gold catalyst, and the N_2 and O_2 fractions were subsequently separated cryogenically. Pure O_2 was used for the mass spectrometric analysis. We collected air samples by in situ cryogenic trapping of N_2O and CO_2 from 1800 liters of air (*16*). All isotopic values are reported with the standard delta notation with respect to atmospheric O_2 (*32*).
14. M. H. Thiemens and W. C. Trogler, *Science* **251**, 932 (1991).
15. S. S. Cliff and M. H. Thiemens, *Anal. Chem.* **66**, 2791 (1994).
16. Atmospheric N_2O was extracted and purified from 1800 liters of air in a portable in situ cryogenic collection system. We predried ambient air to a dew point of about −70°C by first passing it through a Nafion (water permeable membrane, Perma Pure, Toms River, NJ) tube and subsequently through a polyvinyl chloride tube 2.5 cm in diameter and 1 m long containing Drierite (anhydrous $CaSO_4$; W. A. Hammond, Xenia, OH). The air flow was controlled by an MKS Instruments (Andover, MA) Mass Flow Controller (MFC) to a rate of 10 L/min (standard temperature and pressure). The dry air stream then flowed through two specially designed ultrahigh efficiency collection (UHEC) traps bathed in liquid nitrogen for condensation of N_2O, CO_2, and the remaining water. The UHEC traps are constructed of stainless steel and are virtually indestructible, allowing in situ collection in the field without damage to the system. The two UHEC traps in concert remove 99.9989% of CO_2 and N_2O, as demonstrated with ambient air concentrations. The N_2O was purified and transported on ascarite in stainless steel sample tubes to the laboratory for isotopic analysis. Sample sizes were constant at about 23.5 μmol of neat N_2O within the error of the known collected quantity of gas (±1% for MFC) and the error of measurement by a manometrically calibrated toepler pump (about ±1%). A. K. Huff, S. S. Cliff, M. H. Thiemens, *Anal. Chem.* **69**, 4267 (1997).
17. Experiments were performed with a standard N_2O sample subjected to each phase of the work-up procedure as described in (*15*). In addition, about 50 μmol of an isotopically well-defined N_2O sample was equilibrated with about 5 ml of degassed (freeze-pump-thaw cycles) H_2O. This vessel containing the H_2O-N_2O mixture was maintained at room temperature for 1 month. Measurements of the N_2O revealed no isotopic exchange (<0.1 per mil change in $\delta^{18}O$ and $\delta^{17}O$) with water.
18. J. C. Johnston, thesis, University of California, San Diego (1996), chap. 4.
19. ______, S. S. Cliff, M. H. Thiemens, *J. Geophys. Res.* **100**, 16801 (1995).
20. T. Rahn and M. Wahlen, *Science* **278**, 1776 (1997).
21. The enrichment factor (in units of per mil) is defined as $\varepsilon = (\alpha - 1)1000$, where α is the fractionation factor for the process.
22. H. Craig and K.-R. Kim, *Eos (Spring Suppl.)* **78**, S83 (1997).
23. Y. L. Yung and C. E. Miller, *Science* **278**, 1778 (1997).
24. M. McElroy and D. B. Jones, *Global Biogeochem. Cycles* **10**, 651 (1996).
25. E. C. Zipf and S. S. Prasad, *Eos (Spring Suppl.)* **78**, S82 (1997).
26. S. S. Prasad, *J. Geophys. Res.* **99**, 5285 (1994).
27. P. Harteck and S. Dondes, *J. Chem. Phys.* **22**, 758 (1954).
28. W. E. Groth and H. Shierholz, *ibid.* **27**, 973 (1957).
29. S. M. Anderson, K. Mauersberger, J. Morton, in *Progress and Problems in Atmospheric Chemistry*, J. R. Barker, Ed. (World Scientific, Singapore, 1995), pp. 473–497.
30. J. C. Johnston and M. H. Thiemens, *Eos (Fall Suppl.)* **76**, F85 (1995).
31. K. S. Griffith and G. I. Gellene, *J. Chem. Phys.* **96**, 4403 (1992).
32. The delta notation is defined as $\delta^{X}O = [(^{X}R_{SA}/^{X}R_{ST}) - 1]1000$, where $X = 17$ or 18, $^{X}R = {}^{X}O/^{16}O$, and the subscripts SA and ST refer to the sample and standard, respectively. Isotopic enrichment or depletion is reported as parts per thousand or per mil. Isotopic data for N_2O are reported relative to air O_2 by the relations $\delta^{18}O_{ATM} = -23.0 + \delta^{18}O_{SMOW}/1.0235$ and $\delta^{17}O_{ATM} = -12.1 + \delta^{17}O_{SMOW}/1.0122$ (where $\delta^{18}O_{SMOW} = 23.5$ per mil and $\delta^{17}O_{SMOW} = 12.2$ per mil; the subscripts SMOW and ATM are standard mean ocean water and atmospheric O_2, respectively).

