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**Isotope composition  
of middle  
atmospheric H<sub>2</sub>O**

Ch. Bechtel and A. Zahn

# The isotope composition of water vapour: A powerful tool to study transport and chemistry of middle atmospheric water vapour

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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## Abstract

A one-dimensional chemistry model is applied to study the stable hydrogen (D) and stable oxygen isotope ( $^{17}\text{O}$ ,  $^{18}\text{O}$ ) composition of water vapour in stratosphere and mesosphere. The stable isotope ratios of tropospheric  $\text{H}_2\text{O}$  are determined by “physical” fractionation effects, i.e. phase changes, diffusion processes, and mixing of air masses. Due to these processes water vapour entering the stratosphere (i) is mass-dependently fractionated (MDF), i.e. shifts in the isotope ratio  $^{17}\text{O}/^{16}\text{O}$  are  $\sim 0.52$  times of those of  $^{18}\text{O}/^{16}\text{O}$  and (ii) shows isotope shifts in D/H, which are  $\sim 5$  times of those in  $^{18}\text{O}/^{16}\text{O}$ . In stratosphere and mesosphere “chemical” fractionation, that are the oxidation of methane, re-cycling of  $\text{H}_2\text{O}$  via the  $\text{HO}_x$  family, and isotope exchange reactions are shown to considerably enhance the isotope ratios in the imported tropospheric  $\text{H}_2\text{O}$ . Enrichments relative to the isotope ratios at the tropopause are used to derive the partitioning of tropospheric (unmodified), re-cycled and in situ generated  $\text{H}_2\text{O}$ . The model reasonably predicts overall increases of the stable isotope ratios in  $\text{H}_2\text{O}$  by  $\sim 23\%$  for D/H,  $\sim 8.5\%$  for  $^{17}\text{O}/^{16}\text{O}$ , and  $\sim 14\%$  for  $^{18}\text{O}/^{16}\text{O}$ . The  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios in  $\text{H}_2\text{O}$  are shown to be a measure of the partitioning of  $\text{HO}_x$  that receives its O atom either from the reservoirs  $\text{O}_2$  or  $\text{O}_3$ . In the entire middle atmosphere, MDF  $\text{O}_2$  is the major donator of oxygen atoms incorporated in OH and  $\text{HO}_2$  and thus in  $\text{H}_2\text{O}$ . It is demonstrated that in the stratosphere mass-independent fractionation (MIF) in  $\text{O}_3$  in a first step is transferred to the  $\text{NO}_x$  family and only in a second step to  $\text{HO}_x$  and  $\text{H}_2\text{O}$ . In contrast to  $\text{CO}_2$ ,  $\text{O}(^1\text{D})$  only plays a minor role in this MIF transfer. The major uncertainty in our calculation arises from the many badly quantified isotope exchange reactions and kinetic isotope fractionation factors.

## 1. Introduction

Water vapour ( $\text{H}_2\text{O}$ ) belongs to the most important trace gases in the Earth's atmosphere. It plays a key role as partner of homogeneous and heterogeneous chemical

ACPD

3, 3991–4036, 2003

## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

reactions (Lelieveld and Crutzen, 1990, 1994) and in the short-wave and long-wave radiative budget of the atmosphere (IPCC, 2001). Its extremely complex atmospheric cycle is not understood in sufficient detail, particularly as atmospheric H<sub>2</sub>O is present in the gaseous, fluid, and solid phase. Interest in middle atmospheric H<sub>2</sub>O was additionally increased by observations made by Oltmans and Hofmann (1995) and after this by others (SPARC, 2000, and references therein, Rosenlof et al., 2001) who have found increasing H<sub>2</sub>O concentrations of 30-150 nmol/mol yr<sup>-1</sup> in the middle atmosphere since 1954. Not only the cause of this trend but also its consequences on the Earth's climate and the chemistry of the middle atmosphere is a matter of vital discussion (Forster and Shine, 1999, 2002; Kirk-Davidoff et al., 1999).

Mostly, H<sub>2</sub>O concentration measurements, supported by atmospheric circulation models, are used to place constraints on the H<sub>2</sub>O cycle in the middle atmosphere (Dessler et al., 1995; Rosenlof et al., 1997; Randel et al., 2001). A new dimension allows for the analysis of the isotopic composition of water vapour.

Abundances of stable isotopes in water vapour are usually reported as per mil deviation of the 'rare isotope' to the 'most abundant isotope' ratio, relative to the Vienna Standard Mean Ocean Water (V-SMOW) reference. For  $\delta^{18}\text{O}$ , e.g., this  $\delta$  notation is  $\delta^{18}\text{O}(\text{H}_2\text{O}) = (R_{18\text{O, sample}}/R_{18\text{O, V-SMOW}} - 1) \cdot 1000\text{‰}$ , where  $R_{18\text{O}}$  denotes the isotope ratio  $^{18}\text{O}/^{16}\text{O}$  of a sample or V-SMOW, respectively.  $R_{\text{D, V-SMOW}}$  is  $0.31152 \cdot 10^{-3}$  (Hagemann et al., 1970; DeWit et al., 1980; Tse et al., 1980),  $R_{17\text{O, V-SMOW}}$  is  $0.3799 \cdot 10^{-3}$  (Li et al., 1988), and  $R_{18\text{O, V-SMOW}}$  is  $2.0052 \cdot 10^{-3}$  (Baertschi, 1976). All  $\delta\text{D}$ ,  $\delta^{17}\text{O}$ , and  $\delta^{18}\text{O}$  values in this paper are given with respect to V-SMOW.

The major source of atmospheric water vapour is the ocean having the isotope composition of V-SMOW, i.e.,  $\delta^{18}\text{O}(\text{H}_2\text{O}) \approx 0\text{‰}$ . Evaporation into the atmosphere leads to depletion in the rare H<sub>2</sub>O isotopologues, due to their lower vapour pressure compared to the most abundant H<sub>2</sub><sup>16</sup>O, the vapour pressure isotope effect (v.p.i.e.). Typically,  $\delta^{18}\text{O}(\text{H}_2\text{O})$  is  $-12\text{‰}$  and  $\delta\text{D}(\text{H}_2\text{O})$  is  $-85\text{‰}$  just above the ocean (Rozanski et al., 1993). Cooling during upward air movement causes cloud formation and due to

## Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

the v.p.i.e. preferential condensation and subsequent removal of the isotopically substituted  $\text{H}_2\text{O}$  isotopologues by precipitation. The  $\text{D}/\text{H}$ ,  $^{17}\text{O}/^{16}\text{O}$ , and  $^{18}\text{O}/^{16}\text{O}$  isotope ratios in  $\text{H}_2\text{O}$  thus decrease with altitude and reach tropopause values in the range of  $\delta\text{D}(\text{H}_2\text{O}) \approx -(450-750)^\circ\text{‰}$ ,  $\delta^{17}\text{O}(\text{H}_2\text{O}) \approx -(30-70)^\circ\text{‰}$ , and  $\delta^{18}\text{O}(\text{H}_2\text{O}) \approx -(60-130)^\circ\text{‰}$ , respectively (see Sect. 2). This isotopically depleted water vapour is imported into the stratospheric overworld, almost exclusively within the tropics (Holton et al., 1995; Highwood and Hoskins, 1999). As a result of negligible cloud formation and subsequent precipitation or sedimentation, transport within the middle atmosphere virtually does not change this tropopause isotope signature.

In contrast to the troposphere, chemical reactions determine the isotope composition of  $\text{H}_2\text{O}$  in the middle atmosphere such as: (i) methane ( $\text{CH}_4$ ) oxidation, the main in situ source of  $\text{H}_2\text{O}$  in the stratosphere, (ii) exchange of oxygen atoms with molecular oxygen and ozone via the  $\text{HO}_x$  and  $\text{NO}_x$  family, (iii) oxygen isotope exchange reactions e.g. between  $\text{H}_2\text{O}$  and  $\text{OH}$  (Greenblatt and Howard, 1988; Masgrau et al., 1999), and (iv) locally restricted, injection of  $\text{H}_2\text{O}$  by aircraft. All of these processes isotopically enrich the water vapour imported from the troposphere.

Using a one-dimensional (1-D) model it is shown, how these chemical reactions modify the stable isotope composition of middle atmospheric  $\text{H}_2\text{O}$  on the one hand, and vice versa, how  $\text{H}_2\text{O}$  isotope observations can be exploited to infer constraints on these reactions. Three previous model studies on the isotopic composition of stratospheric  $\text{H}_2\text{O}$  have been made. Kaye (1990) studied  $\delta^{18}\text{O}(\text{H}_2\text{O})$  in the middle atmosphere and suggested a remarkable increase in the  $\delta^{18}\text{O}(\text{H}_2\text{O})$  mixing ratio with altitude due to  $^{18}\text{O}$ -rich excess water from the  $\text{CH}_4$  oxidation. Ridal et al. (2001) and Ridal (2002) focused on  $\delta\text{D}(\text{H}_2\text{O})$  in the stratosphere. They found a strong vertical increase of  $\delta\text{D}(\text{H}_2\text{O})$ , also due to  $\text{CH}_4$  oxidation which is additionally modulated by the seasonally varying  $\text{H}_2\text{O}$  input from the troposphere (“tape recorder effect”).

Here, all three stable isotopologues  $\delta\text{D}(\text{H}_2\text{O})$ ,  $\delta^{17}\text{O}(\text{H}_2\text{O})$ , and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  both in the stratosphere as well as in the mesosphere are dealt with. Special emphasis is put on the pathways of  $\text{D}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$  from their reservoirs  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{O}_3$  into the

## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

end product  $\text{H}_2\text{O}$ .

## 2. Available stable isotope data of $\text{H}_2\text{O}$

In view of the difficulties of the measurement techniques listed below, only a few  $\text{H}_2\text{O}$  isotope observations have been conducted so far:

5 (i) Remote-sensing observations by infrared spectroscopy techniques (Abbas et al., 1987; Carli and Park, 1988; Guo et al., 1989; Dinelli et al., 1991, 1997; Rinsland et al., 1984, 1991; Stowasser et al., 1999; Johnson et al., 2001; Kuang et al., 2003). They reveal strong depletions of  $\delta\text{D}(\text{H}_2\text{O})$  with respect to V-SMOW which significantly decrease with altitude, from an average of  $-(660 \pm 80)\text{‰}$  at the low-latitude tropopause  
10 (Moyer et al., 1996; Johnson et al., 2001) to typically  $-(450 \pm 70)\text{‰}$  at 40 km. Observations by Stowasser et al. (1999) indicate extreme  $\delta\text{D}(\text{H}_2\text{O})$  depletions as low as  $-830\text{‰}$  at 17 km inside the Arctic vortex, which was attributed to condensation and subsequent sedimentation of polar stratospheric cloud (PSC) particles.

For  $\delta^{17}\text{O}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$ , most observations indicate values of about 0 to  $-100\text{‰}$  and a weak, but insignificant vertical increase. This insignificance can primarily  
15 be assigned to the large measurement uncertainties of  $50\text{--}120\text{‰}$ . Deviations from this behavior were noticed during early observations by Guo et al. (1989) who retrieved increasing  $\delta^{18}\text{O}(\text{H}_2\text{O})$  values from  $(80 \pm 140)\text{‰}$  at 22 km altitude to  $(400 \pm 250)\text{‰}$  at 37 km. Using a balloon-borne spectrometer, Johnson et al. (2001) obtained low isotope  
20 ratios of  $-(300\text{--}30)\text{‰}$  (on the average,  $-128\text{‰}$ ) for  $\delta^{18}\text{O}(\text{H}_2\text{O})$ , and of  $-(400\text{--}0)\text{‰}$  (on the average,  $-84\text{‰}$ ) for  $\delta^{17}\text{O}(\text{H}_2\text{O})$  at 12–20 km altitude.

