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Evidence for Altitude-dependent photolysis-induced 18O isotopic fractionation in stratospheric ozone

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Abstract

We present vertical profiles of ^{18}O fractionations in ozone, measured by balloon-borne infrared remote sensing between 15 and 40 km. The magnitudes of the $^{16}O^{16}O^{18}O$ ($^{668}O_3$) and $^{16}O^{18}O^{16}O$ ($^{686}O_3$) fractionations are 13.5 +/- 2.7% and 7.7 +/- 2.2%, averaged over the 20-35 km altitude range, in good agreement with previous atmospheric measurements by mass spectrometry and both infrared and far infrared remote sensing spectroscopy. We use our fractionation profiles, together with known fractionation effects of the ozone formation reaction, to deduce fractionations attributable to photolysis. These photolytic fractionation profiles show significant increases with altitude (3.5 +/- 2.2% and 4.0 +/- 1.6% for $^{668}O_3$ and $^{686}O_3$ respectively over the 20-35 km altitude range), indicating that the ozone formation reaction alone does not account for the observed enrichments.

Keywords

Evidence, for, Altitude, dependent, photolysis, induced, 18O, isotopic, fractionation, stratospheric, ozone, GeoQUEST

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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Evidence for altitude-dependent photolysis-induced ^{18}O isotopic fractionation in stratospheric ozone

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[1] We present vertical profiles of ^{18}O fractionations in ozone, measured by balloon-borne infrared remote sensing between 15 and 40 km. The magnitudes of the $^{16}O^{16}O^{18}O$ ($^{668}O_3$) and $^{16}O^{18}O^{16}O$ ($^{686}O_3$) fractionations are 13.5 ± 2.7% and 7.7 ± 2.2%, averaged over the 20–35 km altitude range, in good agreement with previous atmospheric measurements by mass spectrometry and both infrared and far infrared remote sensing spectroscopy. We use our fractionation profiles, together with known fractionation effects of the ozone formation reaction, to deduce fractionations attributable to photolysis. These photolytic fractionation profiles show significant increases with altitude (3.5 ± 2.2% and 4.0 ± 1.6% for $^{668}O_3$ and $^{686}O_3$ respectively over the 20–35 km altitude range), indicating that the ozone formation reaction alone does not account for the observed enrichments. **Citation:** Haverd, V., G. C. Toon, and D. W. T. Griffith (2005), Evidence for altitude-dependent photolysis-induced ^{18}O isotopic fractionation in stratospheric ozone, *Geophys. Res. Lett.*, *32*, L22808, doi:10.1029/2005GL024049.

1. Introduction

[2] Stratospheric ozone is characterized by enrichments in heavy oxygen which are "mass-independent" and anomalously large compared to those of ambient oxygen [e.g., *Weston*, 1999]. Atmospheric observations, combined with accurate modeling of this anomalous isotopic composition, would allow tighter constraints on the ozone budget. In addition, the isotopic signature of ozone is expected to be partially transferred, via $O(^1D)$ formed by ozone photolysis, to stratospheric CO_2 [e.g., *Yung et al.*, 1997]. If the extent of this transfer and the isotopic composition of $O(^1D)$ were known, the isotopic composition of CO_2 would be a powerful tracer of the chemical and dynamical history of the upper atmosphere.

