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## RESEARCH ARTICLE

10.1002/2015JD024187

## Key Points:

- Nitrate in snow at Summit, Greenland is not affected by postdepositional processing
- Three isotopically distinct sources contribute to nitrate at Summit, Greenland
- Local atmospheric influence is not found in the isotopic composition of nitrate in snow

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## Analysis of nitrate in the snow and atmosphere at Summit, Greenland: Chemistry and transport

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**Abstract** As a major sink of atmospheric nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), nitrate ( $\text{NO}_3^-$ ) in polar snow can reflect the long-range transport of  $\text{NO}_x$  and related species (e.g., peroxyacetyl nitrate). On the other hand, because  $\text{NO}_3^-$  in snow can be photolyzed, potentially producing gas phase  $\text{NO}_x$  locally,  $\text{NO}_3^-$  in snow (and thus, ice) may reflect local processes. Here we investigate the relationship between local atmospheric composition at Summit, Greenland ( $72^\circ 35' \text{N}$ ,  $38^\circ 25' \text{W}$ ) and the isotopic composition of  $\text{NO}_3^-$  to determine the degree to which local processes influence atmospheric and snow  $\text{NO}_3^-$ . Based on snow and atmospheric observations during May–June 2010 and 2011, we find no connection between the local atmospheric concentrations of a suite of gases ( $\text{BrO}$ ,  $\text{NO}$ ,  $\text{NO}_y$ ,  $\text{HNO}_3$ , and nitrite ( $\text{NO}_2^-$ )) and the  $\text{NO}_3^-$  isotopic composition or concentration in snow. This suggests that (1) the snow  $\text{NO}_3^-$  at Summit is primarily derived from long-range transport and (2) this  $\text{NO}_3^-$  is largely preserved in the snow. Additionally, three isotopically distinct  $\text{NO}_3^-$  sources were found to be contributing to the  $\text{NO}_3^-$  in the snow at Summit during both 2010 and 2011. Through the complete isotopic composition of  $\text{NO}_3^-$ , we suggest that these sources are local anthropogenic particulate  $\text{NO}_3^-$  from station activities ( $\delta^{15}\text{N} = 16\text{‰}$ ,  $\Delta^{17}\text{O} = 4\text{‰}$ , and  $\delta^{18}\text{O} = 23\text{‰}$ ),  $\text{NO}_3^-$  formed from midlatitude  $\text{NO}_x$  ( $\delta^{15}\text{N} = -10\text{‰}$ ,  $\Delta^{17}\text{O} = 29\text{‰}$ ,  $\delta^{18}\text{O} = 78\text{‰}$ ) and a  $\text{NO}_3^-$  source that is possibly influenced by or derived from stratospheric ozone  $\text{NO}_3^-$  ( $\delta^{15}\text{N} = 5\text{‰}$ ,  $\Delta^{17}\text{O} = 39\text{‰}$ ,  $\delta^{18}\text{O} = 100\text{‰}$ ).

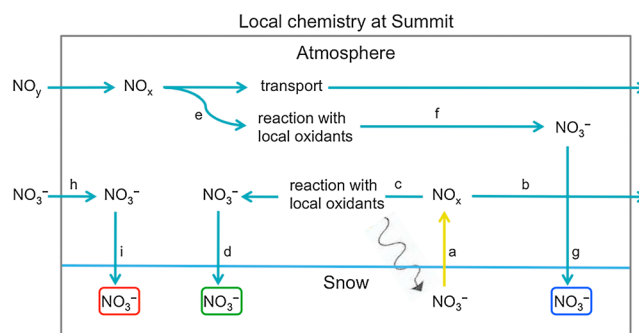
### 1. Introduction

Nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) are short-lived radicals that influence the oxidizing capacity of the atmosphere via interactions with ozone ( $\text{O}_3$ ) and hydroxyl radical ( $\text{OH}$ ). Nitrate ( $\text{NO}_3^-$ ), the end product of  $\text{NO}_x$  oxidation, is an abundant anion in polar snow. Because  $\text{NO}_3^-$  can be subject to postdepositional processes such as photolysis and/or evaporative loss [e.g., Honrath *et al.*, 1999; Rothlisberger *et al.*, 2000],  $\text{NO}_3^-$  in snow can reflect a combination of distant sources and chemistry, as well as local processing and therefore local chemistry. As a result, it can be unclear to what extent  $\text{NO}_3^-$  that is ultimately archived in ice cores reflects local postdepositional processing and/or loss versus that which is representative of regional scale atmospheric chemistry.

The dominant fraction of oxidized nitrogen ( $\text{NO}_y = \text{NO}_x + \text{HNO}_3 + \text{HONO} + \text{PAN} + \dots$ , etc.) transported to Summit is peroxyacetyl nitrate (PAN) [Kramer *et al.*, 2015]. While the amount of PAN transported to Summit decreases in the summer, it remains the dominant species year-round due to formation of PAN in source regions and its long lifetime. PAN can be thermally decomposed to  $\text{NO}_x$  at any point during its transport, but conditions at Summit are nearly always too cold for this to be a significant contributor to local  $\text{NO}_x$  [Kramer *et al.*, 2015]. It is, therefore, thought that a main source of  $\text{NO}_x$  in the lower atmosphere above central Greenland is a photochemical release from snowpack  $\text{NO}_3^-$  [Honrath *et al.*, 1999; Thomas *et al.*, 2012b, 2011].

A number of studies have investigated the degree to which  $\text{NO}_3^-$  is lost from the snow upon photolysis (Figure 1, arrows a and b), with the primary reaction pathways





**Figure 1.** Possible paths for  $\text{NO}_3^-$  deposition and loss at Summit.  $\text{NO}_3^-$  can be photolyzed in surface snow (arrow a) releasing  $\text{NO}_x$  to the atmosphere above, which can be transported away (arrow b) or reacted with local oxidants to regenerate  $\text{NO}_3^-$  (arrow c).  $\text{NO}_3^-$  deposited back to the snow via this mechanism (arrow d) will contain an isotopic composition that reflects photolysis and oxidation by local gases. Alternatively or in addition, snow  $\text{NO}_3^-$  could reflect  $\text{NO}_x$  transported in from outside of Summit that is locally oxidized (arrows e, f, and g) or could represent long-range transported  $\text{NO}_3^-$  that is deposited and preserved in the snow (arrows h and i).

as a result of preferential loss of  $\text{NO}_3^-$  with greater  $^{14}\text{N}$ . Based upon theoretical and laboratory-based predictions of the fractionation factor associated with photolysis of  $\text{NO}_3^-$  (e.g.,  $-40$  to  $-74\text{‰}$  [Berhanu et al., 2014; Frey et al., 2009]), the highly enriched values observed in East Antarctica are explained by significant photolytic loss of  $\text{NO}_3^-$  from the snowpack [Erbland et al., 2013].

In contrast, at Summit, Greenland ( $\sim 65 \text{ cm yr}^{-1}$  snow accumulation), the  $\text{NO}_3^-$  in the snow is largely preserved. Hastings et al. [2004] found little changes in the isotopes of  $\text{NO}_3^-$  in snow sampled on the surface in March and resampled in snowpits at 33 cm depth in August. Recently, Fibiger et al. [2013] found a strong, linear relationship between the oxygen isotopes of  $\text{NO}_3^-$  ( $\delta^{18}\text{O} = ({}^{18}\text{O}/{}^{16}\text{O}_{\text{sample}})/({}^{18}\text{O}/{}^{16}\text{O}_{\text{VSMOW}}) - 1 \times 1000\text{‰}$ , where  $x = 18$  or  $17$ ;  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ). With the current understanding of photolysis of nitrate in snow, the associated isotopic fractionation for  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  in  $\text{NO}_3^-$  remaining in the snow, and possible exchange of oxygen atoms in the snow, this relationship could not be explained in the presence of significant postdepositional loss or processing of  $\text{NO}_3^-$  [Fibiger et al., 2013].

Based on snow  $\text{NO}_3^-$  data from both 2010 and 2011, the relationship found between  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  indicates that  $\text{NO}_3^-$  in the snow at Summit is influenced, primarily, by two oxidants of differing isotopic composition. From the linear relationship ( $\Delta^{17}\text{O} = 0.46 \times \delta^{18}\text{O} - 6.9$ ,  $R^2 = 0.9$ ), the high end-member ( $\delta^{18}\text{O} = 100\text{‰}$  and  $\Delta^{17}\text{O} = 39\text{‰}$ ) is similar to that expected for ozone, while the low end-member ( $\delta^{18}\text{O} = 15\text{‰}$  and  $\Delta^{17}\text{O} = 0\text{‰}$ ) is closest in isotopic composition to diatomic oxygen. In the absence of significant  $\text{NO}_3^-$  loss from the snow,  $\delta^{15}\text{N}$ - $\text{NO}_3^-$  in snow and ice at Summit may reflect  $\text{NO}_x$  sources [Hastings et al., 2009] or some combination of source  $\delta^{15}\text{N}$  and fractionation with processing (e.g., PAN chemistry) during transport. The  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ - $\text{NO}_3^-$ , meanwhile reflect the relative abundance of oxidants implicated in the  $\text{NO}_3^-$  formation pathway [e.g., Hastings et al., 2004; Morin et al., 2008].

While the isotope studies suggest very little loss or redistribution of  $\text{NO}_3^-$  from the snow at Summit, there are significant  $\text{NO}_x$  concentrations observed above the snow [Dibb et al., 2002; Honrath et al., 2002; Yang et al., 2002]. The surprisingly high  $\text{NO}_x$  concentrations, up to 50 pptv measured in the boundary layer, have been ascribed to photolysis of  $\text{NO}_3^-$  in the snow. Based on modeling of observed concentrations of a suite of gases at Summit, only a 2% loss of  $\text{NO}_3^-$  from the snow, prior to burial below the photic zone, is required to explain the  $\text{NO}_x$  concentrations above the snowpack in summertime [Thomas et al., 2011]. This minimal loss fits with isotopic observations of nitrate at Summit thus far. However, recent modeling of the isotopic composition of nitrate under conditions of postdepositional photolytic loss at Dome C on the East Antarctic ice sheet [Erbland et al., 2015] suggests that a significant amount of recycling of  $\text{NO}_3^-$  can take place locally (Figure 1, arrows a, c, and d)—i.e.,  $\text{NO}_3^-$  is photolyzed and  $\text{NO}_x$  escapes the snow, this  $\text{NO}_x$  reacts in the gas phase above the snow and is either transported away (Figure 1, arrow b) or redeposited locally as  $\text{NO}_3^-$  (Figure 1, arrows c and d). If this process was important at Summit as well, the  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  in the snow should reflect both

While the concentration of  $\text{NO}_3^-$  provides some information about processing of  $\text{NO}_3^-$  in the snow, more recent studies have shown that the isotopic composition of nitrate can provide more details.  $\text{NO}_3^-$  in low snow accumulation areas ( $\sim 10 \text{ cm yr}^{-1}$  snow accumulation), such as on the East Antarctic Ice Sheet, shows significant mass loss and redistribution such that a strong decrease in  $\text{NO}_3^-$  concentration is observed with depth [Blunier et al., 2005; Erbland et al., 2013; Frey et al., 2009; Shi et al., 2015]. In these studies, the  $\text{NO}_3^-$  found below the surface in snowpits is generally highly enriched ( $\delta^{15}\text{N} > 300\text{‰}$ ) in the heavier isotope of nitrogen ( $\delta^{15}\text{N} = ({}^{15}\text{N}/{}^{14}\text{N}_{\text{sample}})/({}^{15}\text{N}/{}^{14}\text{N}_{\text{N}_2 \text{ in air (reference)}}) - 1 \times 1000\text{‰}$ ),

photolytic loss and redeposition, while we would expect the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  of  $\text{NO}_3^-$  in the snow to reflect the local oxidant composition and any fractionation with redeposition.

The photolytic processing of  $\text{NO}_3^-$  can also include reactions of the photolytic products which remain in the condensed phase.  $\text{NO}_3^-$  can be photolyzed to  $\text{NO}_2^-$ , which will be converted back to  $\text{NO}_3^-$  in the snow. These reactions will alter the oxygen isotopic composition of the snow  $\text{NO}_3^-$ , without altering the  $\delta^{15}\text{N}$ . The change in  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  depends on the isotopic composition of the water that makes up the snow [McCabe *et al.*, 2005]. This oxygen exchange happens simultaneously with nitrate photolytic loss from the snowpack, and therefore, both isotopic effects are expected.