(ii) Cryogenic in situ sampling and subsequent laboratory-based mass spectrometry (MS) analysis. Apart from observations in the upper troposphere and tropopause region by Ehhalt (1974), Smith (1992), Zahn et al. (1998), and Zahn (2001), there is only  
25 one set of balloon-borne stratospheric  $\delta\text{D}(\text{H}_2\text{O})$  profiles (Pollock et al., 1980). They show a continuous increase in  $\delta\text{D}(\text{H}_2\text{O})$  with altitude, from about  $-450\text{‰}$  at 25 km to about  $-360\text{‰}$  at 35 km. The O isotope composition of stratospheric  $\text{H}_2\text{O}$  has not yet

### Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

been measured by this technique, which is mainly due to the small sample amounts available and their difficult handling and MS analysis.

(iii) In situ measurements by tunable diode laser absorption spectroscopy (TDLAS). This new and challenging technique was recently presented by C. Webster (2003). He reported measurement uncertainties of 30-50‰ for all stable isotope ratios D/H,  $^{17}\text{O}/^{16}\text{O}$ , and  $^{18}\text{O}/^{16}\text{O}$  in  $\text{H}_2\text{O}$  in the UTLS region using the ALIAS instrument onboard the NASA WB57 aircraft.

### 3. Information provided by the $\text{H}_2\text{O}$ isotopic composition

The isotopic composition of tropospheric water vapour is controlled by the hydrological cycle. Hence,  $\text{H}_2\text{O}$  isotope data can be used as tracers for the condensation history of probed air masses (Taylor, 1984), as applied for studying the transport of tropospheric  $\text{H}_2\text{O}$  into the lowermost stratosphere (Zahn, 2001).

Both,  $\delta\text{D}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  are primarily controlled by the v.p.i.e. and thus undergo similar variations. Indeed, in surface precipitation both isotopologues are related closely by the meteoric water line (MWL):  $\delta\text{D}(\text{H}_2\text{O}) \approx m \times \delta^{18}\text{O}(\text{H}_2\text{O}) + 10\text{‰}$ , with  $m = 8$  (Craig, 1961). This relationship was found to be valid even on Mount Logan (Canada) at 5951 m altitude, with  $m = 7.5$  (Holdsworth et al., 1991). At cold temperatures as encountered in the tropical tropopause layer (TTL), however, kinetically limited isotope fractionation during formation of ice cloud particles, their lofting in convective cells and mixing of air masses showing different  $\text{H}_2\text{O}$  isotope compositions are assumed to considerably reduce  $\delta\text{D}(\text{H}_2\text{O})$  depletion compared to  $\delta^{18}\text{O}(\text{H}_2\text{O})$  (Moyer et al., 1996; Keith, 2000; Johnson et al., 2001; Kuang et al., 2003). In fact, using the isotope composition of water vapour entering the stratosphere of  $\delta\text{D}(\text{H}_2\text{O}) = -679\text{‰}$  and  $\delta^{18}\text{O}(\text{H}_2\text{O}) = -128\text{‰}$  measured by Johnson et al. (2001), a slope  $m$  of 5.4 is calculated. Finally and importantly,  $\delta^{17}\text{O}(\text{H}_2\text{O})$  will provide exactly the same information as  $\delta^{18}\text{O}(\text{H}_2\text{O})$ , due to lack of major mass-independent isotope fractionation (MIF) in

## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

the troposphere, that is  $\Delta^{17}\text{O}(\text{H}_2\text{O}) = \delta^{17}\text{O}(\text{H}_2\text{O}) - 0.52 \delta^{18}\text{O}(\text{H}_2\text{O})$  will be 0‰ at the tropical tropopause.

In conclusion, it can be presumed that tropospheric water vapour entering the stratosphere at the tropical tropopause exhibits a  $\delta\text{D}(\text{H}_2\text{O})/\delta^{18}\text{O}(\text{H}_2\text{O})$  ratio of 5-6 and is mass-dependently fractionated (MDF).

Chemical reactions in the middle atmosphere will strongly modify this isotope signature imported from the troposphere, as will be pointed out briefly below and explained in more detail later:

(i) Methane is oxidized in the middle atmosphere by reactions with OH, Cl, and  $\text{O}(^1\text{D})$ , and by photolysis (Lary and Toumi, 1997). Each oxidized  $\text{CH}_4$  molecule leads to the net formation of almost two  $\text{H}_2\text{O}$  molecules (Evans et al., 1999; Zöger et al., 1999; Michelsen et al., 2000). The  $\delta\text{D}$  value of the new  $\text{H}_2\text{O}$  molecule, i.e.  $\delta\text{D}(\text{H}_2\text{O})$ , differs from  $\delta\text{D}(\text{CH}_4)$ , because the  $\text{CH}_4$  loss reactions are accompanied by an unusually strong kinetic isotope fractionation. For instance, at room temperature the D isotope fractionation factor  $\text{KIE}^{\text{D}}$ , that is the ratio of the rate constants  $k(\text{CH}_4)/k(\text{CH}_3\text{D})$ , is  $\text{KIE}^{\text{D}}(\text{OH}) = 1.29$  for the reaction of  $\text{CH}_4$  with OH,  $\text{KIE}^{\text{D}}(\text{Cl}) = 1.51$  for the reaction with Cl, and  $\text{KIE}^{\text{D}}(\text{O}(^1\text{D})) = 1.11$  for the reaction with  $\text{O}(^1\text{D})$  (Saueressig et al., 1996, 2001; Tyler et al., 2000). Since these KIEs differ considerably, the  $\delta\text{D}(\text{H}_2\text{O})$  distribution in the middle atmosphere is expected to mirror the partitioning of the different  $\text{CH}_4$  oxidation reactions. This information cannot be inferred from simultaneous  $\text{CH}_4$  and  $\text{H}_2\text{O}$  concentration measurements.

(ii) Re-cycling of oxygen atoms between  $\text{H}_2\text{O}$  and the oxygen reservoir gases  $\text{O}_2$  and  $\text{O}_3$  via  $\text{HO}_x$  and  $\text{NO}_x$  species and oxygen isotope exchange reactions. Besides net  $\text{H}_2\text{O}$  formation due to  $\text{CH}_4$  oxidation, continuous loss of  $\text{H}_2\text{O}$  and reformation of  $\text{H}_2\text{O}$  lead to an extensive turnover of oxygen atoms between oxygen containing trace gases. This process recycles ~4 times more  $\text{H}_2\text{O}$  molecules than the net production by oxidation of  $\text{CH}_4$  (see Fig. 4). Though a zero-cycle with respect to the  $\text{H}_2\text{O}$  mass, it strongly influences the oxygen isotope composition of  $\text{H}_2\text{O}$ , i.e. in the same manner as addressed in item (i). Therefore, the MIF oxygen isotope signal transferred to middle

## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion



stratospheric H<sub>2</sub>O is strongly amplified compared to the MIF signal originating from CH<sub>4</sub> oxidation alone.

A crucial and exciting point is that more than 99% of all oxygen atoms taken to form H<sub>2</sub>O in the middle atmosphere stem from the hydroxyl radical OH. Hence,  $\delta^{17}\text{O}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  data also provide information on the oxygen isotope composition of OH, and by considering  $\Delta^{17}\text{O}(\text{H}_2\text{O})$  on the affection of MIF enriched O<sub>3</sub> to OH<sub>x</sub> and via OH<sub>x</sub> to many other oxygen containing trace gases in the middle atmosphere. This MIF transfer from O<sub>3</sub> to oxygen - containing radicals was studied by Lyons (2001).

#### 4. Model description

The 1-D model encompasses 64 boxes from 16 to 80 km, each 1 km high. Temperature and pressure profiles are set according to the U.S. Standard Atmosphere (1976). Vertical transport is parameterised by eddy diffusion coefficients K<sub>z</sub>, below 29 km using the “National Academy of Science (1976)” profile, from 29 km to 50 km using the “Hunten” profile, both depicted by Massie and Hunten (1981), and above 50 km employing the profile given by Froidevaux and Yung (1982).

##### 4.1. Peculiarities in modelling isotope ratios

The concept of chemical families frequently applied in atmospheric chemistry models mostly fails if isotopologues are considered. For instance, the reaction chain of CO + OH → CO<sub>2</sub> + H followed by H + O<sub>2</sub> + M → HO<sub>2</sub> + M converts OH in HO<sub>2</sub>, which conserves the sum of HO<sub>x</sub> = OH + HO<sub>2</sub>. The oxygen atom of the initial OH, however, is incorporated in CO<sub>2</sub> and thus leaves the HO<sub>x</sub> family. A new OH bond is formed, which has the oxygen isotope composition of O<sub>2</sub>.

Isotope exchange reactions such as the fast O exchange between O<sub>2</sub> and O(<sup>3</sup>P) (Kaye and Strobel, 1983) also have to be considered. They modify isotope ratios but not the concentration of the participating species.

### Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Finally, when including isotopologues that contain two or more of the isotopes of interest such as  $\text{O}_3$  or  $\text{HO}_2$ , the individual isotopologues have to be considered separately, e.g. the  $\text{OQO}$  and  $\text{OOQ}$  or  $\text{HQO}$  and  $\text{HOQ}$  (with  $\text{Q}$  the rare isotope).

#### 4.2. Trace gas chemistry

5 Due to negligible cloud formation in the middle atmosphere, our model is restricted to gas phase chemistry. Initially, all reactions involved in significant  $\text{H}_2\text{O}$  chemistry and isotope exchange with other gases were assessed carefully for all altitudes considered by the model. The reactions finally used (Tables 1 and 2) always account for more than 95% of the local chemical turnover of  $\text{H}_2\text{O}$  and its isotopes at a given altitude.

10 Water vapour is formed due to H-abstraction by  $\text{OH}$ , i.e.  $\text{XH}_i + \text{OH} \rightarrow \text{XH}_{i-1} + \text{H}_2\text{O}$ , where  $\text{XH}_i$  is  $\text{CH}_4$  (reaction R1),  $\text{CH}_2\text{O}$  (R7),  $\text{HO}_2$  (R15),  $\text{HCl}$  (R20),  $\text{H}_2$  (R25), or  $\text{HNO}_3$  (R28). The major sinks of middle atmospheric  $\text{H}_2\text{O}$  are the reaction with  $\text{O}(^1\text{D})$  (R29) and photolysis at wavelength below 200 nm (R30).

15 Furthermore, all reactions that are necessary to maintain the overall budget of O- and H-atoms balanced are included. To this end a complete methane destruction scheme (LeTexier et al., 1988) is applied which is initialised by photolysis and the reaction of  $\text{CH}_4$  with  $\text{OH}$ ,  $\text{O}(^1\text{D})$ ,  $\text{Cl}$ . All relevant reactions of the  $\text{OH}_x$ -family (Burnett and Burnett, 1995) are also considered.

20 The concentrations and the isotopic compositions of  $\text{H}_2\text{O}$ ,  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{H}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_3$ ,  $\text{CH}_2\text{O}$ ,  $\text{HCO}$ ,  $\text{HNO}_3$ , and  $\text{HCl}$  are explicitly calculated by the model.

#### 4.3. Isotope chemistry

Integration of isotopologues renders the model complex, as shown for the initial steps of the major methane destruction reactions (Table 3).

25 Only for a few of the reactions listed in Table 1 is the isotope fractionation factor  $\text{KIE} = k/k'$  known, with  $k$  the rate constant and the slash marks the isotopically substituted species. All KIEs that have been measured in the laboratory are implemented in the

### Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

model.

For all other reactions KIE is set to  $(\mu'/\mu)^{1/2}$ , with  $\mu$  the reduced mass of the reactants. This accounts for the fact that the rate constant of a certain reaction does not only depend on the reactivity of the reactants, but also on their collision frequency.

