

Heavy ozone enrichments from ATMOS infrared solar spectra

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Abstract. Vertical enrichment profiles of stratospheric $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ (hereafter referred to as $^{668}\text{O}_3$ and $^{686}\text{O}_3$ respectively) have been derived from space-based solar occultation spectra recorded at 0.01 cm^{-1} resolution by the ATMOS (Atmospheric Trace MOlecule Spectroscopy) Fourier-transform infrared (FTIR) spectrometer. The observations, made during the Spacelab 3 and ATLAS-1, -2, and -3 shuttle missions, cover polar, mid-latitude and tropical regions between 26 to 2.6 mb inclusive (≈ 25 to 41 km). Average enrichments, weighted by molecular $^{48}\text{O}_3$ density, of $(15\pm 6)\%$ were found for $^{668}\text{O}_3$ and $(10\pm 7)\%$ for $^{686}\text{O}_3$. Defining the mixing ratio of $^{50}\text{O}_3$ as the sum of those for $^{668}\text{O}_3$ and $^{686}\text{O}_3$, an enrichment of $(13\pm 5)\%$ was found for $^{50}\text{O}_3$ (1σ standard deviation). No latitudinal or vertical gradients were found outside this standard deviation. From a series of ground-based measurements by the ATMOS instrument at Table Mountain, California (34.4°N), an average total column $^{668}\text{O}_3$ enrichment of $(17\pm 4)\%$ (1σ standard deviation) was determined, with no significant seasonal variation discernable. Possible biases in the spectral intensities that affect the determination of absolute enrichments are discussed.

Introduction

Stratospheric enrichment of $^{50}\text{O}_3$ was first reported by Mauersberger [1981], who found enrichments ranging from 0% to 40% using a balloon-borne mass spectrometer. (For the purposes of this paper, % enrichment = $[R_{\text{obs}}/R_{\text{std}} - 1] \times 100$, where R_{obs} is the observed abundance ratio of the heavy isotopomer to the regular isotopomer, and R_{std} is the standard ratio. For $^{50}\text{O}_3$ enrichment, $R_{\text{std}} = 6.01 \times 10^{-3}$, about three times the natural abundance ratio of ^{18}O to ^{16}O ignoring a very small abundance of $^{16}\text{O}^{17}\text{O}^{17}\text{O}$. See IUPAC [1983].) Further stratospheric enrichment of $^{50}\text{O}_3$ has been reported based on mass spectrometry [Mauersberger, 1987], far-infrared emission spectroscopy [Abbas *et al.*, 1987; Carli and Park, 1988], and cryogenic grab-sampling followed by mass spectrometry [Schueler *et al.*, 1990]. These measurements have shown varied consistency with each other. Figure 1 summarizes previous measurements of $^{50}\text{O}_3$ enrichment profiles and averaged results of the analyses presented here.

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Mid-infrared solar absorption Fourier-transform spectrometry has been used to determine column enrichments of $^{668}\text{O}_3$ and $^{686}\text{O}_3$. From Kitt Peak, Arizona (31.9°N), Rinsland *et al.* [1985] determined a column enrichment of $(11\pm 11)\%$ for $^{668}\text{O}_3$ and $(5\pm 7)\%$ for $^{686}\text{O}_3$. Goldman *et al.* [1989], from two balloon-based observations, found column enrichments above 37 km of $(20\pm 14)\%$ and $(40\pm 18)\%$ for $^{668}\text{O}_3$, and $(16\pm 8)\%$ and $(25\pm 12)\%$ for $^{686}\text{O}_3$. From April 1994 to August 1995, Meier and Notholt [1996] took measurements from a high northern latitude of 79°N ; they reported average column enrichments of

