

Interpreting the Isotopic Composition of Sulfate and Nitrate from an Antarctic Ice Core Using GEOS-Chem

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Overview

Atmospheric oxidant concentrations impact the lifetime of reduced trace gases (CH₄, SO₂, NO_x, VOCs) with implications for climate forcing and air pollutants, but there is little direct evidence of paleo-oxidant concentrations. The oxygen isotopic composition ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) of sulfate and nitrate reflect their formation pathways in the atmosphere, and measurements from ice cores in conjunction with atmospheric chemistry modeling have the potential to constrain past oxidant concentrations.

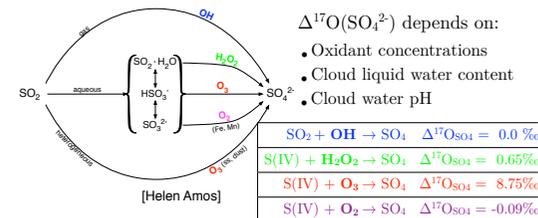
Objective

The first continuous record of $\Delta^{17}\text{O}$ of both sulfate and nitrate has been constructed for the past 2300 years from the WAIS-Divide ice core. Features of the record include:

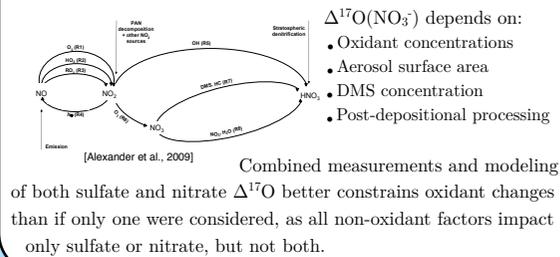
- Increase in $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ and decrease in $\Delta^{17}\text{O}(\text{NO}_3^-)$ between ~1700 CE and present.
- Coincident decreases in $\Delta^{17}\text{O}(\text{SO}_4^{2-})$, $\Delta^{17}\text{O}(\text{NO}_3^-)$, and $\delta^{15}\text{N}$ at ~350 C.E. that exceeds 200 BCE - 1600 CE variability.

The goal of this work is to interpret this new ice core record using sulfate and nitrate box models constrained by GEOS-Chem.