- 5 Additionally, the oxygen exchange reactions listed in Table 4 were included, partially for deriving the necessary isotope parameter profiles.

#### 4.4. Trace gas parameter profiles

Fixed, globally, seasonally and diurnally averaged profiles are used for the following trace gases:  $\text{O}_3$ ,  $\text{O}(^1\text{D})$ ,  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{Cl}$  as retrieved by the 2-D model version of  
10 ECHAM 3 (C. Brühl, Max-Planck-Institute for Chemistry, Mainz), a mean  $\text{O}(^3\text{P})$  profile measured by CHRISTA onboard the Space Shuttle in November 1994 (with the courtesy of M. Kaufmann, University of Wuppertal), and  $\text{CO}$  measured by ISAMS onboard the UARS satellite (López-Valverde et al., 1996).

#### 4.5. Isotope parameter profiles of $\text{O}(^3\text{P})$ , $\text{O}_3$ , $\text{O}(^1\text{D})$ , and $\text{NO}$

- 15 The oxygen isotope compositions assumed for  $\text{O}_2$ ,  $\text{O}(^3\text{P})$ ,  $\text{O}_3$ , and  $\text{O}(^1\text{D})$  are indicated in Fig. 1 together with the calculated profiles for  $\text{NO}$ ,  $\text{OH}$ , and  $\text{HO}_2$ .

The isotope composition of  $\text{O}(^3\text{P})$  is set to the one of  $\text{O}_2$ , i.e.,  $\delta^{17}\text{O}(\text{O}_2) = 11.8\text{‰}$  and  $\delta^{18}\text{O}(\text{O}_2) = 23.8\text{‰}$  (Luz et al., 1999; Coplen et al., 2002), because of the rapid O exchange between  $\text{O}(^3\text{P})$  and  $\text{O}_2$  (Kaye and Strobel, 1983).

- 20 The isotope composition of  $\text{O}_3$  was set to be solely dependent on temperature, as it was found recently that all reliable atmospheric data apparently agree with the enrichments determined in laboratory studies (Mauersberger et al., 2001) and that pressure dependence is negligible below 100 hPa. The (consistent) laboratory data by Thiemens and Jackson (1988, 1990), Morton et al. (1990), and (Günther et al., 1999) are imple-  
25 mented under the assumption that 80% of the isotope enrichment of  $\text{O}_3$  is carried by

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

the asymmetric QOO (Anderson et al., 1989; Janssen et al., 1999; Mauersberger et al., 1999).

$Q(^1D)$  is derived from the isotope enrichment in  $O_3$  under the following assumptions: (i) 80% of the isotope enrichment in  $O_3$  is located in the asymmetric OOQ, (ii) during the photolysis of  $O_3$  only the outer oxygen atoms form  $O(^1D)$ , (iii) there is negligible fractionation during the photolysis of  $O_3$  (Wen and Thieme, 1993), and (iv) mass-dependent collision rates during subsequent quenching of  $O(^1D)$  on  $N_2$  and  $O_2$  to the ground state  $O(^3P)$  lead to an additional isotope enrichment of 19‰ for  $\delta^{17}O$  and 36‰ for  $\delta^{18}O$  in  $O(^1D)$  (calculated by using the formula given in Sect. 4.3).

The oxygen isotope composition of middle atmospheric  $NO_x$  is not controlled by its main source, i.e. oxidation of  $N_2O$  by  $O(^1D)$ , but by O exchange between  $O_x$  and  $NO_x$ :



and the fast O - exchange reactions:



Indeed, over the entire altitude range considered less than 0.5% of all O atoms in NO stem from the oxidation of  $N_2O$  by  $O(^1D)$ . Hence, the isotopic composition of  $N_2O$  that is known to carry MIF into the stratosphere (Cliff and Thieme, 1997; Cliff et al., 1999; Röckmann et al., 2001; Kaiser et al., 2002) does not have to be considered. The O isotope ( $\delta^{17}O$ ,  $\delta^{18}O$ ) parameter profile of NO is derived by calculating the source partitioning of the reactions NO-1 to NO-4. The inferred enrichments exceed the ones calculated by Lyons (2001) by almost a factor of two, as outlined in Sect. 6.4. Because of the dominance of NO-3, the oxygen isotopic composition of NO in the mesosphere is very similar to the one of  $O(^3P)$ .

## Isotope composition of middle atmospheric $H_2O$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

## 4.6. Boundary conditions

At the lower model boundary, i.e., the tropopause (16 km), fixed trace gas and isotope mixing ratios are set as follows:  $[H_2O] = 3.48 \mu\text{mol/mol}$ .  $\delta D(H_2O) = -660\text{‰}$  and  $\delta^{18}O(H_2O) = -128\text{‰}$  (Moyer et al., 1996; Johnson et al., 2001).  $\Delta^{17}O(H_2O)$  is set to  $0\text{‰}$  (as no process is known in the troposphere, which could cause MIF in  $H_2O$ ), so that  $\delta^{17}O(H_2O)$  is  $-66\text{‰}$  (this value agrees with  $-(84 \pm 31)\text{‰}$  observed by Johnson et al. (2001)).  $[CH_4] = 1.7 \mu\text{mol/mol}$ .  $\delta D(CH_4) = -86\text{‰}$  (Quay et al., 1999).  $[H_2] = 0.55 \mu\text{mol/mol}$  (Zöger et al., 1999).  $\delta D(H_2) = 120\text{‰}$  (Friedman and Scholz, 1974). The flux of all considered species across the upper boundary (80 km) is set to zero.

## 5. Model results and comparison with observations

### 5.1. Vertical profile of $\delta D(H_2O)$

The calculated  $\delta D(H_2O)$  profile compares well with observations and the model results obtained by Ridal (2002) (Fig. 2). Apart from the Arctic profile retrieved by (Stowasser et al., 1999), the available observations (Sect. 2) show a vertical increase by  $\sim(150\text{--}200)\text{‰}$  between 20 and 40 km, but partially differ in absolute concentration. Consider however the large measurement uncertainty of all infrared instruments of  $\pm(60\text{--}150)\text{‰}$ . The  $\delta D(H_2O)$  profiles obtained by balloon-borne in situ  $H_2O$  sampling and subsequent laboratory analysis by Pollock et al. (1980) (reported uncertainties:  $\sim 50\text{‰}$ ) reveal significantly higher values compared to the other measurements and the model.

As mentioned in Sect. 3, the strong vertical  $\delta D(H_2O)$  increase in the stratosphere is due to the increasing fraction of  $H_2O$  that originates from the oxidation of  $CH_4$ . The  $\delta D(H_2O)$  value in the mesosphere, which is higher than the tropopause value by  $\sim 250\text{‰}$ , indicate that  $\sim 60\%$  of the mesospheric  $H_2O$  originate from the troposphere and  $\sim 40\%$  stem from the oxidation of  $CH_4$  (see Sect. 6.2).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

## 5.2. Vertical Profiles of $\delta^{17}\text{O}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$

The O isotope ratios in  $\text{H}_2\text{O}$  (Fig. 3) exhibit a vertical profile that is similar to that of  $\delta\text{D}(\text{H}_2\text{O})$ . The reason is oxygen exchange between  $\text{O}_2$  and  $\text{O}_3$  via  $\text{HO}_x$ - and  $\text{NO}_x$ -species rather than the net formation of  $\text{H}_2\text{O}$  as a final product of  $\text{CH}_4$  oxidation than (see Sect. 6.3).

The measurements by Dinelli et al. (1991), Guo et al. (1989), Rinsland et al. (1991), and Johnson et al. (2001) are in reasonable agreement with our model results. However the large measurement errors of  $\pm(50\text{--}120)\text{‰}$  have to be noted, which compares with the calculated total vertical increase by  $85\text{‰}$  for  $\delta^{17}\text{O}(\text{H}_2\text{O})$  and  $140\text{‰}$  for  $\delta^{18}\text{O}(\text{H}_2\text{O})$ .

## 6. Discussion

### 6.1. The middle atmospheric water vapour budget

Figure 4 shows the inferred budgets of  $\text{H}_2\text{O}$ ,  $\delta\text{D}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  of the middle atmosphere. The annual flux of tropospheric water into the stratosphere is set to 788 Mt as given by (Yang and Tung, 1996). In the stratosphere further net production of 50.3 Mt of  $\text{H}_2\text{O}$  (and of 0.4 Mt of  $\text{H}_2$ ) takes place due to the oxidation of  $\text{CH}_4$  with a calculated net  $\text{CH}_4$  destruction rate of  $24 \text{ Mt yr}^{-1}$ . This is slightly lower than the  $(40 \pm 10) \text{ Mt yr}^{-1}$  mostly reported (Crutzen, 1995; Lelieveld et al., 1998), but agrees with Gettelmann et al. (1998) and exceeds earlier values given by Crutzen (1991) and Khalil et al. (1993). The calculated ratios between  $\text{H}_2\text{O}$  and  $\text{H}_2$  production and  $\text{CH}_4$  loss for the entire middle atmosphere are:

$$\frac{\text{P}(\text{H}_2\text{O})}{\text{L}(\text{CH}_4)} = 1.87 \quad \text{and} \quad \frac{\text{P}(\text{H}_2)}{\text{L}(\text{CH}_4)} = 0.13 \quad (1)$$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Using a coupled chemistry/dynamical model (LeTexier et al., 1988) derived  $P(\text{H}_2\text{O})/L(\text{CH}_4) = 1.6$  which is in agreement with satellite observations by Hanson and Robinson (1989). More recent in situ measurements indicated higher values of  $1.94 \pm 0.27$  (Dessler et al., 1994),  $1.82 \pm 0.21$  (Engel et al., 1996),  $1.973 \pm 0.003$  (Hurst et al., 1999), and  $1.975 \pm 0.030$  (Zöger et al., 1999), which are in reasonable agreement with our model results.

Interestingly, although each  $\text{CH}_4$  molecule finally results in the formation of almost 2  $\text{H}_2\text{O}$  molecules (Eq. 1), most hydrogen atoms in  $\text{CH}_4$  make the detour via  $\text{H}_2$ , the  $\text{HO}_x$  family, and other gases to  $\text{H}_2\text{O}$ , as demonstrated in Fig. 5. Only ~15% of all  $\text{H}_2\text{O}$  molecules are formed directly from one of the four H atoms of  $\text{CH}_4$  or intermediate products in the  $\text{CH}_4$  destruction chain (such as formaldehyde,  $\text{CH}_2\text{O}$ ), i.e., they are produced via the following reactions:



This can be explained by the fact that only ~30% of all  $\text{CH}_4$  molecules react with OH, and the majority of ~70% with  $\text{O}(^1\text{D})$  or Cl (Lary and Toumi, 1997), which is in strong contrast to the troposphere where the reaction with OH clearly dominates. The other ~85% of the H atoms in  $\text{CH}_4$  are incorporated first in the  $\text{HO}_x$  family (~60%), in  $\text{H}_2$  (~18%), and other gases such as HCl (~7%), before they end up in  $\text{H}_2\text{O}$ . This detour of the H atoms from  $\text{CH}_4$  to  $\text{H}_2\text{O}$  certainly affects not only the isotope composition of the final product  $\text{H}_2\text{O}$ , but also that of the intermediate products (OH,  $\text{HO}_2$ , HCO, H,  $\text{H}_2$ , HCl etc.).