If the  $\text{NO}_3^-$  in the snow is the result of  $\text{NO}_x$  that is transported in from outside of Summit and then converted to  $\text{NO}_3^-$  and deposited (Figure 1, arrows e, f, and g), then the  $\delta^{15}\text{N}$  should reflect long-range transport of  $\text{NO}_x$  or  $\text{NO}_y$  to Summit as a result of midlatitude  $\text{NO}_x$  emission sources, while the oxygen isotopic composition is expected to reflect local oxidizing conditions. For instance, in the presence of sunlight, any  $\text{NO}_2$  lost from the snow as a result of photolysis will cycle rapidly with  $\text{NO}$ , erasing the original oxygen isotopic content of the  $\text{NO}$ .

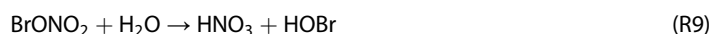
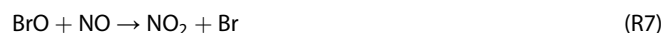


Eventually, the  $\text{NO}_2$ , which now reflects the isotopic composition of local  $\text{O}_3$ , will be further oxidized to  $\text{HNO}_3$ .



In this case, the isotopic composition of  $\text{HNO}_3$  will be two thirds derived from  $\text{O}_3$  and one third from  $\text{OH}$ . The isotopic composition of  $\text{OH}$  is currently not well constrained, but it is assumed to be in isotopic equilibrium with water vapor, depending on local conditions [Morin *et al.*, 2007]. Calculated for average summertime conditions at Summit, the  $\text{OH}$  should contain greater than 98% the isotopic composition of water. This will result in a  $\Delta^{17}\text{O}$  not significantly different than that of  $\text{H}_2\text{O}$  vapor ( $\sim 0\text{‰}$ ) and a  $\delta^{18}\text{O}$  that either directly reflects that of  $\text{H}_2\text{O}$  vapor ( $\sim -10\text{‰}$ ) or includes fractionation. The most current estimate of the fractionation of  $\text{OH}$  in equilibrium with water is  $\sim -40\text{‰}$  [Michalski *et al.*, 2012], and in this case,  $\text{OH}$  at Summit would be expected to have a  $\delta^{18}\text{O}$  of  $\sim -50\text{‰}$ . The isotopic composition of  $\text{O}_3$  is unique among oxidants, with typical  $\Delta^{17}\text{O}$  of  $\sim 26\text{‰}$  and  $\delta^{18}\text{O}$  of  $\sim 115\text{‰}$  [Vicars and Savarino, 2014]. As demonstrated by Vicars and Savarino [2014, and references therein], these values reflect the properties of bulk  $\text{O}_3$ , while the reactions that produce  $\text{NO}_3^-$  interact with the terminal oxygen atoms of  $\text{O}_3$ , such that the isotopic composition transferred to  $\text{NO}_3^-$  is  $\sim 40\text{‰}$  for  $\Delta^{17}\text{O}$  and  $\sim 128\text{‰}$  for  $\delta^{18}\text{O}$ . These isotopic values reflect tropospheric  $\text{O}_3$ , while stratospheric  $\text{O}_3$  values have been observed to be higher, close to  $35\text{‰}$  for bulk  $\Delta^{17}\text{O}$  ( $53\text{‰}$  for terminal  $\Delta^{17}\text{O}$ ) [Krankowsky *et al.*, 2007].

Attempts to model the oxygen isotopic composition of  $\text{NO}_3^-$  at Summit, Greenland, generally underestimate the  $\Delta^{17}\text{O}\text{-NO}_3^-$  observed in spring and summer due to the expected dominance of (R5) [Alexander *et al.*, 2009; Kunasek *et al.*, 2008]. Both Alexander *et al.* [2009] and Kunasek *et al.* [2008] posited that local halogen chemistry could account for this difference. In particular, the spring  $\text{BrO}$  concentrations of up to 5.5 pptv [Liao *et al.*, 2011b] at Summit could be high enough to increase the simulated  $\Delta^{17}\text{O}\text{-NO}_3^-$  to better match observations.  $\text{BrO}$  imparts a high  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  on to  $\text{NO}_3^-$  because its oxygen originates from  $\text{O}_3$ , as follows:



The resulting  $\text{HNO}_3$  in (R9) would have a much higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}\text{-NO}_3^-$  than that formed in (R5) because of the greater influence of  $\text{O}_3$  [e.g., Morin *et al.*, 2012, and references therein]. The higher than predicted snow  $\text{NO}_3^-$  oxygen isotopic values would then be explained as a result of the local recycling of photolysis-derived  $\text{NO}_x$  and redeposition of  $\text{NO}_3^-$  (Figure 1, arrows a, c, and d) [Alexander *et al.*, 2009; Kunasek *et al.*, 2008]. Jarvis *et al.* [2009] also suggested that local recycling of  $\text{NO}_3^-$  (Figure 1, arrows a, c, and d) at Summit may influence the  $\text{NO}_3^-$  in the snow, based on an observed offset in  $\delta^{18}\text{O}\text{-NO}_3^-$  in the snow and air, despite similar  $\delta^{15}\text{N}\text{-NO}_3^-$  in snow  $\text{NO}_3^-$  and  $\text{HNO}_3$  captured from the air (via mist chamber). Fieber *et al.* [2013], however,

found that postdepositional loss and/or recycling are not prominent processes at Summit during spring and early summer. The  $\text{NO}_3^-$  in snow, rather, is interpreted as a direct, atmospheric signal, which is representative of long-range transport (Figure 1, arrows h and i). We investigate these contrasting findings by examining whether there are direct connections between atmospheric composition and the concentration and isotopic composition of  $\text{NO}_3^-$  in surface snow and the atmosphere at Summit.

## 2. Methods

### 2.1. Snow Concentration and Isotope Measurements

Two 5 week field seasons were conducted in late spring at Summit, Greenland: 17 May to 22 June 2010 and 24 May to 26 June 2011. Throughout both seasons, surface snow samples comprising the dominant stratigraphic layer, as described in *Dibb et al.* [2007], were collected at 4 or 12 h intervals. This surface layer typically ranged from 0.5 to 3.0 cm in depth and 100 to 400  $\text{cm}^2$ . All snow samples were collected within a  $2 \times 10$  m area in the clean air sector (approximately 1.0 km to the south of the station). This area is generally upwind of the station, though there are periods of “north winds” during each field season when air passes over the station before the sampling area or the winds are low enough that there may be station influence on the snow. North wind conditions are defined as wind between 342 and 72° or less than  $2 \text{ m s}^{-1}$ . During these events, camp activities that may pollute the snow are limited as much as possible, though the generator is run continuously. At each time point three adjacent samples of 100–400  $\text{cm}^2$  were collected. (The mass of each sample is reported with the data set at ACADIS, see Acknowledgments below.) Every tenth bottle, a blank was collected, which was handled identically to the samples, with approximately 10 mL of 18 M $\Omega$  water added in place of the snow. Samples were stored frozen in high-density polyethylene (HDPE) bottles until analysis in laboratories at University of New Hampshire (UNH) and Brown University. Snow samples were first analyzed on a Dionex ion chromatograph (IC) for a suite of ion concentrations, including chloride ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ),  $\text{NO}_3^-$ , sodium ( $\text{Na}^+$ ), ammonium ( $\text{NH}_4^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), and calcium ( $\text{Ca}^{2+}$ ). Immediately upon melting in the UNH lab, aliquots were taken for the IC analysis, and the remainder was refrozen for subsequent transfer to Brown. The analysis and QA/QC followed protocols described in *Dibb et al.* [2007] and yielded an uncertainty of 10%.

The  $\text{NO}_3^-$  was analyzed for the complete isotopic composition ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ ) at Brown University. The isotopes were determined using the bacterial denitrifier method, explained in detail in *Casciotti et al.* [2002], *Sigman et al.* [2001], and *Kaiser et al.* [2007]. In short, denitrifying bacteria that lack the  $\text{N}_2\text{O}$  reductase enzyme quantitatively convert  $\text{NO}_3^-$  (and  $\text{NO}_2^-$ ) in solution to gaseous  $\text{N}_2\text{O}$ . Using helium as a carrier gas, the analyte  $\text{N}_2\text{O}$  is then measured on a Thermo-Finnegan Delta Plus isotope ratio mass spectrometer at  $m/z$  44, 45, and 46 to determine  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$ . Isotopic reference materials, USGS34, USGS35, and IAEA-N3 were prepared in 18.2 M $\Omega$  water and analyzed in each set via the same analytical process as samples, and the samples are corrected to a linear fit of the standard values [*Kaiser et al.*, 2007]. (Note that USGS35 is not used as a standard for  $\delta^{15}\text{N}$ .) For the  $\delta^{15}\text{N}/\delta^{18}\text{O}$  analysis, all samples and standards were injected so the amount of  $\text{NO}_3^-$  was 10 nmol. For determination of  $\Delta^{17}\text{O}-\text{NO}_3^-$  ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ), the  $\text{N}_2\text{O}$  was passed through a gold tube heated to 770°C, resulting in  $\text{N}_2$  and  $\text{O}_2$  [*Kaiser et al.*, 2007]. The  $\text{O}_2$  is then measured at  $m/z$  32, 33, and 34 and corrected based upon linearly fitting reference materials USGS35 and USGS34 to known values. All  $\Delta^{17}\text{O}$  analysis was done on 50 nmol of  $\text{NO}_3^-$ . The reference material values and reproducibility for each isotopic quantity are detailed in Table 1.

To calculate the isotopic composition of  $\text{NO}_3^-$  for each snow-sampling event, a weighted average of the values for the triplicate samples was taken. For example:

$$\delta^{18}\text{O} - \text{NO}_3^- = \frac{[\text{NO}_3^-]_1(\text{H}_2\text{Omass})_1\delta^{18}\text{O}_1 + [\text{NO}_3^-]_2(\text{H}_2\text{Omass})_2\delta^{18}\text{O}_2 + [\text{NO}_3^-]_3(\text{H}_2\text{Omass})_3\delta^{18}\text{O}_3}{[\text{NO}_3^-]_1(\text{H}_2\text{Omass})_1 + [\text{NO}_3^-]_2(\text{H}_2\text{Omass})_2 + [\text{NO}_3^-]_3(\text{H}_2\text{Omass})_3} \quad (1)$$

where  $\text{H}_2\text{Omass}$  is the mass of snow collected and the same process used for  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ .

### 2.2. Atmospheric Concentration and Isotope Measurements

Atmospheric gas phase soluble ion concentrations ( $\text{Br}^-$ , nitrite ( $\text{NO}_2^-$ ),  $\text{NO}_3^-$ ) were measured in 0.5 h intervals using a mist-chamber (MC) system coupled to a Dionex IC. The automated two-channel sampling and analysis system has been described previously [*Dibb et al.*, 2010]. In previous studies independent inlets were

**Table 1.** Error Statistics for Isotopic Standards and Snow Sample Replicates

	$\delta^{18}\text{O}$ , $1\sigma_p$ (‰) <sup>a</sup>	$\delta^{18}\text{O}$ , $n$ <sup>b</sup>	$\delta^{18}\text{O}$ Standard Value (‰) <sup>c</sup>	$\Delta^{17}\text{O}$ , $1\sigma_p$ (‰) <sup>a</sup>	$\Delta^{17}\text{O}$ , $n$ <sup>b</sup>	$\Delta^{17}\text{O}$ Standard Value (‰) <sup>c</sup>	$\delta^{15}\text{N}$ , $1\sigma_p$ (‰) <sup>a</sup>	$\delta^{15}\text{N}$ Standard Value (‰) <sup>c</sup>
IAEA-N3	0.37	160	25.6	--	--	--	0.02	4.7
USGS34	0.79	158	-27.9	0.48	246	-0.292	0.02	-1.8
USGS35	0.46	160	57.5	0.72	241	21.6	--	--
Sample replicates	0.7	271	--	0.9	271	--	0.2	--

<sup>a</sup> $\sigma_p = \sqrt{\sum_{i=1}^k (n_i - 1)s_i^2 / \sum_{i=1}^k (n_i - 1)}$ , where  $n_i$  and  $s_i^2$  are the size and variance of the  $i$ th set of samples, respectively, and  $k$  is the total number of sample sets.

<sup>b</sup> $n$  is the number of standards or sample replicates ( $n$  is the same for  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$ ).

<sup>c</sup> $\delta^{18}\text{O}$  standard values from Böhlke *et al.* [2003] and  $\Delta^{17}\text{O}$  standard values recalculated from Böhlke *et al.* [2003] using the linear  $\Delta^{17}\text{O}$  ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ).

used for each channel to assess gradients (with height above the snow, or between firn air and the atmosphere). In this study a single inlet fitted with a Millipore 90 mm Fluoropore PTFE 1  $\mu\text{M}$  pore size filter to remove particulates was employed to sample air approximately 1 m above the snow throughout the field season, resulting in paired samples in 2010. Particulate  $\text{NO}_3^-$  is a very small fraction of  $\text{NO}_3^-$  found in Greenland; only about 3% of total atmospheric  $\text{NO}_3^-$  at Summit is in the aerosol phase [Dibb *et al.*, 1994; Jaffrezo and Davidson, 1993; Silvente and Legrand, 1995]. Therefore, the mist chamber  $\text{HNO}_3$  is expected to be representative of  $\text{NO}_3^-$  in the atmosphere at Summit. The filter was changed every 2–3 days or when blocked by snow. In 2011, a third MC was added to increase the volume of air sampled during each sampling interval, and hence the mass of  $\text{NO}_3^-$  collected, to facilitate the isotopic measurements. The atmospheric sampling was located ~200 m from the snow sampling.