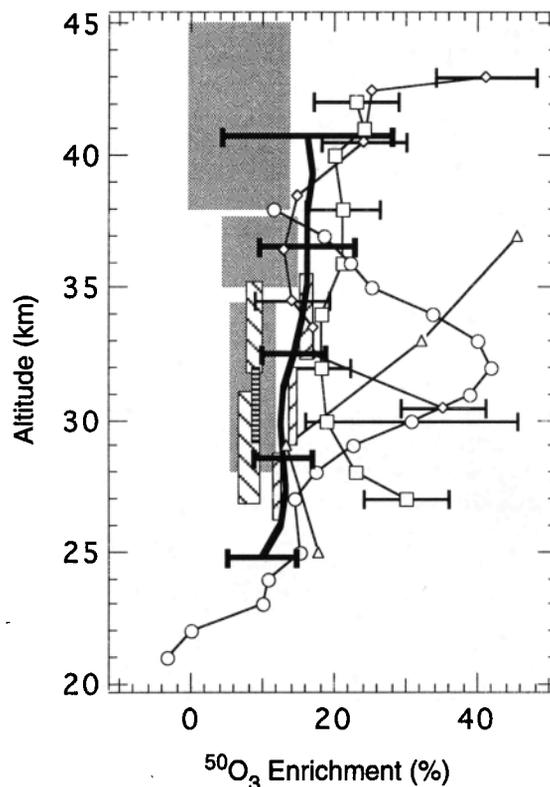


Figure 1. Previously reported and globally averaged ATMOS space-borne measurements of $^{50}\text{O}_3$ enrichment profiles. ATMOS altitudes are approximate and ATMOS $^{50}\text{O}_3$ enrichments are assumed to be the sum of two-thirds the $^{668}\text{O}_3$ enrichment and one-third the $^{686}\text{O}_3$ enrichment (c. f. Figure 2). The error bars on the ATMOS measurements are the 1σ standard deviations, and do not include systematic error. For clarity, error bars for many of the data points have been omitted, and altitudes for Mauersberger [1987], flight a, have been shifted upwards by 0.5 km. Data from Carli and Park [1988] are the range of their measurements. Mauersberger [1981]: \circ ; Mauersberger [1987], flight a: \diamond flight b: \square ; Abbas *et al.* [1987]: \triangle ; Carli and Park [1988]: hatched ; Scheueler *et al.* [1990] flight I: Z flight II: cross-hatched flight III: $\text{horizontal stripes}$; ATMOS Spacelab 3 and ATLAS-1, -2 and -3 average: thick solid line .

(15.4±0.9)% for $^{668}\text{O}_3$ and (11.2±1.4)% for $^{686}\text{O}_3$ from solar absorption spectra, and (9.0±3.3)% for $^{668}\text{O}_3$ and (8.5±2.5)% for $^{686}\text{O}_3$ from lunar absorption spectra recorded during the polar night. Using mass spectrometry, enrichment of $^{50}\text{O}_3$ from about 8 to 10% in tropospheric urban air was reported by *Krankowsky et al.* [1995]; no apparent variation in the enrichment with tropospheric O_3 mixing ratio was found.

Heavy ozone enrichment has also been observed in laboratory measurements. *Anderson et al.* [1989] found ozone created using an electric discharge (which can produce excited states of O and O_2) was enriched primarily in the asymmetric isotopomers, such as $^{668}\text{O}_3$. *Morton et al.* [1990] found that enrichment can occur via the reaction of ground-state atomic and molecular oxygen, $\text{O}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) + \text{M} \rightarrow \text{O}_3 + \text{M}$, the so-called Chapman formation reaction; under these conditions, *Mauersberger et al.* [1993] found enrichment only in the asymmetric isotopomers. *Miller et al.* [1994] proposed that the reaction of vibrationally hot O_2 ($v \geq 26$) with another O_2 molecule can lead to heavy ozone enrichment via preferential potential energy curve-crossing of heteronuclear O_2 from the $\text{O}_2(^1\Delta_g)$ to the $\text{O}_2(^3\Sigma_g^-)$ state (see *Valentini* [1987]). However, appreciable production of such vibrationally hot O_2 was predicted to occur only above about 35 km, with the enrichment produced less than 5% at 40 km.

