

## REVIEW – REFEREE#1

This paper presents a new 120,000 year record of Br measured in the Renland ice core. It then interprets this in terms of sea ice extent. The analytical record is an interesting and potentially important one, and the paper should eventually become publishable in *Climate of the Past*. It is written in a clear style. However there are a number of issues that need to be addressed before it can be published. These fall principally into three areas, the meaning of Br<sub>enr</sub>, dating of the ice, and the transformation the authors adopt.

We thank the Reviewer for the time she/he took to review the manuscript. We agree with her/his comments and incorporated the suggested modifications, except for the ice core chronology, which is still not published. In particular, the introduction (Sect. 1.) is centered on the meaning/limitations of Br<sub>enr</sub>. The transformation has been removed. An extended section (Sect. 3.) has been added to deal with the calculation of ssNa (sea-salt sodium) concentrations, needed to calculate Br<sub>enr</sub>. Now three methods are used: chlorine, magnesium and calcium. The analytical records of this paper now include bromine, sodium, calcium, magnesium and chlorine. All time series are presented in the figures in the main text and the measurements are explained in the Methods section (Sect. 2.2). Two marine PIP records from the Norwegian Sea have been added.

1. The idea that some measure of Br enrichment may be associated with mainly first year sea ice (FYSI) is plausible and the authors have, in previous papers, made some kind of argument for it. However it is far from established and the paper is far too definite about that. It needs to spell out the caveats, and use the word “suggest”, “might” and “may” a lot more. I would also argue to add a question mark to the title.

The idea that Br<sub>enr</sub> is a FYSI proxy relies on a number of assumptions.

(a) The Br activation process leads to production of activated Br and to a depletion of Br in the salty surface on which it happens. As a result there can be both enhancements and depletions in what is deposited as snowfall, depending on the relative importance of depleted sea salt aerosol and gas-phase Br compounds that eventually get transported as (presumably) HBr. The implicit assumption used here is that the gas phase Br is transported to (in this case) Renland much more efficiently than the depleted sea salt aerosol. I agree with this, which is consistent with eg Simpson et al 2004. However the assumption needs to be stated, especially as this group has been inconsistent on that question, with Spolaor et al (2013), the first paper on this proxy, asserting exactly the opposite.

(b) There is also an assumption that HBr is produced only by the photochemical Br activation and not by a reaction between salt and acid analogous to that described on page 3, line 10 for Br. Again, the weak Cl fractionation suggests this may be true, but it needs stating.

(c) The paper assumes that Br activation takes place only on FYSI and not at all on MYSI. This is highly unlikely to be true, and the production ratio between these two forms of sea ice will be crucial to the interpretation. This is also the case for sea salt aerosol itself as shown in a modelling study by Rhodes et al (2018), where the use of sea salt as a sea ice proxy is crucially dependent on the extent to which FY and MYSI are involved in aerosol production. I don't expect a full modelling study here, but again it needs to be acknowledged that production on MYSI would affect the interpretation.

(d) Finally the authors essentially assume that their untransformed proxy equates to FYSI, taking no account of transport distance. It's actually quite plausible that their proxy decreases in very cold periods not because there is less FYSI but because it's much further from Renland. This may still argue for a

similar interpretation to the data, but is a more subtle mechanistic point that will eventually need to be tested in models.

I therefore ask the authors to state their assumptions and the caveats more fully, and I will suggest some places in the text where the interpretation should be more tentative.

The introduction (Sect. 1.) now consists of a description of *Br<sub>enr</sub>* as a potential sea ice proxy and the limitations and uncertainties that still remain. We thus proceed with the interpretation of the *Br<sub>enr</sub>* record as a record of FYSI, but it is now clearly stated that a number of uncertainties still exist. A question mark to the title has been added. Please find the added text in italics.

