Clim. Past Discuss.,
doi:10.5194/cp-2016-49-RC2, 2016

Climate of the Past Discussions

Interactive comment on "Sea ice and pollution-modulated changes in Greenland ice core methanesulfonate and bromine" *by* O. J. Maselli et al.

Anonymous Referee #2

Received and published: 12 June 2016

Maselli and coauthors present a study investigating the behaviour of two possible sea ice proxies, Br and MSA, from two Greenlandic ice cores, Tunu and Summit. This is an interesting dataset and discussion, however I hold some significant doubts regarding the interpretations and methods. Most of my concerns relate to the production and interpretation of the MSA record. This would be the first time that a convincing MSA record has been published from Greenland ice cores, and the first time ever that such data has come from a continuous melting system. Given the significance of such data, it is surprising that the technique description and validation is so limited. I also have doubts regarding the assumption to calibrate Br trends using MSA, as the two have different production processes with respect to sea ice. Further, such a calibration is

performed for a period where there is no independent reliable observational data. Can the authors be sure they are not comparing proxy with different meaning? There is a lot of impressive data presented in this work but the authors should not put the cart before the horse: A thorough demonstration of the reliability of the data presented; a more complete investigation of the divergent trends between MSA and Br, and between Tunu and Summit; and a more detailed consideration of the potential impacts of acidity on the stability of Br and MSA in ice cores, would make this work a considerable contribution to the literature and our understanding of these important possible sea ice proxies. The following comments on the manuscript are divided into topics instead of referring to particular lines or sections.

Major comments MSA record Many papers have been written about the measurement of MSA (Legrand et al., 1993; Curran et al., 2001) as well as the problems of stability and mobility (Abram et al., 2008; Smith et al., 2004; Curran et al., 2002) as well as challenges of interpretation (Abram et al., 2013, Wolff et al., 2006; Legrand and Mayewski, 1995). Given the length of time that the community has required to tackle the distribution and stability of such a challenging ion, a thorough validation of the measurement method is required. Have replicate measurements been carried out? Have parallel discrete samples been measured (ie, samples that have not been exposed to the melter?). How do these results compare to other recent observations of MSA in Greenland (e.g Kuramoto et al., 2011, Jaffrezo et al., 1994)? Is it possible that MSA is destabilized at the melthead or when acid is added to the meltstream? These are critical questions as there is no pre-existing MSA record for comparison and in this manuscript MSA is used as a calibratiuon reference for the Br data.

Br measures Line 143. In the text the authors refer to Bromine as the sum of all bromine species that could be present into ice core samples. Equation 4 shows a calculation for Br enrichment, which has been used previously through the work of Spolaor and coauthors (2013) whereas in this manuscript the authors always use total bromine for discussion. Total Br follows sea salt and its components such as sodium. It is the

difference, or the additional amount of Br produced beyond the sea salt component, that must be evaluated, at least if you want to consider Br as a sea ice tracer.

Br summer peak and biological production Br emission from sea ice is well documented from both satellite observations of BrO and aerosol measurements. It is detected from the beginning of March, the arrival of solar radiation, to early June. The data show a maximum in Br in mid-June (also shown in figure S1). The results are in agreement with those obtained from NEEM (Spolaor et al., 2014) of maximum Br enrichment in summer. The authors claim that biological production could be a factor influencing the total Br concentration however I am not convinced of this for the following reasons: MSA, biologically produced, has its greatest snow concentration during spring, with consistently lower values during summer. Ardyna et al 2013 (Biogeosciences, 10, 4383–4404) report annual time series of surface chlorophyll for the Arctic and show that the main production is concentrated in spring with less production in summer. There could be an influence of biogenic bromine in spring but this is not supported by satellite observations, where the highest atmospheric concentrations are over sea ice. Release of biogenic bromine from sea ice through percolation is quite unlikely due to the low porosity of Arctic spring sea ice (Zhou et al 2013, JGR: Oceans, Vol. 118, 3172–3189, 2013) Finally, during summer satellites do not detect BrO in the polar atmosphere

