# The impact of bromine chemistry on the isotopic composition of nitrate at Summit (2009-2013, NSF OPP 0909734)

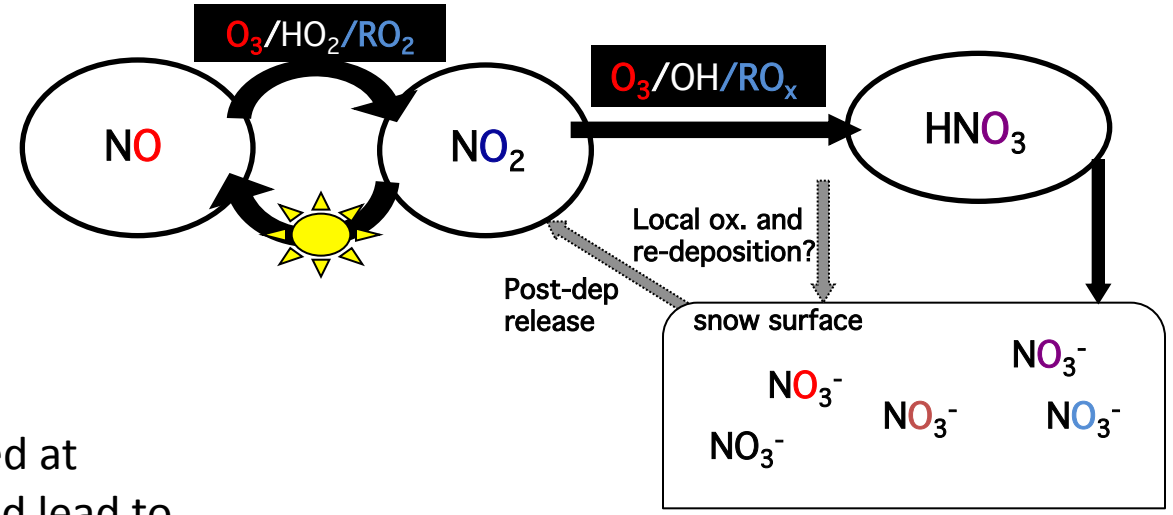
Dorothy Fibiger (Brown)
M.G. Hastings (Brown), J.E. Dibb (UNH), L.G. Huey (GA Tech)

The oxygen isotopic composition ($\Delta^{17}O$) varies among oxidants in the atmosphere
($\Delta^{17}O \approx \Delta^{17}O - 0.52 \times \delta^{18}O$)

The $\Delta^{17}O$ of $NO_3^-$ in the atmosphere is determined by the oxidant(s) that make $NO_2$ and the additional oxidation of $NO_2$ to $HNO_3$

pptv levels of BrO have been detected at Summit; BrO reaction with $NO_2$ would lead to higher $\Delta^{17}O$ in $HNO_3$ b/c of Br-$O_3$ interaction:

$Br + O_3 \rightarrow BrO + O_2$
$BrO + NO \rightarrow NO_2 + Br$
$BrO + NO_2 \rightarrow BrONO_2$
$BrONO_2 + H_2O \rightarrow HNO_3 + HOBr$




Tropospheric Oxidant Isotopes:

$\Delta^{17}O$ of $O_3$ (f(T,P)) = 35 ± 3‰

$\Delta^{17}O$ of $HO_2$ = 0.9 - 1.8‰ (~ 0 ‰)