Figure 6 presents the vertical profile of  $\text{H}_2\text{O}$  production  $P(\text{H}_2\text{O})$  and loss  $L(\text{H}_2\text{O})$ . Both  $P(\text{H}_2\text{O})$  (dominated by the reaction  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  (Kaye, 1990)) and  $L(\text{H}_2\text{O})$  (more than 99% of which are due to the reaction of  $\text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2 \text{OH}$ ) peak at ~38 km altitude. The net rate,  $P(\text{H}_2\text{O}) - L(\text{H}_2\text{O})$ , amounts to ~25% of  $P(\text{H}_2\text{O})$  only. It shows a wide maximum centred at 35-40 km, that is ~5 km above the maximum of the

## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

CH<sub>4</sub> loss rate (for better comparison  $2 \times L(\text{CH}_4)$  is shown, dotted line). This again emphasises that (i) most H atoms from CH<sub>4</sub> are first incorporated in intermediate species (that experience spatial redistribution) before ending up in H<sub>2</sub>O, and (ii) a considerable turnover of H<sub>2</sub>O molecules occurs in the middle atmosphere which significantly exceeds the net production of H<sub>2</sub>O.

Division of the local H<sub>2</sub>O concentration by the local H<sub>2</sub>O loss rate  $L(\text{H}_2\text{O})$  yields the chemical lifetime of H<sub>2</sub>O,  $\tau(\text{H}_2\text{O})$ , at a certain altitude (Fig. 6b). In the entire middle atmosphere  $\tau(\text{H}_2\text{O})$  considerably exceeds the vertical transport time scale, i.e. H<sub>2</sub>O never is in photochemical equilibrium. Only between 30 and 50 km altitude, the transport lifetime  $H^2/K_z$  ( $H$  being the local scale height and  $K_z$  the vertical eddy diffusion coefficient) almost compare with the photochemical lifetime of H<sub>2</sub>O, in agreement with (LeTexier et al., 1988).

This long chemical lifetime of H<sub>2</sub>O implies that below 30-35 km (where  $\tau(\text{H}_2\text{O})$  exceeds ~5 years) the D/H isotope ratio of H<sub>2</sub>O is simply due to the mixing of the  $\delta\text{D}(\text{H}_2\text{O})$  isotope signature imported from the troposphere and the one present in the upper stratosphere. This finding does not apply to  $\delta^{17}\text{O}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$ , because of the considerable oxygen exchange of H<sub>2</sub>O with other gases, which also occurs in the lower stratosphere.

## 6.2. $\delta\text{D}(\text{H}_2\text{O})$ as tracer for CH<sub>4</sub> oxidation

Tropospheric H<sub>2</sub>O is imported into the stratosphere with  $\delta\text{D}(\text{H}_2\text{O}) \approx -660\text{‰}$  (Moyer et al., 1996, Johnson et al., 2001). Tropospheric CH<sub>4</sub> carries much higher  $\delta\text{D}$  values of roughly  $-86\text{‰}$  (Quay et al., 1999) into the stratosphere. Neglecting the small net formation of H<sub>2</sub> due to CH<sub>4</sub> oxidation ( $\sim 0.4 \text{ Mt yr}^{-1}$ , see Fig. 4a), a simple mass balance

## Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion



for  $\delta D$  yields an average  $\delta D(\text{H}_2\text{O})$  value in the middle atmosphere  $\delta D_0$  of:

$$\underbrace{\delta D_0}_{\text{mean}} \underbrace{M_0}_{838} = \underbrace{\delta D_t}_{-660\text{‰}} \underbrace{M_t}_{788} + \underbrace{\delta D_m}_{-86\text{‰}} \underbrace{M_m}_{50} \quad (2)$$

import from troposphere                      production from  $\text{CH}_4$  oxidation

where  $M_i$  denotes the  $\text{H}_2\text{O}$  mass fluxes of the different components and  $\delta D_i$  their  $D$  isotope signature. The numbers are given in per mil for  $\delta D_i$  and in  $\text{Mt yr}^{-1}$  for  $M_i$ , as shown in Fig. 4a and b. Equation (2) gives an average middle atmospheric  $\delta D(\text{H}_2\text{O})$  value of  $\delta D_0 = -626\text{‰}$ , which exceeds the value at the tropopause by  $34\text{‰}$  only. This small isotope excess reflects the fact that net  $\text{H}_2\text{O}$  production from  $\text{CH}_4$  oxidation ( $\sim 50 \text{ Mt yr}^{-1}$ ) is small compared to the  $\text{H}_2\text{O}$  inflow from the troposphere ( $\sim 788 \text{ Mt yr}^{-1}$ ).

The vertically increasing contribution of  $\text{H}_2\text{O}$  produced by the oxidation of  $\text{CH}_4$  is described by the upper  $x$  axis of Fig. 2. It shows the local fraction of  $\text{H}_2\text{O}$  from  $\text{CH}_4$  oxidation  $\mathcal{F}$ , that is the ratio between the difference of the local  $\delta D(\text{H}_2\text{O})$  value to the tropopause value ( $-660\text{‰}$ ) and the difference of the  $\delta D(\text{H}_2\text{O})$  from the  $\text{CH}_4$  oxidation (set to  $-86\text{‰}$ ) and the  $\delta D(\text{H}_2\text{O})$  tropopause value, i.e.,  $\mathcal{F} = (\delta D(\text{H}_2\text{O}) - (-660\text{‰})) / (-86\text{‰} - (-660\text{‰}))$ . Figure 2 indicates that  $\sim 40\%$  of the  $\text{H}_2\text{O}$  above 40 km originate from the oxidation of  $\text{CH}_4$ .

It might be argued that this estimation is not correct, since the high kinetic isotope fraction factors KIEs of the  $\text{CH}_4$  oxidation reactions (Sect. 3) result in a strong vertical change of the  $\delta D$  value of freshly produced  $\text{H}_2\text{O}$ . Although this comment is correct, influence on  $\delta D(\text{H}_2\text{O})$  is weak, as demonstrated by Fig. 7. Because of the large KIEs,  $\delta D(\text{CH}_4)$  increases from  $-86\text{‰}$  at the tropopause to about  $+190\text{‰}$  at the stratopause. Over the same altitude range,  $\delta D(\text{H}_2\text{O})$  rises from  $-660\text{‰}$  to  $-445\text{‰}$ , but only by  $20\text{‰}$  more to  $-425\text{‰}$  if isotope fractionation is not considered (KIEs = 1). This small difference is due to the fact that around 38 km, where the major destruction of  $\text{CH}_4$  occurs (Fig. 6),  $\delta D(\text{CH}_4)$  is about  $+70\text{‰}$  vs. VSMOW (or 1.070 absolute) and the mean KIE is  $\sim 1.2$  only (as there  $\sim 60\%$  of all  $\text{CH}_4$  molecules are removed by the reaction with

## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

O( $^1D$ ) which is associated with weak isotope fractionation). Therefore, the  $H_2O$  produced at 38 km shows a mean  $\delta D$  value of  $1.070/1.2 = 0.892$  absolute or  $-108\text{‰}$  vs. VSMOW. This value does not differ much from  $\delta D(CH_4) = -86\text{‰}$  and indeed demonstrates that the high KIEs of the  $CH_4$  loss reactions cause a weak shift in  $\delta D(H_2O)$  only.

Unfortunately, this finding also documents that the  $\delta D(H_2O)$  value does not constitute a sensitive tracer to distinguish between the different  $CH_4$  loss reaction chains, contrary to its initial assumption. Such a distinction could only be made with the aid of precise mass-spectrometry measurements on middle atmospheric  $H_2O$  samples (which are not available to date).

Another surprising feature is that both, the  $\delta D$  value of the source molecule  $CH_4$  and the one of the end product  $H_2O$  increase with altitude (Fig. 7), although mass conservation for  $\delta D$  suggests the opposite behaviour, at a first glance. In all methane oxidation reactions the most abundant  $CH_4$  reacts faster than the isotopically substituted  $CH_3D$  (Sect. 3). Therefore, the remaining  $CH_4$  is continuously enriched in D/H with altitude (solid line in Fig. 7), while that of the freshly formed  $H_2O$  molecule is always significantly lower (dotted line) compared to the remaining  $CH_4$ . Despite this D depletion with respect to  $\delta D(CH_4)$ , freshly formed  $H_2O$  still shows much higher  $\delta D$  values than the  $H_2O$  lofted from below.

### 6.3. $\delta^{17}O(H_2O)$ and $\delta^{18}O(H_2O)$ as tracer for transport and chemistry

As outlined in Sect. 3, the oxygen isotope signature atom of middle atmospheric water vapour is determined by the partitioning of four oxygen isotope sources: (1) mass-dependently fractionated (MDF)  $H_2O$  imported from the troposphere, (2) mass-independently fractionated (MIF)  $H_2O$  formed as a final product of the oxidation of  $CH_4$ , (3) likewise MIF carrying  $H_2O$  from the recycling of  $H_2O$  via the  $HO_x$  family and (4) oxygen atom exchange between  $H_2O$  and other gases.

The  $\delta^{17}O$  and  $\delta^{18}O$  values of source (1), i.e. of  $H_2O$  imported from the troposphere, are about  $-67\text{‰}$  and  $-128\text{‰}$ , respectively (see Sect. 4.6). The  $\delta O$  values of the iso-

## Isotope composition of middle atmospheric $H_2O$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

## Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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tope sources (2) to (4), i.e. of the chemical reactions leading to new H<sub>2</sub>O molecules, are adopted from the respective educt molecules. As outlined by Kaye (1990) and confirmed by our calculations, more than 99% of all H<sub>2</sub>O molecules generated in the middle atmosphere are due to hydrogen abstraction from H-containing molecules by OH. Thus, the isotope sources (2) and (3) will show the O isotope signature of OH at the respective altitude. H<sub>2</sub>O undergoes oxygen isotope exchange (i.e. isotope source 4) with OH and NO<sub>2</sub> (Table 4). Both oxygen exchange reactions are too slow to significantly affect the isotope composition of H<sub>2</sub>O in the middle atmosphere.

Therefore, modifications of the oxygen isotope composition of middle atmospheric H<sub>2</sub>O are almost exclusively controlled by reactions with OH. For this reason, the sources of OH and their oxygen isotope signatures will be studied next. As the reaction chains, by means of which OH is converted into HO<sub>2</sub> and back into OH without breaking the initial OH bond, form a zero cycle with respect to the oxygen isotopic composition, only the reactions forming new OH bonds need to be considered.

### 6.3.1. The formation of new OH bonds

Four classes of reactions, distinguished by the O isotope signal transferred, form new OH<sub>x</sub> bonds:

(i) HO<sub>x</sub> that receives the oxygen isotope signature from molecular oxygen via



Reactions R5 and R11 are part of the CH<sub>4</sub> oxidation chain and only play a role below 40 km. Reaction R12 dominates the formation of new OH bonds over the entire middle atmosphere. In addition, oxygen isotope exchange between OH<sub>x</sub> and O<sub>2</sub> may occur via:





Assuming the rate constants of reactions R34 and R35 at their estimated upper limit, this oxygen isotope exchange with the  $\text{O}_2$  reservoir will remarkably influence the isotope composition of  $\text{OH}_x$  and thus of  $\text{H}_2\text{O}$ , as shown by Lyons (2001) and verified here (Fig. 3).

(ii)  $\text{HO}_x$  that receives the oxygen isotope signature from MIF carrying ozone via



which is important above 40 km only. Although  $\text{O}_3$  also influences the isotope composition of  $\text{HO}_2$  via  $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ , new OH bonds are not formed. The reason is that the oxygen atom OH receives from  $\text{O}_3$  is lost again, simply because  $\text{HO}_2$  is an asymmetric molecule ( $\text{H}-\text{O}-\text{O}$ ).

(iii)  $\text{HO}_x$  that receives the oxygen signature from MIF carrying  $\text{O}(^1\text{D})$  and, in the case of reaction R29, from  $\text{H}_2\text{O}$ :



with reaction R29 clearly dominating in the entire middle atmosphere.

