**Atmospheric
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Discussions**

The sensitivity of the oxygen isotopes of ice core sulfate to changing oxidant concentrations since the preindustrial

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**Preindustrial
oxidants and
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Abstract

Changes in tropospheric oxidant concentrations since preindustrial times have implications for the ozone radiative forcing, lifetimes of reduced trace gases, aerosol formation, and human health but are highly uncertain. Measurements of the triple oxygen isotopes of sulfate in ice cores (described by $\Delta^{17}O_{SO_4} = \delta^{17}O - 0.52 \times \delta^{18}O$) provide one of the few constraints on paleo-oxidants. We use the GEOS-Chem global atmospheric chemical transport model to simulate changes in oxidant concentrations and the $\Delta^{17}O_{SO_4}$ between 1850 and 1990 to assess the sensitivity of $\Delta^{17}O_{SO_4}$ measurements in Greenland and Antarctic ice cores to changing tropospheric oxidant concentrations. The model indicates a 42% increase in the concentration of global mean tropospheric O_3, a 10% decrease in OH, and a 58% increase in H_2O_2 between the preindustrial and present. Modeled $\Delta^{17}O_{SO_4}$ is consistent with measurements from ice core and aerosol samples. Model results indicate that the observed decrease in the Arctic $\Delta^{17}O_{SO_4}$ in spite of increasing O_3 is due to the combined effects of increased sulfate formation by O_2 catalyzed by anthropogenic transition metals and increased cloud water acidity. In Antarctica, the $\Delta^{17}O_{SO_4}$ is sensitive to relative changes of oxidant concentrations, but in a nonlinear fashion. Sensitivity studies explore the uncertainties in preindustrial emissions of oxidant precursors.

1 Preindustrial oxidants

The concentrations of the tropospheric oxidants, including ozone (O_3), hydroxyl radical (OH), and hydrogen peroxide (H_2O_2), are described collectively as the "oxidizing capacity of the atmosphere" (Thompson, 1992). Variations in the oxidizing capacity impact the lifetimes of chemically and radiatively important reduced trace gases, such as carbon monoxide (CO), methane (CH_4), and halocarbons. However, the extent to which the oxidizing capacity of the troposphere has changed between the preindustrial

Holocene (PI; ~1850 CE) and present-day (PD) due to anthropogenic activity remains highly uncertain.

Measurements of H_2O_2 concentrations (Sigg and Neftel, 1991) and CH_2O/CH_4 (Staffelbach et al., 1991) in ice cores have been studied as potential proxies of the past oxidizing capacity of the atmosphere. However, both are sensitive to post-depositional processing. There are also reconstructions of O_3 measurements from the nineteenth century made with the Schönbein method (Marenco et al., 1994; Pavelin et al., 1999) and oxidation of arsenate (Volz and Kley, 1988). These reconstructions suggest very low surface O_3 concentrations, on the order of 5–15 ppbv.

Due to the challenges in interpreting these records, the community relies on models to quantify the past oxidizing capacity of the atmosphere. However, between model studies, the fractional change in global mean oxidant concentrations between PI and PD (PD-PI) scenarios varies greatly (e.g., Wang and Jacob, 1998; Thompson et al., 1993; Grenfell et al., 2001; Lamarque et al., 2005). Models predict PD-PI changes of +30 to +65% in mean O_3, −33% to +10% in OH, and +40% to +140% in H_2O_2. Inter-model variability in oxidants is due to differing meteorological fields, differing choices of CH_4 concentrations, uncertainties in PI biogenic and biomass-burning emissions, and inherent variations in PD models related to NO_x and volatile organic compound (VOC) emissions and stratosphere-troposphere exchange of O_3 (Wu et al., 2007). In addition to inter-model variability, Mickley et al. (2001) points out that most PI simulations overestimate O_3 relative to the late-1800s measurements described above. To achieve agreement with these measurements, models require dramatically lower emissions of soil and lightning NO_x and higher emissions of biogenic VOCs.