While *Miller et al.* [1994] may have provided an explanation for some of the enrichment in the mid-stratosphere, the bulk of the enrichment lacks a generally accepted theoretical explanation. Indeed, detailed statistical mechanical analyses by *Kaye and Strobel* [1983] and *Kaye* [1986] predicted a slight depletion of $^{50}\text{O}_3$ under stratospheric conditions. This discrepancy between observation and theory indicates that current understanding of ozone formation is incomplete (see, for example, *Anderson et al.* [1992]). However, a promising advance in finding an enrichment mechanism is the recent discovery of several electronically excited states of ozone near the dissociation threshold [*Anderson and Mauersberger*, 1995]. It is possible that the formation of ozone via the Chapman mechanism goes through one or more of these states whose quantum properties (such as lifetime) are dependent on the isotopic composition of the reactants.

From Figure 1, no vertical gradient consistently appears within the assembly of previous measurements, and data are lacking on latitudinal gradients in the stratosphere. In this study, we take advantage of the high vertical and latitudinal range of the ATMOS data set from the Spacelab3 and ATLAS series missions to constrain any vertical or latitudinal variability. We also evaluate $^{668}\text{O}_3$ column enrichments from ground-based spectra taken from Table Mountain Facility (TMF), Wrightwood, California, (34.4°N, 117.7°W, 2.2 km altitude) to examine seasonal variations in the column enrichment from a mid-latitude site.

Data Acquisition

Information about the ATMOS instrument and its use on the shuttle can be found in *Gunson et al.* [this issue]. The spectral filters used for analyses described here, filters 1, 9 and 12, had ranges of 650-1100 cm^{-1} , 650-2450 cm^{-1} , and 625-1400 cm^{-1} respectively. The number of vertical profiles used for this study were 4 from Spacelab 3, 39 from ATLAS-1, 29 from ATLAS-2 and 87 from ATLAS-3. Using the ATMOS instrument from Table Mountain Facility (TMF), ground-based total column measurements were made on 48 separate days from

Table 1. Spectral intervals used for heavy ozone profile analyses from space

| Window center frequency (cm^{-1}) | Window width (cm^{-1}) | Line centers (cm^{-1}) | Line intensity at 296K ($\times 10^{22}$ cm molecule $^{-1}$) | Ground state energy (cm^{-1}) | Temperature sensitivity of intensity (%/K at 220K) |
|--|-----------------------------------|-----------------------------------|---|--|--|
| $^{668}\text{O}_3$ | | | | | |
| 1090.445 | 0.55 | unresolved | 2.14(a) | 203(b) | -0.1 |
| $^{686}\text{O}_3$ | | | | | |
| 975.27 | 0.12 | 975.2503 | 0.169 | 546 | 1.0 |
| | | 975.2838 | 0.230 | 495 | 0.7 |
| 981.715 | 0.14 | 981.6756 | 3.54 | 363 | 0.4 |
| | | 981.7107 | 4.46 | 328 | 0.3 |
| 985.09 | 0.44 | 984.9062 | 4.32 | 298 | 0.2 |
| | | 984.9062 | 5.48 | 264 | 0.1 |
| | | 985.0321 | 2.20 | 395 | 0.5 |
| | | 985.1031 | 4.78 | 279 | 0.1 |
| | | 985.1578 | 3.32 | 334 | 0.3 |
| | | 985.2171 | 5.10 | 268 | 0.1 |
| 990.422 | 0.14 | 990.3889 | 1.55 | 493 | 1.3 |
| | | 990.3895 | 1.74 | 567 | 1.3 |
| | | 990.3918 | 1.74 | 567 | 1.1 |

Notes: (a) Sum of intensities between 1090.1 and 1090.6 cm^{-1} .
(b) Average weighted by the intensity of the individual lines.

October, 1985 through July, 1990, usually at solar zenith angles corresponding to about 1, 5 and 10 airmasses. Further discussion of ATMOS measurements from TMF may be found in *Gunson and Irion* [1991].

