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Jack E. Dibb

University of New Hampshire, jack.dibb@unh.edu

Luke D. Ziemba

NASA

J Luxford

University of New Hampshire - Main Campus

P Beckman

University of New Hampshire - Main Campus

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Bromide and other ions in the snow, firn air, and atmospheric boundary layer at Summit during GSHOX

J. E. Dibb¹, L. D. Ziemba^{1,*}, J. Luxford¹, and P. Beckman¹

¹Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH, USA

* now at: NASA Langley Research Center, Hampton, VA, USA

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Abstract. Measurements of gas phase soluble bromide in the boundary layer and in firn air, and Br[−] in aerosol and snow, were made at Summit, Greenland (72.5° N, 38.4° W, 3200 m a.s.l.) as part of a larger investigation into the influence of Br chemistry on HO_x cycling. The soluble bromide measurements confirm that photochemical activation of Br[−] in the snow causes release of active Br to the overlying air despite trace concentrations of Br[−] in the snow (means 15 and 8 nmol Br[−] kg^{−1} of snow in 2007 and 2008, respectively). Mixing ratios of soluble bromide above the snow were also found to be very small (mean < 1 ppt both years, with maxima of 3 and 4 ppt in 2007 and 2008, respectively), but these levels clearly oxidize and deposit long-lived gaseous elemental mercury and may perturb HO_x partitioning. Concentrations of Br[−] in surface snow tended to increase/decrease in parallel with the specific activities of the aerosol-associated radionuclides ⁷Be and ²¹⁰Pb. Earlier work has shown that ventilation of the boundary layer causes simultaneous increases in ⁷Be and ²¹⁰Pb at Summit, suggesting there is a pool of Br in the free troposphere above Summit in summer time. Speciation and the source of this free tropospheric Br[−] are not well constrained, but we suggest it may be linked to extensive regions of active Br chemistry in the Arctic basin which are known to cause ozone and mercury depletion events shortly after polar sunrise. If this hypothesis is correct, it implies persistence of the free troposphere Br[−] for several months after peak Br activation in March/April. Alternatively, there may be a ubiquitous pool of Br[−] in the free troposphere, sustained by currently unknown sources and processes.

1 Introduction

The discovery in 1998 that NO_x was photochemically produced in snow at Summit, Greenland (Honrath et al., 1999) led to the realization that sunlit snow is a chemically dynamic environment. Follow up studies have been undertaken at a large number of research sites, in both polar regions and in temperate snowpacks (e.g., Grannas et al., 2007). At Summit it soon became apparent that a large number of very active compounds were produced in the snow pack and released to the overlying air (see the 2002 special issue of Atmospheric Environment on snow photochemical investigations at Summit, volume 36, issues 15–16). Calculations with a photochemical box model indicated that the snow to air fluxes of H₂O₂, HCHO and HONO enhanced their mixing ratios significantly and should result in extremely elevated mixing ratios of HO_x (OH plus HO₂) just above the snow at Summit in summer (Yang et al., 2002).

In 2003 and 2004 the first campaigns to include measurements of OH and HO₂ plus RO₂, along with all precursors and sinks anticipated to be significant, at Summit were mounted to confirm the predicted enhancements of HO_x and test whether HO_x cycling and partitioning were consistent with established homogeneous tropospheric chemistry. In the summer 2003 campaign median values of HO₂ plus RO₂ and OH around their midday peaks were 4.1 × 10⁸ and 8.4 × 10⁶ molecule cm^{−3}, respectively (Sjostedt et al., 2007). Fully constrained box model calculations predicted similar levels of HO₂ plus RO₂ (and by extension HO_x) but observed OH exceeded predicted levels by more than a factor of two. Sjostedt et al. (2007) suggested that the good agreement between measured and predicted HO_x indicated that no large sources or sinks of HO_x at Summit were being overlooked, but the large underprediction of OH pointed to poor



Correspondence to: J. E. Dibb
(jack.dibb@unh.edu)

simulation of the cycling between OH and HO₂ in this unique environment. They speculated that active Br chemistry (not included in the standard model) would push HO_x partitioning to favor OH, and suggested that as little as 10 ppt of BrO could largely eliminate the difference between modeled and measured OH and the HO₂/OH ratio.

Sjostedt et al. (2007) readily admitted that active Br chemistry was not expected at Summit, given that the site is 3 km above sea level and several 100 km from the coast (assuming that sea salt would be the most likely source of Br reaching Summit). However, they outlined several lines of indirect evidence that supported the possibility of active Br chemistry at Summit, and suggested three possible sources: photochemical production in the snow, rapid advection of marine boundary layer air to Summit, and/or downward mixing of free tropospheric air. The GSHOX campaigns in 2007 and 2008 were conducted to confirm whether active Br chemistry was significant at Summit, and attempt to determine the relative importance of the different potential sources of Br suggested by Sjostedt et al. (2007). Seven different research groups combined to seek both direct and indirect evidence of Br chemistry at Summit, as well as measuring reactive gases and meteorological parameters required to model the complex chemical cycling in and above the snow at Summit (see the overview paper by Dibb et al. (2010) for the design of GSHOX and the contributions from all team members). This paper focuses on measurements of soluble ions in the gas phase, associated with aerosol, and in snow made by the University of New Hampshire, with particular attention paid to Br⁻.

