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Are methyl halides produced on all ice surfaces? Observations from snow-laden field sites

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Abstract

We present data collected from a number of snow-covered environments including two polar locations (Summit, Greenland and the South Pole) and two mid-latitude regions (a remote site in northern Michigan, and Niwot Ridge, Colorado). At each site, concentrations of CH_3I and $\text{C}_2\text{H}_5\text{I}$ were enhanced within the interstitial air near the snow surface, compared to levels in boundary layer air. Fluxes of CH_3Br from surface snow to the atmosphere were observed at each site except Niwot Ridge, where CH_3Br appeared to have a sink. The mid-latitude sites showed significant emissions of CH_3Cl , mostly originating at the ground surface and traveling up through the snow, while at the polar locations CH_3Cl emissions from firn air were relatively small. In general, methyl halide mixing ratios in firn air were significantly greater at Summit than at the South Pole, with Summit showing a strong diurnal cycle in the production of alkyl halides that was well correlated with actinic radiation and firn temperature. We suggest that the most likely route to alkyl halide formation is through an acid catalyzed nucleophilic substitution of an alcohol type function by a halide, both of which should be preferentially segregated to the quasi-liquid layer at the surface of the snow grains. A series of experiments using a snow-filled quartz chamber irradiated by natural sunlight allowed estimation of emission trends that were hard to measure in the natural snowpack. These static chamber experiments confirmed significant production of the primary alkyl halides, following the order $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{C}_2\text{H}_5\text{Cl} > \text{CH}_3\text{I} > \text{C}_2\text{H}_5\text{Br} > \text{C}_2\text{H}_5\text{I} > 1\text{-C}_3\text{H}_7\text{Br} > 1\text{-C}_3\text{H}_7\text{I}$. Our observations at all four locations, including polar and mid-latitude sites, imply that alkyl halide production may be associated with all surface snows.

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Keywords: Snow chemistry; Methyl iodide; Methyl bromide; Organohalides; Snow composition

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1. Introduction

Post-depositional processes within surface snows have become an increasingly important topic over

the past several decades. In several different polar field investigations the surface snowpack has been shown to be more photolytically active than previously considered, inducing rapid exchange of gases between the snowpack and the overlying boundary layer (BL) (Bottenheim et al., 2002; Davis et al., 2004). Coincident evidence from laboratory experiments have also shown that organic chromophores in snow and ice such as ketones (Klan et al., 2000, 2001), nitrophenols (Dubowski and Hoffmann, 2000), and a large number of substituted aromatics (Klan and Holoubek, 2002), can be photolyzed by actinic radiation, transforming the post-depositional composition of snow and ice.

A wide range of volatile organic species have been measured at high concentrations in surface snowpacks, such as C₁–C₂ organic acids (Dibb and Arsenault, 2002), aldehydes (Couch et al., 2000), alkenes, alkyl nitrates, and methyl halides (Swanson et al., 2002), with the emission of all of these compounds being tied to actinic radiation. Early results, which showed photochemically driven production of HCHO from organic chromophores in the snowpack interstitial air, suggested that net flux to the BL would both increase the oxidative capacity of the BL and increase ozone depletion in the Arctic by inducing Br₂ emissions from the snow (Sumner and Shepson, 1999). Evidence of these processes occurring in natural snowpacks was subsequently collected at Alert, Canada in 2000, where Br₂ was shown to be twice as concentrated in firn pore air just below the snow surface compared to overlying air (Foster et al., 2001). However, the relationship between organic and reactive halogen species first suggested by Sumner and Shepson (1999) has not received much attention. Most research dealing with halogens in arctic regions or areas impacted by snowfall have focused on bromine oxidation of ozone.

A different investigation has pointed out the connections between enhancements of BrO and CH₃Br during ozone depletion events within the BL in the Canadian Springtime (Wingenter et al., 2003). Additionally, several investigations have found similar results within irradiated snowpacks where emissions of organics, reactive halogens and alkyl halides are coupled with the rapid depletion of ozone in the snowpack (Couch et al., 2000; Dibb and Arsenault, 2002; Foster et al., 2001; Peterson and Honrath, 2001; Sumner and Shepson, 1999; Swanson et al., 2002). Thus, it would appear there is a direct connection between halides and organic

carbon species in the snow that upon irradiation participate in the release of reactive halogens and alkyl halides.

In this study we compare and contrast measurements of mono-substituted alkyl halides (C₁–C₂ RX; X = Cl, Br, and I) made in the interstitial firn air and the overlying BL air at four remote sites: two polar locations (Summit Research Camp, Greenland, and the South Pole Observatory, Antarctica) and two mid-latitude sites (northern Michigan, and Niwot Ridge, Colorado).

2. Experimental methods

2.1. Field sampling projects

Whole air samples were collected within the surface snow (firn) at polar locations during two different field campaigns: “Investigation of Sulfur Chemistry in the Antarctic Troposphere” (ISCAT) at the South Pole and “Investigation of Photochemical Transformations within Snow and Their Effect on Snow and Atmospheric Composition” at Summit, Greenland, and are the focus of two separate special issue publications; Davis et al. (2004) and Bottenheim et al. (2002), respectively. This paper focuses on selected sample sets collected as small components of these larger projects. For this work, samples from the South Pole Atmospheric Research Observatory (ARO) were collected on December 23, 2000, while the Summit firn profile samples were collected on June 23, 2000. Therefore, both data sets were collected at the time of summer solstice in their hemisphere. At Summit the collection of firn pore-air samples to a depth of 2 m was repeated three times over a single day, extending from maximum to minimum solar zenith angle, while at ARO a single midday firn profile was sampled to 1.5 m depth. There is 24 h sunlight at both Summit and South Pole during summer, but Summit experiences a strong solar diurnal variation because of its lower latitude (72°N). At South Pole the solar zenith angle is essentially constant over 24 h intervals. Fig. 1 shows modeled photolysis rates for $J(\text{O}^1\text{D})$ and $J(\text{NO}_2)$ that depict the difference in UV-B and visible/infrared radiation, respectively, between the South Pole, Summit, Niwot Ridge, and northern Michigan. The total ozone columns used in the modeling, as well as the basic meteorological parameters for all sites are listed in Table 1.

The Niwot Ridge, Colorado, data set was collected on April 18, 2003. It represents samples

