Sources of the oxygen isotopic anomaly in atmospheric N\(_2\)O

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[1] One-dimensional and two-dimensional models are used to investigate the isotopic composition of atmospheric N\(_2\)O. The sources of N\(_2\)O in the atmosphere are based on recent laboratory measurements of the N\(_2\)O quantum yield in the mixture of O\(_3\)/O\(_2\)/N\(_2\) (Estupiñán et al., 2002). Two recently proposed pathways (Estupiñán et al., 2002; Prasad, 2005) are evaluated in the model. We find that the new atmospheric sources constitute a few percent of the total N\(_2\)O source, but can account for \(\sim 50-100\%\) of the \(\Delta^{17}\)O anomaly observed in N\(_2\)O. The essence of the mechanism is to transfer a heavy oxygen atom originally in O\(_3\) to N\(_2\)O. The magnitude of \(\Delta^{17}\)O in N\(_2\)O is a linear function of the strength of these new N\(_2\)O sources. Laboratory and atmospheric measurements are proposed to confirm the chemical pathways. The potential of \(\Delta^{17}\)O in N\(_2\)O for providing a new tool to probe ozone levels in paleoatmospheres is discussed.


1. Introduction

[2] Nitrous oxide is a potent greenhouse molecule as well as the major source of stratospheric NO\(_x\), which catalyzes the loss of ozone in the stratosphere. The primary sources of N\(_2\)O are anthropogenic and oceanic microbial activity as a by-product of nitrification and denitrification reactions, and the major sink is in the stratosphere by UV photolysis [see, e.g., review by Stein and Yung, 2003]. The recent discovery [Cliff and Thiemens, 1997; Cliff et al., 1999; Röckmann et al., 2001] of an oxygen isotope anomaly in atmospheric N\(_2\)O suggests a gap in our understanding of the N\(_2\)O budget. The isotopic compositions are reported as \(\delta^{17}\)O and \(\delta^{18}\)O, and we define them as

\[
\delta^{17}\text{O}(\text{N}_2\text{O}) = \frac{2([^{17}\text{O}]\text{N}_2\text{O})/([^{16}\text{O}]\text{N}_2\text{O}) - 1}{\text{O}(\text{N}_2\text{O})} - 1 \tag{1}
\]

\[
\delta^{18}\text{O}(\text{N}_2\text{O}) = \frac{2([^{18}\text{O}]\text{N}_2\text{O})/([^{16}\text{O}]\text{N}_2\text{O}) - 1}{\text{O}(\text{N}_2\text{O})} - 1. \tag{2}
\]

[3] Unless otherwise stated, the \(\delta\) values reported in this paper are referenced relative to atmospheric O\(_2\), rather than the more commonly employed Vienna Standard Mean Ocean Water (V-SMOW). The magnitudes of the atmospheric \(\delta^{17}\)O(O\(_2\)) and \(\delta^{18}\)O(O\(_2\)) are 11.75 and 23.5\% referenced to V-SMOW, respectively, while the values are zero as referenced to O\(_2\) itself. The unit \% reads per mil or one part in thousand. The mass-dependent isotopic fractionation follows

\[
\delta^{17}\text{O} \approx 0.515 \delta^{18}\text{O}. \tag{3}
\]

[4] The oxygen anomaly is defined as the residual from the above equation, or

\[
\Delta^{17}\text{O} \approx \delta^{17}\text{O} - 0.515 \delta^{18}\text{O}. \tag{4}
\]

[5] It was discovered that tropospheric N\(_2\)O samples [Cliff and Thiemens, 1997] have \(\Delta^{17}\)O \(\approx 1\). Subsequent measurements [Cliff et al., 1999; Röckmann et al., 2001] confirmed and extended the result into the stratosphere. The latter reference gives \(\Delta^{17}\)O = 1.0 \pm 0.2\% at \(\delta^{18}\)O = 20.7 \pm 0.3\%.

[6] Several chemical processes have been proposed to explain this anomaly: NO\(_3\)/NO\(_3\)\(^+\)\(_2\) [Zellner et al., 1992], CO\(_3\)\(^+\) + N\(_2\) [McElroy and Jones, 1996], O(\(^1\)D) + N\(_2\) [Estupiñán et al., 2002], O\(_3\) + N\(_2\) [Zipf and Prasad, 1998; Prasad, 2002, 2005], NH\(_2\) + NO\(_2\) [Röckmann et al., 2001], and N + NO\(_2\) [Mclinden et al., 2003]. These processes have been summarized and discussed by Mclinden et al. [2003] and Kaiser and Röckmann [2005]. In addition to the aforementioned proposals that generate nonzero \(\Delta^{17}\)O in the atmosphere, it has also been suggested that microbial production of N\(_2\)O in the biosphere [Michalski et al., 2003; Kaiser et al., 2004; Kaiser and Röckmann, 2005] could contribute the observed oxygen anomaly. A recent calculation by Kaiser and Röckmann [2005] suggests that microbial nitrification and denitrification, O(\(^1\)D) + N\(_2\), and NH\(_2\) + NO\(_2\) contribute 0.30, 0.36, and 0.18\% to \(\Delta^{17}\)O, respectively, summing to a total of 0.82 to 0.90\%. Biomass burning and industrial processes only make a small contribution to \(\Delta^{17}\)O.