[3] Previous observations of stratospheric ozone isotopic composition are considered largely consistent with expected fractionations of 7–11% induced by ozone formation. [*Brenninkmeijer et al.*, 2003] Temperature dependences of the formation rates of $^{668}O_3$ and $^{686}O_3$ [*Janssen et al.*, 2003] translate to increases in $^{668}O_3$ and $^{686}O_3$ fractionations of 2.5% and 0.1% over an altitude range of 20–40 km, with a typical temperature increase of 50 K. Thus vertical profile measurements of $^{668}O_3$ and $^{686}O_3$ fractionations could clarify whether stratospheric ozone isotopic composition is controlled by the formation reaction alone. However, the vertical fractionation profiles reported to date have not done so, since they suffer from either a lack of precision or a lack of symmetry resolution. Mass spectrometric data in the 22–32 km altitude range (with the exception of the rejected higher (>12%) values) support the "fractionation-only-during-formation" hypothesis, inasmuch as the variability of the data is consistent with the variability of stratospheric temperature, but do not discriminate between $^{668}O_3$ and $^{686}O_3$ [*Mauersberger et al.*, 2001]. Symmetry-resolved fractionation profiles of $^{668}O_3$ and $^{686}O_3$ have been reported by *Irion et al.* [1996] (space-based infrared absorption solar occultation spectra) and *Johnson et al.* [2000] (balloon-based far-infrared thermal emission solar occultation spectra). Neither shows statistically significant altitudinal variation in the 25–40 km altitude range. However the large uncertainties in both studies would mask any altitudinal variation of less than ~10% in ^{18}O fractionation.

[4] Further investigation of altitudinal variations in ozone isotopic composition is warranted in order to establish whether they are controlled by ozone formation alone. In this work we present fourteen stratospheric vertical profiles of $^{668}O_3$ and $^{686}O_3$ fractionations, measured by balloon-based solar remote sensing FTIR absorption spectroscopy, and test the current understanding of ozone isotopic fractionation against our observations.

2. Measurements

[5] We have determined $^{668}O_3$ and $^{686}O_3$ enrichments by analysis of 14 occultations of balloon-based solar infrared absorption spectra, collected between 1992 and 2003 from Fort Sumner, New Mexico (34°N), Fairbanks, Alaska (65°N) and Esrange, Sweden (68°N). The spectra were collected using the Jet Propulsion Laboratory MkIV Fourier transform infrared spectrometer [*Toon*, 1991] at balloon altitudes of 33–40 km in solar occultation mode, in which the spectrum of the rising or setting sun is obtained through the limb of the earth's atmosphere. Retrievals of $^{668}O_3$ and $^{686}O_3$ slant column abundances were achieved by least squares fitting of calculated spectra to the measured spectra in the ν_1 band (982–1016 cm^{-1} and 966–1011 cm^{-1} for $^{668}O_3$ and $^{686}O_3$ respectively). The ν_3, ν_2 and $\nu_2 + 2\,\nu_3$ bands (1096–1167 cm^{-1}, 767–793 cm^{-1} and 2735–2796 cm^{-1}) were used to retrieve $^{666}O_3$. Spectral intervals are listed in the Supplementary Data[1]. Although $^{666}O_3$ absorbs in the intervals used for the retrievals of

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[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2005GL024049.

