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Photochemically induced production of CH_3Br, CH_3I, C_2H_5I, ethene, and propene within surface snow at Summit, Greenland

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Abstract

Measurements at Summit, Greenland, performed from June–August 1999, showed significant enhancement in concentrations of several trace gases in the snowpack (firn) pore air relative to the atmosphere. We report here measurements of alkenes, halocarbons, and alkyl nitrates that are typically a factor of 2–10 higher in concentration within the firn air than in the ambient air 1–10 m above the snow. Profiles of concentration to a depth of 2 m into the firn show that maximum values of these trace gases occur between the surface and 60 cm depth. The alkenes show highest pore mixing ratios very close to the surface, with mixing ratios in the order ethene > propene > 1-butene. Mixing ratios of the alkyl iodides and alkyl nitrates peak slightly deeper in the firn, with mixing ratios in order of methyl > ethyl > propyl. These variations are likely consistent with different near-surface photochemical production mechanisms. Diurnal mixing ratio variations within the firn correlate well with actinic flux for all these gases, with a temporal offset between the solar maximum and peak concentrations, lengthening with depth. Using a snow-filled chamber under constant flow conditions, we calculated production rates for the halocarbons and alkenes that ranged between 10^3–10^5 and 10^6 molecules cm^{-3} s^{-1}, respectively. Taken together, these results suggest that photochemistry associated with the surface snowpack environment plays an important role in the oxidative capacity of the local atmospheric boundary layer, and influences post-depositional chemistry, which in turn may affect the interpretation of certain aspects of the ice core records collected previously at Summit. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Snowpack photochemistry; Methyl bromide; Methyl iodide; Alkenes; Alkyl nitrates

1. Introduction

Investigations during the past decade at Summit, Greenland, indicate that the composition of surface and near-surface snow changes significantly within days to months after deposition (Dibb and Jaffrezo, 1997).

Several groups have shown that photochemical processes occurring within the firn (unconsolidated snow) alter the pore air composition on a temporal scale of minutes to hours. For example, nitrogen oxides (NO_x) and HONO are produced within the Summit firn (Honrath et al., 1999, 2002; Dibb et al., 2002), possibly as a result of nitrate ion photolysis (Honrath et al., 2000). Sumner and Shepson (1999) reported photochemical production of formaldehyde (HCHO) from the snow at Alert, Canada, and suggested the source may

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be photolysis of organic matter within the snowpack. They proposed that HCHO released from the firn could compete in importance with its formation through the oxidation of methane in the polar troposphere, and that photolysis of HCHO may be the primary source of radicals in the polar boundary layer. These results suggest a strong coupling in chemical processes between the surface atmosphere and snowpack.

Compositional changes after deposition may also affect trace gas concentrations at depths far below the snow surface. At South Pole, Antarctica, methyl bromide (CH_3Br) concentrations in firn cores gradually decreased with depth down to 120 m (Butler et al., 2000; Sturges et al., 2001), consistent with modeled changes in the global atmospheric mixing ratio of CH_3Br over the past century estimated from increasing industrial emissions and biomass burning (Sturges et al., 2001). By contrast, results from firn cores in Greenland and Devon Island, Canada, show that mixing ratios of CH_3Br, as well as some other trace gases increase with depth down to firn close-off (Butler et al., 2000; Sturges et al., 2001), which implies a significant post-depositional change. Enrichment with depth is known to occur through primarily physical processes, such as gravitational diffusion (Severinghaus et al., 2001, and references therein). Temperature gradients (caused by seasonal temperature fluctuations) within the first 5–15 m of firn can lead to increased concentrations of heavier gases within 10 m of the surface during summer (Severinghaus et al., 2001). In addition, chemical changes in trace gas concentration from atmosphere to firn may affect the interpretation of ice-core species sensitive to chemical reactions within the snow such as H_2O_2, CO, HNO_3, HCHO, and possibly even CH_4. For example, significant changes in the $HCHO:CH_4$ ratio in ice cores can perturb the determination of past atmospheric oxidative capacities (Staffelbach et al., 1991). Post-depositional chemical changes have also been suggested to explain interhemispheric differences in the concentrations of CO_2 in ice (Anklin et al., 1995). Any such changes must be verified and understood if accurate reconstructions of past atmospheric composition based on chemical records recovered from glacial ice are to be possible (Dibb and Jaffrezo, 1997).

Summit is the location of the Greenland Ice Sheet Project 2 (GISP2) and the Greenland Ice Core Project (GRIP) deep-drilling programs (Dibb and Jaffrezo, 1997). Both ice cores recovered from these projects have offered the longest high-resolution historical record of past atmospheric conditions in the Northern Hemisphere. The low mean annual air temperature at Summit and the minimal melting make it an ideal site from which to recover deep ice cores (Mayewski et al., 1994). For the same reasons, Summit is also an ideal place to study atmosphere-to-snow interactions and to understand their significance to post-depositional changes and

polar tropospheric chemistry. Data presented here were collected at Summit, Greenland, as part of the NSF-funded "Air–Snow Exchange of Reactive Nitrogen Oxides" project intended to characterize the boundary layer NO_y budget at Summit. The data are representative of trace gas concentrations within the surface atmosphere and pore air of the surface snowpack during summer at the remote Summit research camp.

2. Experiment

Whole air samples were collected at Summit in 2-l stainless steel canisters pressurized with a metal bellows pump. A small, enclosed structure that was buried a meter below the surface of the snow housed the sampling pumps and inlet manifold. Six Dekaron sample lines (all 30 m in length) ran from the surface down a conduit into the buried trench and were connected to the inlet manifold. Three of the inlet lines were used for ambient air sampling on the tower, usually at 1, 4, and 8 m heights. The other lines were used for sampling within the firn, for firn depth profiles, and for snow chamber experiments. All firn pore air was pulled through a stainless steel filter, into a Dekaron line, and to the sampling manifold. Unfortunately, when sampling firn pore air, a large portion of the sample tends to be pulled vertically down the hole made by the sample line (Albert et al., 2002). Therefore, our firn air samples represent an averaged mix of surface and firn air, which we have not yet been able to quantify.