[7] The essence of the above mechanisms is to transfer a heavy oxygen atom originally in O\(_3\) to N\(_2\)O. It is known that atmospheric O\(_3\) is enriched in heavy isotopologues

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Table 1. Summary of Reactions for the Production of Atmospheric N$_2$O$^a$

<table>
<thead>
<tr>
<th>Mechanism$^*$</th>
<th>Reactions</th>
<th>Production(N$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>JPL06 recommended reactions</td>
<td>$4.24 \times 10^{-15}$</td>
</tr>
<tr>
<td></td>
<td>$O^*(D) + N_2 \rightarrow N_2O + M$</td>
<td>$4.1 \times 10^7$</td>
</tr>
<tr>
<td></td>
<td>$\Rightarrow$ $\phi\alpha[O^*(D)][N_2](1.2 \times 10^{-10}/9.65 \times 10^{15})$</td>
<td>$6.0 \times 10^3$</td>
</tr>
<tr>
<td>B1</td>
<td>Prasad’s interpretation</td>
<td>$5.3 \times 10^7$</td>
</tr>
<tr>
<td></td>
<td>$O^<em>(D) + O_3 \rightarrow O_2^</em>(B_1) + O^*(P)$</td>
<td>$\phi\alpha[O^*(D)][N_2]$</td>
</tr>
<tr>
<td></td>
<td>$\Rightarrow$ $\phi\alpha[O^*(D)][N_2] + M \rightarrow N_2O + M$</td>
<td>$8.9 \times 10^5$</td>
</tr>
</tbody>
</table>

*Kaiser and Röckmann [2005]*

$NH_3 + OH \rightarrow NH_2 + H_2O$

$NH_2 + NO_2 \rightarrow N_2O + H_2O$ $1 \times 10^7$

$McLinden et al. [2003]*

NO + hv $\rightarrow N + O$

$N + NO_2 \rightarrow N_2O + O$ $3 \times 10^6$

$^a$For this particular model, the tropospheric O$_3$ level is about 20–30 ppbv. Production (N$_2$O) denotes the column integrated N$_2$O production rate (molecules cm$^{-2}$ s$^{-1}$). The surface steady state N$_2$O upwelling flux is taken to be 1.95 \times 10^{15}$ molecules cm$^{-2}$ s$^{-1}$ (or 14.3 TgN/year), which gives a tropospheric N$_2$O abundance $\sim$320 ppbv; the flux is about $\sim$10% lower than 16.4 TgN/year reported in IPCC [2001], because the present atmosphere is not in steady state. The conversion factor from molecules cm$^{-2}$ s$^{-1}$ to TgN/year is 7.52 \times 10^{-5}. Note that densities used in the expression are in units of cm$^{-3}$.

$^b$The arrows indicate the expressions used for the production of N$_2$O in the model.

$^c$The value 1.2 \times 10^{-15} is the rate coefficient of the reaction O$(^3D) + O_3 \rightarrow 2 O_2$. The division by 9.65 \times 10^{15} is to account for that $\phi\alpha$ was obtained for this O$_3$ concentration.

$^d$The product of 1.2 \times 10^{-11} \times (110/T)[O^*(D)][N_2]$ represents the quenching rate of O$(^3D)$ with N$_2$.

