OZONE ISOTOPES RETRIEVALS

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Abstract

The isotopic ratios of stratospheric ozone can be used as valuable tracers for many processes in the atmosphere. Here we compare stratospheric enrichments of heavy ozone obtained from two limb sounders: MIPAS (Michelson Interferometer for Passive Atmospheric Sounding), on board Envisat, SMR (Sub-Millimetre Radiometer), on board the Odin satellite.

1 Ozone isotopic anomaly

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. The isotopic composition is often regarded as an isotopic fingerprint of the source.

The theoretical foundations for our understanding of isotope fractionation processes rely on the fact that the fractionation processes are based on differences in chemical and physical properties, which depend on mass. In the case of oxygen with its three isotopes, ^{16}O, ^{17}O and ^{18}O, such mass dependent isotope effects cause a strict correlation in the fractionations: $\delta^{17}\mathrm{O} = 0.52\ \delta^{18}\mathrm{O}$.

The name "mass independent fractionation" has become established to describe any process that deviates from the expected strict mass dependence. Such anomalous or mass independent fractionation was first observed in meteoric material. However, this mass independent fractionation can also occur in chemical reactions and is quite common in atmosphere. The prime example is ozone, whose anomalous enrichment has been studied in detail in numerous laboratory experiments [1]. This isotope effect has been observed in tropospheric [2] and stratospheric [3] ozone. Despite the progress that has been made during the past 10 years, a convincing physical explanation of the process that results in enrichments is still missing. However, these measurements find that ozone is enriched in both ^{17}O and ^{18}O.

In atmosphere, this isotope effect is not restricted to ozone alone, other gases (e.g CO_2, CO, N_2O, H_2O_2, sulfate and nitrate aerosols) show a mass independent fractionation. These anomalies offer the opportunity to advance the science of atmospheric chemistry and to relate its finding to fundamental atomic and molecular processes.

The relative abundances of oxygen atoms in standard mean ocean water [4], ^{16}O:^{17}O:^{18}O, are approximately 1: 1/2700:1/500. Here we consider only singly substituted isotopic variants, symmetric (O_3-sym-17 and O_3-sym-18) and asymmetric (O_3-asym-17 and O_3-asym-18). For ozone species $^{49}O_3$ and $^{50}O_3$, about one-third of all molecules are symmetric and two-thirds are asymmetric.

As isotopic variations are usually small, relative deviations of measured isotope ratio R, such as $R = [^{50}O]/[^{48}O]$, where $[X]$ signifies the volume mixing ratio of X, are typically reported relative to a standard ratio R_0, often using δ notation:

$$\delta(\%) = 100 \cdot \left(\frac{R}{R_0} - 1\right). \qquad (1)$$

2 ODIN-SMR

The Sub-Millimetre Radiometer (SMR) is one of two instruments on the Swedish Small Satellite Project for Astronomical and Atmospheric Research (ODIN). The ODIN satellite was launched on February 21, 2001 into a quasi-polar orbit at 600 km. The instrument observes thermal emissions originating from the Earth's limb as well as astronomical targets. It employs 4 tunable single-sideband Schottky diode heterodyne receivers operating within the 485-580 GHz spectral range. Atmospheric spectra are recorded by means of two high resolution auto-correlator spectrometers [5].
Aeronomy mode measurements are dedicated to the investigation of stratospheric and mesospheric chemistry and dynamics. The main target species are O_3, ClO, N_2O, HNO_3, H_2O, NO, CO and isotopes of H_2O and O_3. These so called stratospheric mode measurements are typically scheduled on one day out of three, time-shared with other aeronomy measurement modes as well as with astronomical observations. A typical stratospheric mode scan covers the altitude range from 7 to 70 km with step of $\sim$ 1.5 km below 50 km and of $\sim$ 5.5 km above.

3 MIPAS

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a Fourier transform spectrometer with a spectral resolution of 0.025 cm^{-1}. MIPAS operates on board Envisat satellite, launched on March 1, 2002, and measures limb emission spectra over a wide spectral range in the middle infrared region (685 - 2410 cm^{-1}, 4.15 - 14.6 micron).
MIPAS observations allow a global geographical coverage, including the polar regions, during both day and night. MIPAS observes sequences of spectra at different limb heights to allow for the retrieval of species concentration profiles. A nominal elevation scan starts at 68 km, descend in 5/8 km steps to 42 km and from 42 km to 9 km in 3 km steps. From these measurements, profiles of pressure, temperature and volume mixing ratio profiles of six key species (H_2O, O_3, HNO_3, CH_4, N_2O and NO_2) are continuously retrieved in near real time by ESA [6]. However, MIPAS spectra contain also information on isotopes of ozone.