Data Analysis

ATMOS analysis techniques for space-based observations have been described by *Norton and Rinsland* [1991]. For $^{48}\text{O}_3$, large spectral windows (from 14.5 to 16 cm^{-1} wide) covering regions of the ν_1 , ν_2 , and ν_3 bands were used for analyses, while additionally for the broadband filter 9, smaller windows (≤ 1 cm^{-1} wide) containing lines from the $\nu_1+\nu_2$, $\nu_1+\nu_3$, and $2\nu_2$ bands were used. (A fuller discussion of ATMOS $^{48}\text{O}_3$ retrievals and comparison with other instruments may be found in M. C. Abrams et al., "An evaluation of stratospheric ozone observed by the Atmospheric Trace Molecule Spectroscopy (ATMOS) Experiment During April 1992," in preparation for *J. Geophys. Res.*, 1996.) For $^{668}\text{O}_3$, the narrow, unresolved ν_1 band Q-branch centered at 1090.35 cm^{-1} was analyzed, as were several lines of the ν_3 band P-branch for $^{686}\text{O}_3$ (see Table 1). Spectral parameters for all lines were from the ATMOS linelist [*Brown et al.*, 1996], which currently incorporates the ozone parameters given by *Flaud et al.* [1986; 1990] and *Camy-Peyret et al.* [1986]. Error sources for stratospheric measurements are discussed by *Abrams et al.* [this issue]. However, as discussed by *Meier and Notholt* [1996], an uncertainty exists in the spectral line intensities of $^{668}\text{O}_3$ due to what may have been an incorrect assumption for the isotopic makeup of the reference gas used in the experiments of *Flaud et al.* [1986] and *Camy-Peyret et al.* [1986]. Furthermore, any errors in the line intensities of $^{686}\text{O}_3$ (which were derived from theory) will impact those of $^{668}\text{O}_3$. As will be seen, these uncertainties can affect the interpretation of our results. The average 1 σ random errors for an enrichment from a single spectrum, mostly from signal-to-noise error and interfering lines for spectral windows featuring the heavy isotopomers, are 20% for $^{686}\text{O}_3$ and 18% for $^{668}\text{O}_3$.

Table 2. Spectral intervals used for column density analyses from Table Mountain

| Line Center (a) (cm ⁻¹) | Line Intensity (x10 ²² cm molec. ⁻¹) | Ground State Energy (cm ⁻¹) | Temperature Sensitivity of Intensity (%/K at 220K) | Airmass Range |
|--|--|---|--|---------------|
| ⁴⁸O₃ | | | | |
| 1095.1008 | 5.19 | 310.3 | 0.2 | < 1.5 |
| 1114.8233 | 1.03 | 77.1 | -0.5 | 3-10 |
| 1123.4234 | 6.85 | 120.3 | -0.4 | <3 |
| 1126.2511 | 2.49 | 42.9 | -0.5 | <5 |
| 1140.9448 | 1.02 | 190.2 | -0.1 | 3-10 |
| 1163.4222 | 2.57 | 253.9 | 0.04 | <5 |
| 1176.1047 | 1.41 | 353.3 | 0.3 | 3-10 |
| ⁶⁶⁸O₃ | | | | |
| (b) | 2.14(c) | 203(d) | -0.1 (d) | all |

Notes: (a) Interval width for all ⁴⁸O₃ windows was 0.16 cm⁻¹. The window for ⁶⁶⁸O₃ was 1090.35 cm⁻¹ with a width of 0.5 cm⁻¹.
 (b) Several unresolved lines between 1090.1 and 1090.6 cm⁻¹
 (c) Sum of intensities between 1090.1 and 1090.6 cm⁻¹
 (d) Average weighted by the intensities of the individual lines.

For the TMF ground-based retrievals of ⁴⁸O₃ and ⁶⁶⁸O₃, an assumed vertical ozone mixing ratio profile was scaled by a single multiplicative factor until a best fit was obtained between observed and calculated spectra. Assumed vertical ozone profiles were created using monthly-averaged profiles from the JPL Lidar on TMF [McDermid, 1993]. Vertical temperature and pressure profiles were adapted from daily National Meteorological Center data and merged with the U.S. Standard Atmosphere [1976] for higher altitudes. These profiles were then adjusted so that the atmosphere was in hydrostatic equilibrium. To achieve better fits and improved consistency in the column retrievals among the different airmasses sampled within a day, the height registration of the assumed ozone profiles was shifted vertically up to ±3 km. Measurement of column ⁴⁸O₃ by the ATMOS instrument at TMF was previously reported by Gunson and Irion [1991], however, as some of the ⁴⁸O₃ lines used in that study may have been saturated at high airmasses, the ⁴⁸O₃ columns have been re-analyzed for this study. Table 2 describes the lines used for TMF retrievals. The ⁶⁸⁶O₃ column from TMF was not retrieved because interference by neighboring ⁴⁸O₃, H₂O and CO₂ lines was too large to achieve acceptable fits. Random error for TMF retrievals, mostly from errors in the pressure/temperature profile and the assumed O₃ profiles, averaged about 9% for the ⁶⁶⁸O₃ enrichments.