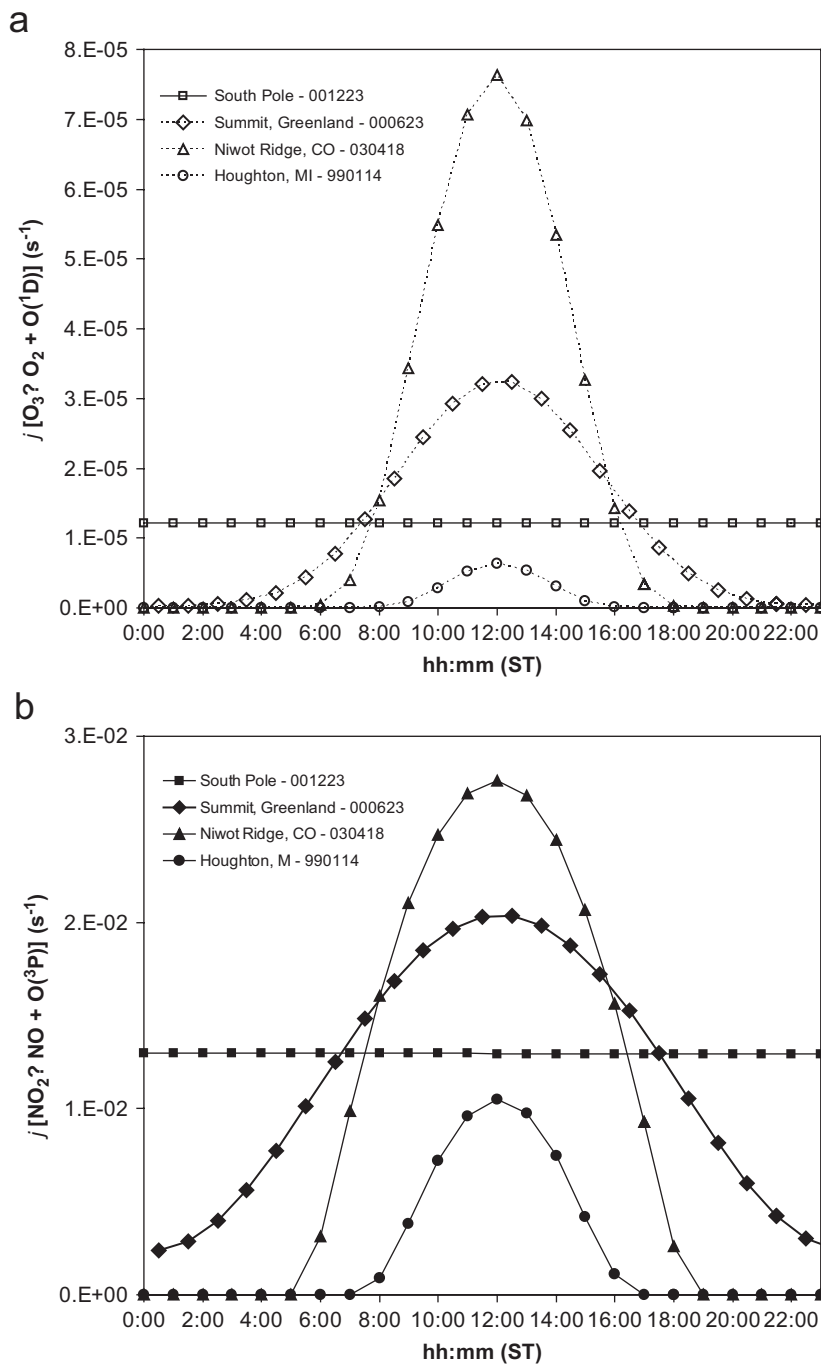


Fig. 1. (a) and (b) Photolysis rates modeled for each site at the time of the firn profile: 14/01/1999 for Michigan, 23/06/2000 for Summit, 23/12/2000 for South Pole, and 18/04/2003 for Niwot Ridge. Figs. A and B show $J(\text{O}(^1\text{D}))$ and $J(\text{NO}_2)$ representing UV-B and IR wavelengths, respectively. The ozone columns and elevations used for the calculation are shown in Table 1. Measurements at the South Pole agree well with the radiative transfer model results (Lefer et al., 2001).

of interstitial air collected within a snowpack of 1.1 m depth overlying forest soil. The sampling location was in a clearing between mixed hardwood

and conifer forests at the high alpine research site (3000 m), operated by the University of Colorado (Swanson et al., 2005). The fourth set of samples

Table 1
Meteorological and chemical parameters of sites

Location	Air T (°C)	Firn T at –10 cm (°C)	Wind speed (m s ^{–1})	Ozone column (DU)	Elevation (m)				
South Pole	–28.4 ± 0.7	~ –30	4.6 ± 1.3	282	2849				
Summit, GN	–12.4 ± 0.5	–17.8 ± 0.1	2.9 ± 0.3	351	3207				
Niwot Ridge	3.7 ± 2.9	0 ± 0.5	~0	348	3350				
Michigan	–10 to –18	~ –15	0.6 ± 0.3	357	338				
	TOC (mg l ^{–1})	Formate (nmol g ^{–1})	Acetate (nmol g ^{–1})	NO ₃ [–] (nmol g ^{–1})	SO ₄ [–] (nmol g ^{–1})	NH ₄ ⁺ (nmol g ^{–1})	Cl [–] (nmol g ^{–1})	Br [–] (nmol g ^{–1})	
South Pole	0.04–0.18	0.11 ± 0.08	0.11 ± 0.05	4.9 ± 2.5	0.43 ± 0.10	0.072 ± 0.031	0.56 ± 0.20	0.036 ± 0.004	
Summit, GN	0.56	1.3 ± 1.9	0.87 ± 1.1	5.3 ± 1.3	0.88 ± 0.09	0.99 ± 0.28	0.94 ± 0.14	0.006 ± 0.002	
Niwot Ridge	0.66 ± 0.33	1.23 ± 2.34	0.21 ± 0.20	10.8 ± 8.6	4.4 ± 4.8	3.7 ± 4.1	3.25 ± 4.54	NA	
Michigan	0.69 ± 0.46	0.29 ± 0.20	0.39 ± 0.25	17.8 ± 18.1	6.6 ± 6.4	12 ± 22	12.8 ± 7.8	NA	

Meteorological conditions are for mid-day the date of the firn profile sampling. At Summit the 6 pm and midnight profiles had air and firn temperatures of –13.6 ± 0.5 and –26.0 ± 1.0 °C, and –17.2 ± 0.1 and –17.4 ± 0.1 °C, respectively, with 1–2 m s^{–1} wind speed for both. Total ozone columns are from TOMS data.

TOC, Total Organic Carbon; South Pole and Summit are from Grannas et al. (2002), Niwot Ridge is from Dibb (unpublished), and Michigan Is from Sarah Green at Michigan Technological University from SNOW-99.

Summit major ions are averages for the month of June from 5 years of snow samples (Dibb et al., this issue).

South Pole major ions are from three pits collected in November–December, 2000.

Niwot Ridge major ions are from samples collected from same snowpit as whole air canisters sampled in April 2005.

Michigan major ions are from all the snow samples collected during the project in 1999.

reported here were also collected within a clearing in a forested site in a remote area of the upper peninsula of northern Michigan, on January 14, 1999, during the Snow Nitrogen and Oxidants in Winter (SNOW-99) study (Honrath et al., 2000). The SNOW-99 samples represent one profile into a 0.6 m deep snowpack overlying soil.

2.2. Analytical method

The sampling and analytical method is covered in great detail by Colman et al. (2001). All whole air samples were collected in 21 stainless steel canisters. These canisters were preconditioned with ultra-pure whole air then evacuated, followed by addition of ~2.4 kPa water vapor (Colman et al., 2001). Samples were collected with a Parker all-stainless steel bellows pump used to pressurize each canister to three atmospheres at sample flow rates of 1 lpm. Firn air samples were collected at the polar and Niwot Ridge sites by placing sample lines into cored holes (2.5 cm wide) of a various depths in the snow followed by firmly backfilling the holes with snow. To collect the SNOW-99 samples a 5 cm wide hole was first cored out from the firn, then sample lines were placed at different depths. During sampling, a Teflon plastic film blocked the entrance to the hole and covered the snow surface for a radius of about

30 cm around to block surface ventilation, but the hole was not backfilled.

The samples were all analyzed by gas chromatography methods using mass spectrometry, flame ionization, and electron capture detection (Swanson et al., 2005). The samples were analyzed for more than 50 trace gases, including hydrocarbons (HC), halocarbons, sulfur species, and alkyl nitrates. The detection limits for the alkyl halides are as follows: CH₃I, C₂H₅I, and 1-C₃H₇I are 0.01 pptv, CH₃Br, C₂H₅Br, and 1-C₃H₇Br are 0.1 pptv, and CH₃Cl and C₂H₅Cl are 5 pptv. The analytical precision limits for CH₃I, CH₃Br and CH₃Cl are 1.1, 1.7, and 1.5%, respectively (Colman et al., 2001). The precision limits for the higher alkyl halides are all considered to be better than ±20%. Ethyl iodide is systematically undetectable when samples contain high water concentrations, which were encountered occasionally when the stainless steel sampling lines heated up when exposed to radiation. To minimize this effect, where possible the sample lines were buried in the surface snowpack before being directed to the pump.

2.3. Snow chamber experiments

A series of additional experiments to probe the oxidative capacity of the snowpack were performed

during the Summit 2000 project, using a snow chamber (SC). The chamber was designed by Michigan Tech University (R. Honrath), and is a 1 m long cylindrical quartz tube (30 cm diameter) with Teflon end caps (Picture 1). It was designed to allow full exposure of the snow placed in the chamber to solar radiation, but under controlled airflow conditions. For these experiments, sampling ports were attached to the intake and exhaust manifolds of the chamber by connection to the Teflon end caps. Total flow through the chamber ranged from 3 to 24 lpm depending on the number and type of sample lines hooked up to the chamber. The flow rate for the SC (Table 2) experiments was about 24 lpm, but during the HC doping tests, when only the whole air sampling lines were connected, flow through the chamber was only 3 lpm. The HC doping experiments utilized a reactive mix of HCs (C_2 – C_6 parafins, plus several refractive CFC tracers) that was introduced into the quartz chamber at mixing ratios between 0.5 and 5 ppbv, similar to the experiments described by Beyersdorf et al. (2007). Several blank experiments were also performed under constant airflow conditions, with the blank representing an empty chamber with and without the addition of HCs (Empty SC and Empty + HC, respectively).

