

## RESEARCH ARTICLE

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## Key Points:

- O<sub>3</sub> photochemistry and temperature control clumped isotopes in atmospheric O<sub>2</sub>
- Stratospheric and tropospheric Δ<sub>36</sub> signatures are distinct
- Circulation-sensitive distribution of tropospheric O<sub>3</sub> controls tropospheric Δ<sub>36</sub>

## Supporting Information:

- Supporting Information S1

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## Isotopic ordering in atmospheric O<sub>2</sub> as a tracer of ozone photochemistry and the tropical atmosphere

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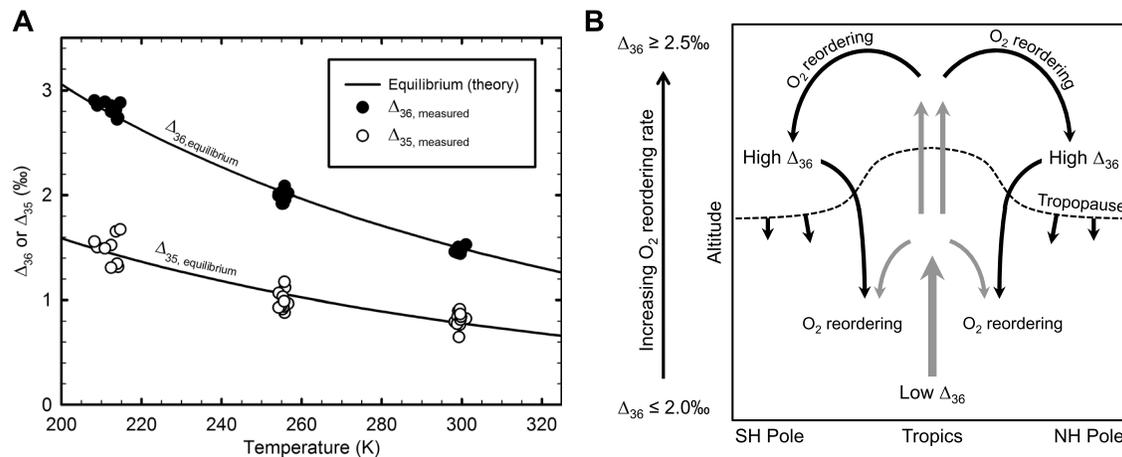
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**Abstract** The distribution of isotopes within O<sub>2</sub> molecules can be rapidly altered when they react with atomic oxygen. This mechanism is globally important: while other contributions to the global budget of O<sub>2</sub> impart isotopic signatures, the O(<sup>3</sup>P) + O<sub>2</sub> reaction resets all such signatures in the atmosphere on subdecadal timescales. Consequently, the isotopic distribution within O<sub>2</sub> is determined by O<sub>3</sub> photochemistry and the circulation patterns that control where that photochemistry occurs. The variability of isotopic ordering in O<sub>2</sub> has not been established, however. We present new measurements of <sup>18</sup>O<sup>18</sup>O in air (reported as Δ<sub>36</sub> values) from the surface to 33 km altitude. They confirm the basic features of the clumped-isotope budget of O<sub>2</sub>: Stratospheric air has higher Δ<sub>36</sub> values than tropospheric air (i.e., more <sup>18</sup>O<sup>18</sup>O), reflecting colder temperatures and fast photochemical cycling of O<sub>3</sub>. Lower Δ<sub>36</sub> values in the troposphere arise from photochemistry at warmer temperatures balanced by the influx of high-Δ<sub>36</sub> air from the stratosphere. These observations agree with predictions derived from the GEOS-Chem chemical transport model, which provides additional insight. We find a link between tropical circulation patterns and regions where Δ<sub>36</sub> values are reset in the troposphere. The dynamics of these regions influences lapse rates, vertical and horizontal patterns of O<sub>2</sub> reordering, and thus the isotopic distribution toward which O<sub>2</sub> is driven in the troposphere. Temporal variations in Δ<sub>36</sub> values at the surface should therefore reflect changes in tropospheric temperatures, photochemistry, and circulation. Our results suggest that the tropospheric O<sub>3</sub> burden has remained within a ±10% range since 1978.

### 1. Introduction

Global patterns of atmospheric circulation have changed dramatically with climate in the past [Mayewski et al., 1997; Vecchi et al., 2006; Eagle et al., 2013; Oster et al., 2015]. They are expected to change in the future, but accurately predicting the changes in heat and moisture transport, trace gases, and climate sensitivity remains a challenge [Schneider et al., 2010; Shepherd, 2014; Sherwood et al., 2014; Bony et al., 2015]. The paleoclimate record of circulation could be a guide; it is typically inferred from the analysis of hydroclimate [Wang et al., 2008; Yoshimura et al., 2008; Risi et al., 2010] and mineral dust records [Mayewski et al., 1997]. However, these records tend only to represent patterns of variability at the surface. The record of dynamic “vertical” properties of the atmosphere such as the strength of tropical upwelling must be inferred from these horizontal patterns using general circulation models [Haigh, 1996; Shindell et al., 2001; Partin et al., 2007; Schneider et al., 2010; Tripathi et al., 2014]. These inferences are difficult to test given the paucity of geological records for these processes, so their behavior on climatically relevant timescales is not well known. In this manuscript, we explore the viability of clumped isotopes in O<sub>2</sub> as a tracer of atmospheric chemistry and physics on decadal and longer timescales.

The tracer—the proportional abundance of <sup>18</sup>O<sup>18</sup>O in O<sub>2</sub>, quantified as the Δ<sub>36</sub> value—is sensitive to thermal and photochemical properties of the atmosphere (Figure 1). Ozone photochemistry (or, more precisely, the O(<sup>3</sup>P) + O<sub>2</sub> isotope exchange reaction) drives the proportions of <sup>18</sup>O<sup>18</sup>O and <sup>17</sup>O<sup>18</sup>O toward isotopic



**Figure 1.** Factors controlling isotopic ordering in  $O_2$  on decadal timescales. (a) Photochemically catalyzed  $O(^3P) + O_2$  isotope exchange equilibrium yields nonstochastic enrichments in  $^{18}O^{18}O$  and  $^{17}O^{18}O$  (shown as  $\Delta_{36}$  and  $\Delta_{35}$  values). Data points from the instrument at Rice University are compared with theoretical predictions for the equilibrium temperature dependence. (b) Schematic of the atmospheric  $\Delta_{36}$  budget. Oxygen isotope exchange reactions occur throughout the atmosphere, but the rates of reaction generally increase with altitude. Also, temperature decreases with altitude and transport mixes air from different altitudes. Therefore, the  $\Delta_{36}$  budget is characterized by  $O_2$  isotope exchange reactions occurring at different temperatures, modulated by air mass mixing. The troposphere has  $\Delta_{36}$  values that reflect the balance of photochemical isotope exchange kinetics (i.e., locally incomplete isotopic equilibration), tropospheric circulation, and STT. Biological cycling of  $O_2$  has negligible effects on the global  $\Delta_{36}$  budget on decadal timescales.

equilibrium. Subtle differences in vibrational energies of the  $O_2$  isotopologues favors  $^{18}O^{18}O$  and  $^{17}O^{18}O$  formation more so than chance alone would dictate. As temperatures decrease, the preference for  $^{18}O^{18}O$  formation increases by  $0.010\text{‰}/K$  to  $0.024\text{‰}/K$  at Earth surface temperatures, resulting in equilibrium  $\Delta_{36}$  values that range from  $1.49\text{‰}$  to  $3.06\text{‰}$  between  $300\text{ K}$  and  $200\text{ K}$ , respectively (see Figure 1a; excesses in  $^{17}O^{18}O$ —i.e.,  $\Delta_{35}$  values—are about half those for  $^{18}O^{18}O$  at equilibrium) [Wang *et al.*, 2004]. Ozone photochemistry in cold regions of the atmosphere tends to increase  $\Delta_{36}$  values, while  $O_3$  photochemistry in warmer regions tends to decrease  $\Delta_{36}$  values, within these limits. The approach to local isotopic equilibrium in the atmosphere is kinetically limited by  $O(^3P)$  concentrations, which can vary by many orders magnitude depending on altitude [Yeung *et al.*, 2014].

In the stratosphere,  $O_3$  photochemistry rearranges the isotopes in  $O_2$  on timescales of months or less toward  $\Delta_{36} \geq 2.3\text{‰}$ , corresponding to stratospheric temperatures below  $\sim 240\text{ K}$  [Yeung *et al.*, 2012, 2014]. In the troposphere,  $O_3$  photochemistry rearranges isotopes in  $O_2$  as well, but orders of magnitude more slowly and at warmer temperatures (Figure 1b). This contrast has two consequences. First,  $\Delta_{36}$  values are lower in the troposphere because isotope reordering generally occurs at warmer temperatures. Second, tropospheric  $\Delta_{36}$  values reflect the balance of tropospheric and stratospheric processes—both photochemical and dynamical—that can vary on a range of timescales.

The spatial patterns of  $O_3$  photochemistry determine tropospheric and stratospheric contributions to the atmospheric  $\Delta_{36}$  budget. They are driven by precursor emissions as well as mass transport. Regions of deep convection in the midlatitudes, for example, are associated with mass exchange between the surface and the lowermost stratosphere that has global consequences for the budget of  $O_3$  [Stohl *et al.*, 2003; Wu *et al.*, 2007; Škerlak *et al.*, 2014; Barth *et al.*, 2015]. The distribution of these features, as well as others that transport  $O_3$  and its precursors, affect atmospheric  $\Delta_{36}$  values by determining the rates and temperatures at which  $\Delta_{36}$  values are reset.

Evidence for the importance of the  $O_3$  distribution in the troposphere can be found in the measured  $\Delta_{36}$  values at the surface. Air in Los Angeles had a  $\Delta_{36}$  value of  $1.97 \pm 0.07\text{‰}$  in 2012–2014 (2 SE,  $n = 23$ ), corresponding to an effective temperature of  $260 \pm 5\text{ K}$  [Yeung *et al.*, 2014]. This temperature is significantly colder than local mean-annual temperatures ( $290\text{ K}$ ), yet warmer than typical stratospheric temperatures. While stratosphere-troposphere exchange (STE) and mixing is undoubtedly important, patterns of  $O_3$  photochemistry in the free troposphere, which are governed by surface emissions and atmospheric circulation, may play a primary role in determining tropospheric  $\Delta_{36}$  values. Increasing rates of  $O_3$  photochemistry

near the surface, for example, would tend to drive tropospheric  $\Delta_{36}$  values lower toward warmer effective temperatures, all else being equal.