Due to the widely varying model approaches and the nonlinearity of oxidant chemistry, a proxy is needed for model validation of PI oxidant concentrations. In this study, we consider the oxygen isotopes of atmospheric sulfate extracted from ice cores as a potential constraint for oxidant concentrations in a global model.

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2 Oxygen isotopic composition of sulfate

In the gas phase, sulfate (SO_4^{2-}) forms through oxidation of sulfur dioxide gas (SO_2) by OH. In water, SO_2 dissolves, speciating into $SO_2 \cdot H_2O + HSO_3^- + SO_3^{2-}$, the total of which is described as S(IV). Aqueous-phase sulfate forms by the oxidation of S(IV) by O_3,

5 H_2O_2, and by molecular oxygen (O_2) catalyzed by metals (mainly Fe and Mn). Also, SO_4^{2-} forms through heterogeneous-phase oxidation by O_3 on alkaline sea salt and dust aerosols. Additional sulfate-formation pathways are thought to be minor contributors to the global sulfur budget (Faloona, 2009).

Triple-isotope measurements (^{16}O, ^{17}O, ^{18}O) of the oxygen in sulfate provide in-
10 sight into the oxidation pathway by which sulfate formed, due to the anomalous "mass-independent" isotopic signature that is passed to SO_4^{2-} by O_3 and H_2O_2 (Savarino et al., 2000).

This mass-independent signature is described by

$$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O, \qquad (1)$$

15 where

$$\delta^n O = \frac{(^nO/^{16}O)_{sample}}{(^nO/^{16}O)_{standard}} - 1. \qquad (2)$$

Both δ and Δ are expressed as a parts-per-thousand deviation from a standard (SMOW) in units of "per mil" (‰).

Field, laboratory, and modeling studies find that tropospheric O_3 has a mean $\Delta^{17}O$ of
20 ~25‰–35‰, H_2O_2 has a $\Delta^{17}O = 0.9$–2.2‰, and O_2 and OH have $\Delta^{17}O \approx 0$ (Johnston and Thiemens, 1997; Janssen et al., 1999; Krankowsky et al., 1995; Mauersberger et al., 1999; Lyons, 2001; Savarino and Thiemens, 1999; Luz et al., 1999). The resulting mean $\Delta^{17}O$ of atmospheric sulfate ($\Delta^{17}O_{SO_4}$) depends on the $\Delta^{17}O$ transferred to sulfate by each oxidant and the fraction of sulfate formed through each oxidation
25 pathway. The latter depends on oxidant concentrations, cloud liquid water content,

cloud-water pH, atmospheric metal concentrations, and aerosol surface area. The $\Delta^{17}O_{SO_4}$ of sulfate deposited to polar ice is well-preserved, enabling its use as a proxy of atmospheric sulfate formation pathways.

3 Model description

We use version 8-01-01 of the GEOS-Chem global, three-dimensional atmospheric chemical transport model (http://www.geos-chem.org) at 4°×5° resolution to simulate oxidant concentrations and the resulting $\Delta^{17}O_{SO_4}$ of the PI and PD atmosphere. The model is driven by assimilated Goddard Earth Observing System (GEOS) 1989–1991 meteorology. The PD simulation relies on the standard GEOS-Chem emissions inventories – GEIA fossil fuel, fertilizer, biogenic, and biofuel emissions (Wang et al., 1998) scaled by national energy and CO_2 emission data to 1989–1991, MEGAN 2.0 biogenics (Millet et al., 2008), GFED2 biomass burning from the year 1997 (Giglio and Werf, 2006), and 1700 ppbv CH_4. For PI simulations, we turn off fossil fuel and fertilizer emissions, scale biomass burning emissions to 10% of PD levels (following Crutzen and Zimmermann, 1991, and others); biofuel, lightning, and biogenic emissions remain at their PD levels. We set PI CH_4 to 1850 CE levels of 792 ppbv (Etheridge et al., 2002).

