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Regular isotopic observation of stratospheric ozone and its implications for the ozone formation theory

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Abstract

For the periods 20-Nov-1996 to 25-Mar-1997 and 15 to 22-Aug-1997 we present a data set of 340 observations of the isotopic abundances of the two most abundant heavy isotopomers of ozone for the site of Kiruna in northern Scandinavia. The isotopic abundances are retrieved from ground-based solar and lunar FTIR-spectra and represent in spite of its total column character mainly stratospheric conditions.

Instead of a continuously high enrichment, as observed earlier on Spitsbergen under polar day conditions, with a slow relaxation in polar night, we observe significant changes on diurnal timescales and an overall high variability. Isotopic enrichments relative to ordinary atmospheric oxygen vary from -5 to +30 percent.

So far no theoretical ozone formation model is able to give a correct quantitative understanding of the strong isotopic signals observed by a variety of different experimental methods [4]. One may argue that the direct effect of changes on a 10 percent scale in an ozone species which itself is barely abundant on the permil scale has any direct effect to global ozone. But the ozone formation process runs at a high rates. Thus, even small parameterization errors caused by our incomplete understanding of the ozone formation process may effect the ozone equilibrium concentration significantly.

Experimental

The isotopic ratios of ozone are derived from solar and lunar IR absorption spectra recorded in the 10 μm spectral region with a ground-based BRUKER 120 HR FT-spectrometer at IRF Kiruna (67.84°N, 20.41°E, 419 m amsl). Lunar and solar spectra are recorded with 45 cm and 180 cm OPD, respectively (boxcar apodization). The *quicklook* data is processed as described in detail in [5]. For the most recent data (after 11-Feb-97) the number of spectral microwindows analyzed has been increased by 5 (all 16-18-16 ozone) as described in [7], the retrieval software and spectroscopic data base are upgraded to SFIT Vers. 1.09e and HITRAN96 (based on [1&2]), respectively. Finally, preliminary results from the retrieval of 16-16-17 ozone are included, which are the first ever reported from ground for stratospheric $^{49}\text{O}_3$. The spectroscopic data used for ozone of mass 49 is from a most recent study by *C. Camy-Peyret* and *A. Perrin* (priv. comm., 1997).

Discussion

The 'quicklook' data:

Figure 1 shows an overview over 240 observations between 20-Nov-1996 and 04-Mar-1997. In polar night only lunar spectra are available during full moon phases. For many days in early winter no ozone VMR profile from local ECC ozone sondes was available. Typical uncertainties are 1 to 2 % enrichment in solar and 3 to 5 % enrichment in lunar spectra (plus systematic uncertainties of the spectroscopic data as discussed in [5]), but may

