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First measurement of the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios in stratospheric nitrous oxide: A mass-independent anomaly

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Abstract. The first multi-oxygen isotopic analysis of nitrous oxide samples from the lower stratosphere has a mass-independent composition. This study extends the results from tropospheric nitrous oxide samples. Measurements are reported from two 8 - 12 km altitude airplane flights from New Zealand to the Antarctic in June and October 1993. The observed isotopic results strengthen the previous argument that an atmospheric process, source, sink, or exchange reaction, involving nitrous oxide must exist in the atmosphere, and they further define its signature.

1. Introduction

Nitrous oxide (N_2O) is an important gas in the Earth's atmosphere because of its absorption of infrared radiation as well as its ozone depletion potential [World Meteorological Organization (WMO), 1995]. Concentration measurements of atmospheric N_2O indicate an increase in the atmospheric loading of this molecule at a rate of 0.2-0.3%/yr. Current understanding of the budget of atmospheric N_2O is limited to large, sometimes up to a factor of 10, ranges in the predicted strengths of individual sources. Recent data for tropospheric N_2O samples [*Cliff and Thiemens*, 1997] have indicated a mass-independent fractionation in the isotopes of oxygen. Although the cause of this specific type of fractionation is as yet unknown, it implies new sources and/or sinks of N_2O in the atmosphere.

Several features of the isotopic chemistry of atmospheric N_2O raise questions about the mechanisms which produce and destroy this molecule. The discovery of an isotopic enrichment in ^{15}N and ^{18}O in stratospheric N_2O [*Kim and Craig*, 1993; *Rahn and Wahlen*, 1997] suggests a process in the atmosphere that preferentially destroys light oxygen and nitrogen isotopes in N_2O.

(R1) $N_2O + h\nu \rightarrow N_2 + O(^1D)$, ($\lambda < 240$ nm) (90%)
(R2a) $N_2O + O(^1D) \rightarrow NO + NO$ (6%)
(R2b) $N_2O + O(^1D) \rightarrow N_2 + O_2$ (4%)

Measurement of the fractionation factors for the stratospheric sink reactions (R1), and (R2a), and (R2b) indicates essentially no fractionation in the photolysis reaction (R1) at 185 nm and a small, mass-dependent fractionation in the photooxidation reactions (R2a) and (R2b) [*Johnston et al.*, 1995]. The combined results of these atmospheric and laboratory measurements imply that unrealized processes occur in the stratosphere that destroy N_2O [*Cliff and Thiemens*, 1997]. A recent theoretical treatment of the wavelength isotopic dependency in N_2O photolysis, however, raises new issues with regard to stratospheric sinks [*Yung and Miller*, 1997]. Laboratory experiments apparently confirm a wavelength dependency [*Rahn et al.*, 1998], although these experiments exceed the fractionation predicted by *Yung and Miller* [1997]. Further experiments are needed to quantify this effect, particularly for the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios. Although new atmospheric sinks based on the discrepancy between laboratory measurements of N_2O photolysis [*Johnston et al.*, 1995] and stratospheric isotopic observations [*Kim and Craig*, 1993; *Rahn and Wahlen*, 1997] seem unlikely, the source of the mass-independent observation in atmospheric N_2O [*Cliff and Thiemens*, 1997] remains unexplained.

A mass-independent isotopic anomaly may derive from stratospheric N_2O photolysis, but it is not predicted by the model calculation of *Yung and Miller* [1997]. Their model relies on the change in absorption cross section with changing wavelength in the photolysis (reaction (R1)) of N_2O. These absorption cross-section variations are based on the differences in zero point energy (ZPE) of the isotopically substituted species. We will denote the isotopic N_2O species 446, 456, 546, 447, and 448 for $^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{17}O$, and $^{14}N^{14}N^{18}O$, respectively. A relative increase in the photodestruction rate from 446 to 447 to 448 will occur based on the Yung and Miller model calculation. However, this model relies on ZPE differences in the isotopically substituted species; therefore the fractionation is expected to be strictly mass-

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dependent. No model calculation was made for the expected fractionation of 447/448 ratio relative to 446 N_2O [*Yung and Miller*, 1997]. Simultaneous $\delta^{17}O$ and $\delta^{18}O$ measurements of the wavelength-dependent N_2O photolysis process are clearly needed.