Parker all-stainless steel bellow pumps were used to pressurize each stainless steel canister to 30 psig. Sample filling times were approximately 10 min at a $1 \, l \, min^{-1}$ flow rate. Sampling canisters were preconditioned at our University of California, Irvine (UCI) lab by evacuation to $<10^{-2}$ Torr followed by the addition of 20 Torr of water, as described by Wingenter et al. (1999). After sampling, all canisters were shipped back to UCI for analysis of nonmethane hydrocarbons (NMHCs), halocarbons (CFCs, HCFCs, and alkyl halides), alkyl nitrates ($RONO_2$), methane (CH_4), and carbon monoxide (CO). The analysis for all trace gases, except CH_4 and CO, was performed on a single preconcentrated sample, which was split to five detectors: two gas chromatographs (GCs) with flame ionization detection (GC-FID); two GCs with electron capture detection (GC-ECD); and one GC with mass spectrometry detection (GC-MS), as described by Sive (1998) and Colman et al. (2001). Methane and CO were analyzed on separate systems, both using GC-FIDs, as described by Blake and Rowland (1986) and Hurst (1990), respectively.

Seven hundred and seventy whole air samples were collected during the 60 day June–August 1999, experimental season. Several periods of calm or stable

weather, usually lasting no longer than 2 days, were utilized for high-resolution diurnal firn sampling. One firn depth profile was collected to a depth of nearly 2 m. This profile constituted sampling at 40, 20, and 1 cm above the firn, followed by sampling in the firn at 20, 40, 80, 122, 152, and 183 cm at consecutive 30 min intervals.

Other experiments performed during the project employed a snow chamber (SC) designed by Michigan Tech University. The chamber was a snow-filled, Teflon-coated 34 l (10 cm depth) aluminum rectangular box with a transparent Teflon top (Honrath et al., 2000). Sampling lines were attached to the intake and exhaust manifolds. Total flow through the chamber was $\approx 25\,l\,min^{-1}$. Diurnal chamber experiments were performed over 48-h periods under constant flow conditions. Light/dark experiments were performed over 24 h study periods in which the snow chamber was alternately covered and then exposed to solar radiation. Because Teflon is a potential contaminant for halocarbons, blank experiments were performed. When we

sampled zero air in the dry empty chamber while it was exposed to sunlight, we observed no enhancements of methyl halides, alkenes or alkyl nitrates caused by outgassing.

3. Results

3.1. Firn measurements

Fig. 1 shows the observed concentrations of ethene (C_2H_4), ethane (C_2H_6), CH_3Br, methyl iodide (CH_3I), ethyl iodide (C_2H_5I), and methyl nitrate (CH_3ONO_2) during the firn diurnal experiment on 8–9 July at 1 and 8 m (in the atmosphere) and −10 and −80 cm (in the firn). A sample at 14:10 at −10 cm in the firn (the third data point) was removed for both ethane and ethene because the concentrations were erroneously high, the possible result of contamination by zero air being employed as part of parallel experiments. Ethene mixing
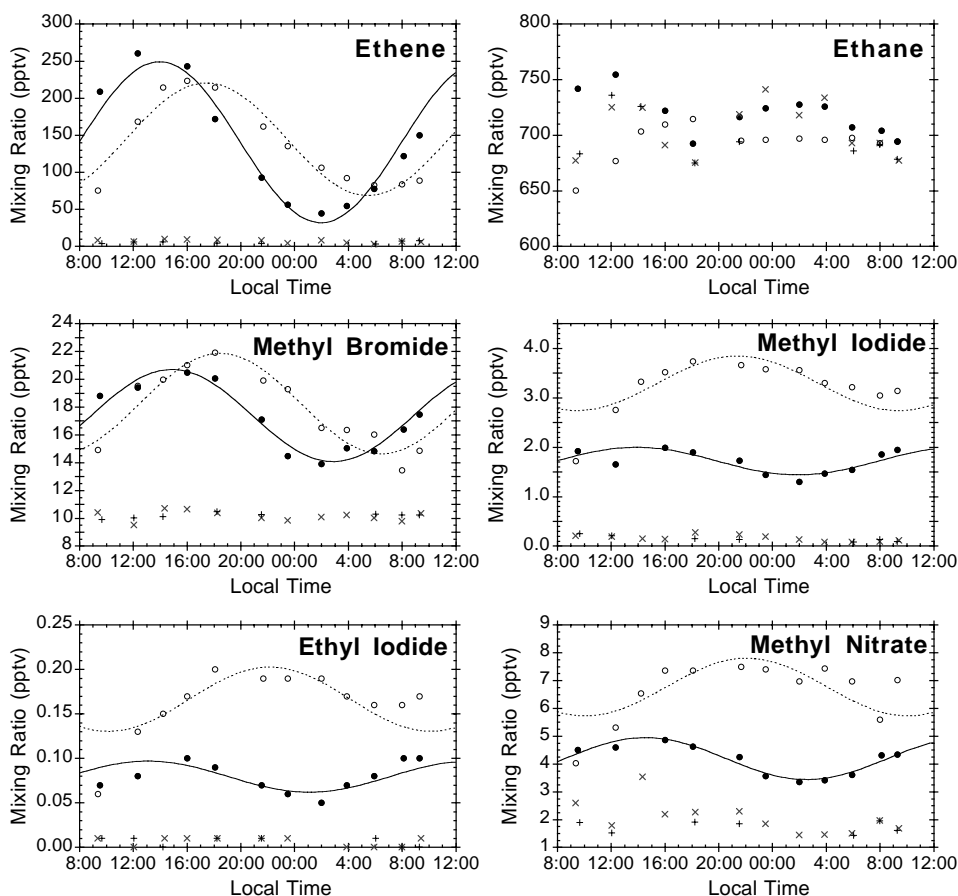