Here we test the link between circulation,  $O_3$ , and  $\Delta_{36}$  values in a combined observational and modeling study. We obtain empirical constraints on the global budget of clumped isotopes in  $O_2$  using a new set of atmospheric  $\Delta_{36}$  measurements, which we interpret with the aid of the GEOS-Chem global 3-D chemical transport model. We confirm that the primary control on  $\Delta_{36}$  values in both the stratosphere and troposphere is the spatial pattern of  $O_3$  photochemistry. In the stratosphere,  $\Delta_{36}$  values resembling local equilibrium are associated with rapid isotope reordering and high concentrations of  $O_3$ . In the troposphere, patterns of  $O_2$  isotope reordering rates are closely associated with features of the tropical overturning circulation. When integrated globally, these patterns explain the observed surface  $\Delta_{36}$  values after including the effects of STE. Our modeling results indicate that anthropogenic effects on tropospheric  $O_3$  concentrations over the past century may be detectable in the ice-core record of  $\Delta_{36}$ . Furthermore, changes in free-troposphere temperatures may be detectable on longer timescales.

## 2. Methods

### 2.1. Clumped-Isotope Measurements

Isotopic ordering in  $O_2$  is quantified in reference to the stochastic (random) distribution of isotopes according to the definition  $\Delta_{36} = ({}^{36}R_{\text{sample}}/{}^{36}R_{\text{stochastic}} - 1)$ , where  ${}^{36}R_{\text{sample}} = {}^{36}O_2/{}^{32}O_2$  and  ${}^{36}R_{\text{stochastic}} = ({}^{18}O/{}^{16}O)^2$ . Similarly,  $\Delta_{35} = ({}^{35}R_{\text{sample}}/{}^{35}R_{\text{stochastic}} - 1)$ , where  ${}^{35}R_{\text{sample}} = {}^{35}O_2/{}^{32}O_2$  and  ${}^{35}R_{\text{stochastic}} = 2 \times ({}^{18}O/{}^{16}O) \times ({}^{17}O/{}^{16}O)$ . Isotopologue measurements were performed at UCLA and Rice University after gas chromatographic separation of  $O_2$  from other components of air according to established techniques [Yeung *et al.*, 2012]. They were calibrated using photochemically and thermally catalyzed equilibrations of standard gases at known temperatures performed during the same analytical sessions [Yeung *et al.*, 2014]. The theoretical equilibrium temperature dependence of  $\Delta_{36}$  and  $\Delta_{35}$  values are calculated from partition function ratios and harmonic vibrational frequencies for the  $O_2$  isotopologues; they are likely accurate within 0.01‰ [Wang *et al.*, 2004].

Measurements performed at UCLA have an external reproducibility of  $\pm 0.17\%$  in  $\Delta_{36}$  ( $1\sigma$ , on a ThermoScientific MAT 253) based on replicate analyses of air [Yeung *et al.*, 2014], whereas measurements performed at Rice University on a high-resolution isotope ratio mass spectrometer (a modified Nu Instruments *Perspective IS*) had significantly better external reproducibility of  $\pm 0.038\%$  in  $\Delta_{36}$  ( $1\sigma$ ). The latter reproducibility corresponds to the pooled standard deviation of 11 samples in this study that were analyzed in duplicate or triplicate at Rice (see Table S1 in the supporting information), which is similar to the instrumental uncertainty (1 SE for 2000s integration time using ion currents of 40 nA and 0.2 pA for  ${}^{16}O^{16}O^+$  and  ${}^{18}O^{18}O^+$ , respectively).

We analyzed whole-air samples from the stratosphere and troposphere collected during three Northern Hemisphere field campaigns between 2000 and 2012: The SOLVE campaign in the boreal winter of 1999/2000 [Newman *et al.*, 2002], a scientific balloon flight from Fort Sumner, NM (USA) in September 2004 [Froidevaux *et al.*, 2006; Wiegel *et al.*, 2013], and the DC3 campaign in the Southeastern USA in May/June 2012 [Barth *et al.*, 2015]. Atmospheric samples were obtained as whole-air samples using the methods described in earlier publications [Lueb *et al.*, 1975]. In addition, we measured subsamples of archived air from Cape Grim, Australia in the Southern Hemisphere between 1978 and 2013 [Langenfelds *et al.*, 1996].

### 2.2. Two-Box Modeling of Atmospheric $\Delta_{36}$ Values

We employed the two-box model of the stratosphere and troposphere described in Yeung *et al.* [2012] to obtain insights into the budget of clumped isotopes in atmospheric  $O_2$ . Briefly, the tropospheric  ${}^{18}O^{18}O$  budget can be represented by the following mass balance equation at steady state:

$$F_{ST}\chi_S^{36} - F_{TS}\chi_T^{36} + F_P\chi_P^{36} - F_R\chi_T^{36}a_{36,R} - E_{\text{trop}}(\chi_T^{36} - \chi_{\text{Tequil}}^{36}) = 0 \quad (1)$$

with similar equations for the other  $O_2$  isotopologues. The first and second terms represent isotopic fluxes due to STE, with  $F_{ST}$  and  $F_{TS}$  being the stratosphere-to-troposphere and troposphere-to-stratosphere fluxes of  $O_2$ , respectively. We used annual net mass fluxes of  $4.6 \times 10^{18} \text{ mol } O_2 \text{ yr}^{-1}$  obtained by applying the method of Appenzeller *et al.* [1996] on monthly mean air mass data. They are similar to literature estimates [Schoeberl, 2004] and allow our atmospheric simulations to be evaluated using their own transport schemes.

Biological cycling is expressed in the third and fourth terms, with  $F_P$  and  $F_R$  being the  $O_2$  fluxes due to photosynthesis and respiration, respectively ( $3.43 \times 10^{16} \text{ mol } O_2 \text{ yr}^{-1}$  [Blunier et al., 2012]). The fifth term represents the tropospheric equilibration flux of  $O_2$ , with  $E_{\text{trop}}$  being the tropospheric isotope exchange rate. The mole fractions  $\chi$  represent end-member isotopologue abundances of mixing end-members (subscripts  $S$  and  $T$  for stratosphere and troposphere) and process signatures (subscripts  $P$  and  $T_{\text{equil}}$  for photosynthesis and tropospheric isotope equilibration). The  $\alpha_R$  value is the isotopic fractionation factor for respiration. Generally, biological cycling terms are small because while biological cycling alters the isotopic composition in  $O_2$  on centennial to millennial timescales [Bender et al., 1994; Severinghaus et al., 2009], the whole-troposphere  $O_2$  reordering timescale is subdecadal [Yeung et al., 2012].

Assuming tropospheric  $O_2$  is well mixed on annual timescales, equation (1) can be approximated by

$$F_{ST}\Delta_{36,\text{strat}} - F_{TS}\Delta_{36,\text{trop}} - E_{\text{trop}}(\Delta_{36,\text{trop}} - \Delta_{36,\text{Tequil}}) \approx 0 \quad (2)$$

in which  $\Delta_{36,\text{strat}}$  is the end-member composition of stratospheric  $O_2$  entering the troposphere,  $\Delta_{36,\text{trop}}$  is the mean  $\Delta_{36}$  value of tropospheric  $O_2$ , and  $\Delta_{36,\text{Tequil}}$  is the whole-troposphere equilibration end-member (see section 2.3). The use of  $\Delta_{36}$  values rather than mole fractions in equation (2) is reasonably accurate because isotope exchange reactions do not detectably alter the bulk isotopic composition of  $O_2$ ;  $\Delta_{36}$  values therefore vary linearly upon mixing. The approximate equation above illustrates the balance of stratospheric and tropospheric processes governing the  $\Delta_{36}$  budget on annual timescales: Mass transport (first two terms) is balanced by tropospheric isotope reordering (third term). Biological cycling decreases the steady state  $\Delta_{36,\text{trop}}$  value by  $\sim 0.01\text{‰}$  [Yeung et al., 2015] and varies minimally on these timescales [Severinghaus et al., 2009].

### 2.3. Chemical Transport Modeling Using GEOS-Chem

GEOS-Chem (version 10-01d; <http://www.geos-chem.org>) is a global three-dimensional chemical transport model of atmospheric photochemistry and aerosols driven by assimilated meteorology from the NASA Global Modeling and Assimilation Office. Here we used both the Modern-Era Retrospective Analysis for Research and Applications (MERRA) [Rienecker et al., 2011] and the Goddard Earth Observing System version 4 (GEOS-4) meteorological reanalyses [Bloom et al., 2005] to separately drive the model for the year 2005. MERRA is available at  $1/2^\circ$  latitude by  $2/3^\circ$  longitude horizontal resolution with 72 vertical layers ( $\sim 38$  in the tropical troposphere) up to 0.01 hPa. GEOS-4 is available at  $1^\circ$  latitude by  $1.25^\circ$  longitude horizontal resolution with 55 vertical layers ( $\sim 17$  in the troposphere) up to 0.01 hPa. We degraded both products to  $2^\circ$  latitude by  $2.5^\circ$  longitude horizontal resolution for input to GEOS-Chem while maintaining native vertical resolution. We used the Unified Chemical Mechanism (UCX) that fully resolves both tropospheric and stratospheric chemistry [Eastham et al., 2014], including online calculation of  $O(^3P)$  and  $O(^1D)$  chemistry. This mechanism yields modeled  $O_3$  within  $\pm 17\%$  of ozonesonde data ( $\pm 11\%$  in the tropics) when driven by GEOS-5 meteorology. Each simulation was repeatedly cycled over 2004 and 2005 for five iterations, with the first 9 years discarded as initialization.