2. Method

In this paper we present oxygen isotopic measurements of the lowermost stratospheric N_2O. These results are the first $\delta^{18}O$ and $\delta^{17}O$ measurements of stratospheric N_2O. A total of 14 stratospheric N_2O samples were isotopically analyzed. Twenty-four air samples were taken from aboard a U.S. Air Force C-141 (Starlifter), 8 on June 6 and 16 between three flights on October 22-25, 1993. Four more samples were collected aboard a C130 (Hercules) on October 21, 1993. Flights were from Christchurch, New Zealand, to either McMurdo or the South Pole and back, along an approximately 170°E longitude. June flight samples were collected between 10 and 12 km pressure altitude, while the tropopause level was consistently below the flight for all samples taken [*Thiemens et al.*, 1995]. October flight samples were taken between 8 and 11 km pressure altitude. Description of flight parameters and atmospheric dynamics is reported by *Thiemens et al.* [1995] and *Brenninkmeijer et al.* [1995] for the June flight and by *Brenninkmeijer et al.* [1996] for the October flight. N_2O samples for isotopic analysis were combined from two individual air sample collections on the basis of similarity in ^{14}CO activity, which correlated with potential vorticity measurements for the individual samples. Combination of samples was necessary because of the sample size requirement for isotopic analysis at the time of measurement. A sample collection represents a horizontal span of approximately 200 km; thus the combined samples represent approximately 400 km. The dried air samples were compressed into 10 L Al cylinders, followed by CO_2/N_2O extraction in the laboratory. The sampling procedure is described by *Brenninkmeijer et al.* [1995, 1996 and references therein], and the extraction system is described by *Brenninkmeijer* [1993]. Oxygen isotopic analysis of N_2O was carried out according to the method described by *Cliff and Thiemens* [1994]. Typical errors for collection and analysis of atmospheric N_2O are 0.2‰ for $\delta^{18}O$ and 0.1‰ for $\delta^{17}O$ [*Cliff*, 1998]. The error associated with collection of these samples is negligible as N_2O recovery is quantitative with over 99.9% of N_2O removed from the stratospheric whole air samples [*Brenninkmeijer*, 1993]. For the N_2O isotopic measurements, errors are typically 0.1‰ for $\delta^{17}O$ and $\delta^{18}O$ [*Cliff and Thiemens*, 1994]. Results (Figures 1-3) are presented using the standard delta notation with respect to air O_2. The delta notation is defined as: $\delta^X O$ (‰)=$(^XR_{SA}/^XR_{ST} - 1)1000$ (X=18, 17), where $^XR=^XO/^{16}O$ and the subscripts SA and ST refer to the sample and standard, respectively. Isotopic enrichment or depletion is reported as per mil (‰). Isotopic data for N_2O are, by convention, reported relative to air O_2 ($\delta^{18}O_{SMOW}$=23.5‰ and $\delta^{17}O_{SMOW}$=12.2‰, where SMOW is standard mean ocean water) converted by the relation $\delta^{18}O_{ATM}$=-23.0 + $\delta^{18}O_{SMOW}$/1.0235 and $\delta^{17}O_{ATM}$=-12.1 + $\delta^{17}O_{SMOW}$/1.0122, where ATM is the isotopic enrichment or depletion with respect to atmospheric O_2.

3. Results and Discussion

The data for the two Antarctic flights are plotted on three-isotope diagrams with $\delta^{17}O$ on the y axis and $\delta^{18}O$ on the x axis (Figures 1-3). The mass-dependent fractionation line is displayed in each. Deviation from this line is termed mass-independent and is quantified by the value $^{17}\Delta$, where $^{17}\Delta=\delta^{17}O - [(0.515)\delta^{18}O]$. The $^{17}\Delta$ is the vertical difference between an individual datum and the mass-dependent fractionation line. Any potential fractionation associated with collection and analysis procedures has been determined to be mass-dependent ($^{17}\Delta$ = 0). The N_2O mass-dependent fractionation line was experimentally determined [*Cliff and Thiemens*, 1997]. Figure 1 illustrates the entire atmospheric N_2O data set from several surface-air field collections [*Cliff and Thiemens*, 1997], and the stratosphere plotted with the mass-dependent fractionation line. The encircled area in Figure 1 encompasses all atmospheric $\delta^{18}O$ and $\delta^{17}O$ data, and the mass-dependent fractionation line extending through SMOW is shown for reference.

