GLOBAL OBSERVATIONS OF OZONE ISOTOPIC RATIOS FROM MIPAS LIMB EMISSION SPECTRA

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1. INTRODUCTION

The observed variations in the isotope ratios often reveal information about the relative strengths of different sources and sinks of the trace gas in question, and about the transport processes which influence its distribution. With the magnitude of the heavy ozone isotope effect known, the isotopes can serve as markers for atmospheric transport and chemical reactions. The enrichment observed in stratospheric CO_2 is just one of the possible transfers of an isotopic signature from ozone to another minor constituent.
Ozone isotopes of molecular mass 49 and 50 are difficult to measure in the atmosphere since they are present in parts per billion range or below. Measurements of stratospheric ozone [1, 2] and of ozone generated in the laboratory using a variety of techniques consistently find that ozone is enriched relative to O_2 in both ^{17}O and ^{18}O. The measurements also suggest that a mass-independent process is involved. In this study we present the feasibility of retrieving the different isotopes of ozone and their global distributions and enrichments observed by MIPAS.

2. MIPAS

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is an infrared limb-sounding Fourier transform interferometer on board the Envisat satellite, launched in March 2002 [3, 4]. It acquires spectra over the range 685 – 2410 cm^{-1} (14.5 – 4.1 μm), which includes the vibration-rotation bands of many molecules of interest. It is capable of measuring continuously around an orbit in both day and night and a nearly complete global coverage is obtained in 24 hours.
From July 2002 until March 2004 MIPAS was operated at full spectral resolution (0.025 cm^{-1}) with a nominal limb-scanning sequence of 17 steps from 68 – 6 km with 3 km tangent height spacing in the troposphere and stratosphere, generating complete profiles spaced approximately every 500 km along the orbit. However, in March 2004 operations were suspended following problems with the interferometer slide mechanism. Operations were resumed in January 2005 with a 35% duty cycle and reduced spectral resolution (0.0625 cm^{-1}).
For the high-resolution mission ESA have processed pT (pressure-temperature) and 6 target species. However, MIPAS spectra contain also information on isotopes of ozone as well as other species.

3. MICROWINDOW SELECTION AND ERROR ANALYSIS

The relative abundances of oxygen atoms ^{16}O:^{18}O:^{17}O in standard mean ocean water (SNOW) are approximately 1:1/500:1/2700.
In this study we consider only singly substituted isotopic variants, so that asymmetric $^{50}O_3$=$^{18}O^{16}O^{16}O$, symmetric $^{50}O_3$=$^{16}O^{18}O^{16}O$, asymmetric $^{49}O_3$=$^{17}O^{16}O^{16}O$ and symmetric $^{49}O_3$=$^{16}O^{17}O^{16}O$.
The microwindows have been selected for retrieving simultaneosly the all 5 O_3 isotopic variants (the main isotope $^{48}O_3$=$^{16}O^{16}O^{16}O$ and the four singly substituted isotopic variants listed above). Figure 1 shows Jacobian contributions at 21 km for the 5 different O_3 isotopic variants. The error analysis resulting from the microwindow selection is shown here for the 5 different O_3 isotopic variants (see Fig. 2). Each plot shows the total error (% VMR for a single profile) as a function of altitude. The total error (solid line) is given by random (dotted line) and the systematic (dashed line) profiles; the different symbols represent the major systematic components that affect the accuracy of the retrieval.