Base anthropogenic emissions are from the EDGAR v3.2-FT2000 inventory for inorganic compounds [Olivier et al., 2005] and from the RETRO inventory for organic compounds [Schultz et al., 2007], with regional overwrites for the United States (EPA National Emissions Inventory 2005), Canada (National Pollutant Release Inventory), Mexico [Kuhns et al., 2005], Europe [Auvray and Bey, 2005], and South and East Asia [Streets et al., 2006] and are all scaled to year 2005 on the basis of economic data [van Donkelaar et al., 2008]. Separate inventories are used for ammonia [Bouwman et al., 1997], black carbon [Leibensperger et al., 2012], and ethane [Xiao et al., 2008]. Methane is prescribed at the surface to a global mean of 1780 ppbv and allowed to advect and be consumed, with similar treatment of chlorofluorocarbons and other long-lived stratospheric ozone-depleting substances [Eastham et al., 2014]. Aircraft emissions are described by Stettler et al. [2011] and distributed at altitude along flight corridors. Shipping emissions are described by Vinken et al. [2011]. Biomass burning emissions are from the Global Fire Emissions Database version 3 [van der Werf et al., 2010]. Biogenic hydrocarbon emissions from terrestrial plants follow the Model of Emissions of Gases and Aerosols from Nature scheme version 2.1 [Guenther et al., 2012]. Lightning  $NO_x$  emissions are computed online in active deep convection, as described by Murray et al. [2012]. Soil microbial  $NO_x$  emissions are described by Hudman et al. [2012]. In addition to the base 2005 emission simulation, we also perform a preindustrial-like emissions scenario, in which fuel combustion and industrial and agricultural emissions are removed and surface methane is set to 730 ppbv.

Note that GEOS-Chem does not yet have the capability to treat oxygen isotopes and isotopologues explicitly. Explicit treatment imposes a significant computational burden (>300 additional reactions for the O<sub>2</sub> photochemical system alone [Yeung *et al.*, 2014]) and a parameterization for their temporal evolution has not yet been developed. Consequently, the detailed transport histories of O<sub>2</sub> isotopologues are not known, and spatial variations in Δ<sub>36</sub> are not simulated. Some inferences can be made by comparing simulated isotope equilibration timescales with empirically constrained transport timescales, however. Furthermore, if Δ<sub>36</sub> is well mixed in the troposphere, quantities integrated over the whole troposphere can be compared to the surface observations using the two-box model described in section 2.2.

We used modeled O(<sup>3</sup>P) and O<sub>2</sub> concentrations, known isotope exchange rates ( $k_{\text{exch}}$ , which are weakly temperature dependent) [Wiegell *et al.*, 1997], temperature ( $T$ ), air mass ( $m$ ), and residence times ( $\tau_{\text{box}}$ ) in each grid box to calculate the tropospheric rate of isotope exchange ( $E_{\text{trop}}$ ) and the mean temperature at which O<sub>2</sub> isotope exchange occurs in the troposphere ( $T_{\text{equil}}$ , yielding a corresponding Δ<sub>36,Tequil</sub>). Unless otherwise specified, we used annual-mean concentrations and temperatures to calculate the quantities described below. Using daytime values yielded identical results at the reported level of precision.

Formally,  $E_{\text{trop}}$  (mol yr<sup>-1</sup>) can be defined as the mass- and time-weighted integral of equilibration rates  $E_V$  in all tropospheric volumes  $dV$ :

$$E_{\text{trop}} = \frac{\int_{V_{\text{trop}}} E_V([O(^3P)], [O_2], k_{\text{exch}}(T)) m_V \tau_{\text{trop},V} dV}{\int_{V_{\text{trop}}} m_V \tau_{\text{trop},V} dV} \times V_{\text{trop}} \quad (3)$$

for which  $\int V_{\text{trop}} dV = V_{\text{trop}}$ . Equation (3) can be discretized as

$$E_{\text{trop}} \approx \frac{\sum_{\text{trop grid boxes}} \{k_{\text{exch}}(T) [O(^3P)] [O_2] \times m_{\text{box}} \times \tau_{\text{box}}\}}{\sum_{\text{trop grid boxes}} \{m_{\text{box}} \times \tau_{\text{box}}\}} \times V_{\text{trop}} \quad (4)$$

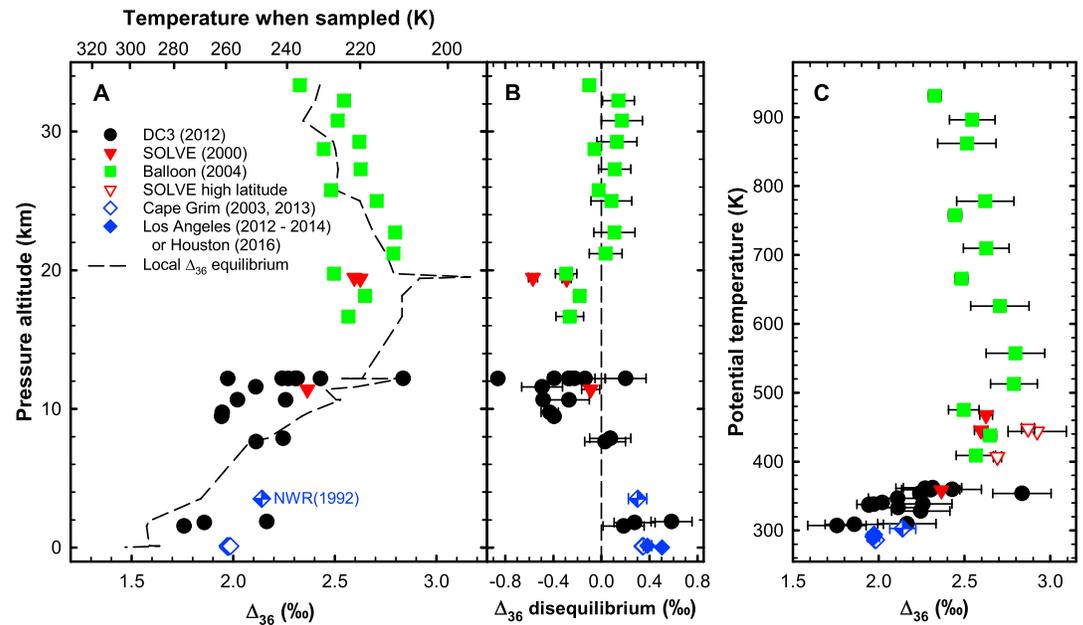
$$T_{\text{equil}} \approx \frac{\sum_{\text{trop grid boxes}} \{k_{\text{exch}}(T) [O(^3P)] [O_2] \times m_{\text{box}} \times \tau_{\text{box}} \times T_{\text{box}}\}}{\sum_{\text{trop grid boxes}} \{k_{\text{exch}}(T) [O(^3P)] [O_2] \times m_{\text{box}} \times \tau_{\text{box}}\}} \quad (5)$$

The first term in equation (4) represents the mass-weighted mean rate of isotope equilibration in mol m<sup>-3</sup> yr<sup>-1</sup>. For the purposes of weighting, residence times in each grid box (allowing for reentry) are assumed to be proportional to the air density at steady state (see the Appendix A). The total volume of the troposphere ( $V_{\text{trop}}$ ) depends on the mean altitude of the tropopause, which varies according to how the tropopause is defined. It was not independently varied in this study but ranges from 4 to 8 × 10<sup>18</sup> m<sup>3</sup> for mean tropopause altitudes between 8 km and 15 km. For this study, we use the air mass and density in each grid box, combined with the dynamical tropopause as defined by each meteorological scheme, to calculate the volume of the troposphere. Equation (5) represents the tropospheric  $T_{\text{equil}}$  resulting from the weighting scheme in equation (3). The whole-troposphere Δ<sub>36,Tequil</sub> values were calculated using the theoretical temperature dependence of Δ<sub>36</sub> at isotopic equilibrium [Wang *et al.*, 2004]. Uncertainties in  $E_{\text{trop}}$  and  $T_{\text{equil}}$  arise from the definition of the tropopause, parameterization of transport (residence times for each tropospheric box, in particular), as well as the intrinsic model-dependent uncertainties. A discussion of these uncertainties can be found in the Appendix A.

### 3. Results

#### 3.1. Measurements of the Present-Day Atmosphere

In the stratosphere, measured Δ<sub>36</sub> values were typically between 2.5 and 3.0‰, consistent across field campaigns, while Δ<sub>36</sub> values were between 1.8 and 2.3‰ in the troposphere (Figures 2a and 2c). Elevated Δ<sub>36</sub> values in the midlatitude lower and middle stratosphere resemble the equilibrium values for the temperatures measured at the time of sampling (Figure 2b). Evidence for elevated Δ<sub>35</sub> values consistent with isotopic equilibrium was also observed (see Table S1), but the observations were less precise due to lower natural abundances of <sup>17</sup>O<sup>18</sup>O. The bulk isotopic composition is constant within analytical uncertainties (i.e., δ<sup>18</sup>O and δ<sup>17</sup>O; Table S1), indicating that mesospheric influences are likely negligible [Thiemens *et al.*, 1995; Liang *et al.*, 2007; Yeung *et al.*, 2009].

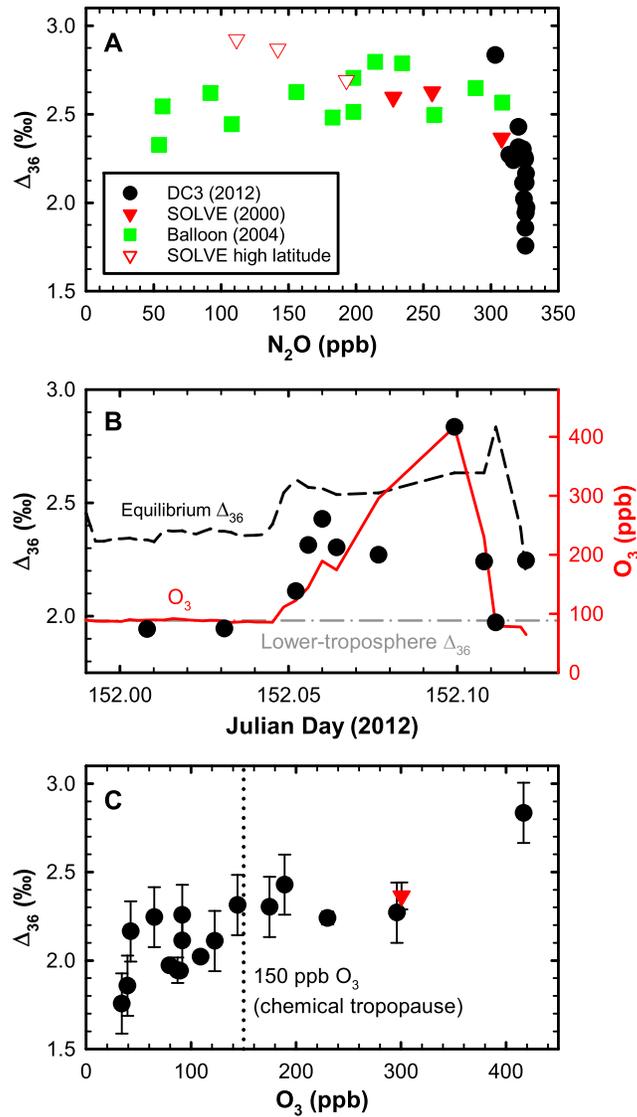


**Figure 2.** Measured atmospheric  $\Delta_{36}$  values versus height. Pressure-altitude versus (a)  $\Delta_{36}$  values and (b)  $\Delta_{36}$  disequilibrium in the midlatitudes are shown, as well as (c) potential temperature,  $\theta$ , versus  $\Delta_{36}$  values for the entire data set. The checked symbol corresponds to air sampled at Niwot Ridge, Colorado (NWR, 40.05°N, -105.6°W; 3523 m asl) in 1992. Dashed lines show equilibrium  $\Delta_{36}$  values corresponding to the temperatures at which the air was sampled. Error bars represent 1 $\sigma$  uncertainties, except for surface samples, for which the error bars represent 1 standard error of the mean. Error bars have been omitted from Figure 2a for clarity.