---

and isotopomers with mass-independent fractionation [Mauersberger, 1987; Krankowsky et al., 2000; Mauersberger et al., 2001; Lümmertzahl et al., 2002; Brenninkmeijer et al., 2003; Thiemens, 2006]. The isotopic composition of atmospheric O$_3$ [Liang et al., 2006] can be well explained by two processes: formation [Thiemens and Heidenreich, 1983; Mauersberger et al., 1999; Gao and Marcus, 2001] and photolysis [Johnson et al., 2001; Bhattacharya et al., 2002; Blake et al., 2003; Liang et al., 2004; Miller et al., 2005; Prakash et al., 2005]. We briefly summarize the basic features of the O$_3$ isotopic anomaly. The isotopic enrichment is primarily caused by the formation of O$_3$. As a consequence of finite lifetime of O$_3$ complex in the intermediate state, symmetric molecules in their intermediate states tend to have greater deviation from their statistical density of states, compared with asymmetric isotopomers. This deviation is known as the “$\eta$ effect” [e.g., see Gao and Marcus, 2001]. This formation process results in $\delta^{48}O_3 \approx $ $\delta^{38}O_3 \approx 100\%$, relative to atmospheric O$_2$. In addition, about 10% of the observed O$_3$ isotopic enrichment is due to photolytic processes. The photolysis effect provides an explanation for the observed altitude variation of the O$_3$ isotopic composition in the stratosphere. See Liang et al. [2006] for details.

$^8$In this paper, we simulate the isotopic fractionation of O$_3$ and N$_2$O in one-dimensional (height) and two-dimensional (latitude and height) modes. The modeling of the longitudinal variation requires a three-dimensional model and will be deferred to a later paper. The calculated isotopic composition of O$_3$ is then used to evaluate new sources of N$_2$O and their associated oxygen anomaly. The paper is organized as follows. We summarize in section 2 a new interpretation [Prasad, 2002, 2005] of the laboratory measurements of the N$_2$O quantum yield in the mixture of O$_3$/O$_2$/N$_2$. To provide deeper insight into the physics of new N$_2$O sources, one-dimensional model results are presented and discussed in detail in section 3. The two-dimensional simulations that extend the results of one-dimensional models are shown in section 4. Implications for paleoatmospheric O$_3$ and concluding remarks are presented in section 5.

2. Sources of N$_2$O

[9] The current globally averaged surface abundance of N$_2$O is $\sim$320 ppbv, with a few parts per billion by volume more in the Northern Hemisphere than in the Southern Hemisphere. Several known sources of N$_2$O are reported in IPCC report [Intergovernmental Panel on Climate Change (IPCC), 2001], summing to a total emission of 16.4 TgN/year or 2.2 \times 10^9 molecules cm$^{-2}$ s$^{-1}$; about half of N$_2$O is emitted naturally and the rest is produced by anthropogenic activities. (The conversion factor for N$_2$O emission from molecules cm$^{-2}$ s$^{-1}$ to TgN/year is 7.52 \times 10^{-9}.) The identified major sinks for N$_2$O are photolysis (90%) and the reaction with O$(^3D)$ (10%). Both reactions occur primarily in the stratosphere, resulting in a lifetime of $\sim$120 years for N$_2$O. Consequently, there are only small vertical and horizontal gradients in N$_2$O in the troposphere.

[10] Isotopic measurements have been used to constrain the global N$_2$O budget. The observed $\delta^{15}N$ and $\delta^{18}O$ are 7.0 and 20.7% [Kim and Craig, 1993] relative to atmospheric N$_2$ and O$_2$, respectively. The atmospheric cycle of N$_2$O is as follows. Tropical rain forest, fertilized soils, and ocean are major source regions in the troposphere. Compared with the mean tropospheric values, the land source is strongly depleted in $^{15}N$ and $^{18}O$; the oceanic source is moderately depleted. The back flux of N$_2$O from the stratosphere is highly enriched in both $^{15}N$ and $^{18}O$. The budget of the isotopologues and isotopomers of N$_2$O is nearly balanced.

[11] The discovery of mass-independent oxygen anomaly in N$_2$O [Cliff and Thiemens, 1997; Cliff et al., 1999; Röckmann et al., 2001] suggests that its sources and sinks have not yet been completely understood. Several mechanisms that transfer heavy oxygen atom from O$_3$ to N$_2$O have
been proposed (see above). Of these proposals, the reactions of N₂ with O(¹D) and O₅ are supported by laboratory measurements [DeMore and Raper, 1962; Gaedtke et al., 1972; Kajimoto and Cvetanovic, 1976; Maric and Burrows, 1992; Estupiñán et al., 2002]. These processes provide a new source of N₂O in the atmosphere, contrary to the current belief that the source of N₂O in the atmosphere is negligible. The mechanism [Yung et al., 2004] that exchanges O atoms, Q(¹D) + N₂O → O + N₂Q, where Q = ¹⁸O or ¹⁷O, has been ruled out by laboratory experiments [Kaiser and Röckmann, 2005].

[12] In this paper, we follow the recommendation of Sander et al. [2006, JPL06 hereafter] for the production of N₂O from O(¹D) + N₂ [Estupiñán et al., 2002]. The JPL06 recommended reaction and the rate coefficient are taken to be our reference model and are denoted as mechanism A (Table 1). We also consider the interpretation of Prasad [2002, 2005], denoted as mechanism B, in which O₅ in its excited state reacting with N₂, instead of O(¹D) + N₂,

dominates the production of N₂O in the atmosphere. Prasad’s interpretation is briefly described below.