Results

The solid lines in Figure 2 illustrate average vertical enrichment profiles for ⁶⁶⁸O₃ and ⁶⁸⁶O₃ measured by ATMOS over the four shuttle missions, while the dashed lines indicate 1σ standard deviations. (The standard error for the average is nowhere more than 2%.) The individual points on Figure 2 show enrichments averaged for latitude and mission and weighted by inverse square random error. For these latitudinal averages, the standard errors average 8% for ⁶⁶⁸O₃ and 10% for ⁶⁸⁶O₃. No significant variation with latitude or altitude could be determined. Figure 1 illustrates previously published and the average ATMOS ⁵⁰O₃ enrichment profiles determined by averaging results across constant pressure surfaces and assigning an approximate altitude. Weighted by the ⁴⁸O₃ density, the globally averaged ⁵⁰O₃ enrichment between 2.6 and 26 mb inclusive is

(13±5)%, while that for ⁶⁶⁸O₃ and ⁶⁸⁶O₃ are (15±6)% and (10±7)%, respectively (1σ standard deviation).

Figure 3 shows the ⁶⁶⁸O₃ enrichment measured above TMF. The average random error for the data is 9%. No seasonal variation in the enrichment can be discerned. Ignoring systematic error, the average column enrichment is (17±4)% (1σ standard deviation), in good agreement with the ⁶⁶⁸O₃ enrichment derived from the ATMOS stratospheric profiles. This is also in agreement with Meier and Notholt [1996] for their solar spectra, (15.4±0.9)%, but higher than their average of (9.0±3.3)% for lunar spectra taken during the polar night.

