6
DSS1213 core	1987-2012	25	115	106	4355	2		0.2	0.67	0.06	1.8	0.1
DSS0506 core	1927-1986	59	77	74	571	3.3		9.7	0.88	0.57	2.5	0.6

Table 2. Correlations between bromine and iodine enrichments and First year Sea Ice (FYSI) areas calculated for two sectors adjacent to Law Dome. Correlations that are significant at the 99% level or above are shown in bold.

Ln($\mathrm{Br_{enr}}$)	# years	FYSI 90-110 °E		FYSI 110-130 °E	
		r^2	p-value	r^2	p-value
Jan-Dec (summer-summer)	35	**0.357**	**<0.001**	0.006	ns
Jul-Jun (winter-winter)	35	0.17	<0.05	**0.20**	**<0.01**
Sep-Nov (Spring only)	35	0.18	<0.05	0.02	ns

$\mathrm{I_{enr}}$	# years	FYSI 90-110 °E		FYSI 110-130 °E	
		r^2	p-value	r^2	p-value
Jan-Dec (summer-summer)	12	0.07	ns	0.24	ns
Jul-Jun (winter-winter)	12	0.02	ns	0.03	ns
Sep-Nov (Spring only)	12	0.09	ns	0.005	ns

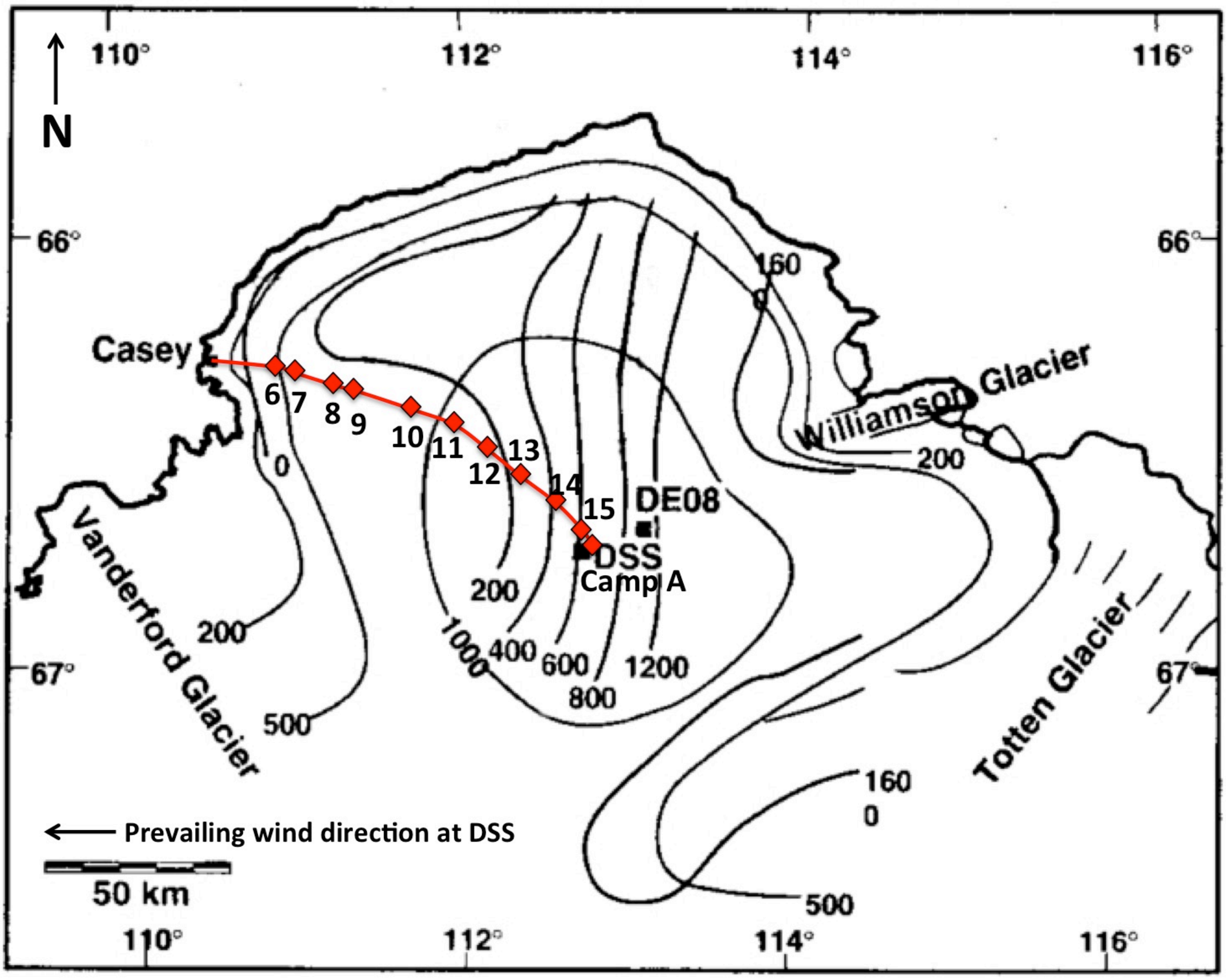


Figure 1: Map of Law Dome with contours of elevation (m asl) and accumulation (kg m^{-2} a^{-1}). The red line indicates the traverse route from Casey station to Camp A located near the Law Dome Summit. Red diamonds indicate the LDT surface snow sampling stations. DSS1516, DSS1213 and DSS0506 sampling sites are all in the vicinity of Camp A.