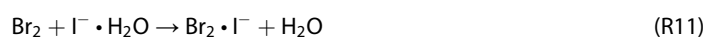
At the end of each sampling interval 5 ml of the ultrapure water in one of the samplers was injected into the IC. For  $\text{NO}_2^-$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$ , there is a detection limit of 0.5 pptv and uncertainty of 15%. Any sample solution remaining in that MC was transferred into an amber HDPE bottle. The entire samples in the second (2010 and 2011) and third (2011) MCs were transferred to separate HDPE bottles. The collection bottles for isotope analysis were changed every 12 h and then frozen for shipment to the laboratory at Brown for analysis of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$ .

In these MC samples,  $[\text{NO}_3^-]$  was low enough that they could not be analyzed directly via the bacterial denitrifier method. The samples were concentrated by anion exchange resin, which has been used previously by several groups [Erbland *et al.*, 2013; Frey *et al.*, 2009; Silva *et al.*, 2000]. A 0.3  $\text{cm}^3$  Bio-Rad AG 1-X8 200–400 mesh chloride form ion exchange resin was used to capture  $\text{NO}_3^-$  from the sample; the  $\text{NO}_3^-$  was then eluted from the resin with 10 mL of 1 M NaCl solution. The NaCl always has a small, but significant,  $\text{NO}_3^-$  blank or  $\text{NO}_3^-$  impurity associated with it. Within a single batch of NaCl (Fisher brand) the  $\text{NO}_3^-$  had a constant concentration and isotopic composition. For the NaCl used with samples here, different bottles were found to have a range of 0.5–1  $\mu\text{M}$   $\text{NO}_3^-$  in 1 M NaCl solution (determined colorimetrically by a Westco Scientific SmartChem 200 discrete chemistry analyzer). The  $\delta^{15}\text{N}$  of the NaCl ranged from -2.7 to +0.6‰ and the  $\delta^{18}\text{O}$  from 13.4 to 30.6‰, depending on the batch of NaCl used. To eliminate the influence of the  $\text{NO}_3^-$  impurity on sample isotope measurements, 18.2 M $\Omega$  water of a similar volume to the samples was put through the same conditions as samples with each sample set. The resultant concentration and isotopic values were corrected out of the sample and reference materials. This is important, even in higher concentration samples, if the isotopic value of  $\text{NO}_3^-$  in NaCl is significantly different from that of the material being analyzed. Additionally, there is some fractionation associated with the concentrating method, so 0.1  $\mu\text{M}$  standards USGS34, USGS35, and IAEA-N3, were put through the concentration method with each analytical set. Thus, a three-step correction was required: first, all concentrated samples, concentrated standard materials, and NaCl impurity “blanks” were linearly corrected to typical USGS34, USGS35, and IAEA-N3 that are analyzed with every sample set to account for the denitrifier method and mass spectrometry uncertainties [Kaiser *et al.*, 2007]; second, the  $\text{NO}_3^-$  contained in the NaCl solution was subtracted out by mass balance to remove the influence of this impurity; finally, the samples were corrected based on linear fitting to the known reference material values (USGS34, USGS35) that had been run through the concentration method. In general, the additional corrections (second and third) resulted in a 2–3‰ change in the  $\delta^{15}\text{N}$ , with a maximum change of 5‰ and a 5–15‰ change in  $\delta^{18}\text{O}$  of the standards, with a maximum change of 25‰. The  $\text{NO}_3^-$  impurities accounted for the vast majority of this additional correction and the positive  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  in the NaCl accounts for the large range in  $\delta^{18}\text{O}$  corrections. Despite the use of the concentrating method,

there were times when several samples had to be combined for the 10 nmol of  $\text{NO}_3^-$  required for analysis. This caused variable time resolution (12–48 h, sometimes discontinuous) and eliminated most of the duplicate samples at any time point. Additionally, there was insufficient  $\text{NO}_3^-$  in the atmospheric samples for analysis of  $\Delta^{17}\text{O}$ . BrO was measured by Chemical Ionization Mass spectrometry (CIMS). The configuration of the CIMS has been described by *Liao et al.* [2011b]. The primary reagent ion was  $\text{I}^- \cdot \text{H}_2\text{O}$ . BrO was ionized inside the CIMS and measured as  $\text{BrO} \cdot \text{I}^-$  [*Neuman et al.*, 2010].



Due to the unstable nature of BrO, direct calibration of BrO in the field was unavailable.  $\text{Br}_2$  from a permeation tube (Kin-tek) was added periodically into the inlet to track the CIMS sensitivities in the field (R10), while the sensitivities to BrO were obtained in the laboratory by comparing sensitivities to BrO and  $\text{Br}_2$  [*Liao et al.*, 2011b]. The emission rate of  $\text{Br}_2$  permeation tube was measured in the field by spectrophotometric technique [*Wu et al.*, 1963].

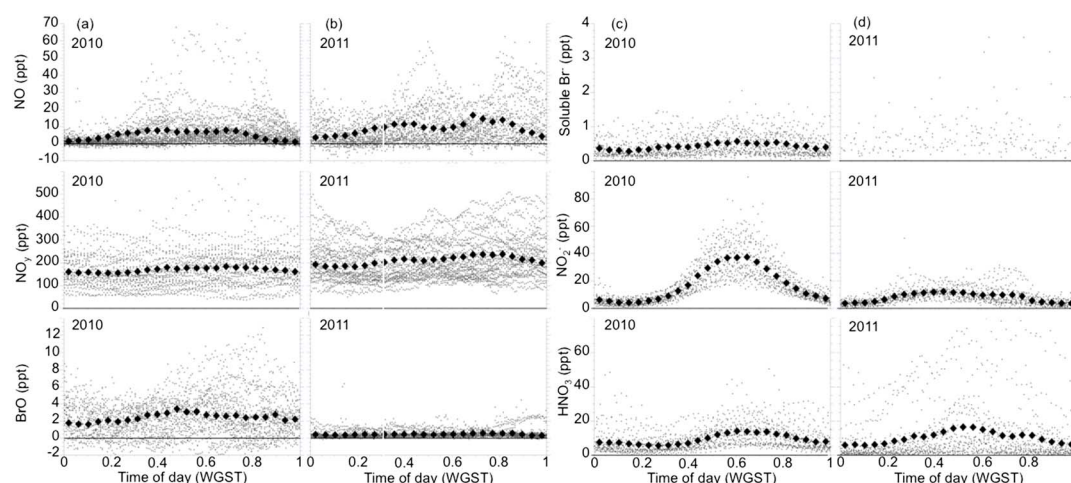


During the 2010 campaign, sensitivity to BrO was 5–15 Hz pptv $^{-1}$  and the detection limit was  $\sim 1$ –1.5 pptv based on 1 min averaged data. During the 2011 campaign, sensitivity to BrO was 10–35 Hz pptv $^{-1}$  and the detection limit was  $< 0.3$  pptv based on 1 min averaged data. The detection limit was significantly improved during the 2011 campaign, partially due to increased sensitivities with a new detector and ion source. The total uncertainty was  $\sim 30\%$  for BrO measurements in both years.

$\text{NO}$  and  $\text{NO}_y$  were measured by the chemiluminescence method described by *Ryerson et al.* [2000]. The instrument has two channels: one channel measured  $\text{NO}$  directly by chemiluminescence, and the other was equipped with a heated Molybdenum converter which converts all  $\text{NO}_y$  species into  $\text{NO}$ , and the product  $\text{NO}$  was measured to quantify  $\text{NO}_y$ . During the 2011 campaign, high-frequency noise was observed on both  $\text{NO}$  and  $\text{NO}_y$  channels, probably due to a deteriorating photomultiplier; therefore, a low-pass filter with a cutoff of 0.05 Hz was applied to the raw data. During the two campaigns the detection limit was  $\sim 1$ –1.5 pptv, and the total uncertainty was  $\sim 10\%$  for both  $\text{NO}$  and  $\text{NO}_y$  channels.

### 2.3. Transport Modeling

We used the Lagrangian FLEXible PARTicle Dispersion Model (FLEXPART) [*Stohl et al.*, 2005] to evaluate (1) the seasonal transport patterns at Summit during our two seasons in 2010 and 2011 and (2) transport events on 22–25 May 2010 and 24–26 June 2011. In both model investigations, FLEXPART was driven using European Center for Medium-range Weather Forecasting model ( $0.25^\circ \times 0.25^\circ$  horizontal resolution, 92 vertical levels) global meteorological fields. FLEXPART was run in two ways. First, the model is used to study seasonal transport to Summit during the two campaign years (2010 and 2011 seasons). For this, we calculate the mean transport during 17 May to 22 June 2010 and 24 May to 26 June 2011. Simulations are conducted backward in time, as this provides a more efficient way to calculate a source-receptor relationship when one is interested in a single receptor. The model was configured with 3-hourly releases of 90,000 particles each from a grid box local to Summit. The particles were parameterized as a passive tracer with a 20 day lifetime. This parameterization removes the particles after 20 days and is intended only to provide an air mass history. In this configuration, one may use the FLEXPART model to produce maps of potential emission sensitivity (PES) (in units of  $\text{s kg}^{-1}$ ), which is proportional to the particle residence time in that cell. It is a measure for the simulated mixing ratio at the receptor that a source of unit strength ( $1 \text{ kg s}^{-1}$ ) in the respective grid cell would produce. By taking the lowest model layer ( $< 100$  m above ground level) one can create a map of residence time or sensitivity to source regions. This provides information on where and when the air mass would be sensitive to surface emissions. When conducting transport simulations over a long period (e.g., several weeks of the campaign), these values must be normalized so that patterns separate from immediate local transport can be seen. We normalized the seasonal average using the long-term mean transport climatology from Summit for the period of January 2000 to December 2011. The resulting data provides seasonal transport anomaly from the long-term mean transport for each season. Second, the model is run for specific events. Separate FLEXPART runs in backward mode were completed for each day with releases (100,000 particles) from 9:00–17:00 UTC in 2010 and 13:00–21:00 UTC in 2011, bracketing the times of largest isotope anomaly. Using the plume-clustering algorithm included in FLEXPART, we are able to map the air mass transport history immediately prior to the observations [*Dorling et al.*, 1992; *Stohl et al.*, 2002].



**Figure 2.** Hourly averages (black diamonds) and all data (grey points) for gas phase NO, NO<sub>y</sub>, and BrO in (a) 2010 and (b) 2011. Soluble Br<sup>-</sup>, NO<sub>2</sub><sup>-</sup> and HNO<sub>3</sub> in (c) 2010 and (d) 2011 in Western Greenland Standard Time (WGST). BrO values are significantly higher in 2010 than 2011, while NO and NO<sub>y</sub> have similar average values, but different distributions. Br<sup>-</sup> and soluble NO<sub>2</sub><sup>-</sup> values are significantly higher in 2010 than 2011, HNO<sub>3</sub> has similar values with a different time distribution. No hourly averages of soluble Br<sup>-</sup> are reported in 2011 because there are too few data points above the detection limit.

### 3. Results

In both the 2010 and 2011 campaigns, the same suite of gas phase and snow measurements was made. Both campaigns showed high variability in both concentration and isotope measurements, which is typical of what has been observed at Summit in the past (detailed below). We first consider the gas phase concentrations of NO, NO<sub>y</sub>, BrO, and soluble gases, followed by the snow NO<sub>3</sub><sup>-</sup> concentration and isotopes, and, finally, context for our discussion and interpretation based on transport modeling.

