

# Anthropogenic Influence on Atmospheric Oxidants and the Sulfur Budget

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## ABSTRACT

We use a global chemical transport model constrained by observations of ice core sulfate oxygen isotopes to simulate anthropogenic impacts on oxidant ( $\text{OH}$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ) and sulfur budgets. The Arctic ice core sulfate  $\delta^{18}\text{O}$ -isotope observations are insensitive to changes in oxidant concentrations on the preindustrial-industrial timescale due to the rising importance of metal catalyzed  $\text{S}(\text{IV})$  oxidation in mid- to high-northern latitudes resulting from anthropogenic metal emissions. The small change in Antarctic ice core sulfate  $\delta^{18}\text{O}$ -isotope observations on this timescale are consistent with simultaneous increases in boundary layer  $\text{O}_3$  (32%) and  $\text{H}_2\text{O}_2$  (49%) concentrations in the southern hemisphere, which have opposing effects on the sulfate  $\text{O}$ -isotope anomaly. Despite large changes in global oxidant abundances and sulfur emissions since preindustrial times, the relative importance of gas- versus aqueous-phase sulfate formation has remained constant.

## I. INTRODUCTION

The oxidation capacity of the atmosphere (usually defined by global mean OH abundance) has large implications for GHG (e.g.  $\text{CH}_4$ ) and pollutant (e.g. CO) concentrations. Little to no information exists on how oxidant abundances have varied in the past. Hence we rely on models; however, modeled changes in OH and  $\text{O}_3$  in the past show disagreement among different studies due to large uncertainties in emissions of  $\text{O}_3$  precursors.

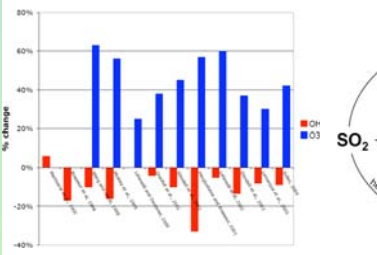


Figure 1. Modeled percent change in annual-mean tropospheric OH and  $\text{O}_3$  concentrations in the present day relative to the preindustrial from different studies.

The  $\Delta^{17}\text{O}$  value of sulfate and nitrate from ice cores currently provides the most promising proxy for paleo oxidant concentrations. The  $\Delta^{17}\text{O}$  value of sulfate is a function of the relative importance of its various oxidation pathways, which is in large part determined by atmospheric oxidant abundance (in addition to pH and liquid water content of clouds). It can also be used as an indicator of the relative importance of gas- versus aqueous-phase sulfate formation, which has implications for the direct and indirect forcing of sulfate aerosol.

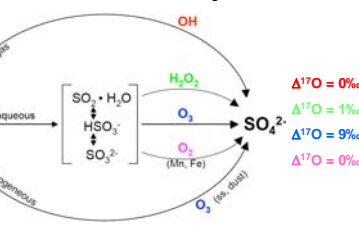


Figure 2.  $\text{S}(\text{IV})$  oxidation pathways and their corresponding  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5 \times \delta^{18}\text{O}$ ) [Savarnino et al., 2000].

## II. ICE CORE OBSERVATIONS

Arctic  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  ice core and aerosol observations show an unexpected decrease throughout the industrial period. This decrease is unexpected due to known increases in  $\text{O}_3$  concentrations over this time period.

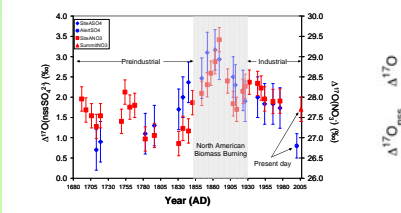


Figure 3.  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{nitrate})$  ice core observations since 1680 A.D. from Greenland ice core and snowpit and Arctic aerosol observations (produced using data from Alexander et al. [2004], McCabe et al. [2006] and Kunasek et al. [2009]).

Antarctic  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  ice core observations show a small increase from the mid- to late-1700s leveling off in the mid- to late-1800s. The timing of this increase is coincident with increases in southern hemisphere biomass burning [Marlon et al., 2008].