The  $\Delta_{36}$  values decrease with altitude from ~18 km to the surface ( $\theta < 500$  K), across all latitudes and years (Figure 2c). Replicate  $\Delta_{36}$  measurements at the surface in both hemispheres indicate that surface air is not at isotopic equilibrium with local temperatures (e.g.,  $p < 5 \times 10^{-9}$  in Houston; Table S1). These observations are consistent with our expectations of rapid isotope reordering in the middle stratosphere and slower isotope reordering in the lower stratosphere and troposphere.

We observe no correlation between  $\Delta_{36}$  and  $N_2O$  above the lowermost stratosphere in the Fort Sumner balloon samples ( $r^2 = 0.23$  for  $\theta > 380$  K), but a negative correlation for the SOLVE samples ( $r^2 = 0.95$ ; Figure 3a). The former is consistent with an isotope reordering timescale faster than the timescale for mixing in the lower stratosphere (i.e., several months [Boering et al., 1996; Plumb, 2007]). The latter may be related to the altitudes from which they were sampled: both the Fort Sumner balloon samples and SOLVE samples from 16 to 20 km ( $400 \text{ K} < \theta < 500 \text{ K}$ ) are in isotopic disequilibrium to a similar degree (Figure 2b). If the isotope exchange rates in the lower stratosphere are sufficiently slow compared to timescales of mixing, isotopic disequilibrium would be expected because the  $\Delta_{36}$  values of these samples would represent isotopic exchange reactions integrated along their transport pathway, thus bearing little resemblance to the temperatures at time of sampling except by coincidence. Yet the short timescales of isotope equilibration in that region may be too short for the observed correlation to represent a global “slope equilibrium” [after Plumb and Ko, 1992] that could be used to derive a net isotope flux between stratosphere and troposphere. Additional measurements on similar samples may address the generality of this correlation in the lower troposphere and its potential utility for constraining STE fluxes of  $\Delta_{36}$ .

The  $\Delta_{36}$  values for samples taken during a nearly isentropic and isothermal (within 3 K) flight across the tropopause indicate that mixing strongly modulates  $\Delta_{36}$  values near the tropopause (Figure 3b). The timescales of isentropic transport are equal to or shorter than the timescales for isotopic equilibration in that region ( $\tau_{\text{equilibration}} \sim \text{months}$  versus transport within weeks [Boering et al., 1996]), so the samples likely represent mixtures of air from different regions. A 0.9‰ range was observed during the initial tropopause crossing when a 0.3‰ range would be expected based on temperatures alone (Figure 3b). Similarly elevated  $\Delta_{36}$  values were observed for some samples obtained from the upper troposphere, where intrusions of



**Figure 3.** Comparison of atmospheric  $\Delta_{36}$  values with other tracers. (a)  $\Delta_{36}$  values plotted against  $N_2O$ . A correlation implies that timescales of  $O_2$  isotope reordering are longer than those of mass transport. The correlation observed for SOLVE samples requires more data to verify (see section 3.1). (b) Measured  $\Delta_{36}$  values for a cross-tropopause flight during the DC3 campaign, plotted with  $O_3$  concentrations and  $\Delta_{36}$  values for local isotopic equilibrium. (c) Measured  $\Delta_{36}$  versus  $O_3$  near the 150 ppb chemical tropopause. Note the data from the SOLVE mission (red triangle; mean  $\pm 1\sigma$ ,  $n = 3$ ), which is consistent with the DC3 data despite the 12 year difference in sampling date. Error bars have been omitted from Figures 3a and 3b for clarity.

stratospheric air masses often occur [Stohl *et al.*, 2003; Škerlak *et al.*, 2014]. Tropospheric air from 8 to 12 km ( $\theta \approx 330\text{--}350$  K) sampled during the DC3 campaign was up to 0.3‰ higher in  $\Delta_{36}$  than in surface air (Figures 2 and 3). Air sampled from Niwot Ridge, CO (3523 m above sea level (asl)) in 1992, also has a  $\Delta_{36}$  value  $0.15 \pm 0.08\text{‰}$  ( $1\sigma$ ) higher than air sampled from Cape Grim that same year (94 m asl; Figure 2a and Table S1). These variations may be episodic, as not all upper troposphere samples had elevated  $\Delta_{36}$  values. Many of the DC3 samples were sampled in deep convective midlatitude storms that are associated with STE, and Niwot Ridge is influenced by periodic stratosphere-to-troposphere transport (STT) of air [Pan *et al.*, 2014; Schroeder *et al.*, 2014; Sullivan *et al.*, 2015]. Some  $\Delta_{36}$  values nevertheless appear close to local isotopic equilibrium (Figure 2b). These agreements are probably coincidental, as air mass residence times in this region are far shorter than expected local isotope equilibration timescales ( $\tau_{\text{equilibration}} > 1$  year).

**Table 1.**  $\Delta_{36}$  Values Measured in Archived Surface Air

Sample	Date(s)	Latitude (°N)	Longitude (°W)	$\Delta_{36} \pm 1 \text{ SE}$ (‰)	<i>n</i>
Houston	2016	29.76	95.37	$1.972 \pm 0.011$	17
Los Angeles <sup>a</sup>	2012–2014	34.07	118.44	$1.97 \pm 0.03$	23
Cape Grim (G050-211)	7/5/2013	−40.68	−144.69	$1.978 \pm 0.011$	3
Cape Grim (G050-209)	2/17/2003	−40.68	−144.69	$1.985 \pm 0.017$	3
Cape Grim (G050-208)	9/23/1992	−40.68	−144.69	$1.963 \pm 0.020$	3
Cape Grim (G050-207)	2/6/1986	−40.68	−144.69	$1.978 \pm 0.024$	3
Cape Grim (G050-206)	4/26/1978	−40.68	−144.69	$1.974 \pm 0.027$	3

<sup>a</sup>From Yeung *et al.* [2014].

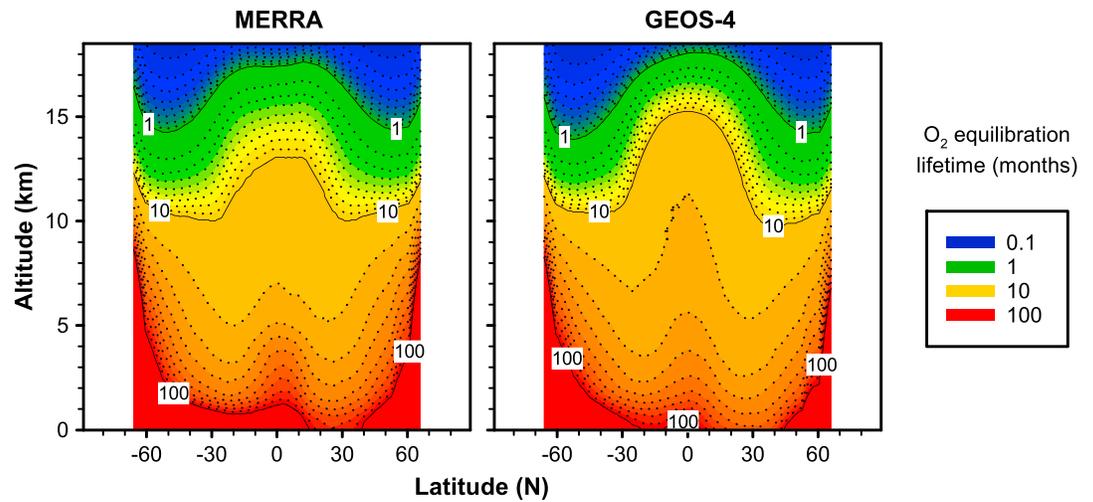
The mean of air measurements in Los Angeles ( $\Delta_{36} = 1.97 \pm 0.03\text{‰}$ , 1 SE), Houston ( $\Delta_{36} = 1.972 \pm 0.011\text{‰}$ , 1 SE), and Cape Grim (e.g.,  $\Delta_{36} = 1.978 \pm 0.011\text{‰}$  in 2013, 1 SE; see Table 1) were indistinguishable within analytical uncertainties. Furthermore,  $\Delta_{36}$  values from 1 to 2 km, sampled during DC3 ( $\Delta_{36} = 1.93 \pm 0.12\text{‰}$ ; 1 SE, analyzed at UCLA), are also similar to surface  $\Delta_{36}$  values. This close correspondence in  $\Delta_{36}$  between Northern and Southern Hemisphere sites, including one from a high- $\text{O}_3$  region (Los Angeles basin) and one from a low- $\text{O}_3$  region (Cape Grim), suggests that surface  $\Delta_{36}$  values are insensitive to the local differences in photochemistry set by abundances of nitrogen oxide radicals and volatile organic compounds. Moreover, surface  $\Delta_{36}$  values are not at isotopic equilibrium with their surroundings, and they are too low to be stratospheric in origin (where  $\Delta_{36} \geq 2.3\text{‰}$ ). They must reflect  $\text{O}_3$  photochemistry taking place elsewhere in the troposphere. We suggest that mean  $\Delta_{36}$  values at the surface reflect  $\text{O}_3$  photochemistry integrated at least hemispherically, if not throughout the whole troposphere: Rapid tropospheric stirring [Wofsy, 2011; Waugh *et al.*, 2013] will lead to a narrow distribution of  $\Delta_{36}$  values at the surface if isotopic equilibration is slower than the  $\sim 1$  year mixing timescale of the troposphere. Intrusions of stratospheric air into the lower troposphere may cause short-term variability in  $\Delta_{36}$  values at the surface, but mean  $\Delta_{36}$  values within  $\pm 0.01\text{‰}$  in both hemispheres indicate that, at least on annual timescales, local influences on the clumped-isotope distribution of  $\text{O}_2$  at the surface are negligible.