Figure 2 is an enlargement of the encircled area from Figure 1, illustrating only the stratospheric N_2O isotopic data. The data shown in Figure 2 indicate a variable mass-independent enrichment of the heavy isotopes of oxygen in stratospheric N_2O. A range in $\delta^{18}O$ of approximately 3‰ and in $^{17}\Delta$ of 0.5‰ is given for all flights, owing to variations in air mass between sample collections. Since the data in Figure 2 were collected from a horizontal flight path, vertical correlations of isotopic values with altitude are not available. Also, N_2O concentration measurements were not made, but a methane (CH_4) concentration variation of about 150 ppb is reported for these samples [*Brenninkmeijer et al.*, 1995, 1996]. Typically, a CH_4

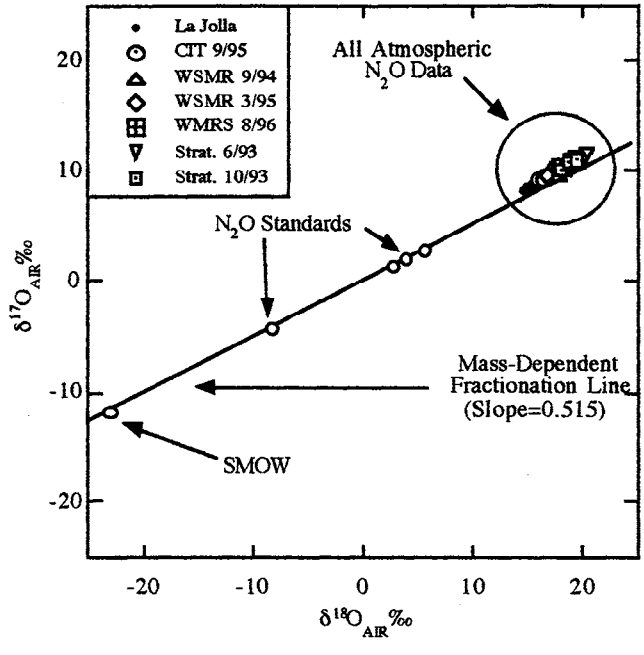

Figure 1. Three-isotope diagram of $\delta^{18}O$ and $\delta^{17}O$ for all atmospheric N_2O samples. Data are from La Jolla, California Institute of Technology (CIT), White Sands Missile Range (WSMR), White Mountain Research Station (WMRS), and the stratosphere (Strat.) and the mass-dependent fractionation line is from *Cliff and Thiemens* [1997]. The mass-dependent fractionation line is determined by replicate analysis of many laboratory standards. Note that all standards are not shown as some values overlap atmospheric data. The encircled area represents the bulk N_2O isotopic data set. SMOW is plotted for reference.

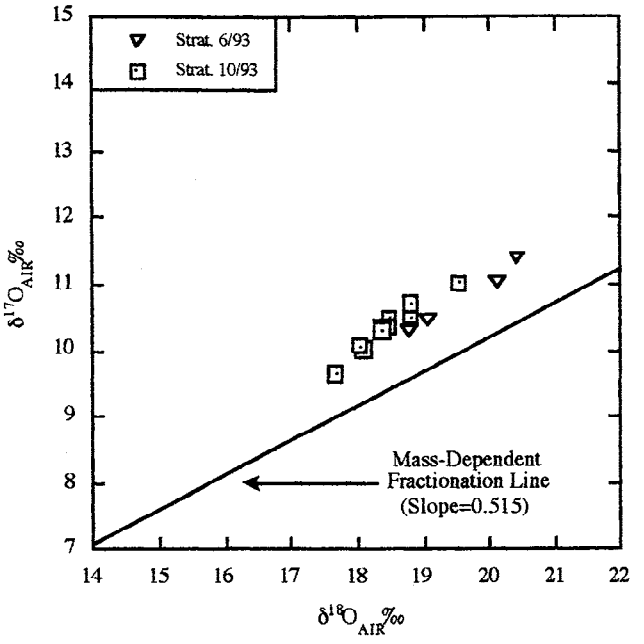

Figure 2. Three-isotope diagram of stratospheric N_2O data from Antarctic flights.

concentration variation of 100 ppb is associated with a 16 ppb N_2O concentration variation in the stratosphere. Therefore the N_2O concentration variation in these samples is extrapolated to be approximately 24 ppb. Furthermore, *Thiemens et al.* [1995] observed a strong linear correlation between the $^{17}\Delta$ in CO_2 and ^{14}CO abundance for these same samples. The mass-independent isotopic enrichment in CO_2 is known to derive from its exchange with $O(^1D)$ produced from stratospheric O_3 photolysis [*Wen and Thiemens*, 1993]. The positive correlation of high ^{14}CO abundance with high $^{17}\Delta$ in CO_2, each a relative index of altitude, suggests sampling of variable air masses along the horizontal flight track. Because stratospheric N_2O is known to be enriched in ^{18}O [*Kim and Craig*, 1993; *Rahn and Wahlen*, 1997], the enhanced $\delta^{18}O$ in these samples (Figure 2) combined with the inferred N_2O concentration variation confirms sampling of stratospheric air. Finally, the observations of Thiemens et al. independently verify stratospheric air character in these samples.

