

RESPONSES TO REFEREE 2

General Comments:

1) Activation of a certain amount of bromine into the atmosphere can come from a small fraction of activation of a saline (bromide-rich) snow/ice, which would lead to a small enhancement in the Cl-/Br- ratio (choice of ratio as in the text, but not preferred), but a large total amount of reactive Br produced. Alternatively, for the same amount of reactive Br production, a snow/ice sample that happened to have less bromide to start with (e.g. a less saline sample) would show a larger enhancement in the Cl-/Br- ratio. Therefore, the plot shown in Figure 3 does not tell the complete story. Specifically, how much Br- and/or Cl- are present in each of these samples? If the blowing snow at higher altitude (e.g. 550 cm) has much less total salinity, little reactive bromine would have been produced from this sample. The authors need to include the full measurements of Cl- and Br- in their samples in some manner so that readers could explore other hypotheses. Inclusion of the data as a supplementary data table could be a good solution, and just indicating that the data are on a website, which is not archival, is not sufficient. The discussion of ranges on page 11992 is not sufficient to get a full picture of the data, and the large ranges shown on that page motivation the need for inclusion of more data. The authors should also explore the total mass of Br- lost from samples as a function of height. Even though the fractional Br- lost is highest at 550cm, the lower portion of the column could be releasing more Br-, if it is more saline.

We thank Referee #2 for recognizing the need to also present the raw anion concentrations in addition to the mass ratios. We have added a supplement to the revised manuscript that has tables reporting the chloride, bromide, sulfate, and nitrate concentrations for all 83 samples. As can be seen in the data, there is not a trend between anion concentrations and height. In addition, even replicate samples collected from the same basket had drastically different anion concentrations, suggesting that the snow originated from a variety of locations. We feel that the small sample size is not sufficient to estimate the total mass of bromide lost as a function of height

and therefore did not include this estimate in the revised manuscript. We find the hypothesis of greater Br^- mass loss at lower heights interesting but unlikely, as very saline samples were collected from the upper baskets. The following three tables have been included as a supplement to the revised manuscript:

Table 1: Raw anion concentrations of blowing snow samples collected on 25 October, 2012, and measured using a Dionex-600 IC system.

Site	Height (m)	Cl^- (g/m^3)	Br^- (g/m^3)	SO_4^{2-} (g/m^3)	NO_3^- (g/m^3)
Butter Pt	0.3	400	1.3	26	0.4
Butter Pt	0.3	460	1.6	28	0.4
Butter Pt	2.0	23	0.1	1	0.3
Butter Pt	2.0	62	0.2	4	0.4
Butter Pt	2.0	63	0.2	4	0.5
Butter Pt	3.0	4,500	9.5	160	20
Butter Pt	3.0	670	1.3	18	4.3
Butter Pt	5.5	1,400	1.4	47	9.9
Butter Pt	5.5	4,900	6.0	210	30
Iceberg	0.3	150	0.5	14	0.2
Iceberg	0.3	280	1.3	59	0.4
Iceberg	2.0	6,700	18.5	240	13
Iceberg	3.0	2,600	6.0	100	8.3
Iceberg	5.5	3,900	4.9	150	23

Table 2: Raw anion concentrations of surface snow samples collected in October – November, 2012, and measured using a Dionex-600 IC system. All nitrate samples marked BQL were below the quantification limit of 0.1 g/m³.

