

# Photochemistry and nature of organic matter in Arctic and Antarctic snow

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[1] It has been shown that sunlit snowpacks are photochemically active, producing a number of species that can significantly impact the overlying atmosphere. Here we investigate the origin of the flux of low molecular weight carbonyl compounds (formaldehyde and acetaldehyde) from sunlit snow obtained from both Arctic (Alert, Canada, and Summit, Greenland) and Antarctic (South Pole) sources. In addition, efforts to characterize the potential snow-phase organic matter (SPOM) precursors were undertaken. Using chemically characterized SPOM, we find that formaldehyde and acetaldehyde are produced upon irradiation, and that production is enhanced with the addition of nitrate (a precursor to OH radicals). SPOM from both Alert and Summit is found to be derived from a variety of sources, including vascular plants. This indicates deposition of atmospheric particulate matter containing vascular tissue to high-altitude Arctic snow. These findings open a potential window for a rich record of variations in terrestrial vegetation-derived aerosol signals that could be preserved in ice

cores. *INDEX TERMS*: 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1827 Hydrology: Glaciology (1863); 1863 Hydrology: Snow and ice (1827); *KEYWORDS*: snowpack photochemistry, ice cores, atmospheric particulate matter, lignin phenols, dissolved organic matter (DOM), biomarkers

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## 1. Introduction

[2] Recent observations in the Arctic indicate that the snowpack is photochemically active, producing and emitting to the atmosphere a variety of photochemically active compounds such as HCHO [Sumner and Shepson, 1999], NO<sub>x</sub> [Honrath *et al.*, 2000], HONO [Zhou *et al.*, 2001], molecular halogens [Foster *et al.*, 2001], alkyl halides [Swanson *et al.*, 2002], and CH<sub>3</sub>CHO and acetone [Grannas *et al.*, 2002], which can significantly impact the composition of the overlying atmosphere [Dominé and Shepson, 2002]. Debate exists as to whether the emission of carbonyl compounds is due to a physical uptake-release mechanism [Hutterli *et al.*, 1999] or one involving photochemical oxidation of snow-phase organic matter (SPOM).

[3] As part of a series of studies of the role of carbonyl compounds in lower atmosphere ozone depletion in the

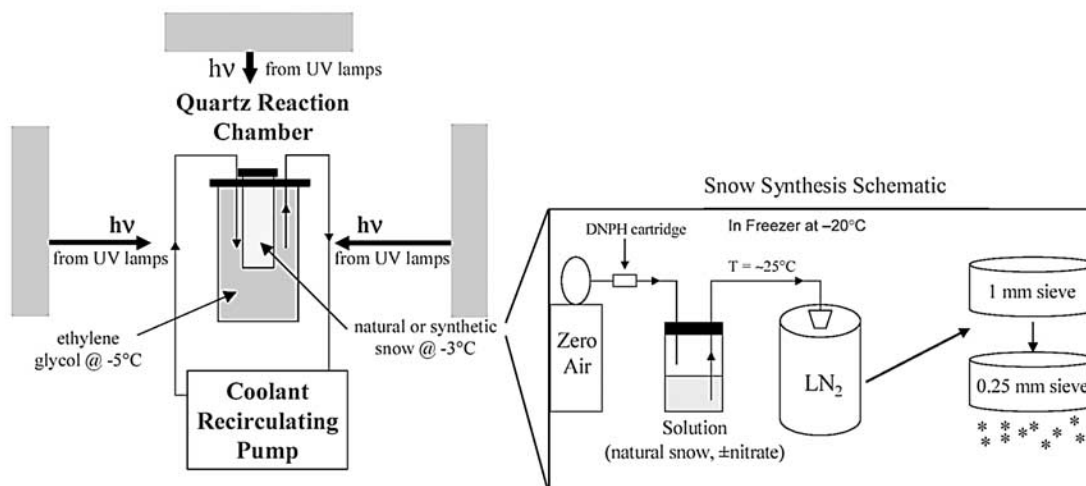
Arctic, Sumner and Shepson [1999] first proposed the importance of photochemical oxidation of organic material present in snow, and hypothesized that this type of chemistry could result in the observed flux of HCHO from the sunlit snowpack at Alert, Canada. However, the possibility of a condensed phase production mechanism was inferred based on gas phase measurements of HCHO in the snowpack interstitial air. Although it was clear that there was a flux of HCHO from the snowpack, and that the flux could significantly impact the atmosphere, the fundamental cause of the flux was not certain, nor was the nature and source of the SPOM.

[4] Honrath *et al.* [2000] have shown that the photolysis of nitrate in irradiated snowpacks leads to the evolution of NO<sub>x</sub>, and likely HONO [Zhou *et al.*, 2001]. This chemistry also generates condensed phase OH radicals, as shown in reactions (1)–(3),

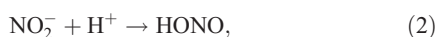


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**Figure 1.** Schematic of irradiation apparatus and snow generation process, used for snow irradiation experiments.



The OH radicals can oxidize SPOM to low molecular weight carbonyl compounds in the condensed phase, similar to what has been demonstrated in ocean surface waters [Mopper and Zhou, 1990; Mopper *et al.*, 1991]. OH radical generation by Fenton [1894] chemistry or from the breakdown of organic material itself [Qian *et al.*, 2000] is also likely to occur in irradiated snow. Additionally, oxidizing species such as singlet oxygen, superoxide, and ozone might play a role. Studies of the photochemistry, sources, and chemical composition of SPOM are lacking, but are essential to gain full accounting of potential precursors and production mechanisms of carbonyl compounds (and other products) in irradiated snow. In this work, we chemically characterized and studied photochemical processes in natural surface snow samples from three polar sites: Alert, Canada, a coastal Arctic Ocean site; Summit, Greenland, a high-altitude glacial site; and South Pole.

