

## ***Interactive comment on “Sea ice dynamics influence halogen deposition to Svalbard” by A. Spolaor et al.***

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### ANSWER REFEREE 3

This manuscript shows observations of halogens (bromine and iodine) in a firn core extracted from a glacial cap on Svalbard. The manuscript is generally well written and readable and of interest to ice core and atmospheric scientists. The firn core is dated by oxygen isotope measurements as well as glaciological methods. Core extraction, sample preparation, and analysis of bromine and iodine are well documented and appear sufficient. The paper makes some interesting direct findings, such as: Bromine is enriched in nearly all samples, although at lesser values than prior snow work (see below). Iodine is greatly enriched compared to sea salt tracers, as the authors indicate that "...sea salt I was found to consistently account for less than 2% of iodine

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concentrations". While it is exciting to see these observations from glacial records, interpretation of the manuscript appears overreaching given the lack of understanding of post-depositional processes for these species, use of pan-Arctic ice indices for what are likely regional processes, and indications in the data that post-depositional processes may be active.

We agree with the referee and we have modified the paragraph in the manuscript. In particular we thoroughly investigated local wind patterns and regional sea ice changes (see also our responses to referees 1 and 2).

The lack of seasonality in the halogen data is of concern in the light of the fact that the oxygen isotope data indicate that seasonal layers exist and are not sufficiently influenced by snow melting and percolation to destroy seasonal information. Specifically, the authors state on page 1083, line 11 that "melt events have only a minor influence on the seasonal climatic signal determined from the delta-18O signal in Svalbard cores". This statement seems to say that seasonal information should exist in the firn core for halogens. The fact that seasonal cycles are not very evident for the halogens then seems to indicate that post-depositional processes may affect the halogens, which would cloud the interpretation here. Specifically, Fig. 3 doesn't seem to show any annual cycling, and Fig 4 is said to show annual cycling in "in the upper part of the core". The annual cycling seems to be two years, which is not very convincing given the apparent lack of cycling in prior years. If the argument being made is that Br and I are enriched during early springtime (March-May), why doesn't the data show that? Toom-Sauntry and Barrie (Atmos. Env. 36, p2683, 2002) show a very strong seasonal peak for bromide enrichment in March-April-May, with enrichment factors compared to sea salt ratios using sodium as a sea salt tracer having values up approaching 100x sea water ratios, while fall and winter values are much closer to sea water ratios. It seems surprising that such a strong seasonal cycle should not be retained in the snowpack. Possibly in the case of I, the season is longer, and arguments are made for Autumn I production, so one might expect I to show less annual cycling. Overall, my point is

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that why should water show annual cycling but halogens, which are hopefully faithfully archived, not show annual cycling?

Following the findings by (Pohjola et al., 2002) the conservation of the  $\delta^{18}\text{O}$  profile suggests the preservation of the climate signal in at least the observed temperature profile. However, we never state that the seasonality of the other species are preserved, and indeed we note that the bromine enrichment signal could have been smoothed by percolation. We agree with the referee that the disappearance of seasonality below 150 cm w.e. depth is likely due to the presence of meltwater percolation. On account of this likely mobilisation of bromine due to percolation, we focus our attention on the bromine/sodium concentration ratio. As suggested by (Bales et al., 1989) these two elements have a similar percolation "speed" meaning that the ratio is not strongly influenced, however the loss of seasonality seems to confirm that percolation probably smooths this signal. As the referee suggests, the loss of seasonality, especially for bromine, can be associated with summer melt and percolation. The most important parameter influencing bromine enrichment seems to be the bromine explosion events occurring in seasonal sea ice during springtime. Unfortunately the quality of the Svalbard core is not equal to those from Antarctica or Greenland, however we can recognise the influence of sea ice in the halogen deposition record. Regarding halogen enrichment, (Sturges and Barrie, 1988) first detected a bromine enrichment ratio of approximately 100 at Alert station, subsequently confirmed by Toom-Sauntry and Barrie in 2002. We need to consider that they studied coastal areas, very close to the sea ice regions where bromine explosions occur. We also measured bromine enrichment in the Antarctic Talos Dome ice core (Spolaor et al., 2013) and identified sea ice to be the main source for bromine enrichment. The importance of transport processes must be stressed, due to the fast rate of HBr deposition compared to sea salt aerosol. The Talos Dome ice core results (Holocene Br enrichment ratio approximately 3) are of the same order as the results obtained from the Høltedahlfonna shallow core. It is likely that the strong enrichment observed at the Greenland coast could be modified and lost during transport (Spolaor et al., 2013). We need to remember that the Høltedahlfonna core

