

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

Anonymous Referee #1

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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

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consider spatial variability in the Br/Na relationship around Law Dome.

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

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

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Br is transport/deposited as gaseous HBr or sea salt aerosol (see Simpson et al. 2005, GRL).

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

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.

The significant, but rather weak, correlation between $\ln(\text{Br enr})$ 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.

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

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

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measured in both labs? - 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. - 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? - 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. - Sect 3.2, pg. 9 line 26: Levine et al. (2014) do not discuss post-depositional remobilization, please add another citation here. line 27: do you mean "seasonality" of sea salt deposition? line 30: How is the correlation "consistent", with what? - Sect 3.4, pg 10, line 30: Do you mean iodine enrichment in snow, not sea ice? - Sect 3.4, pg 10, line 31: Do heterogeneous reactions really "release" particulate species? - 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? - Sect 3.5, pg11 line 31: Brenr is not a concentration. - 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. - 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. - Figure 2: This would be easier to interpret quickly if axes were degrees, rather than arbitrary grid. Is the blue color meaningful, probably outlining the two regions is enough? - 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

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could also be moved to the supplement. - 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.

Technical notes - abstract, line 23. Change “particularly” to specifically – correlation only found for the one sector. - line 23: Iodate should be iodate

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