Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine air-snow chemistry during springtime

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[1] We measured halide concentrations of snow and frost flowers in the vicinity of Barrow, Alaska. We find that the ratio of bromide to sodium in frost flowers is slightly enhanced ($\approx$10%) as compared to sea water. In contrast, the ratio of bromide to sodium in some snow samples is more than an order of magnitude enhanced, and in other samples is more than an order of magnitude depleted. We interpret the bromide depleted snow as having been processed by heterogeneous chemistry and providing reactive halogen compounds to the atmosphere. The eventual end product of reactive bromine chemistry is HBr that is then deposited over a wide region, enhancing bromide in inland snow samples. Although frost flowers or open leads are likely to be the original source of halides that become reactive halogen gases, we find that the bromide release often occurs subsequent to production of aerosol from marine sources. **Citation:** Simpson, W. R., L. Alvarez-Aviles, T. A. Douglas, M. Sturm, and F. Domine (2005), Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine air-snow chemistry during springtime, *Geophys. Res. Lett.*, *32*, L04811, doi:10.1029/2004GL021748.

1. Introduction

[2] Reactive halogens strongly impact the troposphere in polar regions during springtime. Ozone is depleted from background levels to near zero, and at the same time, elemental mercury is oxidized to reactive gaseous mercury that deposits to snow. Early studies implicated bromine in these ozone depletion [*Barrie et al.*, 1988] and mercury deposition events [*Schroeder et al.*, 1998]. Ground-based [e.g., *Hausmann and Platt*, 1994] and satellite-based observations have subsequently shown that reactive bromine clouds (clouds containing bromine monoxide, BrO) are ubiquitous in the polar springtime troposphere [e.g., *Wagner and Platt*, 1998; *Richter et al.*, 1998]. These BrO-rich air masses generally occur over snow-covered sea-ice surfaces [*Richter et al.*, 1998; *Wagner and Platt*, 1998], especially in regions where leads and polynyas commonly form [*Zeng et al.*, 2003; *Kaleschke et al.*, 2004]. While the source of

bromine is certainly sea salt, many questions remain regarding how sea salt is transformed into gas-phase reactive halogens. Frost flowers have been proposed as an important intermediate step in halogen activation [*Rankin et al.*, 2002; *Kaleschke et al.*, 2004], although there are other sea-salt sources such as bubble-bursting, wave action, and convective lead processes. The proposed mechanism of halogen release from ice surfaces involves the reaction of HOBr with halides (Br^- and Cl^-) on acidic ice surfaces forming BrCl and Br_2 that are subsequently photolysed to form reactive halogen atoms [*Fan and Jacob*, 1992; *McConnell et al.*, 1992; *Huff and Abbatt*, 2002; *Adams et al.*, 2002]. Reactive halogen compounds are eventually deactivated by reaction with organic compounds, such as aldehydes, leading to HBr and HCl. These acids are then scavenged by snow or particulate matter. Some studies have examined bromide in aerosols [e.g., *Berg et al.*, 1983; *Barrie et al.*, 1988; *Ianniello et al.*, 2002], but only a few papers investigate bromide in snow [*Toom-Sauntry and Barrie*, 2002; *Domine et al.*, 2004]. Therefore, we focus here on observations of bromide and chloride in surface snow. These studies are a part of larger projects aimed at understanding the relationship of reactive halogen chemistry and sea-ice leads to mercury deposition [*Douglas et al.*, 2005].

## 2. Snow Sampling and Chemical Analysis Methods

[3] Because satellite observations of BrO show strong contrasts between offshore and inland atmospheric conditions, transects were chosen to observe snow in differing chemical environments. The sampled area extended from the edges of leads on the sea ice near Barrow Alaska, across the North Slope of Alaska, and into the Brooks range ($\approx$280 km from Barrow). Snow was sampled during three field phases from 1 March 2004 to 10 May 2004 and with reference to snow stratigraphic layer. For the present investigation, we selected snow samples that were deposited after polar sunrise. Snow and frost flowers were sampled using clean procedures to prevent contamination [e.g., *Douglas and Sturm*, 2004]. Multiple samples were collected at each location to assess variability between replicate samplings. All samples were transported and stored frozen in the dark (approximately 4 months) before analysis. Anions were analyzed by ion chromatography (Dionex DX320, AS17 column), and sodium was analyzed by direct-aspiration flame atomic absorption spectroscopy (Perkin Elmer). Samples were sorted by conductivity and diluted appropriately to maintain the high dynamic range required to quantify accurately the small bromide concentrations in the presence of approximately 1000-fold excess of chloride. Extended