Site	Date	Cl ⁻ (g/m ³)	Br ⁻ (g/m ³)	SO ₄ ²⁻ (g/m ³)	NO ₃ ⁻ (g/m ³)
Butter Pt	10/15	3,400	13	1,600	0.3
Butter Pt	10/15	2,400	8.0	350	0.3
Butter Pt	10/15	950	3.7	150	BQL
Butter Pt	10/17	940	3.0	120	0.5
Butter Pt	10/25	780	2.8	78	BQL
Butter Pt	10/25	1,800	6.9	210	BQL
Butter Pt	10/25	2,700	9.5	210	BQL
Butter Pt	10/25	420	1.5	29	BQL
Butter Pt	10/25	920	3.7	120	BQL
Butter Pt	10/25	1,300	4.9	250	BQL
Butter Pt	10/26	330	1.2	20	0.5
Butter Pt	10/29	350	1.2	50	BQL
Butter Pt	10/31	470	2.0	77	BQL
Butter Pt	11/02	2,200	7.8	210	BQL
Butter Pt	11/06	3,700	13	590	1.2
Iceberg	10/11	1,400	4.4	87	0.3
Iceberg	10/15	4,600	15	1,200	0.9
Iceberg	10/15	550	2.1	160	0.1
Iceberg	10/15	440	1.7	34	BQL
Iceberg	10/17	3,700	13	1,100	0.5
Iceberg	10/19	1,100	4.7	1,600	BQL
Iceberg	10/25	2,100	7.3	140	BQL
Iceberg	10/25	1,100	4.4	58	BQL
Iceberg	10/25	3,700	13	1,600	BQL
Iceberg	10/25	2,300	8.2	2,300	BQL
Iceberg	10/26	370	1.2	100	0.5
Iceberg	10/29	1700	5.1	480	BQL
Iceberg	10/31	150	0.5	74	0.2
Iceberg	11/02	2,000	6.5	160	BQL
Iceberg	11/06	1,400	5.2	540	BQL
Iceberg	11/08	2,300	7.8	240	BQL

Table 3: Raw anion concentrations of sub-samples taken every 10-cm for the length of two ice cores collected at Butter Point Site and Iceberg Site, respectively, and measured using a Dionex-600 IC system. All nitrate measurements in the two ice cores were below the quantification limit of 0.1 g/m³.

Site	Depth (m)	Cl ⁻ (g/m ³)	Br ⁻ (g/m ³)	SO ₄ ²⁻ (g/m ³)
Butter Pt	0	7,600	25	1,800
Butter Pt	10	5,500	19	1,300
Butter Pt	20	5,200	17	1,900
Butter Pt	30	3,500	11	670
Butter Pt	40	3,800	11	1,400
Butter Pt	50	3,200	11	490
Butter Pt	60	2,900	9.7	570
Butter Pt	70	3,800	13	470
Butter Pt	80	2,500	8.0	420
Butter Pt	90	3,600	12	330
Butter Pt	100	2,900	9.8	680
Butter Pt	110	2,600	8.7	480
Butter Pt	120	2,800	8.9	590
Butter Pt	130	1,900	5.6	440
Butter Pt	140	2,100	6.2	410
Butter Pt	150	2,200	8.6	440
Butter Pt	160	3,300	11	610
Butter Pt	170	3,200	11	690
Iceberg	0	8,000	30	3,100
Iceberg	10	6,000	21	1,200
Iceberg	20	3,200	13	520
Iceberg	30	3,700	13	450
Iceberg	40	3,300	12	1,600
Iceberg	50	2,900	9.7	230
Iceberg	60	3,000	8.9	840
Iceberg	70	2,800	9.8	270
Iceberg	80	3,100	11	490
Iceberg	90	3,100	12	390
Iceberg	100	2,600	9.5	370
Iceberg	110	3,400	12	690
Iceberg	120	2,500	8.2	480
Iceberg	130	3,200	11	560
Iceberg	140	2,700	8.7	460
Iceberg	150	2,300	7.4	440
Iceberg	160	2,200	8.0	420
Iceberg	170	3,000	11	480
Iceberg	180	3,500	13	460
Iceberg	190	9,100	34	1,400

2a) The authors made a good design for collecting blowing snow, but the design still leaves some challenges in interpretation. Specifically, snow in the basket is being exposed to ambient air, which could be leading to depletion of Br- after sampling snow. One could argue that the authors have produced a snowpack that is being held aloft (in baskets) and wind is ventilating this snowpack and causing depletion of halogens in a snowpack-like process. The greater windspeed at higher altitude could then cause the profile observed in Fig. 3. It is not clear if the snow in the baskets is permeable to air. The authors should give a description of what the snow looked like (was a fine dust or a packed windslab that might not be very permeable). That description could possibly help in the interpretation, but I think that both the possibility of depletion of Br- from the blowing snow phase and post-sampling depletion of Br- need to be discussed.

