論文紹介（2012-07-10）

Isotopic fractionation through water vapor condensation: The Deuteropause, a cold trap for deuterium in the atmosphere of Mars

J.-L. Bertaux & F. Montmessin, JGR 106, 2001

佐川英夫 (NICT)

rev. 2

abstract

- 1998年のハッブル望遠鏡観測で，火星上層大気中のHD/H2が下層大気中のHDO/H2Oよりも 11倍小さいことが示された [Krasnopolsky et al., 1998].

- この非常に強いD/Hの鉛直勾配を説明するのに Photolysis Induced Fractionation Effect, PHIFE（光解離過程における同位体分別）が提案されていたが，本論文では，水蒸気の凝結蒸発に伴なう同位体分別 Condensation/Evaporation Fractionation Effect, CEFE の寄与を考察.

- 雲微物理を含んだ火星GCMによる数値実験を行なった結果，PHIFE による 下層/上層のDepletion比が 2.5倍なのに対して，CEFEでは 3.5 倍になった（両者が働くと 9.5倍となり，ハッブルの観測を説明しうる）.

- CEFE (+PHIFE) メカニズムの意義＝HDOの存在上限高度(HDO-cold trap/Deuteropause)の存在．火星大気から D は殆ど逃げていないことを示唆.

導入:同位体分別

物質の定量といったレベルから一歩踏み込み そこで何が起きているのかというプロセス(物質循環)を知る手掛かり.

REVIEWS OF GEOPHYSICS, VOL. 25, NO. 8, PAGES 1609–1658, NOVEMBER 1987

Mechanisms and Observations for Isotope Fractionation of Molecular Species in Planetary Atmospheres

JACK A. KAYE

NASA Goddard Space Flight Center, Greenbelt, Maryland

Chemical and physical processes which may give rise to isotope fractionation of molecular species in the atmospheres of both Earth and other planets are reviewed, along with observations of isotopically substituted molecules in planetary atmospheres. Mechanisms for production of isotope fractionation considered include escape and effect of isotope substitution on equilibrium constants (including those of phase changes), photolysis rates, and chemical reaction rates. The isotopes considered for compounds in the terrestrial atmosphere include D, T, ^{13}C, ^{14}C, ^{15}N, ^{18}O, and ^{34}S. Compounds for which data about isotopic composition in the terrestrial atmosphere are summarized include CO, CO_2, O_3, N_2O, NH_3, SO_2, H_2S, H_2O, H, H_2, and CH_4. Planetary atmospheres discussed include those of Venus, Mars, Jupiter, Saturn, Uranus, and Titan; isotopes reviewed are D, ^{13}C, ^{15}N, and ^{18}O. Suggestions for additional research in the area of isotopically substituted molecules in atmospheres are offered.

導入：同位体分別

- 大気散逸過程における 質量に依存した同位体分別（軽い分子ほど逃げ易い）[e.g., Hunten et al., Icarus 1987]
- 相変化に伴う同位体分別（飽和蒸気圧の違い；軽い分子ほど気体になり易い： CEFE）
- 光解離定数の違いによる同位体分別（吸収断面積の違い，太陽UVがどこまで深く届くか，解離する分子の鉛直分布：PHIFE）
- 大気化学反応に伴う分別
- 他にも色々（熱平衡定数の違い，重力に伴なう質量依存分別 他）

ce Flight Center, Greenbelt, Maryland

Chemical and physical processes give rise to isotope fractionation of molecular species in the atmospheres of both Earth and other ets are reviewed, along with observations of isotopically substituted molecules in planetary atmospheres. Mechanisms for production of isotope fractionation considered include escape and effect of isotope substitution on equilibrium constants (including those of phase changes), photolysis rates, and chemical reaction rates. The isotopes considered for compounds in the terrestrial atmosphere include D, T, ^{13}C, ^{14}C, ^{15}N, ^{18}O, and ^{34}S. Compounds for which data about isotopic composition in the terrestrial atmosphere are summarized include CO, CO_2, O_3, N_2O, NH_3, SO_2, H_2S, H_2O, H, H_2, and CH_4. Planetary atmospheres discussed include those of Venus, Mars, Jupiter, Saturn, Uranus, and Titan; isotopes reviewed are D, ^{13}C, ^{15}N, and ^{18}O. Suggestions for additional research in the area of isotopically substituted molecules in atmospheres are offered.