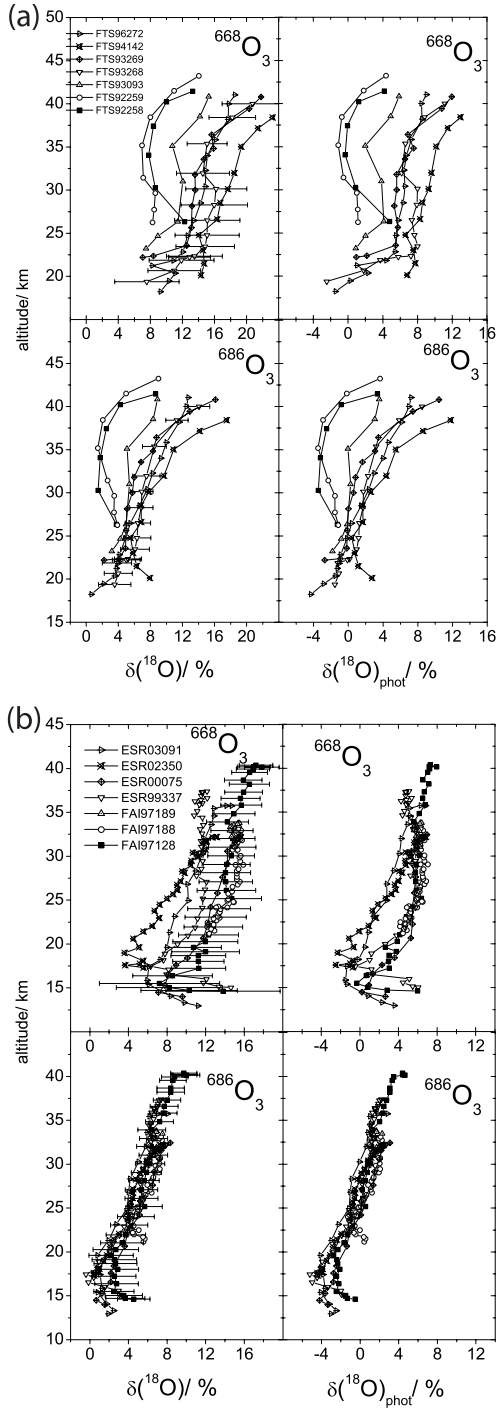

Figure 1. (a) Fort Sumner flights. Vertical profiles of $\delta^{668}O_3$ (top left) and $\delta^{686}O_3$ (bottom left), calculated from slant column abundances. Corresponding inferred photolytic fractionations are shown on the right. The vertical scale is the mean altitude, weighted by ozone density for each slant column. Flight dates and locations are given in the legend; the 5-digit code is the date in yyddd format. (b) Corresponding data for Esrange and Fairbanks flights.

the minor isotopomers, separate intervals were used for $^{666}O_3$ retrievals in order to avoid saturated lines. Spectral calculations and fitting were performed with the GFIT algorithm, discussed by *Goldman et al.* [1999], using HITRAN-2K line parameters [*Rothman et al.*, 2003].

3. Results and Discussion

[6] The left-hand panels of Figure 1 show the $\delta^{668}O_3$ and $\delta^{686}O_3$ vertical profiles from the 14 flights. We report isotopic fractionations in the usual δ form. For example, for $^{668}O_3$,

$$\delta^{668}O_3 = (R_{668}(\text{sample})/R_{668}(\text{reference}) - 1) \times 100\%.$$

[7] Here R_{668}(sample) is the ratio of the $^{668}O_3$ to the $^{666}O_3$ slant column abundance and R_{668}(reference) is the corresponding statistically expected value, based on the isotopic composition of molecular oxygen ($^{18}O/^{16}O$ = 0.002052). (Note that, for ease of comparison with model calculations and published mass-spectrometric data, we have used molecular O_2 as the isotopic reference, instead of the SMOW reference inherent in the Hitran-2K database ($^{18}O/^{16}O$ = 0.0020052). When comparing our measurements with other published spectroscopic measurements, we first correct the published measurements for differences in the definition of the isotopic reference, as also done by *Johnson et al.* [2000]. Conventionally, R is the ratio of the local concentrations, rather than the integrated slant columns. However at the mean altitude of the slant path, weighted by ozone density, the slant column ratio is a good approximation to the local ratio. This altitude is given by

$$\bar{z} = \frac{\int_{s=0}^{s=\infty} z(s)\rho(s)x(s)ds}{\int_{s=0}^{s=\infty} \rho(s)x(s)ds} \quad (1)$$

where s is the distance along the slant column path, ρ is the total density and x is the ozone volume mixing ratio. We use this approximation because the resulting errors in the local ^{18}O fractionation are small compared to the uncertainties introduced by inverse-model-based profile retrievals [*Sen et al.*, 1995]. Errors resulting from the use of Equation 1, along with other contributions to uncertainties in our reported fractionations are shown in Figure 2. Random errors (1σ) were estimated from the root-mean-squared residuals from the fits obtained in the various spectral windows. Uncertainties arising from errors in the spectrum-model parameters are reported as sensitivities to perturbations of these parameters by 2% (pressure broadening coefficients), 5 K (temperature profile) and 1% (zero-offset). A relatively large systematic uncertainty exists due to uncertainty in the line strengths of the heavy isotopomers. As discussed by *Janssen* [2005], this uncertainty is difficult to quantify, but is expected to be in the several % range, giving rise to constant biases in the reported enrichments, which may differ for $\delta^{668}O_3$ and $\delta^{686}O_3$. We emphasize that the uncertainties reported in Figure 2 refer to the precision of our measurements, not the absolute accuracy. As such, the data in Figure 1 are useful for assessing relative changes

