

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

Aaron L. Swanson^{a,b,*}, Nicola J. Blake^a, Donald R. Blake^a, F. Sherwood Rowland^a, Jack E. Dibb^c, Barry L. Lefer^d, Elliot Atlas^e

^aDepartment of Chemistry, University of California, Irvine, USA

^bChemistry Technology Department, One Space Park Drive; O1/2030e, Redondo Beach, Chemistry Technology Division, Northrop Grumman Space Technologies, CA 90278, USA

^cInstitute for the Study of Earth, Oceans, and Space, University of New Hampshire, NH, USA

^dDepartment of Geology, University of Houston, Houston, TX, USA

^eDivision of Marine and Atmospheric Chemistry, University of Miami, Miami, FL 33149, USA

Received 28 November 2005; received in revised form 6 November 2006; accepted 6 November 2006

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.

© 2007 Elsevier Ltd. All rights reserved.

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

*Corresponding author. Chemistry Technology Department, One Space Park Drive; O1/2030e, Redondo Beach, CA 90278, USA.

E-mail address: Aaron.Swanson@NGC.com (A.L. Swanson).

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

Download English Version:

<https://daneshyari.com/en/article/4443500>

Download Persian Version:

<https://daneshyari.com/article/4443500>

[Daneshyari.com](https://daneshyari.com)