2 Methods

2.1 Sampling location

All measurements and sample collection for this experiment except DOAS were made at a satellite camp 1.5 km SSW of the center of Summit station in the clean air sector. The active (long-path) DOAS system was installed in a temporary shelter on the south edge of the station, with retroreflector arrays located in the clean air sector. The light paths between the DOAS telescope and reflectors were approximately 0.5 km to the east of the satellite camp. Winds at Summit are not consistently steady in speed or direction, but the least frequent direction is from due north, so all atmospheric sampling has been on the southern, “upwind” side of camp. Hagler et al. (2008) pointed out that, on average, during the summers of 2003 through 2006, winds arriving at the satellite camp location passed through a northern, potentially polluted, sector (defined by point sources of pollution in the camp as well as areas where heavy equipment often was operating), 19% of the time. These authors recommended use of sector control to interrupt sampling, particularly for experiments that integrated over long periods (days or longer). Our group em-

ployed sector control for 2-day filter sampling that targeted organic aerosol, but not for any of the measurements described herein, preferring to filter fast continuous data using clear pollution spikes in NO. However, it may be important to note that in 2007 the sector controller flagged 5.5% of all sampling time as having wind direction that passed through the potentially camp-influenced sector, compared to 33% of the 2008 season. It should be noted that the “bad air” sector is defined conservatively, to account for mobile sources that are not always present (e.g., equipment grooming the runway or moving snow). Hagler et al. (2008) observed that during summer 2006 the winds were out of the defined camp sector 21% of the time, but local pollution (identified by very large enhancements in aerosol absorption monitored continuously) impacted the satellite camp just 7.6% of the time

2.2 Soluble gases

As in several previous experiments at Summit, we used mist chamber samplers to collect soluble gases, which were quantified in near-real-time by ion chromatography (e.g., Dibb et al., 1994, 1998, 2002; Chen et al., 2007; Sjostedt et al., 2007). In all previous campaigns samples were collected manually and then immediately analyzed in a nearby laboratory, for this study we deployed an automated two-channel mist chamber/ion chromatography (MC/IC) system developed for use on ship cruises (Dibb et al., 2004a) and urban air quality studies (Stutz et al., 2010a; Ziemba et al., 2010). This system uses syringe pumps to automatically load/unload the samplers and make injections into the ICs that are packaged in the same enclosure. As in previous Summit experiments, each sampler had its own inlet (3-m long heated 1.25 cm OD Teflon tubing that was wrapped for insulation and to exclude light and equipped with Zefluor inlet filter to exclude aerosol), and simultaneous samples were collected in the two samplers. For most of the 2007 season one of the inlets was positioned just a few cm above the snow while the second was 1 m above the snow, in a largely unsuccessful attempt to measure gradients (e.g., Honrath et al., 2002). In 2008 we used one sampler to monitor ambient air 1 m above the surface while the second was primarily used to sample firn air (the air filling pore spaces in the snowpack) at approximately 10 cm depth. In both years the two inlets were placed next to each other 1 m above the snow for 20% of sampling time to assess agreement between the two systems.

Samples were collected for integration intervals of 17.5 min. Emptying the samplers, making injections into the ICs, and then refilling the samplers took 2.5 min, thus we collected 3 samples h⁻¹. Every 2.5 to 3 days IC eluents and the sampler fill water were replenished, and the IC response was recalibrated using mixed aqueous standards. This routine maintenance resulted in data gaps of 2–3 h, efforts were made to perform maintenance at varied times of day in order to avoid any bias in sampling diurnal variations.

The MC samplers remove soluble gases from the airstream in a dense mist of fine, ultrapure, water droplets and continually concentrate the collected gases during sampling (Scheuer et al., 2003; Talbot et al., 1990). Resulting aqueous samples can be analyzed by technique of choice, we chose ion chromatography to quantify very low concentrations of several target ions; bromide, nitrite, and nitrate in this study. Soluble nitrate is overwhelmingly contributed by HNO_3 in the sampled air (Talbot et al., 1990) and is reported as HNO_3 . For bromide and nitrite the speciation of the atmospheric molecules collected in the MC is less certain. Lab tests have confirmed that HONO is quantitatively collected (and analyzed as nitrite) but field campaigns indicate positive interference by unknown additional compounds can be significant at times. In Houston, soluble nitrite measured by MC/IC agreed with HONO measured by long-path DOAS except on a few heavily polluted afternoons when a photochemically produced interferant (not identified) contributed to the soluble nitrite signal (Stutz et al., 2010a). At South Pole and Summit if soluble nitrite is assumed to be HONO it cannot be reconciled with observed NO and OH and established chemistry (Chen et al., 2004, 2007; Liao et al., 2006). Pernitric acid may contribute to the nitrite captured in MC samplers in polar regions, but poor correlation between HO_2NO_2 and soluble nitrite was observed at South Pole (Dibb et al., 2004b). At Summit the soluble nitrite is clearly photochemically produced in the snow pack and plays an important part in cycling of nitrogen oxides (Dibb et al., 2002; Honrath et al., 2002) so we continue to measure and report it despite uncertainty of speciation. Our first observations of bromide in MC samples were made from the NCAR C-130 during TOPSE where it was strongly anticorrelated with O_3 in the boundary layer over the Arctic sea ice (Evans et al., 2003; Ridley et al., 2003) and considered to be similar to “filterable Br^- ” observed in ODEs at Alert (Barrie et al., 1988). We have quantified bromide in all subsequent Summit campaigns (e.g., Sjostedt et al., 2007) and in MC/IC samples collected from the NASA DC-8 during the April, 2008 ARCTAS deployment (Neuman et al., 2010). We had speculated that gas phase soluble bromide was dominantly HBr plus HOBr but laboratory tests after ARCTAS indicate $\sim 50\%$ of Br_2 , HOBr, and BrO (presented as pure Br_2 , and variable mixtures of Br_2 plus HOBr and Br_2 plus BrO) are captured by the MC and measured as bromide by IC (Liao et al., 2010a). Testing with a pure HBr source, and mixtures of HBr with the other Br gases, is planned. The soluble bromide measured by MC/IC therefore provides a lower limit constraint on the abundance of reactive Br (sum of BrO, Br_2 , HOBr and HBr) in the sampled air.

2.3 Aerosol

Aerosol samples were collected onto 90 mm diameter 2 micron Zefluor filters. The open face filter holders were suspended 1.5 m above the snow from an aluminum pole.

Each filter was exposed for nominally 24 h, starting at 10:00 WGD. Sample flow rates were essentially constant at 62 standard liters min^{-1} , yielding sample volumes near 90 standard m^3 . Blank filters were taken every third day by loading a filter into the holder, mounting it on the pole and then removing it with no air flow. Filters (samples and blanks) were stored frozen for up to 9 days (accumulated until there were 12), and were then extracted and analyzed for major anions and cations by IC in the field. Extraction entailed wetting each filter with 0.5 ml of HPLC grade methanol then shaking and soaking in 20 ml of ultrapure (MilliQ) water, as described by Dibb et al. (2003).