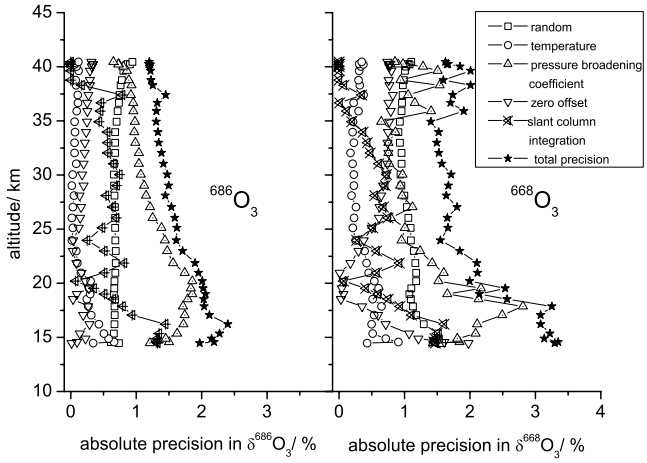

Figure 2. Absolute (not fractional) precisions (see text) as a function of altitude for $\delta^{686}O_3$ (left) and $\delta^{668}O_3$ (right) retrievals.

in fractionation, rather than absolute fractionations. The general increases in both $\delta^{668}O_3$ and $\delta^{686}O_3$ with altitude are interpreted in the following discussion.

[8] Ozone formation,

$$O + O_2 + M \rightarrow O_3 \quad (2)$$

is generally considered the major source of ozone isotopic fractionation in the stratosphere [e.g., *Brenninkmeijer et al.*, 2003]. However laboratory experiments on ozone photodissociation [e.g., *Bhattacharya and Thiemens*, 1988] and recent analysis by *Miller et al.* [2005] suggest that ozone photolysis should also cause significant isotopic fractionation. Here we infer the photolytic fractionations, $(\delta^{686}O_3)_{phot}$ and $(\delta^{668}O_3)_{phot}$ from our observations of total fractionations $\delta^{686}O_3$ and $\delta^{668}O_3$, using a model comprising reactions (2)–(8) with Q = ^{18}O.

$$O_3 + h\nu \rightarrow O_2 + O \quad (3)$$

$$O_2 + Q + M \rightarrow OOQ + M \quad (4)$$

$$OOQ + h\nu \rightarrow O_2 + Q \quad (5a)$$

$$\rightarrow O + OQ \quad (5b)$$

$$OQ + O + M \rightarrow OOQ + M \quad (6a)$$

$$\rightarrow OQO + M \quad (6b)$$

$$OQO + h\nu \rightarrow O + OQ \quad (7)$$

$$Q + O_2 \rightarrow O + OQ \quad (8a)$$

$$O + OQ \rightarrow Q + O_2 \quad (8b)$$

We assume that no other reactions significantly affect the isotopic composition of ozone. In particular, we do not include ozone removal processes other than photolysis; in the 12–40 km altitude range, these will have a negligible effect on ozone isotopic composition, since the sum of the reaction rates of these processes is at least 2 orders of magnitude less than the photolysis rate. Following *Johnson et al.* [2000], we assume that O_3, $^{668}O_3$ and $^{686}O_3$ are in photochemical steady state and obtain the following expressions for the modeled fractionations,