A subset of samples were collected during the HC doping experiments where airflow through the chamber was stopped (static chamber), and the air within the chamber remained static for 2–3 h,

effectively allowing the interstitial air to be irradiated with sunlight for an extended period. Two of these static chamber experiments were performed, with three samples collected after the chamber had been closed off. The third sample was collected immediately after the second, so its lower values should simply reflect dilution with ambient air. No empty or non-HC static chamber blanks were collected, which is unfortunate because temperatures rose during the static chamber experiments, causing melting near the edges of the chamber. However, a number of blanks were performed under airflow conditions, including one experiment where the chamber was heated intentionally to partially melt the snow in the chamber (heated SC). These will have to represent blank conditions associated with the significant thermal heating that accompanied radiation of the static as well as airflow chamber experiments.

3. Results

3.1. Firn profiles

Comparison of three snowpack profiles collected at Summit over a 24 h period (Fig. 2) reveals a significant diurnal signal. Firn concentrations of CH_3Cl , CH_3Br , and C_2H_5Br peaked at solar noon, while the C_2H_5I peak corresponded to the 6 pm profile, and CH_3I shows similar firn concentrations at both noon and 6 pm. Mixing ratios of all the



Picture 1. Shows the snow chamber used for the hydrocarbon reactivity experiments.

Table 2
Snow chamber results

	Static chambers	HC	Empty + HC	SC	Empty SC	Heated SC
CFC-12						
Average inlet value	527.1	527.2	533.0	537.7	535.2	535.4
Average change (pptv)	5.9	2.6	0.1	1.5	−0.7	2.7
STDev of delta	NA	2.6	3.3	3.5	2.0	NA
Ave percentage change from mean (%)	1.1	0.5	0.0	0.3	−0.1	0.5
CH₃Cl						
Average inlet value	522.5	513.3	536.2	524.2	537.7	508.5
Average change (pptv)	305.5	11.3	4.9	5.7	4.5	4.9
STDev of delta	NA	9.6	13.7	12.0	17.3	NA
Ave percentage change from mean (%)	58.5	2.1	0.9	1.1	0.8	1.0
CH₃Br						
Average inlet value	11.1	11.2	11.3	9.8	10.3	9.4
Average change (pptv)	60.9	3.1	1.2	0.2	0.1	0.3
STDev of delta	NA	1.0	0.5	0.6	0.9	NA
Ave percentage change from mean (%)	549	21	9	2	1	3
CH₃I						
Average inlet value	0.57	0.59	0.63	0.22	0.12	0.10
Average change (pptv)	12.93	0.61	0.27	0.11	0.08	0.02
STDev of delta	NA	0.23	0.09	0.09	0.06	NA
Ave percentage change from mean (%)	2249	48	30	35	40	18
C₂H₅Br						
Average inlet value	0.3	0.3	0.3	0.1	0.2	ND
Average change (pptv)	3.2	0.2	0.1	0.0	0.0	NA
STDev of delta	NA	0.1	0.1	0.1	0.1	NA
Ave percentage change from mean	1172	37	22	9	−26	NA
C₂H₅I						
Average inlet value	0.05	0.05	0.04	0.10	0.03	0.02
Average change (pptv)	0.54	0.03	0.02	−0.01	0.00	−0.01
STDev of delta	NA	0.01	0.01	0.06	0.01	NA
Ave percentage change from mean (%)	1113	31	32	−9	9	−50
CCl₄						
Average inlet value	98.4	98.3	99.2	98.6	99.2	98.7
Average change (pptv)	−1.1	−0.1	0.0	0.4	0.0	0.4
STDev of delta	NA	0.8	0.4	0.9	0.6	NA
Ave percentage change from mean (%)	−1.2	−0.1	0.0	0.4	0.0	0.4
Ethane						
Average inlet value	4693.2	4178.7	2270.4	1018.2	1015.4	956.4
Average change (pptv)	−689.5	−395.4	176.0	1.5	−4.9	9.0
STDev of delta	NA	404.2	58.4	11.2	18.2	NA
Ave percentage change from mean (%)	−14.7	−12.5	7.2	0.1	−0.5	0.9
Ethene						
Average inlet value	84.4	107.7	139.1	13.0	21.3	10.4
Average change (pptv)	2238.6	147.2	96.4	10.3	33.2	8.3
STDev of delta	NA	71.3	37.8	6.5	27.7	NA
Ave percentage change from mean (%)	2653	54.2	40.9	44.1	61.0	44.6
Number of Samples sets	3	22	12	28	11	1

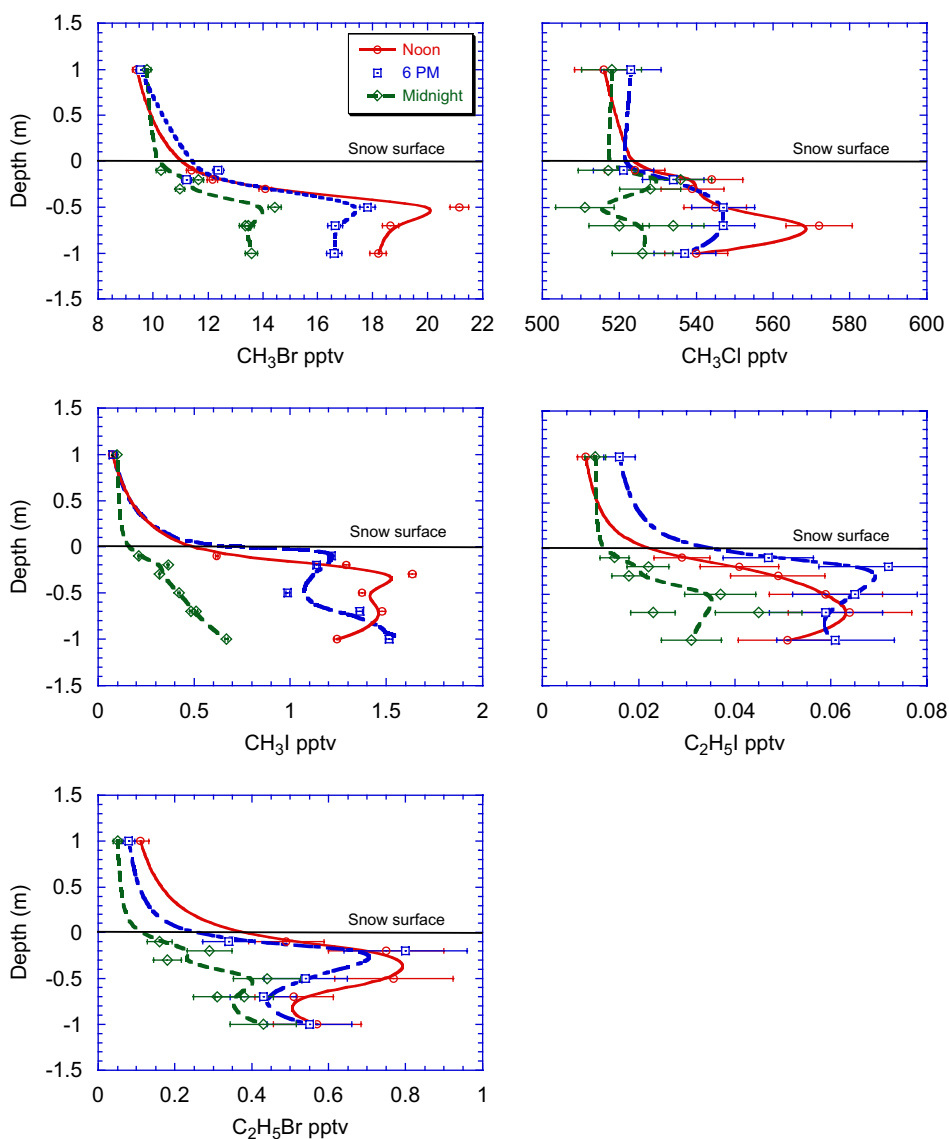


Fig. 2. Methyl and ethyl halide diurnal firn profiles at Summit, Greenland, June 23, 2000. The curves are smooth fits to the data. Error bars represent the analytical precision of the measurements. The curves are simple smooth fits to the data. (Note: The data are shown with error bars for the precision of the analytical method.)

compounds were clearly elevated during the day compared to midnight, when solar insolation is at a minimum, although not zero (Fig. 1). The largest firn/air CH_3Br gradient measured for all the sites was the noon Summit profile where CH_3Br mixing ratios were 9.4 pptv at 1 m above the snow but peaked at 21.2 pptv at 50 cm into the firn (Figs. 2–4).