$\Delta^{17}\text{O}$ of Sulfate



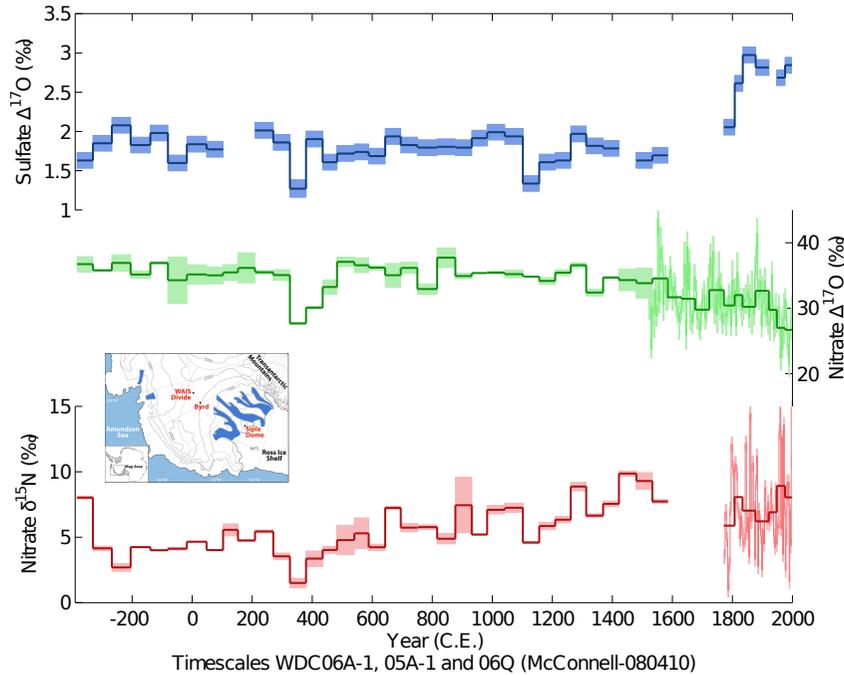
$\Delta^{17}\text{O}$ of Nitrate



Acknowledgments

This work was supported by NSF grants NSF-OPP 0538049 and NSF-AGS 0704169. The authors appreciate the support of the WAIS Divide Science Coordination Office at the Desert Research Institute of Reno Nevada for the collection and distribution of the WAIS Divide ice core and related tasks (Kendrick Taylor, NSF Grants 0440817 and 0230396). The National Science Foundation Office of Polar Programs also funds the Ice Drilling Program Office and Ice Drilling Design and Operations group for coring activities; Raytheon Polar Services for logistics support in Antarctica; and the 109th New York Air National Guard for airlift in Antarctica. The National Ice Core Laboratory, which curated the core and performed core processing, is jointly funded by the National Science Foundation and the United States Geological Survey.

WAIS-Divide Ice Core Sulfate $\Delta^{17}\text{O}$, Nitrate $\Delta^{17}\text{O}$, and Nitrate $\delta^{15}\text{N}$



Preliminary Interpretation

- **Long-term:** Changing post-depositional processing (due to changing snow accumulation) can explain the trend in nitrate $\Delta^{17}\text{O}$ and $\delta^{15}\text{N}$.
- **1700 CE-Present:** Ice core indicators of non-oxidant factors (LWC, pH, aerosol surface area, DMS, post-depositional processing) do not show changes consistent with the changes in the $\Delta^{17}\text{O}$ of sulfate and nitrate. **The changes in the $\Delta^{17}\text{O}$ of sulfate and nitrate may reflect changes in the oxidant concentrations in the different source regions of sulfate and nitrate.**

Nitrate

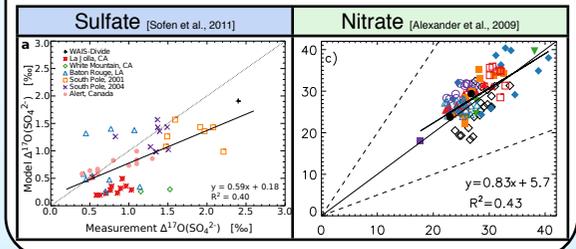
- Sources: Biomass burning, lightning, soil NO_x emissions; stratospheric denitrification.
- Nitrate forms in NO_x emission regions.
- Increased NO_x increases OH locally.
- Decreases $\Delta^{17}\text{O}(\text{NO}_3^-)$.
- Alternative: Increased PAN transport imparts local summer $\Delta^{17}\text{O}(\text{NO}_3^-)$.

Sulfate

- Source: Southern Ocean DMS emissions.
- Sulfate forms in remote ocean areas.
- OH in remote regions has decreased since the preindustrial due to increased CH₄ concentrations.
- Increases $\Delta^{17}\text{O}(\text{SO}_4^{2-})$.

Model-Measurement Comparison

Comparison of GEOS-Chem to measurements of present-day sulfate and nitrate $\Delta^{17}\text{O}$ from aerosol, cloud, and firn samples.



Preindustrial Oxidants and $\Delta^{17}\text{O}(\text{SO}_4^{2-})$

GEOS-Chem modeled changes in annual mean tropospheric (a) O₃, (b) OH, and (c) H₂O₂ concentrations and the corresponding change in (d) $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ between the preindustrial and present. In the Arctic, increased metal-catalyzed oxidation and decreased cloud pH render $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ insensitive to changing oxidant concentrations. In the Antarctic, $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ is sensitive to oxidants, but there is little change in $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ because the relative changes in oxidant concentrations have opposing isotopic effects [Sofen et al., 2011]. GEOS-Chem does not reproduce the observed ~1‰ 1600 CE-present increase in $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ using standard preindustrial assumptions.

Box Model Monte Carlo Simulations

Box models of sulfate and nitrate formation will be run with a range of conditions representative of present-day and preindustrial conditions based on GEOS-Chem simulations or relevant literature. $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ are calculated and compared to the ice core record to assess which sets of conditions (e.g. oxidants, LWC, pH, DMS, aerosol surface area) are consistent with the observations.



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