(iv)  $\text{HO}_x$  that receives the oxygen isotope signature from  $\text{NO}_x$ :



while the oxygen isotope composition of  $\text{NO}_x$  is controlled by reactions with the  $\text{O}_2$  and  $\text{O}_3$  reservoirs (Sect. 4.4).

## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

### 6.3.2. The origin of oxygen atoms incorporated in H<sub>2</sub>O

On the basis of Sect. 6.3.1, the influence of each oxygen emission source (O<sub>2</sub>, O<sub>3</sub>, O(<sup>1</sup>D), and NO<sub>x</sub>) on the oxygen isotope composition of freshly produced H<sub>2</sub>O is assessed. As demonstrated in Fig. 8 and listed in Table 5, molecular oxygen clearly dominates as source of oxygen atoms transferred to water vapour in the entire middle atmosphere. When neglecting the additional not yet quantified oxygen exchange with O<sub>2</sub> (reactions R34 and R35, Sect. 6.3.1), of all oxygen isotopes incorporated in H<sub>2</sub>O in stratosphere and mesosphere, respectively, ~78% and ~70% stem from O<sub>2</sub>, ~17% and ~30% from O<sub>3</sub>, ~2% and ~0% from O(<sup>1</sup>D), and ~2% and ~0% from other gases such as HNO<sub>3</sub> or H<sub>2</sub>O itself. When assuming the additional oxygen exchange reactions R34 and R35 at their estimated upper limit, the oxygen isotope source partitioning will hardly change in the mesosphere. On the contrary, in the stratosphere the hydroxyl radical and thus the water molecules freshly produced will almost completely adopt the oxygen isotopic composition of O<sub>2</sub>. In this case, no mass-independent fractionation is transferred to H<sub>2</sub>O. Another finding is that in the stratosphere ~50% of the overall oxygen isotope transfer to H<sub>2</sub>O proceed in two steps (Fig. 8), i.e. from O<sub>2</sub> and O<sub>3</sub> to NO<sub>x</sub> and from there via HO<sub>x</sub> to H<sub>2</sub>O.

The oxygen isotope source partitioning just described is reflected by the strongly structured vertical profiles of  $\delta^{17}\text{O}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  of freshly produced H<sub>2</sub>O (Fig. 9). Two maxima occur, both by oxygen atom transfer from O<sub>3</sub> to H<sub>2</sub>O. In the stratosphere, it is due to the oxygen transfer chain  $\text{O}_3 \xrightarrow{\text{O}} \text{NO}_x \xrightarrow{\text{O}} \text{HO}_x \xrightarrow{\text{O}} \text{H}_2\text{O}$ . In the mesosphere, it is caused by  $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$  (reaction R13) and subsequent O transfer from OH to H<sub>2</sub>O due to the strongly increasing concentrations of atomic hydrogen. If the oxygen exchange reactions R34 and R35 are additionally considered, freshly produced H<sub>2</sub>O in the stratosphere will have the  $\delta^{17}\text{O}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  values of O<sub>2</sub>.

## Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

### 6.3.3. $\Delta^{17}\text{O}(\text{H}_2\text{O})$ as a tracer of MIF transfer from $\text{O}_3$ to $\text{H}_2\text{O}$

The last Sect. 6.3.2 revealed that the pathway of MIF from  $\text{O}_3$  to  $\text{H}_2\text{O}$  is different compared to the one from  $\text{O}_3$  to  $\text{CO}_2$ .  $\text{CO}_2$  is assumed to receive the MIF signal exclusively from  $\text{O}(^1\text{D})$  (produced by the photolysis of  $\text{O}_3$ ) via the short-lived intermediate  $\text{CO}_3$  (Yung et al., 1991, 1997; Barth and Zahn, 1997). In the case of  $\text{H}_2\text{O}$ ,  $\text{O}(^1\text{D})$  is only weakly involved in the oxygen isotope transfer (Table 5). In the stratosphere water vapour receives only  $\sim 15\%$  of its MIF signal from  $\text{O}(^1\text{D})$ . In the mesosphere  $\text{O}(^1\text{D})$  does not play any role at all.

As indicated in Fig. 8, in the stratosphere MIF transfer from  $\text{O}_3$  to  $\text{H}_2\text{O}$  basically proceeds in three steps, first MIF transfer from  $\text{O}_3$  to  $\text{NO}_x$  species (via reaction NO-1:  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ , Sect. 4.5), then from  $\text{NO}_x$  to  $\text{OH}_x$  and finally transfer to  $\text{H}_2\text{O}$  due to H-abstraction by OH. This quite efficient oxygen transfer chain leads to peaking  $\Delta^{17}\text{O}(\text{H}_2\text{O})$  values of  $\sim 10\text{‰}$  at  $\sim 35\text{ km}$  altitude (Fig. 10). In the mesosphere,  $\text{NO}_x$  species are not involved. There, the entire MIF transfer from  $\text{O}_3$  to  $\text{HO}_x$  (and from there to  $\text{H}_2\text{O}$ ) proceeds via reaction R13:  $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$ .

### 6.4. Assessment Of results

A simple 1-D box model that considers relatively few chemical reactions was applied. This approach was chosen deliberately, since its simplicity allows to precisely track the pathway of hydrogen and oxygen isotopes from their sources (for hydrogen  $\text{CH}_4$ , and for oxygen  $\text{O}_2$  and  $\text{O}_3$ ) to  $\text{H}_2\text{O}$ . The isotope fractionation factors of many reactions involved in the isotope transfer have not been measured up to now. Thus, the additional outcome of using a more sophisticated model is limited. As shown by Lyons (2001) and verified here (see Figs. 3, 9, and 10, and Table 5) a major unknown is the possible oxygen isotope exchange of  $\text{O}_2$  with  $\text{NO}_x$  and  $\text{HO}_x$ . If the relevant reactions R34 and R35 are considered at their estimated upper limit, only a very weak mass-independent oxygen isotope signature is transferred to  $\text{HO}_x$  and  $\text{H}_2\text{O}$ .

## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Independent of the importance of reactions R34 and R35, the MIF signal transferred to  $\text{HO}_x$  (Fig. 1) and thus to  $\text{H}_2\text{O}$  as calculated by our model is only half as large as the one determined by Lyons (2001). This discrepancy arises from the different  $\Delta^{17}\text{O}$  signatures assumed for the asymmetric  $\text{O}_3$  molecule and  $\text{O}(^1\text{D})$ . Lyons (2001) used the branching ratios of 0.43 and 0.57 measured for  $\delta^{18}\text{O}$  in the reaction of  $\text{O} + \text{QO} \rightarrow \text{QOQ}, \text{QOO}$  by (Janssen et al. (1999) also for  $\delta^{17}\text{O}$ , and the fractionation factors for this reaction measured by Mauersberger et al. (1999). This assumption led to  $\Delta^{17}\text{O}$  values of asymmetric  $\text{O}_3$  of  $\Delta^{17}\text{O}(\text{QOO}) = \sim 85\text{‰}$ , and together with the mean  $\Delta^{17}\text{O}$  values of  $\text{O}_3$  of  $\Delta^{17}\text{O}(\text{O}_3) = \sim 38\text{‰}$ , to  $\Delta^{17}\text{O}$  values of symmetric  $\text{O}_3$  of  $\Delta^{17}\text{O}(\text{OQO}) = -50\text{‰}$  (because  $\Delta^{17}\text{O}(\text{O}_3) = 2/3 \Delta^{17}\text{O}(\text{QOO}) + 1/3 \Delta^{17}\text{O}(\text{OQO})$ ). Such a strong  $\delta^{17}\text{O}$  depletion of symmetric ozone is unlikely (C. Janssen, personal communication). In contrast, we assumed identical ratios of the enrichments of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  in QOO and OQO. That is, in the stratosphere we assume mean  $\Delta^{17}\text{O}$  values of  $34\text{‰}$  for  $\text{O}_3$ , which is in agreement with Lyons (2001), but  $\Delta^{17}\text{O}$  values of  $39\text{‰}$  for QOO, and  $25\text{‰}$  for OQO.

## 7. Conclusions

A simple 1-D isotope chemistry box model is applied to derive vertical profiles of the stable isotope ratios  $\text{D}/\text{H}$ ,  $^{17}\text{O}/^{16}\text{O}$ , and  $^{18}\text{O}/^{16}\text{O}$  in middle atmospheric water vapour. It was demonstrated that a number of chemical reactions with diverse gases cause isotope fractionation in  $\text{H}_2\text{O}$  relative to values at the tropopause. This makes a description more complicated compared to other trace gases such as  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ .

$\delta\text{D}(\text{H}_2\text{O})$  was modelled to increase from  $-660\text{‰}$  at the tropopause to  $-430\text{‰}$  above 40 km, which is in excellent agreement with the observations. This increase by  $\sim 230\text{‰}$  corresponds to a fraction of  $\sim 40\%$  of  $\text{H}_2\text{O}$  produced as end product of the oxidation of  $\text{CH}_4$ . Although the D fractionation factors of the individual  $\text{CH}_4$  oxidation reactions with OH,  $\text{O}(^1\text{D})$ , and Cl differ strongly, the  $\delta\text{D}(\text{H}_2\text{O})$  value turned out to be no sensitive

## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

tracer to distinguish between the different CH<sub>4</sub> oxidation chains. This has two reasons. First, the major CH<sub>4</sub> loss occurs in the middle and upper stratosphere where the reactions with O(<sup>1</sup>D) dominate, accompanied by weak isotope fractionation dominates. Second, the chemical lifetime of H<sub>2</sub>O is long in the middle atmosphere. This allows for significant mixing and thus weakening of the spatial gradients of δD(H<sub>2</sub>O).

The oxygen isotope ratios δ<sup>17</sup>O(H<sub>2</sub>O) and δ<sup>18</sup>O(H<sub>2</sub>O) are calculated to increase relative to the tropopause by up to ~85‰ and ~140‰, respectively, which is also in agreement with the observations. Fractionation of the oxygen isotope ratios in H<sub>2</sub>O was demonstrated to be determined almost exclusively by the isotope signature of OH. The oxygen isotopic composition of OH, in turn, is mainly controlled by the one of mass-dependently fractionated O<sub>2</sub>. Depending on the altitude and assumed reaction rates for isotope exchange reactions with O<sub>2</sub> (reactions R34 and R35) between 60 and almost 100% of all oxygen atoms transferred to H<sub>2</sub>O stem from O<sub>2</sub>, while 40 to 0% originate from O<sub>3</sub>. The transfer of mass-independent fractionation in O<sub>3</sub> to OH and thus to H<sub>2</sub>O in the stratosphere proceed primarily via NO<sub>x</sub> species. In the mesosphere, however, it directly takes place via the reaction of H + O<sub>3</sub> → OH + O<sub>2</sub>. Maximum Δ<sup>17</sup>O(H<sub>2</sub>O) values of 10‰ around 35 km are calculated.

The largest unknowns in our calculations are the unquantified reaction rates of a few oxygen isotope exchange reactions, in particular of OH<sub>x</sub> and NO<sub>x</sub> with O<sub>2</sub>, and the many unquantified isotope fractionation factors of the reactions involved in the isotope transfer to H<sub>2</sub>O. In this respect, the most urgent need in this research field is the development of more precise techniques to measure the isotope composition of water vapour both in the laboratory and atmosphere.