4. RETRIEVAL APPROACH

The MORSE (MIPAS Orbital Retrieval using Sequential Estimation) retrieval algorithm uses an Optimal Estimation Technique with a-priori information to constrain the retrieval [5]. The retrieval is based on the use of selected spectral intervals (microwindows) containing the best information on the target parameters [6] and the line-by-line radiative transfer forward model used is the RFM (Reference Forward Model). Since it is expected that there is little difference between the atmospheric O_3 isotopes profiles within a10 degree latitude band, the pre-

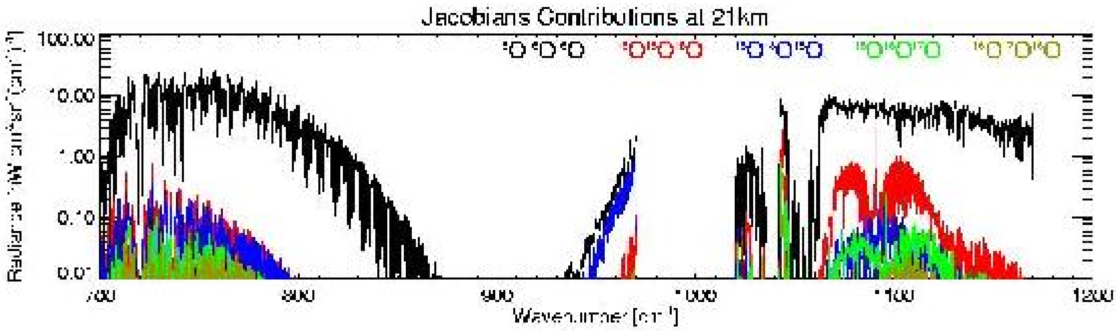

Figure 1. Jacobians contributions at 21 km for the 5 O_3 isotopic variants.

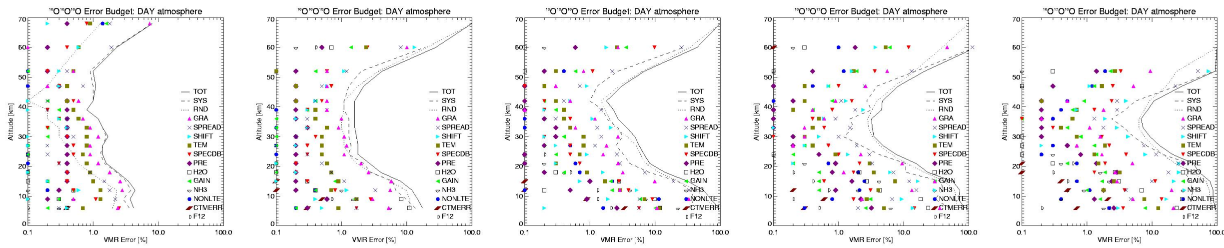

Figure 2. Estimated error budgets for the 5 O_3 isotopic variants of single profile retrievals from the microwindow selection.

vious MIPAS limb measurement (within the same latitude band) can provide prior information about O_3 isotopic variants at the current time. Here, we use the resulting profile (and associated covariance) as the starting point for the next retrieval (Kalman filter approach). In this way the prior information enters the retrieval only once and the random error on the final profile should be greatly reduced (approximately to a tenth of an individual retrieval). Before the O_3 isotope retrievals, pT, H_2O, O_3, CH_4 and N_2O retrievals were performed in sequence using the ESA OFL operational microwindows. O_3 profiles are used to initialize the Kalman filter in each latitude bands instead of using the climatological profile to jointly retrieve the 5 O_3 isotopic variants.

5. ZONAL MEANS AND ISOTOPIC RATIOS

The results shown here are presented in terms of zonal means, calculated for 10 degree latitude bands. An example of the zonal fields for the 5 O_3 isotopic variants is shown in Fig. 3.

As isotopic variations are usually small, measurements of an isotope ratio R, such as R = [$^{50}O_3$]/[$^{48}O_3$], where [X] signifies the volume mixing ratio (VMR) of X, are typically reported relative to a standard ratio R_0, often using delta notation: $\delta(\%) = 100\ (R/R_0 - 1)$.