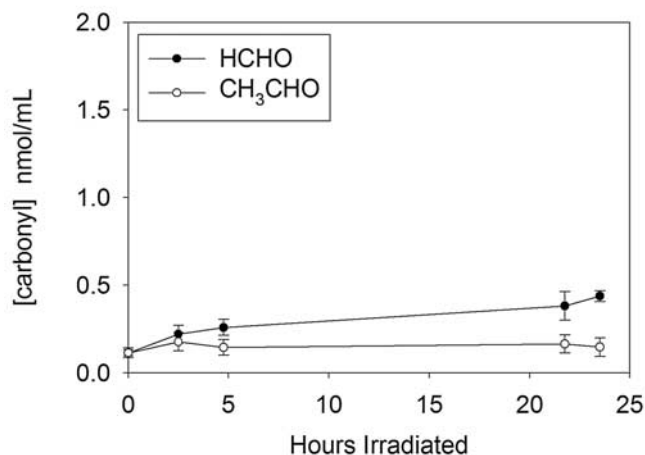
## 2. Methods

### 2.1. Natural Snow Processing and Synthetic Snow Generation

[5] Surface snow samples were collected at three major snow covered sites: the Arctic (Alert, Nunavut, Canada (82.5°N, 62.3°W)), the Greenland glacier (Summit, Greenland (72.3°N, 38.8°W)) and Antarctica (South Pole station). The Alert and Summit samples were collected using high-density polyethylene (HDPE) scoops and stored in 20-L HDPE carboys during shipment ( $T = 283 \text{ K}$ ). The Alert snow sample was collected approximately 6 km inland from the Arctic Ocean and consisted of snow from  $\sim 10 \text{ cm}$  above the ground surface (to avoid direct sampling of soil or

potential plant tissues) to the top of the snowpack (approximately 30 cm deep), from an area of approximately  $1 \text{ m}^2$ . The Summit snow sample consisted of four separate samples obtained at four different depths, representing the last year's snow accumulation (segregated by season) from an area of approximately  $30 \text{ cm}^2$ . Tests prior to sampling indicated that the carboys caused no significant contamination of the sample. After shipment, samples were refrozen and stored until analysis ( $T = \sim 263 \text{ K}$ ). The Antarctic samples were collected in Whirl-Pak polyethylene bags and kept frozen during shipment and until analysis.

[6] Snow meltwater was processed by first filtering through glass fiber filters (Whatman type GF/F) of  $0.7\text{-}\mu\text{m}$  nominal pore size and then using cross-flow ultrafiltration [Guo *et al.*, 2000] at 1 KDa (kiloDalton) to remove colloidal and particulate organic matter. The dissolved organic species filtered to  $<1 \text{ KDa}$  in size were reserved for artificial snow production. Portions of the  $<1\text{-KDa}$  fractions were spiked with  $\text{NaNO}_3$  to a concentration of  $1 \times 10^{-2} \text{ M}$  prior to snow production. Laboratory snow was generated as described by Burkhardt *et al.* [2002] from environmental snowmeltwater obtained from Alert and Summit and used in photolysis experiments. Snow samples from South Pole were maintained frozen during transport and used unaltered (no ultrafiltration or nitrate amendment) in the experiments. The natural and laboratory-generated snow crystals (average size  $\sim 250 \mu\text{m}$  in diameter, density  $\sim 0.3 \text{ g/cm}^3$ ) were placed in a quartz tube, cooled to and maintained at  $270 \text{ K}$  using an ethylene glycol circulating bath (which is transparent to the wavelengths emitted by the light source), and irradiated with UV radiation (UV lamps, model TL20W/12, Philips Lighting Company), for periods of  $\sim 1\text{--}60$  hours (see Figure 1). The emission spectrum of the lamps ( $\lambda_{\text{max}} = 310 \text{ nm}$ ; peak width at half height =  $\sim 30 \text{ nm}$ ) overlaps with the absorption spectrum of nitrate, but intensities fall off significantly below 310 nm. It is known that solar radiation in the 300–320 nm range (i.e., actinic radiation) constitutes the driving force of tropospheric photochemistry [Finlayson-



**Figure 2.** Blank irradiations (snow made from ultrapure water containing <10 ppb organic carbon).

Pitts and Pitts, 1999], even though intensities decrease rapidly toward the 300-nm end. Although the lamps used to irradiate the samples do not represent a true “solar spectrum” (in that longer wavelengths are not represented), the actinic portion of the solar spectrum important to tropospheric photochemistry is emitted by the lamps. To determine if the intensity of these wavelengths was comparable to sunlight in the Arctic, we performed experiments measuring the OH produced from nitrate photolysis, using CH<sub>3</sub>OH as an OH radical trap (producing HCHO) [Zhou and Mopper, 1997]. It was determined that OH radicals were produced in the condensed phase at a rate of 440 nmol/mL·hr per 1 M NO<sub>3</sub><sup>-</sup> added to the snow. Thus the calculated value for J(NO<sub>3</sub><sup>-</sup>) ( $3 \times 10^{-7} \text{ s}^{-1}$ ) for the irradiation experiments is comparable to J(NO<sub>3</sub><sup>-</sup>) values measured in Summit Greenland [Qui et al., 2002] ( $5 \times 10^{-7} \text{ s}^{-1}$  in early June) and Alert, Canada [Simpson et al., 2002] ( $7 \times 10^{-8} \text{ s}^{-1}$  in early April). Since the measured J-rates are comparable, we conclude that the irradiation impinging on the samples is similar to that in a natural snowpack, for the wavelengths emitted by the lamp, and that the wavelengths used in these experiments are appropriate for study of polar snow photochemistry.