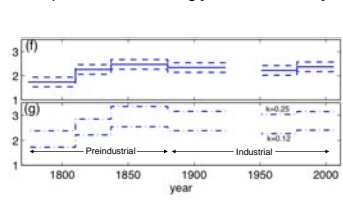


Figure 4. Raw  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\Delta^{17}\text{O}(\text{nssSO}_4^{2-})$  since 1770 A.D. from the West Antarctic Ice Sheet (WAIS) Divide ice core (Figure 2 from Kunasek et al., manuscript in prep). Note: A values represent different assumptions regarding the  $\text{SO}_2$ -N ratio in sea-water.

## III. METHODS

We use the GEOS-Chem model [Bey et al., 2001], a global 3D chemical transport model driven by assimilated meteorology at  $4^\circ \times 5^\circ$  horizontal resolution and 30 sigma vertical levels, to simulate oxidant concentrations and  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  in the present day and preindustrial time periods.

Model Configuration	Preindustrial	Industrial
Meteorology	GEOS-4 1989-1991	GEOS-4 1989-1991
Fossil Fuel Emissions	OFF	GEIA
Fertilizer Emissions	OFF	GEIA
Biomass Burning Emissions	scaled to 10% of industrial	Duncan et al./GFED2
Biogenic Emissions	GEIA/MEGAN	GEIA/MEGAN
Biofuel Emissions	GEIA	GEIA
$\text{CO}_2$	285 ppmv	355 ppmv
$\text{CH}_4$	792 ppbv	1700 ppbv