#### 3.1. Gas Phase Concentrations

The mixing ratios of reactive nitrogen oxides and active bromine above the snow at Summit were quite different in some regard, between the two field campaigns. Focusing first on compounds that are believed to be dominated by emissions from the snowpack [Thomas *et al.*, 2012a], we note that hourly means (and medians, not shown) of NO were consistently higher by several pptv during summer 2011; this enhancement was largest (>4 pptv) from 17:00 to 23:00 Western Greenland Standard Time (WGST) (Figures 2a and 2b). In contrast, soluble NO<sub>2</sub><sup>-</sup> mixing ratios were much higher in 2010, particularly from about 11:00–23:00 WGST (Figures 2c and 2d). Reactive bromine (both BrO and the soluble Br<sup>-</sup> measured by MC/IC) was also higher by at least a factor of 5 throughout the day during 2010 (Figure 2). Nitric acid above the snow can be enhanced by long-range transport events, but it has been suggested that local production from NO and HO<sub>x</sub> emitted from the snowpack can be the dominant source for much of the summer at Summit [e.g., Dibb *et al.*, 2002; Dibb and Fehsenfeld, 2004; Thomas *et al.*, 2011]. Hourly mean HNO<sub>3</sub> mixing ratios were similar in 2010 and 2011, but we observed several hour offset in the timing of the daily peak (12:00–14:00 WGST in 2011 versus 14:00–18:00 in 2010) and note that the nighttime minimum was not as deep in 2010 (Figures 2c and 2d). The afternoon and evening enhancement of HNO<sub>3</sub> in the 2010 campaign is more pronounced in the hourly medians (not shown). Mixing ratios of NO<sub>y</sub> increased just 10–20 pptv from early morning minima to broad afternoon maxima in both seasons, 2011 had higher levels by 20–30 pptv throughout the average daily cycle (Figures 2a and 2b).

The nitrogen oxide species have been measured in a series of Summit campaigns extending back to 1998, but the only previous measurements of reactive bromine were made as part of the Greenland Summit Halogen-HO<sub>x</sub> Experiment (GSHOX) experiment in 2007 and 2008 (summarized in Thomas *et al.* [2012b]). Most of these prior campaigns emphasized the fast photochemistry linking NO<sub>x</sub> and HO<sub>x</sub> cycles above the snow and focused on model simulations around midday when this chemistry was most active. Comparing our observations during midday to those from GSHOX reveals that NO mean and median mixing ratios were quite low in 2010 (Table 2). Looking further back, the NO means and medians in 2008, 2010, and 2011 were all 1.5–2.5-fold lower than reports for midday during campaigns in 1999, 2000 [Yang *et al.*, 2002], 2003 [Chen *et al.*, 2007], and a



**Table 2.** Mean (Median) Midday (10:00–15:00 WGST) Gas Phase Mixing Ratios (pptv) During Recent Campaigns at Summit

	2011	2010	2008 <sup>a</sup>	2007 <sup>a</sup>
Species	5/24 to 6/26	5/17 to 6/22	5/13 to 6/13	6/10 to 7/8
NO	9.8 (8.1)	7.5 (4.6)	11.4 (8.6)	17.2 (12.8)
NO <sub>2</sub> <sup>-b</sup>	11.2 (10.6)	32.5 (30.9)	5.8 (4.7)	7.3 (6.5)
HNO <sub>3</sub>	15.5 (8.3)	11.7 (11.0)	11.5 (5.5)	15.9 (12.9)
BrO	0.5 (0.4)	3.0 (2.9)	2.0 (1.5)	2.0 (1.8)
Soluble Br <sup>-c</sup>	– <sup>d</sup> (– <sup>d</sup> )	0.5 (0.3)	0.3 (0.3)	0.7 (0.6)

<sup>a</sup>From Liao et al. [2011a] and Dibb et al. [2010].

<sup>b</sup>This is strictly soluble nitrite (NO<sub>2</sub><sup>-</sup>) as sampled and quantified by the MC/IC system.

<sup>c</sup>See Liao et al. [2012] for discussion of soluble bromide.

<sup>d</sup>During the 2011 season bromide was only above detection limits in 211 out of 1406 half-hour mist chamber samples, making summary statistics highly uncertain.

springtime campaign in 2004 [Grannas et al., 2007]. On the other hand, midday soluble NO<sub>2</sub><sup>-</sup> in 2010 was more than fourfold higher than during either GSHOX campaign (Table 2). The mean and median soluble NO<sub>2</sub><sup>-</sup> mixing ratios reported in 2008, however, were the lowest out of nine campaigns, with the 1999, 2000, 2003, and 2004 results all in the 7–13 pptv range like 2007, and in 1998 the midday mean (median) was 42.7 (42.1) pptv [Grannas et al., 2007]. Midday HNO<sub>3</sub> during our recent campaign varied between the two years, but was within the same range

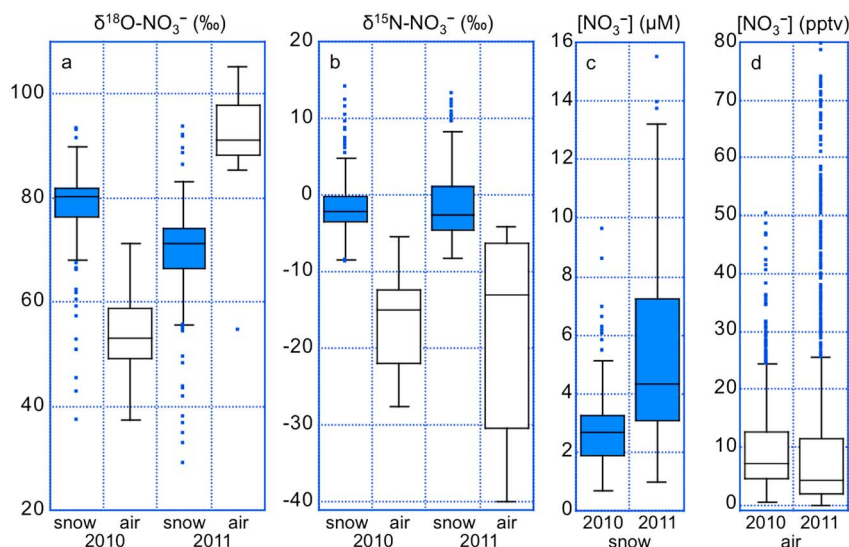
reported for GSHOX (Table 2). During the 1999 and 1998 campaigns midday HNO<sub>3</sub> mean (median) mixing ratios were 16.9 (9.4) and 44.3 (9.4) pptv, respectively [Grannas et al., 2007].

### 3.2. Snow Nitrate Concentration

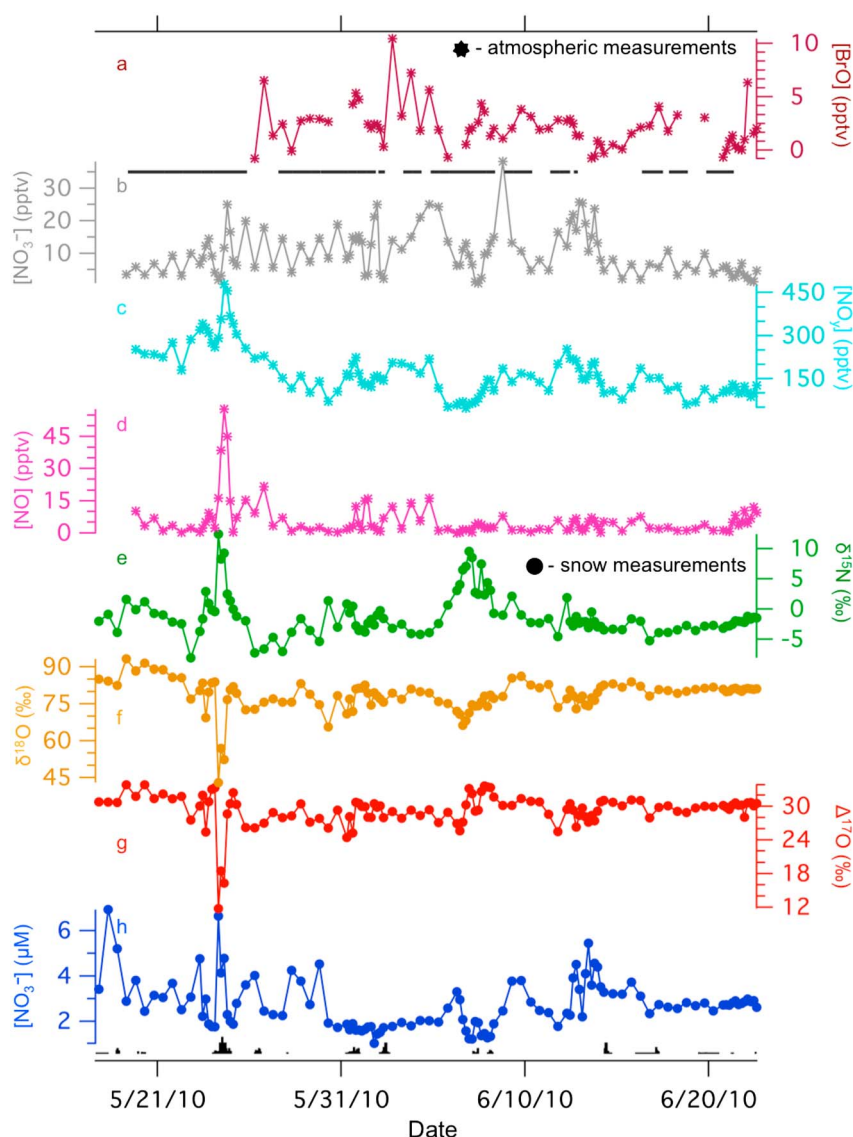
In the surface snow, the NO<sub>3</sub><sup>-</sup> varied significantly between the 2010 and 2011 seasons sampled at Summit (Figure 3). The [NO<sub>3</sub><sup>-</sup>] in the snow ranged from 0.7 to 9.7 μM in 2010, with a mean of 2.8 μM, and in 2011 it ranged from 1.0 to 15.5 μM with a mean of 5.16 μM. This range of [NO<sub>3</sub><sup>-</sup>] is similar to that observed in surface snow in May/June 2006 by Jarvis et al. [2009] (1 to 6 μM), Honrath et al. [2002] (1.2 to 8 μM), and Hastings et al. [2004] (0.8 to 5.9 μM).

### 3.3. Isotope Measurements

The snow δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> in 2010 ranges from 37.4 to 93.4‰ with a mean of 78.5‰; while the range is similar in 2011 (28.9 to 93.6‰), the mean of 70.1‰ is significantly different. In contrast, the δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> has similar mean values in the two years (–1.3 and –1.4‰) as well as similar ranges (2010: –8.7 to +14.1‰, 2011: –8.2 to +13.4‰). The snow NO<sub>3</sub><sup>-</sup> oxygen isotopic composition is similar in range to that observed by Jarvis et al. [2009], where they



**Figure 3.** Comparison of snow and air NO<sub>3</sub><sup>-</sup> isotopic composition and concentration. Snow (blue) and air (white) from 2010 and 2011 are compared for (a) δ<sup>18</sup>O and (b) δ<sup>15</sup>N. NO<sub>3</sub><sup>-</sup> concentration for both years is compared for (c) snow and (d) air. The lines in each diagram show the median value, the boxes show the upper and lower quartiles. The individual points are more than 1.5 times the interquartile distance. Note that the snow NO<sub>3</sub><sup>-</sup> concentration and δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> above, in addition to the Δ<sup>17</sup>O-NO<sub>3</sub><sup>-</sup> of the same samples, are reported in Fibiger et al. [2013].

