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Sensitivity of Oxygen Isotopes of Sulfate in Ice Cores to Past Changes in Atmospheric Oxidant Concentrations

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Overview

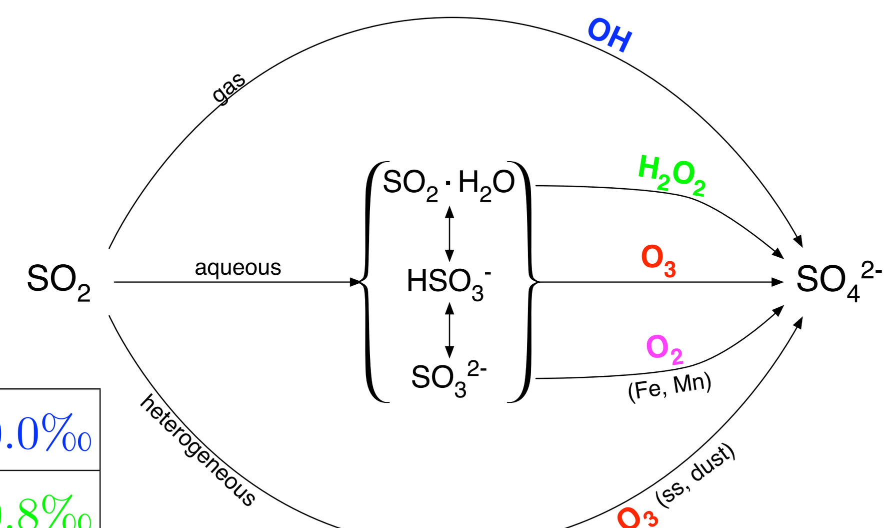
Oxidant concentrations impact the lifetime of reduced atmospheric trace gases (CH_4, SO_2, NO_x, VOCs) with implications for climate forcing and pollutants. Without direct evidence of paleo-oxidant concentrations, we have relied on atmospheric chemistry models. We simulate oxidant chemistry and the $\Delta^{17}O_{SO4}$ in the present (**PRES**), preindustrial Holocene (**PIH**) and Last Glacial Maximum (**LGM**), using the GEOS-Chem model, and use measurements of the $\Delta^{17}O_{SO4}$ from Greenland (**Site-A** [*Alexander et al., 2004*]) and Antarctic (**WAIS-Divide** [*Kunasek et al., in prep*] and **Vostok** [*Alexander et al., 2002*]) ice cores as constraints. The GEOS-Chem model is run with assimilated meteorology (GEOS4) and general circulation model meteorology (GISS ModelE). For ModelE simulations, LGM boundary conditions are from CLIMAP, 1981 (*warm*) and Webb et al., 1997 (*cold*). LAI and vegetation type are from BIOME4-TG. Simulations are consistent with ice core measurements of the $\Delta^{17}O_{SO4}$ on the PIH-PRES timescale, but preliminary LGM simulations do not reproduce the measurements of $\Delta^{17}O_{SO4}$ from the Vostok core.

$\Delta^{17}O$ of Sulfate

$\Delta^{17}O_{SO4}$ depends on:

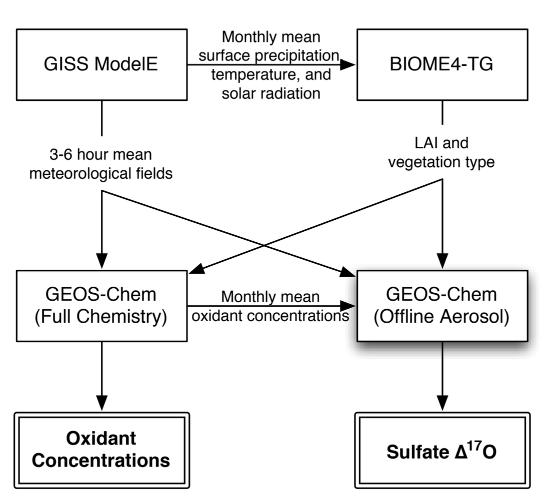
- Oxidant Concentrations
- Cloud liquid water content
- Cloud water pH