### 3.2. Comparison of Present-Day Measurements With GEOS-Chem Model Results

We ran chemical transport simulations of the atmosphere for the present-day atmosphere using the GEOS-Chem atmospheric chemistry model forced by either the MERRA or GEOS-4 meteorological reanalyses for the year 2005. Both model implementations show that  $\text{O}_3$  and  $\text{O}(^3\text{P})$  covary throughout the atmosphere because of rapid  $\text{O}_3$  photolysis and recombination (Figures 5a–5d). Photolysis of nitrogen dioxide ( $\text{NO}_2$ ), although important in polluted air masses in the northern midlatitudes, has a much smaller effect on tropospheric atomic oxygen in the rest of the atmosphere, contributing  $< 2\%$  to tropospheric  $\text{O}(^3\text{P})$  production (Figures 5e and 5f; note the difference in scale relative to Figures 5c and 5d).

At  $> 20$  km altitude, our model and several others [e.g., Brasseur *et al.*, 1990] predict that timescales of isotope equilibration are several days or less. Generally, our observations in this region are consistent with these model results, as the air in that region appears to be near isotopic equilibrium with local temperatures (Figure 2b). The disequilibria observed between 16 km and 20 km altitude noted in section 3.1 also do not seem unreasonable given the timescales of isotope equilibration there (Figure 4): equilibration takes a week to a month, comparable to the timescales for horizontal transport in this region ( $< 1$  month [Boering *et al.*, 1996]). As noted previously by others [Boering *et al.*, 1996; Mote *et al.*, 1996; Schoeberl *et al.*, 2006], a significant fraction of the air in the lower stratosphere has only recently entered the stratosphere, so we hypothesize that it has not yet been fully reequilibrated at stratospheric temperatures.

We calculated a whole-troposphere isotopic equilibration rate of  $E_{\text{trop}} = 1.3 \times 10^{19} \text{ mol O}_2 \text{ yr}^{-1}$  using modeled isotope exchange rates, air masses, and air density in each grid box (see section 2.3 and Appendix A). About one half to one third of the tropospheric  $\text{O}_2$  inventory ( $3 \times 10^{19} \text{ mol O}_2$ ) undergoes isotope exchange annually. This tropospheric rate of isotope reordering is  $\sim 400$  times faster than biological  $\text{O}_2$  cycling [Blunier *et al.*, 2012] and similar to that of whole-troposphere tracer mixing [Waugh *et al.*, 2013]. It justifies our treatment of the troposphere as a geochemical box within which  $\Delta_{36}$  values are driven toward an equilibrium end-member,  $\Delta_{36, \text{Tequil}}$ , by photochemistry on annual timescales. This end-member can be calculated



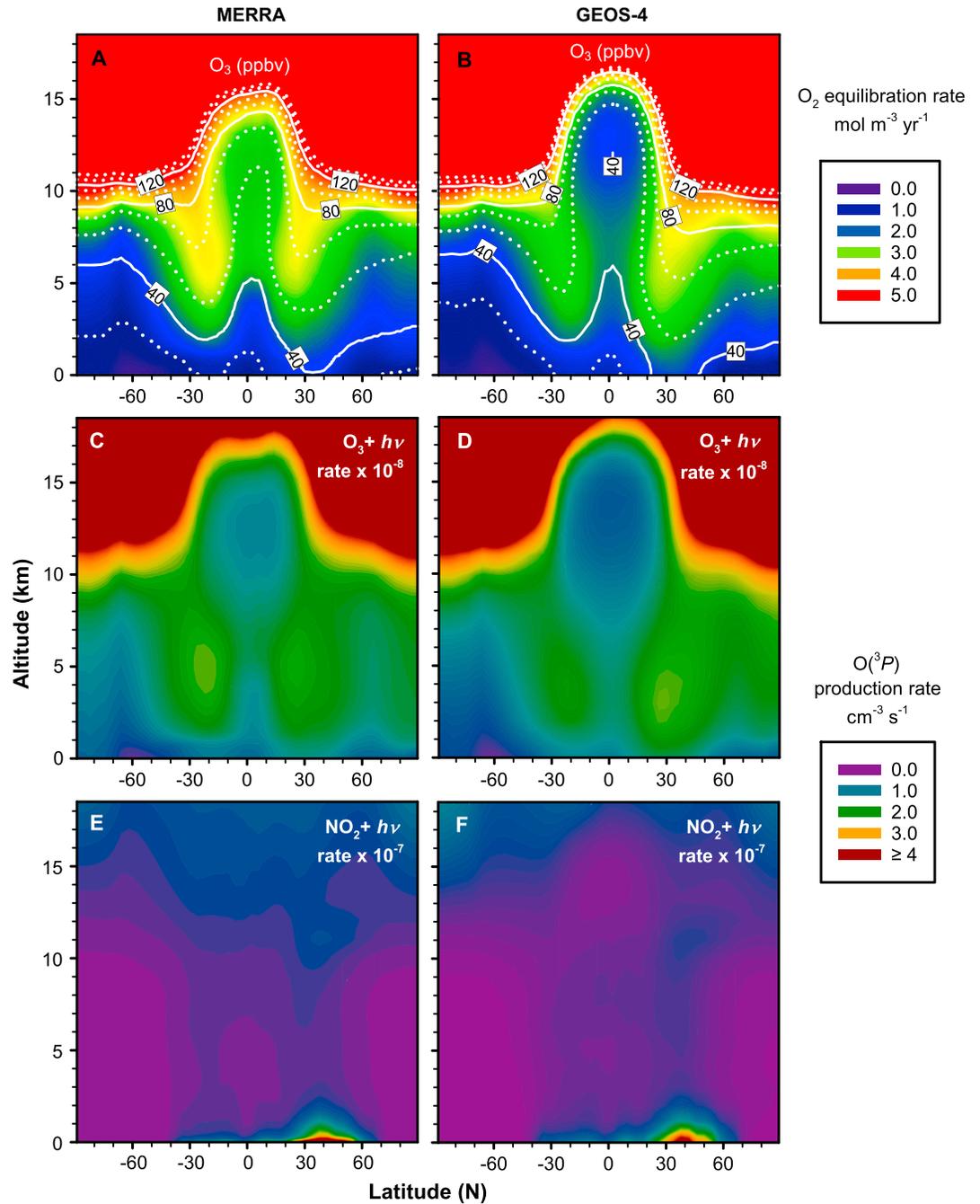
**Figure 4.** Calculated zonal-mean O<sub>2</sub> equilibration lifetimes in the troposphere and lower stratosphere. Labeled and colored contours depict the lifetimes, i.e.,  $\tau = (k_{\text{exch}} \times [\text{O}(\text{}^3\text{P})])^{-1}$ , expressed in months, shown on a logarithmic scale. Equilibration lifetimes for polar latitudes are not shown; they are exceedingly long because negligible atomic oxygen is produced there during polar night.

using annually averaged spatial distributions of O<sub>3</sub> (via atomic oxygen), temperature, air mass in each grid box, and air density (a proxy for residence time; see section 2.3).

The calculated whole-troposphere equilibrium end-members are  $\Delta_{36, \text{Tequil}} = 1.93\text{‰}$  for MERRA and  $1.90\text{‰}$  for GEOS-4 meteorology in 2005. Isotopic reordering in the subtropical free troposphere (4–6 km) contributes the most to the weighting of  $\Delta_{36, \text{Tequil}}$  values (Figures 5 and 6). The spatial weighting patterns for MERRA and GEOS-4 are similar, but the maxima are at higher altitudes in MERRA, perhaps reflecting its weaker vertical fluxes of low-O<sub>3</sub> air from the marine boundary layer into the upper troposphere [Liu *et al.*, 2010]. For example, at 215 hPa (~11 km), the vertical velocities in the MERRA meteorology are about a factor of 2 lower than in GEOS-4 [Liu *et al.*, 2013b]. A larger proportion of tropospheric O<sub>3</sub> photochemistry occurs in the upper troposphere in MERRA/GEOS-Chem simulations as a result (Figures 5a and 5b), yielding a higher whole-troposphere  $\Delta_{36, \text{Tequil}}$  value. Slightly higher cloud top heights in the MERRA meteorology [Murray *et al.*, 2012] may also contribute to the differences in calculated whole-troposphere  $\Delta_{36, \text{Tequil}}$  values.