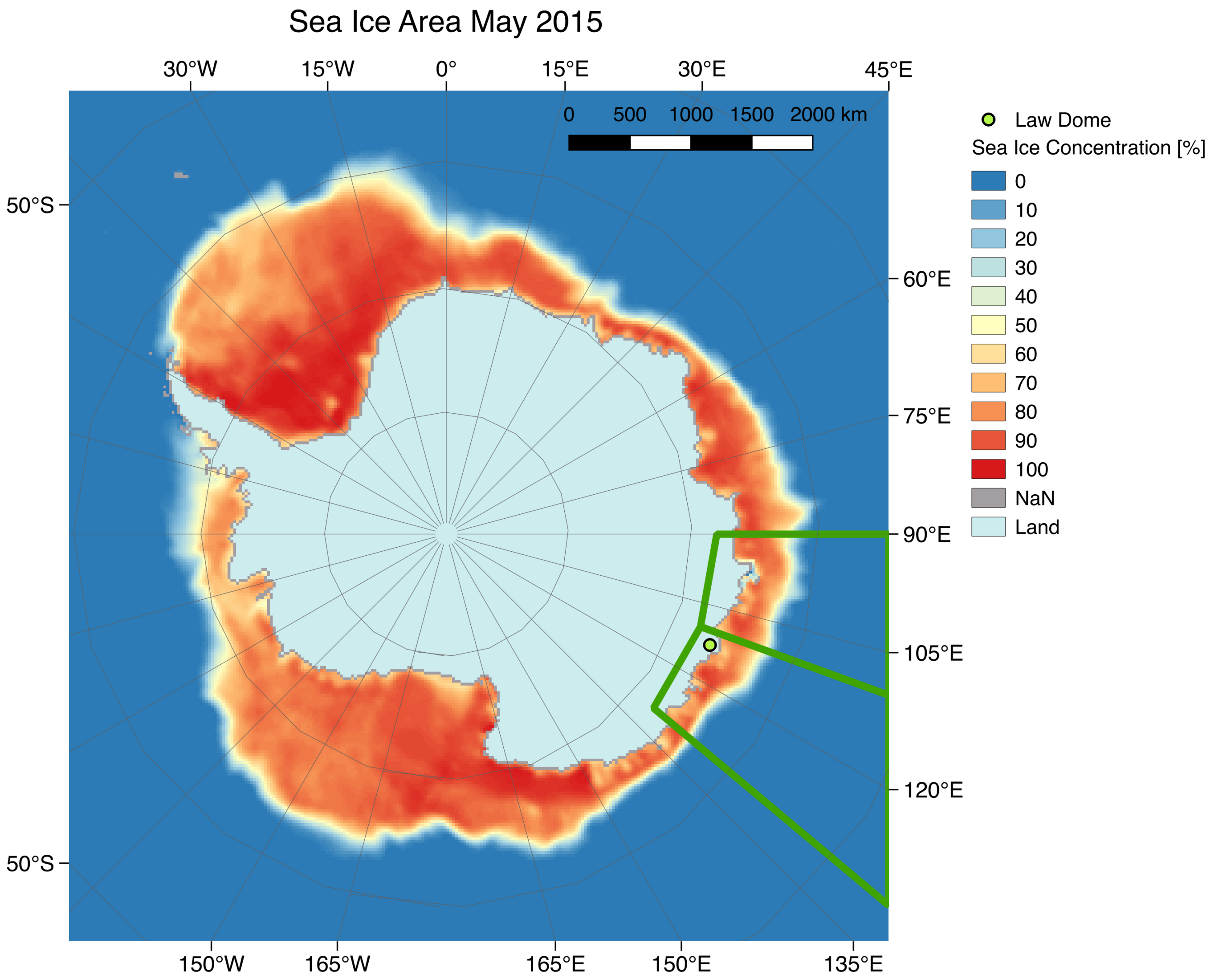


Figure 2: Antarctic sectors used for evaluating sea ice trends. Two sectors (90-110° E and 110-130° E) adjacent to Law Dome have been isolated and used to calculate past sea ice area. The image shows and example of sea ice area for the month of May 2015 given as sea ice concentration (%) per grid cell.