Fig. 1. Diurnal variation study for 8–9 July 1999. Mixing ratios for ethene, ethane, methyl bromide, methyl iodide, ethyl iodide, and methyl nitrate sampled at depths of 10 cm in the firn (●), and 80 cm in the firn (○), also at 1 m (×) and 8 m (+) above the snow surface.

ratios in the firn are much higher than in the atmosphere above. Ethene at -10 cm exhibits a strong diurnal signal peaking at 260 pptv at about 14:00 and minimizing at about 40 pptv around 02:00 local time. At -80 cm, ethene peaks at a somewhat lower mixing ratio at 17:00 and minimizes at about 80 pptv around 06:00. Over the same period, ethene mixing ratios at 1 and 8 m remain between 3 and 10 pptv. By contrast, ethane levels vary between 675 and 750 pptv at all heights (Fig. 1) and show no correlation with the large ethene diurnal signal seen in the firn.

Maximum CH_3Br mixing ratios in the firn are similar at both the firn depths and more than double of those at 1 and 8 m above the surface (Fig. 1). The firn levels of both CH_3I and C_2H_5I are enhanced by more than a factor of 10, with highest levels at the deeper (-80 cm) firn depth (Fig. 1). By contrast, atmospheric levels of both gases are very low, with several C_2H_5I samples below our analytical detection limit of 1 ppqv (1 part in 10^{15}). Methyl nitrate follows a similar pattern to the alkyl iodides (Fig. 1). All C_1–C_4 alkyl nitrates show elevated concentrations of about a factor of 2 in the firn versus 1 m.

The ethene measurements are compared with measured J_{NO_2} values and temperature at 1 m and -10 cm in Fig. 2. This figure shows that the ethene oscillations within the firn closely match those of actinic flux, but that the maxima are delayed by ≈ 1–2 and 4–6 h at -10 and -80 cm, respectively. The time lag suggests diffusion or transport of ethene formed near the surface deeper into the firn. We attempt to model this with a 1D box model (see Section 6). The firn temperature at -10 cm lags the diurnal oscillations of the trace gases sampled at -10 cm. Near the surface, the snow temperature tracks the air temperature very closely,

but temperature changes in the surface snow are transferred less efficiently deeper into the snowpack. At a depth of 50 cm, no diurnal changes are apparent (K. Steffen, unpublished data from Summit 2000).

The surface ethene mixing ratios reveal small fluctuations that are similar in pattern to those seen in the firn. The values at 1 m are on average 2 pptv higher than those at 8 m. Higher resolution sampling over the diurnal time frame would be needed to confirm this relatively low-amplitude atmospheric diurnal variation and to quantify a flux.

Alkenes are known to be subject to growth during storage of air in our stainless steel canisters by as much as 0.1–0.2 pptv per day over a 2-month period for ethene and propene (Sive, 1998). For the firn diurnal on 8–9 July, the highest 1 m concentrations were ≈ 10, 6, and 4 pptv for ethene, propene, and 1-butene, respectively. These levels are low enough to have been adversely affected by growth within the canisters and so are of questionable value. However, such low measured concentrations are useful for setting upper limits to any canister growth that occurred during sample storage for this experiment. By contrast, alkene concentrations in the firn are high enough not to have been affected significantly.

4. Firn depth profile

Fig. 3 shows results from the depth profile sampled on 4 August for the C_2–C_4 alkanes and alkenes, anthropogenic tracers (C_2Cl_4, CFC-113, CCl_4, and CH_3CCl_3), alkyl halides (CH_3I, C_2H_5I, and CH_3Br), and the alkyl nitrates. The gases chosen as anthropogenic tracers are species that are all long lived, so they should be well
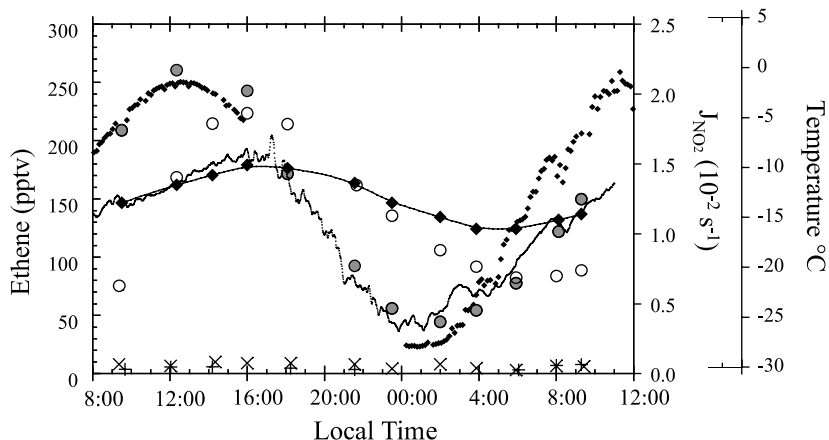

