

Sensitivity of the Oxygen Isotopes of Ice Core Sulfate to Glacial-Interglacial Changes in Climate and Chemistry

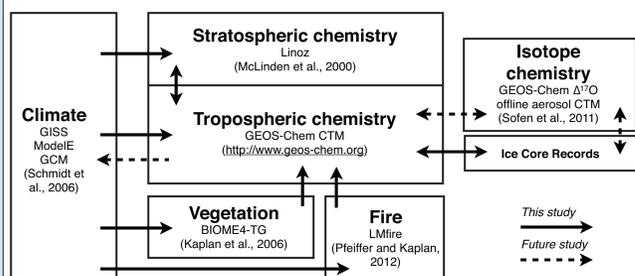
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Background

Attempts to reconcile glacial-interglacial changes in CH₄ from ice cores with terrestrial biosphere models and the possible role of changes in the CH₄ lifetime have inspired broader investigations into how atmospheric chemistry has changed on the glacial-interglacial timescale. The large-scale climate changes between ice ages and warm periods drive changes in trace gas emissions, temperature, water vapor, lightning, and atmospheric dynamics, all of which influence atmospheric oxidant abundances, but their combined impact is highly uncertain. Ice core measurements of the three oxygen isotopes of sulfate have been suggested as a potential proxy for paleo-oxidant abundances. The oxygen isotopic composition of sulfate reflects its formation pathways in the atmosphere. Ice core observations from Vostok, Antarctica are consistent with greater sulfate formation by OH during the last glacial period than during the preindustrial Holocene (PIH). Here, we use the ICECAP (ICE age Chemistry And Proxies) version of the GEOS-Chem model to investigate the sensitivity of Δ¹⁷O to changes in climate and chemistry on the glacial-interglacial timescale.

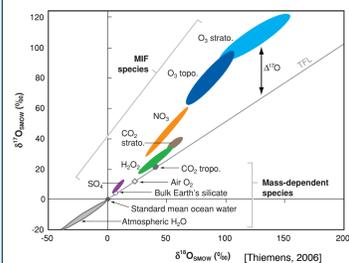
ICECAP Model Framework



See Lee Murray's talk.

Sulfate Chemistry and Isotopes

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$$

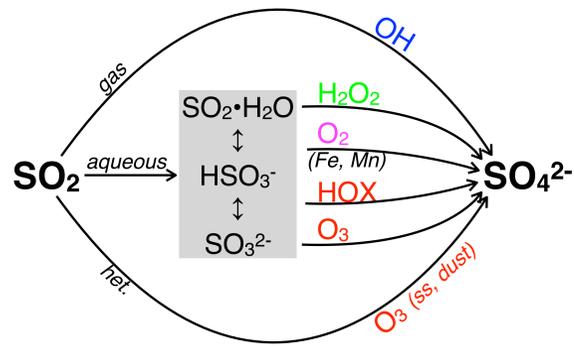


Isotopic Assumptions

- Δ¹⁷O(O₃) = 25-35 ‰
- Δ¹⁷O(O₂) = -0.34 ‰
- Δ¹⁷O(OH) = 0 ‰
- Δ¹⁷O(H₂O₂) = 1.3 ‰
- Δ¹⁷O(HOX) = 0 ‰

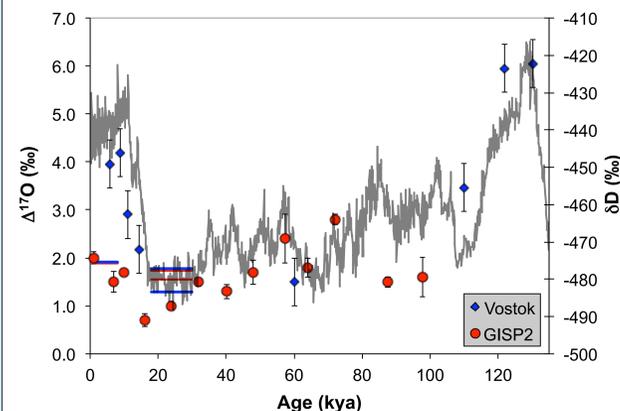
Δ¹⁷O(SO₄²⁻) depends on:

- (1) Oxidant concentrations
- (2) Cloud liquid water content
- (3) Cloud water pH



