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Atmospheric
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Discussions

Interactive comment on "The isotope composition of water vapour: A powerful tool to study transport and chemistry of middle atmospheric water vapour" *by* Ch. Bechtel and A. Zahn

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General comments:

The paper by Bechtel & Zahn (2003) describes a one-dimensional model of stratospheric and mesospheric water vapour isotopes. Stable hydrogen and oxygen isotopes are considered and predictions of the transfer of oxygen isotope anomalies between different reactive species are made. Within the large experimental errors, the model results agree well with in situ observations. Improvements over previous one-dimensional model results (Lyons et al., 2001) for the predicted oxygen isotope anomaly are achieved. The main limitations for the model calculations are missing reaction rate constants for isotopically substituted species and unknown equilibrium fractionation constants for isotope exchange reaction. As stated appropriately by the

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authors, the precision that can be achieved with current optical techniques is not sufficient to provide additional constraints to the kinetic data. Ongoing developments of high-precision mass-spectrometric techniques promise to provide better estimates of stratospheric water vapour isotopes, and the present model results will become very useful for future interpretations of new experimental data.

The paper is generally very well written and methodologically sound (within the limitations of a 1D model). However, a number of corrections, improvements and clarifications still need to be made before the paper is acceptable for publication in ACP. My specific comments are detailed below. Some typos and technical corrections are also pointed out.

Specific comments:

The title of the paper should be changed. It is rather long, repetitive ("water vapour"), and does not agree with the conclusion that deltaD(H2O) is not a very sensitive tracer to distinguish between the different CH4 reaction chains and that major uncertainties exist in the isotope exchange equilibria and kinetic fractionation factors. The claim about water vapour isotopes to be a "powerful" tool is therefore too strong. I suggest a title such as "Modelling of transport and chemistry of middle atmospheric water vapour isotopes".

Vertical profiles of H2O, CH4, and H2 concentrations should be shown including a comparison with in situ measurements so that an appraisal of the model quality can be made.

The transport of hydrogen from the troposphere into the stratosphere is currently missing from the model and the budget calculations. Please quantify. Important relevant references may be [Gerst and Quay, 2000; Gerst and Quay, 2001; Tromp et al., 2003] and a recent paper by Röckmann et al. that appeared in ACPD next to the present paper. If H2 is important for the isotope budget, isotopic fractionation by its sinks might also need consideration.

p. 4006 and Fig. 4: Give the fluxes in megatons H2 equivalents per year to make them comparable for the different compounds (H2, CH4, H2O). Consider that CH4 corresponds to two H2 equivalents.

It needs to be spelled out clearly that oxygen isotope anomalies can also arise from differences in three-isotope relationships, i.e. the relative enrichments in 17O can be between 0.5 and 0.53 times the relative enrichment in 18O. These differences can lead to positive or negative Delta17O values [Miller, 2002; Young et al., 2002] that differ significantly from zero, especially if amplified by Rayleigh fractionation processes. For instance, the relationship between ln(1+delta17O) and ln(1+delta18O) for meteoric waters is characterized by a slope of 0.528 whereas the reaction between CH3 and O2 would have a "mass-dependent" beta value as defined in Young et al. [2002] of 0.513. Evaporation and condensation may modify the relationship for meteoric waters so that it is not clear which Delta17O value atmospheric water vapour has and whether the relative enrichments in 17O/16O really scale by a factor of 0.52 to changes in the relative 18O/16O enrichments (p. 3992, l. 7, and elsewhere). Moreover, atmospheric O2 is known to have small negative Delta17O value of -0.26 per mill [Luz and Barkan, 2000]. Table 5 and references to O2 in the text therefore require correction. It needs to be clarified whether these rather small effects have an impact on the results of the present study.

A revised version should comprise corrections and improvements of the kinetic model. First of all, the updated NASA-JPL kinetic data evaluation (2003) should be used. Several differences to the JPL97 results are evident and some typos might also be present in the tables of the present paper, e.g. in case of reactions nos. 7, 9, 11, 14, 16, 19, 21, and 24. The reaction CH3O2 + NO -> CH3O + NO2 is conspicuously missing. Is it also missing in the model implementation? Isotope exchange by this reaction should also be considered. The reaction OH + OH + M -> H2O2 + M is missing. Could this reaction explain the oxygen isotope anomaly in Savariono and Thiemens [1999a]? Obviously, the absence or presence of isotopic exchnange by reactions R34 and R35 is important in this context. Moreover, isotopic fractionation by Hx, Ox reactions was studied by Savarino and Thiemens [1999b] and should given a critical assessment whether it is relevant. Discuss whether H2O2 might give some additional constraints on these different aspects.