MSA/Br correction (line 331) The authors suggest a correction for Br using MSA in the preindustrial era. To do this, a linear relationship has been used between the two parameters. I am not convinced about this approach because the relationship between Br, and its enrichment over seasonal sea ice is not linear but logarithmic. This is explained by Br chemistry over sea ice – very briefly, one Br radical produces two radicals causing the explosion. The relationship between MSA and the location of the sea ice edge, or as proposed by the authors, with open water leads in the ice pack, is linear. What is the correlation between Br and MSA? What is the relationship used? No chart has been presented in the paper although this is one of the central discussions of the

manuscript. In Fig 3 (and other work in the literature) it is shown that MSA can undergo remobilization (the seasonal cycle of MSA is changed completely) and smoothing in the ice. How much does this interfere with the Br correction? Again I mention my comment about the dangers of comparing a proxy with a proxy. Do MSA and Br represent the same source processes at the two sites investigated? Abram et al. (2013) have reviewed at least 5 different interpretations for MSA records around Antarctica alone. In this work, how can the authors correct a proxy (Br) influenced by the presence of seasonal sea ice with a proxy (MSA) that seems to quantify open water leads in the ice pack? Again my comment that more careful attention must be given to the discrepancies between the records. Infigure 2 there is a positive correlation until 1870 for Summit while for Tunu it persists until 1950. Then the correlation between Br and MSA seems negative. Why there is this discrepancy between the two cores? Tunu is a low accumulation site, Summit is far away from the coast; how much should these two sites be expected to demonstrate a similar sea ice signal? Are they even sampling the same sea ice regions? It has been demonstrated that sea ice cannot be reconstructed from MSA in central East Antarctica (Wolff et al., 2006) – a similar level of criticism needs to be applied to records from central Greenland. Br after 1950 The authors have investigated the Br increase of Br after 1950 in both cores. In the Summit core Br increases significantly from 1930 while in the Tunu core the increase is sharper and starts around 1950. The authors investigated different possible explanations, suggesting that anthropogenic pollution plays an extremely marginal role compared to biogenic contributions and acidity which can play a more central role. As discussed previously biological production can contribute to total bromine emission but a major influence on Br deposition is not supported by satellite observations of BrO. Acidity can play a role in the process, primarily for halogen recycling in sea salt aerosols and not so much for heterogeneous recycling on sea surfaces. Nevertheless, acidity is dependent on sea ice to have any effect: without sea ice the role of acidity would be zero. Therefore, the first order influence on Br recycling is from sea ice and a second or third order influence may be attributed to acidity. The links drawn between nitrate and Br are extremely

interesting but the data presented does not satisfactorily describe the influence of acidity. The authors are correct that the data points to more of an influence from nitrate than from sulphate, but none of the correlations in Fig 9 are strong, even if some are significant. How much of the significance between Br and nitrate can be ascribed to autocorrelation based on their seasonality?

Back trajectory and sea ice correlation Back trajectories shown in Figure 5 indicate that for Summit the main atmospheric pattern, or the source regions, originate from the south and south-east of Greenland while for Tunu the main source is Baffin Bay with sporadic incursions from southeast Greenland. Figure 6 shows correlation maps of monthly sea ice concentration (SIC) derived from the HadISST1 ICE dataset from 1900-2012. Why is it that the area used for correlation is different to the south and south-east secotrs of Greenland, where the Summit backtrajectories originate from? For panel b of figure 6, how is the correlation value in the graph (0.45) related to the data in the satellite maps, where none of the data approach a value of 0.45? For Tunu (Figure 7), as for Summit, the main correlation with sea ice is detected in northeast Greenland where BT analysis do not suggest an atmospheric source region. On what basis was the correlation window chosen? Again, why does the graph in panel b include a correlation of r=0.53 when this value is not shown in the correlation maps? For both sites, what would the correlations be if "outliers" were included? Other comments Line 101. Bromine is not normally measured in low resolution due to interference from 40Ar39K. What were the relative sizes of baseline to signal and was there a significant background when quantifying Br in low resolution? Line 225. Why has bromine been referenced to chloride? Chloride can undergo atmospheric reactions and is not recommended for evaluating Br enrichment. For consistency, as well as due to its stability, sodium should be used. Line 472. Although the effect of springtime Arctic haze is well described, the high springtime concentrations of sulphate and nitrate cited by the authors may be associated with biological production. Lehrer et al 1997 conducted their study in Ny-Alesund, a research facility right on the coast. Such a site is therefore susceptible to oceanic productivity, especially in connection to the springtime opening

of sea ice in the adjacent fjord. Line 557-559. Br and its enrichment in ice cores has been used for reconstructing sea ice changes in recent periods in the Arctic. The authors haven't provided a satisfying explanation for why bromine doesn't work at Tunu or Summit but does work at other Arctic sites. Acidity should play a role in influencing reactive halogens such as bromine but without sea ice no reactions will occur. It is further dissatisfying that the large acid peaks observed in the record do not have a consistent effect on either Br or MSA. Figure 2. It would be easier to look at the data if they do not overlap.

Interactive comment on Clim. Past Discuss., doi:10.5194/cp-2016-49, 2016.