33. We thank G. J. Wasserburg for the use of his laboratory for the CIT samples, WMRS for their assistance in sampling at Mount Barcroft, and E. Zipf for assistance in sampling at WSRM. Funding for this project has been provided by NSF (grant CHE9632311) and the U.S. Environmental Protection Agency (grant R822264-01-0).

17 July 1997; accepted 17 October 1997

Stable Isotope Enrichment in Stratospheric Nitrous Oxide

Thom Rahn* and Martin Wahlen

Nitrous oxide is a greenhouse gas that also plays a role in the cycling of stratospheric ozone. Air samples from the lower stratosphere exhibit $^{15}N/^{14}N$ and $^{18}O/^{16}O$ enrichment in nitrous oxide, which can be accounted for with a simple model describing an irreversible destruction process. The observed enrichments are quite large and incompatible with those determined for the main stratospheric nitrous oxide loss processes of photolysis and reaction with excited atomic oxygen. Thus, although no stratospheric source needs to be invoked, the data indicate that present understanding of stratospheric nitrous oxide chemistry is incomplete.

Nitrous oxide (N_2O) is an atmospheric trace gas that contributes to the greenhouse effect. It is also involved in the catalytic destruction of ozone in the stratosphere and is increasing in concentration by about 0.25% per year (*1*). The increase is believed to result from fertilizer use, emissions from internal combustion engines, biomass burning, and industrial processes (*2*). It is naturally produced by nitrification and denitrification in soils and in the oceans, and is destroyed in the stratosphere via photolysis (90%) and reaction with excited atomic oxygen [$O(^1D)$] (10%). Its atmospheric lifetime is between 100 and 150 years (*1*). Although the major sources and sinks of N_2O are known, they are poorly quantified and inadequately balanced, both in terms of mass exchange and in their N and O isotopic composition (*1–3*).

Stable isotopes have been used in the past to constrain sources and sinks of other atmospheric trace gases (*4*) but have yet to be successfully applied to N_2O. The isotopic approach to a global N_2O budget is hindered by the wide range of observed isotopic values for each of the major natural sources, making it difficult to assign a unique value to each of the source terms. Soil flux samples have been shown to be variable but consistently depleted in both ^{15}N and ^{18}O relative to atmospheric N_2O (*3*). Oceanic samples have exhibited a trend similar to typical nutrient profiles, with slightly depleted surface waters becoming progressively enriched along the nutricline and stabilizing with depth (*5*, *6*). Early analytical methods employed infrared absorption techniques (*7*) or required decomposition of N_2O with subsequent analyses of N_2 and CO_2 (*5*, *8*, *9*). The use of direct injection techniques was introduced in 1993 when Kim and Craig (*3*) reported heavy enrichment in both the N and O isotopes in two samples of stratospheric air. They proposed that a stratosphere to troposphere return flux of heavy N_2O could balance the observed isotopically light source terms, although a simple mass-balance model showed that this led to a considerable overcorrection. Direct injection of N_2O was subsequently shown to result in erroneous enrichment of $\delta^{15}N$ and $\delta^{18}O$ (*10*) when contaminated by trace amounts of CO_2 (*11*).

We present results for $\delta^{15}N$ and $\delta^{18}O$ of N_2O obtained from samples collected in the lower stratosphere (Table 1) (*12*). Five samples were collected at midnorthern latitudes on board NASA's WB-57 aircraft (*13*), and two samples were collected at high northern latitude during the 1988 Juelich balloon campaign (*14*). We also measured, for comparison, the isotopic composition of tropospheric N_2O sampled in La Jolla, California, under clean air conditions. Nitrous oxide mixing ratios decreased with height above the tropopause, whereas the heavy-isotope composition of the remnant N_2O was found to be increasingly enriched. If the process responsible for this enrichment is an irreversible sink and if the fractionation factor remains constant, the data should obey what is known as a Rayleigh distillation, in which the resulting isotopic enrichment is related to the fraction remaining by the equation

---

Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093–0220, USA.