## REFERENCES

Alexander, B., Savarnino, J., Baek, N. I., Delmas, R. J., and Thériault, M. H., Climate driven changes in the oxidation pathways of atmospheric sulfur, *Geophys. Res. Lett.*, 29, 10.1029/2003GL018479, 2002.  
 Logan, J. A., Platt, B. D., Frost, A. M. L., Q. Liu, X. Y., Molina, L. J., and Schmitt, M. G., Global modeling of nonaqueous chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, 106, 23073-23096, 2001.  
 Braaten, P. D., Koff, T. J., Miller, F. J., Schneider, T., Gnanou, C., Tai, X., Hauglusteiner, and D., Past and future changes in global tropospheric ozone: Impact on radiative forcing, *Geophysical Research Letters*, 25, 3807-3810, 1998.  
 Fehsenfeld, G. P., Mihir, J. B., White, J. W., Ebersole, D. M., Lussary, K. R., Lewis, D. C., M. M. Deiner, M. F., Trudinger, C. M., Omern, T. D., and Langenfeldt, R. L., Unexpected changes to the Global Methane Budget over the Past 2000 Years, *Science*, 309, 1714-1717, 10.1126/science.1114519, 2005.  
 Grenfell, J. L., Shindell, T. T., Koch, D., and Rind, D., Chemistry-climate interactions in the Goddard Institute for Space Studies general circulation model 2: New insights into modeling the preindustrial atmosphere, *J. Geophys. Res.*, 106, 32435-32461, 2001.  
 Hauglusteiner, G. A., and Braaten, P. D., Evolution of tropospheric ozone under anthropogenic activities and associated radiative forcing of climate, *Journal of Geophysical Research Atmospheres*, 106, 22317-22362, 2001.  
 Kaplan, D. J., Fildes, D., and Hauglusteiner, G. A., Role of methane and biogenic volatile organic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations, *Global Biogeochemistry*, 20, 26-10.1029/2005GB002590, 2006.  
 Karim, I. I., Frost, A. A., and Kleiser, A. A., Radiative-chemical modeling of the annually averaged composition and temperature of the global atmosphere during the last glacial and interglacial periods, *J. Geophys. Res.*, 100, 7291-7301, 1995.  
 Kunasek, S. A., Alexander, B., Jackman, T. L., Thériault, M. H., and Arnold, H. M., Complete isotope composition of sulfate in 70-meter ice cores from the West Antarctic ice Sheet Divide (WDC05A), manuscript in preparation.  
 Kunasek, S. A., Alexander, B., Hastings, M. G., Stimp, E. J., Gleason, D. J., and Jarvis, J. J., Measurements and modeling of global nitrate in a snowfall from Summit, Greenland, *J. Geophys. Res.*, 111, D24322, doi:10.1029/2006JD007103, 2006.  
 Lamarque, J.-F., Neus, P., Brimble, L., Bjak, L., Wang, W., and Strasser, A. C., Tropospheric ozone evolution between 1850 and 1990, *J. Geophys. Res.*, 105, 20034-20045, 2000.  
 Lavee, J., and Denner, F. J., What controls tropospheric ozone?, *J. Geophys. Res.*, 105, 3531-3551, 2000.  
 Lavee, J., Peters, W., Denner, F. J., Koch, and MC, Stability of tropospheric hydroxyl chemistry, *J. Geophys. Res.*, 107, 4715, doi:10.1029/2002JD002772, 2002.  
 Marlon, J. R., Battar, P. J., Caraculac, C., Gavr, D. G., Harrison, S. P., Hoggan, P. E., Joshi, P., Pauer, M. J., and Pitterich, J. C., Climate and human influences on global biomass burning over the past two millennia, *Nature Geosci.*, 1, 697-702, 2008.  
 Marnett, P., Braaten, C. P., and Granier, C., The chemical composition of ancient atmospheric  $\text{O}_2$  model study constrained by ice core data, *J. Geophys. Res.*, 100, 14,201-14,204, 1995.  
 McCabe, J. R., Savarnino, J., Alexander, B., Gong, S., and Thériault, M. H., Isotope constraints on nonphotochemical sulfate production in the Arctic winter, *Geophys. Res. Lett.*, 33, doi:10.1029/2005GL02164, 2006.  
 Mackley, L. M., P. F., Jacob, D. J., Logan, J. A., Frost, D., and Koch, D., Radiative forcing from tropospheric ozone calculated with a unified chemistry-climate model, *J. Geophys. Res.*, 106, 163,163-163, 1999.  
 Savarnino, J., Liu, C. C. W., and Thériault, M. H., Laboratory oxygen isotope study of sulfur (IV) oxidation: Origin of the mass-independent isotopic anomaly in atmospheric sulfates and sulfate mineral deposits on Earth, *J. Geophys. Res.*, 105, 20079, 2000.  
 Shindell, T. T., Grenfell, J. L., Rind, D., and Drew, V., Chemistry-climate interactions in the Goddard Institute for Space Studies general circulation model. 1: Tropospheric chemistry model description and evaluation, *J. Geophys. Res.*, 106, 8047-8075, 2001.  
 Shindell, T. D., Faluvee, G., Ball, and N., Preindustrial-to-present-day radiative forcing by atmospheric sulfate and sulfate mineral deposits with the GEOS chemistry-climate GCM, *Atmospheric Chemistry and Physics*, 3, 1679-1702, 2003.  
 Thompson, A. M., Chappellaz, J. A., and Fehsenfeld, G. P., The atmospheric  $\text{CH}_4$  increase since the Last Glacial Maximum, *Geophys. Res. Lett.*, 45B, 2457-2457, 1993.  
 Yavelov, F. J., Beerling, D. J., and Johnson, C. E., The ice age methane budget, *Geophys. Res. Lett.*, 32, L07044, 2005.  
 Wang, Y. H., and Jacob, D. J., Anthropogenic forcing on tropospheric ozone and OH since preindustrial times, *J. Geophys. Res.*, 103, 11,923-11,938, 1998.

## IV. MODEL RESULTS

Calculated global mean changes in tropospheric OH (-9%),  $\text{O}_3$  (+42%) and  $\text{H}_2\text{O}_2$  (+58%) in the present day relative to the preindustrial are consistent with previous modeling studies (see also Figure 1).

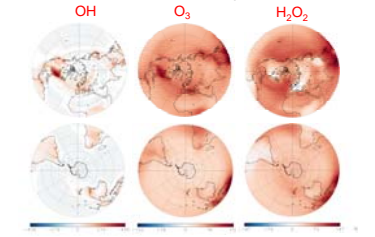


Figure 5. Percent change in boundary layer oxidant concentrations in the present day relative to the preindustrial.

The fraction of sulfate formed in the gas-phase, important for direct and indirect radiative forcing of sulfate aerosols, does not change despite large changes in the sulfur and oxidant budgets.