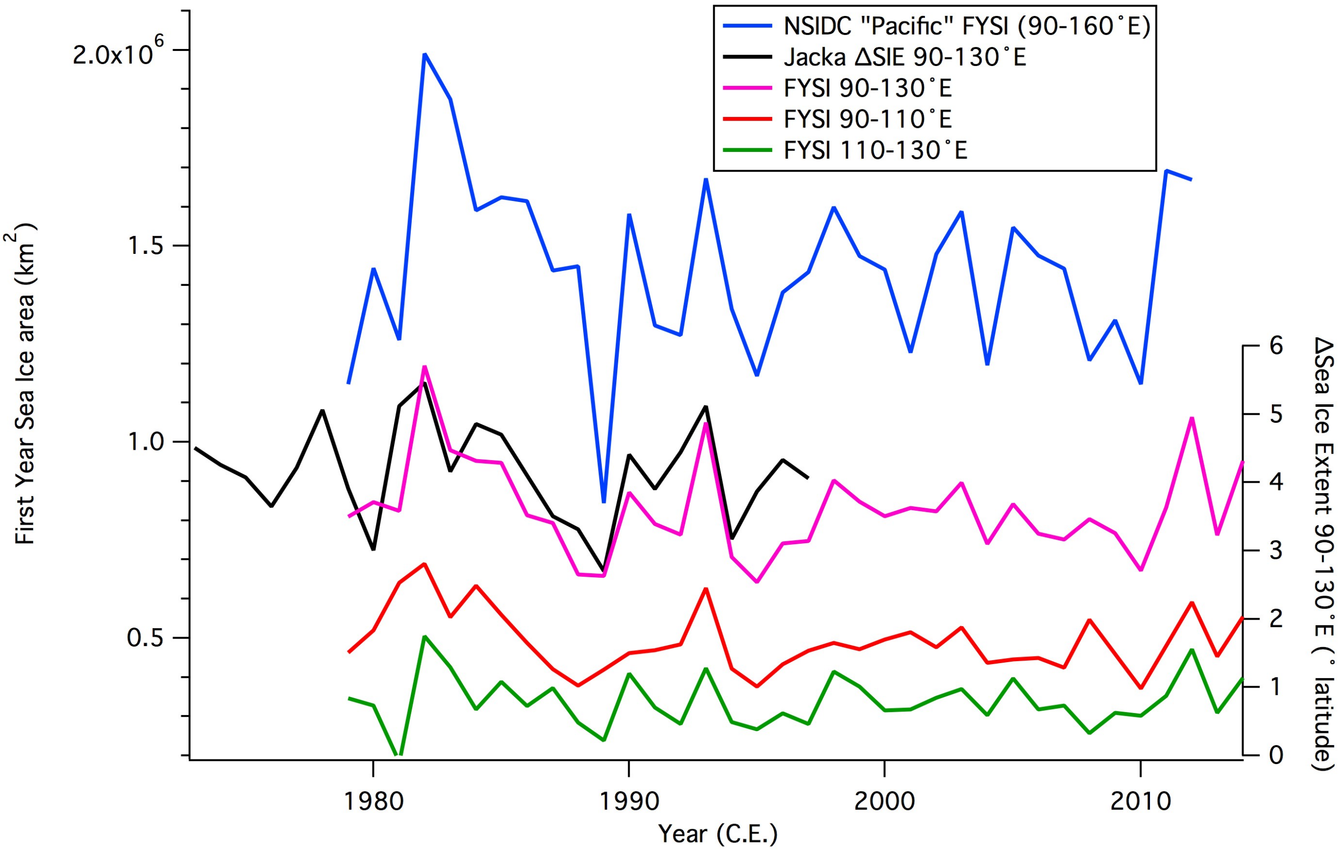


Figure 3: First year sea ice (FYSI) areas calculated from satellite microwave radiometer observations. The 90-110° E and 110-130° E data shown here correspond to the two sectors indicated in Fig. 2. The 90-130° E FYSI data series (fuchsia) is the sum of the 90-110° E (red) and 110-130° E (green) data series'. For comparison to previous studies, we include corresponding data series from Jo Jacka (Jacka, 1998) and NSIDC (Fetterer et al., 2002). Note the NSIDC Pacific sector covers a larger sector (90-160°E) than the other records shown here.