## 2.2. Measurement of Condensed Phase Carbonyl Compounds

[7] During irradiation experiments, an aliquot of the snow sample was melted, and the condensed phase carbonyl compounds were determined by derivitization to the corresponding hydrazone via reaction with 2,4-dinitrophenylhydrazine, followed by separation via HPLC (C-8 column, CH<sub>3</sub>CN/H<sub>2</sub>O gradient elution) with absorption detection at 360 nm. The estimated accuracy of the derivitization/detection scheme is  $\pm 5\%$  with a measurement precision of  $\pm 2\%$ . To test whether the snow-making process or sample handling led to a detectable signal of carbonyl compounds, triplicate blank experiments (Figure 2) were conducted by irradiating snow made from ultrapure water (<10 ppb organic carbon). The small production of HCHO

is attributed to the trace organic material present in the water, while CH<sub>3</sub>CHO production in the blank was not statistically significant. Generally, the absolute concentrations for the blank samples did not statistically significantly exceed the amount measured in the natural snow samples before irradiation commenced.

## 2.3. Total Organic Carbon Measurements

[8] TOC analysis of snow samples was conducted using a high sensitivity TOC analyzer (Shimadzu Corporation, Model TOC-VCPH) with a detection limit of 4 ppb ( $\mu\text{g/L}$ ) organic carbon. The total carbon content of a sample was determined by measuring the total carbon signal by combustion of the sample on a catalyst at 953 K with subsequent measurement of the CO<sub>2</sub> produced (via NDIR measurement). The inorganic carbon content of the sample was then determined by acidification of the sample with phosphoric acid (converting all of the carbonate carbon to CO<sub>2</sub>) followed by quantification of the CO<sub>2</sub> produced. The difference in these two measurements was then assumed to represent the organic carbon content of the sample. Replicate analyses of a potassium hydrogen phthalate standard (for organic carbon) and a sodium bicarbonate/sodium carbonate standard (for inorganic carbon), both at 100 ppb, indicated a precision for the organic carbon concentration determination of  $\pm 15\%$ . Blanks were determined by measuring the carbon content of the same ultrapure water used to generate the organic and inorganic carbon standards.

## 2.4. CuO Oxidation of Particulate Material

[9] Particulate SPOM on GF/F was extracted for lignin-phenols using the cupric oxide method [Hedges and Ertel, 1982] in a Prime Focus, Inc., bomb apparatus. Eight lignin phenols, vanillin, acetovanillone, syringaldehyde, vanillic acid, acetosyringone, syringic acid, *p*-hydroxycinnamic acid, and ferulic acid, were quantified and used as indicators for source and diagenetic state of vascular plant tissue. Lignin phenols were determined using a Shimadzu QP5050A Gas Chromatograph/Mass Spectrometric Detector (GC/MS) using a 30-m Restek RTX-5 capillary column upon derivitization of the products with trimethylsilane using BSTFA. Quantification was based on use of the internal standards ethyl vanillin and 3,4-dimethoxy benzoic acid (a recovery standard) using a calibration curve generated by integration of selected mass fragments of the target compounds. The average mean deviations, based on two replicates ( $n = 2$ ), for the sum of lignin phenols is less than 12%, while that for individual compounds ranged from 5 to 25%. Mono and diacid quantification was based on calibration curves generated for silylated undecanoic diacid and hexadecanoic acid. Response factors for each of the quantified acids were assumed to be identical to the standard.

[10] Because the glass fiber filter was analyzed as part of the sample (the entire filter was ground and added to the reaction vessel), a blank was determined by grinding a clean glass fiber filter by the same procedure used for the sample filters. The filter was then added to a reaction vessel, reacted, and extracted using the same procedure as described above for the samples. In the triplicate analysis of three separate blank filters, no lignin monomers were observed to be present in any

**Table 1.** Organic Carbon Composition of Arctic Snow Samples<sup>a</sup>

	Alert May 2002	Alert Feb. 2002	Summit Spring 2001	Summit Summer 2001	Summit Fall 2001	Summit Winter 2002
	<i>Organic Carbon Content</i>					
Original snow, mg/L	0.70	0.20	0.58	0.56	0.40	0.43
Fraction > 0.7 µm	18%	12%	16%	14%	n/a	n/a
0.7 µm to 1000 Da	21%	38%	6%	7%	n/a	n/a
<1000 Da	61%	50%	78%	79%	n/a	n/a
	<i>Lignin Source</i>					
Vanillyl phenols	0.56	3.40	0.42	0.41	0.45	1.21
Syringyl phenols	0.35	1.31	0.07	0.12	0.04	0.38
Cinnamyl phenols	0.20	0.05	–	0.05	–	0.04
p-hydroxyacetophenone	0.16	0.03	0.02	0.02	0.02	0.02
p-hydroxybenzaldehyde	0.69	0.20	0.19	0.09	0.07	0.12
Total lignin	1.96	4.99	0.70	0.69	0.58	1.77
	<i>Lignin Composition Indicators</i>					
C/V	0.36	0.01	–	0.12	–	0.03
S/V	0.63	0.39	0.17	0.29	0.10	0.31
Acid/Ald-v	0.41	0.25	0.71	0.40	0.57	0.49
Acid/Ald-s	0.27	0.15	0.40	0.29	–	0.22
	<i>Lipid Sources</i>					
<i>Monoacids</i>						
Octanoic acid (C8)	0.07	1.20	0.69	0.73	0.65	0.74
Nonanoic acid (C9)	–	0.32	0.19	0.28	0.33	0.31
Decanoic acid (C10)	0.02	0.67	0.37	0.48	0.57	0.28
Dodecanoic acid (C12)	–	–	–	0.68	1.63	0.43
Tetradecanoic acid (C14)	0.04	0.69	0.39	–	1.2	0.38
Hexadecanoic acid (C16)	0.06	2.14	1.04	1.15	2.44	1.08
Octadecanoic acid (C18)	–	0.03	0.16	0.07	0.76	0.03
<i>Diacids</i>						
Pentanedioic acid (C5)	0.02	–	–	–	–	–
Hexanedioic acid (C6)	0.02	–	–	–	–	–
Heptanedioic acid (C7)	0.04	–	–	0.11	–	0.04
Octanedioic acid (C8)	0.07	0.24	–	0.25	0.19	0.14
Nonanedioic acid (C9)	0.22	–	0.18	0.15	0.09	0.15
Decanedioic acid (C10)	0.02	–	–	–	–	0.02
Undecanedioic acid (C11)	0.02	–	–	–	–	–
1,4-butene dioic acid	0.17	–	–	–	–	–
Butanedioic acid	0.05	–	–	–	–	–
Total monoacids	0.19	5.05	2.84	3.39	7.58	3.25
Total diacids	0.63	0.24	0.18	0.51	0.28	0.35