Referee #2 raises a good observation regarding the design of the experiment and potential source of error. We do note that an improved future design should try to eliminate any exposure to ambient air of collected snow in the basket. However, the current post-collection exposure is small enough that it does not significantly affect the main conclusions of the manuscript. We have added more field observations that should help alleviate some of these concerns. Section 4 of the revised manuscript has been revised to reflect these changes and now reads:

Previously, bromine activation and ODEs were observed in both low (< 5 m/s) and high (> 12 m/s) winds (Jones et al., 2009). Here, the blowing snow event occurred during moderate winds of approximately 10 m/s. Since the wind was from the south and there was no new precipitation, it is safe to assume that the snow originated from the surface of first-year sea ice. It is noted that the blowing snow event lasted approximately 4 – 6 hours, and that snow samples from the baskets were not collected until 10 – 12 hours later. During this time, wind speeds dropped to less than 5 m/s, and it is possible that the collected snow was exposed to further wind scouring. However, all baskets would have experienced a similar degree of scouring in these minimal winds and the effect would be minor over the short time period prior to collection. Further, the collected snow was mostly windpacked, suggesting it was unlikely the wind penetrated both the 150 μm nylon monofilament mesh

of the basket and the interior bulk of the snow. Future studies, however, may attempt to better seal off collected blown snow.

2b) Along the lines of this discussion, blowing snow clearly suspends surface area that presumably contains bromide, but to the extent that the snow moves with the airstream, the relative velocity of air as compared to ice surface decreases as compared to the fixed snowpack situation. Snow blowing at the windspeed has no relative motion compared to the gases, and then gas-phase diffusion to the snowgrain becomes the mass transfer limitation for halogen activation. For large particles (above a few micron diameter), the diffusion limitation dominates the mass transfer of gases to the surface. This point should be discussed more fully in the manuscript. Saltating (bouncing) snowgrains present an intermediate case, where there is some slip velocity between air and particle.

The observations raised by Referee #2 have been further explored in the discussion. The first paragraph of Section 4 has been revised and now reads:

Observation of bromide depletion relative to other salts is an indication of heterogeneous atmospheric chemical reactions and bromine activation (Adams et al., 2002; Huff et al., 2002; Simpson et al., 2005). Although there was some variability in Br^-/Cl^- mass ratios for sea ice and surface snow, these ratios were remarkably constant, just over 1 : 300. As shown in Fig. 3, signs of bromide depletion occur above the snowpack, with greater depletion occurring at greater heights, reaching mass ratios of nearly 1 : 1000 at heights of 5.5 m. This is consistent with aerosol observations by (Duce et al., 1971) that measured increased bromide depletion with height, albeit at tropical latitudes. They noted a strong particle size dependence with increased bromide depletion corresponding to mid-sized aerosol particles. Further studies have shown that particle size influences the mode of transport and it may not be realistic to differentiate snow saltation and suspension based solely on wind speed and height (Nemoto et al., 2004). Nevertheless, both processes greatly increase the snow surface area exposed for gas-phase reactions by as much as 3,000 times that of surface snow (Pomeroy et al., 2001). It is noted that snow blowing at the windspeed will have no relative motion compared to the gases and gas-phase diffusion becomes an important consideration, especially

for large grain particles. Local turbulence however, will help help overcome some these diffusion limitations (Nemoto et al., 2004).

Specific Comments:

Abstract, p11986 line 11. It is not clear what mechanism causes "replenishment" of bromide in the snow. I dont think that this sentence in the abstract is well justified in the manuscript. Eliminate from abstract or explain more. Again, the mass balance aspects (point 1 above) of the problem are lost by this ratio-based analysis, and the mass balance needs more discussion.

The two points alluded to here have both been addressed elsewhere in the revised manuscript. Raw anion concentrations have now been included as a supplement to the revised manuscript. The paragraph addressing replenishment of bromide has been rewritten.

p11986, line 16 Does sea ice coverage change a lot in springtime?

The change referred to in this sentence is the large Antarctic seasonal change from winter to summer. Antarctic winter sea ice extent is roughly 19 million km², while summer extent is roughly between 3 – 4 million km².

p11986, line 19 In the polar regions, halogens are often the dominant oxidizers. Halogens oxidize hydrocarbons, and that signature is clear in VOC data. This sentence needs modification to indicate that halogens are themselves oxidizers.