Fig. 2. Mixing ratios of ethene measured at depths of 10 (●) and 80 cm (○) below the snow surface and 1 (×) and 8 m (+) above the surface. Also plotted are the J_{NO_2} photolysis rate constant (◆) and temperature (·) measured at 1 m above the surface, and temperature measured at 10 cm depth in the firn (◇ with smooth fit).
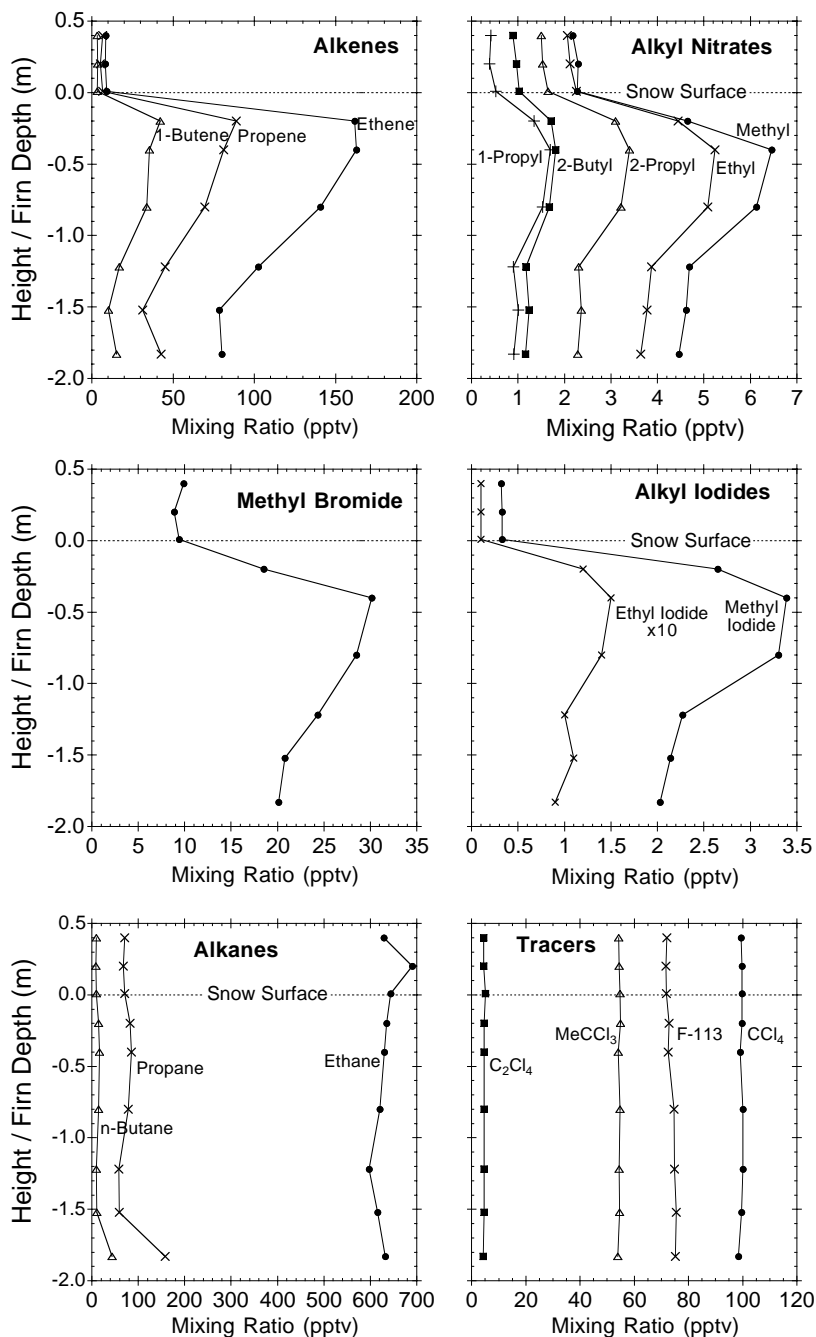
Fig. 3. Profile of mixing ratio versus height/firn depth for light alkenes, alkyl nitrates, methyl bromide, alkyl iodides, alkanes and selected anthropogenic tracers.

mixed within the remote atmosphere of Summit. Fig. 3 confirms that these tracers are indeed all relatively constant with depth, indicating that good sampling, storage, and analytical integrity was maintained for each of these samples.

All the three alkyl halides increase in concentration to a broad maximum mixing ratio at about 60 cm depth, followed by a gradual decrease to the lowest measurement depth of ~ 2 m. The maximum firn enhancements above mean surface mixing ratios are 20, 3.1, and

Table 1
Concentration depth profiles

Compound	Peak depth (cm)	Average surface concentration between 0 and 40 cm (pptv)	Maximum firn concentration (pptv)	Concentration increase (pptv)	Percentage increase
CH_3Br	40	9.40	30.2	20.8	220
CH_3I	40	0.33	3.39	3.06	940
C_2H_5I	40	0.01	0.15	0.14	1200
CH_3ONO_2	40	2.25	6.46	4.22	190
$C_2H_5ONO_2$	40	2.14	5.24	3.09	140
$2\text{-}C_3H_7ONO_2$	40	1.56	3.40	1.84	120
$n\text{-}C_3H_7ONO_2$	40	0.44	1.69	1.25	290
$2\text{-}C_4H_9ONO_2$	40	0.97	1.81	0.85	90
Ethene	20, 40	8.7	163	154	1800
Propene	20	6.2	89	83	1300
1-Butene	20	3.3	42	39	1200

0.14 pptv for CH_3Br, CH_3I, and C_2H_5I, respectively (Table 1). Also listed in Table 1 are all other species measured that were significantly elevated in the firn, along with their percentage increase and depth at which they reached their peak value. (Note, the only other mono-substituted alkyl halide measured during the 1999 season was methyl chloride (CH_3Cl), but no discernible firn enhancement was seen.)

The alkenes exhibited concentration maxima at the shallowest depth within the firn. Ethene, propene, and 1-butene revealed absolute increases of 152, 82, and 39 pptv, respectively, compared to their mean surface concentrations, which were all <10 pptv (Fig. 3, Table 1). However, their corresponding alkanes show a dissimilar pattern (Fig. 3). Ethane remains between 597 and 645 pptv with little evidence for structured change within the firn, while propane and n-butane show small increases down to 1 m. The lowest sampling point at 1.82 m unfortunately shows evidence for contamination of both propane and n-butane. It was also very high for HCFC-142b, 1,3-butadiene, and octane, for unknown reasons. Disregarding this deepest point, propane and n-butane increased from a mean surface concentration of 69 and 9 pptv to peak concentrations at 40 cm of 86 and 16 pptv, respectively. This is a relative increase of 23% for propane and 70% for n-butane, far less than the increase in alkenes.