Table 2. Calculated sulfur budget in the present day and preindustrial.	Preindustrial	Present day
Sulfur Emissions (Tg yr <sup>-1</sup> )	23.6	92.0
Sulfur Burden (Tg)	0.42	0.97
Fraction of sulfate formed via gas-phase SO <sub>2</sub> + OH	23%	26%

## V. CONCLUSIONS

- A decrease in modeled  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  (-0.7%) in Greenland in the present day relative to the preindustrial is consistent with the Greenland ice core record (-0.7±0.4%) [Alexander et al., 2004]. The unexpected decrease in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  on this timescale is explained by the rising dominance of metal catalyzed  $\text{S}(\text{IV})$  oxidation from anthropogenic metal emissions, despite large increases in  $\text{O}_3$  concentrations (50%) in the northern hemisphere.
- A small decrease in modeled  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  (-0.2%) in Antarctica in the present day relative to the preindustrial is consistent with a small change in the Antarctic observations (+0.2±0.5%) [Kunasek et al., manuscript in prep.]. The lack of a significant change in Antarctic  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  on this timescale is consistent with simultaneous increases in  $\text{O}_3$  (32%) and  $\text{H}_2\text{O}_2$  (49%) concentrations in the southern hemisphere which have opposing effects on  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ .

## VI. FUTURE DIRECTIONS

$\Delta^{17}\text{O}(\text{SO}_4^{2-})$  from the Vostok ice core shows large (3.5%) changes on the glacial-interglacial timescale, consistent with increased OH (and  $\text{CH}_4$  sink) during the last glacial.

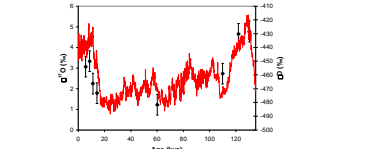


Figure 7.  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and  $\delta\text{D}$  over the last glacial-interglacial cycle from the Vostok ice core (Figure 1 from Alexander et al. [2002]).

Impact of oxidant changes on  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  and comparison with ice core observations

	Model (base)	Model (with metal catalyzed S(IV) oxidation)	Ice core observations
Arctic (Greenland and Alerø)	+0.2	-0.7	-0.7±0.4
Antarctic (WAIS)	+0.2	-0.2	+0.2±0.5

\*base scenario includes  $\text{S}(\text{IV})$  oxidation by OH,  $\text{H}_2\text{O}_2$ , and  $\text{O}_3$   
 \*Alexander et al. [2004] (see Figure 3)  
 \*McCabe et al. [2006] (see Figure 3)  
 \*Kunasek et al., manuscript in prep. (see Figure 4)  
 \*error represents the 1σ standard deviation of the preindustrial observations

Sulfate formed via metal catalyzed oxidation is dominated by anthropogenic metal emissions in mid- to high-northern latitudes in the present day, and represents up to -half of (annual mean) total sulfate formation.

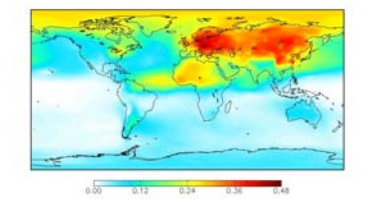


Figure 6. Annual mean fraction of total sulfate at the surface formed via metal catalyzed oxidation (Figure 4 from Alexander et al. [2009]).

Modeled changes in OH and  $\text{O}_3$  in the LGM relative to the preindustrial show large disagreement among different studies.

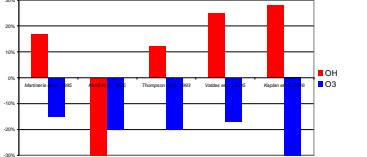


Figure 8. Modeled percent change in global-mean tropospheric OH and  $\text{O}_3$  concentrations in the LGM relative to the P.I.

In collaboration with Loretta Mickley, Gavin Schmidt, Jed Kaplan and others, we are simulating oxidant concentrations and  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  on the glacial-interglacial timescale using an offline coupling between GEOS-Chem (CENTM, GISS ModelE (GCM), and BIOME-4 (global terrestrial vegetation model). We are testing the sensitivity of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  to changes in oxidants on this timescale in order to provide an observational constraint for oxidant concentrations in the past.

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