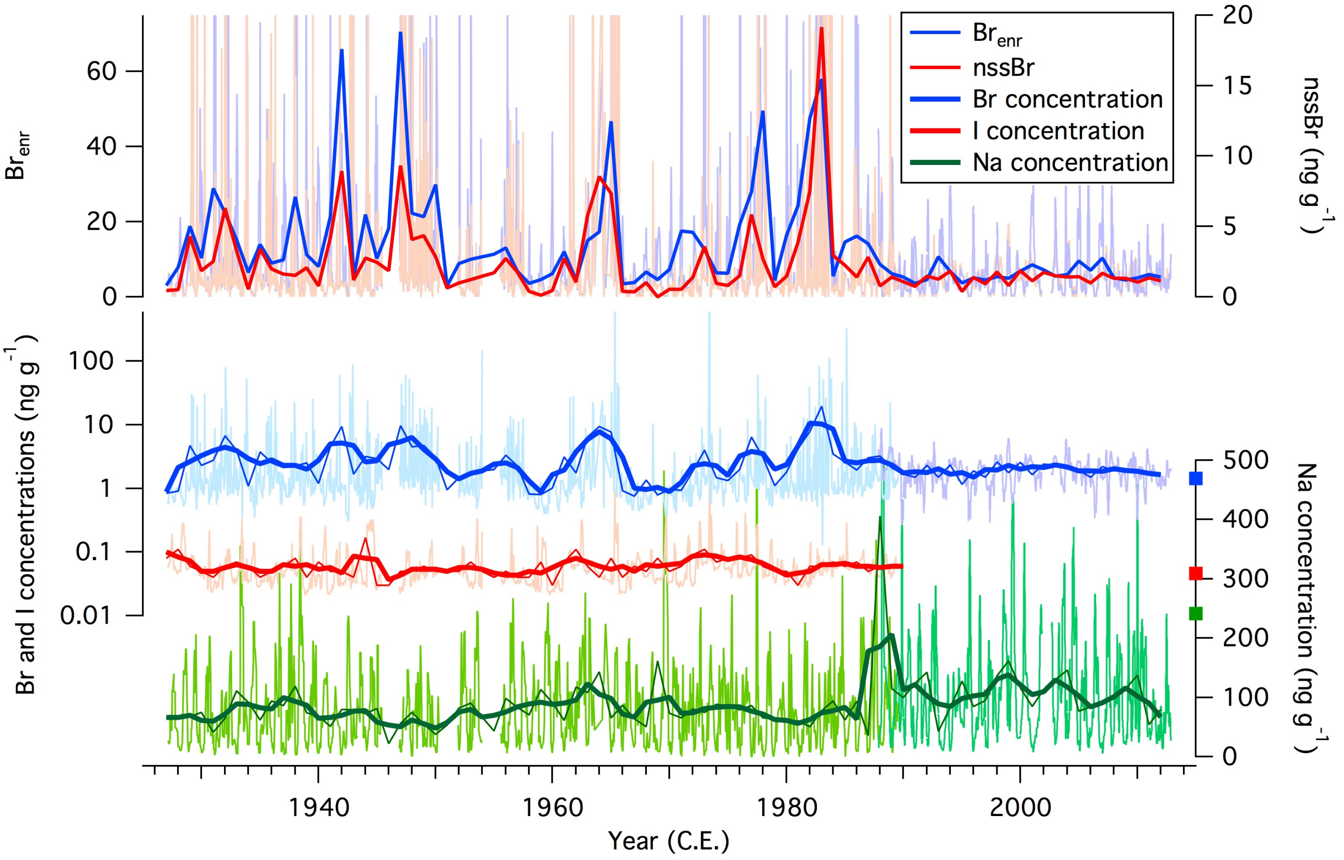


Figure 4: Time series' of sodium, iodine and bromine concentrations as well as nssBr and Br$_{enr}$ at Law Dome. Raw data are shown in pale colours, with annual means shown by a thin line and three-year running means shown by a thick line. For nssBr and Br$_{enr}$, only raw data (pale colours) and annual averages (thick line) are shown. Different shades of blue and green are used to distinguish data from DSS0506 (1927-1989) and DSS1213 (1987-2013). The squares indicate average values from the DSS1516 snow pit.