Of the alkenes that were elevated within the firn, the primary alkene appears to be the most abundant isomer. 1-butene was the dominant C_4 alkene with little evidence of 2-butene, *cis*-2-butene, or *trans*-2-butene within the near-surface firn pore air. There was also evidence for 1-pentene and 1-hexene at concentrations up to 10–20 pptv within the first 20 cm of firn, but again no evidence for their isomers. In general, firn concentrations of these alkenes decreased with increasing carbon number. The alkyl nitrates showed firn concentration profiles with

peak values at a depth of 40 cm (Fig. 3, Table 1). The increases over ambient levels for the alkyl nitrates are similar to the alkyl iodides, but closer to CH_3Br on a percentage basis. Again, the increase over ambient levels decreases with increasing carbon number, $C_1 > C_2 > 2\text{-}C_3 > 1\text{-}C_3 > C_4$, similar to the alkenes. However, 1-propyl nitrate exhibits the greatest relative increase (290%), probably as a result of its very low concentration above the surface (<0.5 pptv). This difference in relative increase between $1\text{-}C_3$ and $2\text{-}C_3$ is evidence of a formation mechanism other than atmospheric (Hauff et al., 1998) and will be examined in the discussion.

5. Snow chamber experiments

Separating the effects of temperature and irradiation is an important step in determining whether the cause of the enhanced firn concentrations described above is most likely to be physical desorption or photochemical production. The snow chamber's characteristic of a closed partially controlled system aided in this aspect. To minimize temperature fluctuations, the chamber was sunk into the firn so that only the surface Teflon cover was exposed to the sun. Ideally, the chamber was a proxy for the firn between the surface and 10 cm, under controlled airflow and mass exchange. During light/dark experiments, the chamber tracked the firn temperature closely, changing by at most $1\,^\circ C$ when changed from dark to light exposed periods.

The light/dark experiment performed on 25 July showed significant fluctuations in the concentrations of the alkenes and alkyl iodides (Fig. 4). Exhaust mixing ratios of ethene, propene, and 1-butene increased by >200% once exposed to sunlight for nearly a 2-h period centered on local noon after the chamber had been covered for the previous 10 h (since midnight). The
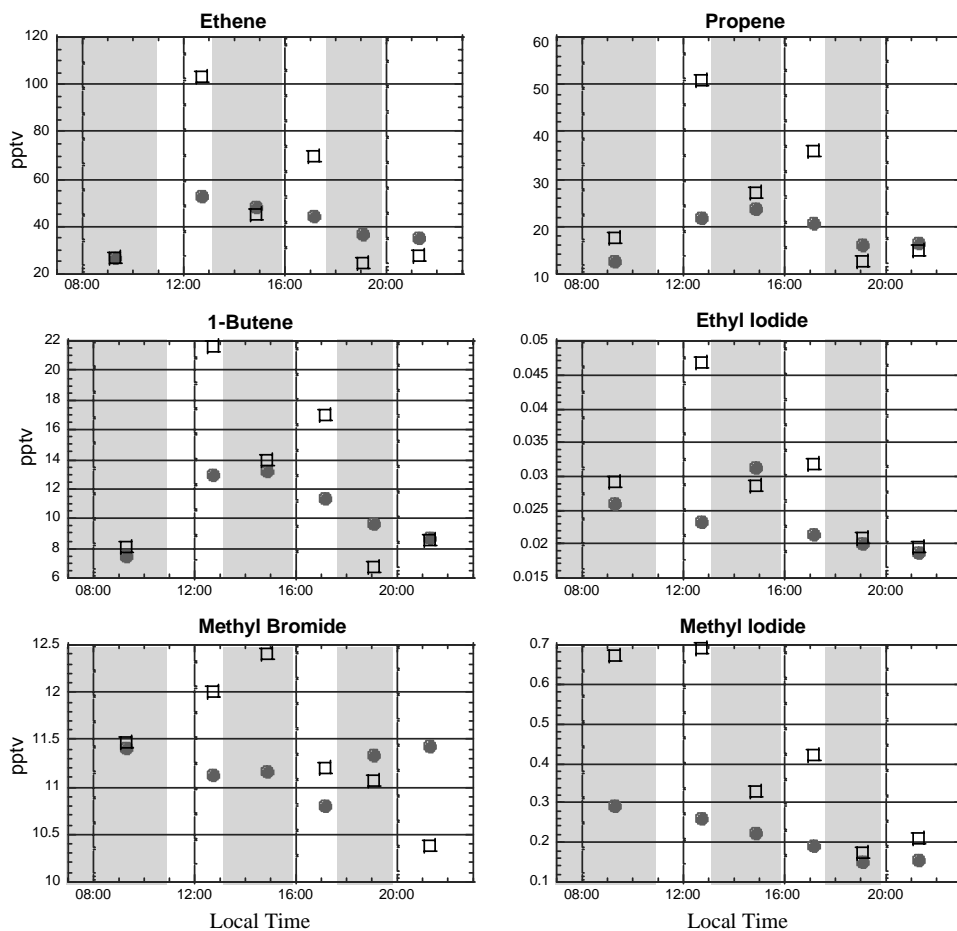
Fig. 4. Light/dark snow chamber experiment on 25 June. Dark periods are shown in gray. Squares are the exhaust values from the chamber, circles are inlet values and are equivalent to ambient values at 20 cm above the snow surface.

alkenes consistently increased upon exposure to sunlight during all the three uncovered periods, but with decreasing magnitudes later in the day. Ethyl iodide also showed distinct increases after the first two periods of exposure to light. Methyl iodide levels were very high before the first exposure, but showed increases in all lighted periods. The responses of CH_3Br and the alkyl nitrates (not shown) were more variable. In all the snow chamber experiments, CH_3Br and the alkyl nitrates were highly variable and did not exhibit distinct increases with exposure to light. CH_3Br has a measurement uncertainty of 3%, which is lower than its typical variability through the snow chamber (11 ± 2 pptv), and so the observed variability did not reflect analytical uncertainty.