Ice Core Time Series

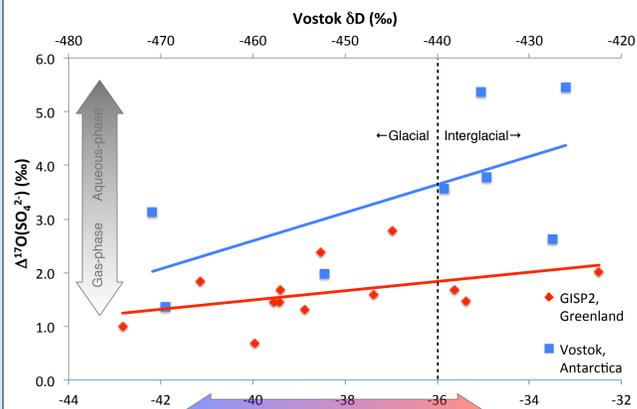
Ice core measurements of sulfate Δ¹⁷O from Vostok, Antarctica and GISP2, Greenland are plotted with Vostok deuterium, a temperature proxy over a complete glacial-interglacial cycle.



See Lei Geng's poster on Greenland Δ¹⁷O measurements.

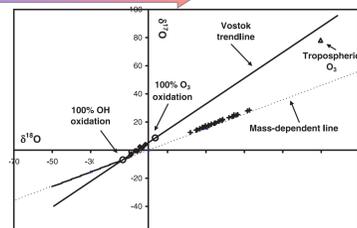
Ice Core Δ¹⁷O Variations Related to Chemistry and Climate

Greenland and Antarctic Δ¹⁷O is qualitatively consistent with higher OH in sulfate formation regions during the cold periods of the last glacial period than during the warm periods of the preindustrial Holocene.



Observations fall on a mixing line between O₃ and OH [Alexander et al., 2002]:

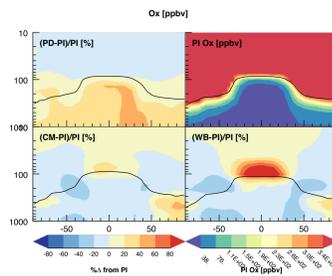
Is this due to changes in [OH] and [O₃] or clouds (gas- vs. aqueous-phase sulfate formation)?



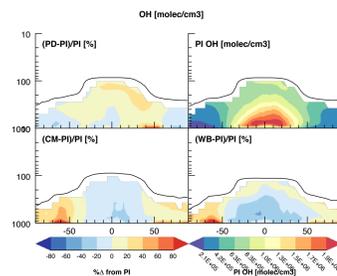
ICECAP Modeled Oxidants

Δ¹⁷O is sensitive to the relative changes in oxidant abundances, so we look at the fractional changes in O₃, OH, and H₂O₂. There is an overall reduction in the net oxidative capacity in both Last Glacial Maximum (LGM) scenarios (CLIMAP and Webb et al., 1997) relative to the PIH.

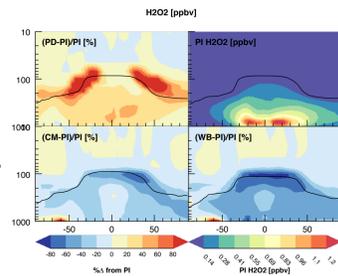
Ozone decreases in polar regions in the LGM, although there is more stratospheric O₃ and STE.



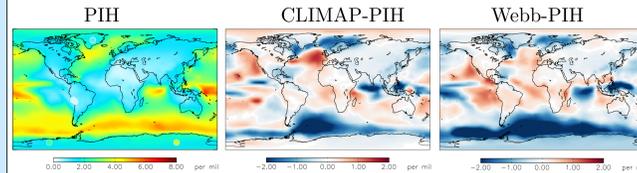
Hydroxyl radical is enhanced in polar regions in the LGM due to reduced loss to CH₄ and increased UV photolysis of O₃ (especially over ice).



Hydrogen peroxide is generally reduced during the LGM, except over the wintertime Southern Hemisphere extratropics. H₂O₂ is highly sensitive to biomass burning emissions.

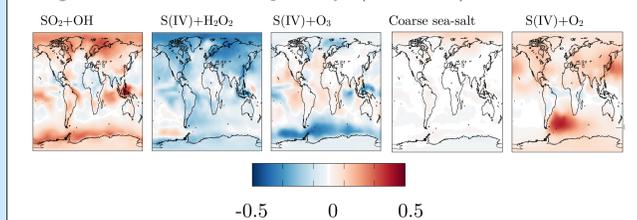


ICECAP Modeled Sulfate Δ¹⁷O



Modeled Δ¹⁷O is qualitatively consistent with ice core observations, but underestimates the preindustrial Holocene (PIH) observations at Vostok, Antarctica.

