Atmos. Chem. Phys. Discuss., 5, S2481–S2483, 2005
www.atmos-chem-phys.org/acpd/5/S2481/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Interactive comment on "High-precision isotope measurements of $H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$, and the -anomaly of water vapor in the southern lowermost stratosphere" *by* P. Franz and T. Röckmann

C. Webster (Referee)

Chris.R.Webster@jpl.nasa.gov

Received and published: 9 September 2005

This is an excellent paper that presents interesting and important results. It is well-written, communicates simply but with the meticulous detail required for contribution to furthering our understanding of transport and mixing between troposphere and stratosphere through the subtlety of departures from MDF.

This excellent work stands on its own, and the authors do not need to provide such

strong criticism of earlier work in the field. First of all, the discussion on page 5389 concerning the Webster and Heymsfield (W&H) delta-17O measurements is somewhat staged and reported in an unnecessarily negative light. To claim that W&H report “an extreme isotope anomalyĚ.” and “ Ě.this huge anomaly...” that needs careful analysis is later deflated by the conclusion that “...(the W&H anomaly) is not statistically different from zero”. The reader can understand this immediately from the quoted error bars. I suggest that this section be shortened to focus on the much higher precision and accuracy for delta-17O achieved by this work in a spirit of positive progress. Also, this paper should point out that the W&H measurements of delta-D, delta-18O, and delta-17O were truly pioneering in that they were the first simultaneous measurements of these isotope ratios made in situ in real time as an aircraft flew in and out of clouds, with a time resolution and sensitivity that allowed cloud features to be studied in detail. The delta-17O measurements of W&H were very much secondary, as the work focused on the much more prominent changes in delta-D and delta-18O that are much more indicative of atmospheric processes. For the delta-D and delta-18O measurements, W&H had precision and accuracies well above what was needed to observe the large changes (e.g up to 900 per mil in delta-D) accompanying the atmospheric processes.

Regarding the introductory statements (page 5377 line 10+) about “Available instruments can be classified into two groups: opticalĚ and cryogenic”, this needs to be re-written to reflect less bias against optical methods and not present the reader with inaccurate, misleading statements. To say that “Optical methods have a high potential for isotope measurements in the upper stratosphere, where interference from the water-rich troposphere is small” is unfairly dismissive, and confuses high-altitude remote sensing optical capability (for which this is true only for some optical techniques) with in situ optical (laser) methods, for which this is certainly not true. For the latter, isotope ratios measurements can be made from the stratosphere all the way to the ground with excellent sensitivity, since for small path lengths the chosen optical lines in the 6 micron region do not overlap nor saturate even with 10,000 ppmv water vapor. The space-based Aura satellite Tropospheric Emission Spectrometer (TES) optical in-

ACPD

5, S2481–S2483, 2005

Interactive Comment

strument is reporting delta-D measurements near 720 mbar pressure (Worden et al., private communication), with validation from the same aircraft in situ laser spectrometer (ALIAS) that produced the W&H isotope data.

While it is true that cryogenic sampling with later lab-based GCMS analysis can produce isotope ratios of higher precision and accuracy than optical methods, these cryogenic samples are few and far between and do not offer the "real time" sampling of in situ laser-based methods. For Earth atmospheric studies, in situ laser-based sampling with its superior time resolution with capability to ˜20 per mil is very adequate for monitoring the observed changes in delta-D and delta-18O (up to 900 per mil, and 200 per mil, respectively), but inadequate for detailing the changes in delta-17O and thereby studying oxygen MDF in water isotopes. To this end, the statement (p. 5377, line 5) that "One major drawbackĚ(to earlier measurements of all isotope ratios)Ěis that delta-D can usually be measured with errors larger than 20 per milĚ." is completely wrong and out of context unless the range of deltas is included. Rather, because delta-D changes by up to 900 per mil, an error of 20 per mil is very acceptable. Somewhere in the introduction, the authors should point out the magnitude of the relative changes in delta-D, delta-18O, and delta-17O to put these statements and their own study in perspective.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5373, 2005.