The Summit methyl chloride profile is the only one where mixing ratios at midnight were equivalent for both firn and ambient. All the other organohalides remained substantially elevated in firn air, even at night (Fig. 2). This likely reflects the higher vapor

pressure of CH_3Cl , compared to the other gases, as well as its small relative enhancement (10.8% at noon) compared to its natural background of 516 ± 16 pptv for all ambient air samples collected during summer at Summit in 2000. However, if we consider maximum absolute mixing ratio increase from ambient to firn, the order of production in the firn interstitial air is: $\Delta\text{CH}_3\text{Cl}(\sim 56 \text{ pptv}) > \Delta\text{CH}_3\text{Br}(11.4 \text{ pptv}) > \Delta\text{CH}_3\text{I}(1.49 \text{ pptv}) > \Delta\text{C}_2\text{H}_5\text{Br}(\sim 0.67 \text{ pptv}) > \Delta\text{C}_2\text{H}_5\text{I}(\sim 0.039 \text{ pptv})$. Whereas, the relative increases over the average BL mixing ratio at 1 m displays the order of: (species (% relative

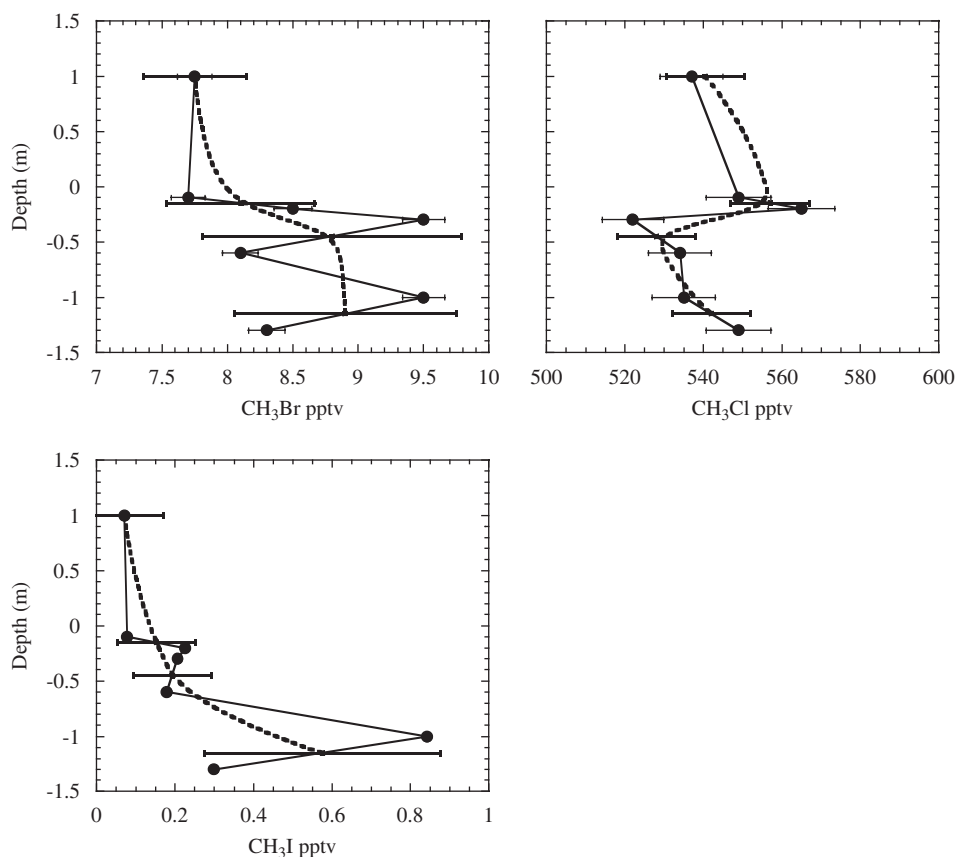


Fig. 3. Firn profiles for CH_3Cl , CH_3Br and CH_3I within the surface snow at the South Pole, December 23, 2000. The solid circle datapoints represent each individual whole air sample collected within the interstitial air with the analytical precision shown as error bars. The dashed line curve represents a smooth fit to the average of 20 cm binned samples with the standard deviation of the bins shown as the error bars.

change, summer background)) $\Delta\text{CH}_3\text{I}$ (1070%, 0.14 ± 0.08 pptv) $>$ $\Delta\text{C}_2\text{H}_5\text{Br}$ (520%, 0.13 ± 0.06 pptv) $>$ $\Delta\text{C}_2\text{H}_5\text{I}$ (120%, 0.033 ± 0.041 pptv) $>$ $\Delta\text{CH}_3\text{Br}$ (120%, 9.7 ± 1.3 pptv) $>$ $\Delta\text{CH}_3\text{Cl}$ (10.8%, 516 ± 16 pptv). It seems clear that the absolute amount of alkyl halide produced is dependent on the availability of precursor species (Table 1), where Cl^- is 20–150 times greater than Br^- . The amount of I^- was estimated to be one tenth that of Br^- , although there are no measurements directly at any of the sites (Swanson et al., 2002). However, the relative increases favor iodides over bromides over chlorides, which would seem to suggest a mechanism that favors the larger halides.

The five snowpack samples that represent the South Pole profile (Fig. 3) are associated with relatively high variability, probably caused by high wind speeds ($\sim 5 \text{ m s}^{-1}$) and a relatively rudimentary sampling protocol (see “Discussion” below). The corresponding ambient data (Fig. 3) represents

average values at 1 m above the snow surface for 10 days surrounding the date that the South Pole firn profile was collected. These values also compare well with ambient values for November 17 to December 31, 2000, for CH_3Cl , CH_3Br , and CH_3I of 538 ± 13 , 7.6 ± 0.8 , and 0.08 ± 0.07 pptv, respectively. Ambient mixing ratios were relatively constant for this period of the ISCAT project. In general the alkyl halide firn profile results for South Pole exhibit much smaller firn profile enhancements compared to Summit. At South Pole, both CH_3Br and CH_3I exhibit only slight enhancements of approximately 1 and 0.5 pptv, respectively, for firn interstitial air compared to ambient air (Fig. 3). Methyl chloride shows no significant trend with depth. The ethyl halides were not quantified in these samples.

