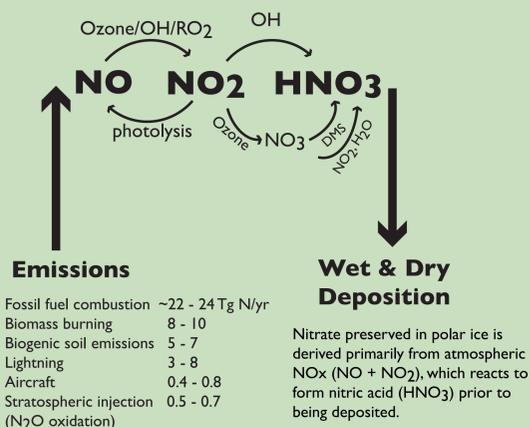
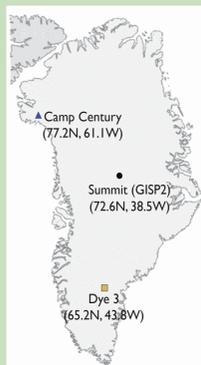


Evaluating source and chemistry changes based on the isotopes of atmospheric nitrate in ice cores

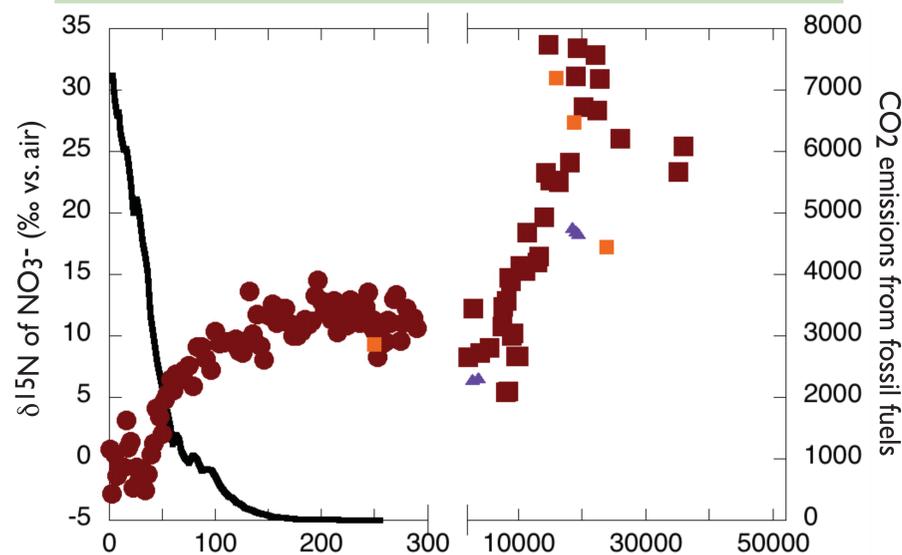
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Where does nitrate in ice cores come from?

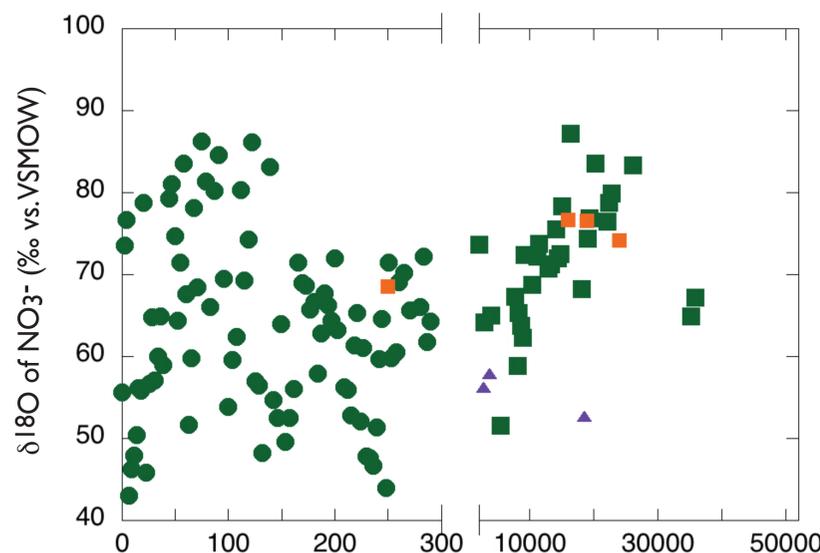


How do we interpret the significant changes in the isotopic composition of nitrate over time?



$\delta^{15}\text{N}$ of nitrate from a 100-meter ice core drilled at Summit, Greenland in 2006 (red circles) spanning ~1718 to 2006. $\delta^{15}\text{N}$ of nitrate is also shown for ice samples from GISP2 (red squares), Camp Century (purple triangles) and Dye 3 (orange squares). For the last 350 years, each datapoint represents ~2-3 years of accumulation; for ~2000-18,000 yrs BP each point represents ~1 year of accumulation; and for samples >18,000 yrs BP datapoints represent ~3 years of accumulation. Also shown is an estimate of global CO_2 emissions from fossil fuels since 1750 (solid black line; millions of metric tons C) (3).

