**Atmospheric
Chemistry
and Physics**
Discussions

Interactive comment on "Halogen species record
Antarctic sea ice extent over glacial-interglacial
periods" *by* A. Spolaor et al.

A. Spolaor et al.

andrea.spolaor@unive.it

Received and published: 10 June 2013

REFEREE 2: ANSWER MAIN QUESTION 1. Landfast sea ice extent vs. seasonal sea ice extent The authors underline that bromine explosions are frequently associated to frost flowers events on sea ice, and these are usually associated to young sea ice (<20 cm thick). This would typically occur in seasonal sea ice (first‐year sea ice), as opposed to multiyear sea ice, which is thicker and confined to protected coastal areas. For the transport distance argument used (and modelled) by the authors to be a valid explanation for depleted bromide during glacials, we need to look at the glacial extent of multiyear sea ice, and not seasonal sea ice. I am not sure we have proper documentation of the glacial extent of multiyear sea ice. If we do, then it is

crucial that the authors put it forward in their manuscript, otherwise their argument doesn't necessarily hold. In other words, if glacials are mainly characterized by an increase of seasonal sea ice cover (with no significant change of multiyear sea ice), then glacial periods would also favour frost flore formation on a larger surface area and not significantly further away from the coast)

The referee is correct in saying that we propose multiyear sea ice (MYSI) extension as the main driver to explain our bromine data. There are few, and sometimes contradictory, data available regarding MYSI extension during glacials. The available data do suggest a more extended seasonal sea ice (SSI) during glacials, but for multi year sea ice the approach is more complicated. (Gersonde et al., 2005) suggest that an increase of MYSI occurred but this has not been demonstrated for all sectors of the Antarctic coast. Our data are compatible with an increased MYSI extent during glacials. It is important to recognize that seasonal sea ice is the hotspot for bromine enrichment (as also has been suggested for Arctic bromine fluxes) while MYSI is unsuitable for gas phase bromine production as it is not an area of frost flower formation. We agree with the referee that a thorough explanation of the observed bromine fluxes and depletion has to account for both multiyear and seasonal sea ice behaviour. To answer the referee in detail, we need to consider both bromine fluxes (fig.3) and bromine depletion (fig.4). First of all the referee suggests that "if glacials are mainly characterized by an increase of seasonal sea ice cover (with no significant change of multiyear sea ice), then glacial periods would also favour frost flower formation on a larger surface area and not significantly further away from the coast". We have also considered the possibility of biological Br production, but the poor correlation between Bromide, MSA and nss-sulphate seem to suggest only a marginal role of biological production in the total bromide flux. Greater bromine fluxes during interglacials are therefore most likely explained by a reduced total extent of MYSI and SSI during interglacials.

Total bromine fluxes do not indicate if only one of MYSI or SSI was reduced during interglacials, but it does indicate that there was a reduction of at least one type of

Antarctic sea ice. This uncertainty can be resolved by evaluating the depletion (or enrichment) of bromine with respect to sea salts, in this case we use sodium. The key factor here is the observation that Br and Na have different deposition velocities, hence there will be a depletion of Br with respect to Na as they are transported from their emission sources. Both Br and Na are sourced from the open ocean (hence the SSI margin) although Bromine is enriched above seasonal sea ice during bromine explosion events. Br- is reactive and can be removed from sea spray droplets by conversion to HBr while in the gas phase form, or due to absorption into aerosol droplets. Bromine will be enriched with respect to Na above seasonal sea ice, but will become depleted with respect to Na as it travels over MYSI and into the interior of Antarctica. If, during the glacial, the main change in sea ice extension was due only to an increase in seasonal sea ice extent, we should expect to have an enrichment in bromine compared to sodium. Instead, we observe a depletion of Br during glacials, which can only be explained by either a substantial reduction of SSI (incompatible with the findings of Gersonde et al., 2005), or an increased glacial extension of MYSI. Multiyear sea ice is effective in increasing the sea salt aerosol travel time and therefore promoting the depletion of bromine with respect to sodium. Based on the available data, an increase in multiyear sea ice is the most likely explanation for both the bromine flux decrease and aerosol depletion observed during the last two glacial periods.