$SO_2 + \mathbf{OH} \rightarrow SO_4$	$\Delta^{17}O_{SO4} = 0.0‰$
$S(IV) + \mathbf{H_2O_2} \rightarrow SO_4$	$\Delta^{17}O_{SO4} = 0.8‰$
$S(IV) + \mathbf{O_3} \rightarrow SO_4$	$\Delta^{17}O_{SO4} = 8.8‰$
$S(IV) + \mathbf{O_2} \rightarrow SO_4$	$\Delta^{17}O_{SO4} = 0.0‰$



Model Configuration

	PRESENT	PIH	LGM
Meteorology	GEOS4 (1990s)/ ModelE	GEOS4 (1990s)/ ModelE	ModelE Webb/ Climap
Anthropogenic	GEIA & regional	OFF	OFF
Biomass Burning	GFED2	10% GFED2	10% GFED2
Biofuels	GEIA	OFF	OFF
Biogenic	MEGAN	MEGAN/BIOME4	BIOME4
CH_4	1730 ppbv	730 ppbv	370 ppbv



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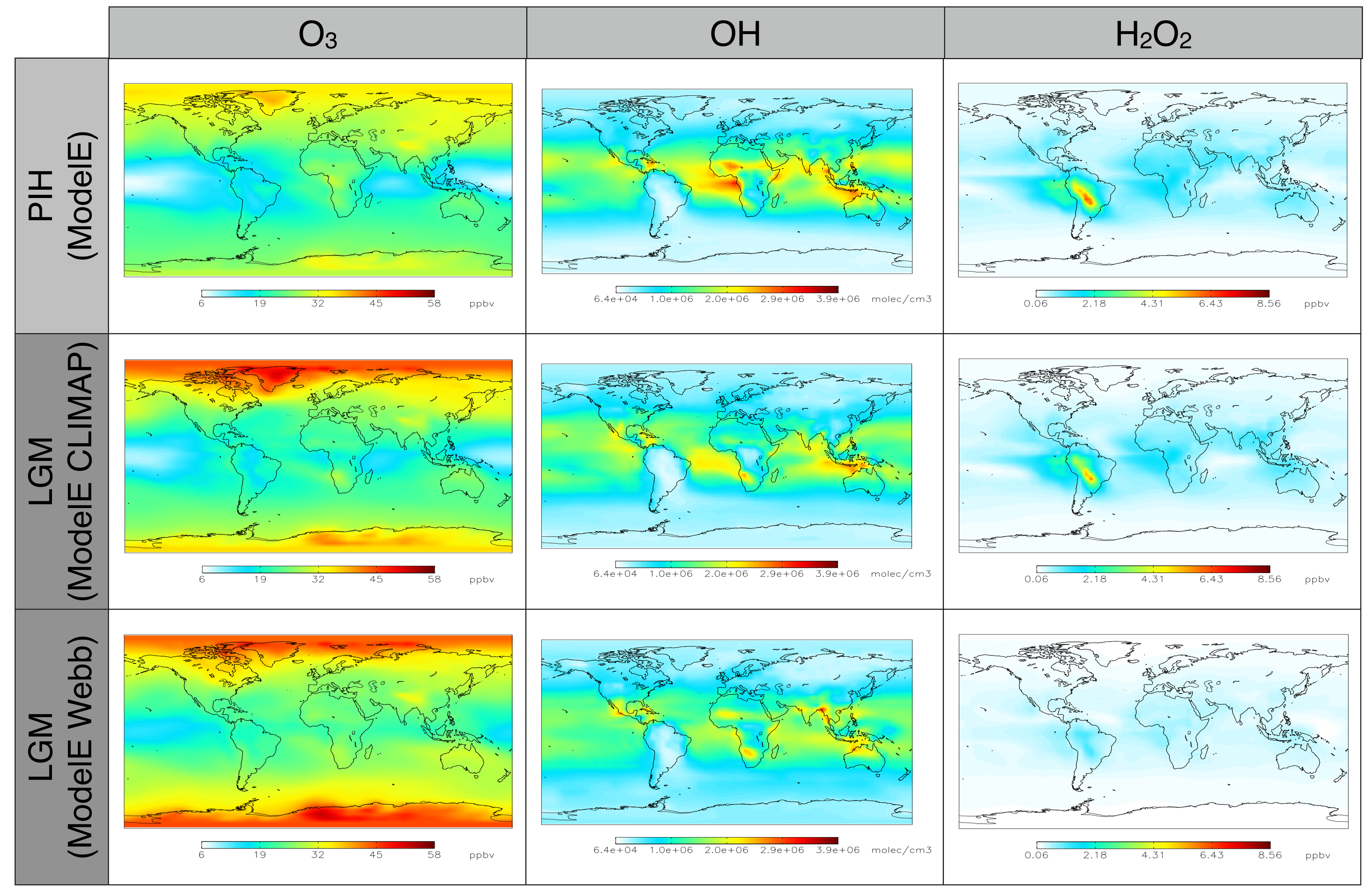
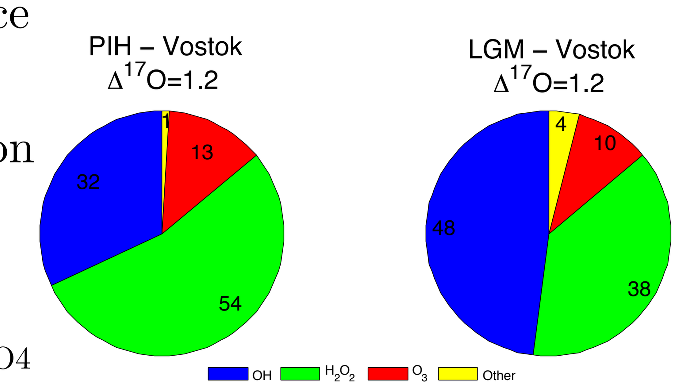
Oxidant Concentrations: ModelE LGM