The ratio of VMRs, R, is a function of two variables, x and y where x is the VMR of the minor isotope and y is the VMR of the main isotope. The error covariance of the ratio, R, can be then expressed as follows: $\mathbf{S_R} = \mathbf{S_x^{rnd}} + \mathbf{S_y^{rnd}} + \sum_k \mathbf{S_{x-y}^k}$, where $\mathbf{S_x^{rnd}}$ and $\mathbf{S_y^{rnd}}$ describe the

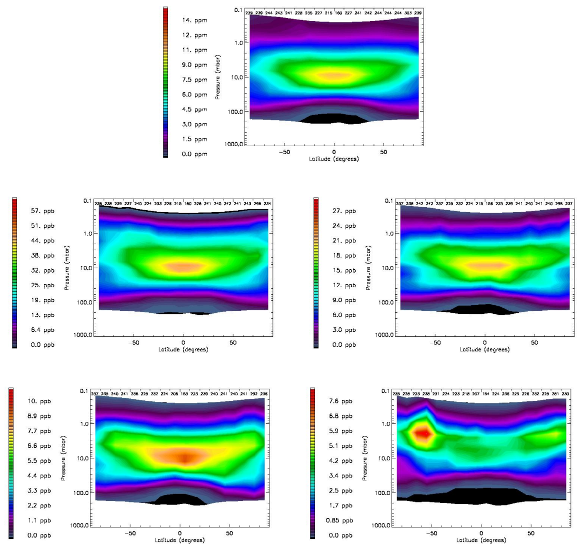

Figure 3. Zonal mean fields of 5 O_3 isotopic variants: main $^{48}O_3$=$^{16}O^{16}O^{16}O$, asymmetric $^{50}O_3$=$^{18}O^{16}O^{16}O$, symmetric $^{50}O_3$=$^{16}O^{18}O^{16}O$, asymmetric $^{49}O_3$=$^{17}O^{16}O^{16}O$ and symmetric $^{49}O_3$=$^{16}O^{17}O^{16}O$, respectively.

random error on x and y respectively (with the assumption that there are no correlations between errors on the VMRs of the minor and major isotope) and $\mathbf{S_{x-y}^k}$ the covariance of the difference of the systematic error k in x and y (assuming that for any particular systematic error k, the errors in the VMRs of the minor and major isotopes are completely correlated). If the main systematic error terms in both x and y are approximately equal, then the total error benefits from their cancellation.

Fig. 4 shows zonal means distributions of asymmetric (top), symmetric (middle) and total (bottom) δ-18 (left) and δ-17 (right), respectively. Net enrichments for $^{50}O_3$ and $^{49}O_3$ are given by [2δ(QOO)+δ(OQO)]/3 where Q stands for ^{18}O and ^{17}O, respectively.

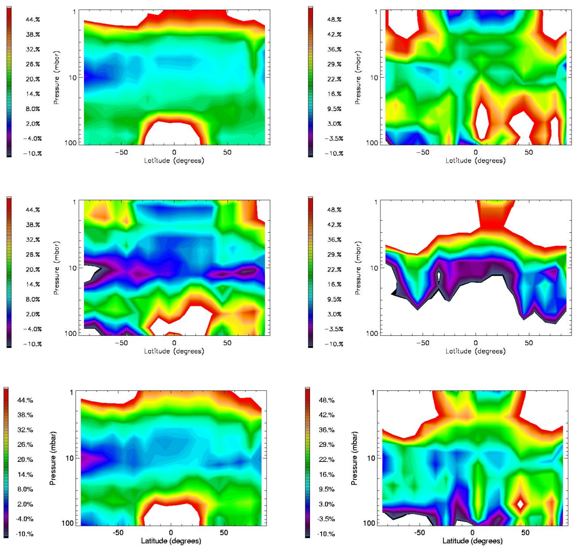

Figure 4. Zonal mean distributions of asymmetric (top), symmetric (middle) and total (bottom) δ-18 (left) and δ-17 (right), respectively.