### **1. Introduction: *Br<sub>enr</sub>* as a potential indicator for past sea ice conditions**

*The connection between Arctic sea ice and bromine was first identified through an anticorrelation between springtime ground level ozone (O<sub>3</sub>) and filterable bromine air concentrations (Barrie et al., 1988). Large bromine oxide (BrO) column enhancements and simultaneous tropospheric ozone depletion were later found in Antarctica (Kreher et al., 1997). Satellite observations reveal geographically-widespread ‘bromine explosions’, the sudden increase of atmospheric bromine concentrations during springtime occurring in both polar regions (Chance, 1998; Richter et al., 1998; Wagner and Platt, 1998). The mechanism proceeds via springtime photochemical heterogeneous reactions that lead to the activation of bromide, followed by the release and exponential increase of gas-phase bromine species in the polar troposphere (Vogt et al., 1996). Several saline substrates on fresh sea ice surfaces (hereafter referred as first-year sea ice, FYSI) were suggested as reservoirs of reactive sea salt aerosols (SSA) capable of sustaining bromine recycling (Abbatt et al., 2012; Saiz-Lopez and von Glasow, 2012). To date, both model studies (Yang et al., 2008, 2010) and experimental evidence (Pratt et al., 2013; Zhao et al., 2016) consider the deposited snow layer on FYSI (known as salty blowing snow) to be the most efficient substrate for SSA release and bromine activation. Atmospheric bromine and sodium thus originate from both oceanic and FYSI sea salt aerosol, where their concentration ratio is that of sea water mass: (Br/Na)<sub>m</sub> = 0.0062 (the subscript indicates ‘marine’, Millero et al. (2008)). *Br<sub>enr</sub>* values in ice core records, i.e. the bromine-to-sodium mass ratios beyond the sea water value (Eq. 1) were introduced by Spolaor et al. (2013b) as a potential proxy for past FYSI conditions within the ocean region influencing the ice core location. The basic assumption behind this idea is that bromine recycling on FYSI surfaces would increase the bromine-to-sodium mass ratio beyond the sea water value in the atmosphere and at the ice core location, thus isolating effect of FYSI- induced bromine recycling from the sea salt aerosol contribution, the latter being interfered by oceanic emissions. Further studies have provided some evidence on the validity of *Br<sub>enr</sub>* as a FYSI indicator (Spolaor et al., 2013a, 2014, 2016a). At present, however, this interpretation is still challenged by several uncertainties related to the different variables which play a role in the involved chemical and physical processes. These can be grouped into three categories: bromine activation, transport and deposition/postdeposition. They are briefly discussed here. Pratt et al. (2013) showed that saline snow collected on Arctic tundra or first-year sea ice surfaces can serve as an efficient reservoir for bromine activation. They point out, however, that acidity of snow is a pre-requisite for bromine activation, as well as internal snow pack air chemistry (e.g. concentration of ·OH, NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub>). A modification in these factors would alter the bromine production efficiency at constant FYSI extent. Aged sea ice (second-year sea ice or older) is possibly contributing to bromine activation due to a non-zero salt content, but the amount of this second order source effect is unknown. Bromine travels from the source region to the ice core location both in the aerosol and gas phases, while sodium is only found in the aerosol phase. To date, the partitioning of bromine species between the two phases isn’t clear. Additionally, some studies have reported that bromine recycling takes place*

*within the plume even during the transport (Zhao et al., 2016), leading to possible bromine depletion from the aerosol in favor to the gas phase. Overall, the final observed Brenr values in ice samples depend on the relative importance of aerosol and gas-phase bromine. It appears that fine aerosol are enriched in bromine, while coarse particles are depleted (Legrand et al. 2016, Koenig pers. Comm.). Additionally, the two phases likely have different atmospheric residence time, thus the final bromine-to-sodium ratio found in the snow might be function of the transport duration. On this topic, Simpson et al. (2005) experimentally showed that sodium is washed out from the atmosphere faster than bromine, suggesting the role of longer lasting gas-phase bromine. On the other hand, a model run by Spolaor et al. (2013b) showed opposite results. To which extent transport processes can interfere with a source effect is yet to be resolved. The last set of uncertainties relates to the variables associated to the deposition of bromine and sodium, such as the variability in accumulation rates over long time scales, which would impact the relative importance of the wet and dry contributions of the two species. Finally, photolytic reemission of bromine from the snowpack could be responsible for bromine loss and decreased Brenr values.*

*We acknowledge the above-mentioned open questions on the validity of Brenr as a FYSI proxy and clearly point out that further studies are needed to shade light to these uncertainties. We thus proceed with the interpretation of Brenr as a FYSI proxy bearing in mind that other interpretations could, at present, explain a Brenr record. Here, we consider the available evidence regarding past sea ice conditions in the Nordic Seas, and present a bromine enrichment record from the RECAP ice core, located in coastal East Greenland. Because of its location, RECAP should record the fingerprint of sea ice in the North Atlantic. We compare our the RECAP Brenr record with sea ice reconstructions from five marine sediment cores drilled within the Renland source area: the Fram Strait, the Norwegian Sea and the North Icelandic shelf.*

2. This seems to be the first paper in which RECAP data have been presented covering the glacial, and is therefore the one in which the age model is effectively first presented. Dating Renland is far from simple, and it is completely unacceptable to rely on a reference to an in preparation paper (Simonsen) which the reader has no sight of. If this is the first paper published then this one needs to demonstrate that the dating is plausible – in the appendix or SI I would expect at minimum an age-depth profile, a table of tie points, and an estimate of age uncertainty. Without that, the reader has no idea how robust the comparisons to the NGRIP isotope record are (ideally we would see the Renland water isotope record in this paper but I appreciate that must be the subject of another paper and that this paper is out of sequence). In the absence of a substantial dating appendix/SI, this paper should not be published until a full description of the dating has been published in another paper.