<sup>a</sup>Total organic carbon content of Arctic snow samples is reported as mg C per L snowmelt. Ultrafiltration was used to obtain the <1000-Da material. The approximate pore size of this filter was 10 Å. Particulate matter composition is listed according to likely sources, reported as mg of compound per 100 mg particulate organic carbon.

of the blanks. One blank sample evidenced a small amount of p-hydroxybenzoic acid (with a peak area of about 3% that of the same monomer found in the May 2002 Alert sample). Two fatty acids were found in all of the triplicate blanks, nonanoic acid and hexanedioic acid. The peak areas measured in the snow particulate matter samples were above (>2 times) the calculated detection limit based on the standard deviation of the blank. In one blank sample, small amounts of decanoic acid, dodecanoic acid, tetradecanoic and hexadecanoic acid were found, and those peak areas were subtracted from the peak areas measured in the particulate matter samples.

### 3. Results and Discussion

#### 3.1. Characterization of SPOM

[11] Total organic carbon (TOC) was measured for each original snow sample as well as associated fractions

obtained after melting and ultrafiltration from Alert, Canada, and Summit, Greenland, to determine the size distribution of TOC in snow (see results in Table 1). For both locations the majority of the organic carbon is present as species <1000 Da in size (~56% at Alert and 78% at Summit). Carbon as particulate organic matter (POM; greater than ~0.7 µm isolated on GF/F) accounts for less than 20% of the total. It is interesting to note that the total amount of organic carbon in Alert and Summit snow is comparable, despite the vastly different geographical location (sea level versus 3200 m altitude) and existence of vegetation at the base of the relatively shallow (<60 cm) Alert snowpack. This points to the possible importance of atmospheric transport followed by deposition to the snowpack as the main mechanism of incorporation of organic material into polar snowpacks, as discussed below. For comparison, we also found a comparable average TOC of

0.40 ( $\pm 0.13$ ) mg/L in a South Pole snow sample. We performed a molecular analysis of the POM fraction using the alkaline CuO oxidation techniques as described by Hedges *et al.* [1988]. Such an analysis of molecular biological markers, which include aliphatic acids from lipids and aliphatic biopolymers, protein degradation products, and lignin phenols, is a useful approach to qualitatively determine the important sources, and potentially assess the relative degradation state of carbon in natural samples [Hedges *et al.*, 1988; Opsahl and Benner, 1995].

[12] Upon analysis of the POM fraction at Alert and Summit, a variety of compounds were identified, which are uniquely attributable to vascular tissue (lignin phenols), as well as terrestrial and algal lipids (fatty and aliphatic diacids) and proteins (butene-1,4-dioic acid). The species identified (and potential sources) are shown in Table 1, with their quantity (after blank subtraction) normalized to total particulate organic carbon. The presence of lignin monomers for Summit, at 3.2 km altitude, is quite significant as it demonstrates atmospheric input of vascular plant-derived materials.

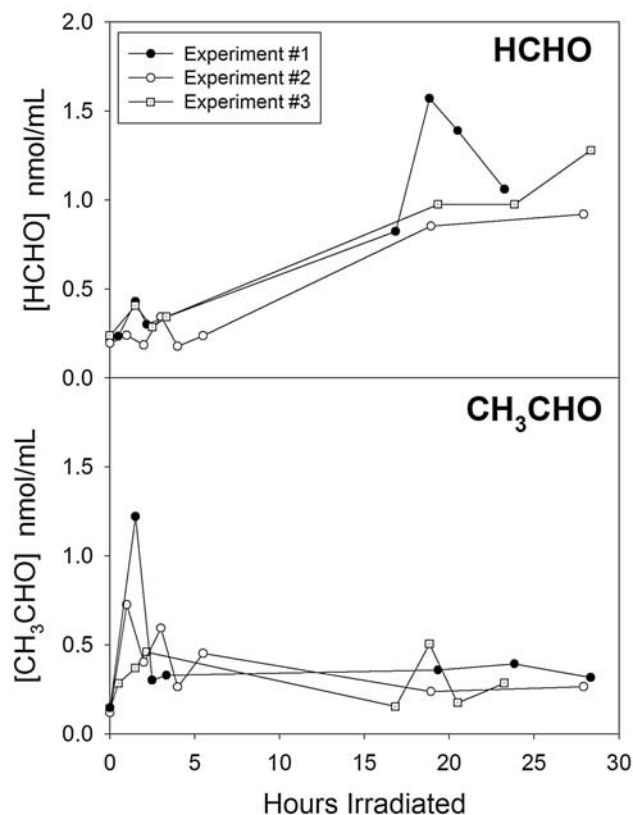
[13] Syringyl:Vanillyl (S/V) and Cinnamyl:Vanillyl (C/V) compound ratios are useful in determining the relative importance of woody versus non-woody tissues and angiosperm versus gymnosperm inputs to the lignin signal [Hedges and Mann, 1979]. Additionally, the diagenetic state of the lignin material can be inferred from the acid:aldehyde ratios of the vanillyl and syringyl compounds [Opsahl and Benner, 1995]. Higher ratios ( $>0.4$ ) are characteristic of a relatively highly degraded lignin material. For both the vanillyl and syringyl monomers, the May 2002 Alert particulate matter evidences a higher acid/aldehyde ratio than that of February 2002, indicating a more highly degraded sample in May. This could point (as expected) to the greater importance of photochemical degradation during transport and after deposition in spring (after polar sunrise) as compared to the February sample, which was transported (at least partially) and deposited during polar night. Although little data is available on the CuO products of exclusively abiotic degradation of lignin, Opsahl and Benner [1998] found that acid:aldehyde ratios increased upon irradiation of natural water samples (Mississippi River) containing lignin materials and attributed this change to the photochemical degradation of the lignin. Although the aerosol lignin may have a unique structural distribution, it is reasonable to hypothesize that the same condensed phase photooxidation processes occur.