2.4 Snow

Surface snow was sampled daily in 2007 (just after the aerosol filter changes) and twice daily ($\sim 10:00$ 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.

3 Results

3.1 Soluble gases

In 2007 the mixing ratio of soluble nitrite approximately 1 m above the snow consistently varied from minima of 1–3 ppt at night to maxima near 10 ppt shortly after local noon (Fig. 1). The midday peak approached 15 ppt on several days and briefly exceeded 20 ppt on just one day. Soluble bromide also tended to increase and decrease with solar elevation, though the lower mixing ratios overall (< 1 ppt in most sampling intervals) make the diurnal variations less clear on some days (Fig. 1). Nitric acid frequently exceeded 20 ppt, reaching 105 ppt briefly on 9 June, but intervals of enhanced HNO_3 were not always associated with the early afternoon peaks in soluble nitrite (and bromide) (Fig. 1).

During the 2008 campaign soluble nitrite again tended to reach minima very early in the morning ($\sim 1:00$ local time) but the relatively smooth daytime peaks seen in 2007 were obscured by frequent spikes exceeding 20 ppt (as

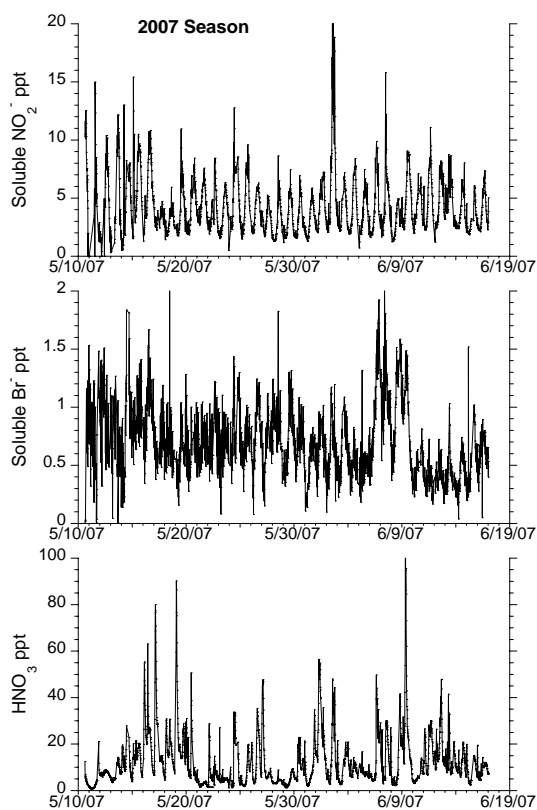


Fig. 1. Mixing ratios of soluble gases from the MC/IC system at Summit in the 2007 season. The inlet was nominally 1 m above the snow surface (adjusted at least daily in response to drifting), sampling rate was three samples per hour.

high as 80 ppt) (Fig. 2). For several days early in the season (9–14 June) soluble nitrite mixing ratios remained >5 ppt even through the night (Fig. 2), again unlike 2007 (Fig. 1). Nitric acid mixing ratios were also enhanced in early June 2008, compared both to 2007 and to most of the 2008 season (after 18 June) (Figs. 1 and 2). In contrast, soluble bromide mixing ratios tended to be lower throughout the 2008 season (Fig. 2) compared to 2007 (Fig. 1). The numerous spikes in soluble nitrite during 2008 are a reflection of the more frequent advection of camp pollution to the satellite camp in that season. Nitric acid is rarely enhanced in camp plumes, perhaps reflecting too little time to convert emitted NO to NO_2 and then produce HNO_3 during the 1.5 km of plume transport from the generator or diesel-powered heavy equipment to the sampling site. It is important to note that soluble bromide shows no apparent enhancements in sampling intervals impacted by camp pollution (reflected as soluble nitrite spikes in Fig. 2).

To assess whether the 2007 and 2008 seasons were representative of conditions at Summit in spring and summer, MC/IC results are summarized for the two campaigns in Table 1. We have published HNO_3 observations for six Summit campaigns in 1993–1995, and 1998–2000 with mean mixing

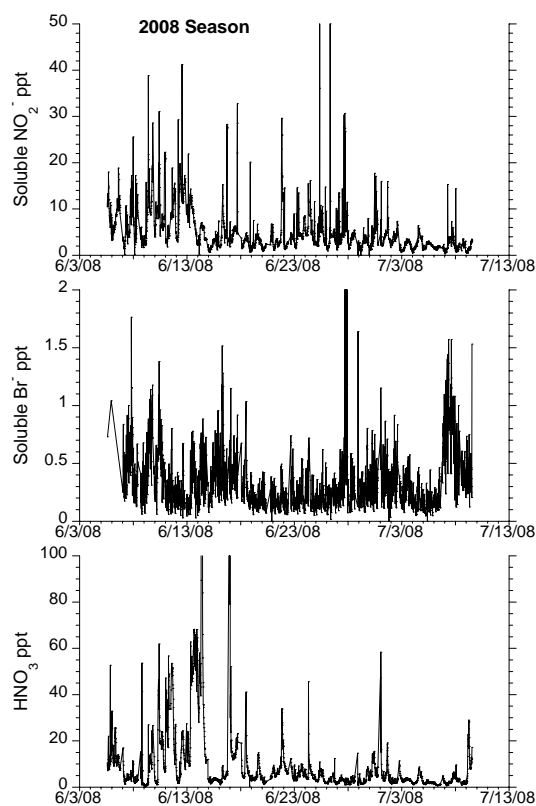


Fig. 2. As in Fig. 1, but for the 2008 season. Note the scale change for soluble nitrite.

