First measurement of the $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ 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 ($\text{N}_2\text{O}$) 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 $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ is limited to large, sometimes up to a factor of 10, ranges in the predicted strengths of individual sources. Recent data for tropospheric $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ in the atmosphere.

Several features of the isotopic chemistry of atmospheric $\text{N}_2\text{O}$ raise questions about the mechanisms which produce and destroy this molecule. The discovery of an isotopic enrichment in $^{15}\text{N}$ and $^{18}\text{O}$ in stratospheric $\text{N}_2\text{O}$ [Kim and Craig, 1993; Rahn and Wahlen, 1991] suggests a process in the atmosphere that preferentially destroys light oxygen and nitrogen isotopes in $\text{N}_2\text{O}$.

(R1) \[ \text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}(^{1}D), \ (\lambda < 240 \text{ nm}) \ (49\%) \]

(R2a) \[ \text{N}_2\text{O} + \text{O}(^{1}D) \rightarrow \text{NO} + \text{NO} \ (6\%) \]

(R2b) \[ \text{N}_2\text{O} + \text{O}(^{1}D) \rightarrow \text{N}_2 + \text{O}_3 \ (4\%) \]

Measurements 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 photodissociation 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 $\text{N}_2\text{O}$ [Cliff and Thiemens, 1997].

A recent theoretical treatment of the wavelength isotopic dependency in $\text{N}_2\text{O}$ 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 $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios. Although new atmospheric sinks based on the discrepancy between laboratory measurements of $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ [Cliff and Thiemens, 1997] remains unexplained.

A mass-independent isotopic anomaly may derive from stratospheric $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$. 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 $\text{N}_2\text{O}$ species 446, 456, 546, 447, and 448 for $^{15}\text{N}_2^{18}\text{O}$, $^{15}\text{N}_2^{17}\text{O}$, $^{15}\text{N}_2^{16}\text{O}$, $^{14}\text{N}_2^{17}\text{O}$, and $^{14}\text{N}_2^{16}\text{O}$, 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-
dependent. No model calculation was made for the expected fractionation of 447/448 ratio relative to 446 N2 (Tung and Miller, 1997). Simultaneous δ^{18}O and δ^{17}O measurements of the wavelength-dependent N2O photolysis process are clearly needed.

2. Method

In this paper we present oxygen isotopic measurements of the lowermost stratospheric N2O. These results are the first δ^{18}O and δ^{17}O measurements of stratospheric N2O. A total of 14 stratospheric N2O 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. N2O samples for isotopic analysis were taken from two individual air sample collections on the basis of similarity in 14CO activity, which correlated with potential vorticity measurements for the individual samples. Combines 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 101. 1L cylinders, followed by CO2/N2O 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 N2O was carried out according to the method described by Cliff and Thiemens [1994]. Typical errors for collection and analysis of atmospheric N2O are 0.2% for δ^{18}O and 0.1% for δ^{17}O [Cliff, 1998]. The error associated with collection of these samples is negligible as N2O recovery is quantitative with the over 99.9% of N2O removed from the stratospheric whole air samples [Brenninkmeijer, 1993]. For the N2O isotopic measurements, errors are typically 0.1% for δ^{18}O and 0.0% [Cliff and Thiemens, 1994]. Results (Figures 1-3) are presented using the standard delta notation with respect to air O2. The delta notation is defined as δε = 1000 * (Rsample/Rstandard - 1), where R represents the ratio of isotopes, 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 N2O are, by convention, reported relative to air O2 (δ^{18}O_{SMOW}=25.5% and δ^{17}O_{SMOW}=12.2%, where SMOW is standard mean ocean water) converted by the relation δ^{18}O_{ATM}=23.0 + δ^{18}O_{SMOW}/0.0235 and δ^{17}O_{ATM}=12.1 + δ^{17}O_{SMOW}/0.0122, where ATM is the isotopic enrichment or depletion with respect to atmospheric O2.