3.1 Microwindow Selection and Error Budget

Rather than using all the available measurements, it is usual to select narrow spectral intervals, called "microwindows", containing the best information on the target parameters [7]. The use of microwindows avoids the analysis of spectral regions that are more affected by systematic errors. The microwindow selection process selects spectral regions by simulating a full profile retrieval including the propagation of the random noise and the systematic components (total error) through the retrieval.

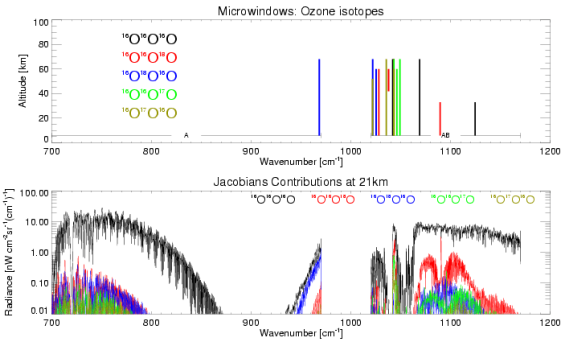

Figure 1: Position of MIPAS microwindows in the spectral and altitude domain (top) and isotope jacobians at 21 km (bottom).

The upper panel of Fig. 1 shows the location (altitude vs spectral domain) of the microwindows for the different ozone isotopes. These microwindows are located in band A (685-970 cm^{-1}) and AB (1020-1170 cm^{-1}) of MIPAS in the altitude range 6-68 km. Since the selection process is altitude dependent, the altitude range of each microwindow is reported in the plot. The lower panel of Fig. 1 shows the jacobians of the different ozone isotopes (same color code as upper panel) at 21 km for bands A and AB of MIPAS.
Fig. 2-4 show five panels for the five ozone isotopes. Each panel represents the percentage VMR error as a function of altitude. The total (solid line) is given by systematic (dashed line) and random (dotted line) profiles. In each plot the major systematic components (different symbols in the plots), that affect the accuracy of the retrieval, are shown as a function of altitude. Such errors are, for instance, calibration errors, uncertain spectroscopic

data, interference of non-target species, non local thermodynamic equilibrium (NLTE) and line mixing effects. For the main isotope (Fig. 2) the accuracy (∼1%) on a single profile is limited by the systematic components, mainly spectroscopic errors at low altitude and ILS at high altitude. For the other isotopes the limitation on a single profile is the random noise, 2-3% for $^{50}O_3$ and 3-6% for $^{49}O_3$, so that the total error can be reduce by averaging profiles.

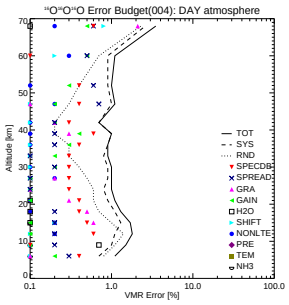

Figure 2: VMR (%) total error for the main isotope.

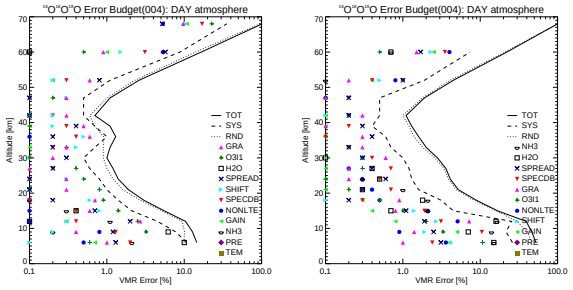

Figure 3: VMR (%) total error for O_3-asym-18 (left) and O_3-sym-18 (right).