導入：同位体分別

- 大気散逸過程における
逃げ易い）[e.g., Hunten
- 相変化に伴う同位体分
なり易い：CEFE）
- 光解離定数の違いによ
がどこまで深く届くか，解
- 大気化学反応に伴う分
- 他にも色々（熱平衡定

Chemical and physical processes
the atmospheres of both Earth an
substituted molecules in planetary
considered include escape and effe
phase changes), photolysis rates, an
the terrestrial atmosphere include
isotopic composition in the terrest
SO_2, H_2S, H_2O, H, H_2, and CH
Jupiter, Saturn, Uranus, and Titan
ditional research in the area of isoto

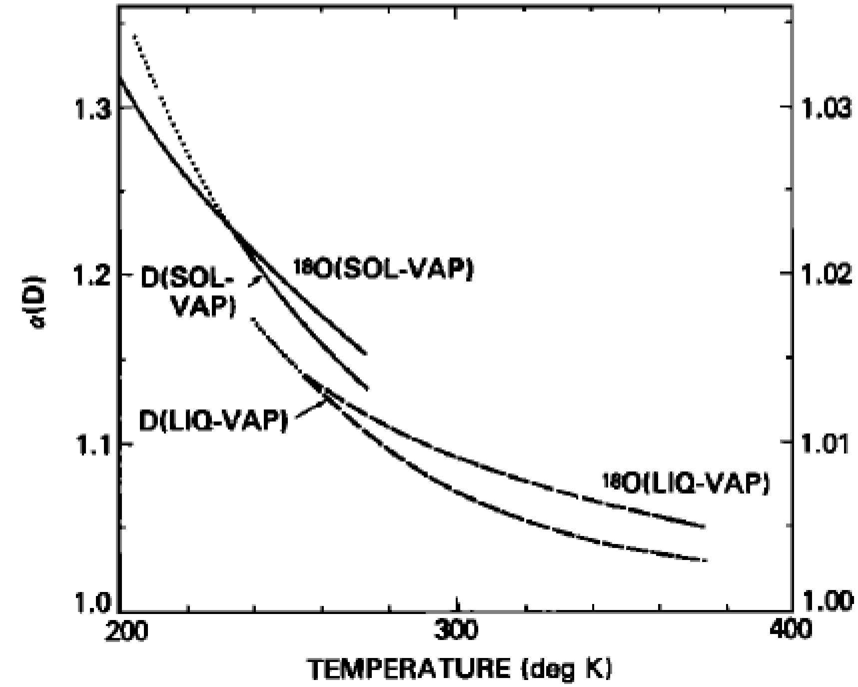


Fig. 2. Plot of equilibrium fractionation factor α associated with HDO and $H_2{}^{18}O$ vapor pressure isotope effects as a function of temperature. HDO curves (left ordinate) are for solid-vapor (solid line) and liquid-vapor (dashed line). Data are from *Merlivat and Nief* [1967] and *Dansgaard* [1964]. Dotted lines are extrapolations to temperatures below those of *Merlivat and Nief* [1967]. $H_2{}^{18}O$ curves (right ordinate) for solid-vapor (solid line) and liquid-vapor (dashed line) data are from *Jancso and van Hook* [1974] and *Dansgaard* [1964]. Dotted lines are low-temperature extrapolations.