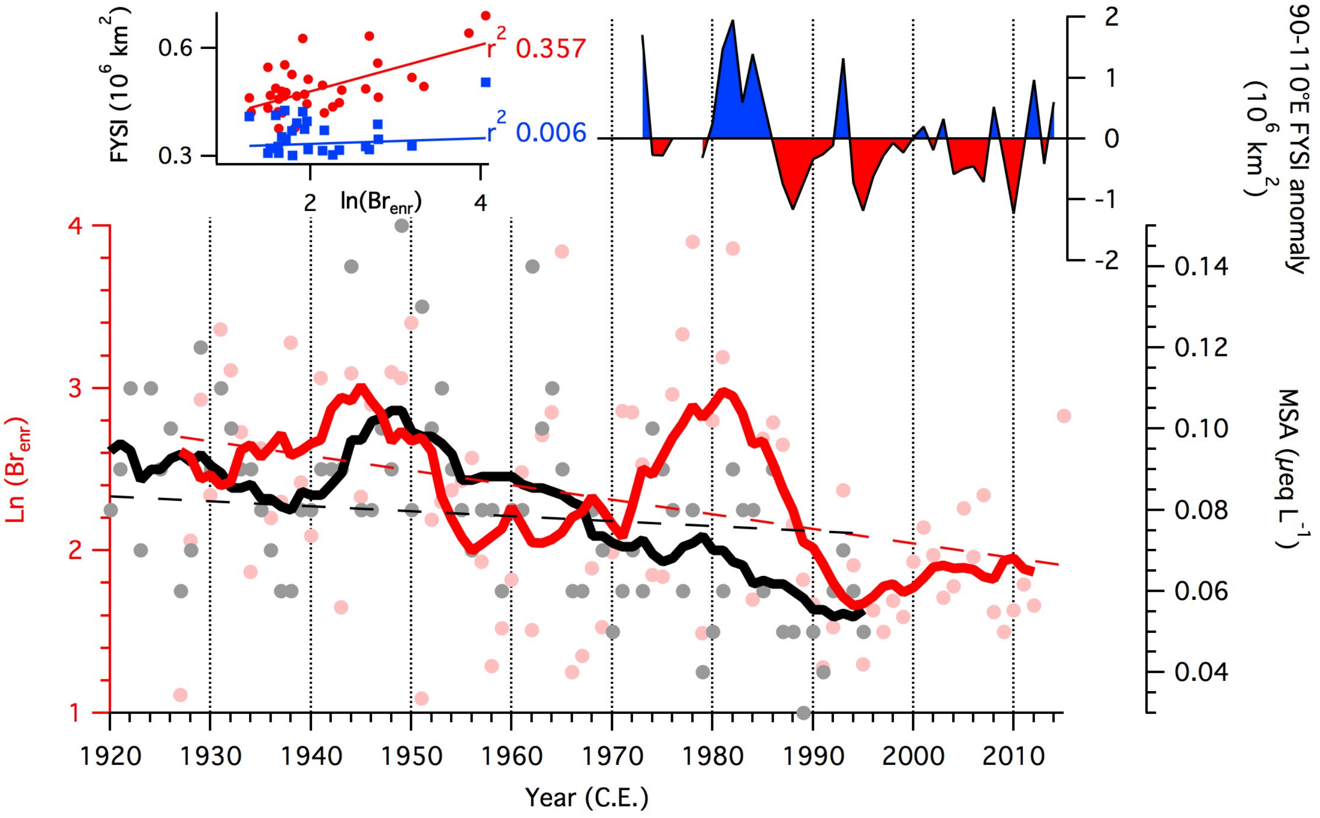


Figure 5: Bromine enrichment (Br$_{enr}$, red), MSA (black) and First Year Sea Ice (FYSI) at Law Dome. Bromine enrichment and MSA data are shown as annual averages (circles) as well as 11-year (thick lines) running means. Linear regression trends are shown as dotted lines. FYSI areas in the 90-110° E sector (top right) are shown as annual anomalies from the 1973-2014 average. Shown in the top left panel are correlations between Br$_{enr}$ and FYSI areas in the 90-110°E (red) and 110-130°E (blue) sector.