*To whom correspondence should be addressed. E-mail: trahn@sdcc3.ucsd.edu

$$R = R_o \times f^{(\alpha-1)} \quad (1)$$

where R and R_o are the residual (stratospheric) and initial (tropospheric) heavy-to-light isotope ratios, respectively; f is the fraction of N_2O remaining (residual concentration divided by the initial concentration); and α is the ratio of the heavy-to-light reaction or photolysis rates. This relationship can be approximated by the equation

$$\delta \cong \delta_o + \varepsilon \times \ln(f) \quad (2)$$

where $\varepsilon = 1000(\alpha - 1)$ expressed in per mil; δ and δ_o are the residual and initial delta values, respectively; and the slope of Eq. 2, ε, is the enrichment factor. The stratospheric data from the WB-57 samples fit the Rayleigh distillation model well with a continuous fit through the tropospheric values (Fig. 1). The derived enrichment factors of $\varepsilon = -14.5$ per mil for $^{15}N_2O$ and $\varepsilon = -12.9$ per mil for $N_2{}^{18}O$ are large and of similar magnitude for both isotopes. The low-altitude balloon data compare favorably with the WB-57 results, whereas the high-altitude balloon data lie above the least squares fits, by far for $\delta^{15}N$ and less so for $\delta^{18}O$. Although the errors are significantly larger for the balloon samples because of their small sample size, we have no reason to regard these data differently. Therefore, we suggest that either competing loss processes (with different α's) change relative strengths as a function of altitude or that enrichment factors are increasing above a certain altitude, possibly as a function of changes in incident radiation.

The only stratospheric N_2O data for comparison are a single datum for $\delta^{15}N$ from Moore (*8*) and the two results of Kim and Craig (*3*) for both $\delta^{15}N$ and $\delta^{18}O$. The result of Moore was from a sample collected at a height of 20.8 km at 34°S with $\delta^{15}N = 19.2$ per mil (with no concentration indicated). This is intermediate with respect to the high-altitude balloon sample (27.3 per mil) and the upper limit of the WB-57 samples (13.9 per mil). The results of Kim and Craig are included in Fig. 1. Both samples are within the concentration range of the WB-57 data and yet are offset from the least squares fits. The possibility exists that the differences are real. However, inspection of the WB-57 data show that although they were collected over a period of 1 year and 3 months and at latitudes from 33° to 48° north, they are well correlated. This indicates that the processes involved are not latitude dependent (at least over the midlatitudes) nor do they appear to be seasonal in nature. Furthermore, extrapolation of data from Kim and Craig does not intercept tropospheric values for either $\delta^{15}N$ or $\delta^{18}O$. This trend could be interpreted as a non-Rayleigh process, but the steep initial slopes (about 70 and 100 per mil for $\delta^{15}N$ and $\delta^{18}O$, followed by abrupt transitions to slopes of 19 and 13 per mil) require that at least two different and isolated processes are operating and that the lower altitude one is associated with an extremely high enrichment factor. If a downward flux of N_2O with high $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios were responsible, the inflection would be expected to be reversed, steepening with altitude and the concomitant decrease in concentration. Finally, the balloon samples analyzed by Kim and Craig are contemporaneous with the balloon samples we analyzed. Although our high-altitude balloon data is elevated relative to the least squares fits, the lower altitude balloon data are consistent with the WB-57 data. At the time when the analyses of Kim and Craig were performed, the consequences of CO_2 contamination had not been reported. Because no check for CO_2 contamination was reported, the offset is most likely a result of trace amounts of contaminant CO_2.

We conclude that the data are most likely the result of a Rayleigh distillation process and reflect large isotopic fractionations for both N and O in either the known stratospheric sink processes or indicate the existence of additional sink processes. This simple Rayleigh process illustrates the working of the stratosphere. Tropospheric air, introduced into the stratosphere in the tropics, mixes both zonally and meridionally on short time scales (months) but is vertically stratified (years) along isentropic surfaces above the local tropopause. Species with stratospheric sinks but no sources exhibit simple relationships to this age stratification in terms of their isotopic signatures. Similar results reflecting Rayleigh distillation in the stratosphere have been obtained for $\delta^{13}C$ and δ^2H in methane (*15*). Stratospheric sources (*16*) can virtually be ruled out, because it is highly unlikely that source products could perfectly mimic a Rayleigh distillation process. The intersection of the data with the isotopic values of tropospheric N_2O also suggests that a sink process is causing the observed enrichments.

