Global Observations of Ozone Isotopic Ratios from MIPAS limb emission spectra

C. Piccolo[1], A. Dudhia[1], V. Payne[2]

[1]Atmospheric, Oceanic and Planetary Physics, Department of Physics, Oxford University, Oxford, UK

[2]Atmospheric and Environmental Research Inc, Lexington, MA, USA

piccolo@atm.ox.ac.uk

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 [Yung et al, 1991] 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 [Irion et al, 1996, Mauersberg et al, 2001] 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.

MIPAS: The Michelson Interferometer for Passive Atmospheric Sounding is a high resolution Fourier transform spectrometer flying on Envisat satellite. MIPAS measures limb emission spectra over a wide spectral range in the middle infrared region (685-2410 cm^{-1}). From July 2002 until March 2004 MIPAS was operated at full spectral resolution (0.025cm^{-1}) with a nominal scanning sequence covering an altitude range of 6-68 km. For the high-resolution mission ESA have processed pT (pressure-temperature) and six target species. However, MIPAS spectra contain also information on isotopes of ozone as well as other species.

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 $^{49}O_3$≡$^{16}O^{17}O^{16}O$.

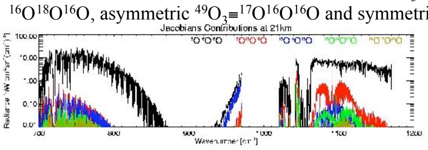
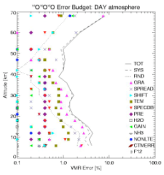
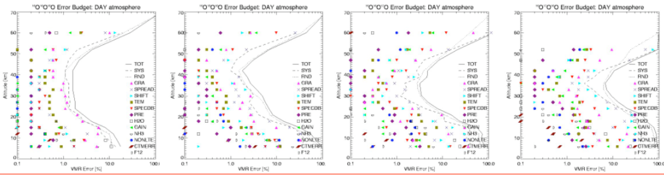


Fig. 1: Jacobian contributions at 21 km for the 5 different O_3 isotopic variants (left pannel) and Error budget (5 panels below)

Microwindow selection and Error analysis

The microwindow have been selecting for retrieving simultaneosly the all 5 O_3 isotopic variants. The error analysis resulting from the microwindow selection is shown here for the 5 different O_3 isotopic variants. 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.





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 [Rodgers, 2000]. The retrieval is based on the use of selected spectral intervals (microwindows) containing the best information on the target parameters [Dudhia et al., 2002] 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 previous 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).

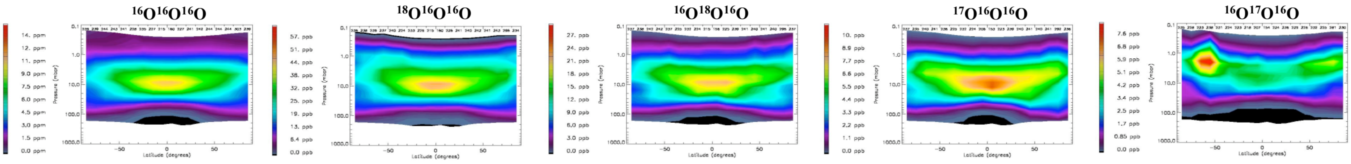
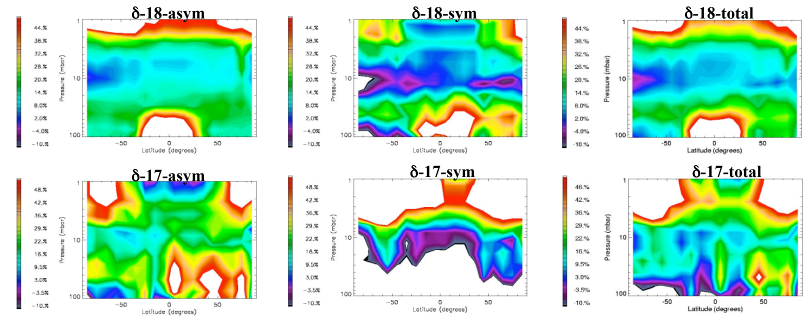


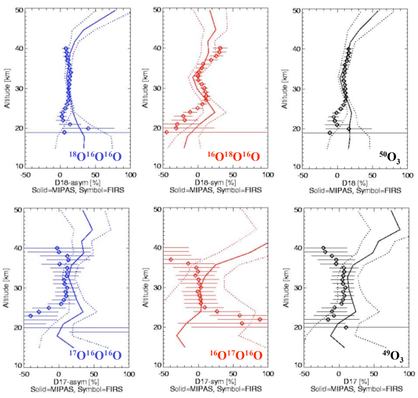
Fig. 2: Zonal mean fields of $^{16}O^{16}O^{16}O$, $^{18}O^{16}O^{16}O$, $^{16}O^{18}O^{16}O$, $^{17}O^{16}O^{16}O$, $^{16}O^{17}O^{16}O$, respectively.



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

Fig. 3: Zonal mean of asymmetric (left), symmentric (middle) and total (right) δ-18 and δ-17, 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.

FIRS: The FIRS-2 is remote-sensing Fourier transform spectrometer which observes the thermal emission of the atmosphere [Johnson et al., 1995]. 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±1.0%, 6.1±1.8% and 10.2±0.9%, respectively, and the average enhancements for for asymmetric, symmetric and total $^{49}O_3$ are 8.0 ±5.2%, 1.6 ±7.6% and 7.3 ±4.3%, respectively.



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

Summary and further work

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. Possible seasonal and annual variations will also be investigated in the next future.

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