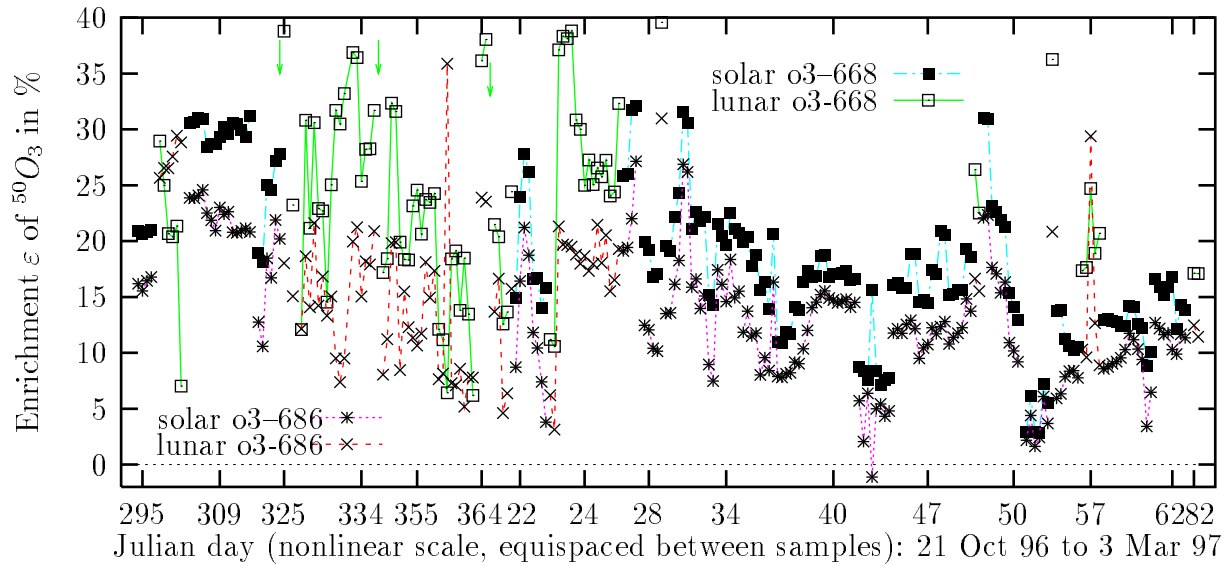


Figure 1: Quicklook data: Enrichment of ^{18}O in ozone relative to atmospheric O_2 .

occasionally be larger in particular in lunar spectra. The major features seen are expected to be verified when all data is reprocessed with the improved techniques described above. This expectation is based on the comparison of the data from Feb/Mar 97, which is included both in the quicklook data (Fig. 1, individual samples) and in the detailed analysis (Fig. 2, daily mean values).

The data show strong enrichments in heavy ozone of mass 50 relative to the isotopic ratios in atmospheric O_2 . The variability is much higher than one might expect from satellite data [3] or from earlier studies with an FTS on Spitsbergen [5]. Values range from virtually no enrichment to 30 % and more, with the asymmetric species typically showing higher enrichments than the symmetric 16-18-16 ozone, but several exceptions can be seen.

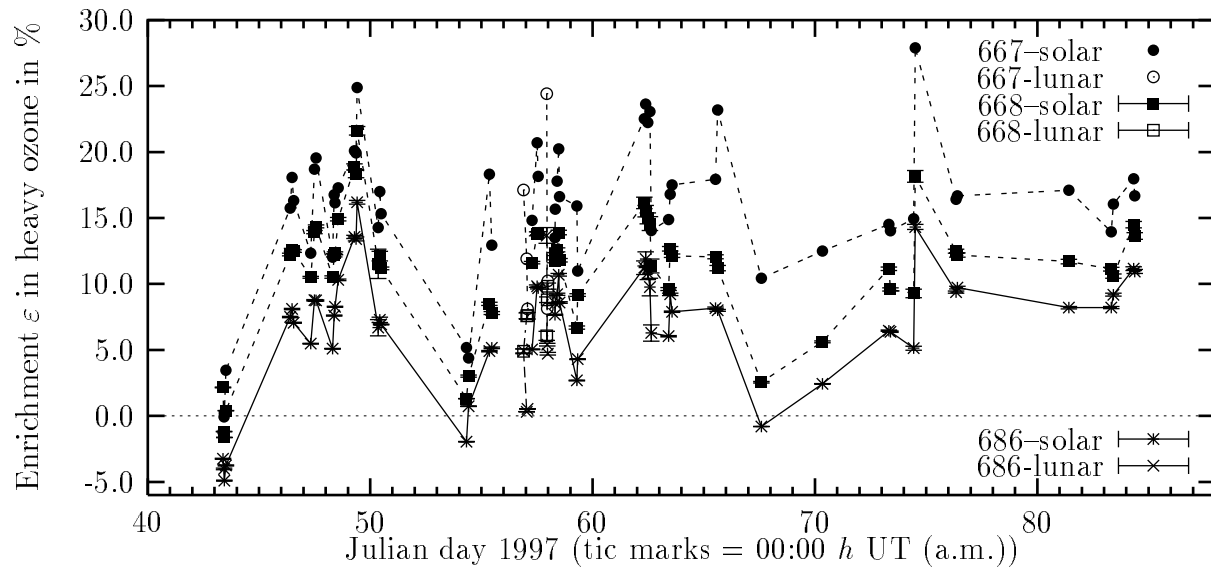


Figure 2: Enrichment in heavy ozone in Feb/Mar 1997 (daily mean values).