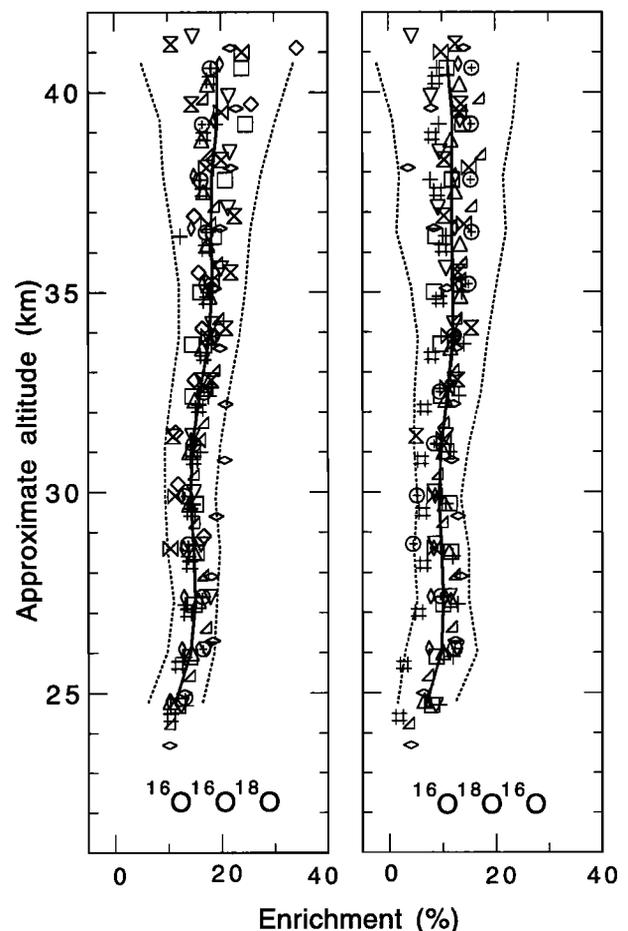


Figure 2. ⁶⁶⁸O₃ and ⁶⁸⁶O₃ global and latitudinally-averaged enrichments from ATMOS space observations. All averages were done on a fixed pressure scale; the altitude shown is the average altitude at each pressure level in its particular latitude bin. All latitudinal averages were weighted by the inverse random error of the measurement and at least three observations were averaged for each point. The error ranges for the globally averaged profiles are the 1σ standard deviations. See text and Abrams et al. [this issue] for discussion of systematic errors. ATLAS-3 (Nov. 1994): ▽ 80°S-60°S, outside vortex; ⊖ 80°S-60°S, inside vortex; + 0°-10°N; □ 10°N-30°N; △ 30°N-60°N. ATLAS-2 (May 1993): ⊕ 60°S-30°S; # 60°N-80°N, outside vortex; ▲ 60°N-80°N, inside vortex. ATLAS-1 (Apr 1992): † 60°S-30°S; ◇ 30°S-10°S; ✕ 10°S-10°N; ✕ 10°N-30°N. Spacelab-3 (Apr 1985): ∇ ≈50°S; ▴ ≈30°N. — Global average; 1σ standard deviation.

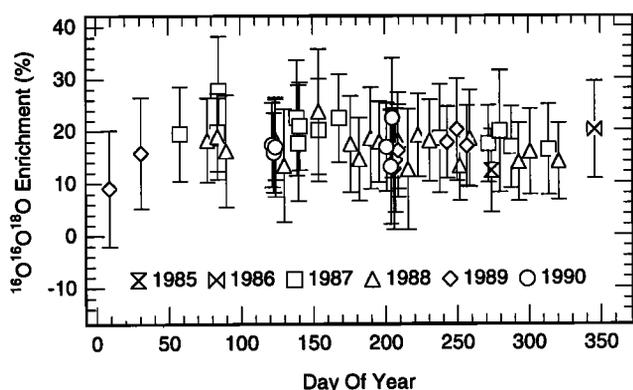


Figure 3. Column $^{668}\text{O}_3$ enrichments from Table Mountain. The error bars do not include systematic error.

Conclusions

We have analyzed ATMOS stratospheric spectra for the enrichments of $^{668}\text{O}_3$ and $^{686}\text{O}_3$, and ground-based spectra for the column enrichment of $^{668}\text{O}_3$. While some previous studies, most notably Mauersberger [1981; 1987] and Abbas *et al.* [1987], have shown large vertical gradients, results here indicate that the vertical and latitudinal variability of the enrichment is generally small. We can find no discernable seasonal variability in the $^{668}\text{O}_3$ column enrichment over Table Mountain. These observations suggest the enrichment of heavy ozone in the sunlit stratosphere is relatively constant, and perhaps only weakly regulated by temperature and pressure.

Although previous studies have not ruled out other enrichment processes, laboratory measurements have shown the most significant enrichment in the Chapman reaction, with O and O_2 reactants in the electronic ground state. Noting that the Chapman mechanism has been shown to produce no enrichment for the $^{686}\text{O}_3$ isotopomer, our determination of a $^{686}\text{O}_3$ enrichment of $(10 \pm 7)\%$ (1σ standard deviation) suggests that the $^{686}\text{O}_3$ line intensities may be biased too low by 10% with respect to the line intensities of $^{48}\text{O}_3$. However, it may be possible that other unknown processes are operating to enrich stratospheric $^{686}\text{O}_3$, much as ozone produced in an electric discharge becomes enriched in $^{686}\text{O}_3$. Furthermore, since the $^{668}\text{O}_3$ line intensities derived by Camy-Peyret *et al.* [1986] were determined making use of the $^{686}\text{O}_3$ line intensities, then if these are incorrect, the $^{668}\text{O}_3$ line intensities may also be too low. Laboratory measurement of the $^{668}\text{O}_3$ and $^{686}\text{O}_3$ spectral line intensities are necessary for calibration of the absolute stratospheric enrichments described here and the interpretation thereof. Since Flaud *et al.* [1986] and Camy-Peyret *et al.* [1986] reported good model fittings to their laboratory spectra, such laboratory measurements would probably produce a constant, corrective scaling of the line intensities (though not necessarily the same amount for both isotopomers), and would not affect the precision of the enrichments described here.

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