ratios ranging from 10–45 ppt (Dibb et al., 1998; Grannas et al., 2007). If the 1998 season is excluded the range is just 10–20 ppt, which suggests that our 2007 and 2008 campaigns encountered the low end of normal HNO_3 mixing ratios, with means of 12 and 10 ppt, respectively. Similarly, mean mixing ratios of soluble nitrite in 2007 and 2008 (Table 1) were lower than the mean of 13 ppt in 1999 by as much as a factor of three but more similar to means of 7 and 11 ppt in 2000 and 2003, respectively (Yang et al., 2002; Chen et al., 2007). We are not aware of any published summaries of soluble bromide on the Greenland ice sheet, but the 2007 and 2008 ranges and means are comparable to our own unpublished results from 2003 and 2004. Sjostedt et al. (2007) noted that for most of 2003 soluble bromide mixing ratios ranged 1–2 ppt, though our reliance on manual sampling limited the number of data points collected between $\sim 1:00$ and $8:00$ local time. More nighttime sampling in 2003 may have documented more intervals with mixing ratios < 1 ppt if the nighttime minima in 2007 (Fig. 1) are representative, but it is likely that 2008 would still be the season with lowest soluble bromide observed at Summit to date.

Table 1. Statistical summary of the ambient mixing ratios (ppt) measured by MC/IC above the snow at Summit.

	Soluble Nitrite	Soluble Bromide	Nitric Acid
2007 Season 10 May to 17 June			
Mean (sdev)	4.3 (2.4)	0.7 (0.3)	12.4 (11.4)
Median	3.6	0.6	8.5
Maximum	20.9	2.7	105.1
2008 Season 5 June to 9 July			
Mean (sdev)	5.1 (5.0)	0.3 (0.3)	9.7 (16.4)
Median	3.5	0.3	4.2
Maximum	79.5	4.1	203.8

3.2 Aerosol

As expected from previous campaigns on the Greenland ice sheet (e.g., Davidson et al., 1993; Bergin et al., 1995; Dibb and Jaffrezo, 1997) the aerosol is dominated by sulfate, which is only partially neutralized by ammonium (Table 2). The mean (median) values of the molar ratio $\text{NH}_4^+/\text{SO}_4^-$ were 0.8 (0.7) and 1.2 (1.2) in 2007 and 2008, respectively, characteristic of acidic aerosol. All other ions were much less abundant than SO_4^- and NH_4^+ in both seasons. Smaller mixing ratios of dust tracers (Mg^{2+} and Ca^{2+}) in mid summer (2008) compared to early summer (2007) are consistent with peak dust delivery to Summit in April (Dibb et al., 2007) and may explain the smaller mixing ratios of NO_3^- in 2008 as well (Jordan et al., 2003). (Excess SO_4^- compared to NH_4^+ suggests that aerosol NO_3^- is likely to be associated with coarse aerosol, rather than forming fine NH_4NO_3 .) On average, Br^- was a trace contributor to the ionic burden in aerosol at Summit (Table 2) but the mean (median) Br^-/Na^+ ratio was 34 (16) and 9 (8) times larger than the seasalt ratio in 2007 and 2008, respectively.

3.3 Snow

Nitrate is the dominant ion in summertime surface snow at Summit (Dibb et al., 1994, 1998) and this was certainly true in 2007 and 2008 (Table 3). The abundance of NO_3^- and excess Cl^- combine to make the snow quite acidic, with average excess anions (assumed to be balanced by H^+) amounting to 3525 and 4730 nequiv kg^{-1} in 2007 and 2008, respectively. The molar ratio of $\text{NH}_4^+/\text{SO}_4^-$ also indicates that the snow was more acidic than the aerosol, with mean (median) values of 0.8 (0.2) and 0.5 (0.5) in 2007 and 2008. As noted for the aerosol, the concentrations of dust tracers in surface snow were nearly a factor of three lower in 2008 than 2007, reflecting strong seasonality in transport of dust to Summit (more generally, transport of Asian dust throughout the Northern Hemisphere, Dibb et al., 2007).

Overall, the composition of the snow during this experiment was as expected. Anions reflect the dominance of gaseous acids (HNO_3 and HCl) and partially neutralized accumulation mode SO_4^- aerosols as summer time sources of ions in snow at Summit. Sources of cations other than NH_4^+ are much weaker in mid summer and appear to be dominated by long-range transport of dust and episodic advection of biomass burning plumes over Summit. Dibb et al. (2007) presented results of three years of daily sampling at Summit for the major ions (not including NO_2^- and Br^-) and discussed seasonality of their transport and sources. In all cases except for C_2O_4^- the 2007 and 2008 means and medians (Table 3) are near the midrange of monthly values for May, June, and July observed in that study. Oxalate concentrations in both years of the present study were roughly three-fold lower than those in the lowest month of the prior study (May, 2002) and nearly an order of magnitude smaller than in June/July 2001, suggesting smaller influence from boreal wild fires than in several recent years.

We are not aware of prior measurements of NO_2^- and Br^- in Greenland snow that would provide context for the 2007 and 2008 results. It should be noted that NO_2^- concentrations in snow were lower in 2008 than 2007 (Table 3) despite the higher mean, and frequent spikes, in gas phase soluble NO_2^- (Table 1, Fig. 2), suggesting that camp pollution plumes were depositing little NO_2^- to the snow so close to the source (or that it was not retained in the snow). In contrast, Br^- in both the gas phase and the snow was about a factor of two lower in 2008 than 2007 (Tables 1 and 3). 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 suggested as evidence of active Br chemistry in the Arctic basin (e.g., Toom-Sauntry and Barrie, 2002; Simpson et al., 2005).

4 Discussion

4.1 Implications of gas phase observations

The time series of soluble gases measured by MC/IC in 2007 hinted that soluble nitrite and bromide tracked solar elevation on most days, with a less obvious diurnal variation in HNO_3 (Fig. 1). This early afternoon peak is quite clear in the hourly average mixing ratios of soluble nitrite over the entire 2007 campaign (Fig. 3, recall that local noon is at 14:00 GMT). Soluble Br^- and HNO_3 also showed daytime peaks in 2007, albeit less pronounced and broader than that of soluble nitrite (Fig. 3). Mixing ratios of BrO measured by both long path DOAS and CIMS in 2007 tended

Table 2. Statistical summary of the mixing ratios (ppt) of ions measured in aqueous extracts of 24 h bulk filter samples.