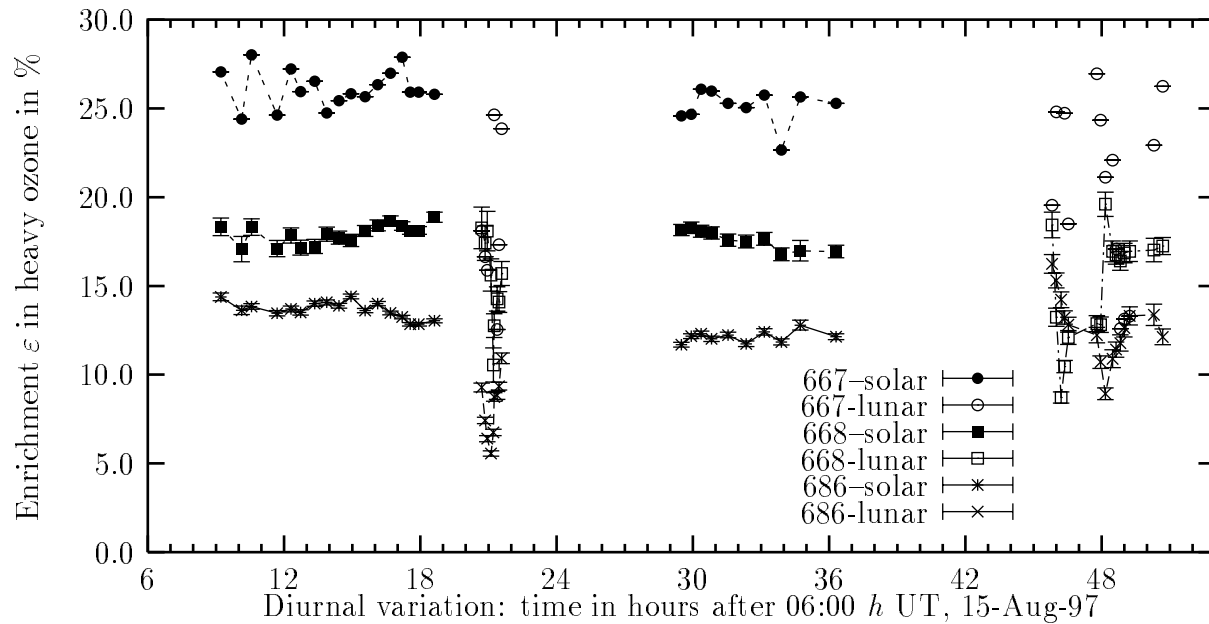


Figure 3: *Enrichment in heavy ozone in Aug 1997 (individual spectra).*

Feb/Mar 1997 detailed study:

In addition to the improvements in the retrieval as described under 'Experimental' a set of chemical key species and dynamical parameters (subsidence) has been derived. Though the results for the end of February show somewhat lower enrichments compared to the quicklook data, the general features are preserved. The negative enrichment in 16-18-16 ozone on day 43 (12-Feb) is confirmed as well as at least one value exceeding 20 %.

The first results tentatively shown for 16-16-17 ozone are based on the retrieval of rather weak features in only 3 microwindows near 1044 cm^{-1} . Error bars are about 10 % enrichment (not plotted). However, the results look promising and basically the same features are seen as in the other 2 heavy isotopomers studied.

No clear correlation can be seen neither with the total column amount of ozone (mass 48) nor with potential vorticity or any other species like HNO_3 , HCl , $ClONO_2$. (Size restrictions did not allow to include all these plots from the poster.)

August 1997 detailed study:

This data is included for two important reasons: First, an 'undisturbed' reference period is needed and, second, on the 16-Aug-97 almost the same air mass was sampled by *Max-Planck-Institut für Kernphysik*, Heidelberg, with a new in-situ ozone isotope sampler carried on a stratospheric balloon launched from Esrange, thereby providing a unique intercomparison of two completely different techniques.