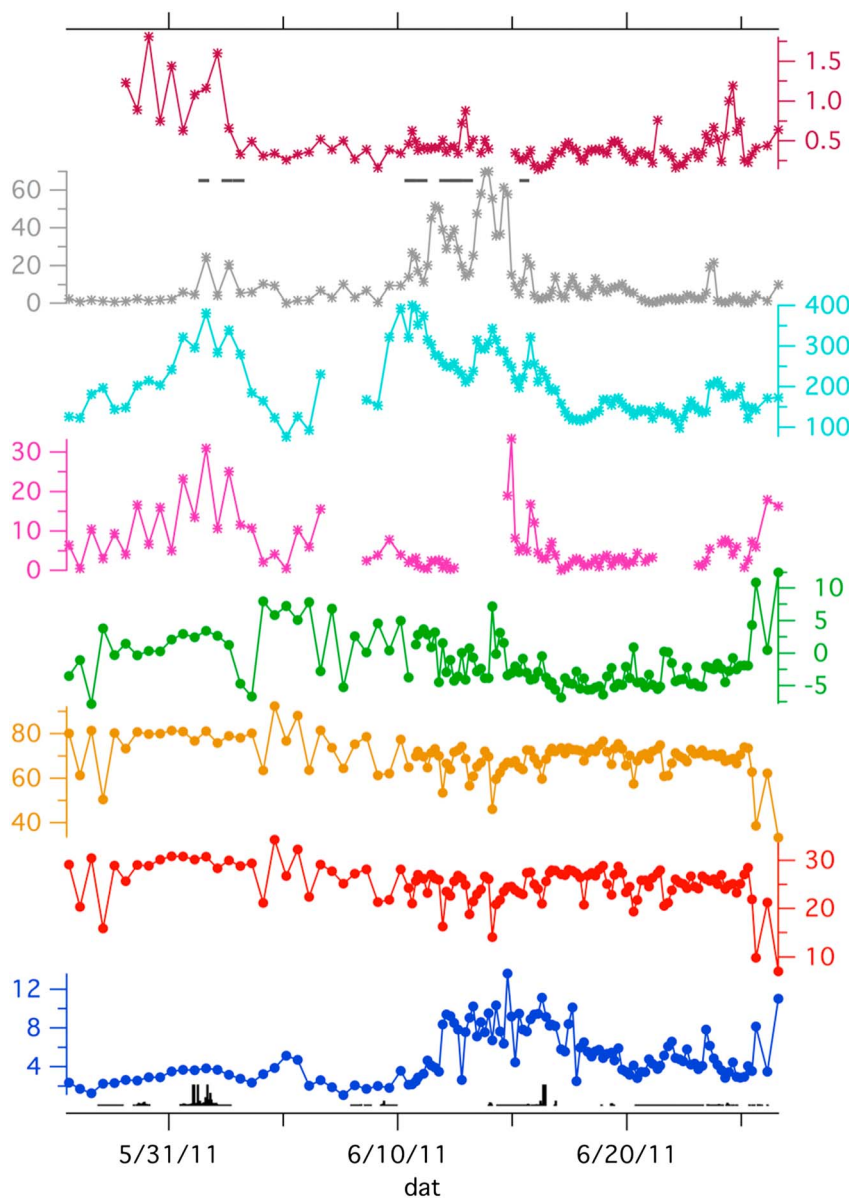


**Figure 4.** Time series of atmospheric (a–d) and snow (e–h) data for 2010. The atmospheric constituents are on top and marked with stars. The snow measurements are indicated with dots. The black bars at the bottom indicate times Summit Station was under north wind conditions (winds between  $342$  and  $72^\circ$  or less than  $2\text{ m s}^{-1}$ ). The bar length indicates the inverse of the wind speed (longer bars are slower speeds). The dark grey line between Figures 4a and 4b shows the time coverage of the atmospheric  $\text{NO}_3^-$  isotopic values summarized in Figure 3. All snow samples were collected at 4 or 12 h time intervals in triplicate. The  $[\text{NO}_3^-]$  is a mean of the triplicates, while the isotopic values are weighted by  $\text{NO}_3^-$  amount (see section 2.1). The atmospheric observations represent 5 h back averages from the time each snow sample was collected.

found  $\delta^{18}\text{O}\text{-NO}_3^-$  from 40 to 110‰. The  $\delta^{15}\text{N}\text{-NO}_3^-$  in snow observed by *Jarvis et al.* [2009], however, is lower ( $\delta^{15}\text{N}\text{-NO}_3^-$  from  $-15$  to  $+5$ ‰) than seen in 2010 or 2011.

In contrast to Jarvis, however, the  $\delta^{15}\text{N}\text{-NO}_3^-$  in the snow is significantly different from the  $\delta^{15}\text{N}\text{-HNO}_3$  in the air. Both seasons had similar  $\delta^{15}\text{N}\text{-HNO}_3$  in the atmospheric samples, whereas  $\delta^{18}\text{O}\text{-HNO}_3$  was very different between the years. (Figure 3). In 2010, the mean  $\delta^{15}\text{N}\text{-HNO}_3$  in the atmosphere was  $-16$ ‰, and in 2011,  $-13$ ‰. The  $\delta^{18}\text{O}\text{-HNO}_3$  was 54‰ in 2010 and 91‰ in 2011. The atmospheric isotopic data, however, represent only 60% of the 2010 field season and 10% of the field season in 2011. In 2010, these data are evenly distributed over the season, while in 2011, all atmospheric data fall during the period of high  $[\text{HNO}_3]$  from 10 June to 16 June (Figure 5).

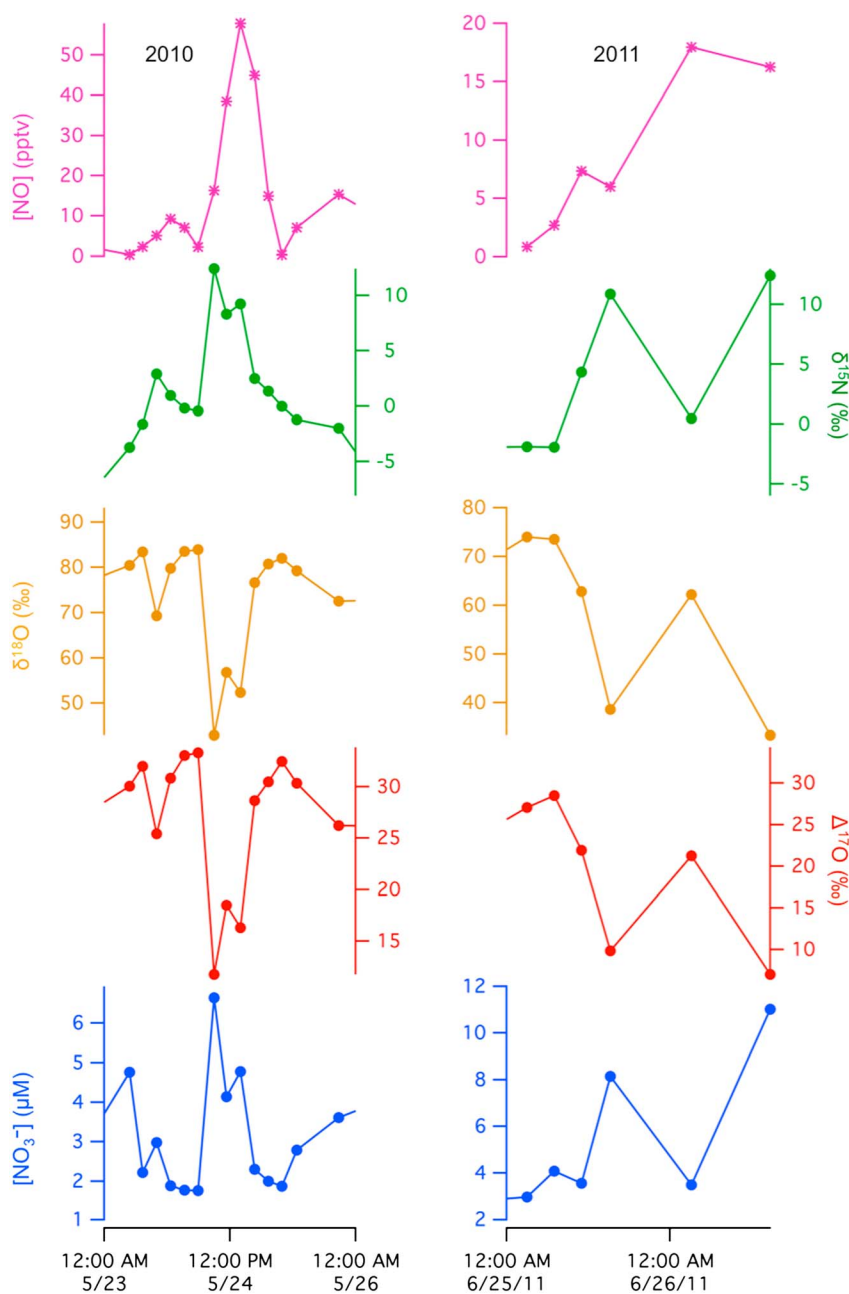
In both 2010 and 2011 there is a strong correlation between  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  of  $\text{NO}_3^-$  in the snow. As shown in *Fibiger et al.* [2013], the relationship of  $\Delta^{17}\text{O} = 0.46 \times \delta^{18}\text{O} - 6.9$  cannot be explained with any significant



**Figure 5.** The time series of atmospheric (a–d) and snow (e–h) data for 2011. (a–d) The atmospheric constituents are on top and marked with stars. (e–h) The snow measurements are indicated with dots. The black bars at the bottom indicate times Summit Station was under north wind conditions (winds between  $342$  and  $72^\circ$  or less than  $2 \text{ m s}^{-1}$ ). The bar length indicates the inverse of the wind speed (longer bars are slower speeds). The dark grey line between Figures 5a and 5b shows the time coverage of the  $\text{NO}_3^-$  atmospheric isotopic values summarized in Figure 3. All snow samples were collected at 4 or 12 h time intervals in triplicate. The  $[\text{NO}_3^-]$  is a mean of the triplicates, while the isotopic values are weighted by  $\text{NO}_3^-$  amount (see section 2.1). The atmospheric concentrations represent 5 h back averages from the time each snow sample was collected.

postdepositional processing of  $\text{NO}_3^-$  in the snow.  $\text{NO}_3^-$  loss or local recycling of  $\text{NO}_3^-$  would perturb the linear relationship. Instead, the  $\text{NO}_3^-$  in the snow is interpreted as a direct atmospheric signal of long-range transported  $\text{NO}_3^-$ . There is no relationship found between any of the isotopes of  $\text{NO}_3^-$  in the snow and any of the atmospheric constituents measured (Figures 4 and 5). Additionally, in the snow, there is no correlation between  $\delta^{15}\text{N}-\text{NO}_3^-$  and the oxygen isotopes of  $\text{NO}_3^-$ . In the atmospheric samples, there is no relationship between  $\delta^{15}\text{N}-\text{HNO}_3$  and  $\delta^{18}\text{O}-\text{HNO}_3$ .

In both seasons, there occur isotope deviations in the  $\text{NO}_3^-$  in the snow, in which the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  both decrease significantly while the  $\delta^{15}\text{N}$  increases (Figure 6). The most obvious event occurs in 2010 on 25 May. In 2011, these excursions bookend the observations: occurring in the first days of sampling (27 and 28 May) and

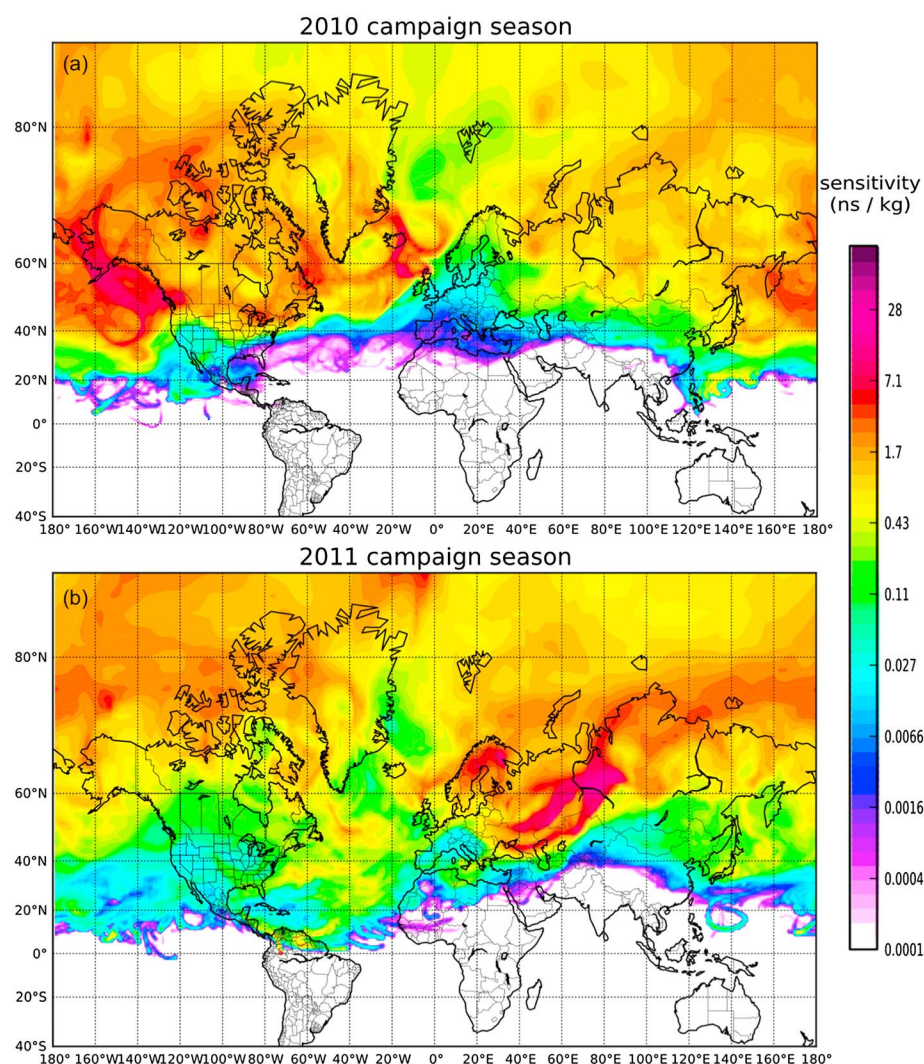


**Figure 6.** A more detailed look at the  $\text{NO}_3^-$  isotope and concentration behavior during an isotope deviation in 2010 and one in 2011. Gas phase data is a 5 h back average from the time point of snow collection. Both deviations occur at the same time as the highest NO concentration, indicating the presence of local anthropogenic pollution. Both excursions show a large decrease in  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ , with a simultaneous increase in  $\delta^{15}\text{N}$  and  $[\text{NO}_3^-]$ .

at the very end of the season (26 June). These events do not correspond with any significant changes in atmospheric  $\text{NO}_3^-$ , BrO, or  $\text{NO}_y$ . They all, however, happen concurrently with relatively high concentrations of NO, with the 2010 and 26 June 2011 events corresponding with season-high NO concentrations (Figure 6). These unusual NO events seem to be driven by pollution from the camp. Additionally, all the events occur during times when winds are bringing air over camp and then over the sampling area or when the wind speed is less than  $0.5 \text{ m s}^{-1}$ , indicating that  $\text{NO}_3^-$  pollution from camp may be impacting the samples collected during this time.