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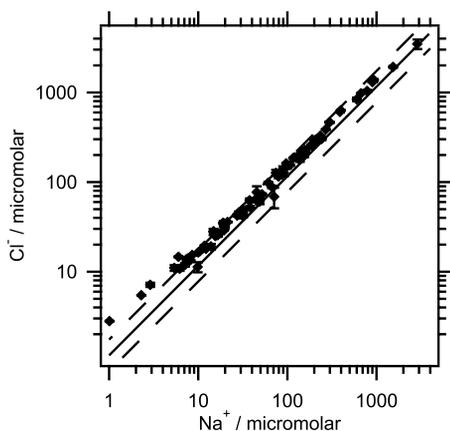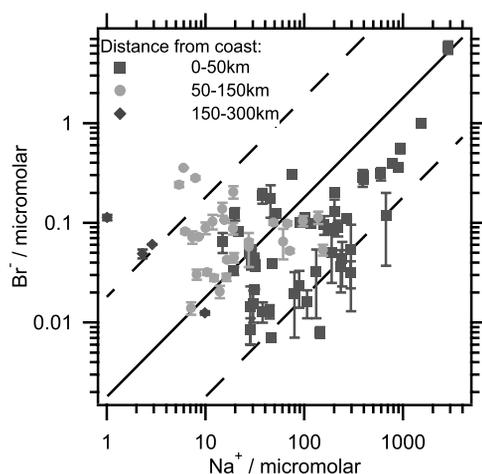
Figure 1. Chloride versus sodium concentrations in springtime snow pack. Both scales are logarithmic. The ends of the error bars show the two field replicates, and the marker their average. In many samples the error bars are too small to be seen. The solid diagonal line represents the chloride versus sodium concentration that results from dilution of sea water. The upper and lower dashed lines represent 1.5 and 2/3 times the sea-salt dilution line.

details of the analytical procedures will be discussed elsewhere. Analysis of a sea water sample taken from the Arctic Ocean shows ratios of chloride and bromide to sodium are within analytical errors (<10%) of literature values [*Quimby-Hunt and Turekian*, 1983].

3. Results

[4] Because sea-salt aerosol is very likely to provide the majority of sodium in snow, sodium is an excellent tracer for the influence of marine aerosols on snow. Figures 1 and 2 show the concentration of chloride and bromide, respectively, versus the sodium ion concentration. The solid diagonal lines represent the sea-salt ratio that would result from dilution of sea-salt. The end points of the error bars represent the two field replicate measurements, and the symbol is their average. Figure 1 shows that, except for a

Figure 2. Bromide versus chloride, as in Figure 1, except here the upper and lower dashed lines represent 10 and 0.1 times the sea salt dilution line. See color version of this figure in the HTML.

few samples with very low sodium concentration, our snow samples are below the 50% enhancement line. On the other hand, Figure 2 shows that bromide concentrations are much more poorly correlated to sodium and that numerous samples are enhanced or depleted by over an order of magnitude. Figure 2 also shows that the absolute variation in bromide concentrations is less than that of chloride and sodium ions. Table 1 shows halide and sodium ion concentrations for sea-water and frost flower samples and shows only slight alterations of the ratios of bromide and chloride to sodium, from sea water to frost flowers, in concordance with [*Rankin et al.*, 2002]. These slightly enhanced halide to sodium ratios are caused by depletion of sodium through formation of mirabilite ($Na_2SO_4 \cdot 10\ H_2O$) [*Wagenbach et al.*, 1998; *Rankin et al.*, 2002]. Because the bromide fractionation in frost flowers is much smaller than the observed fractionation in snow, we can not use bromide to separate between frost flowers and other sea salt sources. The small difference of Br/Na ratios between sea water and frost flowers implies that processes subsequent to production of sea salt aerosols are more important in causing the release of bromine from the aerosols than processes from the original frost flowers.

[5] The influence of marine sources on coastal snow can be observed by considering the sodium concentration as a function of distance inland (Figure 3). Our samples were in two classes, either near coastal or along an approximately north-south transect onshore (south) from Barrow. In the former case, we take the distance from the coast to be the distance to the nearest coast, and in the latter case, we take the distance from the Naval Arctic Research Laboratory (71.2°N, 156.4°W) endpoint of the traverses. Because of variations in wind direction and strength, this distance definition is not the transport distance from source to the sampling site and probably causes a great deal of variability in sodium concentration at each location. However, simply plotting all data shows an informative picture of the strong falloff of marine influences inland from the coast. We also plot the bromide concentration as a function of distance from the coast on Figure 3. We see that the decay of bromide concentration with distance from the coast is significantly more gradual than that of sodium. This picture reinforces that of Figure 2, now clearly indicating that sodium, which is transported as an aerosol, deposits relatively rapidly as air masses transport onshore, while bromide is transported much farther onshore.