[14] Typically, for undegraded plant tissue, a C/V from 0.3 to 1.2 can be thought to be derived from herbaceous plants while S/V values greater than 0.9 are indicative of woody angiosperms. C/V values less than 0.3 in combination with S/V values less than 0.9 indicate a woody gymnosperm source. Microbial decomposition of lignin tends to force C/V values toward lower numbers [Opsahl and Benner, 1995]. C/V ratios exhibit a large range at the Alert station (0.01 to 0.36) and at Summit (0.03 and 0.12), while the S/V ratios are less than 0.63 at all sites. The low C/V and S/V values in combination with the high Ad/Al point to the importance of long-range transport of biogenic materials, suggesting that this vascular tissue may be partly derived from woody gymnosperms, as a majority of the

local vegetation at Alert is non-woody in nature [Gould *et al.*, 2003].

[15] Although the amount of lignin phenols at Summit is less than that found at Alert, the presence of vascular plant derived materials at the top of the Greenland glacier summit (3200 m altitude) is remarkable. It is far removed from any direct sources of plant material, and as such, any material found in the snow necessarily results from atmospheric transport and deposition, as might be predicted given the identification of soil-derived acids in Arctic aerosols [Kawamura *et al.*, 1996]. Previous studies have attributed a significant portion (20–30%) of carboxylic acids (such as formate, acetate, and oxalate) measured in Greenland ice cores to biomass burning with subsequent transport to the Greenland glacier [Legrand and DeAngelis, 1996]. In addition, black carbon and sulfate concentrations measured in Greenland have indicated that fossil fuel burning and biomass burning contribute significantly to the various chemical species measured in the Greenland snowpack and ice [Slater *et al.*, 2002]. Such long-range transport of biomass burning products is now visible with remotely sensed data (Naval Research Laboratory, online data, Monterey Aerosol Page <http://www.nrlmry.navy.mil/aerosol>). Iversen [1996] determined (using 5-day back trajectories) that the air masses transported to Greenland originated from the south and west in fall, the west in winter, the south, west, and north in spring, and the south and west in summer. These trajectories confirm the likely importance of transport of organic material from North America to the Greenland glacier. These measurements represent the first direct evidence of vascular plant organic matter in polar snow, and allow for the direct measurement of its biogenic inputs to the glacial ice, rather than as inferred from low molecular weight carboxylic acids and black carbon [Kawamura *et al.*, 1996; Legrand and DeAngelis, 1996; Slater *et al.*, 2002]. However, on the basis of the molecular weight distributions obtained from TOC analysis of the snow samples, it is imperative that future studies focus on the smaller organic materials that make up a large fraction of the total carbon found in snow in these regions.

[16] Homologous suites of monoacids and dicarboxylic acids were also released from the POM by the CuO oxidation reaction and extraction. The monoacids were dominated, almost exclusively, by even chain length numbers from C<sub>8</sub> to C<sub>18</sub>. Without exception, the C<sub>16</sub> fatty acid (palmitic acid) was dominant in all samples. Many zooplankton, phytoplankton, and brown macroalgae produce monoacid and diacid distributions not unlike those seen at both Alert and Summit upon alkaline CuO extraction [Goni and Hedges, 1995; Goni *et al.*, 1998]. Additionally, this process can produce aliphatic diacids from cuticular materials but in much lower yield [Goni and Hedges, 1995]. Dicarboxylic acids are also produced in soils by bacterial oxidations of plant-derived fatty acids [Kawamura and Gagosian, 1990] and have been used as molecular tracers for the atmospheric transport of soil derived materials [Kawamura *et al.*, 1990, 1995]. Kawamura and Gagosian [1987] analyzed aerosol samples at Alert, Canada, and detected a series of  $\alpha,\omega$ -dicarboxylic acids (C<sub>6</sub>–C<sub>26</sub>). They proposed that the predominance of



