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Utilizing isotopes of nitrate to characterize air-ice interactions at Summit, Greenland

D. Fibiger (1), M. Hastings (2), J. Dibb (3), C. Corr (3), and L.G. Huey (4)

(1) Department of Chemistry, Brown University, Providence, RI, United States (dorothy_fibiger@brown.edu), (2) Department of Geological Sciences and Environemental Change Initiative, Brown University, Providence, RI, United States, (3) Earth Systems Research Center, Institute for the Study of the Earth, Oceans and Space, University of New Hampshire, Durham, NH, United States, (4) School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, United States

Atmospheric nitrate results from reactions of NO_x (NO and NO_2) with oxidants in the atmosphere. The concentration and isotopic composition of nitrate in ice cores have been studied with the aims of reconstructing past NO_x concentrations in the atmosphere, modeling past atmospheric oxidant concentrations and exploring variability in NO_x sources. Post-depositional processing at the snow surface, however, complicates our understanding and interpretation of nitrate found in snow and ice cores (Honrath et al., *Atmos. Env.*, 2002; Röthlisberger et al., *JGR*, 2000).

In a campaign consisting of two springtime (May-June) field seasons at Summit, Greenland [72˚35'N, 38˚25'W], atmospheric and surface snow measurements were made to investigate the influence of bromine chemistry (i.e. BrO) on locally processed nitrate versus nitrate transported to Summit. Specifically, we look to use the oxygen isotopic composition of nitrate (Δ^{17}O-NO_3^-) to quantify the effect of BrO on the formation of atmospheric nitrate (i.e. via $BrONO_2$). The major oxidants in tropospheric nitrate formation have distinctive isotopic compositions such that their relative contribution to NO_x oxidation can be quantified based on Δ^{17}O ($\Delta^{17}O \approx \delta^{17}O - 0.52 \times \delta^{18}O$) of nitrate. In particular, ozone has a unique "mass independent fractionation" signature with Δ^{17}O = 25-35‰ (per mil), while OH has a Δ^{17}O of 0‰ḂrO, formed from Br reacting with ozone, is expected to carry a Δ^{17}O = 30-42‰ (Morin et al., *ACP*, 2007).

Models of local photochemical post-depositional processing of nitrate cannot fully explain observed values of Δ^{17}O-NO_3^- in Summit snow, especially in the late spring and summer (Kunasek et al., *JGR*, 2008; Jarvis et al., *GRL*, 2008). These models do not include bromine chemistry, though concentrations of bromine oxide (BrO) >0.5 pptv have been detected regularly above the snowpack at Summit during the spring and early summer. Reactive bromine often shows a diurnal cycle, with concentrations reaching as high as 10 pptv shortly after solar noon, although more typically found to be between 0.5 – 3.0 pptv. During our campaigns, gas phase BrO (CIMS), NO, NO_y (chemiluminescent analyzer) and soluble Br, NO_3^-, and NO_2^- (IC) were measured concurrently. In addition, surface snow samples were collected and analyzed for nitrate concentration and isotopes. While atmospheric concentrations of soluble nitrate generally range from 2-10 pptv, typical concentrations of nitrate in the snow range from 1-3 micromolar with sporadic concentrations up to 10 micromolar.

With comprehensive isotope measurements (δ^{15}N, δ^{18}O, Δ^{17}O) of both atmospheric nitrate (mist chamber collections) and surface snow NO_3^- in both field seasons, ice-air interactions will be characterized seasonally. Comparison of isotope values with the suite of snow (soluble ions) and atmospheric (BrO, NO, NO_y, soluble constituents) concentration measurements will allow for investigation of the influence of local oxidation pathways on post-depositionally processed NO_3^-. In addition, interannual variability will be discussed.