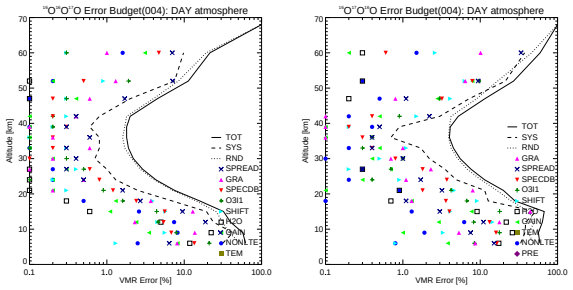

Figure 4: VMR (%) total error for O_3-asym-17 (left) and O_3-sym-17 (right).

4 Comparison between ODIN and MIPAS ozone isotope retrievals

Fig. 5 shows the comparison between ODIN (left) and MIPAS (right) zonal mean measurements of VMR ozone isotopes and enrichments with respect to their standard isotopic ratio for O_3-asym-18 and O_3-sym-18 for the 22^{nd} November 2003.

The zonal mean measurements of the VMR of main isotope (first row of Fig. 5) are qualitatively in agreement. The ODIN VMR retrievals are generally higher than MIPAS (accuracy ∼ 1 ppm). Further investigation is required to explain these differences.

The zonal mean measurements of the VMR of O_3-asym-18 (second row of Fig. 5) present a few differences: ODIN VMR retrievals are generally lower than MIPAS (accuracy ∼ 3.5 ppb) and at equatorial latitudes ODIN shows a minimum while MIPAS is noisier.

The third row of Fig. 5 show the ODIN (left) and MIPAS (right) enrichments of O_3-asym-18 with respect a standard isotopic ratio, as defined in Eq. 1. These plots look quite different: MIPAS shows a latitude and altitude structure with higher enrichments above 10 mbar at equatorial latitudes while ODIN looks noisier with no particular structures. The altitude range is limited by MIPAS accuracy. The expected enrichments are around 0-25%.

The zonal mean measurements of the VMR of O_3-sym-18 (forth row of Fig. 5) are very different: ODIN shows a maximum around 30 mbar while MIPAS, even if noisier at equatorial latitudes, shows its maximum at 10 mbar (accuracy ∼ 3 ppb).

Last row of Fig. 5 shows the comparison between ODIN (left) and MIPAS(right) enrichments of O_3-sym-18. Again the enrichments look very different: ODIN presents high enrichments above 30 mbar, while MIPAS looks noisier but with a latitude and altitude structure. The expected enrichments are of the order of 0-15%.

Further work is required on the MIPAS error analysis and a possible re-selection of the MIPAS microwindows could provide a better agreement with ODIN results. Since the MIPAS retrieval error is limited by the random component, averaging more profiles belonging to more than one day could reduce the total error and provide less noisy and more

realistic results. On the other hand, the ODIN-SMR retrieval error is dominated by the systematic spectroscopic errors on the foreign broadening parameters. New laboratory measurements of foreign broadening parameters with an accuracy of 5% or better could improve ODIN results and therefore the comparison with MIPAS retrievals.

4.1 O_3-asym-17 and O_3-sym-17

MIPAS can also measure O_3-asym-17 and O_3-sym-17 isotopic variants. The retrievable altitude range is limited by MIPAS accuracy ($\sim$1.5 ppb).
Fig. 6 shows the zonal mean measurement of VMR O_3-asym-17 (left) and of its enrichments with respect to its standard isotopic ratio (right) for the 22^{nd} November 2003. O_3-asym-17 presents a maximum at equatorial latitudes of the order of 10 ppb and enrichments of the order of 15-20% below 10 mbar. Above 10 mbar the enrichment might be unrealistic.
Fig. 7 shows the zonal mean measurement of VMR O_3-sym-17 (left) and of its enrichments with respect to its standard isotopic ratio (right) for the 22^{nd} November 2003. O_3-sym-17 presents a kind of two maxima at middle latitudes. Enrichments show a definite pattern, higher at higher altitudes that changes in depletions at lower altitudes.