This is indeed a helpful observation. However, for clarity, the introductory clause to this sentence was removed. The beginning of Section 1 now reads:

The polar springtime is a season of change, most notably in temperature, sea ice coverage, and weather, but it also signals the onset of many photochemically driven atmospheric chemical reactions, such as tropospheric ozone depletion events (ODEs) (e.g., Barrie et al., 1988). Boundary layer ozone in polar regions has been observed to fall dramatically periodically in the spring in both the Arctic (Barrie et al., 1988) and Antarctic (Kreher et al., 1997; Wessel et al., 1998). These tropospheric ODEs are initiated by increased concentrations of reactive bromine gases (BrO and Br) resulting in

a catalytic removal of ozone

p11987, line 12 The use of "fractionation" is not being used appropriately. Fractionation is a process the changing of ratios of ions from sea salt ratios to different ratios. This section needs rewording to be consistent.

The sentence has been revised to read as:

Specific salts precipitate out of solution when solubility limits are reached below -2°C (Light et al., 2003), producing brine with different ion ratios than those found in seawater.

p11989, line 27 the word "unto" is not correct. Possibly "until".

We thank Referee #2 for catching this typo. The word has been corrected to *until*.

p11991, line 3 Winds were mild is indicated. Was ozone measured? If so, was ozone also not depleted often? While the relationship between ozone depletion and halogen activation is complex, it would be valuable to examine if ozone was depleted during these blowing snow events, and/or if ozone depletion was observed during nonblowing snow events.

We did not measure for ozone while in the field. Satellite BrO and O₃ images collected by the Global Ozone Monitoring Experiment-2 (GOME-2) were analyzed over the duration of the field campaign. There was no discernible BrO concentration spike and ODE over the Ross Sea around 24 October. As mentioned above in the response to Referee #1, this suggests that the recorded bromine release was a small-scale event that did not directly lead to a greatly enhanced BrO spot. Further, there was no strong ODE over the 2-month long campaign. As was mentioned, the relationship between ozone depletion and halogen activation is complex, and since the lack of a dramatic BrO spike does not nullify the occurrence of bromine release, this analysis was not included in the revised manuscript.

p11991, line 17 missing an "and" somewhere?

We thank Referee #2 for catching this typo. The final paragraph of Section 2 now begins:

Anion chromatography was completed using a Dionex-600 IC system, equipped with a LC 25 chromatogram oven set at 30 °C, GD 50 gradient pump, CD 25 conductivity detector, AS15 anion column with a AG15 guard column, and an auto-sampler.

p11992, line 9 the unit of kg m⁻³ is used here for chloride, but line 25 on the same page has an overlapping range that is instead written as g m⁻³. Please make consistent. Again, ranges are not sufficient to answer mass balance questions and somewhere this manuscript needs a full data table.

We thank Referee #2 for catching this inconsistency. All concentrations are now in g m⁻³. Additionally, anion concentrations for all samples are given in a supplement to the revised manuscript.

p11994, line 2 the section "...actually decreases due to required HOBr..." is not very clear. Reword.

The first paragraph of the discussion has been reword and now reads:

Observation of bromide depletion relative to other salts is an indication of heterogeneous atmospheric chemical reactions and bromine activation (Adams et al., 2002; Huff et al., 2002; Simpson et al., 2005). Although there was some variability in Br⁻/Cl⁻ mass ratios for sea ice and surface snow, these ratios were remarkably constant, just over 1 : 300. As shown in Fig. 3, signs of bromide depletion occur above the snowpack, with greater depletion occurring at greater heights, reaching mass ratios of nearly 1 : 1000 at heights of 5.5 m. We define a depletion factor (DF) such that DF= 1 signifies no bromine depletion in particles and DF= 0 signifies complete depletion. Averaging the Br⁻/Cl⁻ mass ratios at each height for Butter Point yields DF= 0.04, 0.11, 0.41, and 0.68 for heights of 0.3, 2.0, 3.0, and 5.5 m, respectively. At Iceberg Site, we have DF= -0.08, 0.20, 0.33, and 0.64, respectively. An increased depletion factor can either signify bromide depletion due to bromine release or chloride enrichment from, for example, gaseous HCL uptake. If the later hypothesis were true, one would expect to observe increased chloride concentrations in higher baskets. The lack of an observed

chloride trend with height leads to our interpretation that the decreased mass ratio is a clear indicator of bromine activation. Interestingly, lower Br^-/Cl^- ratios also correspond to a decrease in chlorine release. It has been shown that BrCl plays a critical role in chlorine production, and BrCl release is reliant upon the existence of HOBr from prior bromine activation (Wren et al., 2013).

p11994, line 16 How is surface snow bromide "replenished"? An argument is made about "small proportion of surface snowpack", which starts the discussion of a mass balance (point 1 above). This can be made more quantitative through the inclusion of all concentration data instead of only ratios. The production of HOBr is not really much of a termination reaction $\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$ on snow is the "bromine explosion" reaction, not a termination. Deposition of "aerosol-phase bromine" only represents a "replenishment" if the aerosol-phase bromine is enhanced compared to chloride in the particles. Please clarify this mechanism.