Table 1. Sample locations and altitudes with corresponding concentrations and corrected isotopic data. The isotopic data are reported relative to those of atmospheric N_2 and O_2. The height of the tropopause for the WB-57 samples was determined by averaging radiosonde data from stations surrounding the sampling locations. Most WB-57 samples were collected on transects between Houston, Texas, and Minneapolis, Minnesota. Samples which were of large enough volume were analyzed in duplicate. When analyzed in duplicate, $\delta^{15}N$ values are within 0.2 per mil and $\delta^{18}O$ values are within 0.6 per mil (1σ). Lat./long., latitude and longitude; Alt., altitude; NM, not measured; N/A, not applicable.

Sample number	Sample date	Lat./long.	Alt. (km)	Hgt > TPP (km)†	N_2O (ppbv)	$\delta^{15}N$ Rel. to N_2	$\delta^{18}O$ Rel. to O_2
M2726	1/27/88	46 N/94 W	17.4	6.6	238	10.0	24.6
LL21119	2/10/88	68 N/20 E	14.4	NM	273	7.9	21.6
LL21109	2/10/88	68 N/20 E	22.6	NM	126	27.3	34.8
M0131*	5/10/88	39 N/94 W	18.3	4.8	230	10.7	25.6
E1983	5/10/88	45 N/94 W	16.8	4.4	245	10.0	24.7
E1690*	4/12/89	40 N/94 W	15.3	4.3	248	9.3	23.8
M3033*	4/12/89	48 N/94 W	17.4	6.7	185	13.9	28.1
CDK64284*	5/19/94	33 N/117 W	0	N/A	320	6.4	21.5

*Indicates samples that were analyzed in duplicate. †Hgt > TPP is the height above the local tropopause.

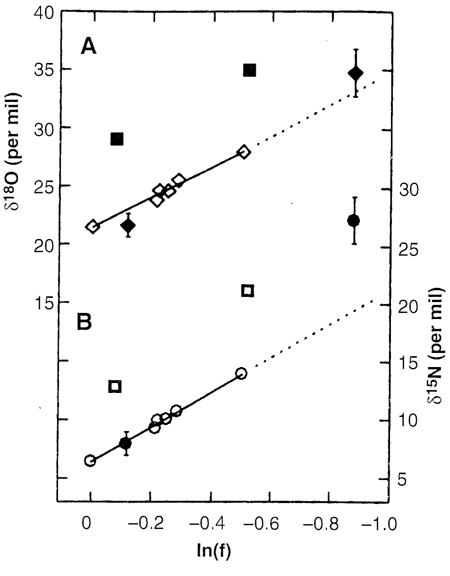

Fig. 1. Nitrous oxide isotopic data plotted against the natural log of the fraction remaining for (**A**) $\delta^{18}O$ and (**B**) $\delta^{15}N$ (see text for details). WB-57 data are indicated by open circles ($\delta^{15}N$) and open diamonds ($\delta^{18}O$). Corresponding filled symbols indicate the Juelich balloon data. Open and filled squares are data of Kim and Craig (*3*) for $\delta^{15}N$ and $\delta^{18}O$, respectively. Unless otherwise indicated, the error (1σ) associated with isotopic analysis is less than or equal to the symbol size, except for data of Kim and Craig which had no analytical error reported. Dotted lines are extrapolations of the regression analyses for the WB-57 data.

Laboratory results from photooxidation and photolysis experiments (17) predict an enrichment factor of $\varepsilon = -0.6$ per mil for ^{18}O, a result which is incompatible with the value of -12.9 per mil derived from our data. If the observed stratospheric enrichments are caused by the known sink reactions, this comparison would indicate that the conditions under which the laboratory data were obtained were not representative of stratospheric conditions, and that these enrichment factors are not applicable to the stratosphere. The laboratory photolysis experiments were conducted at a wavelength of 184.9 nm, near the peak of the N_2O absorption continuum. However, peak photolysis rates in the stratosphere occur between 195 and 205 nm (18) because of the tail of the Schumann-Runge bands of O_2 absorption. A theoretical treatment has been carried out by Yung and Miller (19) which suggests the possibility of a wavelength-dependent fractionation at wavelengths greater than 185 nm. Alternatively, there may be other stratospheric sinks such as heterogeneous reactions on or in aerosols, because the samples originate from close to the Junge layer of peak concentrations of H_2SO_4 and HNO_3 aerosols (20). Finally, there might exist an exchange mechanism wherein isotopically enriched N and O are transferred to molecular N_2O with no apparent loss, but this is unlikely.