The mid-latitude profiles (Fig. 4) contrast with those collected in the Polar Regions because they represent interstitial air collected from a shallow

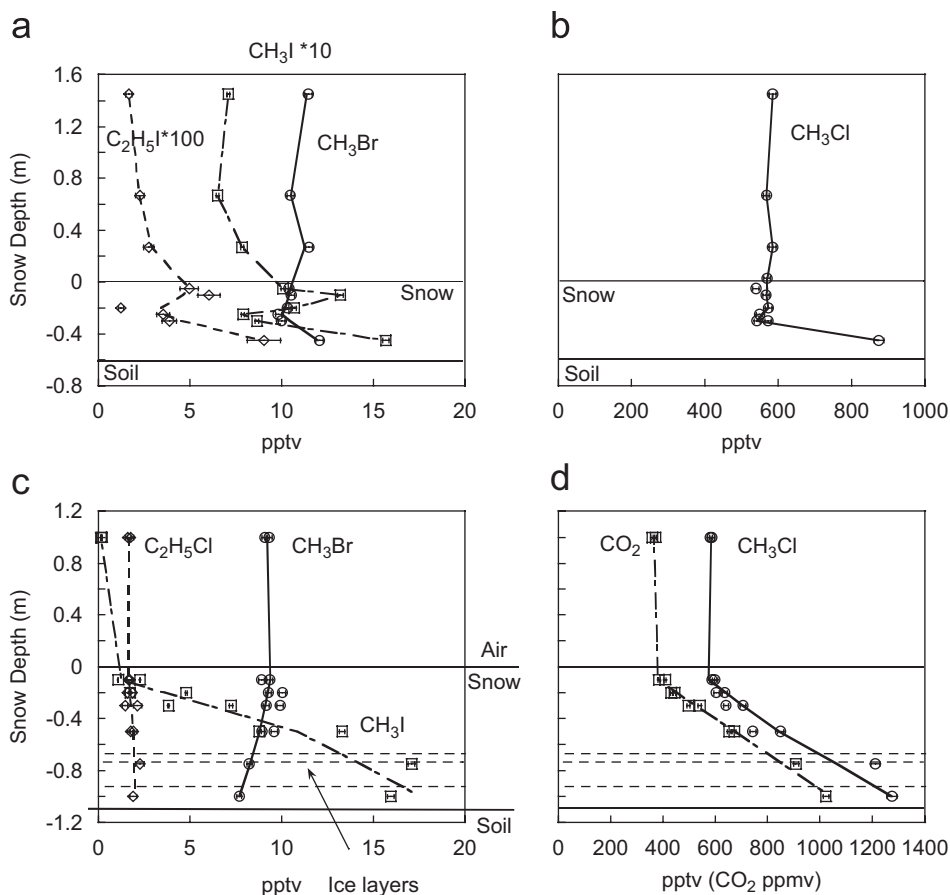


Fig. 4. (a) and (b) show the snow profiles from Michigan, MI, for alkyl halides; CH₃Cl, CH₃Br, CH₃I, and C₂H₅I. (c) and (d) Show the Niwot Ridge snow profiles for alkyl halides; CH₃Cl, C₂H₅Cl, CH₃Br, and CH₃I. Analytical precision is shown for error bars.

snowpack overlying frozen plants and soil, whereas the polar profiles represent the first meter of a 60–80 m thick firn layer, atop ~2 miles of ice. The northern Michigan profile (Fig. 4(a) and (b)) reveals a 2-fold enhancement of CH₃I and C₂H₅I within the firn interstitial air vs. ambient, similar to that seen in Greenland but with a higher degree of variability. In contrast, the Michigan profiles of CH₃Br and CH₃Cl show no significant change (variability <10%) in the first 30 cm of snow, followed by an abrupt mixing ratio increase at 45 cm into the snowpack. The variability of the alkyl iodides in the top part of the firn, but not CH₃Br or CH₃Cl, is evidence that the sampling method captured a mixture of interstitial and BL air. As mentioned in the “Experimental methods” section the sampling hole was left open and covered at the surface with a Teflon film, rather than being back-filled with snow as for the other firn samples reported here. Depending on how well the Teflon film adhered to

the surface snow, air probably penetrated under the film and down the open core. As each sample depth was sampled independently over a period up to 30 min, it is likely that ventilation under the Teflon film and dilution with BL air was greater for some samples than others. Such variable vertical ventilation from the surface into the sampling hole would obviously not alter the mixing ratios of a gas that had no significant surface snow source at this location (like CH₃Br or CH₃Cl) but would perturb measurements for those gases that do have a significant source (i.e., CH₃I and C₂H₅I). The same logic also applies for the samples collected at the South Pole where CH₃Br and CH₃I, but not CH₃Cl, were influenced by dilution of surface air for some samples more greatly than others probably as the result of similarly poor sampling technique.

At Niwot Ridge, CH₃I and CH₃Cl increase nearly linearly from the snow surface towards the bottom of the snowpack (Fig. 4(c) and (d)). At a depth of

1 m, which was 10 cm above the soil, CH_3Cl reaches the extremely high level 1275 pptv. Methyl iodide maximizes at a depth of 75 cm (35 cm above the soil) at a mixing ratio of 17.1 pptv and is still extremely elevated (16 pptv) at the 1 m depth. The increasing mixing ratios with depth and their good correlation with CO_2 (Fig. 4d), which has been shown to have large winter–spring time emissions from alpine soils covered by snowpack (Brooks et al., 1997), suggests a biogenic soil source for both CH_3I and CH_3Cl . However, the fact that CH_3I maximizes before it reaches the greatest sampling depth and that there were discrete ice layers in the snowpack present at several depths between 60 and 100 cm complicate the interpretation for this gas. Interestingly, CH_3Br for the Niwot Ridge profile is the only species to show a slight decreasing trend towards the bottom of the snowpack, suggesting a soil sink of this gas that would be consistent with previous reports of CH_3Br soil uptake (Montzka et al., 2003). The only ethyl halide measured at Niwot Ridge was $\text{C}_2\text{H}_5\text{Cl}$, which revealed no trend within the snow interstitial air. There are a number of studies investigating terrestrial biogenic emissions of alkyl halides (e.g., Swanson et al., 2005 and references therein) but, except to point out that they appear to be substantial at both of the mid-latitude locations sampled and bear further investigation, we do not speculate further on soil emissions in this article.

3.2. Snow chamber experiments

The exhaust minus the inlet concentrations for the experiments performed employing the Michigan

Tech quartz snow chamber were averaged for each type of chamber study (Table 2). The samples collected during the ambient air (SC) and the HC doped (HC) studies had average residence times through the chamber of 10 and 30 min respectively, corresponding to flow rates of about 24 and 3 lpm, respectively.

Much higher mixing ratios were observed in the three samples from the static chamber HC experiments, compared to samples taken for all the HC experiments when there was airflow through the chamber (Table 2). When plotted, the correlations between CH_3I and the other alkyl halides for all the HC experiments (including the three static chamber samples) are very strong, with an r^2 value of 0.99 for both CH_3Br , and $\text{C}_2\text{H}_5\text{I}$, and r^2 values of 0.94 and 0.93 for CH_3I vs. CH_3Cl and $\text{C}_2\text{H}_5\text{Br}$, respectively (Fig. 5). The highest mixing ratios were associated with the samples collected from the static chamber after 2.5 and 3 h entrainments, compared with an average residence time of 30 min for the HC flow studies. The absolute magnitude of alkyl halide production was only slightly higher for the experiments where the chamber was filled with snow (SC and heated SC) than for the blank (empty chamber) experiments. Considering the one-sigma standard deviation within the measurements there is no statistical difference between the filled and unfilled SC studies. The relative production ratios for the different alkyl halides, as expressed by the average percentage change from the mean, were also similar for both snow filled and blank experiments.

The fact that there was alkyl halide production during the blank experiments could possibly be

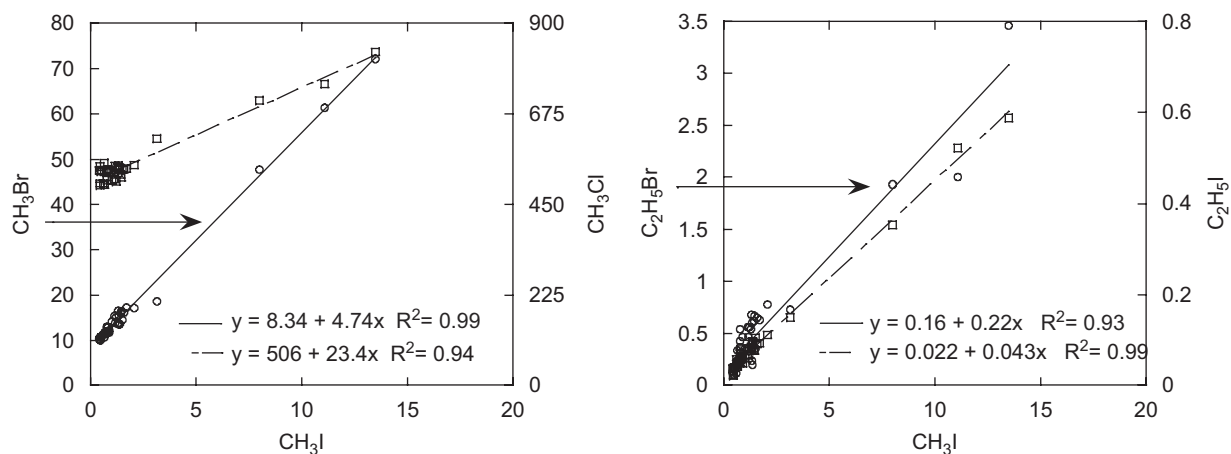


Fig. 5. Alkyl halides for all the HC reaction experiments are plotted against CH_3I to show their relative increases within the snow filled chamber. The alkyl halide on the right y-axis is plotted with the dashed line fit and square symbols.