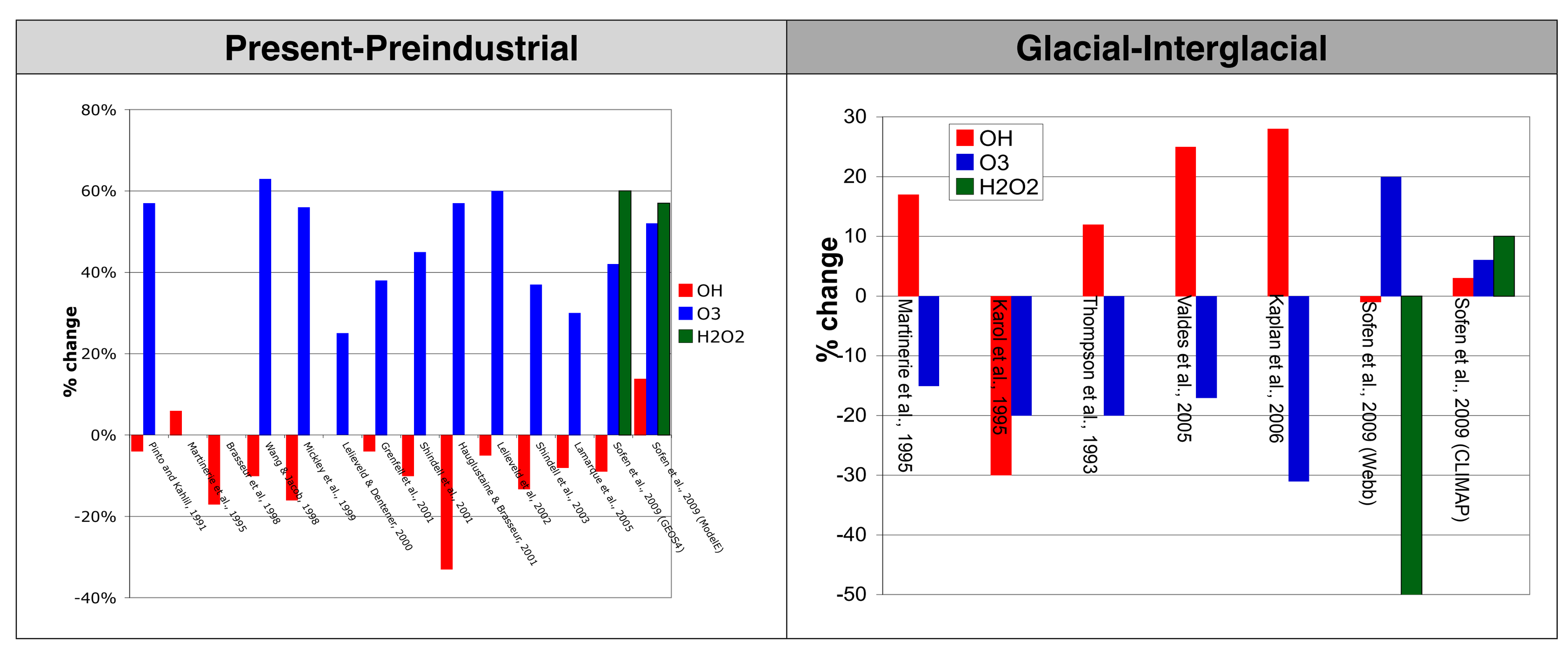
LGM Simulations: Preliminary Conclusions