2. Model for Bromide depletion

The choice for the many inputs in this model is not argumented enough, which gives the impression that it is extremely tuned to provide the adequate outputs. It is therefore dangerous to use it to pull out and compare sea ice extents during the two documented glacials

The purpose of the modelling is to provide a plausible explanation for the variation in Brdep measured at Talos Dome over several glacial cycles. It is not possible to demonstrate unambiguously that the variation in sea-ice extent caused these variations by using a simple 1D transport model where several parameters are poorly known (as

pointed out in the paper). Rather, our objective is to show that by choosing sensible values of these parameters it is possible to explain the variations in bromide depletion levels, and to estimate the change in the sea-ice extent between glacial and interglacial periods which turns out to be in good agreement with an estimate made with microfossil records (Gersonde et al., 2005).

This point is now made at the start of Section 3.1.1 in the revised paper. We obviously hope that the publication of these measurements will encourage more sophisticated modelling efforts in the future.

3. Geometry of the experimental device for IO3 âĂŘ reactivity

The concept and geometry of the experimental device for IO3 âĂŘ reactivity could be more clearly depicted (see detailed comments below). I wonder if the design is not also prone to limit potential degassing of iodine oxide, given the freezing geometry (from the outside to the inside?). I am also not sure that it is a good analogue for processes occurring in the dry polar firn.

The geometry of the experimental device was initially used for study the iodine reactivity in water (also sea water) solutions. The system favours the formation of Iodine oxide particles that can be detected by the TAPCOM instrument. The system has been designed to be robust and able to consistently reproduce the same initial conditions. Studying iodine reactivity is always complicated because this halogen is able to react with many species and by different mechanisms. The importance of having a system that is able to reproduce very similar initial conditions is crucial to determine the variables that influence iodine reactivity. We know that the geometry is not optimized for the reproduction of environmental conditions but it is suitable for understanding which processes act on frozen iodate solutions, much more closely than for liquid water environments.

RESPONSES TO SPECIFIC COMMENTS

40-45. If the open ocean is the main source, then Iodine should not be dominant during glacials, where a larger proportion of the ocean is covered by ice (?)... Or it needs to be proven that the sea ice signal is dominant over the oceanic one for the rationale held in this paper to be valid!... Is it the release of Iodine in the retreating Marginal Ice Zone that dominates the signal? If yes, then the more seasonal ice, the more extended the MIZ and indeed the more iodine is provided...but has this relationship been proven?

There has been a recent change in the scientific community regarding iodine processes and sources around Antarctica. Iodine is emitted from the ocean by the biological production and also by inorganic reaction with ozone in surface waters. However recent satellite measurements have contributed to an improved understanding of iodine chemistry in the Antarctic region, clearly demonstrating that sea ice, particularly thin seasonal sea ice, is a hotspot for iodine emission to the polar atmosphere (Atkinson et al., 2012;Saiz-Lopez et al., 2007). Sea-salt iodine emission from the open ocean is normally less than 1% of the total atmospheric concentration of iodine. The increase of iodine fluxes during the glacial is mostly due to the increase of seasonal sea ice extent during cold periods, which allows an increase in the area of under-ice substrate required for the growth of sea ice algae.

62 – IO3- This would be the case for most of the sea ice, even in the winter when there is no primary production and heterotrophy dominates

No data are available regarding the seasonal variation in the total iodine flux in Antarctica and changes in its speciation. However the aim of this manuscript is not to investigate the seasonality in iodine speciation, and the data reported are unsuitable for the evaluation of seasonal cycles. In addition the accumulation rate at the Talos Dome site is quite low, which could favour the conversion of iodate to iodide.

87-90 Bromine explosions promoted by frost flowers growth. Then, it is the glacials (with increased occurrence of thin ice leads between ice floes) that should show high bromine levels, isn't it? This is a bit misleading for the rationale of the paper...the

whole discussion about source vs. transport...

In general frost flowers and brine growth on the seasonal sea ice surface occurs in both glacial and interglacial periods. During glacials there is evidence of greater seasonal sea ice extent and consequently greater bromine production. Our data indicates lower glacial Br fluxes and Br depletion with respect to Na, for which the most consistent explanation is a substantially increased multiyear sea ice extent during glacials.

112 - 250 ky before present. References?

The reference has been added.