The photolysis rate for H2O photolysis is only valid for the Lyman-alpha line. How much does photolysis in the Schumann Runge bands contribute? The coefficient A should be 5.25(-6), not 5(-6). I could not find the parameterization that Bechtel & Zahn claim to use for CH4 photolysis in the cited reference (Brasseur & Solomon (1986)). Does CH4 photolysis play a role at all? How much of the total CH4 sink is via photolsysis? If photolysis is significant, the reaction channel CH4 -> CH + H2 + H should also be included.

Finally, it would be useful for reference purposes if the table with the kinetic data included the isotopic fractionation factor calculated/used by the authors, even if we know that they would most likely be not correct. It might also be revealing to calculate the beta value in each case, i.e ln 17alpha / ln 18alpha [Young et al., 2002]. Also, the fractionation factors used by the authors for the methane destruction reactions do not always agree with other cited work (e.g., Saueressig et al.). Relative rate measurements are likely to be more reliable than absolute rate measurements of isotopically substituted species. Discuss whether the differences are significant.

Technical corrections:

"Middle atmosphere": This term needs to be clarified or replaced (e.g., p. 4008, l. 4, and elsewhere). Some people understand "middle atmosphere" as "stratosphere", others as "mesosphere", and others as "stratosphere and mesosphere combined".

p. 3992, l. 7: "isotope shifts" refer to the influence of isotopic substitution on physical quantities, especially spectroscopic properties. They should not be used to describe isotopic enrichments and changes in the isotopic composition.

p. 3993, l. 5: A reference to [Engel et al., 1996] should be made.

p. 3993, l. 19: Isotope ratios are defined as atomic ratios, so that RD, V-SMOW is equal to 0.15576 x 10(-3).

p. 3993, l. 24: Terrestrial waters differ significantly in their isotopic composition from ocean waters. How much of total evaporation is really from the ocean? Does it reflect the ocean/landmass distribution, i.e. 70 %? Or is it closer to 90 %? What is the global average delta18O value for evaporating water?

p. 3994, l. 8: Transport does not change the isotope signature in the troposphere either, only evaporation etc. do. Transport may change the apparent fractionation factors, though, due to the interplay of chemistry and diffusion, for example [Kaye, 1987] Rephrase this sentence appropriately.

p. 3995, l. 2: "data"

p. 3997, l. 1: Water vapour may have a Delta17O value at the tropopause that differs significantly from zero, due to the interplay of equilibrium and kinetic isotope fractionation factor with different three-isotope relationships and Rayleigh fractionation. See also my specific comments.

p. 3997, l. 18: "to mirror" is too strong a statement, because additional isotopic fractionation during the CH4 oxidation chain may vary with altitude, temperature, etc.

p. 3998, l. 25: Replace "species" by "compounds" (HDO and H218O are different (isotopic) species, too.)

p. 3999, l. 2: isotopologues "and isotopomers"

p. 3999, l. 3: "(with Q substituting for 17O and 18O")

p. 4000, l. 17: This delta17O value for O2 is not in line with the isotope-anomaly of -0.26 per mill derived by Luz and Barkan [2000] if the definition Delta17O = delta17O Ű 0.52 delta18O is used.

p. 4000, l. 22: "Mauersberger", "that the pressure dependence"

p. 4001, l. 20: The following paper should also be referenced: [Röckmann et al., 2001].

p. 4004, l. 4: Engel et al. (1996) is missing from the reference list.

p. 4005, l. 10: The transport lifetime for a 1D diffusion model is given by 4H/KZ [Kaiser et al., 2002]. Fig. 6b should also be corrected.

p. 4006, l. 24: Delete (or 1.070 absolute). It is redundant.

p. 4006, l. 25: Delete "there"

p. 4007, l. 2: Delete "1.070/1.2 = 0.892 absolute or".

p. 4008, l. 12+13: Delete commas.

p. 4009, l. 1 & p. 4025, Table 4: Use chemical equilibrium arrows.

p. 4009, l. 16: A reaction arrow is missing.

p. 4011, l. 16: "of"

p. 4012, l. 26: "turned"

p. 4014, l. 5: "18O"

p. 4022, Table 1 & p. 4024, Table 3: n=0.917 should not appear in the column "fractionation factor".

p. 4024, Table 3, footnote a: "DeMore" and correct the parameters for the reaction CH3D + OH -> H2O + CDH2. They should be the same as for the following three reactions.

p. 4028, Figure 2: Replace "latitudinal" by "meridional".

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