Webb and CLIMAP simulations fail to reproduce the observed change in the $\Delta^{17}O_{SO4}$ at Vostok, Antarctica, because there is not enough oxidation by O_3 in the PIH simulation to a produce high enough $\Delta^{17}O_{SO4}$. However, the ModelE PIH simulation does agree with the measured $\Delta^{17}O_{SO4}$ at Site-A and WAIS-Divide. Further work is needed to understand the extremely high $\Delta^{17}O_{SO4}$ measured during interglacial periods at Vostok.

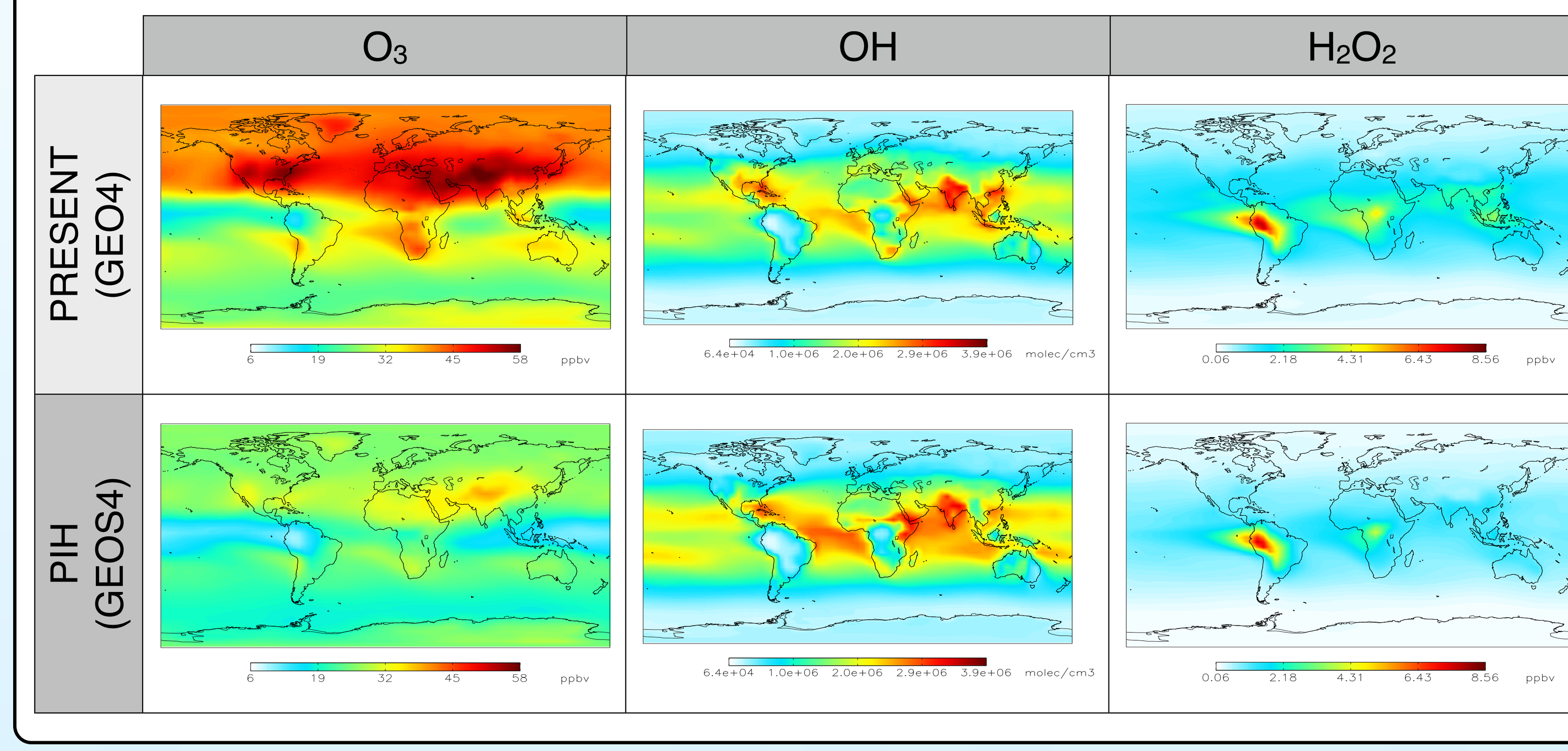


Uncertainties in Paleo-Oxidants

Models vary widely on the calculated change in paleo-oxidants due to uncertainties in emissions or meteorology.



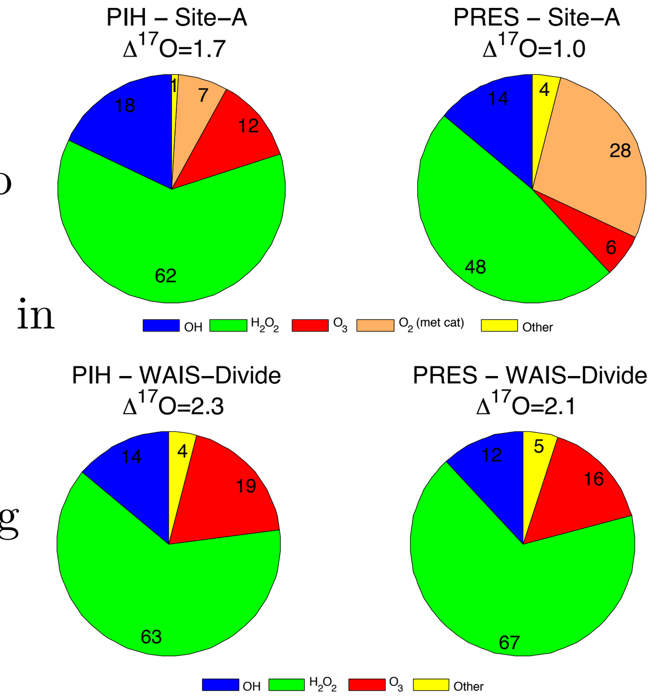
Oxidant Concentrations: GEOS4 Preindustrial