However, there are a number of possible factors that may have adversely impacted the reproducibility of these snow chamber results, including ice/snow in the inlet line, a diurnal signal in the inlet value, the rate of

photochemical formation in the snow, or local camp pollution. For example, a clear diurnal signal can be seen in the concentration of the alkenes at the inlet in Fig. 4. These high daytime inlet levels explain the relatively high exhaust values measured during the second covered (dark) period (Fig. 4). Another factor is the different snow placed in the snow chamber. The 25 June snow was the least concentrated for nitrate (Dibb et al., 2002) and low in chloride (close to 0.5 nmol/g) and so may have been less concentrated for bromide and iodide, which could have masked the production of alkyl bromide and alkyl nitrates in the snow chamber relative to the air entering it. Another primary problem is channeling of air through the chamber as discussed by Honrath et al. (2000), which causes the air to interact with only a portion of the snow and leave a significant portion isolated. For gases that are produced very slowly (CH_3Br and alkyl nitrates), fast ventilation rates obscure consistent production, but when channeling

Table 2
48 h snow chamber production rates of CH_3Br, CH_3I, C_2H_5I, C_2H_4, C_3H_6, and the total concentration required to be present in the firn pore air at the beginning of the experiment to sustain such a rate

Species	Production rate (molecules $cm^{-3} s^{-1}$)	Required firn pore concentrations (pptv)
CH_3Br	0.9×10^5	640
CH_3I	1.0×10^5	720
C_2H_5I	3.7×10^3	26
C_2H_4	1.7×10^6	12,000
C_3H_6	1.2×10^6	8500

pathways in the chamber change to flush isolated pockets of air, those species may experience an increase due to much longer atmospheric lifetimes compared to the alky iodides and alkenes.

Four 48-h chamber experiments (not shown) performed over the summer season show similar alkene and alkyl halide production from the snow during exposure to radiation. The mixing ratios of CH_3I, C_2H_5I, ethene, and propene leaving the chamber were on average always greater than those entering. CH_3Br (as well as 1-butene) showed production in three of the four experiments, with the first (second) experiment showing no increase. Table 2 shows a mass balance calculation of the net increase in the pore air concentrations through the chamber (exhaust minus inlet) for the alkyl halides and alkenes for the four 48 h experiments. Average production rates were calculated for five trace gases by taking the average difference between exhaust and inlet of the SC from the four 48 h experiments, multiplied by the flow through the SC, and divided by the SC volume (34 l). Required firn pore concentration is then the production rate from the air in the firn at an average firn density (~ 0.3 g/cm^3) summed over the entire 48-h period (Table 2). Since the SC air was exchanged approximately every 1.3 min (at a 25 l min^{-1} flow rate), we calculated initial pore air concentrations that would have been required to sustain the production rates listed in Table 2. These calculated pore air concentrations were hundreds of times higher than those observed at Summit and, therefore, must instead represent emission from the snowpack. The alkyl nitrate results gave no conclusive evidence for production from the chamber during the 48-h period. The CH_3Br results are also very uncertain given the small difference between inlet and exhaust concentrations. It is suggested in Section 6 (and above) that this lack of evident production in the snow chamber and higher variability is because these gases (CH_3Br and alkyl nitrates) have slower rates of formation in the snowpack.
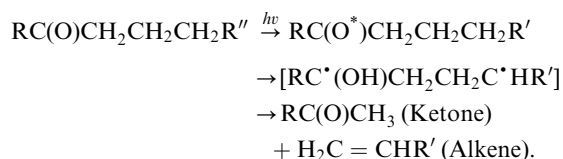
6. Discussion

These summertime ambient and firn measurements suggest that fast (within a 90 min period) sunlight-driven processes lead to emissions of a variety of reactive alkenes, alkyl halides, and alkyl nitrates in the near-surface firn. In the following, we examine the possibility that these processes are physical (driven by desorption from ice surfaces), photochemical (photo-induced oxidation of organic matter), or biological. Also, if they are photochemical, are they associated with homogeneous gas-phase photochemistry or heterogeneous photochemistry?

Significant biological activity is very unlikely, given that the firn temperatures at Summit during the summer season remain below $-10°C$ at the surface and decrease to $-40°C$ at a depth of 10 m (Schwander et al., 1997). Summit therefore is a dry snow zone 365 days a year with temperatures below those considered viable for microbiological activity, primarily due the absence of liquid water (R.W. Hoham, personal communication, 2000). Whether or not there is a quasi-liquid layer of water on firn crystals at sub-zero temperatures is an active area of research and debate.

The magnitude of firn air mixing ratios and their strong response to light suggest that simple degassing or desorption from the snow cannot be the major source to the firn pore air. The alkenes, alkyl halides and alkyl nitrates, are all volatile species with Henry's law constants 10–1000 fold lower than NO_2, HCHO, HONO, and organic acids, which have all been shown to be photochemically produced in the snowpack (Honrath et al., 2002; Dibb and Arsenault, 2002; Sumner et al., 2002). It is therefore unlikely that these gases are physically adsorbed to the snow grains. Analysis of NMHC in snow from a 1 m pit dug in 2000 showed levels of alkenes, alkyl halides and alkyl nitrates, equivalent to blank values reinforcing that these volatile organic gases are not adsorbed to the snow grain surface (Swanson, unpublished data). In addition, the mass balance calculations described earlier were designed to demonstrate that the interstitial firn air itself could not have been the source for the observed alkene and alkyl halide enhancements because high firn air levels (Table 2) would have been required to sustain the observed outputs.