$$\delta^{686}O_3 = \frac{2k_6 j_3 \beta}{k_2 j_7} - 1 \quad (9)$$

$$\delta^{668}O_3 = \frac{j_3}{j_5}\left(\frac{k_4}{k_2 K_{eq}} + \frac{(1-\beta)k_6}{k_2}\right) - 1 \quad (10)$$

where k_i is the rate constant for the ith reaction, j_i is the photolysis rate for the ith reaction, $k_6 = k_{6a} + k_{6b}$, $\beta = k_{6a}/(k_{6a} + k_{6b})$ and $K_{eq} = k_{8f}/k_{8r}$. The pure photolytic fractionations are obtained by setting $k_2/k_4 = k_2/(k_{6a} + k_{6b}) = 1$, $k_{6a}/k_{6b} = 1$ and $k_{8f}/k_{8r} = 2$ in equations (8) and (9) and rearranging in terms of the total fractionations:

$$\left(\delta^{686}O_3\right)_{phot} = \frac{j_3}{j_7} - 1 = \frac{k_2}{2k_6\beta}\left(\delta^{686}O_3 + 1\right) - 1 \quad (11)$$

$$\left(\delta^{668}O_3\right)_{phot} = \frac{j_3}{j_5} - 1 = \left(\frac{k_4}{k_2 K_{eq}} + \frac{(1-\beta)(k_{6a}+k_{6b})}{k_2}\right)^{-1} \cdot \left(\delta^{668}O_3 + 1\right) - 1 \quad (12)$$

We substitute the observed fractionations into (11) and (12), together with the equilibrium constant $K_{eq} = 1.94e^{32/T}$ [*Kaye and Strobel*, 1983] and the ozone-formation rate parameters of *Janssen et al.* [2003]: $k_4/k_2 = 0.93 + 1.03 \times 10^{-3}(T - 298)$; $k_6/k_2 = 1.27 + 2.0 \times 10^{-5}(T - 298)$ and $\beta = 0.427$, evaluated at the local temperature. The local temperature is expected to be the temperature of ozone formation, since the photolytic lifetime of ozone is short

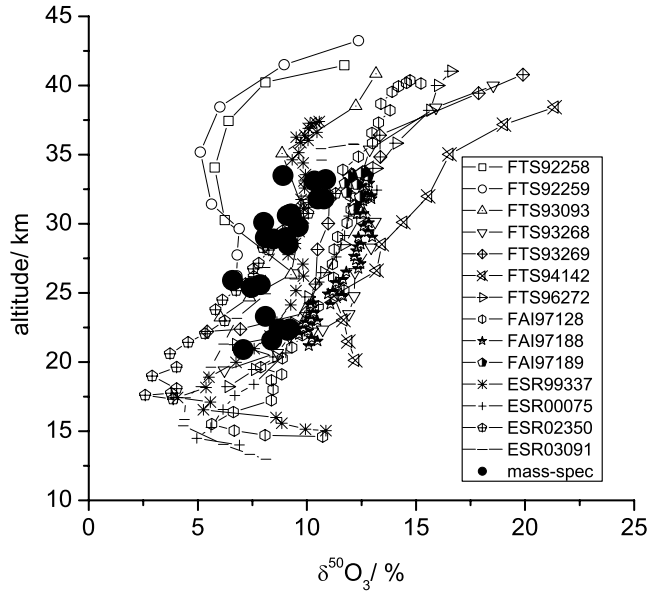

Figure 3. Vertical profiles of $^{50}O_3$. Solid circles: mass-spectrometric data [*Mauersberger et al.*, 2001]. Other symbols: this work.

(~1 hour) compared to the time scale of stratospheric transport.