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site is located at 1150 m.a.s.l and approximately 100 km from the Arctic sea ice edge. Iodine and bromine measurement from glacier snow around Ny-Alesund, at lower altitude (400 m.a.s.l.) and much more exposed to the sea ice in the Kongsfjord show %Brenr values from 20 to 60. This analysis was conducted in 2011, the year before our drilling. It is likely that the enrichment decreases moving from sea level to greater altitudes. For this reason we cannot directly compare the enrichments observed at coastal areas with those at altitude.

The authors attempt to minimize the possible influence of depositional and postdepositional processes. However, we are aware of significant snowpack chemistry of bromine species and snowpack chemistry is also likely for iodine species. Pratt et al. (Nature Geoscience, DOI: 10.1038/NGEO1779) document that irradiated snowpack can produce halogen gases, and observations of bromide ions in snow indicate that some samples can be depleted in bromide (e.g. Krnavek et al., Atmos. Env. 50, p249, 2012). The observations of the highest amounts of iodine in the snowpack near the surface, and lower values in buried snow might also be an indicator of post-depositional loss of iodine. These known post-depositional processes seem likely to be modifiers of snow / firn composition.

Pratt et al. (2013) have greatly improved our understanding of the processes that cause the bromine explosion in sea ice. In addition the paper describes the mechanism that causes bromine emission from snow. The main factors involved in this process are snow acidity and the Br/Cl ratio. Our samples show an average pH of 5.3. Unfortunately we did not measure Cl but assuming that the source of chlorine is almost totally derived from sea spray we can estimate this from Na concentrations (Bigler et al., 2006). The post depositional mobility of chlorine is very poor (Ayers et al., 1999) and it is likely to be conserved in the core. Using this approximation we can calculate the Br/Cl ratio. Without the surface sample (0-5 cm) where the ratio is 1/57 all the other samples show values above 1/200 with an average of 1/333. These results suggest, as denoted by Pratt et al (2013), that bromine emission can occur only in the first centimetres of

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snowpack and is unlikely to occur in lower strata. They also suggest that surface snow (0-8 cm) could be a source of gas phase bromine while the sintered snow (8-18 cm) is a source only at higher ozone concentrations. The post-depositional processes relevant to bromine are quite difficult to estimate. In Antarctica satellite measurements do not show bromine emission above the Antarctic plateau suggesting that re-emission could be negligible. This may be due to temperature; (Oldridge and Abbatt, 2011) suggest the activation of Br is also temperature dependent where no activation has been detected for temperatures below -25°C, theoretically limiting Antarctic Br activation to coastal areas. For the Northern hemisphere, such a temperature limitation only restricts the highest-altitude areas of Greenland. In conclusion we cannot exclude post-depositional bromine emission at our drilling site however considering that almost all samples show enrichment with values similar to Talos Dome; that a decrease in bromine enrichment is plausible from the sea ice level up to higher altitude; and that our samples show similar characteristics to the sintered snow defined by Pratt et al (2013) we can suggest that the re-emission of bromine is a minor aspect controlling the post depositional effect. The main disturbing factor is likely to be meltwater percolation that smooths the signal and destroys seasonal variation.

The use of pan-Arctic tracers of the state of the sea ice seems like a poor choice, at least for bromine chemistry, which is probably much more regional in nature. The general reactivity of iodine, and the observations of Mahajan et al., 2010) that iodine chemistry is associated primarily with upwind open leads or polynyas also indicate a regional nature to iodine chemistry. Therefore, it would seem useful to produce regionally representative sea ice products to compare with the pan-Arctic metrics used here. The authors make what is likely a good argument that Comiso et al. (2002) find that trends in various sectors of the Arctic approximate the overall trend. If this is the case, then regionally representative sea ice metrics would be correlated to the pan-Arctic metrics shown here and the authors would have a stronger argument than what is presented here. Given the availability of high-time-resolution sea ice data for this period, calculation of regional sea ice indexes is achievable.