150 – Reactivity. Does this mean production of iodine gas?...please extend for nonâĂŘspecialists

We have amended the text. We mean to say the capability of iodate to react with other compounds to form reduced species.

151 – Reference

This work.

159- Not clear. I guess the cell was only halfâĂŘfilled to allow the gas to escape and be entrained in the flow? Did the geometry of the freezing allow efficient recovery of the iodine gas phase? It looks like ice growth was centric...which is not good, since all the gases will be concentrated in the (central) last frozen fraction

The referee is right, that the cell has only been half-filled to permit the gas flow to pass above the ice surface. The text has been improved to make this clear. The geometry of the freezing chamber has been kept constant, and we have followed the same procedure, in order to have reproducible results. As the referee points out, the concentric freezing could accumulate the gas in the centre of the ice. However in the absence of light and ozone, no possible reaction could occur with iodate and consequently no gas phase iodine can be formed. After the freezing process the light was switched on and

ozone added into the cell.

162 -The gas phase iodine produced. How? From the freezing process?

The gas phase iodine has been produced after the freezing process, not by a physical process. After the iodate solution has been frozen, we then start to add ozone and switch on the light. Our results suggest that light is the main driver for iodine gas phase formation from an iodate frozen solution

161-167 Please synthesize in an equation, easier to grab for a larger audience

These are a series of reactions and it is not possible to compress them into one. Several aspects work together to produce the iodine oxide particle from the formation of ozone in the mercury lamp, to the combination of tungsten lamp and ozone which contribute to IOP production and growth.

R=0.54 This is really not very strong. Not sure it means anything. For example, at ca. 50 ka, it looks like it is positively correlated. . .

The estimated correlation between sodium and bromide R=-0.54 is statistical significant given the bootstrap 95% confidence interval [-0.40, -0.64]. However, since sodium and bromide have the main reservoir in the ocean, then it is expected a positive correlation between the two elements. The fact that we observed a significant negative correlation is likely a consequence of the unmeasured relationship (sea ice could be the driver) between sodium and bromide. The observed negative correlation between Sodium and Br is of interest because they both feature the ocean as their main reservoir. The observation that these two ocean-derived elements are negatively correlated is indicative of different atmospheric transport, transfer and deposition mechanisms. We attribute this negative correlation to the influence of Br explosion events as well as the removal of gas phase Br from sea salt aerosols as they are transported toward the Antarctic interior.

218-219 This concept is misleading, since it can also indicate enrichment (negative

values). I would choose a more "neutral" and unambiguous expression, such as, for example, "bromide fractionation index/factor/%".

At the present time we know that bromine explosions can inject gas phase bromine into the atmosphere enriching the Br/Na ratio compared to sea water. While in interglacial times we detect an enrichment, during glacials we detect a depletion of bromide compared to the sea water ratio based on sodium. The main finding of the paper is the depletion of bromine during glacials; we try to highlight this aspect and this is where we focus our calculations. However we agree with the referee and we changed the bromide depletion percentage (%Brdep) into Bromide fractionation index (%Brfi)

223 Sea ice presence Measured how? Please give details

Sea ice presence has been calculated by Crosta et al. 2004 using Modern Analog Techniques (MAT5201/31) applied to fossil diatom assemblages in the SO136-111 core, located at 56°40'S and 160°14'E. SIP is expressed as months of sea ice presence per year. This explanation is already included in the text.

230-231 This is ambiguous. Why not in autumn, where sea ice growth starts?...Bromide explosions are generally associated to thin ice formation in leads and brine expulsion under strong cooling, which should decrease in intensity during the Spring, when the ice warms up

Satellite and field measurement clearly demonstrate that bromine explosions occur in the spring time and not in autumn. The referee is correct that during the autumn the strong cooling could favour the formation of frost flowers but the light intensity and environmental conditions are not favourable to produce bromine explosions. In addition a recent paper by (Pratt et al., 2013) suggests that in the Arctic bromine explosions are mainly due to the fresh snow above the sea ice due to its acidic behaviour. However no corresponding data are available for Antarctica so we still consider frost flowers to be the main source.