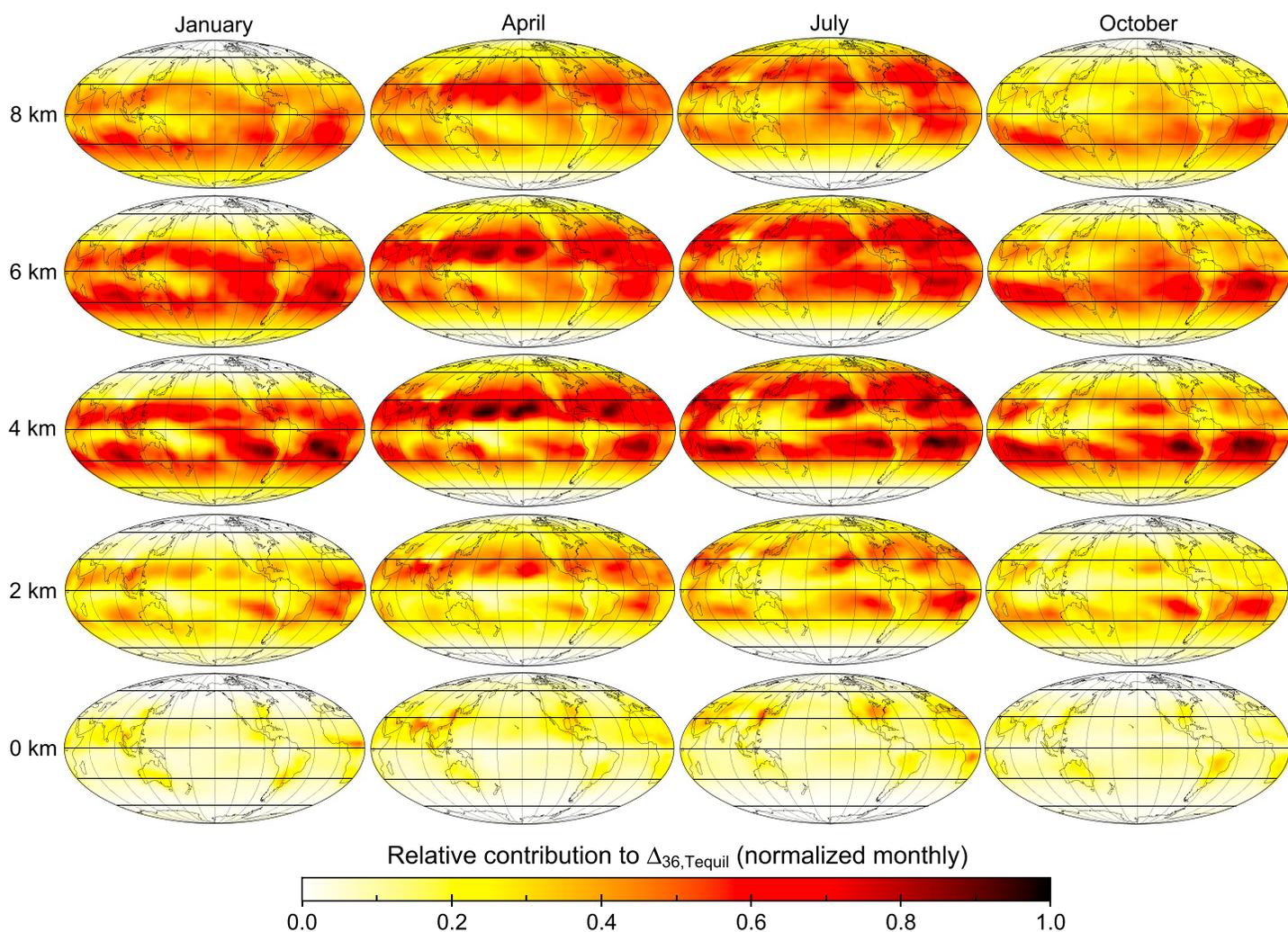
There is a notable minimum of weighting within the intertropical convergence zone in both meteorologies, and seasonal patterns that imply a connection between  $\Delta_{36, \text{Tequil}}$  values and global circulation (i.e., the Hadley, Walker, and Brewer-Dobson circulations; Figure 6). In particular, the altitudes and latitudes of the  $\Delta_{36, \text{Tequil}}$  weighting maxima suggest that  $\Delta_{36, \text{Tequil}}$  is associated with the descending branches of the tropical overturning circulations. Patterns of STT of O<sub>3</sub> are also visible in the extratropics, e.g., a maximum in STT O<sub>3</sub> flux in the late spring and summer in the Northern Hemisphere [Škerlak *et al.*, 2014]. Generally, climatological patterns of O<sub>3</sub> resemble the patterns in Figure 6 [Liu *et al.*, 2013a], supporting a link between O<sub>3</sub>, tropical circulation, and tropospheric  $\Delta_{36}$  values.

Previous studies have associated subtropical O<sub>3</sub> variability with the 30–90 day Madden-Julian Oscillation [Ziemke and Chandra, 2003b] as well as the interannual El Niño–Southern Oscillation [Ziemke and Chandra, 2003a] in the tropical Pacific, the origins of which stem from a combination of O<sub>3</sub> transport, changing precursor emissions from biomass burning, and lightning [Sudo and Takahashi, 2001; Tian *et al.*, 2007; Murray *et al.*, 2013; Sun *et al.*, 2014; Virts and Wallace, 2014; Ziemke *et al.*, 2015]. Other transport mechanisms important in these regions include horizontal mixing between tropical and extratropical air masses and downward transport of O<sub>3</sub> from the stratosphere [Waugh and Polvani, 2000; Hsu *et al.*, 2005; Neu *et al.*, 2014]. The relative importance of these mechanisms is beyond the scope of this report, but we assert that the whole-troposphere  $\Delta_{36, \text{Tequil}}$  value is sensitive to tropical meteorology via the factors that control O<sub>3</sub> in the troposphere.



**Figure 5.** Correspondence between O<sub>3</sub>, O(<sup>3</sup>P), and rates of O<sub>2</sub> isotope equilibration. Left and right columns show annually averaged zonal-mean results from GEOS-Chem simulations (year 2005) using MERRA and GEOS-4 meteorologies, respectively. (a and b) O<sub>3</sub> concentrations (ppbv; white contours) overlay atop isotope equilibration rates (mol m<sup>-3</sup> yr<sup>-1</sup>; colored contours). (c and d) show the strength of the O<sub>3</sub>-photolysis source of O(<sup>3</sup>P); (e and f) the strength of the NO<sub>2</sub> photolysis source of O(<sup>3</sup>P). Note the order-of-magnitude difference in scales for O(<sup>3</sup>P) production rate shown on the plots.

For example, convective and advective transport of O<sub>3</sub>-poor air from the surface to the upper troposphere, mainly in the intertropical convergence zone, reduces the amount of tropospheric O<sub>3</sub> at high tropical altitudes (e.g., Figures 5a and 5b). Subsequent entrainment of O<sub>3</sub>-rich air from the upper troposphere during subsidence increases O<sub>3</sub> at midtropospheric altitudes of the subtropics. These large-scale circulation patterns reduce O<sub>2</sub> isotope exchange rates in the coldest regions of the tropics and enhance O<sub>2</sub> isotope exchange

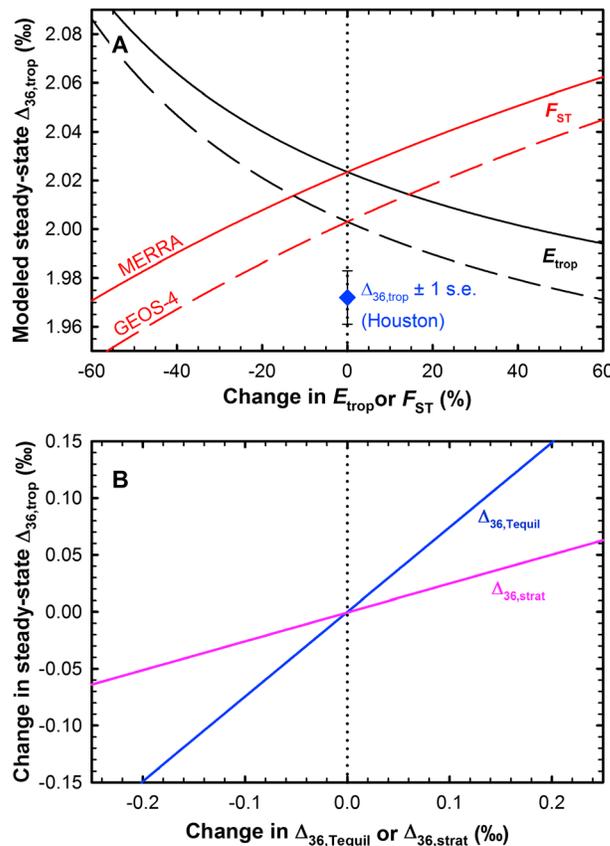


**Figure 6.** Spatial and temporal patterns of isotope reordering derived from GEOS-Chem/MERRA simulations. The maps shown highlight the regions where  $O_2$  isotope reordering occurs during model year 2005. Darker colors indicate a larger contribution to the whole-troposphere  $\Delta_{36,Tequil}$  value. Similar results were obtained for GEOS-4 simulations.

rates in warmer regions (Figures 5c, 5d, and 6). Therefore, the Hadley circulation acts to decrease the whole-troposphere  $\Delta_{36,Tequil}$  value relative to a scenario in which  $O_3$  is uniformly distributed with altitude. Changes in the vertical extent, mass flux, and entrainment that characterize this circulation may affect the whole-troposphere  $\Delta_{36,Tequil}$  value through its effects on  $O_3$  transport and photochemistry [Wu *et al.*, 2007].

The present-day timescale of isotope equilibration in the troposphere (2–3 years) is longer than the timescale of whole-troposphere mixing ( $\sim 1$  year), so spatial variations in  $\Delta_{36}$  values are expected to be small. Indeed, the observational dataset presented in section 3.1 shows no statistically significant tropospheric  $\Delta_{36}$  variations outside of regions with known stratosphere-troposphere mixing. Therefore, we restrict further measurement-model comparison to quantities that integrate  $O_3$  photochemistry on annual timescales—surface  $\Delta_{36}$  values and whole-troposphere  $\Delta_{36,Tequil}$  values—which should be robust in both the measurements and the model.

Mean  $\Delta_{36}$  values measured at the surface (e.g.,  $1.972 \pm 0.011\text{‰}$  in Houston; 1 SE) are similar to calculated whole-troposphere  $\Delta_{36,Tequil}$  values, but slightly higher. We infer that isotopic ordering in  $O_2$  at the surface is nearly equilibrated to the whole-troposphere  $\Delta_{36,Tequil}$  end-member despite the large flux of high- $\Delta_{36}$  air entering the troposphere (STT mass flux =  $4.6 \times 10^{18}$  mol  $O_2$  yr $^{-1}$ ). The stratospheric contributions implied by isotopic mass balance are consistent with the mixing fractions implied by the shorter-lived  $^7Be$  tracer of



**Figure 7.** Sensitivity tests of the two-box atmospheric model. Shown is the dependence of the  $\Delta_{36,trop}$  value on (a) STT mass flux ( $F_{ST}$ ) and whole-troposphere isotope equilibration rate ( $E_{trop}$ ) or (b) the whole-troposphere  $\Delta_{36,Tequil}$  value and the  $\Delta_{36,strat}$  value, keeping all else constant. Two-box model results using both the MERRA and GEOS-4-derived end-members are shown in Figure 7a.

several independent estimates of  $k_{exch}$  near 300 K agree within 10% [Anderson et al., 1985; Wiegell et al., 1997], suggesting that the uncertainty limits reported here are conservative.