To better compare N_2O isotopic data of the stratosphere and troposphere, Figure 3 is presented. Figure 3 is an enlarged diagram of the area in the circle in Figure 1 and represents the total isotopic ($\delta^{17}O$ and $\delta^{18}O$) data set of atmospheric N_2O. The tropospheric values show a qualitatively increasing mass-independent enrichment with increasing altitude or distance from primary sources [*Cliff and Thiemens*, 1997]. The long-term record of data from La Jolla is from samples collected at the same site over a 4 year period without respect to date or atmospheric conditions (e.g., not sampled only when wind is from the west or the ocean) [*Cliff and Thiemens*, 1997]. Isotopic variability in the tropospheric data is consistent with that reported previously [*Wahlen and Yoshinari*, 1985]. From the tropospheric data it was concluded that an atmospheric process is responsible for the enrichment [*Cliff and Thiemens*, 1997]. The data from the lower stratosphere strengthen this conclusion. Figure 3 indicates that the stratospheric N_2O isotopic data are significantly more enriched, by more than 0.5‰ in $\delta^{18}O$ for the heaviest case, than any tropospheric N_2O. A correlation between $^{17}\Delta$ and ^{14}CO is observed for the June flight only, but this correlation is not seen in the October flights. Also, the $^{17}\Delta$ N_2O does not correlate with other measured parameters. However, because the $^{17}\Delta$ is greater in these samples, these data imply a process which increases the $^{17}\Delta$ of N_2O once in the atmosphere. An atmospheric source of the mass-independent anomaly is consistent with this observation.

For ground level N_2O the White Mountain Research Station (WMRS) data (from 3.8 km elevation) were found to have the greatest enhancement in $\delta^{17}O$ and $\delta^{18}O$ [*Cliff and Thiemens*, 1997]. The stratospheric N_2O samples exhibit still greater enrichment. In two of the datum an enrichment in the $\delta^{18}O$ over tropospheric N_2O of almost 1‰ is observed. These data are consistent with a mixing of high $\delta^{18}O$ middle and upper stratospheric N_2O into the troposphere [*Kim and Craig*, 1993].

Although a mass-independent enrichment in the heavy isotopes of oxygen in stratospheric N_2O is observed, this does not necessarily rule out the potential for a tropospheric source of the effect. Since it is known that at least a small enrichment of $\delta^{18}O$ in N_2O occurs in the stratosphere by loss mechanisms (reactions (R2a) and (R2b)) [*Johnston et al.*, 1995], mixing between stratospheric heavy N_2O with ground level mass-dependent N_2O and tropospheric mass-independent N_2O could produce the observations of the lower stratospheric samples. Several potential atmospheric sources and sinks of N_2O are suggested in the literature [*Prasad and Zipf*, 1981; *Prasad*, 1994, 1997; *Prasad et al.*, 1997]. Furthermore, ion-molecule reactions producing enormous (>10,000‰) isotopic fractionations are known to exist [*Griffith and Gellene*, 1992]. Reactions of this type would be consistent with the normally small concentration and isotopic variations reported on atmospheric N_2O and with the model predictions based on these small fluctuations (C.D. Nevison et al., Constraints on N_2O sinks inferred from observed tracer correlation in the lower stratosphere, submitted to *Geophysical Research Letters*, 1998).

Whether the source of the mass-independent anomaly is found to derive from the troposphere or stratosphere, it may still

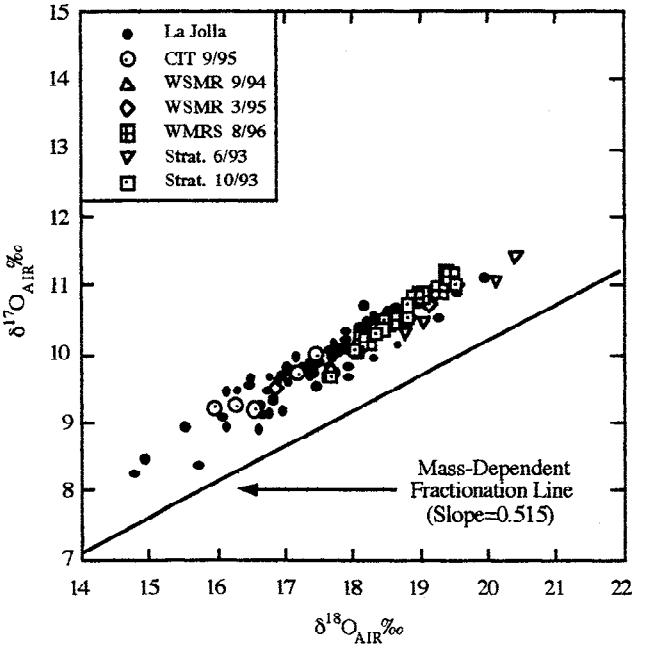

Figure 3. A detail of Figure 1 in the 14‰ ≤ $\delta^{18}O$ ≤ 22‰ region. All data are plotted with respect to air O_2.