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We agree with the referee and have modified our interpretation. Please consider our responses to similar concerns raised by referees 1 and 2.

Minor / technical points:

The manuscript makes use of seasons (e.g. early spring). These periods are not always consistent between past papers, so use of the term plus month (or month range) from the referenced papers would be of assistance in determining that part of the annual cycle is being discussed. Please consistently use either month names or season description with month names in brackets after the description.

We agree with the referee and we improved the manuscript as suggested. We use March-May sea ice to describe the spring sea ice while we keep the term seasonal sea ice.

p1077, line 15: It would be useful to mention the early satellite period average summer minimum sea ice extent. The September 2012 value was just about 50% of the early satellite period, which is an importantly large change

We improved the sentence.

p1084, line 7: If Na is not to be used as a conservative tracer here, should some other normalization be used?

The referee may have misunderstood our intention. We do apply sodium as a well established sea spray deposition proxy and conservative marine aerosol deposition tracer, widely used in the interpretation of ice core data.

p1084, line 25: I think it would be more accurate to say that "It is possibly due to the greater thickness....", as questions of how iodine escapes sea ice are not well established at this point.

The referee is correct that there is no complete explanation for iodine emission from sea ice, only observations. We have improved the sentence. We would like to make note

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of a recent paper by Zhou et al., (2013) suggesting that arctic sea ice is impermeable for almost all of the year except during May.

p1085, line 3: This section is a bit confusing because the maximum I concentration is not seen as peaking in the springtime from the firn core data – no seasonal cycle is evident in the I concentration – but instead, a month-selected ice extent is being compared. One could read this to say that I peaks in the firn core data. Please reword.

We rewrote the sentence

p1086, lines 14-16: I don't see how one can argue for in-situ smoothing of I without in-situ smoothing of water isotopes.

We do not have the data to assess this statement, but Pohjola et al. (2002) conducted a specific study regarding ion remobilization due to percolation phenomena. They studied the re-mobilization of water isotope, acid and others species in the Lomonosovfonna ice core in Spitsbergen, Svalbard (1255 m.a.s.l.). Our shallow core drilling site is located a hundred meters below (1150 masl) and therefore we can consider similar percolation phenomena. The authors clearly state that “As a consequence of percolation, the most mobile acids show up to 50% higher concentrations in bubble-poor ice facies compared with facies that are less affected by melt. Most of the other chemical species are less affected than the strong acids, and the stable water isotopes show little evidence of mobility”. This paper clearly shows that the percolation has a varied effect on ionic species compared to water isotopes. For this reason, though the isotopic signal is well preserved, a smoothing effect for iodine could be possible.

p1087, lines 14-15: The fact that Br is generally enriched indicates that enrichment dominates over depletion, not that depletion doesn't sometimes exist. In fact, enrichment on the order of snow observations from Toom-Sauntry et al. (2002) are much higher than shown here, so the lower values seen here may indicate some depletion in addition to the enrichment process

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As we have responded to a previous question (in the major comments), it would be inappropriate to compare inland bromine enrichment values to those from coastal sites, especially those close to first year sea ice such as Alert or Barrow. It is likely that the enrichment is strongly influenced by altitude and transport processes (Spolaor et al., 2013).

p1087. lines 23-24: This statement is not well supported in the data. Annual cycling that would indicate cool season versus warm season is really only evident in two years of data from Fig. 4. The caption somewhat captures this idea, but the text seems to say that there is general cycling with temperature, which is not seen.

Changed accordingly p1087, line 25: The seasonal peak of Br enrichment is likely due to the high latitude site of Alert and the seasonally later polar sunrise at that location, not really a direct function of temperature.

We added the phrase “during the polar sunrise”.

p1088, lines 2-4: This sentence is awkward and should be reworded.

We changed the sentence to the following: The highest Arctic atmospheric BrO values are located above the seasonal sea ice and decrease above the older multiyear sea ice . . . . .(line 362)

p1090: The conclusions should more clearly point to post-depositional processes as possibly being evident in the data and the need to understand them to interpret these data more fully.

We improved the conclusion as suggested by the referee

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