235–237 Increased multiyear sea ice extent during glacials Do we have proof of this? This is counterintuitive when looking at present–day multiyear sea ice around Antarctica. It is limited and mainly located in bays or areas sheltered by ice shelves or ice–tongues. During glacial times, these areas sheltered from the circumpolar currents should have been less frequent as the ice sheet advanced on the continental platform. This hypothesis is fundamental here, and it should be relying on proxies for landfast sea ice paleo–extent (and not pack ice) – please give reference and elaborate!

The Multi year sea ice presence has been investigated only in a few papers and no specific reference can be cited for its reconstruction. The best available assessment was reported by Gersonde et al. 2005, who evaluated summer sea ice margins, which can give insights into the extent of multi year sea ice. Gersonde et al. 2005 based on sediment core assembly found variable results for the extention of summer sea ice at the LGM, with evidence for a modest increase in LGM summer sea ice extent (around 300 km) in the Indian sector of the southern ocean, and sporadic evidence for a greater increase in summer sea ice extent in the Weddell sea (Atlantic sector) of the southern ocean. Gersonde et al., 2005 (p.891) conclude that 'it can be speculated that the seasonal changes of the sea ice field that at present range between 4 x 106 km2 (summer) and 19x106 km2(winter) (Comiso, 2003) changed to a range between ca 5–6 x 106 km2 (E-LGM summer) and 39 x 106 km2 (E-LGM winter)', suggesting a maximum increase in multiyear sea ice extent of 25 to 50%.

238–247 This is a "corner stone" of the paper...I would strongly recommend it to be illustrated with a "cartoon".

We agree with the referee and we add a cartoon (now Figure 5) illustrating the process proposed. Please see the attach the pdf file for the new figure.

256 Constant Na flux Not clear in Figure 3

Figure 3 has been improved

C3334

270–272 780 km Did Scharchilli et al., 2011 resolve the location of the landfast sea ice margin during the glacials?

Scarchilli and coworkers investigated the modern air mass velocity and transport time in several Antarctic sites. Based on the observed depletion of Br relative to Na in glacial Talos Dome samples, we calculate that the airmasses travelled approximately 780 km from the summer sea ice edge to the deposition site. This value is based upon the availability of Holocene EPICA Dome C samples, located about 900 km from the Antarctic coast, which were used to calibrate our Br depletion model. Considering the distance between Talos Dome and the coast (280 km), we therefore calculate the maximum extent of multiyear sea ice to be 500 km. As noted earlier, Gersonde et al. 2005 found evidence of multi year sea ice at 63°S, extending 300 km furthern than the modern summer sea ice extent in the Weddell sea sector. Scarchilli et al. show that the air mass trajectories reaching TD are cyclonic, and hence are curving southward as they approach the site, therefore we consider the calculated glacial multiyear sea ice extension of 500 km, to be an upper estimate.

276 "typical measured values" Reference?...are these data frequent? Or is this all from Halley data? There must be data from places such as Dumont Durville, which is a bit closer to Talos Dome (?)

Yes, these data are "typical" of Halley Bay in summer, as discussed in (Saiz-Lopez and Boxe, 2008). The data were produced in the large-scale atmospheric chemistry CHABLIS campaign which ran for nearly 2 years. Halley is a coastal station (roughly 20 km from the sea ice edge). of theThis is now made clear, and two more references are added – an overview of the CHABLIS campaign (Jones et al., 2008), and measurements of non-methane hydrocarbons (Read et al., 2007).

280–281 The initial sea–salt aerosol loading was set... Justification? Reference?

The initial sea-salt aerosol loading was chosen to be somewhat higher than the 4-year

C3335

average of 1400 ng m-3 measured at the coastal Antarctic station of Dumont D'Urville, which was stated to be a lower limit because of sampling size cut-offs (Wagenbach et al., 1998). The prevailing wind at Dumont D'Urville is directly onshore (average 9.5 m s-1) and the station is on a small island, and so provides a reasonably close match to the model scenario.

283âĂŘ285 Deposition velocities for HBr , HI, sea salt aerosols set to Please justify those choices and give references.