5 Summary

Comparisons between ODIN and MIPAS ozone isotopes retrievals show a qualitative agreements for the VMRs of the main isotope and the O_3-asym-18 variant, while the VMRs of the O_3-sym-18 isotopic variant are quite different. MIPAS equatorial latitudes retrievals might not be realistic due to lack of statistic. Laboratory measurements of ODIN spectroscopic broadening parameters are required for a better characterization of spectroscopic model errors. Both ODIN and MIPAS retrievals show enrichments of O_3-asym-18 and O_3-sym-18 of the order of 0-25% and 0-15% respectively, in agreement with previous measurements [3]. Further work is required on the error analysis and a possible reselection of the MIPAS microwindows for joint retrievals of the asymmetric and symmetric isotopic variants could provide a better agreement with ODIN results.
Retrievals of O_3-asym-17 and O_3-sym-17 have been performed from MIPAS measurements. In literature there are no other atmospheric measurements of these isotopes enrichments. MIPAS enrichments show latitude and altitude structure. The retrieval error for the minor isotopes is limited by the random component, so averaging profiles for more days could reduce the total error and provide less noisy and more realistic results. Seasonal and annual variations will also be performed in the next future.

References

[1] Mauersberg, K., et al., Multi-isotope study of ozone: Implications for the heavy ozone anomaly, Geophys. Res. Lett., 20, 1993.

[2] Johnston, J. C. et al., The isotopic composition of tropospheric ozone, Geophys. Res. Lett., 102, 1997.

[3] Irion, F. W. et al., Heavy ozone enrichments from ATMOS infrared solar spectra, Geophys. Res. Lett., 23, 1996.

[4] I.U.P.A.C., Isotopic composition of the elements, Pure. Appl. Chem., 55, 1983.

[5] Murtagh, D. et al., An overview of the Odin mission, Can. J. Phys., 80 (4), 2002.

[6] ESA, SP-1229, ESA, ENVISAT-MIPAS: an instrument for atmospheric chemistry and climate research, European Space Agency, ESTEC, Noordwijck, The Netherlands, 2000.

[7] Dudhia, A. et al., Microwindow selection for high spectral resolution sounders, Appl. Opt., 41, 2002.