Thus, our data imply that the observed isotopic enrichments are the result of a stratospheric sink process and that the contribution of a return flux of isotopically enriched N_2O from the stratosphere to the troposphere should indeed help balance the isotopically light, biologically mediated, source terms as proposed by Kim and Craig (3) [although potential terrestrial sources of isotopically enriched N_2O have recently been observed (21)]. The observed enrichment factors, however, are incompatible with those produced in the laboratory and indicate that present understanding of the details of N_2O photochemistry is still incomplete.

REFERENCES AND NOTES

1. "Scientific Assessment of Ozone Depletion: 1994," *WMO Global Ozone Research and Monitoring Project–Report No. 37* (World Meteorological Organization, Geneva, Switzerland, 1995).
2. M. A. K. Khalil and R. A. Rasmussen, *J. Geophys. Res.* **97**, 14651 (1992); A. F. Bouwman, K. W. Van der Hoek, J. G. J. Olivier, *ibid.* **100**, 2785 (1995).
3. K.-R. Kim and H. Craig, *Science* **262**, 1855 (1993).
4. C. D. Keeling *et al.*, in *Aspects of Climate Variability in the Pacific and Western Americas*, D. H. Peterson, Ed. (American Geophysical Union, Washington, DC, 1989), pp. 165–236; C. M. Stevens, in *Atmospheric Methane: Sources, Sinks, and Role in Global Change*, M. A. K. Khalil, Ed. (Springer-Verlag, Berlin/Heidelberg, 1993), pp. 62–88; M. Wahlen *et al.*, *Science* **245**, 286 (1989); M. Wahlen, *Annu. Rev. Earth Planet. Sci.* **21**, 407 (1993); M. Wahlen, in *Stable Isotopes in Ecology and Environmental Science*, K. Lajtha and R. H. Michener, Eds. (Blackwell, Cambridge, MA, 1994), pp. 93–113; P. D. Quay *et al.*, *Global Biogeochem. Cycles* **5**, 25 (1991); C. M. Stevens *et al.*, *Earth Planet. Sci. Lett.* **16**, 147 (1972); M. R. Manning, C. A. M. Brenninkmeijer, W. Allan, *J. Geophys. Res.* **102**, 10673 (1997).
5. K.-R. Kim and H. Craig, *Nature* **347**, 58 (1990).
6. T. Yoshinari *et al.*, *Mar. Chem.* **56**, 253 (1997).
7. M. Wahlen and T. Yoshinari, *Nature* **313**, 780 (1985). T. Yoshinari and M. Wahlen, *ibid.* **317**, 349 (1985).
8. H. Moore, *Tellus* **26**, 169 (1974).
9. N. Yoshida, *Nature* **335**, 528 (1988); ______ and S. Matsuo, *Geochem. J.* **17**, 231 (1983).
10. $\delta = (R_s/R_{std} - 1)1000$ where R_s and R_{std} are the heavy-to-light isotope ratios in the sample and standard, respectively.
11. The mass species measured during direct injection of N_2O—44, 45, and 46 atomic mass units—are subject to interference by the abundant isotopomers of CO_2 of the same mass [N. Tanaka, D. M. Rye, R. O. Rye II, H. Avak, T. Yoshinari, *Int. J. Mass Spectrom. Ion Processes* **142**, 163 (1995); T. A. Rahn and M. Wahlen, *Eos* **77** (no. 17), S51 (1996)].
12. Purified N_2O was cryogenically separated from the air samples after removal of CO_2 with a column of ascarite. Removal of remaining contaminants was achieved by processing through a gas chromatograph fitted with a thermal conductivity detector (we used a 3/8 inch, stainless steel column of 2-m length packed with PorapakQ and operated at a temperature of 18°C with ultrahigh purity helium as carrier gas). The recovered N_2O was then measured directly by stable isotope mass spectrometry on our dual-inlet VG Prism II mass spectrometer (VG Isotech, Manchester, UK). The extraction techniques were tested with artificial air standards made with N_2O working gas of known isotopic composition. To ensure accurate isotopic analyses, we monitored two indicators of CO_2 contamination—the beam intensities of $M/z = 12$ (elemental carbon) and $M/z = 22$ (doubly ionized CO_2) {the second ionization efficiency for N_2O is negligible compared to that for CO_2 [I. Iga, M. V. V. S. Rao, S. K. Srivastrava, *J. Geophys. Res.* **101**, 9261 (1996); H. C. Straub, B. G. Lindsay, K. A. Smith, R. F. Stebbings, *J. Chem. Phys.* **105**, 4015 (1996)]}—and applied corrections when necessary. Corrections were derived from empirical relationships developed by analyses of N_2O standards spiked with known quantities of CO_2. The sensitivity of N_2O isotope analysis to CO_2 contamination in our mass spectrometer is 6.8 per mil/% CO_2 for δ^{15}N and 12.4 per mil/% CO_2 for δ^{18}O. Complete removal of CO_2 has proven difficult to accomplish in the typically small sample sizes [all WB-57 samples were ~10 μl N_2O standard temperature and pressure (STP); balloon samples were ~2 μl N_2O STP]. Corrections are usually on the order of a few tenths of a per mil with corrections of several per mil not uncommon. All sample extractions and isotopic analyses were performed in November and December of 1996. Nitrous oxide mixing ratios in the samples were analyzed by a gas chromatograph with an electron capture detector immediately after collection in 1988 and 1989, and verified before extraction in 1996.
13. Atmospheric Research Equipment, Pressure System Platform, RB-57 (R)F Aircraft, *U.S. Air Force Technical Manual: T. O. 12M5-4-11-2* (1972).
14. U. Schmidt, D. Knapska, S. A. Penkett, *J. Atmos. Chem.* **3**, 363 (1985).
15. M. Wahlen *et al.*, *Eos* **70**, 1017 (1989).
16. M. B. McElroy and D. B. A. Jones, *Global Biogeochem. Cycles* **10**, 651 (1996).
17. J. Johnston, S. Cliff, M. H. Thiemens, *J. Geophys. Res.* **100**, 16801 (1993).
18. L. Froidevaux and Y. L. Yung, *Geophys. Res. Lett.* **9**, 854 (1982); K. Minschwaner, R. J. Salawitch, M. B. McElroy, *J. Geophys. Res.* **98**, 10543 (1995).
19. Y. L. Yung and C. E. Miller, *Science* **278**, 1778 (1997).
20. C. E. Junge, *Air Chemistry and Radioactivity* (Academic Press, New York, 1963).
21. K. Mandernack, T. Rahn, M. Wahlen, J. Bogner, in preparation.
22. We thank H. Weyer and the WB-57 crew for the samples collected on training flights and H. U. Schmidt for the balloon samples. Partially supported by a grant from the Max-Planck Institute of Atmospheric Chemistry, Mainz, Germany. We thank P. Crutzen for this support.