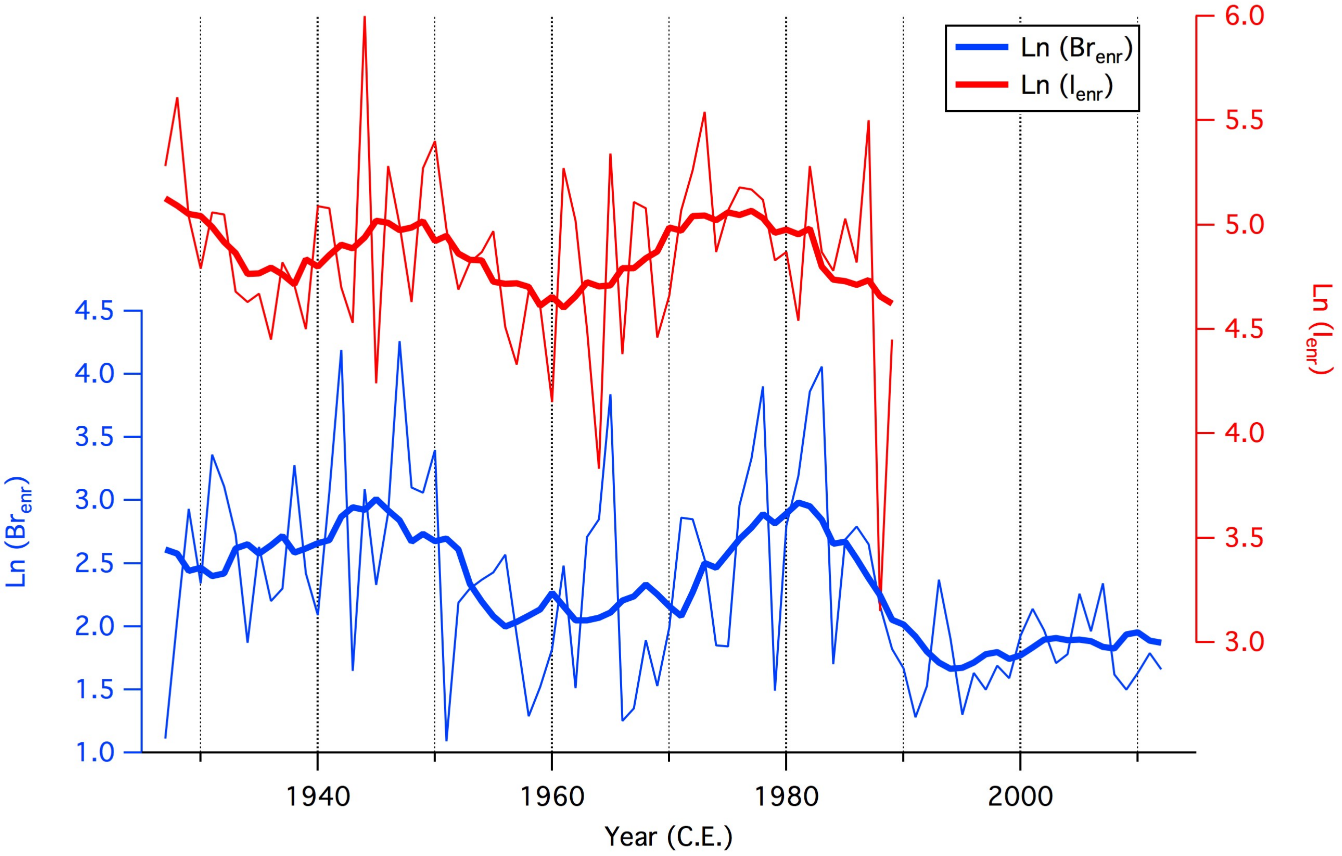


Figure 6: Time series' of bromine and iodine enrichment beyond sea salt concentrations. As described in Sect. 3.2, sea salt is represented by sodium. Bromine and iodine show similar trends, pointing to a common source of variability.

