The nitrogen isotopic composition (δ15N) of nitrate in Greenland ice over the last 300 years shows a clear negative trend that is consistent with the isotopic composition of nitrate over time? 

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

The δ15N of nitrate from a 100-meter ice core drilled at Summit, Greenland in 2006 (red circles) spanning ~1718 to 2006. The δ15N 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 ~2000-1600 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 CO2 emissions from fossil fuels since 1750 (solid black line; millions of metric tons C) (4).

The δ18O 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 δ15N of nitrate from a 100-meter ice core drilled at Summit, Greenland in 2006 and δ18O 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 ±1‰ for δ15N and δ18O.

In contrast to the δ15N record, the δ18O of nitrate shows no consistent trend in the recent past nor on glacial/interglacial timescales. The δ18O of nitrate record is also much more variable. On average the glacial period tends to exhibit higher δ18O values (73.5‰, n=9) than the pre-industrial Holocene (69.9‰, n=57), although the glacial portion of the record is measured at much lower resolution than more recent ice.

Case 1 > Case 2 Case 2 results in nitrate with a higher δ18O and δ17O b/c of the greater influence of O3. In Case 1, OH acts to dilute the high values that result from the interaction of NOx and O3.

What about physical and chemical processing? 

Post-depositional processing of nitrate in surface snow likely affects 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 δ15N and δ18O 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 O3 in the Antarctic atmosphere.

During the glacial period HNO3 was primarily scavenged by alkaline dust particles that contained Ca2+, compared to more recent time periods when HNO3 is primarily taken up by water/ice surfaces. We expect the unidirectional uptake of nitrate onto undivided surfaces of HNO3 on the atmosphere drives the high δ18O values observed in HNO3 and particulate NO3-

References