The choice of deposition velocities has now been explained in more detail. The deposition velocities of HBr and HI are typical of measured velocities of hydrophilic gases – a general reference is now provided. The deposition velocity of the sea salt aerosols is a "tunable" parameter. The deposition velocity is quite size-dependent (being larger than 0.2 cm s-1 for particles smaller than 0.1 μm or larger than 4 μm, and reaching a minimum of about 0.1 cm s-1 for 2 μm diameter particles (Ma and Daggupaty, 2000)). This deposition velocity therefore represents an average over the sea-salt size distribution, and is treated as a fitted parameter in the model.

293 An I2 flux was generated Justify, reference?

This is the flux required in the model to produce this level of IO, so is an adjustable parameter (the term "generated" is misleading and has been changed to "required"). We have also added a comparison to the flux required to generate the higher IO levels observed during summer at Halley Bay.

298âĂŘ299 . . .good agreement. . . This whole paragraph on modelling sounds extremely multituned to reach the observed values at the appropriate distance!...see indeed lines 299âĂŘ300! What should be demonstrated here (with appropriate justifications) with more certainty is that the enrichment at the source is overcompensated by the "en route" depletion. . .

As emphasised in the new opening paragraph of this section of the paper, the purpose

of the modelling is to demonstrate a plausible scenario using sensible choices of parameters. We are not claiming that such a simple model does any more that this. We have added a sentence stating that an important conclusion is that, for the model to predict the change in %Brdep with travel time from the sea-ice edge, the deposition velocity of HBr needs to be at least 3 times larger than the average sea-salt aerosol deposition velocity, which is consistent with dry deposition theory and measurement.

306âĂŘ307 Travelled approximately 300 km How does this compare to presentâĂŘday distance of TD to firstâĂŘyear/multiyear sea ice in the area?

Satellite images clearly show that during summer only a small area of sea ice remains intact. This multi year sea ice is very close to the coast and we considered that the interglacial situation was well represented by this situation. This means that the seasonal sea ice could grow very close to the coast. The distance chosen for the interglacial period of 300 km is the distance between Talos Dome and the coast (on average) which could range from 200 km up to 350 km.

310 estimates . . .Gersonde et al., 2005 Do these estimates really place the limit of multiyear sea ice so far? I would doubt that!... I am not aware of a specific tracer for discriminating first year from multiyear sea ice. . .but maybe it indeed exists!... needs to be mentioned then. If Br explosions are the main driver, since it occurs at frost flowers over thin ice surfaces, it is a general feature of any first year ice. Therefore, it is the limit between multiyear and firstâĂŘyear sea ice that has to be considered. Sea ice was indeed much more extended during glacials, but it could be that it is essentially the result of an increase of the seasonal (firstâĂŘyear) sea ice cover!...

As mentioned previously, no specific reconstruction of multiyear sea ice extent is available for the Talos Dome air mass sector, and only sporadic reconstructions have been produced based on marine sediment records. The available evidence does support a northward extension of summer sea ice by 300 km, which could be compatible with cyclonic airmasses travelling 500 km from the summer sea ice edge to the Antarctic

coastline. The primary aim of this work is to report independent evidence to support the findings of Gersonde et al., (2005) for a persistent glacial extension of MYSI in the Pacific and Indian sectors of Antarctica. This finding is based on our proposed model for interpreting Br depletion with respect to sea salt aerosol. Further modeling and data assimilation will be necessary to fully calibrate and verify this hypothesis.

315 Algae on the underside of the iceAlgae communities are not only located at the underside of the ice, is this the only community documented?...Flooded sea ice (leading to snow ice formation) âĂŘ the proportion of which might change strongly between glacials and interglacialsâĂŘ favours the development of surface communities, are these as efficient in producing iodine?

Atmospheric iodine can be produced by several mechanisms. The role of primary production in open ocean was suggested to be the main driver (Vogt, 1999), however recent developments in satellite measurements and ground truthing clearly show that the sea ice area is a hot spot for gas phase iodine production. In particular, it has been suggested that sea ice algae (Saiz-Lopez and Boxe, 2008;Atkinson et al., 2012) are the main driver of atmospheric iodine concentration in the Antarctic region. The open water surface community are still able to produce iodine however available satellite and field measurements clearly show that the main source of atmospheric iodine is likely the algae growing under the seasonal sea ice.

319-320 Again, if that is the case, then there should be also a higher frequency of bromide explosions events!