*We will provide details on the chronology once it is published.*

3. While it is a clever idea, I am not convinced by the value of the transformation. The paper claims that this “linearizes” the record, but how does it do that? The number that is achieved has not in any sense been shown to be linear with any climate variable, be it FYSI extent, total sea ice extent or anything else. What has been done is to give a spurious air of quantitiveness to a proxy that remains at present qualitative. In Fig 5 the panel where the data are colour coded red or blue is good, and I understand the temptation to try to turn it into a curve that can be compared with the IP25 record in Figure 6 but I feel it should be resisted. If the authors cannot resist producing something I suggest a different alternative: (a) Have the y-axis go up to 7.4 (or whatever the change point is considered to be) and then decreases back to zero again, and plot the actual Br<sub>enr</sub> value either above or below the

line, maintaining its colour coding . (Mathematically this is achieved by making eq5 simply  $Br_{enr} = -Br_{enr}$ , plotting it with axis reversed and using the absolute value of  $Br_{enr}$  as the axis label). To indicate the uncertainty about the T threshold however, you should plot both the actual and the transformed  $Br_{enr}$  values for data within 2 sigma of the chosen temperature threshold so that it is obvious that there are two possible states at some depths. This procedure will produce a curve similar to the one in Figure 6 but without producing spurious new numbers.

The transformation has been removed, and we kept only the records with the two regimes color coded in red and blue.

More detailed comments

Page 1, abstract, needs to be more tentative: line 3 I suggest “and tentatively reconstruct”; line 6 “what we interpret as the transition from MYSO to FYSI started at 17.6 kyr”; line 8 “our proxy interpreted as FYSI reached its maximum”; line 10 “sea ice extent was probably greatest”.

We have now written the abstract clearly stating the uncertainties still exist in the use of  $Brenr$ .

**Abstract.** *Although it has been demonstrated that the speed and magnitude of recent Arctic sea ice decline is unprecedented for the past 1,450 years, few records are available to provide a paleoclimate context for Arctic sea ice extent. Bromine enrichment in ice cores has been suggested to indicate the extent of newly formed sea ice areas. Despite the similarities among sea ice indicators and ice core bromine enrichment records, uncertainties still exist regarding the quantitative linkages between bromine reactive chemistry and the first year sea ice surface. Here we present a 120,000 year record of bromine enrichment from the RECAP ice core, coastal East Greenland, and interpret it as a record of first-year sea ice. We compare it to existing sea ice records from marine cores and tentatively reconstruct past sea ice conditions in the North Atlantic as far north as the Fram Strait (50-85 °N). We find that during the last deglaciation, the transition from multi-year sea ice to first-year sea ice started at ~17.5 kyr, synchronous with sea ice reductions observed in the eastern Nordic seas and with the increase of North Atlantic ocean temperature. First-year sea ice reached its maximum at 12.4-11.8 kyr, after which open-water conditions started to dominate, as supported by sea ice records from the eastern Nordic seas and the North Icelandic shelf. Our results show that over the last 120,000 years, multi-year sea ice extent was greatest during Marine Isotope Stage (MIS) 2 and possibly during MIS 4, with more extended first-year sea ice during MIS 3 and MIS 5. Sea ice extent during the Holocene (MIS 1) has been less than at any time in the last 120,000 years.*

Page 2, line 1 “reservoirs”

Thanks.

Page 3, equations 2-3 and surrounding text. I appreciate that correcting for crustal Na in Greenland is not straightforward, but you need to explain what your rationale is here better, and when you do, it doesn't completely make sense. You are implicitly assuming that when the salt/acid reaction has created excess Cl, there is no terrestrial Na (eq 3); and that if there is a Cl/Na ratio less than 1.8 that is entirely because of terrestrial Na, and not at all because of the salt/acid reaction leading to removal of Cl from aerosol. I am not sure why either of those assumptions should be correct. Normally one would use a crustal element such as Al or perhaps Ca to put limits on the terrestrial correction. In the absence of that you need to revisit your method and at minimum state its limitations and suggest how much it may affect your results.

We greatly thank the referee for rising the issue. We also agree in the fact that both processes (terrestrial sodium inputs and dechlorination processes) could act simultaneously to modify the Na/Cl ratios. By looking at their 1994 paper, Hansson et al. (1994) wrote “The mean ratio between Cl- and Na+ never exceeds the sea water ratio for any climatic stage, i.e. never indicating an excess of Cl-, which is a further indication that the deviation from the sea water ratio is due to an additional (crustal) source of Na+ and not a fractionation process in the atmosphere between the sea salt elements”. Our measurements, show in fact that the Cl/Na do exceed 1.8.