4. Discussion

[6] These data show a number of important points regarding halide concentrations in snow. In most samples, chloride and sodium concentrations lie close to the sea-

Table 1. Analysis of Sea Water and Frost Flowers Sampled on 1 March 2004[a]

Sample	Na+	Cl−	Br−	Cl−/Na+	Br−/Na+
	mmol/L			mol/mol	
Standard sea water ratios	−	−	−	1.16	0.0018
Arctic Ocean sea water	419	519	0.85	1.24	0.0020
Frost flowers (≈4 hour age)	1634	2165	3.53	1.33	0.0021
Frost flowers (≈8 hour age)	1601	2098	3.46	1.31	0.0021

[a]All concentrations are in millimole/L, and ratios are on a molar basis. The sea water sample was from the Arctic Ocean adjacent to the forming frost flowers.
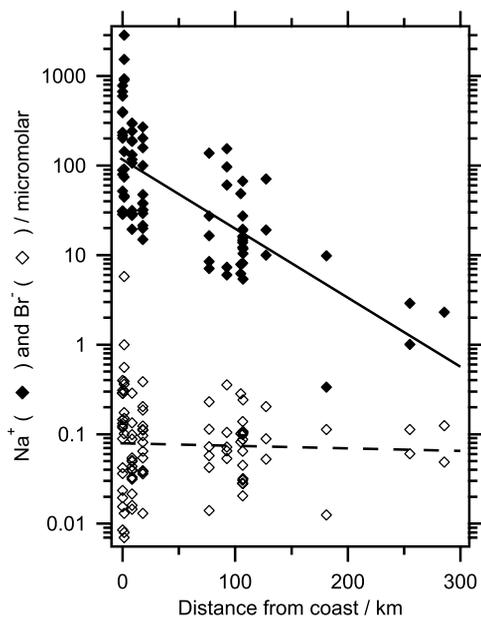
Figure 3. Sodium and bromide in the springtime snow pack as a function of distance from the coast. Distances from the coast are calculated as described in the text. The lines are trend lines made by linear fits of the logarithm of the concentration versus distance from the coast.

water dilution line (Figure 1). Therefore, we see that sodium and chloride in these samples are dominated by marine inputs, in agreement with studies of snow and ice from coastal Antarctica [*Wagenbach et al.*, 1998; *Rankin et al.*, 2002]. Snow that is of low sodium concentration sometimes shows chloride elevation, which is probably due to sticking of gas-phase chloride compounds (e.g., HCl) [*Toom-Sauntry and Barrie*, 2002].

[7] Bromide is poorly correlated to sodium, indicating that, unlike chloride, its presence in snow is not dominated by deposition of sea-salt aerosol (Figure 2). Laboratory studies show that bromide is released from ice surfaces by heterogeneous reactions [e.g., *Huff and Abbatt*, 2002; *Adams et al.*, 2002]. Therefore, the depletions of bromide as compared to sea-salt composition are likely the result of atmospheric chemistry on snow or aerosol surfaces. This bromine release produces gas-phase reactive bromine compounds (e.g., Br and BrO). These gases may subsequently be transported with different dry and wet deposition efficiencies than aerosols. Specifically, they may be transported longer distances onshore than are sea-salt aerosols. Reactive bromine chemistry terminates by reaction with hydrocarbons and production of HBr, which may then be directly deposited to snow or be scavenged by snow or aerosols. If this HBr is added to snow that is low in sodium concentration, it will enhance the bromide compared to sodium in those samples and flatten the onshore decay of bromide compared to sodium, in agreement with observations. Thus atmospheric chemistry appears to be the dominant factor controlling the bromide composition of snow. [*Toom-Sauntry and Barrie*, 2002] showed that snow at Alert, Canada was generally enhanced in bromide, while we find both enhancements and depletions. The fresh snow sampled by [*Toom-Sauntry and Barrie*, 2002] at Alert was low in

sodium concentration, with an annual median sodium concentration of 7 micromolar, placing their samples in a class that we also find to be enhanced in bromide. The finding of less marine influence in springtime at Alert than in the vicinity of Barrow is in agreement with the lack of leads at Alert compared to active leads near Barrow.