Global monthly-mean oxidant fields (O_3, OH, and NO_3 concentrations, H_2O_2 production and photolysis rates) and total inorganic nitrate are archived from NO_x-Oxhydrocarbon-aerosol "full-chemistry" simulations (two-year spin-up, three-year simulation) and used in "offline" tagged-sulfate aerosol simulations as described in Alexander et al. (2009).

The PD model is validated against all available annual, seasonal, and monthly measurements of $\Delta^{17}O_{SO_4}$ from aerosol, precipitation, and firn samples (Fig. 1). The model captures the spatial variability in $\Delta^{17}O_{SO_4}$ measurements (e.g. latitudinal gradient). The best agreement is achieved when cloud water pH values of 4.5 and 5.0 are assumed for the Northern and Southern Hemispheres, respectively. This is consistent with the

increased acidity of Northern Hemisphere precipitation by anthropogenic emissions of nitric and sulfuric acid precursors.

When comparing measured and modeled $\Delta^{17}O_{SO_4}$ on the PI to PD timescale, we focus on the PD-PI change of $\Delta^{17}O_{SO_4}$, rather than the absolute value, to mitigate uncertainties in the $\Delta^{17}O$ of oxidants. Calculated annual average $\Delta^{17}O_{SO_4}$ is compared to measurements from PD aerosol samples in Alert, Canada (McCabe et al., 2006) and ice cores from (PI) Site-A, Greenland (Alexander et al., 2004) and (PD and PI) WAIS-Divide (Kunasek et al., 2010), Antarctica. We also compare PI model results to the measurements of late-1800s O_3 and ice core H_2O_2.

Tropospheric O_3 measurements span a range of $\Delta^{17}O_{O_3}$, and we assume a value at the upper end of the range (35‰). In polar regions, stratospheric O_3 intrusions may increase $\Delta^{17}O_{O_3}$. Also, Morin et al. (2007) has postulated the non-zero $\Delta^{17}O$ of OH formed from O_3 may not be eliminated by isotopic exchange with water vapor in polar regions because of the low water vapor content. These effects may offset modeled $\Delta^{17}O_{SO_4}$ from its true value, but the influence will be similar in both time periods, so the difference in $\Delta^{17}O_{SO_4}$ is largely unaffected. By assuming no change in meteorology, any change in the modeled $\Delta^{17}O_{SO_4}$ is due to a change in oxidant concentrations, pH, or metal emissions.

4 Sensitivity studies

Due to the uncertainties in PI conditions, we conduct four sensitivity studies that involve varying cloud water pH, metal-catalyzed oxidation, biomass burning emissions, and biogenic VOC and NO_x emissions.

The choice of global cloud water pH contributes to uncertainty in $\Delta^{17}O_{SO_4}$, since $S(IV)+O_3$ is highly pH-dependent. Because the Northern Hemisphere has seen an increase in the acidity of precipitation since the PI (Mayewski et al., 1986) while the Southern Hemisphere has not (Cragin et al., 1987), simulations are run at a bulk cloud

water pH=4.5, 5.0, and 5.5. The best-fit pH values from the base simulations are used for all further sensitivity studies.

Alexander et al. (2009) showed that metal-catalyzed sulfate formation is dominated by anthropogenic metals in mid- to high-latitudes during winter and is necessary to model the observed seasonal $\Delta^{17}O_{SO_4}$ cycle in Arctic aerosol. Simulations are run both with and without metal-catalyzed oxidation to test the influence of increasing metal emissions between the PI and PD. Modeled metal emissions are scaled to mineral dust and primary anthropogenic sulfate, following Alexander et al. (2009). Thus, only metal in dust is included in the PI.

Two sensitivity studies explore uncertainties in PI emissions of oxidant precursors and their impact on $\Delta^{17}O_{SO_4}$. The first uses PD biomass burning in a simulation with an otherwise PI configuration. The second sensitivity study is modeled on the work of Mickley et al. (2001). We halve lightning and biomass-burning NO_x and double biogenic VOCs from their PI values to test whether modeled preindustrial oxidants can be consistent with both late-1800s O_3 measurements and ice core $\Delta^{17}O_{SO_4}$.