[13] The measurements of Estupiñán et al. [2002] were taken under atmospheric conditions, i.e., pressure spanning from ~100 to 1000 mbar and temperature from 220 to 324 K. The previous measurements [Kajimoto and Cvetanovic, 1976] of N₂O quantum yield were performed at much higher pressures (27–110 bar). Incorporating the measurements of the N₂O quantum yield in the solution of the mixture of O₅ and N₂ [DeMore and Raper, 1962], Prasad [2005] proposed a three-component model for the density (|M|) and temperature (T) dependence of the N₂O quantum yield, φ(N₂O):

\[ \phi(N₂O) = \phi_0 + \phi_1 + \phi_2, \]  

where \( \phi_0 \) represents the contribution from vibrationally and electronically excited O₅, O₅*(B₁), and has no density dependence (|M|⁰), \( \phi_1 \) represents electronically excited O₅, O₅*(B₂), and is a linear function of density (|M|¹), and \( \phi_2 \) denotes the reaction of O(¹D) + N₂ which has a squared dependence on density (|M|²). The functional forms of \( \phi_0 \), \( \phi_1 \), and \( \phi_2 \) are

\[ \phi_0 = 5.63 \times 10^{-5} \exp(-1899/T) \]  

\[ \phi_1 = 6.99 \times 10^{-26} |M| \Lambda(\lambda) \]  

\[ \phi_2 = \left( \frac{2.95}{T} \right)^{0.6} \chi \left( \frac{3.86 \times 10^{-26}|M| + \frac{|M|}{|M| + 1.98 \times 10^{24}}}{|M| + 8.98 \times 10^{25}} \right), \]  

where \( \chi \) is the volume mixing ratio of N₂, which is about 0.8. \( \phi_2 \) has wavelength dependence, \( \Lambda(\lambda) \), which is unity at wavelengths <300 nm, climbs to ~5 at ~320 nm, and then
drops at >320 nm [see Figure 2 of Prasad, 2002]. This wavelength dependent quantum yield of \( \text{N}_2\text{O} \) production is obtained by fitting the measurements performed in the liquid \( \text{O}_3/\text{N}_2 \) mixture [DeMore and Raper, 1962]. These mechanisms as well as some other proposed pathways are summarized in Table 1. The table shows that the mechanism of McLinden et al. [2003] is less significant, compared with the other three mechanisms.

[14] A one-dimensional model is used to evaluate the contribution from the aforementioned \( \text{N}_2\text{O} \) production pathways. The results are summarized in Table 1. It is shown that in Prasad’s interpretation, \( \phi_1 \) dominates the production of \( \text{N}_2\text{O} \). Therefore in the following discussion, we focus on \( \phi_1 \) as the source of \( \text{N}_2\text{O} \) in Prasad’s mechanism.

3. One-Dimensional Model

[15] To demonstrate the influence of the introduction of these new atmospheric \( \text{N}_2\text{O} \) sources, we first focus on one-dimensional modeling. The model is based on our previous papers on \( \text{O}_3 \) [Liang et al., 2006] and \( \text{CO}_2 \) [Liang et al., 2007] isotopic simulations. The profiles of \( \Delta^{17}\text{O}(\text{O}_3) \) and \( \Delta^{17}\text{O}(\text{O}(^{1}\text{D})) \) are shown in Figure 1. The small \( \Delta^{17}\text{O}(\text{O}(^{1}\text{D})) \) above \( 70 \) km is caused by \( \text{O}_2 \) Lyman-\( \alpha \) photolysis [see Liang et al., 2007]. The \( \Delta^{17}\text{O}(\text{O}_3) \) near the surface used here is greater than the reported values of 20–35\% [e.g., Johnston and Thiemens, 1997]. We note that the difference between model and observations could be reduced by applying more accurate temperature and pressure-dependent formation rates for \( \text{O}_3 \) isotopomers and isotopologues, which are currently not available. Even though our model is less satisfactory in the troposphere, our study on \( \text{N}_2\text{O} \) would not be seriously affected, because >2/3

Figure 4. Sensitivity of the results to the changes of tropospheric \( \text{O}_3 \) abundances and surface \( \text{N}_2\text{O} \) fluxes. Diamonds and crosses represent the model results based on mechanisms A and B, respectively. Asterisks represent the case where atmospheric \( \text{N}_2\text{O} \) sources vanish. Solid line represents a least squares linear fit to the results: \( y = -0.1063 + 37.6142x \).