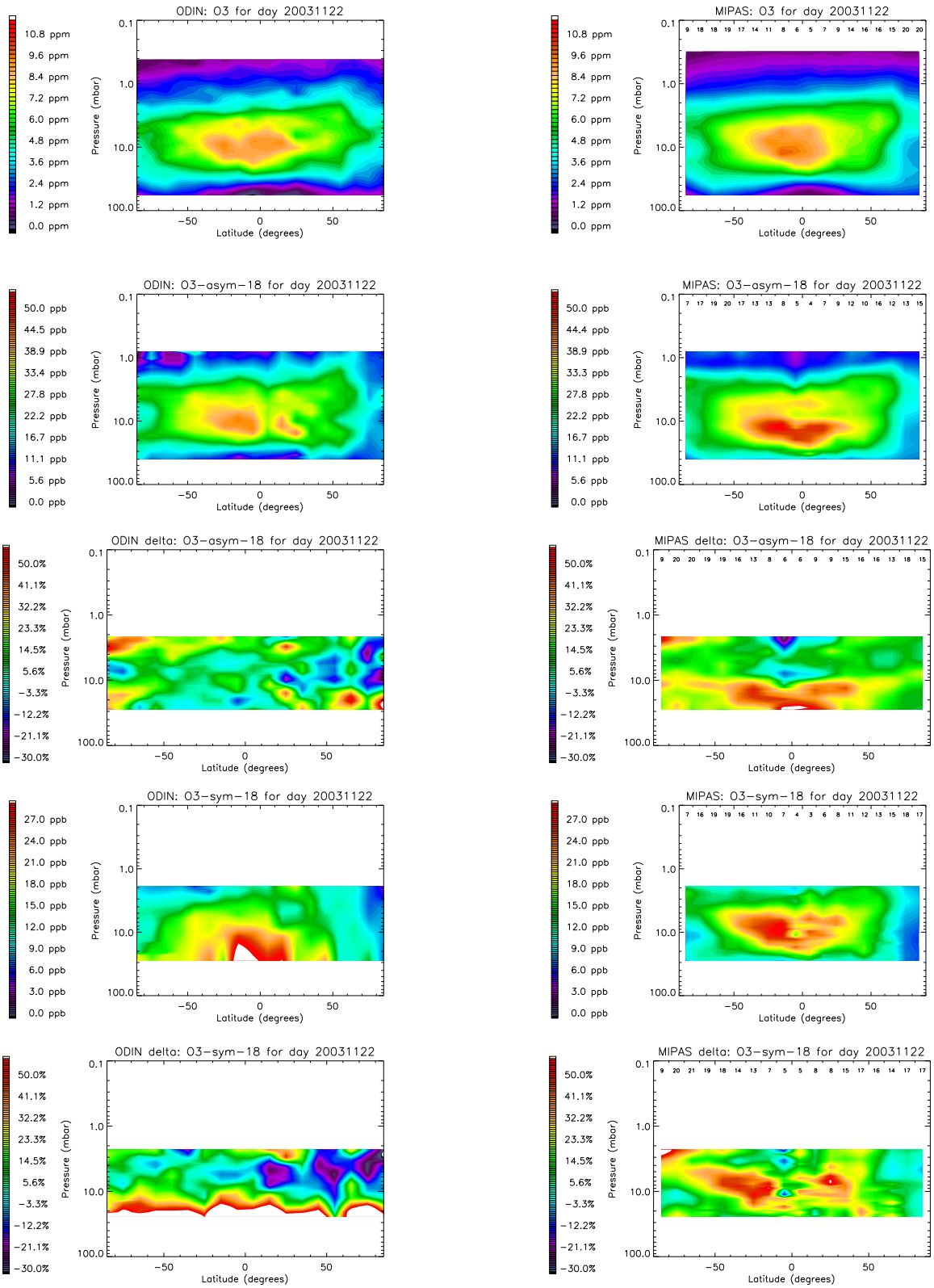

Figure 5: ODIN-SMR (left) and MIPAS (right) zonal mean measurements of VMR ozone isotopes and enrichments with respect to their standard isotopic ratio for O_3-asym-18 and O_3-sym-18 for the 22^{nd} November 2003.

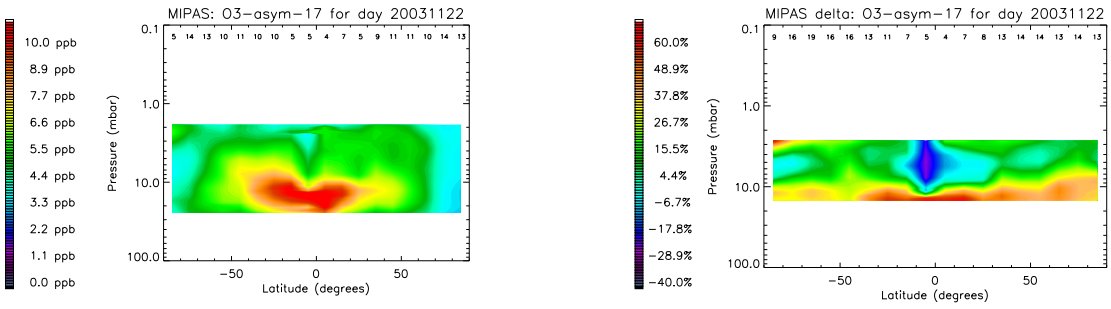

Figure 6: Zonal mean measurement of VMR O_3-asym-17 (left) and of its enrichments with respect to its standard isotopic ratio (right) for the 22^{nd} November 2003.

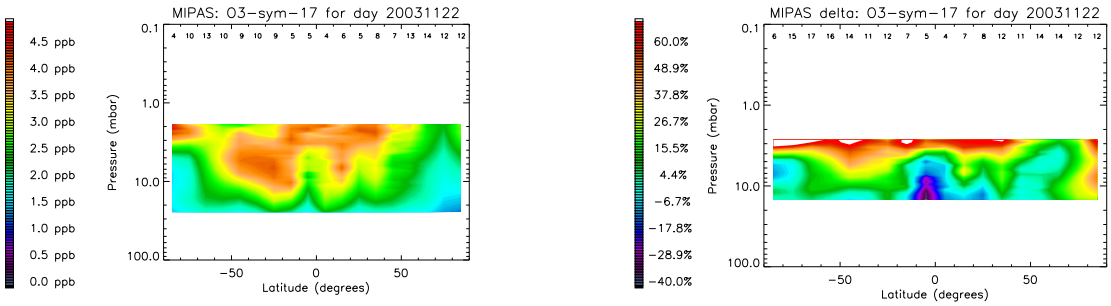

Figure 7: Zonal mean measurement of VMR O_3-sym-17 (left) and of its enrichments with respect to its standard isotopic ratio (right) for the 22^{nd} November 2003.