Sensitivity tests within the two-box model framework indicate that the steady state  $\Delta_{36,trop}$  value is not strongly forced by STT of  $O_2$  (Figure 7); it is instead controlled by tropospheric factors, specifically the whole-troposphere  $\Delta_{36,Tequil}$  value. Changes in the tropospheric steady state  $\Delta_{36,trop}$  value of order 0.01‰ require variations of about 15% in  $F_{ST}$  or 0.04‰ in  $\Delta_{36,strat}$  value (Figures 7a and 7b). Interannual variations in STT mass flux are only large enough to perturb  $\Delta_{36,trop}$  by  $\sim 0.001\%$  [Škerlak et al., 2014]. In addition, a large error in  $\Delta_{36,strat}$  value is unlikely given our observational constraints (Figures 2 and 3) and the insensitivity of steady state  $\Delta_{36,trop}$  value to tropopause definition (see Appendix A). Consequently, a change in  $\Delta_{36,trop}$  value forced by the stratospheric transport term would only occur under extraordinary circumstances. In contrast, a change in  $\Delta_{36,trop}$  value forced by the tropospheric term is plausible: the tropospheric equilibration rate,  $E_{trop}$ , which is three times larger than  $F_{ST}$  in the present day, dominates the tropospheric  $\Delta_{36}$  budget. Furthermore, because tropospheric  $O_2$  is nearly equilibrated to the whole-troposphere  $\Delta_{36,Tequil}$  value, the  $\Delta_{36,trop}$  value is most sensitive to the assumed whole-troposphere  $\Delta_{36,Tequil}$  value in our two-box model (Figure 7b). In general,  $F_{ST}$  and  $E_{trop}$  oppose each other in equation (2), so a decrease in  $E_{trop}$  would result in an increased sensitivity of  $\Delta_{36,trop}$  to the stratospheric terms of the  $\Delta_{36}$  budget and vice versa.

We note that the similarity between whole-troposphere  $\Delta_{36,Tequil}$  values and measured surface  $\Delta_{36}$  values implies that  $O_2$  at the surface has resided in the troposphere for at least 4 years, on average. More precisely, it has not experienced significant photochemical reordering in the stratosphere during that time. Recent

STT (20–30% stratospheric in the northern midlatitudes [Murray et al., 2014]). Furthermore, using these stratospheric and tropospheric end-members in our two-box model yields a mean tropospheric  $\Delta_{36,trop}$  value similar to the observations at steady state, although slightly higher (2.02‰ and 2.00‰ for MERRA and GEOS-4, respectively; these estimates include the effects of biosphere  $O_2$  cycling).

Some uncertainty in these two-box model estimates arises from uncertainties in the kinetic rates of  $O_2$  isotope exchange in the atmosphere, however. The experimental uncertainty in the magnitude of  $k_{exch}$  (the  $O_2$  isotope exchange rate coefficient)  $\pm 30\%$  ( $2\sigma$ ) [Wiegell et al., 1997], affects  $E_{trop}$  values, while the uncertainty in its temperature dependence affects  $\Delta_{36,Tequil}$  values. The former contributes  $^{+0.03}_{-0.02}\%$ , while the latter contributes less than  $\pm 0.01\%$  uncertainty to our steady state  $\Delta_{36,trop}$  estimates, yielding a combined uncertainty of  $^{+0.03}_{-0.02}\%$  ( $2\sigma$ ). Consequently, the  $\Delta_{36,trop}$  estimate derived from the GEOS-4 meteorology appears consistent with the surface  $\Delta_{36}$  measurements, while the MERRA meteorology may be slightly too high, if these are the major sources of systematic error in the tropospheric term within equations (1) and (2). We note that

simulations suggest that one third to one half of air parcel trajectories entering the stratosphere in the tropics return to the troposphere in less than 3 months [Orbe *et al.*, 2014]; if these trajectories tend to remain within the lowermost stratosphere where O<sub>2</sub> reordering timescales are slow (Figure 4), then the air will still be largely “tropospheric” in its  $\Delta_{36}$  value when it exits the stratosphere. We conclude that the surface  $\Delta_{36}$  value is controlled by the whole-troposphere  $\Delta_{36,Tequil}$  value and forced weakly by stratospheric factors.

### 3.3. Archived Air From 1978 to 2013: A Sensitivity Test for Tropospheric $\Delta_{36}$ Values

To investigate the sensitivity of tropospheric  $\Delta_{36}$  values to global changes in atmospheric properties during the twentieth century, we analyzed air samples from the Cape Grim air archive dating back to 1978 [Langenfelds *et al.*, 1996]. Historical ozonesonde measurements indicate that O<sub>3</sub> has increased throughout the troposphere since 1978, by up to 30% at some sites [Logan *et al.*, 2012; Cooper *et al.*, 2014]. Meanwhile, changes in STE mass flux have been observationally constrained to be <10% [Butchart *et al.*, 2006; Škerlak *et al.*, 2014]. Tropopause temperatures have changed less than 2°C [Seidel *et al.*, 2001; Santer *et al.*, 2003], so changes in  $\Delta_{36, strat}$  have a negligible impact on the tropospheric budget. Moreover, tropospheric temperature structure has been relatively constant amidst a global ~1 K warming [Santer *et al.*, 2013]. Finally, a recent global satellite-based time series analysis found that cloud top heights (a proxy for the vertical extent of tropical circulation relevant to  $\Delta_{36, Tequil}$ ) had a long-term trend of  $\leq 2 \text{ m yr}^{-1}$  between 1996 and 2011 [Lelli *et al.*, 2014], too small to be detectable by  $\Delta_{36}$ , even when extrapolated back to 1978. The most important atmospheric trend from 1978 to 2013 for surface  $\Delta_{36}$  values was therefore that of an increasing tropospheric O<sub>3</sub> burden. If the two-box model is an adequate description of the global budget, then one would expect surface  $\Delta_{36}$  values to decrease as the total tropospheric O<sub>3</sub> burden increases. An anthropogenic increase in O<sub>3</sub> near the surface would decrease  $\Delta_{36, Tequil}$  and therefore also surface  $\Delta_{36}$  values over this time period.

We find that  $\Delta_{36}$  values in the archived air samples are all indistinguishable, with mean values within 0.01‰ of recent surface values (see Table 1). We infer that changes in anthropogenic O<sub>3</sub> at the surface since 1978 were smaller than the current limit of detection by  $\Delta_{36}$  values. Holding all else equal, a surface  $\Delta_{36}$  value constant within  $\pm 0.01\text{‰}$  over this time period would imply that the tropospheric O<sub>3</sub> burden has stayed within a  $\sim \pm 10\%$  range since 1978. This result agrees with the 5% increase in the tropospheric O<sub>3</sub> burden since 1980 predicted by the Atmospheric Chemistry-Climate Modeling Intercomparison Project (ACCMIP ensemble mean) [Young *et al.*, 2013]. A more precise measurement-model comparison will require both a higher-precision time series and the inclusion of isotopologue-specific chemistry and transport in the 3-D atmospheric model.

To examine the sensitivity of surface  $\Delta_{36}$  values to anthropogenic O<sub>3</sub> more generally, we ran a GEOS-Chem simulation using the 2005 MERRA meteorology with preindustrial (i.e., 1850 Common Era) nonfire anthropogenic emissions and methane concentrations of 730 ppb. We obtained a  $\Delta_{36, Tequil}$  value for this extreme case, which we input into our two-box model. In that simulation, the largest decreases in O<sub>3</sub> are found at the surface, which leads to a greater proportion of O<sub>3</sub> photochemistry occurring in the middle and upper troposphere. This redistribution of O<sub>3</sub> photochemistry, away from the warm surface and toward the colder free troposphere, results in a  $\Delta_{36, Tequil}$  value that is higher by 0.02‰. The overall tropospheric O<sub>3</sub> burden is 29% lower (256 Tg O<sub>3</sub> versus 362 Tg O<sub>3</sub>), and tropospheric rates of O<sub>2</sub> reordering are reduced by 37% ( $E_{trop} = 8.4 \times 10^{18} \text{ mol O}_2 \text{ yr}^{-1}$  versus  $1.3 \times 10^{19} \text{ mol O}_2 \text{ yr}^{-1}$ ). Consequently, STT is a more important component in the tropospheric  $\Delta_{36}$  budget (i.e., the  $F_{ST}\Delta_{36, strat}$  term in equation (2)), leading to an additional increase of  $\Delta_{36, trop}$  values. The model therefore predicts that these preindustrial  $\Delta_{36, trop}$  values are ~0.05‰ higher than in the present day, all else being equal. Further sensitivity tests indicate that surface  $\Delta_{36}$  values are still insensitive to variations in STT mass flux at these reduced  $E_{trop}$  values: an unprecedented 25% increase in  $F_{ST}$  would be required to increase  $\Delta_{36, trop}$  by 0.02‰.

While O<sub>3</sub> trends since 1978 may not have been detectable in the surface  $\Delta_{36}$  value, the preindustrial-to-industrial increase in O<sub>3</sub> may be observable in ice-core air archives with modest improvements in analytical precision. It is currently limited only by counting statistics and thermal (Johnson) noise on the Rice University instrument, so extending integration times and/or increasing the size of ion currents should yield the factor of 1.5–2 necessary to quantify the anthropogenic decrease in  $\Delta_{36, trop}$  values with high confidence. Note that the  $\Delta_{36, trop}$  value is a proxy for the tropospheric O<sub>3</sub> burden rather than a direct measure of it; however, forward atmospheric modeling can relate changes in  $\Delta_{36, trop}$  value to changes in atmospheric O<sub>3</sub> burden.

#### 4. Summary and Discussion

What atmospheric properties do tropospheric  $\Delta_{36}$  values record? It depends on the timescale of interest. In the upper troposphere and lower stratosphere,  $\Delta_{36}$  values reflect the mass flux between the stratosphere and troposphere on timescales of weeks to months. In the upper troposphere, STT varies the proportion of unaltered “stratospheric” air, which elevates  $\Delta_{36}$  values above mean values characteristic of the surface. In the lower stratosphere, STE of  $O_2$  lowers  $\Delta_{36}$  values from that expected at local isotopic equilibrium. These perturbations can be used as air mass mixing tracers on timescales of up to a year and may be useful in diagnosing STE within a Lagrangian framework. In the lower troposphere,  $\Delta_{36}$  values record quantities related to the concentration and spatial patterns of tropospheric  $O_3$ .