The most likely source of the enhanced trace gases in Summit snow is photochemical production. Analogy with aqueous-phase chemistry employing a liquid-like surface layer suggests that the C_2–C_4 alkenes may be produced by photo-fragmentation of carbonyls, such as has been reported in ocean waters by Riemer et al. (2000). As in our firn measurements, the primary alkene is the dominant ocean product with the order of production ethene > propene > 1-butene. The reaction proceeds by intramolecular hydrogen abstraction

(Norrish type II) as follows:

$$RC(O)CH_2CH_2CH_2R'' \xrightarrow{h\nu} RC(O^*)CH_2CH_2CH_2R'$$

$$\rightarrow [RC^\bullet(OH)CH_2CH_2C^\bullet HR']$$

$$\rightarrow RC(O)CH_3 \text{ (Ketone)}$$

$$+ H_2C = CHR' \text{ (Alkene)}.$$

Hydrogen bonding associated with solvation stabilizes the biradical intermediate above, suppressing disproportionation back to the carbonyl. Preliminary data from Summit (not shown) suggest that acetone levels are enhanced up to 3-fold in the firn compared to ambient levels and behaves similarly to the alkenes in its observed diurnal variations and depth profile. Couch et al. (2000) presented elevated levels of acetone (up to 4 ppbv), acetaldehyde (up to 7 ppbv) and formaldehyde (up to 600 pptv), peaking at about 30 cm below the snow surface in Northern Michigan in January 1999. Total organic carbon (TOC) in Summit snow is high, typically about 100 μg/kg (Currie et al., 1998), with much of it unspeciated, suggesting that the snow may be an abundant source of carbonyls.

Methyl iodide has been shown in laboratory studies to be photochemically produced from seawater, where it is suggested to be produced by the recombination of photochemically produced methyl and iodide radicals (Moore and Zafiriou, 1994), i.e.,

$$RCH_3 + OH^\bullet \rightarrow RCH_2^\bullet + H_2O,$$

$$RCH_2^\bullet + I \rightarrow RCH_2I^\bullet,$$
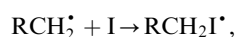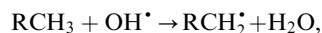
where $R = H$ for the production of CH_3I. At Summit, alkyl radicals are likely produced at high concentrations from the oxidation of the high levels of organic material in the snow as referred to above. Related work at Summit has indeed predicted abundant OH radicals just above the snow surface (Yang et al., 2002). Halide radicals are also formed by the reaction of halide ions with OH radicals (Sumner and Shepson, 1999). Summit snow halide ion concentrations are estimated at about 1–5 pmol/g for I and Br (E. Saltzman, by comparison with Vostok, Antarctica, unpublished data) and Cl abundance is about 1 nmol/g (Dibb et al., 1996). The main competing reaction for formation of organic halides is reaction with molecular oxygen:

$$RCH_2^\bullet + O_2 \rightarrow RCH_2O_2^\bullet.$$
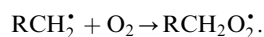
Again, we speculate that snow surface or aqueous-phase type reactions may help to reduce the influence of competing processes. It is also expected that alkyl halide production represents just a small fraction of the available alkyl radicals as most of the alkyl radical reacts to form peroxy and alkoxy radicals, consistent with the results by Yang et al. (2002). A nucleophilic substitution reaction has been shown to produce alkyl

halides during the oxidation of organic matter in soils and may be a more efficient way of producing the alkyl halides due to the avoidance of the free alkyl radical (Keppler et al., 2000). The authors predicted reaction rates for the halides in the order of I > Br > Cl, but stated that absolute production would depend on halide ion concentrations. Our results show production of the iodo and bromo adjuncts, but not CH_3Cl. Absolute production is $CH_3Br > CH_3I$, but from the snow chamber studies, the iodine species show fast production, while CH_3Br is less evident. This probably relates to the rate of formation, I > Br, consistent with Keppler et al. (2000). While the larger magnitude increase for CH_3Br within the firn profile and diurnals relates to the much greater atmospheric lifetime of CH_3Br than CH_3I and C_2H_5I (0.8 years versus less than a week).

Very high levels of OH may additionally play an important role in the photochemical formation of alkyl nitrates. We know that NO levels are very high just below the surface of the snow and the high levels of gas-phase OH radicals referred to earlier are likely to produce significant quantities of RO_2 radicals (see above). Therefore, we would expect to see some production of $RONO_2$ from the reaction:

$$RO_2^\bullet + NO \rightarrow RONO_2.$$
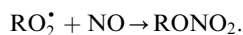
We know that the reaction of CH_3O_2 with NO to form methyl nitrate has a very low yield in the gas phase (Roberts, 1990). However, methyl nitrate is the most abundant alkyl nitrate measured in the surface snow pore spaces. Blake et al. (2002) reported that the abundance of ocean-source alkyl nitrates measured just above the ocean surface are also in the order methyl > ethyl > propyl > butyl. The highest levels of these gases were associated with high-nutrient (nitrate), low chlorophyll equatorial and Antarctic Ocean waters (diminishing further the likelihood of biogenic production playing a role). Thus we again have to invoke analogy with aqueous-phase photochemistry rather than gas-phase chemistry, including stabilization of different intermediate radicals, to explain our snow observations. The increasing ratio of 1-C_3/2-C_3 into the snowpack has been shown previously in snow samples (Hauff et al., 1998) and was suggested to be a result of photolysis of aldehydes similar to that seen in ocean water mentioned above.

The depth of peak concentrations of alkyl nitrates may depend on peak levels of NO and RO_2 radicals, which themselves are likely the product of a dynamic balance between rates of photochemical production and destruction.