Thus, sea salt sodium (ssNa) has been calculated in two additional ways: using calcium and magnesium, both measured by ICP-SFMS (discontinuously in the Holocene, continuously in the glacial section). The analysis is described in Section 3. We also dedicate a section in the Appendix in which we infer from present day studies on desert storms the ratio of Ca/Mg and Ca/Na in ‘asian dust’. These numbers are used to calculate ssNa. As far as calcium is concerned, Renland calcium concentrations showed unexpectedly high values during the glacial. This has been previously shown also in the GRIP core, probably due to the appearance of gypsum/carbonated dust. We thus account for the high calcium levels to provide a calculation of ssNa based on calcium, which turns out very similar to ssNa calculated using magnesium. We therefore consider two ssNa curves and two Brenr curves:  $Br_{enr, Mg}$  and  $Br_{enr, Cl}$ , calculated respectively from chlorine and magnesium concentrations. We will not attach here this whole section since it consists of a number of pages, plots and tables. It will be provided in the modified version of the MS.

Page 3, line 15-20. Thank you for using the word “suggesting” here. However I am not sure what point you are making in line 19-20. Why would we expect Holocene-like ice extent at 120 kyr when we are already well into the glacial inception?

We agree. The sentence has been written more clearly.

Page 3, line 26-28. The modelling study of Rhodes et al (Rhodes, R. H. et al., GRL, 45(11), 5572-5580, doi:10.1029/2018gl077403) doesn’t really support your interpretation, as in present conditions, it says that both sites are overwhelmingly seeing OW conditions (Rhodes was looking at the influence of sea salt aerosol but I imagine modelling Br would produce a similar result).

Thanks for rising this point. Rhodes et al. (2018) modeled an annual SISS/OOSS (sea ice sea salt / open ocean sea salt) of 0.21 at NEEM (fSISS annually integrated, Table S2 and Fig. 1), while at Renland this ratio drops to 0.04, meaning that at NEEM the sea ice influence would be 5 times greater than that at Renland. The ratio of the bromine enrichment values at the two locations are roughly 3-4 (if we consider Holocene averages, Fig. 3 in our manuscript), pointing to a similar conclusion, at least if a relative sea ice vs open ocean contribution are considered. On an absolute scale, it appears from Rhodes et al. (2018) that NEEM is indeed more influenced by open ocean rather than sea ice, at least just considering sodium. We therefore modify the text to better indicate that the different Brenr values at the two locations might reflect the RELATIVE influence of sea ice, being 3 to 5 times higher at NEEM than Renland.

The difference between Holocene values for the two sites could also be partly related to the fact that the  $Br_{enr}$  measure is not really ideal because it does not measure the amount of Br reaching the site but rather the ratio of Br/sea salt aerosol. NGRIP of course receives much less sea salt than Renland so just a small amount of gas phase Br can induce a  $Br_{enr} \gg 1$ . This may not fully explain the difference between the sites but it is a factor. It’s too late now because this measure is embedded in the literature, but the use of  $Br_{excess}$  ( $[Br - Br_{seawater}]$  instead of  $[Br/Br_{seawater}]$ ) would have avoided this problem.

We probably agree, but we point out that a core1-core2 comparison between Br\_excess curves could be interfered by the difference in snow accumulation.

Page 4, line 8 “a number of”  
Thanks.

Page 6, last line “Our reconstruction suggests..”  
Done.

Figure 2. I appreciate that Kindler only goes to 10 kyr but it is unhelpful that we don’t see a climate record from 10-0 kyr. Can you infill with an 18O record to at least indicate to the reader that Holocene temperatures remain warm.

We now used NGRIP  $\delta^{18}\text{O}$  in Fig. 4 and specified that in the caption of Fig. 6.

Fig 3 caption, Fig 6 caption: Tzedakis et al is not an appropriate reference for orbital parameters. Please cite original papers by either Berger or Laskar.

Thanks.

Appendix B. I am wondering why you call this “sea salt aerosol source area” when what you are interested in is the source of the gas phase Br. The back trajectories are for air masses so certainly not specific to aerosol.

Both gas-phase (Br) and aerosols (Br,Na) contribute to Br\_enr, so both need to be considered, so this paragraph (now Sect. 2.3) is now named “*Atmospheric reanalysis: the source region of bromine and sodium for the RECAP ice core*”.

Fig B1 caption line 2 “constraint” (but can you explain what you mean by this constraint).

Only the trajectories that crossed the 900 hPa isosurface were selected and considered for the analysis. The term constraint has been removed.

Fig B1 caption. Sorry for my ignorance but I never heard of a nabla before, can’t you call it an inverted triangle?

We now use diamond symbols.

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