

Interactive
Comment

Interactive comment on “Bromide and other ions in the snow, firn air, and atmospheric boundary layer at Summit during GSHOX” by J. E. Dibb et al.

J. E. Dibb et al.

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We would like to thank both referees for their careful review and, particularly, their very encouraging assessment of this work.

If encouraged to submit a revised manuscript for publication, we would make the following improvements in response to comments made by referee #1.

Typographical error on page 13613 will be corrected.

Regarding more detail about the characteristics of the surface snow samples, we did not determine grain size routinely, and it is difficult to get precise density measurements because our technique focus on the uppermost stratigraphic layer which is not flat either on the bottom or top. Thus while we do know the mass inventory (g snow cm-

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Interactive Discussion

Discussion Paper



2) for every sample, the density is based on an "eyeball" estimate of the mean layer thickness. These generally range 0.15 to 0.35 g cm⁻³. In a revised manuscript we would add additional details to the description of snow sample collection; a proposed new version of section 2.4 is copied below with added text in bold.

Surface snow was sampled daily in 2007 (just after the aerosol filter changes) and twice daily (~ 10:00 and 22:00 local time) in 2008. Following the procedures described by Dibb et al. (2007), three replicates from a known area of the dominant surface layer were transferred into 175 ml precleaned and tared polyethylene bottles, using Lexan scrapers and polyethylene funnels. During intervals with no new snow or drifting the same layer was sampled repeatedly until an event created a new dominant layer. In general, a given layer was replaced every few days, but intervals of calm weather allowed tracking aging of some layers for as long as two weeks. Every tenth bottle was a blank, generated by opening a bottle and placing it next to a sample bottle while the sample was collected. Approximately 20 ml of ultrapure water were subsequently added to each blank. Several shallow pits (at least 50 cm deep) were sampled at 3 cm intervals each season. Snow samples were stored frozen until analysis, which was done by IC in the field on the same days that aerosol filter extracts were analyzed.

We also point out that additional detail about the type of snow sampled each day (new, windblown, fog impacted) is provided in the second and third paragraphs of section 4.3 in original manuscript and would be retained in any revision.

We have not looked any further into whether meteorological conditions during late winter and spring may contribute to the higher abundance of Br at Summit in 2007 compared to 2008. Antecedent conditions likely do have some impact on observations made in any short intensive campaign, but we are becoming convinced that the primary factor accounting for less Br at Summit in 2008 is the fact that sampling extended later into the summer. In 2010 we returned to Summit for an investigation into the potential role of Br chemistry on the isotopic composition of nitrate and made measurements of BrO and soluble Br⁻ from mid May through the 3rd week of June and again observed

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higher concentrations early in the campaign (similar to 2007). Note also that mixing ratios of soluble Br⁻ at end of 2007 were quite comparable to those in early part of 2008 (Figs 1 and 2). Based on these 3 seasons, we suspect that Br chemistry dies down in mid summer at Summit. Additional sampling will be conducted in 2011, currently we are debating the merits of targeting late spring (when this hypothesis suggests Br might be more abundant) or July/August when we now expect much less activity. Either part of the season should support or refute this hypothesis.

In response to comments from referee 2.

We will appreciate guidance from the editorial staff about how to reference manuscripts that are "in prep". One option considered was to delay this response as long as possible (due 23 September) in hopes that some would convert at least to "in review". Many, if not all, of these papers were expected to be companion articles in this special issue. As coordinator of the field campaigns and one of the guest editors for the special issue, J. Dibb has been cajoling collaborators to finalize these manuscripts. Despite assurances that all are nearly ready for submission, none are yet in the hands of ACPD. A near final draft of one Thomas et al. contribution is now circulating among the GSHOX team, allowing us to update at least the title of that paper (though the author list may change). On the plus side, the paper by Neuman et al. has advanced from in press to published, that status has been reflected in our References Cited.

We would revise the end of section 3.4 as shown below to acknowledge that excess Br has previously been observed in snow in the Arctic basin, and thank the referee for pointing out this oversight

The mean (median) Br⁻/Na⁺ ratio in surface snow was 113 (33) and 79 (47) times the sea salt ratio in 2007 and 2008, respectively, indicating even more enrichment of Br⁻ in the snow than in the aerosol. Snowpits suggest that Br⁻ is enriched compared to seasalt nearly all year, with the Br⁻/Na⁺ ratio only approaching 0.0018 (sea salt value) during winter peaks in Na⁺ (not shown). Similar enhancements of this ratio have been

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suggested as evidence of active Br chemistry in the Arctic basin (e.g., Toom-Sauntry and Barrie, 2002; Simpson et al., 2005).

Typographical error on page 13620 will be corrected.

The referee is correct about the relative abundance of Br in the top 0.5 cm of the snow, compared to a hypothetical well-mixed 100 m deep boundary layer. We are not certain whether we made a transcription error, or faulty calculation (changing 0.5 cm to 5.0 cm deep in the snow would make our statements essentially correct). However, as noted by the referee, because the atmospheric burden is a significant fraction of that in surface snow, deposition from the boundary layer (by fog and/or dry deposition) could show up as increasing concentrations in the snow. So, rather than simply changing 0.5 to 5.0, we would revise the end of section 4.2 to both be accurate and emphasize this point, as follows:

compare the abundance of reactive Br in a unit area column from the snow surface to the top of the boundary layer to the amount of Br- in a unit area of the surface layer of snow, it becomes apparent that there is about an order of magnitude more Br- in the top 0.5 cm of snow than there is Br in the hypothetical well-mixed boundary layer above it. Considering that sufficient light to sustain active snow photochemistry penetrates to depths in excess of 10 cm (Galbavy et al., 2007), it thus appears that activation of a small fraction of the Br- in near surface snow could support the observed abundance, and inferred fluxes, of reactive Br just above the snow. Further, it is most likely that reactive Br decreases quickly with distance above the snow source (Thomas et al., this issue), such that activation of an even smaller fraction of snow Br- could sustain active Br chemistry in the lowermost few meters or tens of meters of the atmosphere above Summit. On the other hand, there may be sufficient reactive Br in the boundary layer that deposition could create detectable changes of Br- concentrations in the surface layer (in contrast to NO₃- - HNO₃ where the fraction in snow overwhelmingly dominates the system (Dibb et al., 1998)).

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Note that Galbavy et al. is an additional reference, and would be added to References Cited.

Regarding the Comment from Dorothy Durnford, Dibb responded by personal email and clarified how the two statements were not necessarily contradictory.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 13609, 2010.

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Discussion Paper

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