Figure 5. Latitude-pressure plots of \( \text{O}_3 \) volume mixing ratios for January, April, July, and October.
of the atmospheric sources of N\textsubscript{2}O are in the stratosphere, where our current model can well reproduce the observed isotopic composition of O\textsubscript{3} [see Liang et al., 2006]. An error <50% in the modeled isotopic composition in the tropospheric O\textsubscript{3} results in an error <17% for the $\delta^{17}$O in the new source of N\textsubscript{2}O.

[16] Figure 2 shows the production rates of new N\textsubscript{2}O sources due to two processes: O(\textsuperscript{1}D) + N\textsubscript{2} (solid; mechanism A) and O\textsuperscript{3} + N\textsubscript{2} (dashed; mechanism B), where O\textsuperscript{3} is produced by the photolysis of O\textsubscript{3} in the Hartley-Huggins band (see section 2). The column integrated production rates of N\textsubscript{2}O from these two processes are $4.1 \times 10^7$ (0.3 TgN/year) (mechanism A) and $5.3 \times 10^7$ (0.4 TgN/year) (mechanism B) molecules cm\textsuperscript{-2} s\textsuperscript{-1}. The atmospheric N\textsubscript{2}O source constitutes about 2% of the total N\textsubscript{2}O source, $2 \times 10^9$ molecules cm\textsuperscript{-2} s\textsuperscript{-1} needed to maintain the surface N\textsubscript{2}O concentration of $\sim 320$ ppbv in steady state. [The surface flux ($1.9 \times 10^9$ molecules cm\textsuperscript{-2} s\textsuperscript{-1}) used here is slightly less ($\sim 10\%$) than the IPCC [2001] value, because the present atmosphere is not in steady state.] This suggests that the isotopic anomaly originally in O(\textsuperscript{1}D) or O\textsubscript{3} is diluted by a factor of $\sim 50$ when transferred to N\textsubscript{2}O. For $\Delta^{17}$O = 50$\%$o in O(\textsuperscript{1}D) or O\textsubscript{3}, we expect that $\Delta^{17}$O in N\textsubscript{2}O is 1$\%$.

[17] Calculated profiles of $\Delta^{17}$O for N\textsubscript{2}O are presented in Figure 3. In this model, the tropopause is at 14 km. Below 14 km, high eddy mixing causes the value of $\Delta^{17}$O to be nearly uniform. The sharp increase above 14 km is due to the enhancements of N\textsubscript{2}O production in the stratosphere and the weak stratosphere-troposphere exchange. As the destruction of N\textsubscript{2}O is characterized by a linear loss mechanism, the fractionation of isotopically substituted N\textsubscript{2}O can be considered as a Rayleigh fractionation process, which is...
described by the following formula [e.g., see Morgan et al., 2004 for details]:

\[
\ln \left( \frac{1 + \delta_i}{1 + \delta_{i,0}} \right) = \epsilon_i \ln(f),
\]

(9)

where \(\delta_i\) is the \(\delta\) for species \(i\), \(\delta_{i,0}\) is the initial \(\delta\), \(\epsilon_i\) is the fractionation factor caused by photolysis (see Liang et al. [2004] for a more detail definition and discussion for \(\epsilon\) factor), and \(f\) is the ratio of the remaining \(N_2O\) to that of the initial \(N_2O\) in the air parcel. When \(\delta\) is small, \(\delta\) is a linear function of \(\epsilon\):

\[
\delta_i \approx \delta_{i,0} \epsilon_i \ln(f).
\]

(10)

[18] In this paper, we assume an \(\epsilon\) for \(N_2^{17}O\) that is 0.515 times that for \(N_2^{18}O\), consistent with laboratory measurements [e.g., Kaiser et al., 2004]. This implies that \(\delta^{17}O(N_2^{17}O) \approx 0.515 \delta^{18}O(N_2^{18}O)\). When the \(\delta\) value of \(N_2O\) is as high as \(\sim 100\%\), the linear approximation [equation (10)] no longer holds. To minimize the nonlinearity between \(\delta\) and \(\epsilon\), we use the full expression in equation (9) to calculate \(\Delta^{17}O\), namely

\[
\Delta^{17}O(N_2O) = \delta^{17}O - \left[ (1 + \delta^{18}O)^{0.515} - 1 \right].
\]

(11)

[19] Though this equation can account for the nonlinearity between \(\delta\) and \(\epsilon\), it has a curious effect in that \(\Delta^{17}O(N_2O)\) does not vanish when the atmospheric \(N_2O\) source is zero (dotted line in Figure 3). This is due primarily to the selection of the reference (\(O_2\) here) in which the isotopic ratios deviate from the ratios in the target samples. For example, in the atmospheric \(N_2O\), the back flux of the stratospheric \(N_2O\) enhances the tropospheric \(\delta^{18}O\) in \(N_2^{18}O\) by \(\sim 15\%\). So \(\ln(1 + \delta^{18}O) - \delta^{18}O \approx -0.1\%\), which is still within the statistical error bar of the measurements of 0.2\% [e.g., Röckmann et al., 2001]. The value decreases with \(\delta^{18}O\) or altitude (see Figure 3).