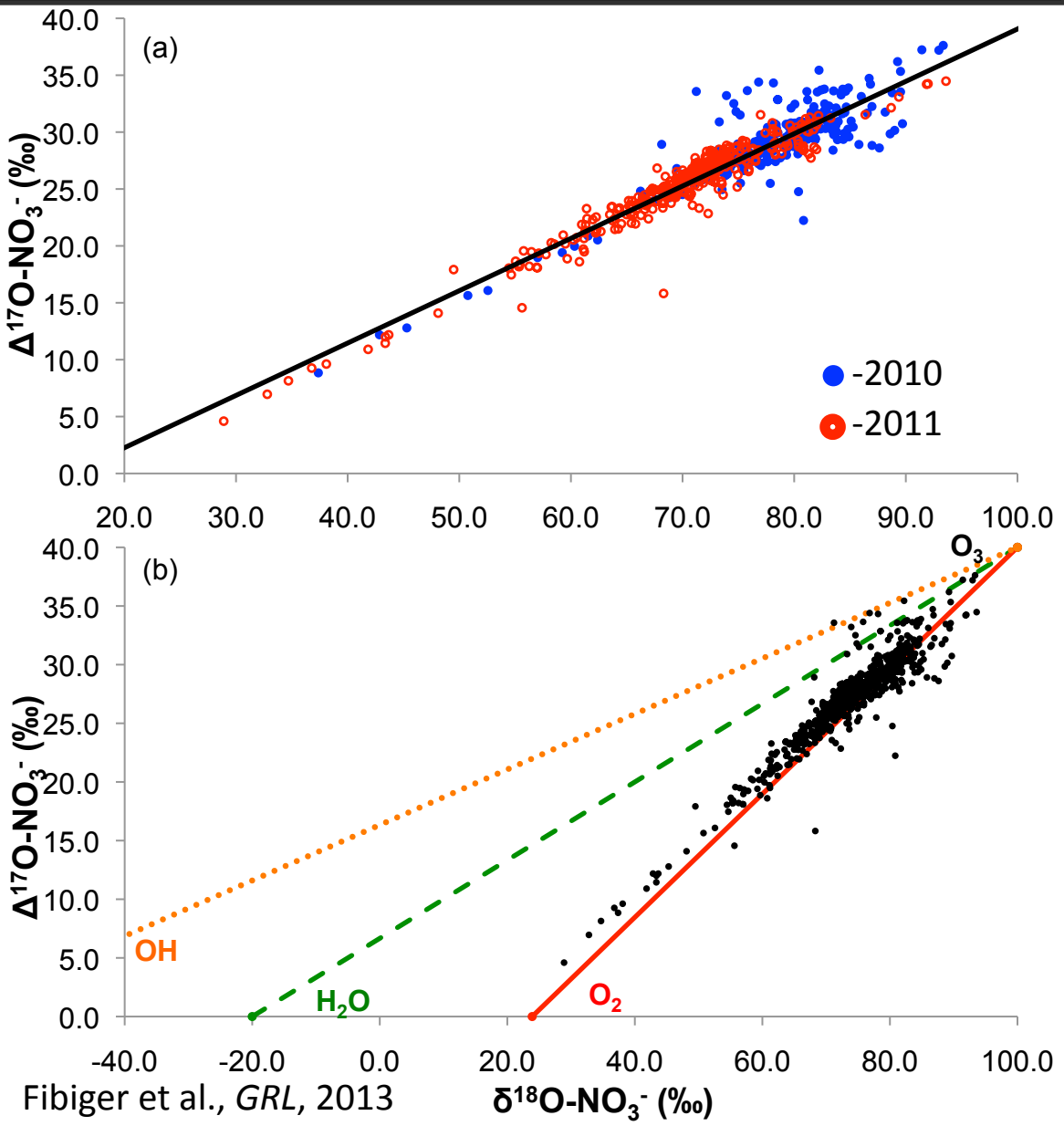
$\Delta^{17}O$ of $H_2O/OH/RO_x/O_2$ = 0‰

# Surface snow $NO_3^-$ oxygen mixing

- May-June 2010 and 2011
- Surface snow (top 1-3 cm) sampled in triplicate every 4-12 hours
- No relationship between [$NO_3^-$] and any isotopic values
- No relationship between any atmospheric concentrations and isotopes

Strong, linear relationship between $\delta^{18}O$ and $\Delta^{17}O$ indicates lack of post-depositional processing- any significant processing would perturb relationship

Relationship reflects direct atmospheric $NO_3^-$ deposition, with mixing between two oxidants, $O_2$ and $O_3$




Fibiger et al., *GRL*, 2013

# Surface snow $NO_3^-$ source mixing

Relationship between $\delta^{18}O$ and $\delta^{15}N$ shows a mixing of three isotopically distinct $NO_3^-$ sources

1 Stratosphere- $\delta^{18}O$ and $\delta^{15}N$ typical of strat. $NO_3^-$

2 Mid-latitude $NO_x$- typical $\delta^{18}O$ and $\delta^{15}N$ found in precipitation

3 Camp pollution- driven by isotope "events" that occur during N. winds, matches iso. values of industrial activities, high $\delta^{15}N$ and low $\delta^{18}O$ found in snow that is typically downwind of generator