because there was always ice accumulation in the inlet lines and on the inside of the chamber. The chamber was resting on the snowpack during the experiments and was always colder than the surrounding air temperature, which would lead to condensation of water in the lines and chamber and eventual ice formation. This means the blanks were never free of ice surfaces, which could account for the non-zero production rates in the blank chamber. This suggests that the bulk composition of the snow might not be the dominant controlling parameter, especially considering the experiments doped with HCs produced the most significant increases in alkyl halides, suggesting the gas phase composition might be a controlling parameter. Another parameter that might be important is temperature and the presence of a liquid layer on the ice. The static chamber experiments heated up in the absence of airflow and caused some melting of the snow at the edges of the chamber and at the exhaust end. One experiment investigating the effects of melting was studied where the SC was wrapped in a brown blanket forcing a large fraction of the snow in the chamber to melt. The one sample set collected during this experiment, marked “heated SC” in Table 2, shows that the heating and melting itself did not lead to increased production of alkyl halides. A sample collected directly after the brown blanket was removed, “Post-heat”, which represents irradiation of a partially melted SC shows that the alkyl iodides increased slightly, while the other alkyl halides showed no change.

Only two samples, other than the static chamber samples, contained detectable levels of the 1-propyl halides. The secondary propyl halides, in contrast, remained below their detection limits for all chamber samples (not shown), which is consistent with results found during Swanson et al. (2002). Ethyl chloride (not shown) was only quantifiable (at levels from 3.3 to 29 pptv) for the HC samples corresponding to the five highest CH_3Cl points. These five samples exhibited an r^2 for correlation with CH_3Cl of 0.94.

In summary, the static SC experiments proved very useful in investigating the absolute production yields of alkyl halides within the surface snow, with average production within the chamber following the order $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{C}_2\text{H}_5\text{Cl} > \text{CH}_3\text{I} > \text{C}_2\text{H}_5\text{Br} > \text{C}_2\text{H}_5\text{I} > 1\text{-C}_3\text{H}_7\text{Br} > 1\text{-C}_3\text{H}_7\text{I}$. The significant production of alkyl halides during HC (paraffin) doped studies suggests that the gas phase composition is a controlling factor on the

alkyl halide production, and that oxidation of paraffins is able to generate alkyl halides. However, clear interpretation of the SC studies becomes somewhat problematic because of ice accumulation on all surfaces and because of the lack of control in the ambient inlet air composition, which was often drawn from directly on top of the snowpack.

4. Discussion

4.1. Sample concentration uncertainty

As noted earlier, when sampling firn pore air a large portion of the sample tends to be pulled vertically down from the surface, even if the sampling line is in direct contact with the surrounding snow (Albert et al., 2002). Any gap between the snow and the sample line formed as a consequence of disturbance and/or melting will allow air to freely travel down the outside of the sample tube, greatly increasing vertical ventilation into the snowpack. Poor sampling technique such as this probably contributed to the high alkyl halide variability seen in the vertical profiles at the South Pole and Michigan. But, as stated earlier, this would only affect a trace gas that had a source (or sink) within the snowpack. We have found that ventilation around the sample line can be minimized by firmly backfilling the sample core hole and firmly packing snow at the surface. However, even when such ventilation is diminished, the measured interstitial firn air still represents a mix of surface and firn air that modifies the true interstitial firn air mixing ratios. For example, while the firn profile at Summit correlates well with the diurnal cycle in solar insolation (Fig. 1), mixing ratios of the alkyl halides peak at a depth of ~ 50 cm (Fig. 2), even though actinic radiation maximizes in the first 1–2 cm and is nearly absent by -50 cm. So peak mixing ratios occur well below the peak in actinic radiation. Snow temperatures fall off just as rapidly with snowpack depth, decreasing from -17.8°C at the surface to -30°C at 1 m depth. We suggest that peak mixing ratios are observed so deep in the snowpack because the near snow surface samples are affected so strongly by dilution with the relatively low mixing ratios present in overlying BL air.

To help us gain further insight into the mixture of air obtained when sampling in the firn we have performed a large number of SF_6 tracer studies at Summit (Albert, unpublished data). Initial results from these experiments indicate that the

above-surface air fraction drops off nearly exponentially with depth from the snow surface to nearly 1 m below the surface, and at -1 m the surface air fraction is still about 30%. We would also like to mention that we plan to address the issue of excessive dilution of near-surface interstitial air with the deployment of a sampling bonnet (Perron et al., 2003), which we hope will allow future surface snow measurements such as those presented here to resolve in-situ photochemical production versus soil emissions at the mid-latitude sites.

While an exponential decrease in the amount of surface air drawn into the snowpack during sampling can explain the shift in peak mixing ratios from the surface to deeper depths, there are several additional parameters that control the total ventilation, advection, and diffusion of gases into and out of the snowpack. Parameters that would be needed to construct a more complete model of the firn air system include snow structure, permeability, and surface wind speeds. The presence of ice layers, which have low permeability and hoar layers, with extremely high permeability play a potentially important role. Ice layers (or lenses) were not a common feature at the polar sites we visited because they experience constant subfreezing temperatures, but three low permeability ice layers were present at the Niwot Ridge site, at 65–69, 75–76, and 92–94 cm depth. No such ice layers were observed at the Michigan site. Ice layers act as barriers to advection and ventilation, as well as slow down diffusion through the vertical layer. These barriers are likely to significantly influence the vertical distribution of any trace gas with a source in or below the snowpack and seemed to play a role in the Niwot Ridge profile. The two samples collected deeper than 50 cm were below several ice lenses that may have trapped CH_3I soil/biogenic emissions over time, leading to high concentrations at depth and peak concentrations being observed at a sampling depth of 75 cm, just below the first ice layer.

Another factor that likely increased variability in the lower snow samples collected at South Pole is high wind speed, leading to rapid ventilation and wind pumping of the shallow surface snow. The wind speeds ($\sim 5 \text{ m s}^{-1}$) on the day the South Pole profile was collected, were likely sufficient to greatly increase ventilation of the near-surface firn. Also, because the firn profile was collected within a few meters of a building due to sample line constraints, the wind strength at this location was

probably highly variable, further encouraging wind pumping of the surface snow (Albert and Shultz, 2002).

4.2. Parameters controlling alkyl halide production

The fact that firn methyl halide (CH_3X) concentrations were so much higher at Summit compared to South Pole suggests a significant difference between the parameters controlling their formation at the two locations. Based on trace gas data and correlations with actinic radiation Swanson et al. (2002) suggested that there was a photochemical mechanism for the formation of the methyl halides within the surface snow. However, the current data provide evidence that parameters, such as temperature and snow composition may be just as significant as actinic radiation to the production rates of methyl halides. The following description addresses the possibility that ionic halides (X^- ; Cl^- , Br^- , I^-) photochemically labile organics within the snow, and the presence of a liquid layer on the ice surface, can contribute to the observed difference between northern and southern Polar regions, and potentially the mid-latitude regions as well.

Summit total organic carbon (TOC) concentrations (Table 1) during summer 2000, were similar to those at the two mid-latitude sites. However, levels of TOC at the South Pole during austral summer were significantly lower (Table 1). Similarly, individual organic compounds such as organic acids measured in surface snow are 2–10 times more concentrated at Summit than at South Pole (Dibb and Arsenault, 2002). Although Summit is relatively isolated from direct biogenic emissions compared to most other northern hemisphere locations, and other trace species appear less prevalent, it appears to be much more heavily influenced in terms of organic composition compared to South Pole (Table 1). This leads us to suggest that organic compounds can be transported over long distances, while the other measured species that are primarily ions undergo deposition more readily before they reach Summit. Certainly, Greenland is in much closer proximity to terrestrial source regions than the Antarctic continent and especially South Pole.