7. Diffusion calculations

The observation that the ethene concentrations at −80 cm in the firn are shifted and attenuated from the

concentrations at -10 cm raises the question of whether diffusion alone can account for the concentration at -80 cm. In order to investigate this question, we employ an analytical solution for 1D diffusion. This solution, which treats ethene as a passive scalar for depths lower than -10 cm, ignores all possible effects from advection or ventilation, and also ignores all generation or destruction within the snow.

The diffusion equation is given by

$$\frac{\partial E}{\partial t} = \kappa \frac{\partial^2 E}{\partial z^2}, \tag{1}$$

where κ is the diffusivity of ethene in snow, E is the ethene concentration, and z is the distance (taken as positive into the firn) from the boundary. For this investigation we will use the measured ethene concentrations at -10 cm as the boundary condition, so that z is the distance into the firn below -10 cm. Because a photolytic reaction would be expected to be a periodic function of time with a period of 24 h, we can represent the measured concentration at -10 cm as

$$E_s = A_0 + A_1 \cos(\omega t - \varepsilon), \tag{2}$$

where A_0, A_1, and ε are chosen to fit the data, and $\omega = 2\pi/24$. When the boundary condition is a periodic function of time of the period $2\pi/\omega$, a solution is derived by Carslaw and Jaeger (1959):

$$E = A_0 + A_1 e^{-x\sqrt{\varpi/2\kappa}} \cos(\omega t - \varepsilon - x\sqrt{\omega/2\kappa}). \tag{3}$$

Fig. 5 shows the diffusion model results for the fit to the measured ethene concentrations at -10 cm propa-gated down to -80 cm by diffusion. We note that the boundary condition fit of Eq. (2) to the -10 cm data is not optimal after about 17 h of the experiment, due to reduced sunlight levels encountered during the morning of the second daylight period of the study. However, this should not have adversely affected the model results for the first 17 h of the experiment. The model results closely reproduce the timing of the peak mixing ratios measured at -80 cm, but the low amplitude of the model results indicate that advection (or ventilation), or further generation of ethene within the snow must participate along with diffusion to achieve the concentrations seen at -80 cm.

The 1D model results above show that diffusion plays a significant role in propagating the diurnal ethene signal deeper into the firn. The other primary alkenes follow similar trends, and so would be consistent with these model results. However, the higher concentrations seen at -80 cm for the alkyl iodides and nitrates (Fig. 1) are very different. In fact, if the distributions of these gases were similarly influenced by gradient-driven diffusion, a delay would be expected to occur between the high mixing ratios at depth and diffusion to the near surface, for which the reverse is observed in Fig. 1. Obviously, diffusion does not play the same role for the firn diurnal signals of the alkyl iodides and nitrates. The reason for this different behavior possibly results from a combination of the sampling process and production mechanisms. Sampling the firn pulls air from a mixture of depths and heights above the surface (Albert et al., 2002) so that the -10 cm firn air is possibly diluted to a
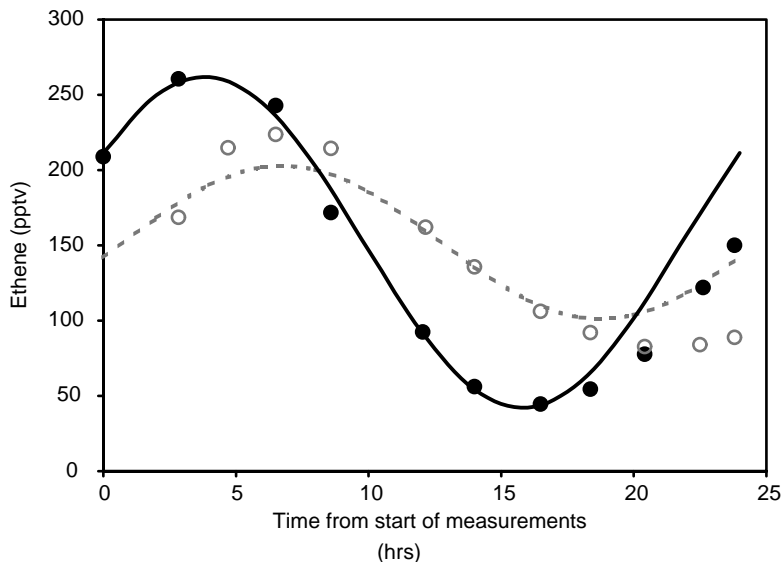

Fig. 5. 1D diffusion model of ethene diurnal on 8–9 July. Measured ethene at 10 cm (●) and 80 cm depth (○) below the snow surface is shown with concentrations at 10 cm fit to a 24 h period (—) and the modeled results at 80 cm depth (- - -). The 10 cm model fit is the boundary condition for the diffusion-driven fit at 80 cm.

greater extent with clean ambient air for the alkyl iodides and nitrates than the alkenes as the result of greater net production occurring at a lower depth. A more thorough analysis of flow patterns within the snow, sampling techniques, and trace gas measurements will be needed to accurately describe these production processes occurring within the snow.

8. Conclusion

During the 1999 summer season, a series of experiments to sample firn pore and ambient air revealed elevated concentrations of alkenes, alkyl halides and alkyl nitrates in near-surface firn air. The strong diurnal variations in surface snow to ~ 1 m depth and light/dark experiments indicate dramatic photochemically induced transformations. Heterogeneous photochemistry (alkenes and alkyl halides) is likely to play an important role for certain gases. However, biological rather than abiotic processes cannot be entirely ruled out. Analyzing the micro-biota within near-surface snow would help to clarify this possibility. The elevated trace gas levels presented here in addition to enhancements of NO_x (Honrath et al., 2002), HONO (Dibb et al., 2002) and HCHO (Sumner et al., 2002), suggest the existence of an extremely reactive and oxidizing environment within and above the snow. A better understanding of the photochemically driven processes occurring within the firn and interactions between atmosphere-to-snow-to-ice is needed to properly understand the polar boundary layer and to interpret ice-core measurements.

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