



South Pole nitrate: isotopic insights into origins and post-depositional processes

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Nitrate in ice cores may contain clues to understanding oxidation capacity, solar activity, and ozone depletion. However, the origin and variation of nitrate in ice cores remains uncertain due to post-depositional reprocessing, which remains the largest obstacle to overcome before using nitrate as a paleo-proxy. The presence of mass independent oxygen in atmospheric nitrate reveals oxidative information about its formation. In addition, recent laboratory studies present isotopic constraints on the role of photochemistry. This study implements a suite of oxygen isotope measurements from South Pole air and snow to show the ability of mass independent studies to provide new insight into the origins of nitrate and the role of post-depositional photochemistry.

Oxygen isotope variations in nitrate ($\Delta^{17}\text{O-NO}_3$) from a 6 meter snow pit vary between 21.3 permil and 33.1 permil with an average of 25.7 permil and display a three-year trend that correlates with surface ozone levels between 1977 and 1990. The breakdown in the $\Delta^{17}\text{O-NO}_3$ -surface ozone connection post-1990 could be attributed in part to aerosol loading during the Mt. Pinatubo event and to an altered photochemical regime during extreme ozone hole events of the 1990s. However, no clear connection exists between the isotope variations and UV flux or total column ozone. In order to understand snow pit variations, we also conducted simultaneous surface snow and aerosol isotope measurements of nitrate. A seasonal variation was found in both with large enrichments during winter ($\Delta^{17}\text{O-NO}_3 = 32 - 38$ permil and lower values ($\Delta^{17}\text{O-NO}_3 = 23 - 29$ permil during summer. We suggest that the large winter enrichments are direct evidence of stratospheric denitrification as the primary source of nitrogen to the plateau while the summer values are a result of photochemical reprocessing within the snowpack and the overlying boundary layer. Comparison between the isotopic composition of aerosol nitrate and Mcmurdo Dry Valley soil ni-

trate (28.9 - 32.7 permil and average surface snow (29.3 permil) indicates that 50% of the original nitrate from the stratosphere is affected by post-depositional photochemistry.