[8] This study, when combined with past studies on aerosols and snow in the arctic, points to an important role for atmospheric chemistry in the snow pack. Measurements of aerosols and filterable bromide [*Berg et al.*, 1983; *Barrie et al.*, 1988] show enhanced bromide in aerosol during ozone depletion events, as confirmed by later observations [*Ianniello et al.*, 2002]. Deposition of this aerosol to snow would then lead to enriched snow in contrast to our observations of numerous depleted coastal snow samples. Therefore, atmospheric chemistry must release the bromide from snow pack over large regions of the coastal zone. Release of bromide from the snow pack was also indicated by higher concentrations of Br_2 observed within the snow pack as compared to air above the snow surface [*Foster et al.*, 2001]. Gas-phase BrCl observed by [*Foster et al.*, 2001] may arise from HOBr reaction on bromide depleted snow, as has been observed in laboratory studies [*Adams et al.*, 2002]. Photolysis of BrCl produces both chlorine and bromine atoms and may be the activation mechanism that provides the chlorine atoms inferred by hydrocarbon loss studies [*Jobson et al.*, 1994].

[9] The atmospheric chemistry that releases bromide from snow requires time to deplete the snow bromide concentration. The amount of bromide in snow would then depend on the initial input of bromide to the snow and the amount of HOBr that is ventilated through the snow pack. Variability in each of these effects may be responsible for the poor correlation of bromide with sodium (Figure 2). Samples with a large reservoir of bromide (e.g., frost flowers or snow with a high input of sea-salt aerosol) require a relatively longer time to show depletion of bromide compared to sodium because their initial bromide concentration is large and a long exposure time is required to deplete this reservoir. This effect is probably the cause of the smaller depletions of the bromide to sodium ratio observed in snow with high sodium concentrations (Figure 2), and the lack of observable bromide loss in fresh frost flowers (Table 1).

[10] The possible role of frost flowers in reactive halogen events has been a major topic of discussion recently [*Rankin et al.*, 2002; *Kaleschke et al.*, 2004]. Our data cannot directly implicate or refute frost flowers as the source of atmospheric reactive halogens. However, our observations show that frost flowers are not depleted in bromide, suggesting that they are not the direct source of bromine to the atmosphere. As discussed above, the large reservoir of bromide in frost flowers may prevent observation of bromide depletion, particularly in the relatively short (<8 hours) lifespan of our samples. However, if bromide release could only occur from frost flowers and frost flowers are not strongly depleted in bromide compared to sodium, strongly depleted snow samples should never be observed. Therefore, our observations of strongly bromide depleted snow samples indicate that frost flowers are not unique in the ability to produce reactive halogen species, and that bromide activation is ubiquitous in coastal regions. It appears likely that sea salt coming from any source can be a source of

reactive halogens and that the main factor controlling reactive halogen release is the amount of sea-salt aerosol produced. Frost flowers may then be correlated with halogen activation because they appear to produce sea-salt aerosol efficiently [*Rankin and Wolff*, 2003].

5. Conclusions

[11]   Our observations of bromide, chloride, and sodium in frost flowers and snow indicate that while chloride and sodium act primarily as tracers of marine influences that are transported inland as aerosols, bromide behaves very differently and in a manner consistent with gross modification through atmospheric chemistry. The Br^-/Na^+ ratio in snow varies by two orders of magnitude and bromide depleted snow samples show that more than 90% of bromide may be removed from snow. The likely cause of this bromide depletion is heterogenous chemistry that produces photolabile halogen compounds and may provide a route to BrCl formation and chlorine activation. In this scenario, bromide is released from sea-salt particles, either in the aerosol phase or contained in snow by heterogeneous reactions. The direct effects are depletion of bromide from affected samples and production of gaseous bromine compounds (Br and BrO). These reactive halogens eventually react with organic compounds producing HBr that deposits on snow, enhancing snow bromide. In this manner, reactive halogens gases and HBr are transported with different loss processes from the aerosols that carry sodium, thus the correlation between bromide and sodium concentrations is poor and the decay of bromide as a function of distance from the coast less drastic than that of sea-salt-aerosol-transported sodium. This flatter distribution for bromide then appears as enhancement of bromide as compared to sodium for low sodium concentration (inland) snow and depletion for high sodium concentration (coastal) snow. We also investigated the possibility that frost-flower formation may affect bromide composition ratios. We found that although frost flowers are more saline than sea water, they are only slightly fractionated in bromide compared to sodium. This finding shows that frost flowers are not the immediate source of bromide-depleted snow and that depletion of bromide must occur either in aerosols derived from marine sources (frost flowers, open sea, or snow on sea ice) or on the surface of snow itself. Overall, we conclude that atmospheric chemistry that produces reactive halogen radicals is the dominant factor controlling the bromide composition of snow.

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