### 3.4. Transport Modeling

Atmospheric transport modeling for each season showed distinct transport patterns and source regions. In 2010 the bulk of air arriving at Summit had a source origin spanning a band from approximately  $40^\circ\text{N}$  to



**Figure 7.** Potential emission sensitivity for transport to Summit, Greenland for (a) 17 May to 22 June 2010 and (b) 24 May to 26 June 2011 as evaluated by the FLEXPART model. The plots show the air mass histories, or residence time, of air in the lowest 100 m of the atmosphere over the period of observation in each of the two seasons. They are normalized by the long-term (2000–2011) mean transport climatologies. It can be seen that during the 2011 season, air was predominately from Eurasia, distinct from the 2010 season which showed typical Westerly transport from North America.

50°N reaching from the western Pacific across central North America and into the North Atlantic. This air mass source region history would indicate preferential sampling of North American emissions, particularly with the strong source region of the North Atlantic, which is a primary transport pathway for emissions leaving the U.S. From a day-by-day analysis (not shown), there were two brief periods early in the season when air masses arrived from Europe, but aside from these episodes transport was distinctly from the west (Figure 7a). This transport pattern is typical of Summit in the early summer period during which sampling took place [Kahl *et al.*, 1997].

During 2011, a more unusual pattern emerges: the source region for air was heavily influenced by Eurasian emissions with a mix of Arctic and North Siberian air masses as well (Figure 7b). The latter two prove to be somewhat episodic but do have an influence on the overall mean climatology. In general, air masses arriving at Summit have a character of both North American and European sensitivity, depending highly on the movement of low-pressure systems south of Greenland as they track across the North Atlantic. Aside from a brief episode from 10 to 13 June (corresponding with the time of higher atmospheric [HNO<sub>3</sub>]), air sampled during the campaign was almost entirely from Europe. Leading up to and following the brief incursion of North American air during mid-June 2011, there was a period of stable regional flow from Europe. The latter half of

the campaign period experienced relatively fast transport, heavily dominated from Europe with 20 day potential emission sensitivity (PES) reaching into the center of the continent.

## 4. Discussion

### 4.1. Local Chemistry at Summit

Previously, it was thought that local recycling of  $\text{NO}_3^-$  might be important at Summit [Jarvis *et al.*, 2009; Kunasek *et al.*, 2008]. If this were true, however, there should be some connection between local gas phase concentrations and the isotopes of  $\text{NO}_3^-$  in the snow. If  $\text{HNO}_3$  were formed locally and deposited by cloud-to-ground scavenging of  $\text{NO}_3^-$  in the snow (Figure 1, arrows d and g), then BrO concentrations above 1 pptv should be influencing  $\text{NO}_3^-$  in the snow [Kunasek *et al.*, 2008; Morin *et al.*, 2007] via reactions (R6) through (R9). In particular, we expect that when BrO is high, the  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of nitrate would also be high, as BrO retains the anomalous isotopic signature of the  $\text{O}_3$  from which it is derived. The local signal, if important, should be present in the snow as the lifetimes of NO and  $\text{HNO}_3$  at Summit are only a few hours. This is evident in the atmospheric  $\text{HNO}_3$  and NO concentrations at Summit, as both approach zero at low solar zenith angle. This is evidence that there is some loss or recycling of  $\text{NO}_3^-$  from the snow in Greenland [Honrath *et al.*, 1999], but as noted above, as little as 2% of  $\text{NO}_3^-$  loss from the snow can account for observed  $\text{NO}_x$  concentrations above the snow [Thomas *et al.*, 2011]. This photolysis of  $\text{NO}_3^-$  to  $\text{NO}_x$  has a significant influence on local  $\text{NO}_x$  concentrations and the  $\delta^{15}\text{N}$ - $\text{HNO}_3$  in the atmosphere at Summit, but appears small enough to not have a significant effect on the residual  $\text{NO}_3^-$  in the snow. If photolysis of  $\text{NO}_3^-$  to  $\text{NO}_x$  followed by deposition of locally formed  $\text{HNO}_3$  (Figure 1, arrows a, c, and d) was having a strong influence on the  $\text{NO}_3^-$  in the snow, we would expect that snow  $\text{NO}_3^-$  concentrations would reflect NO and  $\text{HNO}_3$  atmospheric concentrations. There was, however, no connection found between the local concentrations of BrO, NO, or  $\text{NO}_y$  and any of the isotopes of  $\text{NO}_3^-$  or  $[\text{NO}_3^-]$ . This lack of relationship was found using 3, 5, and 12 h back averages of the gas phase data, from each time point that a snow sample was taken, accounting for potential variations in the lifetime of  $\text{NO}_x$  against deposition as  $\text{NO}_3^-$ . This indicates that local chemistry, either through recycling of  $\text{NO}_3^-$  or local conversion of  $\text{NO}_x$  to  $\text{NO}_3^-$ , is not influencing the  $\text{NO}_3^-$  preserved in the snow. This lack of relationship is true both across each season and over shorter timescales within. For instance, in 2010 the highest BrO concentrations were found between 3 and 6 June, but the  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  of  $\text{NO}_3^-$  in the snow were typical of that found during the field season. Additionally, during that time period the BrO concentration is highly variable and that variation is not reflected in the oxygen isotopic composition of  $\text{NO}_3^-$  found in the snow at Summit. Finally, as shown by Fibiger *et al.* [2013] photolytic processing of the  $\text{NO}_3^-$  does not have a significant influence on the oxygen isotopes of  $\text{NO}_3^-$  observed in the snow at Summit. Taken together, the above all suggest that the  $\text{NO}_3^-$  found in snow at Summit is not a result of local chemistry and scavenging. Rather, the snow  $\text{NO}_3^-$  at Summit represents a larger pool of atmospheric  $\text{NO}_3^-$  that is transported to Summit and deposited.

There are also significant differences in the  $\text{NO}_3^-$  in the snow and atmosphere at Summit in 2010 and 2011, which can be enlightening on their own. First, it is clear that BrO is not having an influence on  $\text{NO}_3^-$  formation at Summit. If it were, we would expect the  $\text{NO}_3^-$  collected in the MC to show a higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  when there is more BrO ( $\Delta^{17}\text{O} = 19.5$  to 35‰,  $\delta^{18}\text{O} = 60$  to 100‰, if it directly reflects  $\text{O}_3$ , both may be up to 1.5 times higher if only the terminal oxygen transfers in formation of BrO [Johnston and Thiemens, 1997; Vicars *et al.*, 2012]). In 2010, the  $\delta^{18}\text{O}$ - $\text{NO}_3^-$  in the atmosphere has an average value of 54‰, while in 2011 it is 91‰. In 2011 there is very little BrO in the atmosphere, with concentrations never exceeding 2.0 pptv, and during the time of high atmospheric  $\text{HNO}_3$  (when atmospheric isotope measurements were possible), it was around 0.5 pptv. In contrast, in 2010 BrO levels ranged between 0 and 10 pptv and were consistently over 2 pptv. This should have resulted in a high  $\delta^{18}\text{O}$ - $\text{HNO}_3$  in 2010 if local chemistry were playing an important role in  $\text{HNO}_3$  formation. The 2010 season, however, had a significantly lower average  $\delta^{18}\text{O}$ - $\text{HNO}_3$  (Figure 3a). Therefore, we conclude that BrO chemistry does not have a significant influence on the formation of local  $\text{HNO}_3$  at Summit.

It has been suggested in a number of studies that the relatively high accumulation rate at Summit may prevent postdepositional processing of  $\text{NO}_3^-$ ; however, it does not appear that snowfall rates, alone, dictate the lack of photolytic processing of snow  $\text{NO}_3^-$ . There was a significant difference in surface height change between the two study periods. In 2010, there was a 14 cm increase in height during the observation time, while during the 2011 study period there was only 3 cm of increased height (from [ftp://summitcamp.org/pub/data/GEOSummit/Bales\\_UCM/Bamboo%20Forest/](ftp://summitcamp.org/pub/data/GEOSummit/Bales_UCM/Bamboo%20Forest/)). The 2010 change would be sufficient to reduce the photolysis of  $\text{NO}_3^-$  by one

e-folding depth (8–10 cm at Summit [Galbavy *et al.*, 2007], but in 2011, the height change should leave all deposited snow in the most active portion of the photic zone. The two years, however, both show the same  $\delta^{18}\text{O}\text{-NO}_3^-$ ,  $\Delta^{17}\text{O}\text{-NO}_3^-$  relationship and the same set of contributing  $\text{NO}_3^-$  sources (section 4.2, below).

Local photochemistry is not a major driver of the variations in  $[\text{NO}_3^-]$  or isotopes of  $\text{NO}_3^-$  in the snow, but there are still differences in the measurements of snow at consecutive time points. The driving force for these variations seems to be, primarily, spatial heterogeneity in the snow. The triplicate samples represent only a few tens of centimeters spatial scale, which should be capturing only about 25% of the variation observed over tens of meters [Dibb and Jaffrezo, 1997].

#### 4.2. Snow and Atmosphere $\text{NO}_3^-$

The relationship between the isotopes and concentrations of  $\text{NO}_3^-$  in the snow and atmosphere at Summit provide further evidence of the lack of locally formed  $\text{HNO}_3$  influencing snow  $\text{NO}_3^-$ . The  $\delta^{18}\text{O}\text{-NO}_3^-$  in the snow is different from the  $\delta^{18}\text{O}\text{-HNO}_3$  in the air and is also significantly different between 2010 and 2011. In fact, in 2010 the  $\delta^{18}\text{O}\text{-HNO}_3$  in the air is significantly lower than  $\delta^{18}\text{O}\text{-NO}_3^-$  in the snow (Figure 3a). In 2011, the relationship is the opposite with  $\delta^{18}\text{O}$  higher in the gas phase than in the snow. In the snow, the  $[\text{NO}_3^-]$  is higher in 2011 than in 2010. In the air, there are higher concentrations achieved in 2011, but the mean concentrations are similar (Figures 3c and 3d). While the atmospheric isotopic samples in 2011 cover a small portion of the season, the snow isotopic values in that period are representative of the season on average.

These interannual differences in air-snow offsets provide further evidence that local gas phase  $\text{HNO}_3$  is not significantly influencing the  $\text{NO}_3^-$  in the snow. If the local gas-phase  $\text{HNO}_3$  were influencing the isotopes in the snow, we would expect the  $\delta^{18}\text{O}\text{-NO}_3^-$  in the snow in 2011 to be higher on average than in 2010, as the isotopes of gas phase  $\text{HNO}_3$  exhibit. The snow, however, shows the opposite pattern with higher  $\delta^{18}\text{O}\text{-NO}_3^-$  in 2010 than 2011.

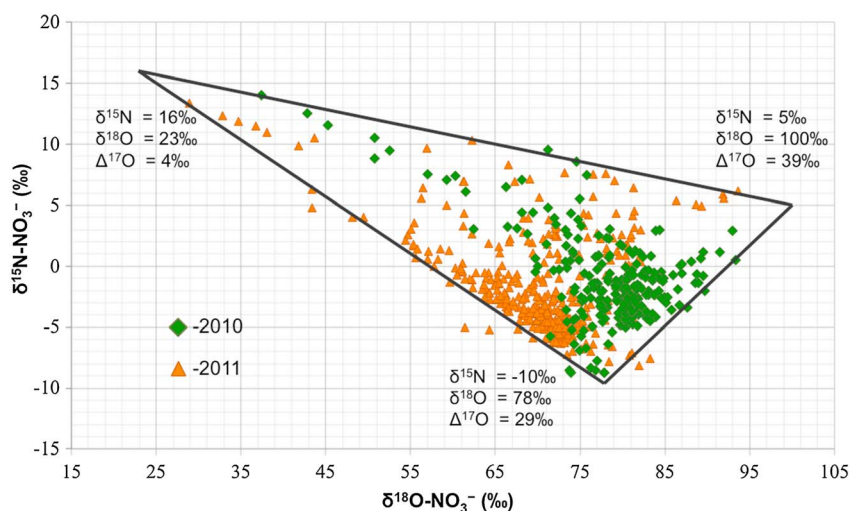
There is a consistent offset between  $\delta^{15}\text{N}\text{-NO}_3^-$  in the snow and air at Summit. In both 2010 and 2011 the difference in mean values is 10‰. Due to the resolution of the atmospheric  $\text{HNO}_3$  isotope measurements, it is not possible to look at the offset at any one point in time. The average offset, however, is markedly different than the only other similar observations [Jarvis *et al.*, 2009], where gas phase  $\text{HNO}_3$  and snow  $\text{NO}_3^-$  were found to have similar  $\delta^{15}\text{N}$  of approximately  $-4\text{‰}$ , similar also to the values found in the snow in 2010 and 2011. The  $\text{HNO}_3$  in the air, however, is distinctly different between the two studies, with mean  $\delta^{15}\text{N}\text{-HNO}_3$  in the air found to be  $-12.6\text{‰}$  in 2010 and  $-17.7\text{‰}$  in 2011. The offset in  $\delta^{15}\text{N}\text{-NO}_3^-$  in the atmosphere and snow could be consistent with photolysis of  $\text{NO}_3^-$  in the snow (Figure 1, arrow a), such that lower  $\delta^{15}\text{N}\text{-NO}_x$  leaves the snow to then form  $\text{HNO}_3$  locally (Figure 1, arrow c). Given the lack of relationship between the atmosphere and snow concentration and isotopes, however, this process must represent a very small portion of the  $\text{NO}_3^-$  in the snow.