[20] To gain insight into the impact of the new sources, we vary tropospheric \(O_3\) abundance and the flux of surface \(N_2O\) sources. The sensitivity of the results to these changes is summarized in Figure 4. It is shown that the oxygen anomaly of \(N_2O\) increases with the contribution from atmospheric \(N_2O\) sources. Note that under the same condition the reaction of \(O_3^*\) and \(N_2\) (mechanism B) tends to produce more \(N_2O\) and hence greater \(\Delta^{17}O\) anomaly (\(\sim 0.3\%\); Figure 3), compared with that of \(O(1D) + N_2\) (mechanism A). This is caused by \(\Lambda(\lambda)\) [equation (7)] that enhances the \(N_2O\) production at longer wavelengths where heavy \(O_3\) is more enriched. For similar \(N_2O\) production, \(\Delta^{17}O\) anomaly from the mechanism B is about 0.1\% in excess of the mechanism A (Figure 4).

4. Two-Dimensional Simulation

[21] To provide a direct comparison with atmospheric measurements, two-dimensional modeling is performed.
Two-dimensional models are sufficient in the stratosphere, where the longitudinal variation is insignificant. Since the N\textsubscript{2}O lifetime is long, two-dimensional modeling is a good approximation for this work. See Morgan et al. [2004] for details about the two-dimensional model.

[22] The isotopic composition of atmospheric O\textsubscript{3} is critical to modeling the oxygen anomaly in atmospheric N\textsubscript{2}O.

To account for the O\textsubscript{2} Lyman-\alpha photolysis [Liang et al., 2007] in the mesosphere, we calculate the isotopic composition of O\textsubscript{3} up to \(~130\) km, which is higher than our previous two-dimensional models of \(~80\) km [e.g., Morgan et al., 2004]. The horizontal and vertical eddy mixing coefficients are taken from Summers et al. [1997].

The two-dimensional advection and zonally averaged temperature are derived from the Whole Atmosphere Community Climate Model (WACCM; data available on the Website http://waccm.acd.ucar.edu/) 3-hourly outputs [Sassi et al., 2002, 2004]. We follow the same technique as in the work of Jiang et al. [2004] to derive the residual circulations [Andrews et al., 1987] needed for transport. The eddy diffusion coefficients, residual circulation, and temperature are then monthly averaged. The WACCM model outputs (winds and temperature) are used only to derive the profiles of O\textsubscript{3} and \(O(\text{^1}\text{D})\). For the simulation of N\textsubscript{2}O, we use the same atmospheric transport and temperature profiles as that in the work of Morgan et al. [2004]. This is to provide a better comparison with our previous N\textsubscript{2}O work [Morgan et al., 2004]. Comparisons between atmospheric circulations will be demonstrated in a later paper (Liang et al., Seasonal cycle of C\textsubscript{16}O\textsubscript{16}O, C\textsubscript{16}O\textsubscript{17}O, and C\textsubscript{16}O\textsubscript{18}O in the middle atmosphere: Implications for mesospheric dynamics and the biogeochemical sources and sinks of CO\textsubscript{2}, submitted to Journal of Geophysical Research: Atmosphere, 2007, hereinafter referred to as Liang et al., submitted manuscript, 2007) which studies the isotopic composition of CO\textsubscript{2}. The

**Figure 9.** Comparison of observed (diamonds) and modeled (solid) concentrations of N\textsubscript{2}O in the terrestrial atmosphere for March at 15\textdegree N. The observations are from the Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) campaigns [e.g., see Morgan et al., 2004].

**Figure 10.** Same as Figure 5 for \(\delta^{18}\text{O}(\text{N}_2\text{O})\) (mechanism A).
reason why we can use different circulations and different temperature profiles to simulate O\textsubscript{3} and N\textsubscript{2}O is that O\textsubscript{3} and O(\textsuperscript{1}D) are both short-lived, compared to dynamical transport, and their isotopic composition is insensitive to the variation of temperature (~0.6\% K\textsuperscript{-1}).