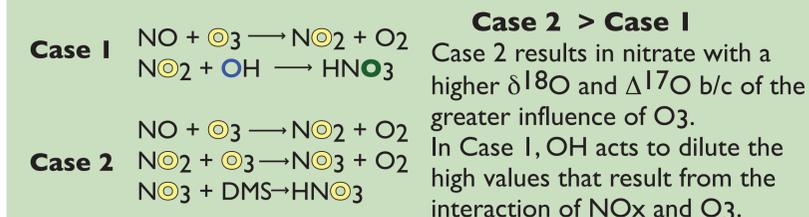
The $\delta^{18}\text{O}$ of nitrate from the 100-meter core is shown as green circles; for GISP2, green squares; Camp Century, purple triangles; and Dye 3, orange squares. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate were determined using the denitrifier method (4,5), which utilizes denitrifying bacteria to convert nitrate samples to nitrous oxide gas that is then measured on an IRMS. The standard error of the mean based on repeated measurements of the sample is $\pm 1\%$ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.



The isotopes of atmospheric nitrate can tell us about oxidizing capacity of the atmosphere

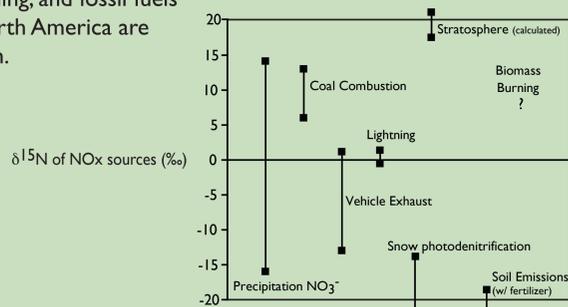
The **oxygen isotopic composition** ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$) of nitrate, in contrast to $\delta^{15}\text{N}$, reflects the isotopic composition of the **oxidation processes that produce nitrate from NOx** in the atmosphere (6). The oxygen isotopic composition of ozone (O_3) is unique, with a very high $\delta^{18}\text{O}$ (~90-120‰ vs VSMOW) and a mass independent relationship between $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ such that $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O} \sim 35\%$ in the troposphere (7). Other oxidant sources such as H_2O (e.g. OH) or O_2 (e.g. RO_2) have much lower isotopic compositions ($\delta^{18}\text{O} \sim -40$ to $+30\%$, $\Delta^{17}\text{O} = 0\%$). The influence of ozone on the production of nitrate in the atmosphere drives the high $\delta^{18}\text{O}$ values observed in HNO_3 and particulate NO_3^- .

In contrast to the $\delta^{15}\text{N}$ record, the $\delta^{18}\text{O}$ of nitrate shows no consistent trend in the recent past nor on glacial/interglacial timescales. The $\delta^{18}\text{O}$ of nitrate record is also much more variable. On average the glacial period tends to exhibit higher $\delta^{18}\text{O}$ values (73.5‰, n=9) than the pre-industrial Holocene (60.9‰, n=57), although the glacial portion of the record is measured at much lower resolution than more recent ice.



The isotopes of atmospheric nitrate can tell us about NOx source changes

The **nitrogen isotopic composition** ($\delta^{15}\text{N}$) of nitrate in Greenland ice over the last 300 years shows a clear negative trend that is consistent with the introduction of nitrogen oxides (NO_x) from fossil fuels combustion starting ~1850 AD (1). While the industrial period shows a change of ~12‰, the $\delta^{15}\text{N}$ of nitrate changes by ~20‰ from a mean pre-industrial Holocene value of 9.7‰ to a mean glacial value of 28.4‰ (2). The more recent ice core record clearly indicates an influence of NO_x emission sources, therefore suggesting that the glacial-interglacial change in $\delta^{15}\text{N}$ may be a record of significant variations in the contribution of **NOx sources**, such as lightning, biomass burning and/or biogenic soil emissions. The isotopic signatures of NO_x emitted from 'natural' soils, biomass burning, and fossil fuels combustion in North America are currently unknown.



Definition of delta (δ):

$$\delta^{15}\text{N} = \left[\frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{std}}} - 1 \right] * 1000 \quad (\text{per mil } (\text{‰}) \text{ units vs atm } \text{N}_2)$$

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{std}}} - 1 \right] * 1000 \quad (\text{per mil } (\text{‰}) \text{ units vs VSMOW})$$

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What about physical and chemical processing?

Post-depositional processing of nitrate in surface snow likely effects the isotopic composition of nitrate that is ultimately preserved in ice. However, this effect should be more pronounced at low accumulation sites, and physical processing of nitrate in surface snow cannot explain the trend observed in recent ice nor the seasonality of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in snow at Summit, Greenland (8,9).

Recent work (10) in Antarctica at a very low accumulation site (Dome C) suggests that the isotopologues of nitrate can be used to trace the photolysis of nitrate in surface snow and that this is dependent upon the amount of O_3 in the Antarctic atmosphere.

During the glacial period HNO_3 was primarily scavenged by alkaline dust particles that contained Ca^{2+} , compared to more recent time periods when HNO_3 is primarily taken up by water/ice surfaces. We expect the unidirectional uptake of nitrate onto dust to produce $\text{Ca}(\text{NO}_3)_2$ to result in a kinetic isotope effect that would result in isotopically lighter particulate NO_3^- than the gas-phase HNO_3 , which is the opposite of the change observed between interglacial and glacial ice (2).

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