[9] The results (see the right-hand panels of Figure 1) provide strong evidence for the existence of altitude-dependent isotopic fractionation of stratospheric ozone by photolysis. There is a general increase in both $(\delta^{668}O_3)_{phot}$ and $(\delta^{686}O_3)_{phot}$ with altitude. The FTS922258 and FTS92259 flights exhibit anomalously low fractionations. The reasons for this are not investigated further here, but we note that these flights sampled the stratosphere when it was heavily loaded with aerosol from the 1991 eruption of Mt Pinatubo. Over the 20–35 km altitude range, absolute values of $(\delta^{686}O_3)_{phot}$ and $(\delta^{668}O_3)_{phot}$ increase on average (excluding FTS92258, FTS92259 and FAI97189 data which do not span this altitude range) by 4.0 ± 1.6% and 3.5 ± 2.2% respectively. These increases are consistent with the 4.0% and 2.4% increases in $(\delta^{686}O_3)_{phot}$ and $(\delta^{668}O_3)_{phot}$, predicted over the same altitude range by *Miller et al.* [2005].

[10] In Figure 3, we report our observations as $\delta^{50}O_3 = (2 \times {}^{668}O_3 + {}^{686}O_3)/3$, to facilitate their comparison with the mass-spectrometric data reviewed by *Mauersberger et al.* [2001]. The two data sets are in reasonable agreement.

[11] Previous remote-sensing spectroscopic results (re-referenced if necessary to atmospheric O_2) also agree well with our measurements. Our mean 20–35 km fractionations, weighted by ozone density and averaged over all occultations (excluding those which do not span this altitude range), are 13.9 ± 2.9% and 7.1 ± 2.6% for $^{668}O_3$ and $^{686}O_3$ respectively. The far-infrared thermal emission study by *Johnson et al.* [2000] reports enhancements of 12.2 ± 1.0% and 6.1 ± 1.8% for $^{668}O_3$ and $^{686}O_3$ respectively, averaged over the 25–35 km altitude range. Space-based infrared solar occultation spectra also give similar average enhancements of 12.3 ± 6.0% and 7.4 ± 7.0% for $^{668}O_3$ and $^{686}O_3$ respectively in the 25–40 km altitude range [*Irion et al.*, 1996]. Ground-based infrared solar absorption measurements returned total integrated column enrichments of 13.5 ± 4.0% for $^{668}O_3$ and 11.9 ± 0.9% [*Meier and Notholt*, 1996] and 11.2 ± 1.4% [*Irion et al.*, 1996] for $^{668}O_3$. The good agreement between our infrared data and the far infrared data of *Johnson et al.* [2000] is particularly satisfying, since independent absorption bands are used in these analyses. Biases in the infrared data resulting from systematic uncertainties in the line strengths remain nevertheless uncertain, but these affect only the offset in the absolute values, not the altitude dependence. A laboratory comparison of infrared spectroscopic and mass-spectrometric measurements on a common set of ozone samples would clarify this uncertainty.

4. Conclusion

[12] Our vertically-resolved observations of ^{18}O fractionations in ozone exhibit significant increases with altitude. Assuming a correct model of ozone isotopic fractionation (Equations 2–8a) and accurate rate parameters (k_6/k_2, k_4/k_2, β, K_{eq}), these observations imply significant altitude-dependent photolysis-induced fractionation of stratospheric ozone. This finding contrasts with those of *Mauersberger et al.* [2001] and *Johnson et al.* [2000], who considered fractionation by ozone formation alone to adequately account for their observations. The difference in findings arises because, although our data are consistent with those of these previous studies, our measurements distinguish between $^{668}O_3$ and $^{686}O_3$ (in contrast to the mass-spectrometric measurements) and are more precise than previous balloon-based spectroscopic measurements. These factors enable us to identify an altitude-dependent photo-induced fractionation effect which was not evident in the other observational data sets. While our inferred increases in $(\delta^{686}O_3)_{phot}$ and $(\delta^{668}O_3)_{phot}$ agree within error with recent calculations by *Miller et al.* [2005], verification by laboratory measurements of $^{686}O_3$ and $^{668}O_3$ photolysis cross sections would further validate these calculations.

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