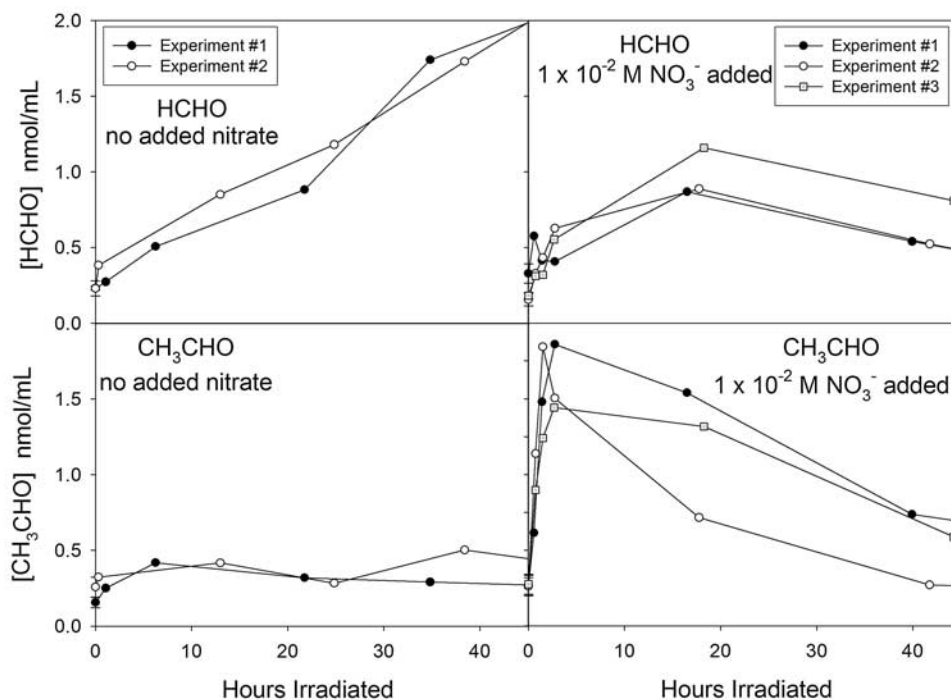
**Figure 3.** South Pole snow irradiation results for HCHO and CH<sub>3</sub>CHO.

the C<sub>9</sub>-diacid (azelaic acid) was a unique tracer of photochemical oxidation of biogenic unsaturated fatty acids (which often contain a double bond at the C-9 position). The absence of azelaic acid in our February Alert snow sample (deposited in 24-hour dark conditions) supports the conclusion that photochemistry of biogenically derived material is its likely source.

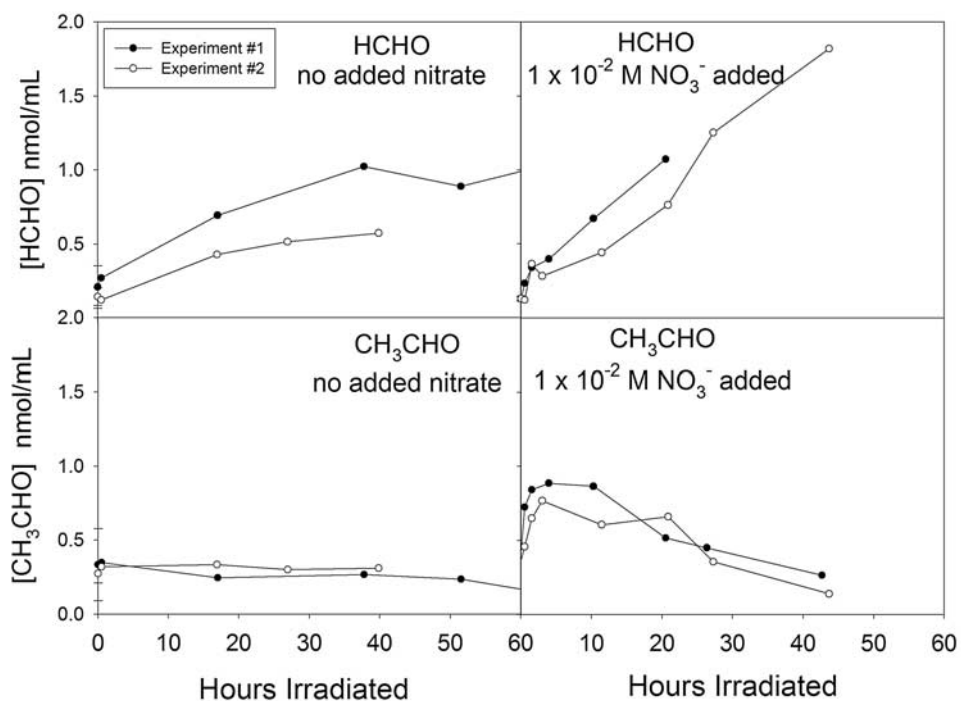
[17] Consideration of the lignin phenol and acid data indicates that they are most likely derived from distinct sources in that the acids are predominantly of algal or bacterial origin, possibly from local sources, while the lignin clearly implies long-range atmospheric transport of vascular tissue to both the Summit and Alert sites. We also note that these analyses were possible for only the POM (due to the small sample size available). The majority of the organic material is less than 1 kDa in size and as yet remains largely uncharacterized [Dassau *et al.*, 2002]. However, knowing that lignin-derived materials and aliphatic acids are present in polar snowpacks, we can approach the experimental production of volatiles from SPOM in a mechanistic fashion, as described below.

### 3.2. Photochemistry of SPOM

[18] To test the hypothesis that low molecular weight carbonyl compounds are produced from SPOM photochemistry, laboratory-generated snow samples were irradiated in a snow-photoreactor. For samples from three unique polar locations (Alert, Summit, and South Pole), HCHO was produced in the native sample when irradiated with UV light (Figures 3–6), although for Alert, the HCHO production rate in snow was not significantly