#### 4.3. $\text{NO}_3^-$ Sources to Summit

There is no correlation between  $\delta^{15}\text{N}$  and the oxygen isotopes of snow  $\text{NO}_3^-$ , but plotting them against each other reveals an interesting relationship (Figure 8). The surface snow samples from both 2010 and 2011 fall within a triangle, indicating a mix of three isotopically distinct forms of  $\text{NO}_3^-$  at Summit. The three sources contribute  $\text{NO}_3^-$  of distinct isotopic composition:  $\delta^{15}\text{N} = 16\text{‰}$ ,  $\Delta^{17}\text{O} = 4\text{‰}$ , and  $\delta^{18}\text{O} = 23\text{‰}$ ;  $\delta^{15}\text{N} = 5\text{‰}$ ,  $\Delta^{17}\text{O} = 39\text{‰}$ , and  $\delta^{18}\text{O} = 100\text{‰}$ ;  $\delta^{15}\text{N} = -10\text{‰}$ ,  $\Delta^{17}\text{O} = 29\text{‰}$ , and  $\delta^{18}\text{O} = 78\text{‰}$ . The relative contribution of each  $\text{NO}_3^-$  source to any snow sample can be quantified by the relative distances from each of the three end-members. While source attribution is difficult due to limited and conflicted studies of  $\delta^{15}\text{N}$  of  $\text{NO}_x$  from various sources [Fibiger *et al.*, 2014; Walters *et al.*, 2015], we can use the complete isotopic composition of the  $\text{NO}_3^-$ , the interannual variations and transport analysis to develop ideas on potential  $\text{NO}_3^-$  sources.

##### 4.3.1. Seasonal Transport to Summit

The 2010 and 2011 seasons at Summit show distinct transport patterns and air source regions. In 2010, the air is primarily derived from North America, while in 2011 it is primarily from Eurasia, with particular influence from the Ob River, an area of heavy industrial activity. It is notable that in 2011 there is a short period of time (10–13 June) when the air is transported from North America and the atmospheric  $[\text{HNO}_3]$  during this time is more reflective of “typical” Summit conditions. The very different transport patterns over the two years are reflected in differing isotopic compositions of  $\text{NO}_3^-$  in the snow across the two years. The interannual isotopic variation may reflect differing isotopic compositions derived from different regional sources, potential fractionations during transport to Summit, or a combination of the two.



**Figure 8.** The relationship between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  in surface snow in both 2010 and 2011. The green diamonds represent 2010 snow samples and the orange triangles represent snow samples from 2011. The samples all fall within a triangle with vertices at  $\delta^{18}\text{O} = 23\text{‰}$ ,  $\delta^{15}\text{N} = 16\text{‰}$ ;  $\delta^{18}\text{O} = 78\text{‰}$ ,  $\delta^{15}\text{N} = -10\text{‰}$ ;  $\delta^{18}\text{O} = 100\text{‰}$ ,  $\delta^{15}\text{N} = 5\text{‰}$ , ( $\Delta^{17}\text{O} = 4$ , 29, and 39‰, respectively, not shown) each representing a distinct  $\text{NO}_3^-$  source to Summit.

#### 4.3.2. Midlatitude $\text{NO}_x$

The  $\text{NO}_3^-$  source end-member with  $\delta^{15}\text{N}$  of  $-10\text{‰}$ ,  $\Delta^{17}\text{O}$  of  $29\text{‰}$ , and  $\delta^{18}\text{O}$  of  $78\text{‰}$  is consistent with observations of midlatitude  $\text{NO}_3^-$ . In a typical spring, the vast majority (85%) of air transported to Summit is sourced from North America, based on 10 day, 700 hPa back trajectories [Kahl *et al.*, 1997]. This air should be influenced by a mixture of anthropogenic and natural  $\text{NO}_x$  sources that can be found in northern North America. Biomass burning should be a prominent natural  $\text{NO}_x$  source in the region [Emmons *et al.*, 2015] and  $\text{NO}_x$  from biomass burning has a  $\delta^{15}\text{N}$  ranging from  $-7$  to  $+12\text{‰}$ , but the value should depend on the biomass type [Fibiger and Hastings, 2013]. Over northern North America significant emissions are derived from burning of boreal forests that are nitrogen limited and contain a negative  $\delta^{15}\text{N}$  [Amundson *et al.*, 2003], so the  $\text{NO}_x$  emitted should be closer to the low end of the above range. In addition, vehicle emissions should be important and have been measured with a  $\delta^{15}\text{N}$  from  $-19$  to  $+10\text{‰}$  [Ammann *et al.*, 1999; Heaton, 1990; Moore, 1977; Walters *et al.*, 2015]. While the entire range ( $-19$  to  $+9.8\text{‰}$ ) has been measured in North America [Walters *et al.*, 2015], it is not clear if those direct tailpipe emissions are reflective of the  $\text{NO}_x$  undergoing long-range transport. The only roadside measurements done by Ammann *et al.* [1999] were collected passively and the study was not conducted in North America, so it is unknown how applicable that range ( $-4.7$  to  $+10\text{‰}$ ) may be. Coal burning for electricity generation should also be a prominent anthropogenic  $\text{NO}_x$  source in North America and the reported  $\delta^{15}\text{N}-\text{NO}_x$  ranges from 9 to  $26\text{‰}$  [Felix *et al.*, 2012; Heaton, 1990; Snape *et al.*, 2003]. Microbial processing of N in soils can also release  $\text{NO}_x$  and the  $\delta^{15}\text{N}$  measured ranged from  $-47$  to  $-28\text{‰}$  during progressive release of  $\text{NO}_x$  over several days in the laboratory [Li and Wang, 2008]. Lightning produces  $\text{NO}_x$  with a  $\delta^{15}\text{N}$  from  $-0.5$  to  $+1.4\text{‰}$  [Hoering, 1957]. Given this large range in  $\text{NO}_x$  emission source isotopic values, many combinations could result in a  $\delta^{15}\text{N}-\text{NO}_x$  close to the noted  $-10\text{‰}$ . Ideally, better-constrained source values could contribute to a more quantitative understanding of the mix of sources [Fibiger *et al.*, 2014].

Still, the 2011 season has a heavy influence of Eurasian emissions, compared with both 2010 and typical climatology for Summit (Figure 7). Thus, the end-member with  $\delta^{15}\text{N}$  of  $-10\text{‰}$ ,  $\delta^{18}\text{O}$  of  $78\text{‰}$ , and  $\Delta^{17}\text{O}$  of  $29\text{‰}$ , which is more important in 2011 than 2010 (Figure 8), may be indicative that the isotopes are sensitive to source region rather than directly representing the  $\delta^{15}\text{N}$  of a  $\text{NO}_x$  emission source.

The oxygen isotopes fall well within the expected range for tropospheric  $\text{O}_3$ , with bulk  $\delta^{18}\text{O}$  ranging from 973 to  $120\text{‰}$  (terminal  $\delta^{18}\text{O}$  103 to  $137\text{‰}$ , calculated from Michalski and Bhattacharya [2009]) and  $\Delta^{17}\text{O}$  from 20 to  $27\text{‰}$  (terminal  $\Delta^{17}\text{O}$  30 to  $40\text{‰}$ ) [Johnston and Thiemens, 1997].

#### 4.3.3. High $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ End-Member

The high  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  end-member has  $\text{NO}_3^-$  with  $\delta^{15}\text{N}$  of  $5\text{‰}$ ,  $\Delta^{17}\text{O}$  of  $39\text{‰}$ , and  $\delta^{18}\text{O}$  of  $100\text{‰}$  (Figure 8). The very high  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  are reflective of a significant influence of  $\text{O}_3$  on the formation of  $\text{NO}_3^-$ . Based on



the ranges observed and the expectation that terminal oxygen isotopes of  $O_3$  are involved in  $NO_3^-$  formation, either tropospheric or stratospheric  $O_3$  could be implicated. The values observed in the snow, however, are very high compared to prior observations of  $\delta^{18}O$  or  $\Delta^{17}O$  of  $NO_3^-$  in the midlatitudes or other regions of the Arctic. Outside of Greenland, Arctic observations are limited, but at Alert, Nunavut, Canada, the maximum  $\Delta^{17}O$ - $NO_3^-$  observed has been 35‰ and the maximum  $\delta^{18}O$  92‰ [Morin *et al.*, 2007; Morin *et al.*, 2008]. In Svalbard, the maximum  $\delta^{18}O$ - $NO_3^-$  found was 81‰ [Vega *et al.*, 2015]. In the midlatitudes, the maximum observed  $\delta^{18}O$  and  $\Delta^{17}O$  of  $NO_3^-$  is even lower, with maximum  $\Delta^{17}O$  of 30‰ and  $\delta^{18}O$  of ~80‰ [Michalski *et al.*, 2012, and references therein]. This makes the observations of  $NO_3^-$  at Summit uniquely high in both  $\Delta^{17}O$  and  $\delta^{18}O$  for the Northern Hemisphere. So this either indicates unusual spring/summer chemistry involving only tropospheric  $O_3$  with no participation of other oxidants (OH,  $HO_2$ , or  $H_2O$ ), or the oxygen isotopes are derived from stratospheric  $O_3$ , with its higher  $\Delta^{17}O$  and  $\delta^{18}O$  and the possibility of involvement of other oxidants.

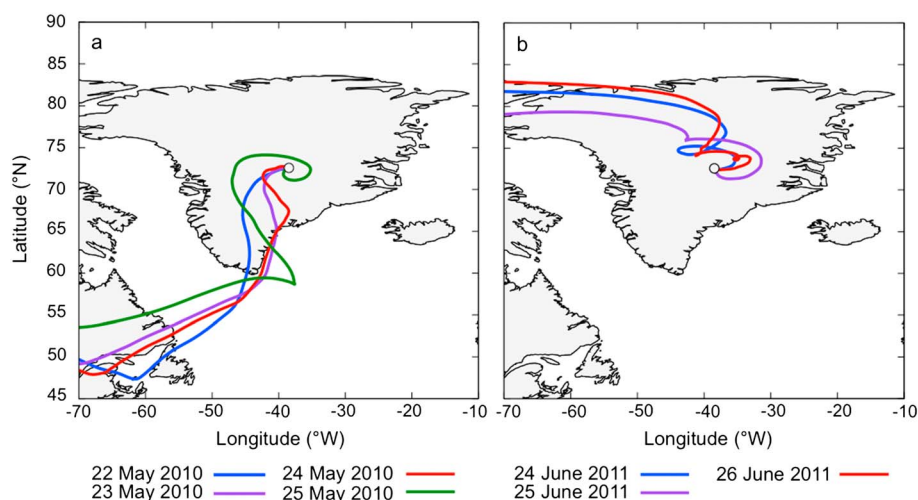
Stratospheric  $O_3$  is a large fraction of the  $O_3$  throughout the Northern Hemisphere in the springtime, and seeing that influence on  $NO_3^-$  production in the troposphere is not unexpected [Wespes *et al.*, 2012]. The  $\delta^{15}N$  of stratospheric  $NO_3^-$  has never been measured directly, but has been calculated as  $19 \pm 3\%$  from the fractionation of the reaction  $N_2O + O(^1D)$ , the primary source of NO in the stratosphere [Savarino *et al.*, 2007] and higher than the observed end-member value of 5‰ (Figure 8). Therefore, the complete isotopic composition raises three possibilities: (1) the  $NO_3^-$  is formed in the stratosphere and the 5‰ reflects additional fractionations in NO oxidation to  $NO_3^-$  and deposition, (2) the  $NO_3^-$  reflects tropospheric sources and chemistry but reflects only  $O_3$  oxidation (which has not been previously reported), or (3) the  $NO_3^-$  is forming in the troposphere but shows oxidation by stratospheric  $O_3$  that has been mixed down. In any case, the high  $\delta^{18}O$ ,  $\Delta^{17}O$  end-member shows greater influence in 2010 than 2011 (Figure 8), so that input must be different between the field seasons.