	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ⁼	C ₂ O ₄ ⁼
2007 Season											
Mean	9.4	63.7	3.7	4.1	16.2	3.2	bdl	0.3	11.2	77.8	1.8
sdev	10.8	38.0	3.0	5.2	18.8	4.4	0.1	0.2	12.3	40.7	0.9
Median	5.4	50.0	2.5	1.8	6.0	2.1	bdl	0.3	7.3	63.7	1.7
2008 Season											
Mean	11.8	44.7	3.6	1.2	6.1	5.8	0.7	0.2	3.1	54.8	1.7
sdev	4.4	25.0	1.7	0.4	2.9	4.4	0.4	0.1	3.2	47.5	1.0
Median	11.3	41.6	3.7	1.2	5.4	4.7	0.6	0.2	1.6	30.3	1.6

Table 3. Statistical summary of the concentrations (nmol kg⁻¹) of ions measured in daily (2007) or twice daily (2008) samples of surface snow at Summit.

	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ⁼	C ₂ O ₄ ⁼
2007 Season											
Mean	175.9	528.6	65.5	65.3	485.8	641.2	14.1	15.3	3143.2	745.8	17.9
sdev	134.3	756.3	73.5	56.8	314.6	370.0	8.0	9.8	1492.3	324.4	10.9
Median	146.5	215.9	30.1	43.5	376.6	526.3	12.7	14.2	2722.2	735.1	13.6
2008 Season											
Mean	115.9	281.6	74.0	23.1	143.7	547.0	3.7	7.7	3855.5	561.3	13.8
sdev	96.4	300.9	49.8	19.0	222.0	362.8	3.0	3.0	3090.5	487.4	15.3
Median	86.1	200.1	66.1	16.1	88.1	533.7	2.5	7.8	3330.0	417.0	9.0

to peak near midday and approach detection limits at night (Stutz et al., 2010b; Liao et al., 2010b). Rapidly depositing reactive gaseous mercury (RGM) also had a pronounced diurnal variation for most of the 2007 season, tracking *j*Br₂ quite closely (Brooks et al., 2010). The magnitude of daytime peaks in RGM increased on days when BrO was more abundant. The diurnal variations of all three gases measured by MC/IC in 2008 were more complicated, with maxima in the two nitrogen oxides not so clearly linked to solar intensity and a reduced range of diurnal variation in soluble bromide at lower mean mixing ratios (Fig. 3). The mixing ratios of BrO were likewise smaller, and diurnal variations less consistent, in 2008 (Stutz et al., 2010b; Liao et al., 2010b; Dibb et al., 2010). Also, RGM was rarely enhanced during the daytime in 2008, but it was observed to increase near midnight when surface air temperatures dropped below -15 °C (Brooks et al., 2010). A secondary peak in HNO₃ in the middle of the night (22:00–2:00 local time) was observed both seasons (Fig. 3). We have not observed nighttime enhancement of HNO₃ in previous campaigns, most likely due to limited sampling through the night in all prior experiments which relied on manual sample collection.

Previous studies have established that the dominant source of soluble nitrite above sunlit snow is photochemical production within the surface layer of the snowpack and subsequent flux into the atmosphere (Dibb et al., 2002; Honrath et al. 2002). Most of the HNO₃ measured above sunlit snow on the polar ice sheets is formed just above the snow by the NO₂ + OH reaction, with photochemical production of NO_x and OH precursors in the snowpack supporting enhanced mixing ratios of NO₂ and OH just above the snow (Dibb et al., 2004b; Chen et al., 2004; Huey et al. 2004). The nighttime enhancements of HNO₃ in 2007 and 2008 likely reflect the importance of NO₃ and N₂O₅ reactions just above the snow (Brown et al., 2004; Dibb et al., 2004a) since the abundances of NO_x and OH decrease markedly when the sun approaches the horizon (Dibb et al., 2002; Sjostedt et al., 2007).

The inference that soluble nitrite is produced in the snow pack and then fluxes out, while HNO₃ is produced above the snow surface from precursors that flux upward out of the snow, is based on firn air measurements which consistently show large enhancements of soluble nitrite and depletions of HNO₃ compared to ambient air just above the snow (Dibb et al., 2002, 2004b). (Snow photochemistry may very well be

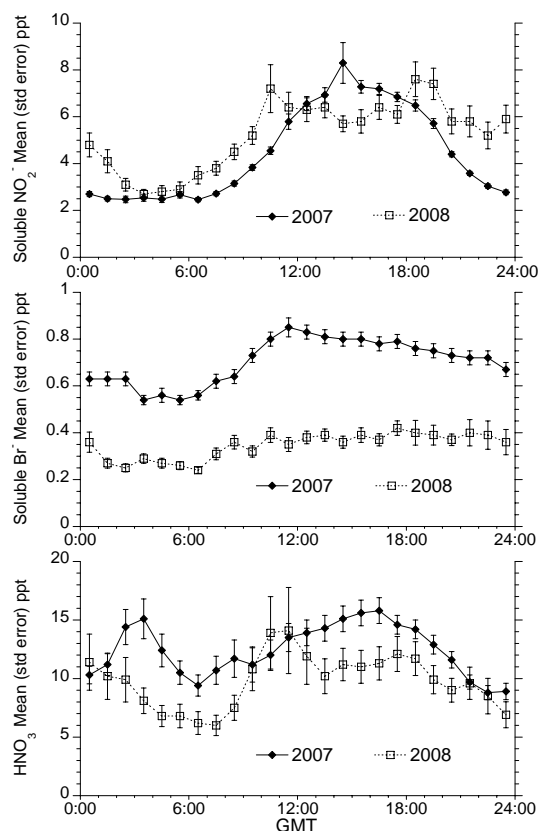


Fig. 3. Mean mixing ratios of soluble nitrite, soluble bromide, and nitric acid in hourly bins for the duration of the 2007 and 2008 campaigns at Summit. Error bars depict the standard error of the mean in each bin. Local Summit time (WGDT) is two hours behind GMT, thus solar noon is $\sim 14:20$ GMT.