Bromide concentrations are higher at the South Pole than at Summit, but confusingly, Cl^- shows the opposite trend (Table 1). Actinic flux values at midday, are much greater at Niwot Ridge and Summit than South Pole and Michigan (Fig. 1). The temperature is also much warmer at Niwot Ridge

than the other sites, and South Pole is clearly the coldest environment (Table 1).

Although the mid-latitude sites do not contain higher organic content in the snowpack than Summit, the mid-latitude sites, specifically Niwot Ridge, actually contained several layers of pine needles, leaves, and particulate matter within the snowpack (Swanson et al., 2005). The Niwot Ridge snowpack had high HC content, as well as the high soil emissions, as seen by the large CO₂ gradient. For example, alpha-pinene concentrations were greater than 1 ppbv at a snowpack depth of 70 cm (Swanson et al., 2005). The evidence from Summit indicating that dilution with ambient air during sampling, as discussed above, shifts evidence for surface production 20–80 cm into the snowpack means that for shallow snowpacks 1 m deep or less, as is the case for northern Michigan, any surface production will be indistinguishable from a soil source. The Niwot Ridge site had such high soil emissions that surface production, even at levels 2–3 times higher than at Summit, Greenland, would still be swamped by emissions from the soil. Therefore, while the organic component of the snow appears to significantly influence trace gas composition in the interstitial air, the many additional influences present for the mid latitude sites, including as pieces of organic material, ice layers and proximity of the soil surface make it much more difficult to identify surface snow sources compared to the relatively simple conditions present at Polar sites.

4.3. Possible CH₃X formation mechanisms

Investigations of halogen compounds in Arctic environments have focused mostly on diatomic halogens and subsequent oxide species due to their direct impact on oxidative capacity, specifically reaction with O₃. These processes are clearly evident in the BL Arctic ozone depletion events which were originally thought to be solely an Arctic phenomena related to photochemical processes initiated at polar sunrise (Barrie and Platt, 1997). However, it is now thought that these processes are initiated on most ice/snow surface and many liquid aerosols (Platt and Moortgat, 1999).

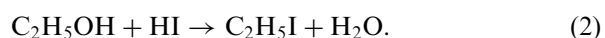
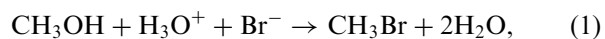
The mechanism for methyl halide formation within the snowpack is based on the hypothesis that CH₃X formation occurs within a heterogeneous medium at the ice–liquid–air interface. There are many assumptions involved with this hypothesis, particularly the existence of a quasi-liquid layer

(QLL) on the ice at subzero temperatures. However, the presence of a QLL is relatively certain at the average temperatures of Summit in Summer (–5–30 °C) and Michigan, but guaranteed to be present at Niwot Ridge temperatures (Table 1), although the QLL thickness will be uncertain (Doppenschmidt and Butt, 2000). A QLL presence will dramatically affect the surface chemistry because of the differences in liquid versus crystalline based dynamics in frozen aqueous media (Klan et al., 2001). It is also uncertain how the presence of trace amounts of salts or organics will affect the thickness or viscosity (mobility) of the QLL, but increasing solute concentration will increase the thickness of the QLL. High surface concentrations of NO₃[–], HNO₃, and organic acids proposed by Jacobi et al. (2004) will greatly increase the acidity of the QLL (above the average bulk snow value for Summit of pH = 4–5).

For the SC experiments, warmer temperatures would be expected to lead to an increase in the thickness of the QLL, and if the QLL is the active media then the increased thickness would help to explain the high mixing ratios observed on irradiation of trapped air. Absolute yields of methyl halides appear to be limited by the concentration of halide ions in the snow, which follow the order Cl > Br > I. However, the relative enhancements suggest alkyl halide formation rates that are similar to those for the oxidation of organic material in soils (Keppler et al., 2000), with halocarbon yields of C₁ > C₂ > C₃ and I > Br > Cl (Swanson et al., 2002). The order of I > Br > Cl is evidently based on the production of methyl halide relative to halide ion, which proceeds in the order of CH₃I/I[–] > CH₃Br/Br[–] > CH₃Cl/Cl[–] (pptv in air nmol^{–1} mol^{–1} in snow). The parallel with the work of Keppler et al. (2000) is appropriate because they were observing alkyl halide production from organic-rich waters where halide abundance was also Cl[–] ≫ Br[–] > I[–].

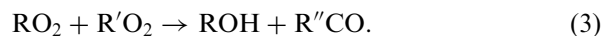
It is useful to note that the order of halide production also follows the ease of which the halogen can be oxidized. To get an idea of what might be happening in the QLL on the ice it is helpful to look at recent aqueous chemical studies. Jungwirth and Tobias (2001) showed that Br[–] and I[–] preferentially migrate from the bulk to surfaces, leading to surface/volume ratios of I[–] > Br[–] > Cl[–] > cations. In addition, measurements of species partitioning to surfaces demonstrates that the hydronium ion shows similar

behavior to the large polarizable anions, I^- and Br^- , and preferentially congregates at the interface (Mucha et al., 2005). If we assume that the hydronium ion does partition to the surface and that nitric acid and organic acids both partition to the interfaces (Jacobi et al., 2004), as well as actively being deposited onto the snow surface, then it follows that the surface layer of the ice grains, or the QLL, would be much more acidic than bulk ice. An acidic snow interface prompts us to suggest that alkyl halides may be formed via an acid catalyzed substitution of an alcohol species, such as methanol or ethanol present in snow at low ppbv levels:

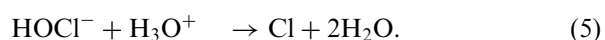


A pH below 4 would promote these reactions. Additionally, It has also been shown that the bromide can be oxidized by O_3 to HOBr followed by reaction with Br^- or Cl^- to form a photo labile dihalogen (Br_2 or $BrCl$) (Oum et al., 1998). This process was employed to explain increases in Br_2 in natural snowpacks at Alert, Canada in 2000 (Foster et al., 2001), and could also be used to explain the presence of reactive iodine, although there are few observations of iodine in snow-covered environments. Iodide at the QLL interface would be much more quickly oxidized by O_3 than would Br^- .

The proposed mechanism seems to contrast with the static SC experiment data in that the presence of large amounts (0.5–5 ppbv) of parafins appear linked with the production of the alkyl halides. However, if the parafins are readily oxidized by OH within the snowpack there is likely a considerable formation of alcohol species simply from RO_2 reactions:



Alcohols, aldehydes, and ketones are the products of these reactions, and have been reported many times as products of surface snow photochemistry (Boudries et al., 2002; Couch et al., 2000; Grannas et al., 2002; Guimbaud et al., 2002; Houdier et al., 2002; Sumner and Shepson, 1999). Other oxidation processes within the snow grains that may play a role in alkyl halide production include the following:



As pointed out by Oum et al. (1998), the dissociation of $HOCl^-$ back to OH and Cl^- occurs in competition with its reaction with H_3O^+ , and reaction (5) is greatly enhanced under acidic conditions. The series of reactions have been proposed to occur in deliquescent sea salt aerosols where a limiting factor is the volume of aqueous media available for the reaction to take place. It can be assumed that the presence of a QLL on the ice in a surface snowpack at just slightly sub-freezing temperatures and under constant irradiation would be substantial and adequate for sustaining the activation of reactive halogens. For bromine and iodine, which will partition much more readily to the interfaces as well as hydronium ion, reactions 4 and 5 will preferentially oxidize $I > Br > Cl$. Once the halides are available within the surface snow reaction with both organics and ozone is a likely outcome.

5. Summary

We presented near-surface snow alkyl halide observations from four remote sites. Alkyl halides are produced in the surface snow at both of the two polar locations: the South Pole and Summit, Greenland. They are also enhanced in the snowpack at two mid-latitude locations: Northern Michigan and Niwot Ridge, CO. However, complications resulting from the proximity of the soil sources for the shallow snowpacks, plus many additional influences, including pieces of organic material and ice layers, make it much more difficult to identify surface snow sources at the mid-latitude sites compared to the relatively simple conditions present at the Polar sites.