In case 1, where the  $NO_3^-$  is stratospheric in origin, there are significant differences in stratospheric chemistry between the two years. This observation fits with the Arctic ozone hole observed in 2011 [Manney *et al.*, 2011], as less stratospheric  $O_3$  should result in lower production of  $NO_3^-$  by the stratospheric  $O_3$  pathway. In case 2, tropospheric sources of  $NO_x$  must be oxidized by  $O_3$  alone, which has not been observed in the middle or high latitudes of the Northern Hemisphere. Observed midlatitude  $\Delta^{17}O$ - and  $\delta^{18}O$ - $NO_3^-$  show seasonal cycles, with highest values in winter (when  $O_3$  chemistry should dominate) and lowest in the summer [Michalski *et al.*, 2012]. The springtime shows intermediate values. There are no observations of spring or summer  $NO_3^-$ , which has only been influenced by tropospheric  $O_3$  and no other oxidants. While local BrO is not affecting the  $NO_3^-$  found in the snow, regional halogen chemistry could influence the  $NO_3^-$  observed [Morin *et al.*, 2007]. If only terminal atoms of  $O_3$  are involved in  $NO_x$  oxidation, BrO should have the same isotopic influence on  $NO_3^-$  as  $O_3$ .

The third case, where the  $NO_3^-$  may be formed in the troposphere but shows influence of stratospheric  $O_3$ , would explain the unusually high  $\delta^{18}O$  and  $\Delta^{17}O$  while still allowing for more typical spring and summer chemistry. As explained by Vickers and Savarino [2014], however, photolysis of  $O_3$ , whether stratospheric or tropospheric in origin, should cause the isotopic composition to reset to local conditions. In Grenoble, France, Vickers and Savarino [2014] estimated this would take approximately 30 min during daylight hours. If the stratospheric  $O_3$  were mixed into the troposphere near dusk or at night, however, this time should be extended up to several hours, particularly, if the  $NO_x$  concentrations are low. While at Summit in May and June, sunlight is constant, this is not true in the midlatitude source regions that influence Summit (Figure 7). In particular, over the remote marine boundary layer,  $NO_x$  concentrations should be very low, so the nighttime lifetime of  $O_3$  against photolysis could allow for significant oxidation of  $NO_x$  to  $NO_3^-$ . There is no diurnal cycle in the frequency of stratospheric intrusion events [Lefohn *et al.*, 2011]. To see the influence of stratospheric  $O_3$ , both the stratosphere-troposphere exchange and the  $NO_x$  oxidation would have to occur near dusk, so this scenario would likely only happen under limited circumstances.

#### 4.3.4. Local Anthropogenic Influence

The final  $NO_3^-$  source, with  $\delta^{15}N$  of 16‰ and  $\delta^{18}O$  of 23‰, has the most surprising isotopic composition. The  $\delta^{18}O$ , which corresponds with a  $\Delta^{17}O$  of 0‰, is extraordinarily low to find in atmospherically derived  $NO_3^-$  [Kendall *et al.*, 2007; Michalski *et al.*, 2012]. This point of the triangle is filled out by  $NO_3^-$  snow samples from the isotope deviations (Figure 6), implying that this  $NO_3^-$  is formed locally at Summit. The  $\delta^{15}N$  and  $\delta^{18}O$  are comparable to measurements by Proemse *et al.* [2012] of  $NO_3^-$  produced in stacks of a bitumen processing facility in the tar sands of Alberta, Canada. The  $PM_{2.5}$  stack emissions had a mean  $\delta^{15}N$  of  $16.1\% \pm 1.2\%$  and



**Figure 9.** The pathway of air arriving at the measurement site on the days preceding, during, and after the anomalous isotope events on (a) 24 May 2010 and (b) 25 June 2011. The trajectories are the centroid locations of the particle clusters from a FLEXPART backward simulation for the period. While transport patterns are very different between the two events, they are very similar in the days surrounding each event.

$\delta^{18}\text{O}$  of  $17.6\text{‰} \pm 1.8\text{‰}$ . Furthermore, snow samples from several shallow snow pits were sampled in an area that is typically downwind of the camp generator. All the samples showed relatively high  $\delta^{15}\text{N}$  and low  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$ . The  $\delta^{15}\text{N}$  in these snowpits ranged from 2 to 10‰, with six out of eight samples  $\delta^{15}\text{N} > 6\text{‰}$ . The  $\delta^{18}\text{O}$  ranged from 42 to 66‰ and  $\Delta^{17}\text{O}$  from 10 to 21‰. The  $\delta^{18}\text{O}-\text{NO}_3^-$  of 23‰ is consistent with the isotopic composition of molecular oxygen, 23.9‰ [Barkan and Luz, 2005], which should be the primary oxidant available in the dark generator stack.

Great efforts are made to minimize the local anthropogenic influence at Summit. It is, however, inevitable that some fossil fuel combustion occurs, particularly a diesel generator (burning Jet A-1 fuel) and several diesel-powered heavy equipment pieces used to groom the skiway and dig snow for water. Heavy equipment usage is minimized during conditions when air is carried over the station before the clean air sector (i.e., north winds) or when wind speed is minimal ( $< 2 \text{ m s}^{-1}$ ). The generator, however, is always operating. Prior work has shown that elemental carbon (EC) from camp activities causes concentrations 1.8–2.4 times higher at 1 km than 10 or 20 km from camp [Hagler et al., 2008]. While this study focused on EC as a tracer of local emissions, it raises the expectation of similar results for other atmospheric species.

Perhaps the most confounding thing about these anomalous isotope events is the fast recovery to prior isotope values (Figure 6). This seems best explained by a physical loss of nitrate from the snow, as any chemical loss should result in fractionation that would not return to prior values in both  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$ . The largest events (14 May in 2010 and 26 June in 2011) occur during very low wind speeds ( $< 2 \text{ m s}^{-1}$ ). The recovery in 2010 occurs after winds increase to over  $2 \text{ m s}^{-1}$ , perhaps resulting in scouring of the top layer of snow. This could remove the snow contaminated with the locally produced  $\text{NO}_3^-$  and return the  $\text{NO}_3^-$  isotopes to their prior values.

Event-based modeling of atmospheric transport to Summit also indicates that this  $\text{NO}_3^-$  is likely derived from local pollution (i.e., the generator). During the largest 2010 event, occurring on 24 May, the air is derived from south of Summit, over maritime Canada (Figure 9a). The two days prior and day following, at the same times as the event (7:00–15:00 WGD, 9:00–17:00 UTC), show very similar origins to air during the event, despite the snow samples having very different isotopic composition. In 2011, during the largest event on 26 June, the air is all derived from north of Summit (Figure 9b). Again, the two days prior to the event (the event occurred on the last day of sampling, so the following day was omitted in 2011) show very similar air mass origins to the day of the event. The difference in air mass source between the two events that show similar isotopic composition indicates that the  $\text{NO}_3^-$  with the anomalous isotopic composition is not being transported in. Additionally, the similarity over the days before and after indicates that it is not a change in air source that is driving the radical change in  $\text{NO}_3^-$  isotopic composition. All of this indicates that the  $\text{NO}_3^-$  during the events is being driven by locally formed  $\text{NO}_3^-$ , but that  $\text{NO}_3^-$  is still not reflecting local atmospheric conditions

measured. This implies that the  $\text{NO}_3^-$  is formed under different chemical conditions than that observed over the clean air sector, likely in the generator stack.

Only while the winds are carrying station pollution directly over the sampling area is local anthropogenic  $\text{NO}_3^-$  the dominant form of  $\text{NO}_3^-$  in the snow, but it is nearly always present in the snow. With the sampling area approximately 1 km away from the main station, it is expected that there is a strong influence of local pollution during certain wind events, but the degree of influence at other times is notable, as the only samples with no influence of local pollution fall directly on the mixing line between the two higher  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  end-members (Figure 8). In both seasons, but particularly in 2011,  $\text{NO}_3^-$  sourced from local combustion is an important portion of the  $\text{NO}_3^-$  pool in the snow.

#### 4.3.5. Role of OH in Nitrate Production

It is surprising that  $\text{NO}_3^-$  derived from midlatitude  $\text{NO}_x$  shows no influence of OH on the oxygen isotopic composition. As shown in *Fibiger et al.* [2013], the closest fit of the linear relationship between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  at Summit is a mixing line between  $\text{O}_2$  ( $\Delta^{17}\text{O} = 0\text{‰}$ ,  $\delta^{18}\text{O} = 23.9\text{‰}$  [Barkan and Luz, 2005]) and  $\text{O}_3$  ( $\Delta^{17}\text{O} = 39\text{‰}$  and  $\delta^{18}\text{O} = 100\text{‰}$ ). This is consistent with the end-members shown in the three-point mixing in Figure 8, with the “local anthropogenic influence” point corresponding to  $\text{O}_2$  isotopic composition and the stratospherically influenced point fitting with the maximum  $\text{O}_3$   $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  presented (39‰ and 100‰, respectively). The “mid-latitude” point on the three-point mixing falls along that line because it is also  $\text{O}_3$ , but with lower  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ .

In contrast, OH is expected to have a  $\delta^{18}\text{O}$  between  $-10\text{‰}$  and  $-50\text{‰}$  (depending on fractionation from the isotopic composition of  $\text{H}_2\text{O}$  [Michalski et al., 2012]) and  $\Delta^{17}\text{O}$  of 0‰. These values are very far from the observed  $\delta^{18}\text{O}$  of 18 to 23‰ for the lowest  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  end-member. One possible explanation is that OH is not involved in the formation of  $\text{NO}_3^-$  in the summertime, though that seems unlikely, based on numerous laboratory, field, and modeling studies [e.g., Donahue et al., 1997; Logan et al., 1981; Monks, 2005; Stroud et al., 2003]. Another possibility is that the assumed isotopic composition of OH is incorrect. The current predicted ranges assume either complete equilibrium with water, fractionation from  $\text{H}_2\text{O}$  or some (minimal) influence of  $\text{O}_3$  as a source of OH [Morin et al., 2007; Michalski et al., 2012]. Either that assumption is wrong or the calculated fractionation of that equilibrium [Michalski et al., 2012] is incorrect. Further isotopic work will be needed to determine which of these scenarios is correct.

## 5. Conclusions

In two May–June field seasons at Summit, Greenland,  $\text{NO}_3^-$  in the surface snow reflects long-range transported  $\text{NO}_3^-$  deposited primarily via snowfall. There is no relationship between the isotopes of  $\text{NO}_3^-$  observed in the snow and the overlying atmospheric composition. Additionally, the interannual variability in the oxygen isotopes of  $\text{NO}_3^-$  in the snow shows the opposite relationship to the oxygen isotopes of  $\text{NO}_3^-$  in the air. There are three, isotopically distinct, sources of  $\text{NO}_3^-$  to Summit. The first, with  $\delta^{15}\text{N} = 5\text{‰}$ ,  $\Delta^{17}\text{O} = 39\text{‰}$ , and  $\delta^{18}\text{O} = 100\text{‰}$  may indicate influence by stratospheric  $\text{O}_3$ , or may be primarily derived from North American emission sources combined with halogen-mediated oxidation chemistry or  $\text{O}_3$  oxidation alone. Another source, with  $\delta^{15}\text{N} = -10\text{‰}$ ,  $\Delta^{17}\text{O} = 29\text{‰}$ , and  $\delta^{18}\text{O} = 78\text{‰}$ , is most appropriately described as  $\text{NO}_3^-$  derived from midlatitude  $\text{NO}_x$ , possibly indicative of Eurasian emissions and tropospheric ozone. The final source,  $\delta^{15}\text{N} = 16\text{‰}$ ,  $\Delta^{17}\text{O} = 4\text{‰}$ , and  $\delta^{18}\text{O} = 23\text{‰}$ , is most fittingly characterized as local anthropogenic pollution from Summit Station activities. Based on the observations, local halogen chemistry cannot explain the underestimation of  $\Delta^{17}\text{O}$  in models [Alexander et al., 2009; Kunasek et al., 2008]. Overall, the observations indicate that local photolytic processing of  $\text{NO}_3^-$  is not important to  $\text{NO}_3^-$  preserved in the snow, as no direct relationships exist between gas phase chemistry, including local atmospheric  $\text{NO}_3^-$  and the snow  $\text{NO}_3^-$  concentrations and isotopic composition.

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