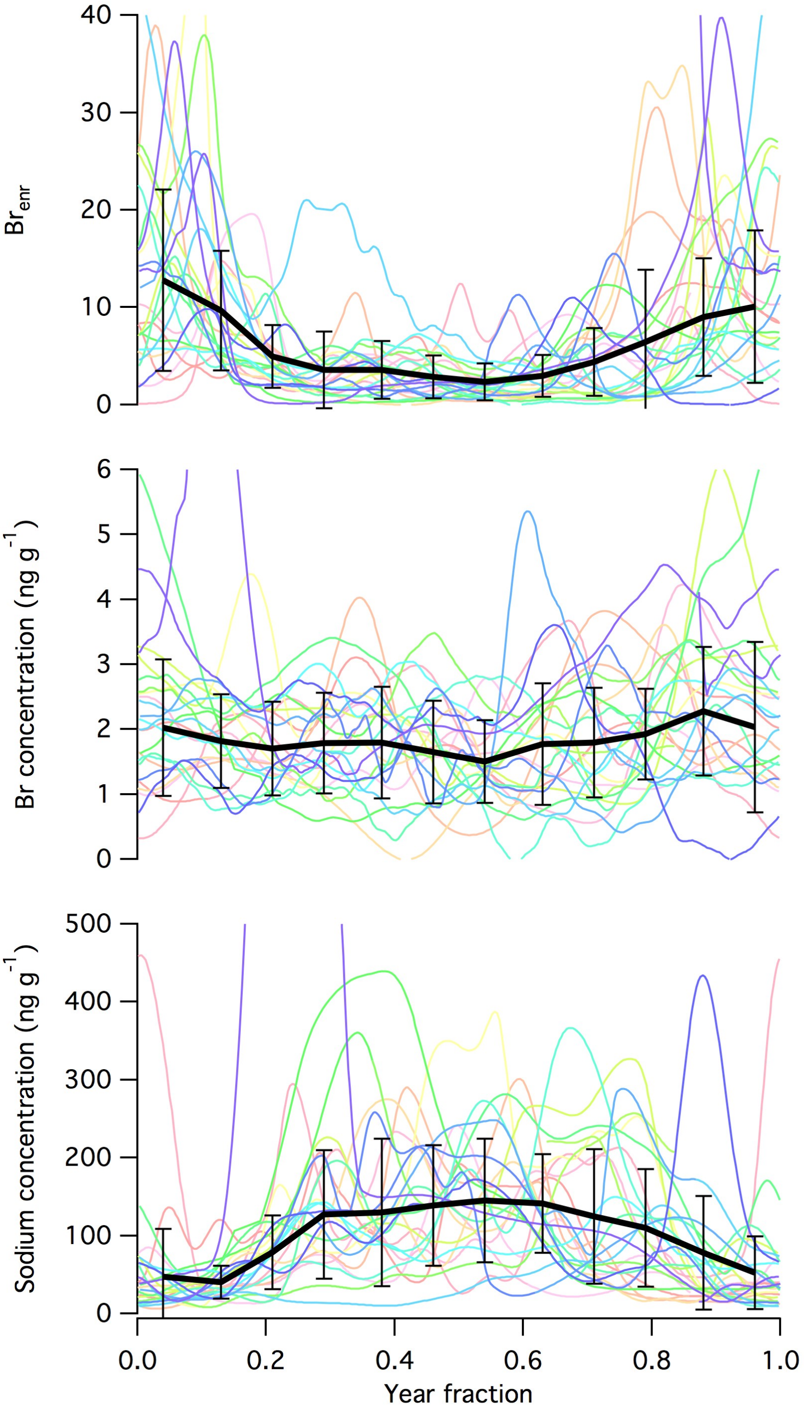
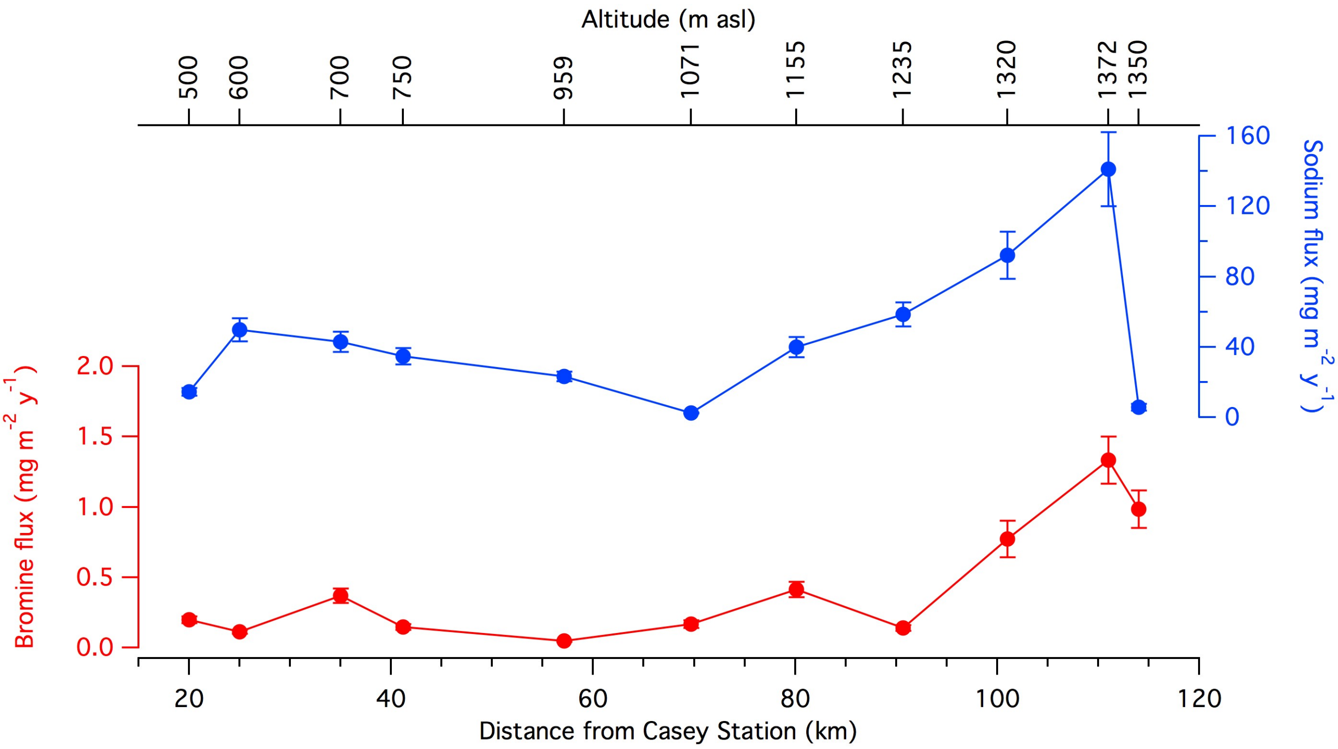


Figure 7: Seasonality of sodium and bromine concentrations and bromine enrichment (Br_{enr}) in the DSS1213 firn core. Each colour corresponds to one year of data with the same year represented by the same colour. The year fraction has been separated into 12 months, with 0.42 representing January and 0.96 representing December. The error bars show 1 standard deviation for the 26 years sampled. 5



5 **Figure 8: Fluxes of sodium and bromine along the 2016 Law Dome Traverse (indicated in Fig. 1).** Uncertainies include uncertainties in the analysis (9% Br, 4% Na) and accumulation (10%).