

## Review of paper :

### Halogen species record Antarctic sea ice extent over glacial-interglacial periods

by Spolaor et al.

#### General Comments:

This paper provides the first record ever of iodine and bromide concentrations in a deep ice core, here the recently drilled Talos Dome Antarctic ice core. The paper shows a clear antinomic behaviour between the two species across the glacial-interglacial cycles, which the authors attribute to a combination of contrasts in sources and transport distances. While bromide is essentially of oceanic abiotic origin (marine aerosols) and often associated to frost flowers formation on thin sea ice, Iodine is produced by sympagic (sea ice hosted) algae. Following the authors, glacials therefore appear as peaks in iodine, because of larger seasonal sea ice extent, and depletions in bromide because of the larger distance of seasonal sea ice to the coast. The reverse is true for interglacials. Signal alterations at the source and during the transport are discussed and a simple model is proposed to simulate bromide depletion from source to deposition. Conclusions are drawn on the past extent of sea ice during LGM and penultimate glacial maximum.

The paper is highly innovative and “at the frontier of science”. It potentially provides a promising alternative to continental ice proxies of sea ice extent such as MSA or  $SO_4$ , the universality of which has been highly debated in the recent decade. The paper is well written and easy to read, even for a larger audience with limited expertise in atmospheric chemistry. Some technical improvements are suggested in the technical table below.

At this stage, I have three main concerns with the paper, which I would like to see better addressed:

#### 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 flower formation on a larger surface area and not significantly further away from the coast)

#### 2. Model for Bromide depletion

The choice for the many inputs in this model is not argued 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

### 3. Geometry of the experimental device for IO<sub>3</sub><sup>-</sup> reactivity

The concept and geometry of the experimental device for IO<sub>3</sub><sup>-</sup> 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.

Given the promising future for these pioneering measurements I would recommend publication with (I hope minor) changes, hoping the authors will be able to adequately address these general comments and the specific comments listed here below.

#### Specific Comments:

40-45	The oceans are the main reservoirs...algae growing under sea ice contribute to the total iodine concentration in the atmosphere	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?
62	IO <sub>3</sub> <sup>-</sup>	This would be the case for most of the sea ice, even in the winter when there is no primary production and heterotrophy dominates
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...
112	250 ky before present	References?
150	Reactivity	Does this mean production of iodine gas?...please extend for non-specialists
151		Give reference
159	The flow cell was filled	Not clear. I guess the cell was only half-filled 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
162	The gas phase iodine produced	How? From the freezing process?
161-167		Please synthesize in an equation, easier to grab for a larger audience
210-211	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...
218-219	Bromide depletion %	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/%"

223	Sea ice presence	Measured how? Please give details
230-231	During Spring...freezing sea water	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
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!
238-247		This is a "corner stone" of the paper...I would strongly recommend it to be illustrated with a "cartoon"
256	Constant Na flux	Not clear in Figure 3
270-272	780 km	Did Scharchilli et al., 2011 resolve the location of the landfast sea ice margin during the glacials?
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 (?)
280-281	The initial sea-salt aerosol loading was set...	Justification? Reference?
283-285	Deposition velocities for HBr, HI, sea salt aerosols set to	Please justify those choices and give references
293	An I <sub>2</sub> flux was generated	Justify, reference?
298-299	...good agreement...	This whole paragraph on modelling sounds extremely multi-tuned to reach the observed values at the appropriate distance!...see indeed lines 299-300! 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...
306-307	Travelled approximately 300 km	How does this compare to present-day distance of TD to first-year/multiyear sea ice in the area?
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 multi-year and first-year 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 (first-year) sea ice cover!...
315	Algae on the underside of the ice	Algae 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) - the proportion of

		which might change strongly between glacials and interglacials- favours the development of surface communities, are these as efficient in producing iodine?
319-320	During glacials are consistent with a greater seasonal sea ice area ...	Again, if that is the case, then there should be also a higher frequency of bromide explosions events!
325	Dust-induced ocean fertilization	<p>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</p> <p>b) There is a peak in dust that is not reflected in I<sup>-</sup> between 170-200 ka</p>
335-336	Assuming a linear... Sea ice extent was approximately double	Given the uncertainties, this simply goes too far in the interpretation!
356	Is present under particular conditions	What arguments do we have to say that IO <sub>3</sub> <sup>-</sup> was initially present everywhere?
366	Within the polar snow pack	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 firm would behave similarly!
386-388	Diffusion through the matrix	Again, this would be very different in cold firm in nature!
402-403	Glacial summer sea ice extent	This is ambiguous. Are you meaning multiyear sea ice extent?
403	500 km	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.
405	Approximate doubling	This is also very speculative, based on an hypothetical linear relationship between maximum sea ice extent and Iodine...
669-670	Rewrite	Figure 3: Plot of Br <sup>-</sup> fluxes (red) as a function of time in the TD ice core. Br <sup>-</sup> fluxes correlate with the δ <sup>18</sup> O (a proxy for the temperature record - black curve) and anti-correlate with Na fluxes (blue curve). Note that Sodium and δ <sup>18</sup> O are recorded as.....at a lower resolution.
672	Suggestion	"% Br <sub>dep</sub> in Talos Dome samples is plotted with sea ice presence (SIP, green area, units?, reference?)..."
673	Suggestion	"..2004). Talos Dome δ <sup>18</sup> O is also shown.
674	Add	(see text for details)
678	Add	"...edge - a proxy for glacial times at Talos Dome)..."
685	Na	Is not seen in Figure 7

**Technical Comments:**

48	percolation...up	Is this a valid expression?
61-62	I suggest rewrite	...in water varies: in anoxic water most of iodine exists as I <sup>-</sup> while in oxygenated waters, ...
70-71	delete	in 1988
127	picogram-per-gram	pgg <sup>-1</sup>
184	Figure 8	Not in the sequence of Figure numbering
225-226	MIS2, 5, 6, 7	Please show these in Figure 4
281	Suggestion	"..volumetric particle surface area...volumetric particle volume..."
335	Suggestion	"..sea ice extent..."
349	Suggestion	"...I <sup>-</sup> /IO <sub>3</sub> <sup>-</sup> . While a study..."
351	Suggestion	"...2004), another study found..."
359	Figure 8	Wrong location for numbering
424	Publication n° xx	Update please
Table 1 caption - 638	Rewrite	IOP (Iodine Oxyde Particles)
638	Delete	Mass production expressed in g cm <sup>-3</sup>
In table	X	X
Figure 2		Color scheme is not clear...too close to each other
Figure 4		Units for SIP?