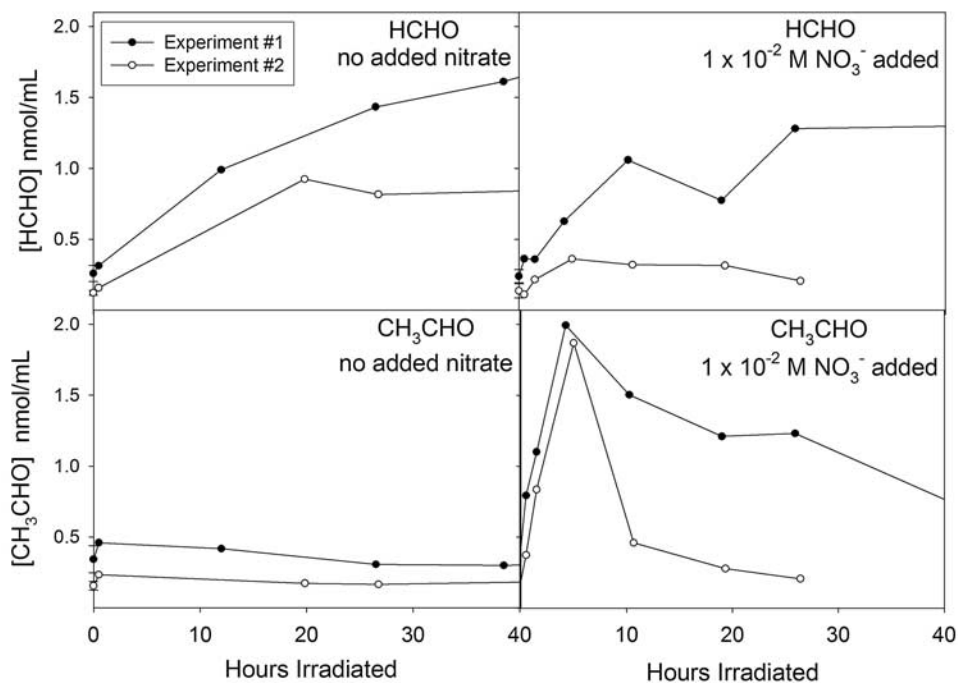
**Figure 4.** Summit, Greenland, snow irradiation results for HCHO and CH<sub>3</sub>CHO (snow containing <1000 Da organic material), with and without nitrate addition.



**Figure 5.** Alert, Canada, snow irradiation results for HCHO and CH<sub>3</sub>CHO (snow containing <1000 Da organic material), with and without nitrate addition.

different from that observed in the blank (as determined by comparing the standard errors of the slopes at the 95% confidence level). Conversely, CH<sub>3</sub>CHO concentrations in irradiated Summit and Alert snow did not vary signifi-

cantly from the dark,  $t = 0$  concentration (Figures 4–6). Interestingly, however, irradiated South Pole snow did produce CH<sub>3</sub>CHO in significant concentrations above the  $t = 0$  concentration (Figure 3).



**Figure 6.** Alert, Canada, snow irradiation results for HCHO and CH<sub>3</sub>CHO (original snow, before filtration), with and without nitrate addition.

**Table 2.** Statistical Analysis of Observed Carbonyl Compound Production Rates and Data Quality of the Regressions<sup>a</sup>

Experiment	Slope (m), nmol mL <sup>-1</sup> hr <sup>-1</sup>	r <sup>2</sup>	σ <sub>m</sub>	Is Slope Significant? (CI = 95%)
Blank	HCHO = 0.011	0.99	HCHO = 0.0015	HCHO = Yes
	CH <sub>3</sub> CHO = 0.001	0.99	CH <sub>3</sub> CHO = 0.001	CH <sub>3</sub> CHO = No
South Pole	HCHO = 0.051	0.92	HCHO = 0.0044	HCHO = Yes
	CH <sub>3</sub> CHO = 0.30	0.94	CH <sub>3</sub> CHO = 0.12	CH <sub>3</sub> CHO = Yes
Summit (<1K Da) no added nitrate	HCHO = 0.033	0.98	HCHO = 0.0015	HCHO = Yes
	CH <sub>3</sub> CHO = 0	–	CH <sub>3</sub> CHO = 0.001	CH <sub>3</sub> CHO = No
Summit (<1K Da) with added nitrate	HCHO = 0.11	0.93	HCHO = 0.022	HCHO = Yes
	CH <sub>3</sub> CHO = 0.56	0.88	CH <sub>3</sub> CHO = 0.05	CH <sub>3</sub> CHO = Yes
Alert (<1 K Da) no added nitrate	HCHO = 0.014	0.93	HCHO = 0.0012	HCHO = No
	CH <sub>3</sub> CHO = 0	–	CH <sub>3</sub> CHO = 0.0011	CH <sub>3</sub> CHO = No
Alert (<1 K Da) with added nitrate	HCHO = 0.026	0.98	HCHO = 0.0033	HCHO = Yes
	CH <sub>3</sub> CHO = 0.12	0.91	CH <sub>3</sub> CHO = 0.021	CH <sub>3</sub> CHO = Yes
Alert (original snow)no added nitrate	HCHO = 0.038	0.89	HCHO = 0.0034	HCHO = Yes
	CH <sub>3</sub> CHO = 0	–	CH <sub>3</sub> CHO = 0.001	CH <sub>3</sub> CHO = No
Alert (original snow) with added nitrate	HCHO = 0.063	0.98	HCHO = 0.016	HCHO = Yes
	CH <sub>3</sub> CHO = 0.35	0.99	CH <sub>3</sub> CHO = 0.030	CH <sub>3</sub> CHO = Yes

<sup>a</sup>The slope (m), standard error of the slope (σ<sub>m</sub>), and whether the slope is statistically significantly different from the blank (for the case HCHO) or zero (for the case of CH<sub>3</sub>CHO) are shown.