5 Results and discussion

Figure 2a–c shows the PD-PI change in annual mean tropospheric oxidant concentrations. Between the PI and PD simulations, global annual mean (3-year average) tropospheric O_3 increases by 42% (32–45 ppbv), OH decreases by 10% (1.3–1.2×10^6 molecules cm^{-3}), and H_2O_2 increases by 58% (0.58–0.92 ppbv). Our base-case simulations represent reasonably mainstream changes in O_3 and OH compared to previous modeling studies. Very few studies report PD-PI H_2O_2 changes (e.g., Thompson et al., 1993; Grenfell et al., 2001), however ice core H_2O_2 measurements are qualitatively consistent with our results (Frey et al., 2006; Sigg and Neftel, 1991).

The sensitivity of $\Delta^{17}O_{SO_4}$ to changing oxidants is best assessed using fractional changes in regional oxidants because $\Delta^{17}O_{SO_4}$ depends on the fraction of SO_4^{2-} formed

by each pathway. Table 1 compares the PD-PI change in modeled $\Delta^{17}O_{SO_4}$ to both Arctic (Site-A and Alert) and Antarctic (WAIS-Divide) measurements. Figure 2d illustrates the PD-PI change in the annual mean $\Delta^{17}O_{SO_4}$ of deposited sulfate across the globe. The largest $\Delta^{17}O_{SO_4}$ decrease occurs in the Eurasian Arctic due to increased

5 metal-catalyzed SO_4^{2-} formation and decreased pH. The largest increase occurs in the Amazon region due to a decrease in the fraction of sulfate formed in the gas-phase.

In the PD, we assume cloud water pH values of 4.5 in the Northern Hemisphere and 5.0 in the Southern Hemisphere, while in the PI, both hemispheres are assumed to have a cloud-water pH of 5.0, due to the lack of anthropogenic acid emissioins. In

10 both time periods, the model agrees well with the Northern Hemisphere $\Delta^{17}O_{SO_4}$ measurements, while slightly underestimating (by 0.4‰) the WAIS-Divide observations. Simulations at pH=5.5 yield unrealistically high $\Delta^{17}O_{SO_4}$ values. A PD Northern Hemisphere pH of 5.0 does not produce the observed decrease in the $\Delta^{17}O_{SO_4}$ at Summit, Greenland (Table 1). The assumed pH values are consistent with SO_4^{2-} and NO_3^-

15 trends in Greenland and Antarctic ice cores. All simulations described below use these pH assumptions.

Sulfate deposited at Alert, Canada is likely emitted from Eurasia and the Arctic, whereas sulfate at Site-A, Greenland is influenced by North America and the northern midlatitudes, as it is better exposed to the free troposphere due to its high elevation

20 (Hirdman et al., 2010). Therefore, we consider the change in oxidants over the entire northern midlatitudes (30°–60° N), where we find modeled PD-PI changes of +51%, −7%, and +72%, respectively, for O_3 OH, and H_2O_2. There is little variation in these values compared with several other sub-regions (North America, Greenland, >60° N) of the Northern Hemisphere. At Site-A, we take the PI period to be prior to 1837 CE, as

25 $\Delta^{17}O_{SO_4}$ increases in the Site A record in the late-1800s due to increased North American biomass burning (Alexander et al., 2004), a condition not considered in these simulations. In spite of the 51% increase in O_3 due to anthropogenic activity, there is a PD-PI decrease of 0.5‰ in the measured $\Delta^{17}O_{SO_4}$. The model reproduces this decrease in

the $\Delta^{17}O_{SO_4}$. Coincident with increased PD O_3 production from anthropogenic precursors, increased anthropogenic metal emissions, primarily from coal-fired power plants, increase the fraction of Site-A sulfate formed by S(IV)+O_2 ($\Delta^{17}O_{O_2}$=0‰) from 7% (PI) to 24% (PD). This increase reduces the fraction of sulfate formed by O_3 and H_2O_2 since the PI. If metal-catalyzed oxidation is not included, PD $\Delta^{17}O_{SO_4}$ at Alert is overestimated by 0.6‰. The decrease in pH between the PI and PD also decreases the fraction of SO_4^{2-} formed by O_3 in the aqueous phase. Both increases in anthropogenic metals and a decrease in pH are needed to explain the observations.