We agree with the referee that during the glacial more bromine explosions were likely however the main factor influencing bromine depletion is the transport time and path length. If, during the glacial, we have more seasonal sea ice then one would expect greater bromine enrichment compared to the interglacial. As the data show the opposite, we have to invoke other mechanisms to explain the observed bromine fractionation. Based on our halogen model and comparisons of Br/Na at Talos Dome and Dome

C, we have attributed differential deposition velocities (determined by air mass transport time) as the dominant factor controlling Br depletion. In the case of more abundant bromine explosions during the glacial, the increased extension of multi year sea ice has the effect of increasing the transport distance of seasonal sea ice and hence favours a greater proportional deposition of bromine compared to sodium.

325 a) Several papers on iron in sea ice suggest that most of the iron is inherited from ocean upwelling and scavenging and that dust fluxes are weak contributors today

We agree with the referee. Iron fertilization is still an open debate since there are many uncertainties regarding iron solubility and the uptake of iron by marine phytoplankton. However a recent study (Vallelonga et al., 2013) suggests that aeolian iron deposition contributes only marginally to the total amount of carbon sequestered by activation of the biological pump. Iodine is only biologically emitted by marine algae, therefore if iron deposition had a strong effect on the biological pump during the glacial we should expect a correlation between iron deposition and iodine concentration. Instead we observe that these elements are only poorly correlated, which is consistent with a minimal influence of dust deposition on marine primary productivity.

b) There is a peak in dust that is not reflected in I- between 170âĂŘ200 ka

As we show by correlations, Iodide shows a similar trend to sodium rather than dust. Only iodate shows a correlation with dust, as this iodine species can accumulate on dust particles and may form metal iodates which are preserved from post-depositional degradation. The correlation between sodium and iodide instead suggests a similar source as well as a similar transport path from the ocean to the Antarctic continent.

335âĂŘ336. Given the uncertainties, this simply goes too far in the interpretation!

The referee is correct that our interpretation is based on a number of assumptions, and there are few reliable studies available to support the assumptions we have made. We acknowledge that one of the most critical assumptions is the assumption that deposi-

tion rates and wind speeds are consistent during glacials and interglacials. Regarding our reconstruction of Pacific sector seasonal sea ice extent, the only study available for comparison is that of Gersonde et al. (2005), which has already been discussed in detail. We note that the estimations of sea ice extent reported by Gersonde et al. 2005 were obtained by evaluating diatom assemblages around Antarctica during LGM, and assessing the presence of cold-water indicating diatoms during periods of summer sea ice coverage. Gersonde et al use a process of deduction to evaluate summer and winter LGM sea ice extents, with sporadic sampling coverage, yet conclude that seasonal sea ice during the LGM did extend further north than present limits, but not as far as earlier estimated by the CLIMAP effort. Other studies, summarised by Gersonde et al (2005) have shown that LGM seasonal sea ice was present up to 56°40' S (Crosta et al., 2004), at least 700 km further north than present seasonal sea ice extent. Despite the speculative nature of our data interpretation, we repeat that our interpretation is based on sound assumptions and that the interpretation is consistent with the most recent and accurate studies reported in the literature.

356 What arguments do we have to say that IO3 was initially present everywhere?

Modern aerosol measurement and atmospheric modelling show and suggest that iodate is the main stable species of iodine in the atmosphere, at least in fresh aerosols (< 2 days). This species is also found commonly in the aerosol fraction. Lab and field experiments show that iodate can be reduced to other species, and it has been suggested that the presence of humic acid could be the key step for the reduction of iodate. Iodate is also present in snow deposition (though at lower concentrations) as found by Gilfedder et al. For the reasons listed above we expected to find iodate in all samples but instead we detected iodate only at colder and dusty time periods.

366 - All the experiments were run by freezing water. Besides the fact that the geometry of the setting might have influenced the amounts of IOP produced, we have to remember that the polar snow pack is devoid of liquid water. The authors should at least comment on the reasons why they think frozen water and cold snow firn would

behave similarly!

The aim of the experiment was to investigate the possibility of iodine reaction in the ice. Laboratory reproduction of natural snow conditions is very difficult because, during different experiments, the distribution of iodate in the snow could change, as well as the diffraction of light from the snow surface, could change thus making the experimental set-up different from one experiment to another. We know that firn and ice can have different behaviours but the intent of the experiment was to identify if iodate reactions could be driven in presence in ice instead of water media. While no IOP formation was detected by irradiating a solution of iodate, IOPs were detected when the solution became frozen. This finding suggests that some reduction of iodate could be promoted in the snow pack. Together with the previous question the absence of iodate in the snow may be explained by these results.