[23] Simplified oxygen chemistry is taken from the work of Liang et al. [2006]. The model is adjusted (with prescribed catalysts for the destruction of O\textsubscript{3}) in order to match the climatological O\textsubscript{3} profiles in the middle atmosphere. In the troposphere, our simplified oxygen chemical model does a less satisfactory job, because NO\textsubscript{x} (NO and NO\textsubscript{2}) chemistry is the major source of O\textsubscript{3} in the troposphere and it is not included in the current model. We scale our calculated O\textsubscript{3} concentration in the troposphere to match the climatological abundances [see, e.g., Morgan et al., 2004]. The same scaling factor is applied to the abundances of the isotopologues and isotopomers of O\textsubscript{3} and O(\textsuperscript{1}D). This scaling does not affect our calculation, as we assume that the isotopic fractionation is caused only by the formation and photolysis of O\textsubscript{3}.

[24] The calculated profiles of the abundance and the isotopic composition of O\textsubscript{3} are presented in Figures 5 and 6, respectively. This represents a generalization for our previous one-dimensional modeling [Liang et al., 2006]. It is shown that the seasonality of $\delta^{56}$O\textsubscript{3} is weak at low latitudes, consistent with temperature seasonality. Above the homopause (~90 km, or ~10\textsuperscript{-3} mbar), the depletion of $\delta^{56}$O\textsubscript{3} is caused by diffusive separation. Figure 7 shows the three-isotope plot of oxygen for O\textsubscript{3}, consistent with the results obtained previously [Liang et al., 2006] that the model overestimates the $\delta$ values of ozone by about 20\%, i.e., biased too high by ~20\%. Further laboratory measurements of the formation rates of O\textsubscript{3} isotopomers and isotopologues at atmospheric conditions are needed in order to resolve the bias.

[25] Figure 8 shows the calculated $\Delta^{17}$O in O\textsubscript{3}. The anomaly is on the order of 50\%. To explain the observed 1\% oxygen anomaly in N\textsubscript{2}O, the atmospheric source of N\textsubscript{2}O needs to be about 2\% of the total source, i.e., a column production of N\textsubscript{2}O ~5 x 10\textsuperscript{7} molecules cm\textsuperscript{-2} s\textsuperscript{-1} or 0.4 TgN/ year, consistent with the suggestion by Kaiser and Röckmann [2005].

[26] With this simplified model, the calculated N\textsubscript{2}O abundance (Figure 9) above ~20 mbar altitude level is slightly lower than our previous work [cf. Figure 2 of Morgan et al., 2004], but the value is still within the statistical variation of the observations. For comparison, the modeled $\delta^{18}$O in N\textsubscript{2}O is presented in Figure 10, which shows that the isotopic composition of $\delta^{18}$O above ~20 mbar level increases faster than previous models [Morgan et al., 2004].

[27] We then calculate the $\Delta^{17}$O of N\textsubscript{2}O based on mechanism A, using the O\textsubscript{3} abundance in Figure 5 and...
$\Delta^{17}\text{O}(\text{O}_3)$ in Figure 8, and the result is shown in Figure 11. The averaged $\Delta^{17}\text{O}$ in tropospheric and lower stratospheric N$_2$O is 0.57%. As described above, given an error <50% in the modeled isotopic composition in the tropospheric O$_3$ and 20% in the stratosphere, the error in the $\Delta^{17}\text{O}$ from the new source of N$_2$O is <30%, suggesting that the magnitude of the oxygen anomaly in N$_2$O produced by mechanism A is >0.40%. For comparison, the result based on mechanism B

Figure 12. Same as Figure 5 for $\Delta^{17}\text{O}$ in N$_2$O (mechanism B).

Figure 13. Seasonal cycle of the isoflux of $\delta^{18}\text{O}(\text{N}_2\text{O})$ (F) across the tropopause. Values are in $\text{%}\text{TgN/year}$. Negative values denote downward flux.
is shown in Figure 12. Using this model, the calculated $\Delta^{17}$O is 1.01 or >0.71‰ after accounting for a possible error in the tropospheric O$_3$.