At WAIS-Divide, the PI period is taken to be 1850 CE, as the $\Delta^{17}O_{SO_4}$ measurements prior to 1850 are influenced by the 1810 and Tambora (1815 CE) volcanic eruptions and may not represent tropospheric chemistry (Kunasek et al., 2010). We assume that most sulfate deposited at WAIS-Divide, Antarctica originates from oxidation of DMS emitted from the Southern Ocean (Patris et al., 2000). Across the Antarctic region (>60° S), relative modeled PD-PI changes in O_3, OH, and H_2O_2 are +22%, −16%, and +52%, respectively. Despite these oxidant changes, only a very slight change (−0.2‰) in the $\Delta^{17}O_{SO_4}$ at WAIS-Divide is modeled, consistent with observations. The greater increase in H_2O_2 than O_3 suppresses S(IV)+O_3. Thus, slightly increased oxidation by H_2O_2, and decreased oxidation by OH and O_3 results in little net change in $\Delta^{17}O_{SO_4}$ due to offsetting effects of $\Delta^{17}O_{OH}$ and $\Delta^{17}O_{O_3}$. That is, $\Delta^{17}O_{SO_4}$ at WAIS-Divide is sensitive to changing oxidant concentrations, but the oxidants change such that there is little net effect on $\Delta^{17}O_{SO_4}$.

The $\Delta^{17}O_{SO_4}$ is used to assess the two sensitivity studies of PI emissions. Increasing biomass burning emissions to PD levels causes changes relative to the PI base simulation of +9%, −4% and +18% in global O_3, OH, and H_2O_2, respectively. However, $\Delta^{17}O_{SO_4}$ is not impacted at either WAIS-Divide or Site-A, because the oxidant changes associated with biomass burning, particularly OH and O_3, are restricted to low latitudes. Following Mickley et al. (2001), we reduce NO_x emissions and double biogenic VOC emissions to try to reproduce late-1800s O_3 measurements. This changes global O_3,

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OH, and H_2O_2 by -14%, -42%, and $+62\%$, respectively. Surface O_3 concentrations at the sites of late-1800s O_3 measurements are reduced from the base PI simulation by ~ 5 ppbv, but are still ~ 5 ppbv higher than both those reported by Mickley et al. (2001) and the measurements. These changes do impact the polar regions, resulting in reductions in the modeled $\Delta^{17}O_{SO_4}$ by >0.2‰ in both regions, relative to the base PI simulation, due to increases in H_2O_2. The modeled $\Delta^{17}O_{SO_4}$ disagrees with WAIS-Divide measurements and with the PI mean at Site-A (Table 1), although it does fall within the range of Site-A PI measurements. These results suggest that a low bias in the late-1800s O_3 reconstructions may be responsible for the discrepancy with PI O_3 modeling results.

6 Conclusions

We modeled PD and PI oxidants and the resulting oxygen isotopic composition of sulfate ($\Delta^{17}O_{SO_4}$). PI oxidants are broadly consistent with past modeling studies, and the PD-PI difference in modeled $\Delta^{17}O_{SO_4}$ is consistent with measurements from Antarctic and Greenland ice cores and aerosol measurements. At WAIS-Divide, Antarctica, $\Delta^{17}O_{SO_4}$ is sensitive to changing oxidant concentrations, but the PD-PI changes in oxidants offset each other, yielding no net change in $\Delta^{17}O_{SO_4}$. In the Arctic, $\Delta^{17}O_{SO_4}$ is made insensitive to PD-PI changes in oxidants by the increased importance of oxidation by O_2 catalyzed by anthropogenic metals in the PD and the decreased pH. Finally, modeled PI oxidant concentrations cannot be consistent with both ice core $\Delta^{17}O_{SO_4}$ and late-1800s O_3 measurements, suggesting that these O_3 measurements are biased low.