Fig. 3 shows the diurnal variation as observed after 06:00 h UT on 15-Aug-97. Data between hours 45 and 51 are from the night 21/22 Aug, which has more favorable lunar zenith angles ($< 75.4^\circ$ compared to $> 86.5^\circ$). As seen in previous studies ([6],[3]), the variability from one solar spectrum to another is very low in summer. The nights considered last only 3 to 4 hours around 20 km altitude (last lunar data are sunlit ozone!). An interesting feature approximately correlating with stratospheric darkness is seen in the

second night shown. A similar drop in enrichment is seen in the first night shown, but the total observation time is shorter and uncertainties are higher due to very high air mass factors.

Conclusions

The most striking new result is the diurnal variation with very fast and strong changes in particular at the day/night lines, which is anticorrelated in direction between symmetric and asymmetric mass 50 ozone, in contrast to sunlit air masses where values are clearly correlated.

The data set presented covers both seasonal and diurnal variations of isotopic enrichments in ozone with a time resolution of up to 20 minutes. The observed enrichments in sunlit air masses are comparable to in-situ, to sampling, to satellite based, and previous studies with an FTS at other locations [3,4,5,6, and references therein]. Compared to satellites, the ground-based FTS covers also night-time conditions during full moon phases and has a higher long-term stability.

The high spectral resolution and improved spectroscopic data allow for the first time to measure 16-16-17 ozone, additionally. The uncertainties are expected to be reducible by a factor of two or better by including a higher number of suitable absorption features.

We have the impression that the irradiation history plays a key role in understanding of any observed isotopic data. In addition to ozone, a number of chemical key species like HNO_3 , HCl , and $ClONO_2$ and dynamical tracers like HF , N_2O , and subsidence are observed simultaneously (see *Blumenstock et al.*, this issue). In particular in arctic winter and spring the isotopic data looks puzzling and might be a complicated function of chemical processing, transport, and the irradiation history.

Neither the high variability in the enrichment is understood nor why occasionally the symmetric species is higher enriched than the asymmetric one.

A trajectory analysis is under process to determine the irradiation history. A correlation check against other geophysical parameter (k-index, cosmic radiation, etc.) that might effect the availability of (excited) odd oxygen will be performed. Data from August is to be compared against the results from the balloon flight of the Heidelberg grab-sampler.

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References

1. Camy-Peyret C. et al., "The hybrid-type Volumes ν_1 and ν_3 of $^{16}O^{16}O^{18}O$: Line positions and intensities", *J. Mol. Spectrosc.*, **118**, 345-354, 1986.
2. Flaud, J.-M. et al., "The ν_1 and ν_3 Volumes of $^{16}O^{18}O^{16}O$: Line positions and intensities", *J. Mol. Spectrosc.*, **118**, 334-344, 1986.
3. Irion, F. W. et al., "Heavy ozone enrichment from ATMOS infrared solar spectra", *Geophys. Res. Let.*, **23**, 2377-2380, 1996.
4. Kaye, J. A., (editor), "Isotope effects in gas-phase chemistry", 438 pp., ACS series 502, Washington DC, 1992.
5. Meier, A. and J. Notholt, "Determination of the isotopic abundances of heavy ozone as observed in arctic ground-based FTIR-spectra", *Geophys. Res. Let.*, **23**, 551-554, 1996.
6. Meier, A., "Determination of atmospheric trace gas amounts and corresponding natural isotopic ratios by means of ground-based FTIR spectroscopy in the high Arctic", Alfred-Wegener-Institut, reports on polar research series, Vol. 236, Bremerhaven 1997.
7. Meier, A., G.C. Toon, C.P. Rinsland, and A. Goldman (editors), "Spectroscopic atlas of atmospheric microwindows in the middle infra-red", IRF preprint 123, 264 pp., Kiruna 1997.