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## Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)



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## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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## Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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## Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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## Isotope composition of middle atmospheric $\text{H}_2\text{O}$

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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## Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion



**Table 1.** Considered gas phase reactions

No	reaction	Rate		Ref. <sup>a</sup>
		A	E	
1	$\text{CH}_4 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{CH}_3$	Table 3		
2	$\text{CH}_4 + \text{O}(^1\text{D}) \longrightarrow \text{OH} + \text{CH}_3$	Table 3		
3	$\text{CH}_4 + \text{Cl} \longrightarrow \text{HCl} + \text{CH}_3$	Table 3		
4	$\text{CH}_4 + \gamma \longrightarrow \text{H} + \text{CH}_3$	Table 3		
5	$\text{CH}_3\text{O} + \text{O}_2 \longrightarrow \text{HO}_2 + \text{H}_2\text{CO}$	3.9(-14)	900	JPL97
6	$\text{CH}_3 + \text{O}_2 + \text{M} \longrightarrow \text{CH}_3\text{O}_2 + \text{M}$	Table 2		
7	$\text{CH}_2\text{O} + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{HCO}$	1.0(-11)	0	JPL97
8	$\text{CH}_2\text{O} + \gamma \longrightarrow \text{H} + \text{HCO}/\text{H}_2 + \text{CO}$	altitude dependent		
9	$\text{CH}_2\text{O} + \text{O}(^3\text{P}) \longrightarrow \text{OH} + \text{HCO}$	3.4(-10)	1600	JPL97
10	$\text{CH}_2\text{O} + \text{Cl} \longrightarrow \text{HCl} + \text{HCO}$	8.1(-11)	30	JPL97
11	$\text{HCO} + \text{O}_2 \longrightarrow \text{HO}_2 + \text{CO}$	3.5(-12)	-140	JPL97
12	$\text{H} + \text{O}_2 + \text{M} \longrightarrow \text{HO}_2 + \text{M}$	Table 2		
13	$\text{H} + \text{O}_3 \longrightarrow \text{OH} + \text{O}_2$	1.4(-10)	470	JPL97
14	$\text{H} + \text{HO}_2 \longrightarrow \text{H}_2\text{O} + \text{O}(^3\text{P})$	3.7(-11)	2300	JPL97
15	$\text{OH} + \text{HO}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$	4.8(-11)	-250	JPL97
16	$\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$	1.6(-12)	940	JPL97
17	$\text{OH} + \text{O}(^3\text{P}) \longrightarrow \text{H} + \text{O}_2$	2.2(-11)	-120	JPL97
18	$\text{OH} + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{O}(^3\text{P})$	4.2(-12)	240	JPL97
19	$\text{OH} + \text{NO}_2 + \text{M} \longrightarrow \text{HNO}_3 + \text{M}$	Table 2		
20	$\text{HCl} + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{Cl}$	2.6(-12)	350	JPL97
21	$\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H}$	1.5(-13)	0	JPL97
22	$\text{HO}_2 + \text{NO} \longrightarrow \text{OH} + \text{NO}_2$	3.5(-12)	-250	JPL97
23	$\text{HO}_2 + \text{O}(^3\text{P}) \longrightarrow \text{OH} + \text{O}_2$	3.0(-11)	-200	JPL97
24	$\text{HO}_2 + \text{O}_3 \longrightarrow \text{OH} + 2 \cdot \text{O}_2$	1.1(-14)	500	JPL97

# Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion



Isotope composition  
of middle  
atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Table 1. Continued

No	reaction	Rate		Ref. <sup>a</sup>
		A	E	
25	H <sub>2</sub> + OH → H <sub>2</sub> O + H	5.5(-12)	2000	JPL97
26	H <sub>2</sub> + O( <sup>1</sup> D) → H + OH	1.1(-10)	0	JPL97
27	H <sub>2</sub> + Cl → H + HCl	3.7(-11)	2300	JPL97
28	HNO <sub>3</sub> + OH → H <sub>2</sub> O + NO <sub>3</sub>			JPL97
29	H <sub>2</sub> O + O( <sup>1</sup> D) → 2 · OH	2.2(-10)	0	JPL97
30	H <sub>2</sub> O + γ → H + OH	5(-6)	-4.4(-19)	n=0.917; BS <sup>b</sup>

<sup>a</sup> JPL97: DeMoore et al. (1997), BS: Brasseur and Solomon (1986)

<sup>b</sup> photolysis rate  $j(z) = A \cdot \exp[E \cdot L(z)^n]$  in s<sup>-1</sup>, L(z) being the number of molecules per cm<sup>2</sup> above altitude z.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Isotope composition  
of middle  
atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

**Table 2.** Termolecular reactions

No.	Reaction	$k_0^{300\ a}$	N	$k_\infty^{300\ b}$	m	Reference
6	$\text{CH}_3 + \text{O}_2 + \text{M} \longrightarrow \text{CH}_3\text{O}_2 + \text{M}$	$4.5 \cdot 10^{-31}$	3.0	$1.8 \cdot 10^{-12}$	1.7	JPL97
12	$\text{H} + \text{O}_2 + \text{M} \longrightarrow \text{HO}_2 + \text{M}$	$5.7 \cdot 10^{-32}$	1.6	$7.5 \cdot 10^{-11}$	0.0	JPL97
19	$\text{OH} + \text{NO}_2 + \text{M} \longrightarrow \text{HNO}_3 + \text{M}$	$2.5 \cdot 10^{-30}$	4.4	$1.6 \cdot 10^{-11}$	1.7	JPL97

$$^a k_0(T) = k_0^{300} \cdot \left(\frac{T}{300}\right)^{-n}$$

$$^b k_\infty(T) = k_\infty^{300} \cdot \left(\frac{T}{300}\right)^{-m}$$

$$\text{rate constant } k(M, T) = \left(\frac{k_0(t)[M]}{1 + (k_0(T)[M]/k_\infty(T))}\right) \cdot 0.6^{(1 + [\log_{10}(k_0(t)[M]/k_\infty(T))]^2)^{-1}}$$

[M] being the number concentrations of air molecules and  $T$  the temperature.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**Table 3.** Detailed description of the initial methane destruction reactions

No	reaction	rate A	E	branching ratio	fractionation factor	Ref. <sup>a</sup>
1	CH <sub>4</sub> + OH → H <sub>2</sub> O + CH <sub>3</sub>	2.45 (–12)	1775	1	1	JPL97
	CH <sub>4</sub> + <sup>17</sup> OH → H <sub>2</sub> <sup>17</sup> O + CH <sub>3</sub>	2.45 (–12)	1775	1	0.986	JPL97
	CH <sub>4</sub> + <sup>18</sup> OH → H <sub>2</sub> <sup>18</sup> O + CH <sub>3</sub>	2.45 (–12)	1775	1	0.973	JPL97
	CH <sub>4</sub> + OD → HD <sup>18</sup> O + CH <sub>3</sub>	2.45 (–12)	1775	1	0.986	JPL97
	CH <sub>3</sub> D + OH → H <sub>2</sub> O + CDH <sub>2</sub>	2.45 (–12)	1775	0.75	1	JPL97
	CH <sub>3</sub> D + OH → HDO + CH <sub>3</sub>	3.5 (–12)	1950	0.25	1	JPL97
	CH <sub>3</sub> D + OD → D <sub>2</sub> O + CH <sub>3</sub>	3.5 (–12)	1950	0.25	0.986	JPL97
	CH <sub>3</sub> D + OD → HDO + CH <sub>2</sub> D	3.5 (–12)	1950	0.75	0.986	JPL97
2	CH <sub>4</sub> + O( <sup>1</sup> D) → OH + CH <sub>3</sub>	1.5 (–10)	0	0.9	1	JPL97
	CH <sub>4</sub> + <sup>17</sup> O( <sup>1</sup> D) → <sup>17</sup> OH + CH <sub>3</sub>	1.5 (–10)	0	0.9	0.985	JPL97
	CH <sub>4</sub> + <sup>18</sup> O( <sup>1</sup> D) → <sup>18</sup> OH + CH <sub>3</sub>	1.5 (–10)	0	0.9	0.972	JPL97
	CH <sub>4</sub> + O( <sup>1</sup> D) → H <sub>2</sub> CO + H <sub>2</sub>	1.5 (–10)	0	0.1	1	JPL97
	CH <sub>4</sub> + <sup>17</sup> O( <sup>1</sup> D) → H <sub>2</sub> C <sup>17</sup> O + H <sub>2</sub>	1.5 (–10)	0	0.1	0.985	JPL97
	CH <sub>4</sub> + <sup>18</sup> O( <sup>1</sup> D) → H <sub>2</sub> C <sup>18</sup> O + H <sub>2</sub>	1.5 (–10)	0	0.1	0.972	JPL97
	CH <sub>3</sub> D + O( <sup>1</sup> D) → OD + CH <sub>3</sub>	1.5 (–10)	0	0.25 · 0.9	–0.037 · exp(0.224/T)	SE01
	CH <sub>3</sub> D + O( <sup>1</sup> D) → OH + CH <sub>2</sub> D	1.5 (–10)	0	0.75 · 0.9	–0.037 · exp(0.224/T)	SE01
	CH <sub>3</sub> D + O( <sup>1</sup> D) → H <sub>2</sub> + HD <sup>18</sup> O	1.5 (–10)	0	0.5 · 0.1	–0.037 · exp(0.224/T)	SE01
	CH <sub>3</sub> D + O( <sup>1</sup> D) → HD + H <sub>2</sub> CO	1.5 (–10)	0	0.5 · 0.1	–0.037 · exp(0.224/T)	SE01
	CH <sub>4</sub> + Cl → CH <sub>3</sub> + HCl	1.1 (–11)	1400	1	1	JPL97
	CH <sub>3</sub> D + Cl → CH <sub>3</sub> + DCl	1.1 (–11)	1400	0.25	1.278 · exp(51.31/T)	SE96
	CH <sub>3</sub> D + Cl → CH <sub>2</sub> D + HCl	1.1 (–11)	1400	0.75	1.278 · exp(51.31/T)	SE96
3	CH <sub>4</sub> + γ → CH <sub>3</sub> + H	5 (–6)	–4.4 (–19)	1	n=0.917	BS <sup>b</sup>
	CH <sub>3</sub> D + γ → CH <sub>3</sub> + D	5 (–6)	–4.4 (–19)	0.25	n=0.917	BS
	CH <sub>3</sub> D + γ → CH <sub>2</sub> D + H	5 (–6)	–4.4 (–19)	0.75	n=0.917	BS

<sup>a</sup> JPL97: DeMoore et al. (1997), BS: Brasseur and Solomon (1986), SE96: Saueressig et al. (1996), SE01: Saueressig et al. (2001).