producing HNO_3 in firn air, but it appears to rapidly adsorb to the ice crystals.) To assess whether daytime peaks of soluble bromide were due to production in, and release from, the snow pack, we sampled firn air at a depth of 10 cm on two days in 2007 and in the 10–15 cm depth range on 22 of the 32 sampling days in 2008. On both days of firn air sampling in 2007, soluble bromide peaked just after 14:00 GMT in both ambient and firn air, with peak mixing ratios in the firn air more than two times higher than those in the air just above the snow (2.5 vs. 1.1 ppt on 26 May and 1.5 vs. 0.7 ppt on 15 June). At night the mixing ratios were similar in and above the snowpack. Similar diurnal patterns in enhancement of soluble bromide were observed on most of the days of firn air sampling in 2008, as reflected in hourly averages calculated for all such days (Fig. 4).

It should be noted that sampling firn air through a probe inserted into the snow pack is prone to significant dilution of the firn air by ambient air rapidly drawn downward to the probe inlet through the highly permeable snowpack (Albert et al., 2002). This effect is more pronounced at shallower depths, and at higher sampling flow rates (like those used

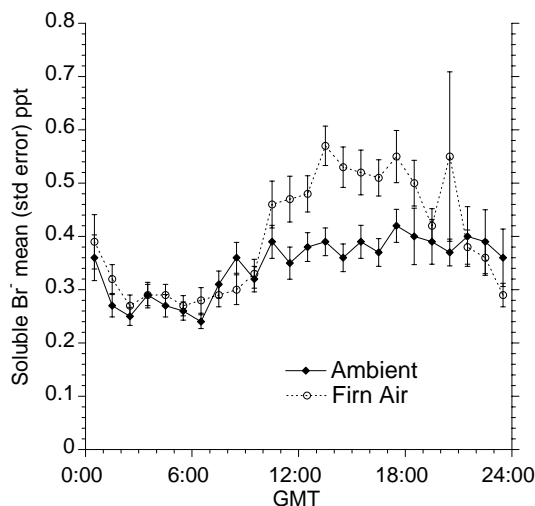


Fig. 4. Comparison of the hourly mean mixing ratios of soluble bromide measured 1 m above (filled diamonds) and 10–15 cm below (open circles) the snow surface during 2008. Error bars depict the standard error of the mean in each bin. Simultaneous ambient and firn air measurements were made on 22 of the 32 sampling days.

here for the MC/IC). As a result, the observed mixing ratios of soluble bromide in shallow firn air are decidedly lower limits, but it is clear that soluble bromide is generally enhanced in firn air compared to ambient air near midday at Summit. Thus, as for soluble nitrite, it appears that soluble bromide is produced in the snowpack by photochemically mediated processes and fluxes upward into the overlying near-surface atmosphere. This hypothesis is central to the one dimensional modeling effort, coupling photochemistry in the upper level of the snowpack to that in the atmospheric boundary layer, described by Thomas et al. (2010).

4.2 Is snow a plausible source of reactive Br at Summit?

Environments where active Br chemistry has been shown to play a significant role in tropospheric chemistry include the coastal Arctic and Antarctic boundary layer (including over sea ice), on the shores of saline lakes or salt pans, some parts of the marine boundary layer, and select volcanic plumes (von Glasow and Crutzen, 2007; Simpson et al., 2007). These all share one key feature, greatly enhanced concentrations of halides compared to those observed in the rest of the troposphere, and available at the surface over most continental regions. Summit would appear to represent nearly the extreme opposite end of the spectrum, with extremely low concentrations of halides in both the aerosol and surface snow (Tables 2 and 3). All of the ions in surface snow at Summit, except possibly NO_3^- , are present in trace concentrations compared to those in terrestrial fresh water throughout the mid and low latitudes (indeed, compared to most treated drinking water) and Br^- is a trace component of the ion loading in Summit snow (Table 3). However, the mixing ratios of

reactive Br (BrO or soluble Br, or even their sum) observed above the snow at Summit rarely exceed a few pptv. If we assume that the atmospheric measurements made just above the snow surface are representative of a well mixed 100 m deep boundary layer, and 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., 2010), 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).

4.3 Source of bromide in the snow?

Despite the relatively low concentration of Br⁻ in surface snow (Table 1), it was greatly enhanced relative to the sea-salt tracer Na⁺ throughout most of the two campaigns (Fig. 5). No clear and consistent relationship between periods with particularly high Br⁻/Na⁺ and the concentration of Br⁻ in snow, nor the mixing ratios of soluble bromide or BrO, were apparent. The sustained high values of Br⁻/Na⁺ in late May–early June 2007 (Fig. 5), partially reflect elevated Br⁻ concentrations (Fig. 6), but the correlation was weak over the 2007 season and there was no trend in Br⁻/Na⁺ with increasing Br⁻ in 2008. Haman et al. (2010) note that several intervals with enhanced BrO reported by the CIMS team and soluble Br⁻ from the MC/IC occurred in the day or two after an increase in Br⁻ concentration in the surface snow. However, this also was not true in all cases. Nor were the observed variations in the concentration of Br⁻ in surface snow consistently linked to deposition events (new snow or fog deposition) or drifting of snow during enhanced winds.