3. Results and Discussion

The data for the two Antarctic flights are plotted on three-isotope diagrams with δ^{17}O on the y axis and δ^{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 \( \delta^\Delta \), where \( \delta^\Delta = \delta^{18}O - (0.515)\delta^{17}O \). The \( \delta^\Delta \) 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-independent (\( \delta^\Delta = 0 \)). The N2O mass-dependent fractionation line was experimentally determined [Cliff and Thiemens, 1997]. Figure 1 illustrates the entire atmospheric N2O 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 δ^{18}O and δ^{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 N2O isotopic data. The data shown in Figure 2 indicate a variable mass-independent enrichment of the heavy isotopes of oxygen in stratospheric N2O. A range in δ^{18}O of approximately 3% and in δ^{17}O 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, N2O concentration measurements were not made, but a methane (CH4) concentration variation of about 150 ppb is reported for these samples [Brenninkmeijer et al., 1995, 1996]. Typically, a CH4...
between $^{17}$A and $^{14}$CO is observed for the June flight only, but this correlation is not seen in the October flights. Also, the $^{17}$A N$_2$O does not correlate with other measured parameters. However, because the $^{17}$A is greater in these samples, these data imply a process which increases the $^{17}$A of N$_2$O once in the atmosphere. An atmospheric source of the mass-independent anomaly is consistent with this observation.

For ground level N$_2$O the White Mountain Research Station (WMRS) data (from 3.8 km elevation) were found to have the greatest enrichment in $^{18}$O (O) [Clifft and Thiemens, 1995]. The stratospheric N$_2$O samples exhibit still greater enrichment. In two of the four N samples in the $^{18}$O over tropospheric N$_2$O of almost 1% is observed. These data are consistent with a mixing of high $^{18}$O middle and upper stratospheric N$_2$O into the troposphere [Kim and Craig, 1993].

Although a mass-independent enrichment in the heavy isotopes of oxygen in stratospheric N$_2$O 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 $^{18}$O in N$_2$O occurs in the stratosphere by loss mechanisms (reactions (R2a) and (R2b)) [Johnston et al., 1995], mixing between stratospheric heavy N$_2$O with ground level mass-dependent N$_2$O and tropospheric mass-independent N$_2$O could produce the observations of the lower stratospheric samples. Several potential atmospheric sources and sinks of N$_2$O are suggested in the literature [Prasad and Zell, 1981; Prasad, 1994, 1997, Prasad et al., 1997]. Furthermore, ion-nucleophile reactions producing enormous (>10,000ppm) isotopic fractionations are known to exist [Griffith and Gellone, 1992]. Reactions of this type would be consistent with the normally small concentration and isotopic variations reported on atmospheric N$_2$O and with the model predictions based on these small fluctuations (C.D. Nevison et al., Constraints on N$_2$O 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 2. Three-isotope diagram of stratospheric N$_2$O data from Antarctic flights.](image-url)

![Figure 3. A detail of Figure 1 in the 14%o $^{18}$O + 22%o region. All data are plotted with respect to air O$_2$.](image-url)
provide a useful tracer of cross-tropopause transport. The \( ^{17} \Lambda \) 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 \( ^{15}O \) 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 \( ^{17} \Lambda \) value is a sensitive tracer of stratospheric \( N_2O \) in the troposphere. The value of \( ^{17} \Lambda \), by definition, is a robust measure of a specific process that is not affected by subsequent mass-dependent fractionations as \( ^{15}O \) and \( ^{15}N \) measurements are. Only the analysis of \( ^{15}O \) and \( ^{18}O \) 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.

Since the abundance ratio of \( ^{15}N/^{14}N \) is approximately 1/10, a 10\% enrichment in the 447 species will be equivalent to a 1\% enrichment in the 340 or 436 species. Only high-precision \( ^{15}O \) and \( ^{18}O \) 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. Fundamentally, more \( ^{15}O \) and \( ^{18}O \) measurements of stratospheric \( N_2O \) are needed. Sampling in the region of the atmosphere where sensitive \( ^{15}N \) and \( ^{18}O \) in \( N_2O \) are reported [Rahn and Wahlen, 1997] is of most interest.

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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 \( ^{15}O \) of ambient \( N_2O \) is variable, (2) atmospheric \( N_2O \) has a mass-independent isotopic component, and (3) a relative mass-independent enrichment in \( ^{15}O \) and \( ^{18}O \) 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 \( ^{15}O \) 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 \( ^{15}O \) and \( ^{18}O \) 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 \( ^{15}O \) and \( ^{18}O \) 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 \( ^{15}N \) and \( ^{18}O \) 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 \( ^{17} \Lambda \) data in atmospheric \( N_2O \) point out a possible source of error in more traditional \( N_2O \) measurements. The measurements of \( ^{15}N \) may be obscured by isobaric interferences at mass 45 between 447 and 546 or 436 \( N_2O \).

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