PIH Simulations: Conclusions

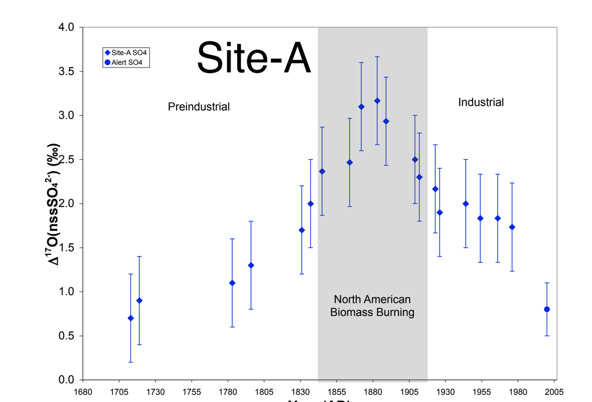
GEOS-Chem reproduces the observed changes in the $\Delta^{17}O_{SO4}$ on the preindustrial-industrial timescale.

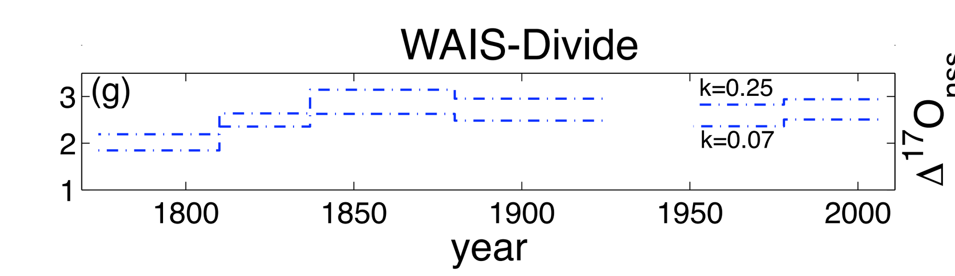
- **Site-A** The small decrease in the $\Delta^{17}O_{SO4}$ between preindustrial and present times is due to the increase in metal-catalyzed oxidation from anthropogenic metals, in spite of a large increase in O_3.
- **WAIS-Divide** Between 1850-2005 there is almost no change in $\Delta^{17}O_{SO4}$ because of offsetting effects on the $\Delta^{17}O$ of increasing oxidation by H_2O_2 and O_3.

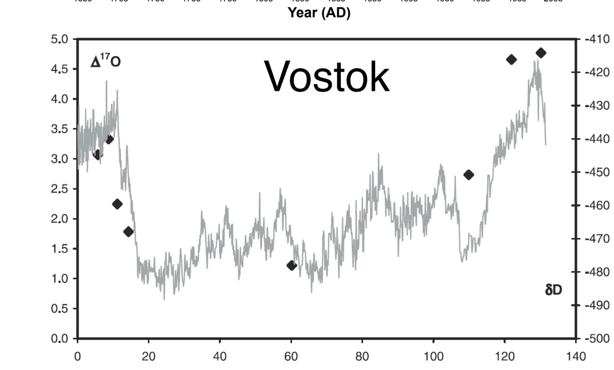


Change in $\Delta^{17}O$ of Sulfate

	Site-A	WAIS-Divide	Vostok
PRES-PIH (Meas)	**-0.5**	**-0.2**	---
PRES-PIH (GEOS)	-0.7	-0.2	-0.1
PRES-PIH (ModelE)	-0.4	-0.1	0.1
PIH-LGM (Meas)	---	---	**1.3**
PIH-LGM (Webb)	1.1	0.7	0.4
PIH-LGM (CLIMAP)	1	0.9	0.2







Future Work

Investigate the sensitivity of $\Delta^{17}O_{SO4}$ and oxidant concentrations in the ModelE LGM simulations to cloud liquid water content, biomass burning and biogenic, sea salt, and dust emissions.