28 July 1997; accepted 27 October 1997

Isotopic Fractionation of Stratospheric Nitrous Oxide

Yuk L. Yung and Charles E. Miller

We propose an isotopic fractionation mechanism, based on photolytic destruction, to explain the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ fractionation of stratospheric nitrous oxide (N_2O) and reconcile laboratory experiments with atmospheric observations. The theory predicts that (i) the isotopomers $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ have very different isotopic fractionations in the stratosphere, and (ii) laboratory photolysis experiments conducted at 205 nanometers should better simulate the observed isotopic fractionation of stratospheric N_2O. Modeling results indicate that there is no compelling reason to invoke a significant chemical source of N_2O in the middle atmosphere and that individual N_2O isotopomers might be useful tracers of stratospheric air parcel motion.

The continued increase of N_2O in the atmosphere is a serious environmental concern because it is an efficient greenhouse gas (1) as well as the principal source of odd nitrogen that regulates the ozone layer (2). Despite its importance, the N_2O budget is currently not well quantified, which makes it difficult to determine the precise source and the cause of its increase (3–6). Recent measurements of isotopic fractionation of N_2O in the stratosphere (7, 8) and laboratory experiments demonstrating an apparent lack of isotopic signature in its principal loss mechanism (9) (photolysis) suggest that the standard atmospheric chemistry

---

Y. L. Yung, Division of Geological and Planetary Sciences, California Institute of Technology, Mail Stop 150-21, Pasadena, CA 91125, USA.
C. L. Miller, Atmospheric Kinetics and Photochemistry Group, Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-901, 4800 Oak Grove Drive, Pasadena, CA 91109-8099, USA.