This method for modeling $\Delta^{17}O_{SO_4}$ is now being applied to glacial-interglacial timescales. In contrast to the PD-PI transition, $\Delta^{17}O_{SO_4}$ varies dramatically (by 3.5‰) on the glacial-interglacial timescale in an Antarctic ice core (Alexander et al., 2002). Modeling the oxygen isotopic composition of both sulfate and nitrate in future work will

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help to further constrain paleo-oxidants, as all non-oxidant factors that impact sulfate or nitrate formation are mutually exclusive.

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Preindustrial oxidants and isotopes of ice core sulfate

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Table 1. Difference in $\Delta^{17}O_{SO_4}$ between PD simulations and the base PI simulation (pH=5.0). Sensitivity studies are also relative to the base PI simulation, and are at a cloud-water pH of 5.0. Italics indicate agreement with measurements within the analytical uncertainty of the measurements. Simulations without metal-catalyzed oxidation by O_2 are indicated by "no met".

Simulation (pH)	Site-A and alert	WAIS-divide
Measurements	−0.5±0.3	−0.2±0.3
PD (4.5)	*−0.7*	−1.3
PD (5.0)	0.0	*−0.2*
PD (4.5), no met.	0.0	−1.2
PD (5.0), no met.	2.2	−0.6
Sensitivity studies		
PD biomass burning	*0.0*	*0.0*
Low-O_3	*−0.2*	−0.4

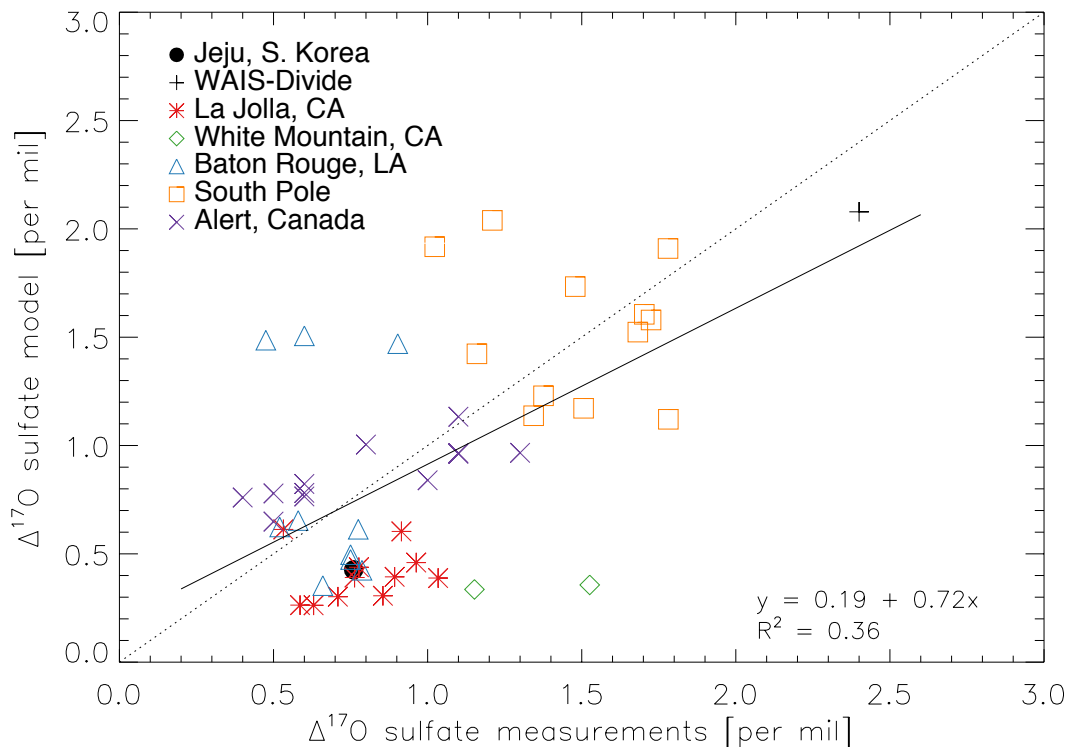**Fig. 1.** Comparison of modeled PD $\Delta^{17}O_{SO_4}$ at the surface to measurements of annual (WAIS-divide, Antarctica: Kunasek et al., 2010), seasonal (Jeju, South Korea: J. McCabe, personal communication, 2001), and monthly (La Jolla, CA, White Mountain Research Station, CA: Lee, 2000; Baton Rouge, LA: Jenkins and Bao, 2006; South Pole, Antarctica: G. Michalski, personal communication, 2001; J. McCabe, personal communication, 2004; Alert Canada: McCabe et al., 2006) $\Delta^{17}O_{SO_4}$ from firn, aerosols, and precipitation. The linear least-squares regression line (solid) and $y=x$ line (dotted) are shown.