<sup>b</sup> photolysis rate  $j(z) = A \cdot \exp[E \cdot L(z)^n]$  in s<sup>–1</sup>,  $L(z)$  being the number of molecules per cm<sup>2</sup> above altitude  $z$ .  
rate constant  $k(T) = A \cdot \exp[-(E \cdot [K]/T)]$  in cm<sup>3</sup>s<sup>–1</sup>

# Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Isotope composition  
of middle  
atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

**Table 4.** Considered oxygen isotope exchange reactions

No	reaction	Rate		Ref.
		A	E	
31	$\text{QH} + \text{NO} \leftrightarrow \text{OH} + \text{NQ}$	1.8(-11)	0	Dubey et al. [1997]
32	$\text{QH} + \text{NO}_2 \leftrightarrow \text{OH} + \text{NOQ}$	1.0(-11)	0	Greenblatt and Howard [1989]
33	$\text{QH} + \text{H}_2\text{O} \leftrightarrow \text{OH} + \text{H}_2\text{Q}$	1.6(-13)	2100	Greenblatt and Howard [1989]
34	$\text{QH} + \text{O}_2 \leftrightarrow \text{OH} + \text{OQ}$	< 1(-17)	0	Greenblatt and Howard [1989]
35	$\text{HOQ} + \text{O}_2 \leftrightarrow \text{HO}_2 + \text{OQ}$	< 3(-17)	0	Sinha et al. [1987]
36	$\text{NOQ} + \text{O}_2 \leftrightarrow \text{NO}_2 + \text{OQ}$	< 1(-24)	0	Sharma et al. [1970]
37	$\text{Q} + \text{O}_2 \leftrightarrow \text{OQ} + \text{O}$			see Sect. 4.5
38	$\text{Q} + \text{NO} \leftrightarrow \text{O} + \text{NQ}$			see Sect. 4.5

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Isotope composition  
of middle  
atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

**Table 5.** Percentage origin of oxygen isotopes of freshly produced H<sub>2</sub>O averaged over stratosphere and mesosphere

Oxygen Isotope Source		neglecting R33, R34		considering R33, R34	
Species	isotope signature	stratosphere	mesosphere	stratosphere	mesosphere
O <sub>2</sub>	MDF <sup>a</sup>	78.0	70.2	98.1	72.5
O <sub>3</sub>	MIF <sup>b</sup>	17.4	29.8	1.9	27.5
O( <sup>1</sup> D)	MIF <sup>b</sup>	2.3	0	0	0
others		2.3	0	0	0

<sup>a</sup> MDF = mass-dependently fractionated

<sup>b</sup> MIF = mass-independently fractionated

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

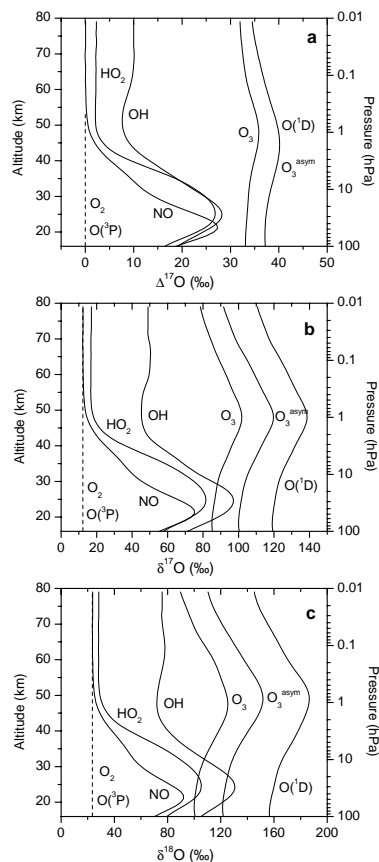
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Print Version

Interactive Discussion

**Isotope composition  
of middle  
atmospheric H<sub>2</sub>O**

Ch. Bechtel and A. Zahn



**Fig. 1.** Vertical profile of  $\Delta^{17}\text{O}$  (graph a),  $\delta^{17}\text{O}$  (graph b), and  $\delta^{18}\text{O}$  (graph c) assumed for  $\text{O}_2$ ,  $\text{O}(^3\text{P})$ ,  $\text{O}_3$ , asymmetric  $\text{O}_3$ , and  $\text{O}(^1\text{D})$ , and calculated for  $\text{NO}$ ,  $\text{OH}$  and  $\text{HO}_2$  (without considering the isotope exchange reactions R34 and R35).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

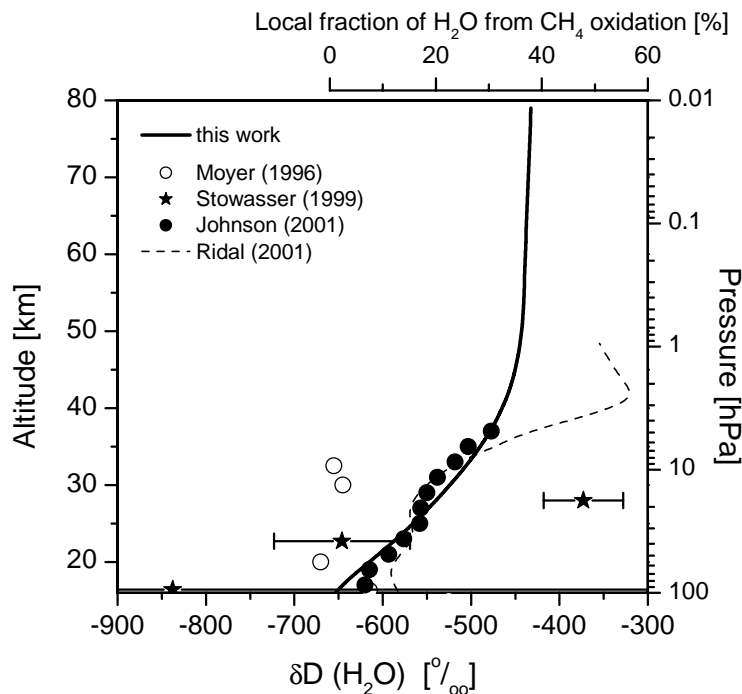
Full Screen / Esc

Print Version

Interactive Discussion

**Isotope composition  
of middle  
atmospheric H<sub>2</sub>O**

Ch. Bechtel and A. Zahn



**Fig. 2.** Calculated vertical profile of  $\delta D(H_2O)$  (solid line) compared to measurements. Open circles: ATMOS FTIR data of near-global latitudinal coverage (Moyer et al., 1996). Full circles: Smithsonian Astrophysical Observatory's far-infrared data by Johnson et al. [2001a]. Stars: Balloon-borne FTIR data inside the Arctic vortex at 68°N (Stowasser et al., 1999). Dashed line: 1-D model result by Ridal et al. (2001). Upper x axis indicates the approximate fraction of H<sub>2</sub>O from the CH<sub>4</sub> oxidation inferred from the  $\delta D(H_2O)$  value (explanation, see Sect. 6.2).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

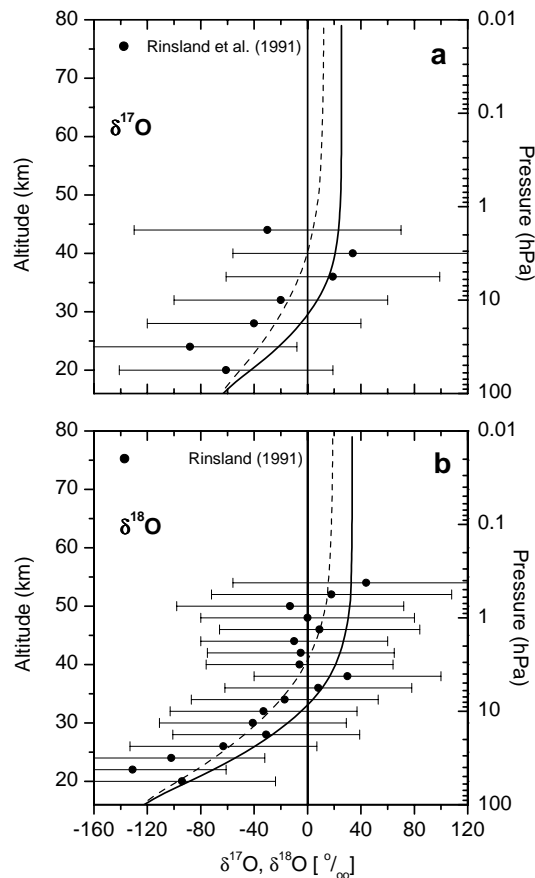
Full Screen / Esc

Print Version

Interactive Discussion

**Isotope composition  
of middle  
atmospheric H<sub>2</sub>O**

Ch. Bechtel and A. Zahn



**Fig. 3.** Calculated vertical profiles of  $\delta^{17}\text{O}(\text{H}_2\text{O})$  (graph a) and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  (graph b) compared to ATMOS Spacelab 3 infrared solar spectra near 30°N [Rinsland et al., 1991]. Straight lines: not quantified oxygen exchange reactions R34 and R35 are omitted. Dashed line: Those reactions are considered at their estimated upper limit.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

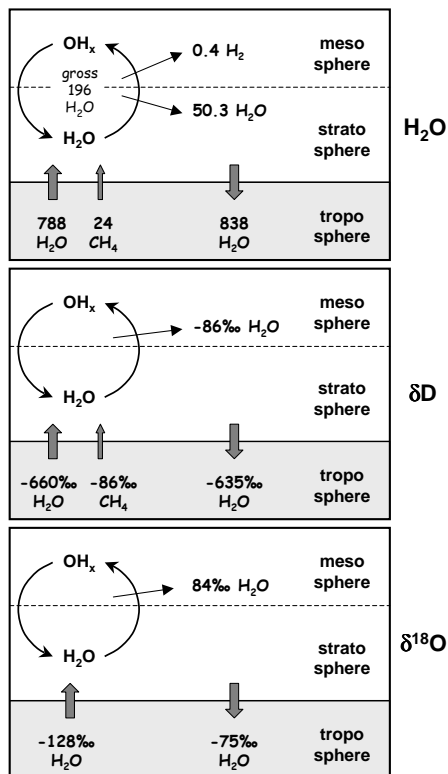
Print Version

Interactive Discussion



# Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn



**Fig. 4.** Middle atmospheric budgets of **a:** H<sub>2</sub>O, numbers are mass fluxes in Mt yr<sup>-1</sup> (the flux into the stratosphere is adopted from Yang and Tung [1996], other numbers are model results), **b:** δD, numbers are mean δD values in ‰ of the individual species, and **c:** δ<sup>18</sup>O, numbers are mean δ<sup>18</sup>O values in ‰.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

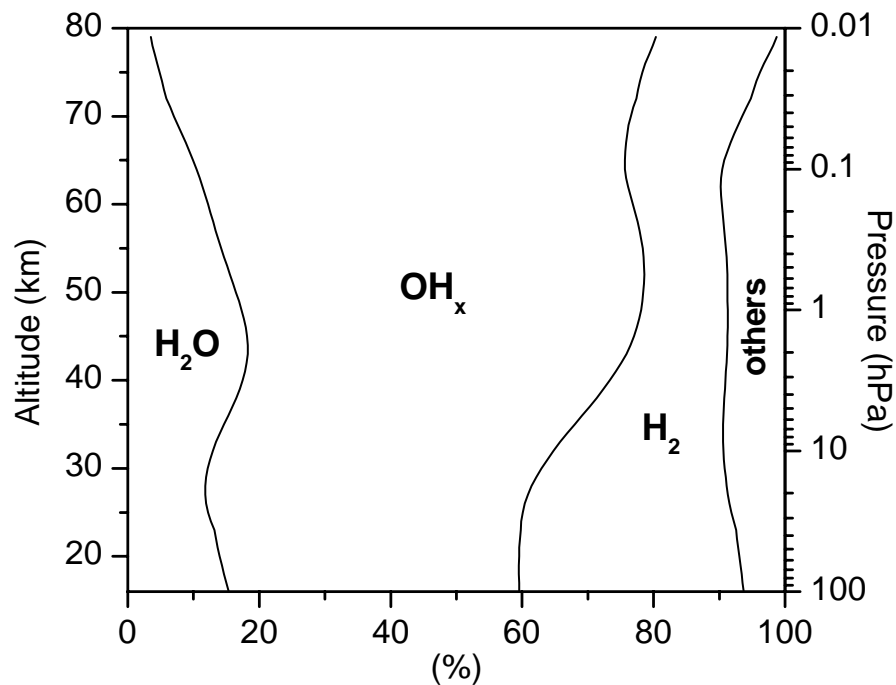
Full Screen / Esc

Print Version

Interactive Discussion

**Isotope composition  
of middle  
atmospheric H<sub>2</sub>O**

Ch. Bechtel and A. Zahn



**Fig. 5.** Calculated percentage fraction of hydrogen atoms that are transferred during the initial oxidation reaction of CH<sub>4</sub> either to H<sub>2</sub>O, OH<sub>x</sub>, H<sub>2</sub>, or other species (such as HCl).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