In 2007 the first eight days of surface snow sampling was conducted under stable conditions with sunny skies, light winds, and significant fog each night, targeting an aging layer that had blown in on 8 May. Through this period concentrations of Br⁻ more or less steadily decreased, and were below detection limits on 22 May (Fig. 6). Stronger winds caused drifting snow through much of the next three days, accompanied by increasing concentrations of Br⁻ in the loose snow

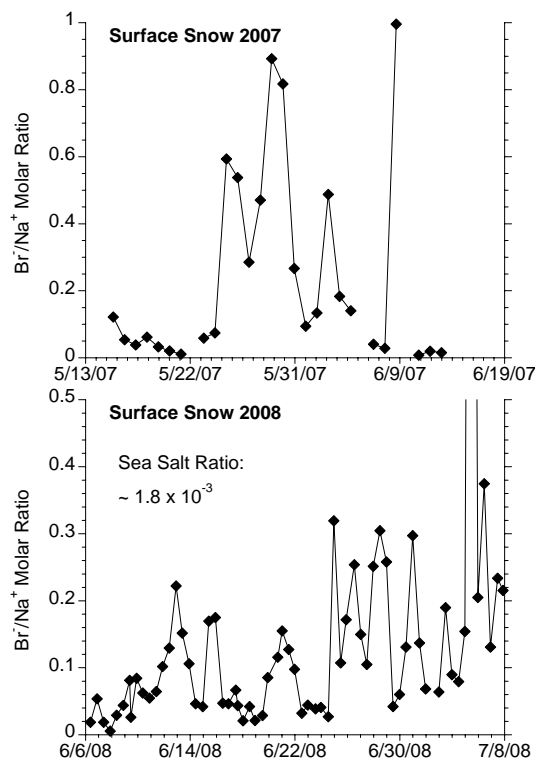


Fig. 5. Ratio of bromide to sodium in surface snow samples. Daily samples in 2007 were collected near 10:00 WGD, in 2008 samples were collected near 10:00 and 22:00. The ratio in nearly all samples is substantially greater than that in seawater. Note that the scales are not the same in the two panels.

sampled as the surface layer on these days. Concentrations dropped again during several calm days with nighttime fog, followed by another blow with drifting snow and enhanced Br⁻ 28 May through the morning of 1 June (Fig. 6). The first significant snowfall event occurred on 2 June, this layer contained ~ 20 nmol Br⁻ L⁻¹, as did additional new snow events sampled on 4 and 5 June. It should be noted that winds were strong enough to cause drifting of the 2 June snowfall, but little change in Br⁻ concentration was seen in the 3 June sample of the drifted new snow. Further, Br⁻ concentrations in new snow events sampled on 6, 14 and 15 June were below detection limits, and drifting during 5 of the last 12 days of sampling did not produce enhancements above 7 nmol Br⁻ L⁻¹ (Fig. 6).

The 2008 sampling season started like 2007 with settled weather and frequent nighttime fog, the first winds strong enough to cause drifting did not occur until the evening of 15 June, and no significant snowfall events were observed until 19 June. Unlike 2007, the settled weather early in 2008 was accompanied by increasing concentrations of Br⁻ in the surface snow, reaching seasonal maximum 14 June before winds increased (Fig. 6). Fresh snow layers sampled 19, 23, 25, 26, 28 and 30 June and 6 and 7 July had Br⁻ concentrations ranging 3–12 nmol L⁻¹.

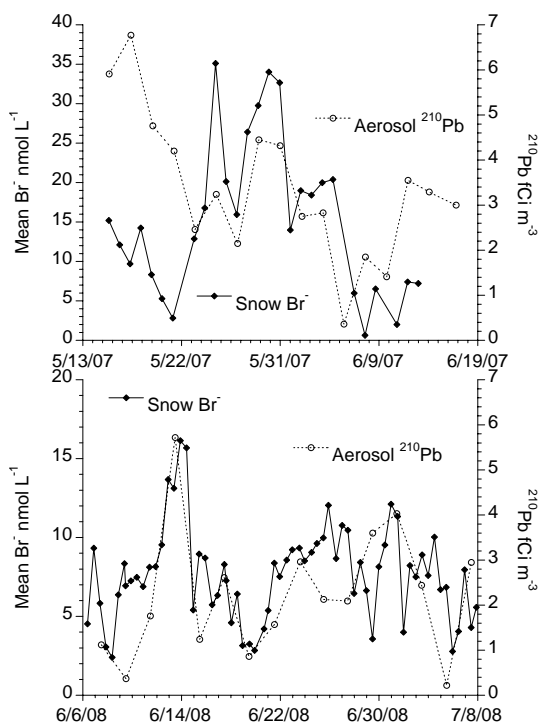


Fig. 6. Time series of bromide concentrations in surface snow compared to the specific activity of ^{210}Pb in bulk aerosol samples. As noted, snow was sampled daily in 2007 and twice daily in 2008. Filter samples for ^{210}Pb integrated over two-day intervals.

The positive relationship between Br^- concentrations in snow and the specific activity of ^{210}Pb (Fig. 6) (also ^7Be , not shown) in aerosol was the most consistent correlation between bromide compounds (in all phases) and any other parameter measured in the two seasons. Collection of 48-h long bulk aerosol samples for quantification of these natural radionuclide tracers is part of the baseline program of the GEOSummit Observatory. Dibb (2007) described the sampling protocol and the implications of covariations in ^7Be and ^{210}Pb observed in the first 5 years of sampling. Briefly, isolation (ventilation) of the boundary layer air above Summit by strong temperature inversions (vertical mixing strong enough to disrupt the inversion) causes aerosol and associated tracers to decrease through fog and dry deposition (increase by replenishment of aerosol). Thus, despite different sources, ^7Be and ^{210}Pb tend to be strongly correlated at Summit, as they were in the 2007 and 2008 seasons (Fig. 7). Increased ^{210}Pb activity is therefore primarily due to downward mixing of fresh aerosol from the free troposphere to the surface at Summit.