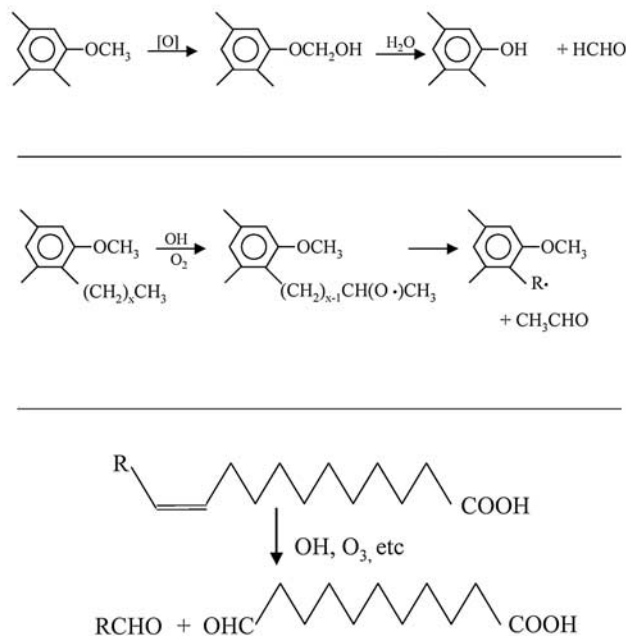
[19] To test the hypothesis that OH chemistry could enhance the condensed phase production of the carbonyl compounds, sodium nitrate was added to the melted Alert and Summit snow samples (at a concentration of  $1 \times 10^{-2}$  M, so that OH production would dominate over other potential mechanisms of carbonyl compound production present in the original snow sample), before being resynthesized into snow crystals (the lamp emission spectrum overlaps with the absorption spectrum of nitrate). The production of HCHO in the condensed phase became significant for the Alert snow sample (as compared to the blank) as shown from Figure 5 (and Table 2), indicating the possible importance of HCHO production via OH mediated chemistry as well as by direct photolytic production. Although CH<sub>3</sub>CHO was not produced in the original snow samples, the production of CH<sub>3</sub>CHO changed dramatically upon addition of nitrate to the snow sample. We suspect that after the initial fast production, destruction of CH<sub>3</sub>CHO via OH reaction becomes relatively more important (likely due to depletion of the reactive organic substrate) than production, and the CH<sub>3</sub>CHO concentration decreases with time. Unfortunately, the volume of frozen snow samples obtained from South Pole was not large enough to be able to melt and then regenerate snow, so experiments with additional nitrate were not possible.

[20] When original Alert snow samples (containing particulates, as well as dissolved material) were irradiated, the initial production rate of HCHO and CH<sub>3</sub>CHO during controlled irradiation experiments was faster than for samples containing only material <1000 Da in size (~60% faster for HCHO and ~40% faster for CH<sub>3</sub>CHO), as shown in Figure 6 and Table 2. This indicates that aldehyde production occurs for a variety of organic substrate molecular weights, i.e., including the particulate organic carbon.

[21] Results of a detailed regression analysis are shown in Table 2 for all of the experiments shown in Figures 3–6 with an analysis of the statistical significance of the slopes. For experiments with added nitrate, only the initial points were used to determine the production rates, due to the fact that OH likely reacts with the carbonyl

compounds over the course of the experiment, causing an eventual decrease in the measured concentrations, as hypothesized above.

[22] With the greater knowledge of the sources of organic matter constituting SPOM in these samples we can proceed to speculate on mechanisms of aldehyde formation upon hydroxyl radical reaction (see Figure 7). Two potential processes are depicted in Figure 7, although there are likely a very large variety of potential mechanisms, given the molecular complexity of the substrate. There is a natural precedence for the production, as depicted in the top panel, of formaldehyde from lignin, as it is thought that many



**Figure 7.** Possible carbonyl compound production schemes from irradiated snow utilizing lignin-derived organic material and fatty acids.

terrestrial fungi decompose woody tissue through the use of hydroxyl radicals. The mechanism presented has been hypothesized as the route by which some microbes are thought to degrade lignin material, where [O] can be species such as OH or superoxide, or oxidizing enzymes [Frick and Crawford, 1983]. In such microbially mediated cases, Fenton type chemistry is thought to be used to generate OH radicals rather than photochemistry [Frick and Crawford, 1983].

#### 4. Conclusions

[23] The results presented here show, for the first time, direct evidence of the photochemical condensed phase production of low molecular weight carbonyl compounds in UV-irradiated snow. The fact that this demonstrates ubiquitous photochemical production in all snows used points to global implications. It is likely that this oxidative chemistry will also occur at midlatitudes, possibly being enhanced due to greater sources of local pollution (e.g., much higher snowpack NO<sub>3</sub><sup>-</sup> and organic material) and local biota. In addition, the type of chemistry proposed in Figure 7 could also occur in the aerosol phase during transport of these materials to polar latitudes. It has been shown that aqueous-phase OH formation in cloud and fog waters is a widespread phenomenon and could significantly affect the atmospheric cycles of such species as peroxides, sulfur, carbon and chlorine [Faust and Allen, 1993]. Reactions of OH with plant materials incorporated in aerosols could serve as partial explanation for the high concentrations of short-lived oxygenated organics measured in the free troposphere, which could not otherwise be modeled or explained using known gas phase chemistry [Singh et al., 2001]. The implications of this finding also extend to the glaciology community, as the interpretation of ice cores as a proctor for past atmospheric concentrations will need to account for the post-depositional photochemical processing that occurs in the condensed phase in irradiated snowpacks. The snowpack and ice core composition is likely to be subject to the variability in long-range transport of oxidants and organic matter that are reactive precursors to snowpack organic chemistry. The presence of vascular plant tissue in Summit, Greenland, snow samples indicates that these materials may in fact be preserved in Greenland glacial ice, and could serve as a rich record of past vegetation inputs. Indeed, the stable carbon isotope composition of plant wax biomarkers in aerosols can provide a detailed temporal record of terrestrial photosynthetic discrimination and shifts in C3 and C4 abundances [Conte and Weber, 2002]. This has wide-reaching implications, as ice core records of terrestrial vegetation biomarkers could provide a unique opportunity to track changes in continental vegetation regimes, and be a compliment to similar studies conducted in lacustrine, riverine, and marine sediments.

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