To first order, the  $\Delta_{36,trop}$  value is an expression of the temperature of the tropical troposphere. The majority of tropospheric  $O_2$  isotope reordering occurs in the subtropics at 4–6 km (Figures 5 and 6), where clear-sky subsidence promotes photochemical  $O_3$  cycling. Stronger convection or advection can decrease upper troposphere  $O_3$  by upwelling more low- $O_3$  air from the boundary layer (e.g., in GEOS-4, Figure 5b), which causes a larger proportion of  $O_3$  photochemistry to occur at warmer temperatures (Figure 5d). Weaker convection/advection has the opposite effect because the upper troposphere will have more  $O_3$  on average (e.g., MERRA, Figure 5a). The former tends to decrease  $\Delta_{36,Tequil}$  and  $\Delta_{36,trop}$  values, while the latter tends to increase them, relative to isotopic equilibrium at a fixed midtropospheric temperature.

The difference between the two-box-modeled  $\Delta_{36,trop}$  value and the mean  $\Delta_{36}$  value measured at the surface may thus constitute an additional benchmark for model parameterizations of vertical transport in the tropical troposphere. The present result, with the MERRA meteorology yielding tropospheric  $\Delta_{36,trop}$  values that are slightly too high (2.02‰ modeled versus 1.97‰ measured), implies that the transport from the boundary layer into the upper troposphere is too weak in the MERRA meteorology; it is consistent with previous work that found that convection detrains at too low an altitude in the tropical upper troposphere in GEOS-5, a nearly identical meteorology. In contrast, the GEOS-4 meteorology better reproduces tropical tropospheric trace gases during convective events [Liu *et al.*, 2010; Mitovski *et al.*, 2012] and also shows better agreement with measured  $\Delta_{36}$  values.

While the STT mass flux is an important part of the atmospheric  $\Delta_{36}$  budget, our sensitivity tests indicate that its variations only perturb  $\Delta_{36,trop}$  values in extraordinary cases. Extreme changes in annually averaged STT mass flux of order several tens of percent or more are required to alter mean  $\Delta_{36}$  values at the surface significantly. Similarly, variations in the tropospheric  $O_3$  burden of ~10% (which affect  $E_{trop}$  values) are near the current limits of detection by  $\Delta_{36}$  values.

Our model predicts that  $\Delta_{36}$  values decreased in response to increasing ground-level  $O_3$  sources during the industrial era. Increasing surface  $O_3$  concentrations leads to a greater proportion of  $O_3$  photochemistry occurring at low altitudes (i.e., warmer temperatures), which lowers  $\Delta_{36,trop}$  values independent of the circulation. The timing and magnitude of changes in  $\Delta_{36}$  values over the past century might therefore constrain the increase in tropospheric  $O_3$  burden, which is presently uncertain. Early measurements of ground-level  $O_3$  suggest that it has increased by a factor of 2–3 since the late nineteenth century, but atmospheric models have struggled to reproduce such a strong  $O_3$  increase [Wang and Jacob, 1998; Stevenson *et al.*, 2013; Young *et al.*, 2013; Cooper *et al.*, 2014]. The  $\Delta_{36}$  tracer may be able to distinguish the twentieth century increase in tropospheric  $O_3$  burden increase predicted by models (resulting in a  $\Delta_{36}$  decrease of –0.05‰ in MERRA) from that implied by historical measurements at the surface (–0.1‰ in  $\Delta_{36}$  [Volz and Kley, 1988; Marengo *et al.*, 1994]). The unknown temporal evolution of circulation and STT mass flux over this time period prevents a more rigorous estimate of the atmospheric  $\Delta_{36}$  evolution at present, but recent work suggests that STT has been either constant or decreasing slightly during the second half of the twentieth century [Škerlak *et al.*, 2014; Oberländer-Hayn *et al.*, 2016]; thus, the sign and magnitude of the twentieth century  $\Delta_{36}$  decrease should be robust. The analytical precision required to provide an unequivocal constraint (i.e., better than  $\pm 0.02$  in  $\Delta_{36}$ ) is likely within the capabilities of current instrumentation.

On longer timescales, the  $\Delta_{36}$  tracer is sensitive to climatic boundary conditions. For example, lower sea surface temperatures during the last glacial maximum [MARGO Project Members, 2009] cool and steepen the lapse rate that characterizes the tropical atmosphere. A cooling of order 10K in the midtroposphere

has been inferred [Thompson *et al.*, 1995; Stansell *et al.*, 2007; Tripathi *et al.*, 2014], which would yield a  $\Delta_{36}$  value about +0.15‰ higher than its mean Holocene values, all else being equal. Significant deviations from this expected value may indicate a shift in hydrologic, dynamical, or chemical properties of the atmosphere influencing tropical lapse rates and/or the global distribution of  $O_3$ . Future modeling studies can test the sensitivity of  $\Delta_{36,trop}$  values to climate-driven changes in tropopause height and  $O_3$ , which are also relevant. Once the governing boundary conditions can be constrained, the  $\Delta_{36}$  tracer may shed light on past changes in the structure of the ancient atmosphere. The  $\Delta_{36}$  tracer can complement more well-known atmospheric temperature proxies such as  $\delta D$  or  $\delta^{18}O$  values of precipitation applied in tropical ice-core records [Thompson *et al.*, 1995] because (1) its equilibrium values are constrained by quantum-mechanical theory and (2) it integrates atmospheric temperature and dynamics across the entire tropics. Importantly, the subdecadal timescale of tropospheric  $O_2$  isotope reordering could in principle be used as a high-resolution stratigraphic marker for synchronization of atmospheric composition and tropical climate using gases extracted from well-preserved polar ice cores.

The measurements and modeling can be improved in several respects to facilitate these applications. First, tighter constraints on the magnitude and temperature dependence of the  $O(^3P) + O_2$  isotope exchange rate coefficient will reduce uncertainties in  $E_{trop}$  and  $\Delta_{36,Tequil}$  values for all model implementations. Second, grid-scale online calculation of atmospheric  $\Delta_{36}$  values may reveal subtle spatial variations that will be relevant when comparing model outputs and ice-core  $\Delta_{36}$  records obtained from high-latitude sites. Third, improvements in the control of photochemical calibration temperatures, combined with increased measurement precision arising from longer integration times, may enable  $\Delta_{36}$  analyses with an accuracy of 0.01‰ to 0.02‰ (i.e.,  $\sim 1$  K at isotopic equilibrium). If clumped-isotope signatures in  $O_2$  are preserved in paleoatmospheric records,  $\Delta_{36}$  values could light a path toward understanding how the tropical troposphere evolved during the Pleistocene.

## Appendix A: Uncertainties in Calculations for Global Rate of Isotope Equilibration and Whole-Troposphere $\Delta_{36,Tequil}$

### A1. Definitions of Tropopause Height

Some uncertainty remains for defining the effective height of the tropopause for the budgets of trace gases. Measurements of  $CO_2$  at the tropical tropopause layer suggest that the upper boundary of the well-mixed troposphere is  $\theta = 360$  K in the tropics [Park *et al.*, 2007], whereas tracer-tracer studies suggest that the lapse rate tropopause represents the upper boundary in the extratropics [Pan *et al.*, 2004]. However, because the lapse rate tropopause may not be unique near the subtropical jet, dynamical tropopause definitions (e.g., troposphere  $< 2$  potential vorticity unit) have also been used because it is better represents diabatic flow. Finally, an  $O_3$  concentration is sometimes employed as a threshold for the tropopause when calculating tropospheric burdens, such as  $O_3 < 150$  ppb for the troposphere in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) [Young *et al.*, 2013]. We found that  $E_{trop}$  was generally insensitive to tropopause definition: Values derived from tropopause thresholds of 100–150 ppb  $O_3$  (based on monthly concentration averages) varied  $< 10\%$ . The whole-troposphere  $\Delta_{36,Tequil}$  value varied 0.03‰ in  $\Delta_{36,Tequil}$  over this range in  $O_3$ , with lower  $O_3$  tropopause thresholds yielding lower  $\Delta_{36,Tequil}$  values. Resulting variations in steady state  $\Delta_{36,trop}$  values were  $\sim 0.01\%$ . The dynamical tropopause definitions yielded nearly identical results to those defined by  $O_3$  concentration at 150 ppb ( $V_{trop} = 6.8 \times 10^{18} \text{ m}^3$ ). Our clumped-isotope measurements are consistent with a chemical tropopause of  $\sim 150$  ppb  $O_3$  with a  $\Delta_{36, strat}$  of 2.3‰.

### A2. Residence Times in Tropospheric Boxes

The mass- and residence-time weighting for the calculation of  $E_{trop}$  and whole-troposphere  $T_{equil}$  was used to account for two effects: (i) air mass in each grid box varies with its size and (ii) isotope equilibration toward  $\Delta_{36,Tequil}$  in a given grid box depends on the reaction rate and the residence time of air in that grid box. Accounting for (i) is straightforward—weight each box by the mass contained within it—but accounting for (ii) is more difficult. At a dynamic steady state, assuming ergodicity, the exponentially decreasing density profile of air indicates that air spends more time at low altitudes than at high altitudes; it is kept near the surface by the gravitational potential of the Earth. Its residence time in a given grid box, however, depends on time-varying meteorological fields. While a full Lagrangian trajectory study is ideal for tracking an  $O_2$

molecule's transport history, the calculations are too expensive at present for the >3 year long trajectories in a global chemical-transport model required to model  $\Delta_{36,Tequil}$  values accurately [Owen and Honrath, 2009]. Therefore, we approximate the aggregated Lagrangian residence times in tropospheric grid boxes, relative to each other, using the air density in each box. The air densities reflect the average large-scale behavior at a dynamic steady state, which is appropriate for the multiannual timescales relevant to tropospheric isotope exchange chemistry. Because there is an upper limit for air densities (globally speaking, i.e., surface conditions) and not for residence times, however, our calculated relative residence times at the surface may underestimate the true relative residence times. If so, warm surface temperatures may be underweighted, leading to whole-troposphere  $\Delta_{36,Tequil}$  values that are too high.

### A3. Oxygen Cycling by the Biosphere

Rates of oxygen production and consumption ( $3.43 \times 10^{16}$  mol O<sub>2</sub> yr<sup>-1</sup> [Blunier et al., 2012]) are 400 times slower than the calculated rate of isotopic equilibration ( $1.4 \times 10^{19}$  mol O<sub>2</sub> yr<sup>-1</sup>). Using the biological end-member of  $\Delta_{36} \sim 0$  obtained from a earlier closed-system terrarium study and the global box model for  $\Delta_{36}$  described in Yeung et al. [2012], we calculate that biological O<sub>2</sub> cycling affects tropospheric  $\Delta_{36}$  by approximately  $-0.01\%$  in steady state.

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