The observation that Br^- in snow tends to track variations in ^{210}Pb suggests that vertical mixing from aloft is likewise the source of Br^- reaching the snow surface during summer at Summit. As discussed above, it does not appear that scavenging by snowfall is necessarily required to deliver the Br^- to the surface, but removal by a combination of snow, fog

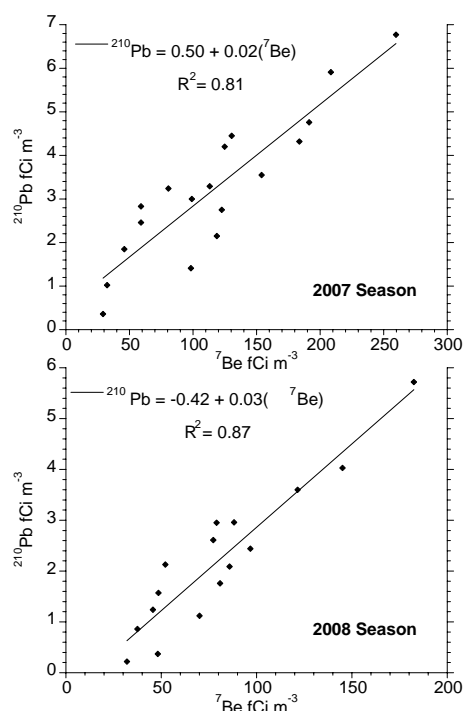


Fig. 7. Scatter plots of ^{210}Pb vs. ^7Be from the bulk aerosol samples collected during the 2007 and 2008 intensive campaigns. Lines are linear least squares regression fits.

and dry deposition must be efficient and rapid since parallel enhancements of gaseous and aerosol-associated Br compounds in the boundary layer above the snow are not generally seen. Our surface snow sampling protocol allows calculation of the inventory of Br^- (or any of the other ions) present per unit area of the surface layer sampled each sampling time (Dibb et al., 1998), with changes in inventory between samples providing insight into net fluxes. Considering observed increases in Br^- inventories provides some constraints on the plausibility of the hypothesis that vertical mixing can provide enough Br^- to account for the net downward fluxes.

In late May 2007 inferred net deposition of Br^- exceeded $19 \text{ nmol m}^{-2} \text{ d}^{-1}$ on 5 days, with the largest change of 41 nmol m^{-2} seen between 23 and 24 May. Complete removal of Br^- from a well mixed atmospheric column 1 km deep with a mixing ratio of 0.9 ppt would support the inferred maximum depositional flux. Assuming deeper vertical mixing would mean lower mixing ratios in the free troposphere would be viable, or would allow relaxing the assumption of complete removal (e.g., a 5 km deep column at 0.18 ppt would also contain 41 nmol of Br^-). We note that neither BrO or soluble Br were detected between 4 and 8 km pressure altitude when the NASA DC-8 spiraled down over Summit on 9 July 2008 (Neumann et al., 2010), however, the detection limit for soluble bromide by MC/IC during the ARCTAS airborne campaign increased from ~ 1 ppt in the

boundary layer to ~ 6 ppt at 12 km. Therefore, it is possible that mixing free tropospheric air down to the surface at Summit could account for even the largest changes of Br^- in the snow. All other observed increases in inventory in both seasons imply net fluxes $< 10 \text{ nmol m}^{-2} \text{ d}^{-1}$. It should also be noted that the steady decrease in Br^- concentration when the same layer of snow was repeatedly sampled early in the 2007 (Fig. 6) season suggests a net flux out of the snow at about $3 \text{ nmol m}^{-2} \text{ d}^{-1}$. Dispersing this into a well mixed 100 m column below the inversion would yield a mixing ratio of 0.7 ppt, comparable to means observed in the air just above the snow (Table 1).

Our observations at the surface at Summit do not provide insight into whether Br^- in the free troposphere is present in the gas or aerosol phase. Higher values of the Br^-/Na^+ ratio in snow than in the aerosol may indicate contributions from a gas phase source in clouds forming snow, or perhaps the aerosol most enriched in Br^- is preferentially taken up by snow. The source of Br^- in the free troposphere above Summit is likewise unknown. Contributions from the North Atlantic and/or the Arctic basin would seem likely. The large enhancements of Br^- relative to Na^+ indicate extensive processing of sea salt (if that is the dominant initial source of Br^-), leading us to speculate that the well documented active Br chemistry in the Arctic in springtime may result in a free tropospheric pool of Br^- at northern high latitudes. Airborne observations during ARCTAS and ARCPAC in April 2008 did suggest significant venting of BrO from the marine boundary layer into the free troposphere in association with some extreme ozone depletion events (Salawitch et al., 2010). Less abundant Br^- in aerosol and snow at Summit in June–July (2008) than May–June (2007) may be consistent with a springtime Arctic source of Br^- getting transported to Summit. Lower concentrations of Br^- in the snow during mid-summer than early summer would then result in lower mixing ratios of soluble bromide and BrO just above the snow, as observed (Thomas et al., 2010). However, non-methane hydrocarbon ratios from year-round sampling provide weak or no evidence of Br chemistry at Summit in March–April when ODE's are common, and Br chemistry is most active, in the Arctic basin (Gorham et al., 2010). Perhaps the strongly stable Arctic atmosphere prevents lofting of Br^- into the free troposphere until later in the year (e.g., Scheuer et al., 2003).

5 Conclusions

Measurements of gas phase soluble bromide in the air just above, and in the pore spaces of, snow at Summit, Greenland confirm that active Br chemistry is occurring at this site, despite extremely small abundance of Br^- (indeed, all halides) in the snow at the crest of the Greenland ice sheet. Despite the trace levels of Br^- in snow, the Br^-/Na^+ ratio is greatly in excess of the seasalt ratio throughout the sum-

mer. Higher mixing ratios of soluble bromide in firm air than the atmosphere, and the tendency for peak mixing ratios to occur near local noon, indicate that photochemical activation of Br^- in the snow sustains active Br chemical cycling above the snow. Companion papers in this issue demonstrate that Br chemistry has significant impacts on speciation of Hg, HO_x cycling, and NMHC ratios at times, despite mixing ratios of soluble bromide and BrO rarely exceeding a few ppt. Bromide concentrations in the surface snow often increased when vertical mixing disrupted strong inversions and allowed free tropospheric air to replenish the boundary layer just above the snow. Speciation of the apparent Br^- reservoir in the free troposphere above Summit is uncertain, as is the relative importance of gaseous vs. aerosol-associated compounds. We hypothesize that widespread Br^- activation leading to ozone depletion in the Arctic basin shortly after polar sunrise also results in the creation of this free tropospheric Br^- pool, which is then not efficiently transported to Summit until early summer. Marine boundary layer processes in the North Atlantic might also be a source of excess Br^- in the free troposphere over Greenland, but this would appear difficult to confirm experimentally.

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