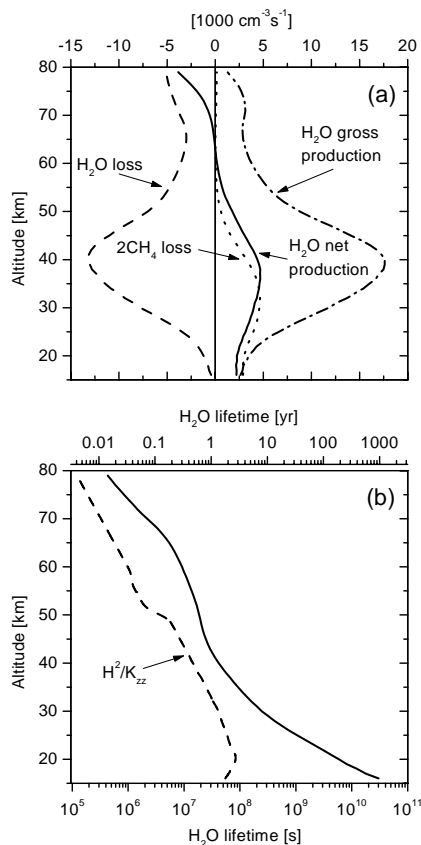
Full Screen / Esc

Print Version

Interactive Discussion

# Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn



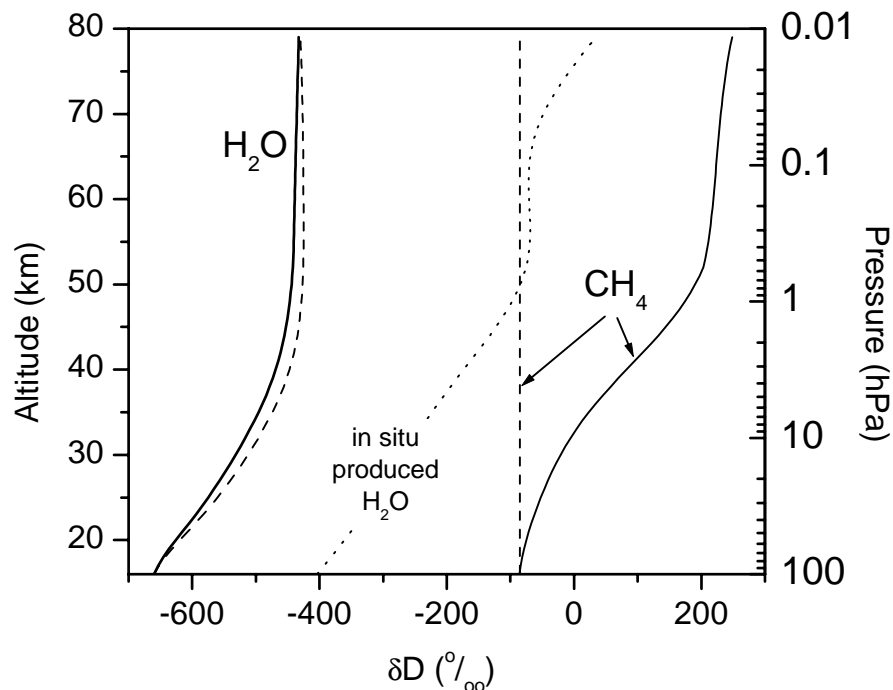
**Fig. 6.** (a) calculated vertical profiles of H<sub>2</sub>O production and loss rates in the middle atmosphere. For comparison, the double CH<sub>4</sub> loss rate is shown (as almost two H<sub>2</sub>O molecules are net produced for each oxidised CH<sub>4</sub> molecule, see Eq. 1). (b) comparison of the photochemical lifetime of water vapour (straight line) with the transport time scale (dashed line).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

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**Isotope composition  
of middle  
atmospheric H<sub>2</sub>O**

Ch. Bechtel and A. Zahn

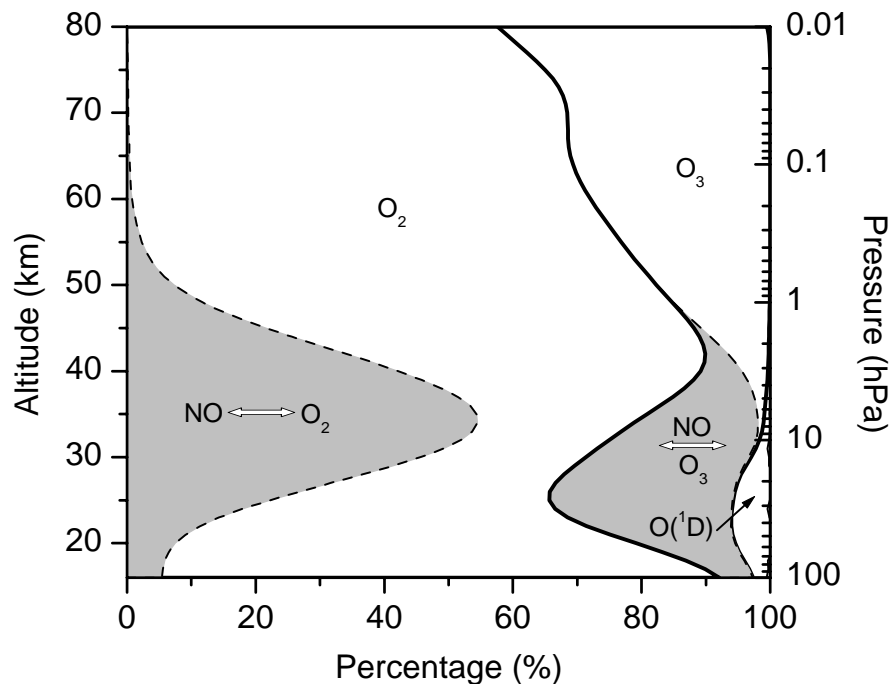


**Fig. 7.** Vertical profiles of  $\delta D(CH_4)$  and  $\delta D(H_2O)$ . Solid lines: Fractionation during the methane decomposition reactions with OH, Cl, and  $O(^1D)$  is allowed. Dashed lines: Fractionation is prevented. Dotted line: Isotope enrichment of freshly produced  $H_2O$  (while fractionation is allowed).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

**Isotope composition  
of middle  
atmospheric H<sub>2</sub>O**

Ch. Bechtel and A. Zahn

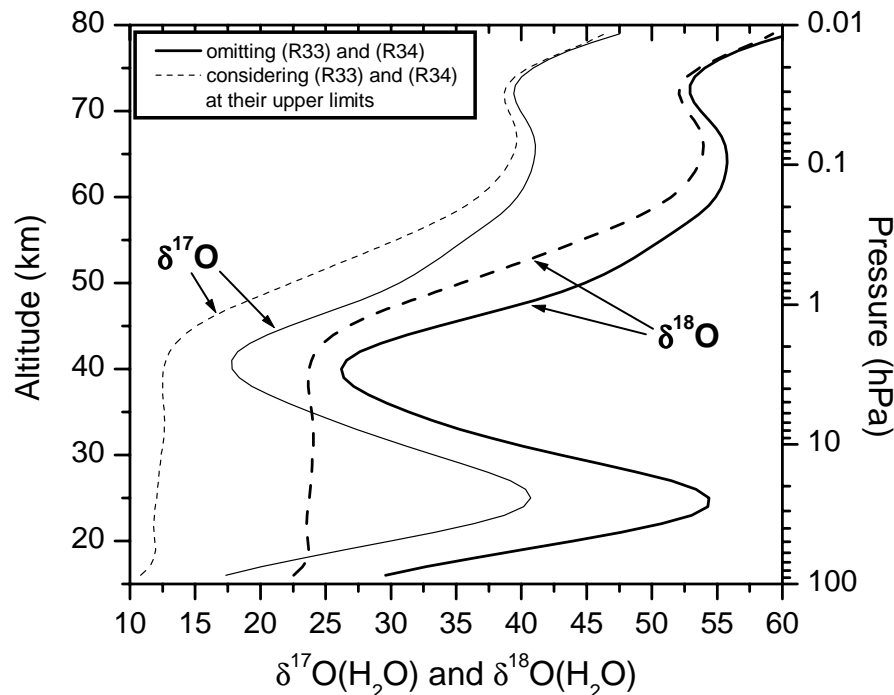


**Fig. 8.** Percentage fraction of oxygen atoms originating from the “reservoirs” O<sub>2</sub>, O<sub>3</sub>, and O(<sup>1</sup>D) in freshly produced H<sub>2</sub>O. Thick straight lines separate the three different reservoirs. In the stratosphere, considerable oxygen transfer from O<sub>2</sub> and O<sub>3</sub> to H<sub>2</sub>O occurs via the NO<sub>x</sub> family (grey areas).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

# Isotope composition of middle atmospheric H<sub>2</sub>O

Ch. Bechtel and A. Zahn

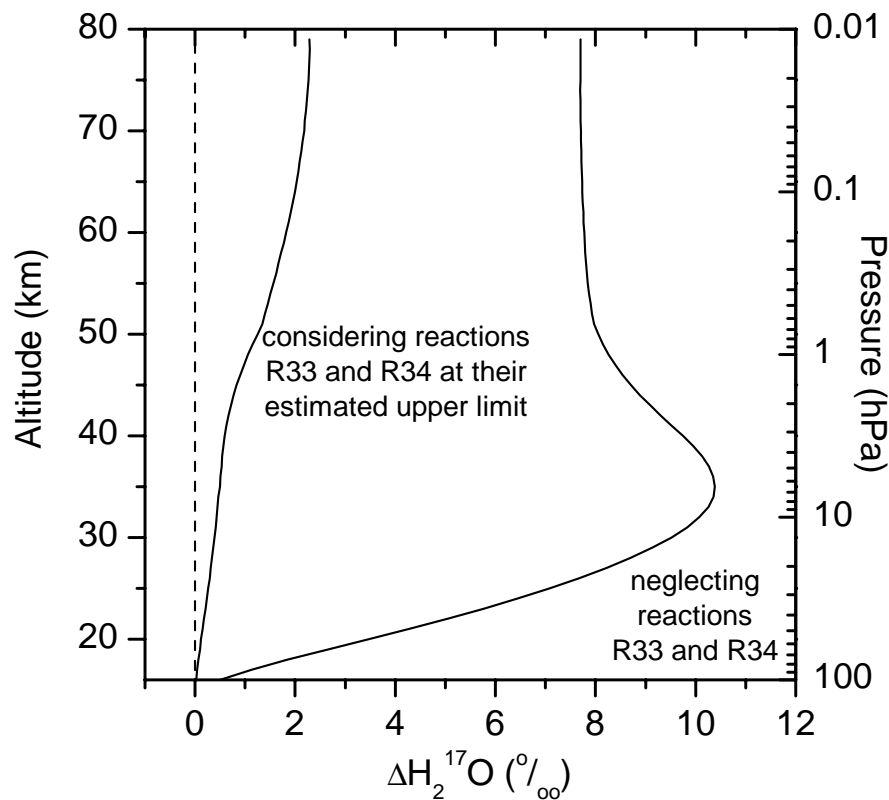


**Fig. 9.** Vertical profiles of  $\delta^{17}\text{O}(\text{H}_2\text{O})$  (thin lines) and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  (thick lines) of freshly produced  $\text{H}_2\text{O}$ . Straight lines: additional oxygen exchange reactions R34 and R35 are neglected. Dashed lines: reactions R34 and R35 are considered using rate constants at their estimated upper limit.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

**Isotope composition  
of middle  
atmospheric H<sub>2</sub>O**

Ch. Bechtel and A. Zahn



**Fig. 10.** Calculated vertical profile of  $\Delta^{17}O(H_2O)$  when considering and neglecting the additional oxygen exchange reactions R34 and R35 at their estimated upper limit.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)