386-388 Again, this would be very different in cold firn in nature!

We agree with the referee. However in the lab we must create conditions that we are able to reproduce to better understand the main reaction steps of IOP formation from a frozen iodate solution.

402âĂŘ403 This is ambiguous. Are you meaning multiyear sea ice extent?

Yes we have used the term "summer sea ice extent" interchangeably with "multiyear sea ice extent". We note that "summer sea ice extent" was the term used by Gersonde et al. (2005) and have amended all mentions of this term for consistency.

403 - As said before, care should be taken here!...if Bromide explosions is susceptible to occur at all seasonal sea ice location , it is the extent of multiyear sea ice that should be considered. . .and I am not convinced the latter was 500 km out during glacials.

Few references are available for a detailed investigation of past Antarctic sea ice extent, although the best available is that of Gersonde et al. 2005. Considering that during the present time, multi year sea ice is almost close to the coast and can be considered

almost absent. During glacial times, sediment cores KR88_22/27/29 suggest that the multi year sea ice edge was located at least 300 km from the present Antarctic coast. We note that these cores are located in the Indian sector of the southern ocean while the area of influence for Talos Dome is mainly located between the Indian and pacific sectors, beyond Victoria Land. Our simple model result suggests a 500 km increase in airmass travel distance from the sea ice edge to Talos Dome. Such an estimate is consistent with the current scientific understanding, despite all of the uncertainties that remain in the bromine transport process and the possible variability of multi year sea ice extent in different Antarctic sectors.

405: This is also very speculative, based on an hypothetic linear relationship between maximum sea ice extent and Iodine. . .

We agree with the referee but repeat that recent satellite observations clearly show that iodine is mainly emitted from the seasonal sea ice regions, and indicate that sea ice algae play a dominant role in controlling iodine concentrations in the polar atmosphere. Additionally, the results obtained by Gersonde et al. 2005 show that the winter(seasonal) sea ice extent increased by 100% compared to the present, which is consistent with our reported findings.

Atkinson, H. M., Huang, R. J., Chance, R., Roscoe, H. K., Hughes, C., Davison, B., Schonhardt, A., Mahajan, A. S., Saiz-Lopez, A., Hoffmann, T., and Liss, P. S.: Iodine emissions from the sea ice of the Weddell Sea, Atmos. Chem. Phys. Discuss., 12, 11595-11639, 2012. Crosta, X., Sturm, A., Armand, L., and Pichon, J.-J.: Late Quaternary sea ice history in the Indian sector of the Southern Ocean as recorded by diatom assemblages, Mar. Micropaleontol., 50, 209-223, 2004. Gersonde, R., Crosta, X., Abelmann, A., and Armand, L.: Sea-surface temperature and sea ice distribution of the Southern Ocean at the EPILOG Last Glacial Maximum–a circum-Antarctic view based on siliceous microfossil records, Quaternary Sci. Rev., 24, 869-896, 2005. Jones, A. E., Wolff, E. W., Salmon, R. A., Bauguitte, S. J. B., Roscoe, H. K., Anderson, P. S., Ames, D., Clemitshaw, K. C., Fleming, Z. L., Bloss, W. J., Heard,