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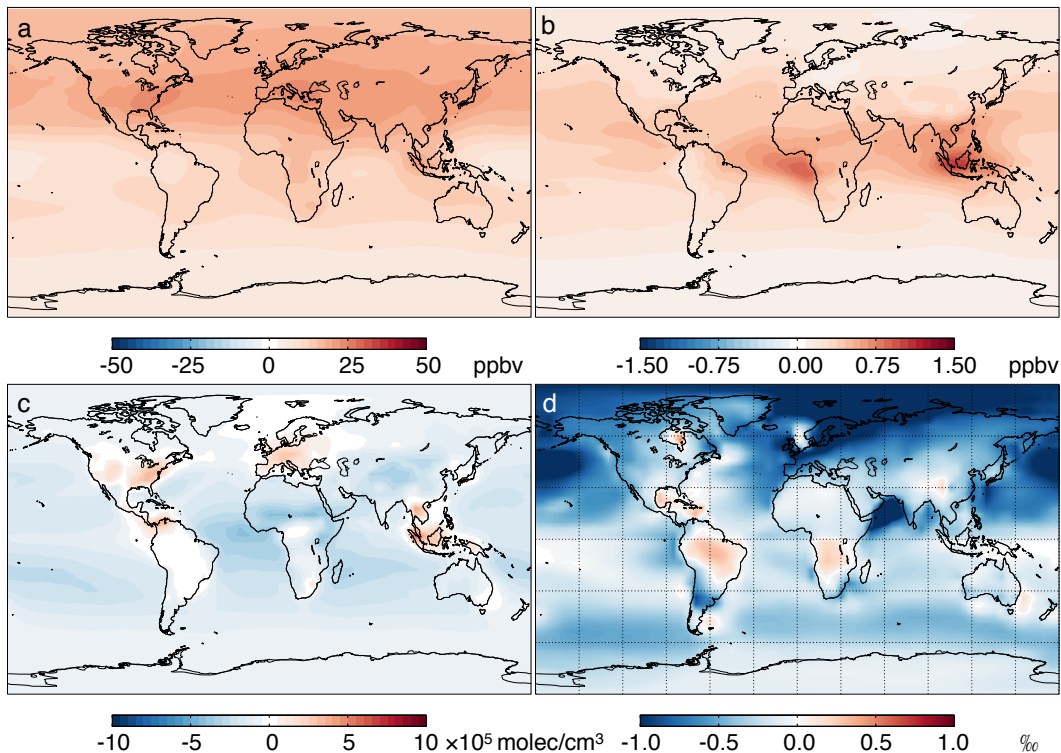
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Fig. 2. PD-PI change in global tropospheric mean concentrations of **(a)** O_3, **(b)** H_2O_2, **(c)** OH, and **(d)** $\Delta^{17}O_{SO_4}$. The $\Delta^{17}O_{SO_4}$ plot is the difference of the PI (pH=5.0) and PD (NH pH=4.5; SH pH=5.0) simulations.