provide a useful tracer of cross-tropopause transport. The $^{17}\Delta$ value of these stratospheric samples (Figure 1) is a reflection of a mixture of N_2O from at least two environments, a mass-independent process and a mass-dependent fractionation that enriches the $\delta^{18}O$ in the stratosphere [*Johnston et al.*, 1995]. If the source of the effect is found to derive from the wavelength dependency in photolysis [*Yung and Miller*, 1997], the $^{17}\Delta$ value is a sensitive tracer of stratospheric N_2O in the troposphere. The value of $^{17}\Delta$, by definition, is a robust measure of a specific process that is not affected by subsequent mass-dependent fractionations as $\delta^{18}O$ and $\delta^{15}N$ measurements are. Only the analysis of $\delta^{17}O$ and $\delta^{18}O$ permit differentiation between mass-dependent and mass-independent processes, and this analysis is requisite for the confirmation of the role of wavelength dependency of N_2O photolysis.

4. Conclusions

Analysis of a substantial number of atmospheric N_2O samples from both the troposphere [*Cliff and Thiemens*, 1997] and the stratosphere reveals a mass-independent isotopic composition in all cases. This mass-independent isotopic component is likely the result of an unrealized atmospheric process. Isotopic data from N_2O samples from a range of environments yield three significant results: (1) The $\delta^{18}O$ of atmospheric N_2O is variable, (2) atmospheric N_2O has a mass-independent isotopic component, and (3) a relative mass-independent enrichment in $\delta^{17}O$ and $\delta^{18}O$ is observed with increasing altitude or distance from primary N_2O sources. These three observations may provide important clues regarding the budget of atmospheric N_2O. The traditional budget allows for ground sources and stratospheric sinks. The observation of a mass-independent isotopic composition of N_2O is consistent with a process or processes which either produce or destroy N_2O in the atmosphere. As asserted, the source of the mass-independent effect does not derive from N_2O photooxidation (reactions (R2a) and (R2b)) or photolysis (reaction (R1)) at 185 nm [*Johnston et al.*, 1995]. Although the origin of the mass-independent isotopic component in atmospheric N_2O has not been discovered, the data suggest that it is consistent with an in situ atmospheric process.

Further research into the isotopic chemistry of atmospheric N_2O and its sources and sinks is necessary. Needed are $\delta^{17}O$ and $\delta^{18}O$ measurements of possible gas phase reactions that produce, exchange, or destroy N_2O in the atmosphere. Ultimately, any reaction that is thought to be a source or sink of N_2O should be isotopically analyzed for both $\delta^{17}O$ and $\delta^{18}O$ to quantify its role in the atmosphere. Also needed are laboratory measurements of the N_2O photolysis reaction at wavelengths that are appropriate to the stratosphere. Measurements of the $\delta^{15}N$ and $\delta^{18}O$ in photolysis fractionation will help explain the results of *Kim and Craig* [1993] and *Rahn and Wahlen* [1997] but will not explain the results of *Cliff and Thiemens* [1997] nor the observation of mass-independently fractionated N_2O in the stratosphere. The $^{17}\Delta$ data in atmospheric N_2O point out a possible source of error in more traditional N_2O measurements. The measurements of $\delta^{15}N$ may be obscured by isobaric interferences at mass 45 between 447 and 546 or 456 N_2O. Since the abundance ratio of $^{15}N/^{17}O$ is approximately 1/10, a 10‰ enrichment in the 447 species will be equivalent to a 1‰ enrichment in the 546 or 456 species. Only high-precision $\delta^{17}O$ and $\delta^{18}O$ measurements of the photolysis study proposed by *Yung and Miller* [1997] will determine if this photochemical process is the source of the observed stratospheric enrichment. Finally, more $\delta^{17}O$ and $\delta^{18}O$ measurements of stratospheric N_2O are needed. Sampling in the region of the atmosphere where sensitive $\delta^{15}N$ and $\delta^{18}O$ in N_2O are reported [*Rahn and Wahlen*, 1997] is of most interest.

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