The wording in the original manuscript was not clear in highlighting the potential sources of bromide replenishment. The relevant paragraph of Section 4 has been rewritten and now reads:

The surface snow Br^-/Cl^- mass ratios at both sites showed little variation and no observed trend with date or meteorology over the month-long campaign. If there was a significant amount of lofted snow being depleted in bromide and then falling back to the snow surface, one might expect to detect a signal in the surface snow chemistry. The lack of recorded bromide depletion in the surface snow may indicate that either surface snow bromide concentration is quickly replenished or that blowing snow represents only a small portion of the surface snowpack. Surface snow will be replenished in bromide through interaction with saline brine (Oldridge et al., 2011), deposition of HOBr as a byproduct of the reaction between BrO and HO_2 , deposition of HBr , and deposition of aerosol-phase bromine. In cold ambient environments, frost flowers, surface snow, and the sea ice surface have been shown to be bromide enriched sources, likely due to the precipitation of NaCl (Kalnajs et al., 2006; Morin et al., 2008). Additionally, recycling of deposited bromine plays a critical role with as much as 75% of deposited bromine being re-emitted into the gas phase as Br_2 or BrCl (Piot et al., 2008). In future

work, it would be informative to collect both surface and blowing snow during stronger wind events.

p11995, line 19 This work examined the ratios of Cl⁻ to Br⁻ in snow deposited in baskets, and did not observe bromine activation (e.g. production of Br and/or BrO). Please clarify.

The first sentence of Section 5 has been reworded and now reads:

In summary, this work examined the mass ratio of Br⁻/Cl⁻ in blowing snow during mid-strength winds to better understand mechanisms leading to bromine activation.

p11995, line 21 The ratio chosen is Cl⁻/Br⁻, but which becomes enhanced in blowing snow. The reason for that enhancement is interpreted as the depletion of the denominator. Therefore, the wording "depletion" in this line is confusing. If the full manuscript were changed to the Br⁻/Cl⁻ ratio, it would read easier. Presumably Cl⁻ is a relatively conserved sea salt tracer, so having that as the denominator makes sense.

We thank Referee #2 for this recommendation. The ratio has been flipped throughout the entire revised manuscript to be Br⁻/Cl⁻ and this should remove any confusion.

p11995, line 23 The conclusion is written in a way stronger than the discussion of the manuscript. The observation is depletion of Br⁻/Cl⁻ in snow in baskets more aloft. The Br⁻ depletion could have happened while the snow was blowing, or could have happened post-catch in the basket but before collection of the basket. Mass balance considerations are absent and not checkable given the data in the manuscript. Diffusion to ice surfaces is not sufficiently discussed, and snow in baskets aloft is probably better ventilated than both snowpack and blowing snow, which moves with the wind. Therefore the statement "...we conclude the blowing snow particles provide an ideal surface for the initial heterogeneous reactions..." is a stretch. Reword to make conclusions from these observations.

As mentioned above, a supplement containing the raw anion concentra-

tions has been added to the revised manuscript to help address the mass balance considerations. In addition, the conclusion has been revised and now reads as:

In summary, this work examined the mass ratio of Br^-/Cl^- in blowing snow during mid-strength winds to better understand mechanisms leading to bromine activation. It was found that while Br^-/Cl^- mass ratios remained relatively constant for sea ice and surface snow, bromide becomes strongly depleted relative to chloride in lofted snow. Thus, we conclude the blowing snow particles provide a very viable surface for the initial heterogeneous reactions initializing ODEs to occur. The findings of this study are consistent with previous modeling results (Yang et al., 2010), suggesting that blowing snow has the capacity to explain the occurrence of ODEs in the polar springtime.