Finally, we update the isoflux of $\delta^{18}$O of N$_2$O across the tropopause that was reported in our previous paper [Morgan et al., 2004]. The results are shown in Figure 13. The stratospheric processes enhance the abundance of N$_2$O relative to that in the troposphere. Negative values denote the isoflux is transported downward. The maximum downward isoflux appears at mid-latitudes of the summer Northern Hemisphere; a similar phenomenon has been seen in the isoflux of $\delta^{18}$O(CO$_2$) (Liang et al., submitted manuscript, 2007). In this work, we follow the same definition (independent of season) of the tropopause as in the work of Morgan et al. [2004], in which the tropopause is approximately at 100 mbar between 30°S and 30°N, 200 mbar between 30° and 60°, and 300 mbar poleward of 60°. The global annual isoflux of $\delta^{18}$O(N$_2$O) across the tropopause is $-95.3$‰ TgN/year, a factor of $\sim$2 less than the value reported by Morgan et al. [2004]. This is because the tropopause was defined at 86 mbar (not 100 mbar) by Morgan et al. [2004] where the $\delta^{18}$O of N$_2$O is greatly enhanced compared with that at lower altitudes at 100–200 mbar.

5. Discussion and Summary

Sources of nonzero $\Delta^{17}$O in atmospheric N$_2$O have long been a puzzle since its discovery in 1997 in tropospheric samples [Cliff and Thiemens, 1997]. Subsequent measurements [Cliff et al., 1999; Röckmann et al., 2001] confirmed the discovery and extended it to the stratosphere. The observed $\Delta^{17}$O is $\sim$1‰. To explain this anomaly, new atmospheric N$_2$O sources are proposed. This atmospheric N$_2$O source has to be of a few percent (Figure 4) of the sum of the anthropogenic and natural N$_2$O sources, contrary to the current belief that the atmospheric N$_2$O source is insignificant. Of the several proposed mechanisms for the new sources, the reactions of O$(^1$D) [Estupiñán et al., 2002] and O$_2$ [Prasad, 2002, 2005] with N$_2$ dominate and are supported by recent laboratory measurements [Estupiñán et al., 2002]. The former pathway is recommended by JPL06 [Sander et al., 2006].

Incorporating the proposed mechanisms into our two-dimensional models, we find that the $\Delta^{17}$O in N$_2$O increases with altitude (Figures 11 and 12). We also find that the seasonality of $\Delta^{17}$O is small at low latitudes but is significant at about 3 mbar in the polar regions. Future atmospheric measurements in these regions are needed to validate our model and to verify the existence of the new N$_2$O sources. Figure 14, which shows a scatterplot of $\Delta^{17}$O and $\delta^{18}$O, provides a direct comparison to observations, illustrating that $\Delta^{17}$O caused by mechanism A increases faster with $\delta^{18}$O than that by mechanism B.

To distinguish between mechanisms A and B, three tests are suggested. For atmospheric observations, the maximum seasonality of $\Delta^{17}$O is about 6% for mechanism A but it is $\sim$3.5% for mechanism B. In the laboratory, more measurements for the N$_2$O quantum yield in the mixture of O$_3$/O$_2$/N$_2$ are needed to be taken under conditions similar to the atmosphere (pressure $\sim$10–1000 mbar, temperature $\sim$200–300 K, and UV photons with wavelengths $\sim$230–350 nm). If mechanism B is correct, the $\Delta^{17}$O in N$_2$O and N$_2$O quantum yield have a stronger wavelength-dependence than that by mechanism A, especially in the Huggins band of O$_3$. One can also add CO$_2$ in laboratory samples. The isotopic composition of CO$_2$ is a powerful tracer for the abundance and the isotopic composition of O$(^1$D) [see Liang et al., 2007]. So an alternative way is to photolyze the O$_3$/O$_2$/N$_2$ mixture at Lyman-$\alpha$. If mechanism A is preferred, one will observe a highly enriched heavy N$_2$O, similar to that in mesospheric CO$_2$ [Liang et al., 2007; Liang et al., submitted manuscript, 2007].

In summary, we have quantitatively modeled the isotopic composition of O$_3$ and N$_2$O in the atmosphere. The calculated $\Delta^{17}$O of N$_2$O is 0.40–1.01‰. The total contribution from microbial nitrification and denitrification, biomass burning, industrial processes, NH$_4$+NO$_2$, and N + NO$_2$ is 0.46‰ [Kaiser and Röckmann, 2005]. These results suggest that either mechanism B is invalid or there are...
undiscovered sinks for $\Delta^{17}$O, if we assume that Kaiser and Röckmann’s estimate of 0.46% is applicable. Paleoa
tmospheric trace gas concentrations preserved in ice cores provide a wealth of information on biogeochemical cycles involving carbon, nitrogen, and oxygen. The $^{18}O$ and $^{17}O$ of N$_2$O over the past 30,000 years have been measured in ice cores [Sowers et al., 2003]. An extension to $^{17}O$ or $\Delta^{17}$O will provide additional information. The linear relationship (Figure 4) between the strength of atmospheric N$_2$O sources and $\Delta^{17}$O anomaly in N$_2$O can be used to constrain ozone levels in paleoa
tmospheres.

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