D. E., Lee, J. D., Read, K. A., Hamer, P., Shallcross, D. E., Jackson, A., Walker, S., Lewis, A. C., Mills, G. P., Plane, J. M. C., Saiz-Lopez, A., Sturges, W. T., and Worton, D. R.: Chemistry of the antarctic boundary layer and the interface with snow: an overview of the CHABLIS campaign, Atmos. Chem. Phys. Discuss., 8, 5137-5181, 10.5194/acpd-8-5137-2008, 2008. Ma, J., and Daggupaty, S. M.: Effective Dry Deposition Velocities for Gases and Particles over Heterogeneous Terrain, Journal of Applied Meteorology, 39, 1379-1390, 10.1175/1520-0450(2000)039<1379:eddvfg>2.0.co;2, 2000. Ordóñez, C., Lamarque, J. F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Sousa Santos, G., Brasseur, G., and Saiz-Lopez, A.: Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources, Atmos. Chem. Phys., 12, 1423-1447, 10.5194/acp-12-1423-2012, 2012. Pratt, K. A., Custard, K. D., Shepson, P. B., Douglas, T. A., Pohler, D., General, S., Zielcke, J., Simpson, W. R., Platt, U., Tanner, D. J., Gregory Huey, L., Carlsen, M., and Stirm, B. H.: Photochemical production of molecular bromine in Arctic surface snowpacks, Nature Geosci, 6, 351-356, 10.1038/ngeo1779 http://www.nature.com/ngeo/journal/v6/n5/abs/ngeo1779.html#supplementary-information, 2013. Read, K. A., Lewis, A. C., Salmon, R. A., Jones, A. E., and Bauguitte, S.: OH and halogen atom influence on the variability of non-methane hydrocarbons in the Antarctic Boundary Layer, Tellus B, 59, 22-38, 10.1111/j.1600-0889.2006.00227.x, 2007. Saiz-Lopez, A., Mahajan, A. S., Salmon, R. A., Bauguitte, S. J. B., Jones, A. E., Roscoe, H. K., and Plane, J. M. C.: Boundary Layer Halogens in Coastal Antarctica, Science, 317, 348-351, 2007. Saiz-Lopez, A., and Boxe, C.: A mechanism for biologically-induced iodine emissions from sea-ice, Atmos. Chem. Phys. Discuss., 8, 2953-2976, 2008. Vallelonga, P., Barbante, C., Cozzi, G., Gabrieli, J., Schüpbach, S., Spolaor, A., and Turetta, C.: Iron fluxes to Talos Dome, Antarctica, over the past 200 kyr, Clim. Past, 9, 597-604, 10.5194/cp-9-597-2013, 2013. Vogt, R.: Iodine compounds in the atmosphere, Fabian P, Singh ON (eds) Reactive Halogen Compounds in the Atmosphere, edited by: Springer-Verlag, Springer-Verlag, Berlin 113-128 pp., 1999. Wagenbach, D., Ducroz, F., Mulvaney, R., Keck, L., Minikin,

A., Legrand, M., Hall, J. S., and Wolff, E. W.: Sea-salt aerosol in coastal Antarctic regions, Journal of Geophysical Research: Atmospheres, 103, 10961-10974, 10.1029/97jd01804, 1998.
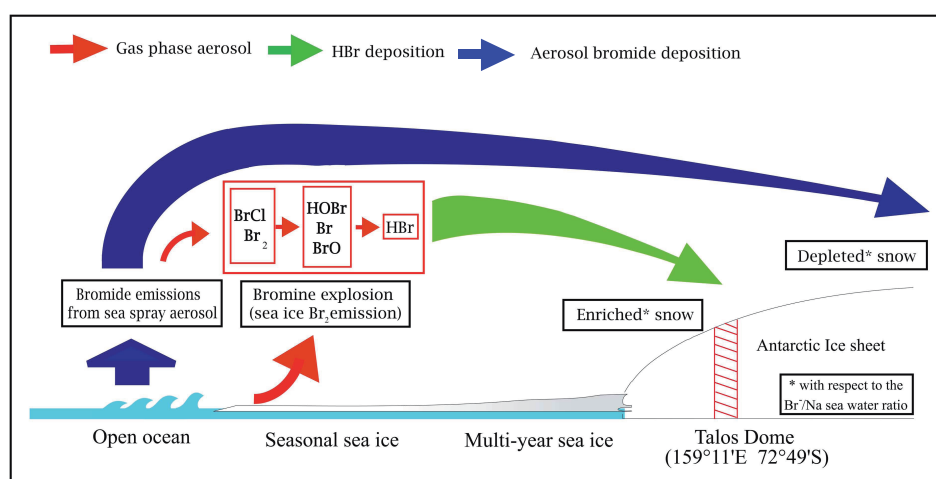
C3344

Fig. 1. Simplified scheme for bromide aerosol deposition in coastal Antarctica. Blue lines indicate the aerosol phase while red lines indicate the gas phase. Green line the HBr deposition.