The observation that production of alkyl halides is associated with snow-covered polar and mid-latitude regions has implications for CH_3X production from all snow/ice environments. The differences in surface snow production at Summit compared to South Pole are mainly attributed to higher concentrations of organic matter in the snowpack and gas phase and a thicker QLL layer caused by higher temperatures at Summit. We further speculate that the production of alkyl halides may be driven by the potentially heterogeneous reaction of halogen ions available at the surface of the ice, with organic species in an acidic interface media. Additionally, alkyl radicals are likely generated in abundance from the photolysis

of photolabile TOC present at the surface or in the bulk snow.

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References

- Albert, M.R., Shultz, E.F., 2002. Snow and firn properties and air–snow transport processes at Summit, Greenland. *Atmospheric Environment* 36 (15–16), 2789–2797.
- Albert, M.R., Grannas, A.M., Bottenheim, J., Shepson, P.B., Perron, F.E., 2002. Processes and properties of snow–air transfer in the high Arctic with application to interstitial ozone at Alert, Canada. *Atmospheric Environment* 36 (15–16), 2779–2787.
- Barrie, L., Platt, U., 1997. Arctic tropospheric chemistry: an overview. *Tellus Series B-Chemical and Physical Meteorology* 49 (5), 450–454.
- Beyersdorf, A.J., et al., 2007. Hydroxyl concentration estimates in the sunlit snowpack at Summit, Greenland. *Atmospheric Environment*, this issue, doi:10.1016/j.atmosenv.2006.08.058.
- Bottenheim, J.W., Dibb, J.E., Honrath, R.E., Shepson, P.B., 2002. An introduction to the ALERT 2000 and SUMMIT 2000 Arctic research studies. *Atmospheric Environment* 36 (15–16), 2467–2469.
- Boudries, H., et al., 2002. Distribution and trends of oxygenated hydrocarbons in the high Arctic derived from measurements in the atmospheric boundary layer and interstitial snow air during the ALERT2000 field campaign. *Atmospheric Environment* 36 (15–16), 2573–2583.
- Brooks, P.D., Schmidt, S.K., Williams, M.W., 1997. Winter production of CO₂ and N₂O from Alpine tundra: environmental controls and relationship to inter-system C and N fluxes. *Oecologia* 110 (3), 403–413.
- Colman, J.J., et al., 2001. Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B. *Analytical Chemistry* 73 (15), 3723–3731.
- Couch, T.L., Sumner, A.L., Dassau, T.M., Shepson, P.B., Honrath, R.E., 2000. An investigation of the interaction of carbonyl compounds with the snowpack. *Geophysical Research Letters* 27 (15), 2241–2244.
- Davis, D.D., et al., 2004. An overview of ISCAT 2000. *Atmospheric Environment* 38 (32), 5363–5373.
- Dibb, J.E., Arsenuit, M., 2002. Shouldn't snowpacks be sources of monocarboxylic acids? *Atmospheric Environment* 36 (15–16), 2513–2522.
- Doppenschmidt, A., Butt, H.J., 2000. Measuring the thickness of the liquid-like layer on ice surfaces with atomic force microscopy. *Langmuir* 16 (16), 6709–6714.
- Dubowski, Y., Hoffmann, M.R., 2000. Photochemical transformations in ice: implications for the fate of chemical species. *Geophysical Research Letters* 27 (20), 3321–3324.
- Foster, K.L., et al., 2001. The role of Br₂ and BrCl in surface ozone destruction at polar sunrise. *Science* 291 (5503), 471–474.
- Grannas, A.M., et al., 2002. A study of photochemical and physical processes affecting carbonyl compounds in the Arctic atmospheric boundary layer. *Atmospheric Environment* 36 (15–16), 2733–2742.
- Guimbaud, C., et al., 2002. Snowpack processing of acetaldehyde and acetone in the Arctic atmospheric boundary layer. *Atmospheric Environment* 36 (15–16), 2743–2752.
- Honrath, R.E., et al., 2000. Release of NO_x from sunlight-irradiated midlatitude snow. *Geophysical Research Letters* 27 (15), 2237–2240.
- Houdier, S., et al., 2002. Acetaldehyde and acetone in the Arctic snowpack during the ALERT2000 campaign. Snowpack composition, incorporation processes and atmospheric impact. *Atmospheric Environment* 36 (15–16), 2609–2618.
- Jacobi, H.W., Bales, R.C., Honrath, R.E., Peterson, M.C., Dibb, J.E., Swanson, A.L., Albert, M.R., 2004. Reactive trace gases measured in the interstitial air of surface snow at Summit, Greenland. *Atmospheric Environment* 38 (12), 1687–1697.
- Jungwirth, P., Tobias, D.J., 2001. Molecular structure of salt solutions: a new view of the interface with implications for heterogeneous atmospheric chemistry. *Journal of Physical Chemistry B* 105 (43), 10468–10472.
- Keppler, F., Eiden, R., Niedan, V., Pracht, J., Scholer, H.F., 2000. Halocarbons produced by natural oxidation processes during degradation of organic matter. *Nature* 403 (6767), 298–301.
- Klan, P., Ansorgova, A., Del Favero, D., Holoubek, I., 2000. Photochemistry of Chlorobenzene in ice. *Tetrahedron Letters* 41 (40), 7785–7789.
- Klan, P., Del Favero, D., Ansorgova, A., Klanova, J., Holoubek, I., 2001. Photodegradation of halobenzenes in water ice. *Environmental Science and Pollution Research* 8 (3), 195–200.
- Klan, P., Holoubek, I., 2002. Ice (photo)chemistry. Ice as a medium for long-term (photo)chemical transformations—environmental implications. *Chemosphere* 46 (8), 1201–1210.
- Lefer, B.L., Hall, S.R., Cinquini, L., Shetter, R.E., 2001. Photolysis frequency measurements at the South Pole during ISCAT-98. *Geophysical Research Letters* 28 (19), 3637–3640.
- Montzka, S.A., et al., 2003. Controlled substances and other source gases, Scientific Assessment of Ozone Depletion: 2002. WMO World Meteorological Organization, Geneva, p. 498 (Chapter 1).
- Mucha, M., et al., 2005. Unified molecular picture of the surfaces of aqueous acid, base, and salt solutions. *Journal of Physical Chemistry B* 109 (16), 7617–7623.
- Oum, K.W., Lakin, M.J., Finlayson-Pitts, B.J., 1998. Bromine activation in the troposphere by the dark reaction of O₃ with seawater ice. *Geophysical Research Letters* 25 (21), 3923–3926.
- Perron, F., Albert, A., Dibb, J., 2003. A new technique for sampling firn air. *AGU Abstracts*, Fall.

- Peterson, M.C., Honrath, R.E., 2001. Observations of rapid photochemical destruction of ozone in snowpack interstitial air. *Geophysical Research Letters* 28 (3), 511–514.
- Platt, U., Moortgat, G.K., 1999. Heterogeneous and homogeneous chemistry of reactive halogen compounds in the lower troposphere—the papers were presented at the XXIII General Assembly of the European Geophysical Society in Nice, France, 20–24 April 1998. *Journal of Atmospheric Chemistry* 34 (1), 1–8.
- Sumner, A.L., Shepson, P.B., 1999. Snowpack production of formaldehyde and its effect on the Arctic troposphere. *Nature* 398 (6724), 230–233.
- Swanson, A.L., et al., 2002. Photochemically induced production of CH₃Br, CH₃I, C₂H₅I, ethene, and propene within surface snow at Summit, Greenland. *Atmospheric Environment* 36 (15–16), 2671–2682.
- Swanson, A.L., Lefer, B.L., Stroud, V., Atlas, E., 2005. Trace gas emissions through a winter snowpack in the subalpine ecosystem at Niwot Ridge, Colorado. *Geophysical Research Letters* 32 (3).
- Wingenter, O.W., Sive, B.C., Blake, D.R., Rowland, F.S., Ridley, B.A., 2003. Unexplained enhancements of CH₃Br in the Arctic and sub-Arctic lower troposphere during TOPSE spring 2000. *Geophysical Research Letters* 30 (22).