6. COMPARISONS AGAINST FIRS

The FIRS-2 is remote-sensing Fourier transform spectrometer which observes the thermal emission of the atmosphere [7]. It has flown from both balloon and aircraft platforms. The spectrometer resolution of 0.004 cm^{-1} (unapodized) is sufficient to resolve individual rotational transactions for $^{16}O^{16}O^{16}O$, $^{18}O^{16}O^{16}O$, $^{16}O^{18}O^{16}O$, $^{17}O^{16}O^{16}O$ and $^{16}O^{17}O^{16}O$. Over the range 25-35 km the average enhancements for for asymmetric, symmetric and total $^{50}O_3$ are 12.2$\pm$1.0%, 6.1$\pm$1.8% and 10.2$\pm$0.9%, respectively, and the average enhancements for for asymmetric, symmetric and total $^{49}O_3$ are 8.0$\pm$5.2%, 1.6$\pm$7.6% and 7.3$\pm$4.3%, respectively [8]. Figure 5 shows the comparison of averaged enrichments between MIPAS (solid lines) and FIRS(symbols). These measurements are in agreement in stratosphere (over the range of about 25-40 km).

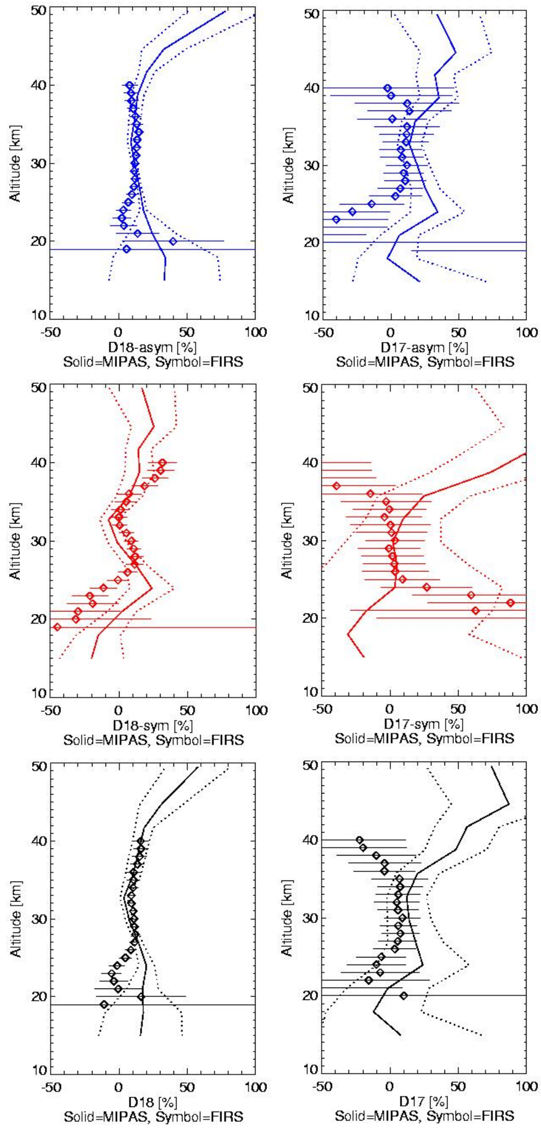

Figure 5. Comparison of averaged enhancements between MIPAS (solid lines) and FIRS (symbols) for asymmetric (top), symmetric (middle) and total (bottom) δ-18 (left) and δ-17 (right), respectively.

7. SUMMARY

Ozone isotope data for $^{50}O_3$ and $^{49}O_3$ are retrieved from MIPAS limb emission spectra. Enrichments for $^{50}O_3$ range 7 to 12% in the middle stratosphere. For $^{49}O_3$ most enrichments are between 7 and 10%. In stratosphere (25-40 km) these measurements are in agreement with previous measurements (e.g. FIRS) and with expectations based on laboratory measurements. Above 40 km and below 25 km, the enrichments of both $^{50}O_3$ and $^{49}O_3$ get larger, from 30 to 50%.

MIPAS enrichments show latitude and altitude structure.

ACKNOWLEDGMENTS

We want to thank David Johnson for providing FIRS measurements of the O_3 isotope enrichments.

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