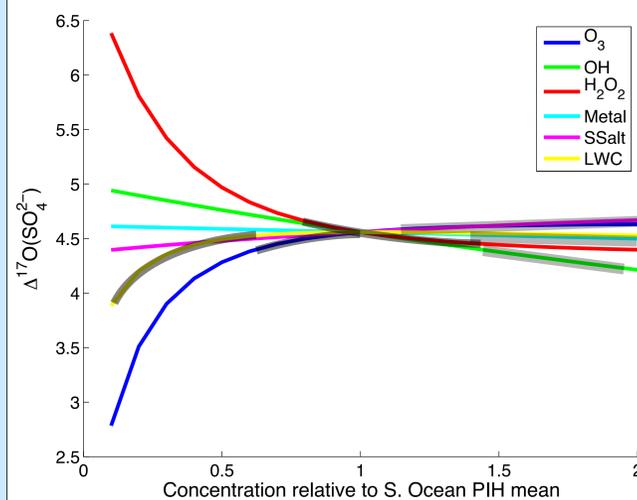
Changes in sulfate formation pathways (Webb-PIH):



Lower LGM Δ¹⁷O at Vostok can be explained by a combination of more sulfate formation by OH, less by H₂O₂ and O₃, and more metal-catalyzed sulfate formation due to more dust during the LGM.

Δ¹⁷O Sensitivity Analysis

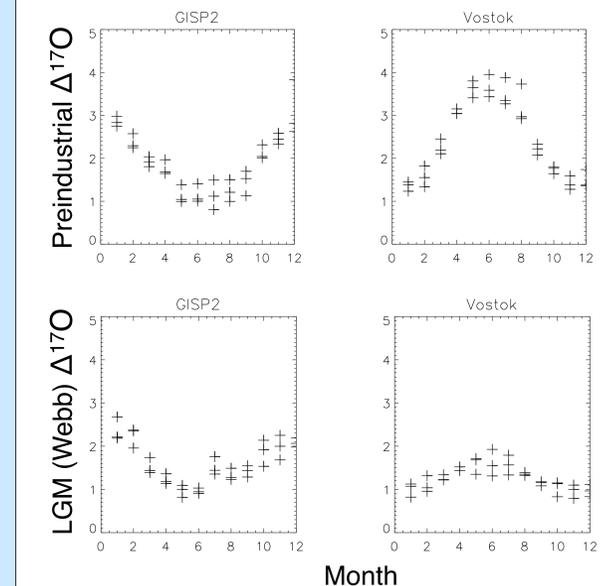
To simplify the assessment of the sensitivity of Antarctic ice core Δ¹⁷O to chemistry, we utilize a box model of sulfate formation and Δ¹⁷O using the sulfate chemistry scheme and Southern Ocean boundary conditions from GEOS-Chem.



Shading indicates the range of each parameter in the LGM from models or observations. The box model suggests that Δ¹⁷O is most sensitive to cloud liquid water content, OH, and sea salt between the PIH and LGM.

Seasonality of Δ¹⁷O

While we will likely never have seasonally resolved ice core measurements of Δ¹⁷O from the LGM, the modeled seasonal cycle provides insight into how Δ¹⁷O changes between climate regimes.



Conclusions

Ice core sulfate Δ¹⁷O vary with climate on glacial-interglacial timescales and suggest greater gas-phase sulfate formation, perhaps due to higher [OH] during the last glacial period compared to interglacial periods. Δ¹⁷O calculated in the ICECAP model is qualitatively consistent in sign with the ice core observations, but underestimates the observed preindustrial Holocene Δ¹⁷O. Large changes in Δ¹⁷O do occur over the Southern Ocean in ICECAP, but do not propagate to Antarctica.

The ICECAP sulfate model indicates that the decrease in Δ¹⁷O is due to a combination of a decreases in sulfate formation by O₃ and H₂O₂ and an increase in sulfate formation by OH and O₂ catalyzed by transition metals from dust.

To assess the sensitivity of Δ¹⁷O to the parameters that impact sulfate formation, a box model of sulfate formation is employed using boundary conditions from the Southern Ocean preindustrial ICECAP simulations. Our preliminary results show that within the range of LGM values, Δ¹⁷O is most sensitive to changes in cloud LWC, OH, and sea salt.

Future work will include further investigation of changes in LWC and the direct impact on gas- versus aqueous-phase sulfate formation and transport, and impact on cloud water pH.