液（固）相/気相間でのHDO/H2OおよびH2^{18}O/H2Oの同位体分別効果．α = P_light/P_heavy．[Kaye, 1987]

導入：同位体分別

- 大気散逸過程における 質量に依存した同位体分別（軽い分子ほど逃げ易い） [e.g., Hunten et al., Icarus 1987]
- 相変化に伴う同位体分別（飽和蒸気圧の違い；軽い分子ほど気体になり易い： CEFE）
- 光解離定数の違いによる同位体分別（吸収断面積の違い，太陽UVがどこまで深く届くか，解離する分子の鉛直分布：PHIFE）
- 大気化学反応に伴う分別
- 他にも色々（熱平衡定数の違い，重力に伴なう質量依存分別 他）

ce Flight Center, Greenbelt, Maryland

Chemical and physical processes ... give rise to isotope fractionation of molecular species in the atmospheres of both Earth and other ...ets are reviewed, along with observations of isotopically substituted molecules in planetary atmospheres. Mechanisms for production of isotope fractionation considered include escape and effect of isotope substitution on equilibrium constants (including those of phase changes), photolysis rates, and chemical reaction rates. The isotopes considered for compounds in the terrestrial atmosphere include D, T, ^{13}C, ^{14}C, ^{15}N, ^{18}O, and ^{34}S. Compounds for which data about isotopic composition in the terrestrial atmosphere are summarized include CO, CO_2, O_3, N_2O, NH_3, SO_2, H_2S, H_2O, H, H_2, and CH_4. Planetary atmospheres discussed include those of Venus, Mars, Jupiter, Saturn, Uranus, and Titan; isotopes reviewed are D, ^{13}C, ^{15}N, and ^{18}O. Suggestions for additional research in the area of isotopically substituted molecules in atmospheres are offered.

導入：同位体分別

- 大気散逸過程における
逃げ易い）[e.g., Hunten
- 相変化に伴う同位体分
なり易い：CEFE）
- 光解離定数の違いによ
がどこまで深く届くか，解
- 大気化学反応に伴う分
- 他にも色々（熱平衡定

Chemical and physical processes
the atmospheres of both Earth and
substituted molecules in planetary
considered include escape and effe
phase changes), photolysis rates, an
the terrestrial atmosphere include
isotopic composition in the terrest
SO_2, H_2S, H_2O, H, H_2, and CH
Jupiter, Saturn, Uranus, and Titan
ditional research in the area of isoto

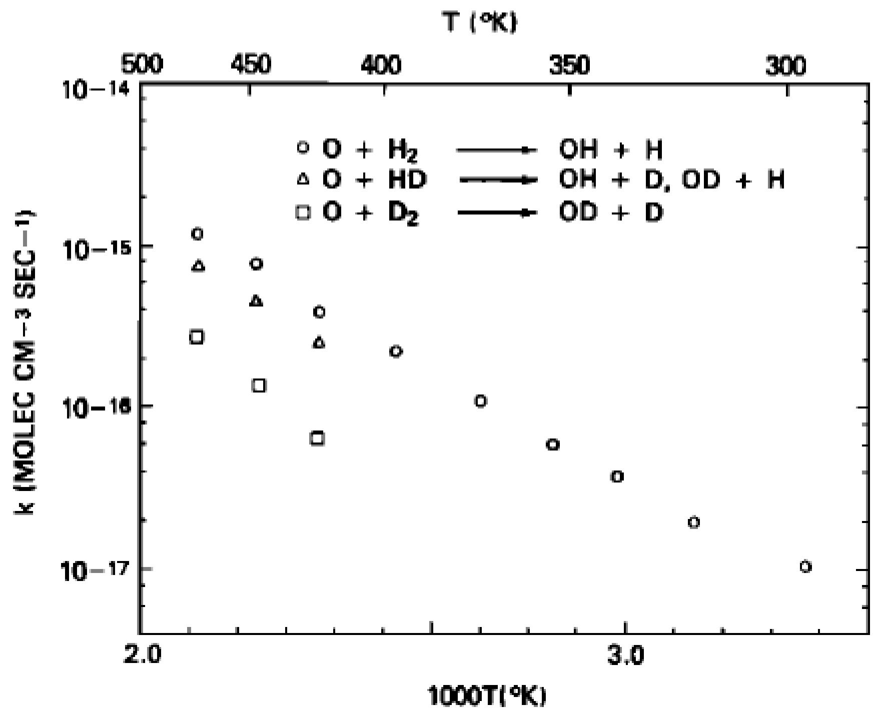
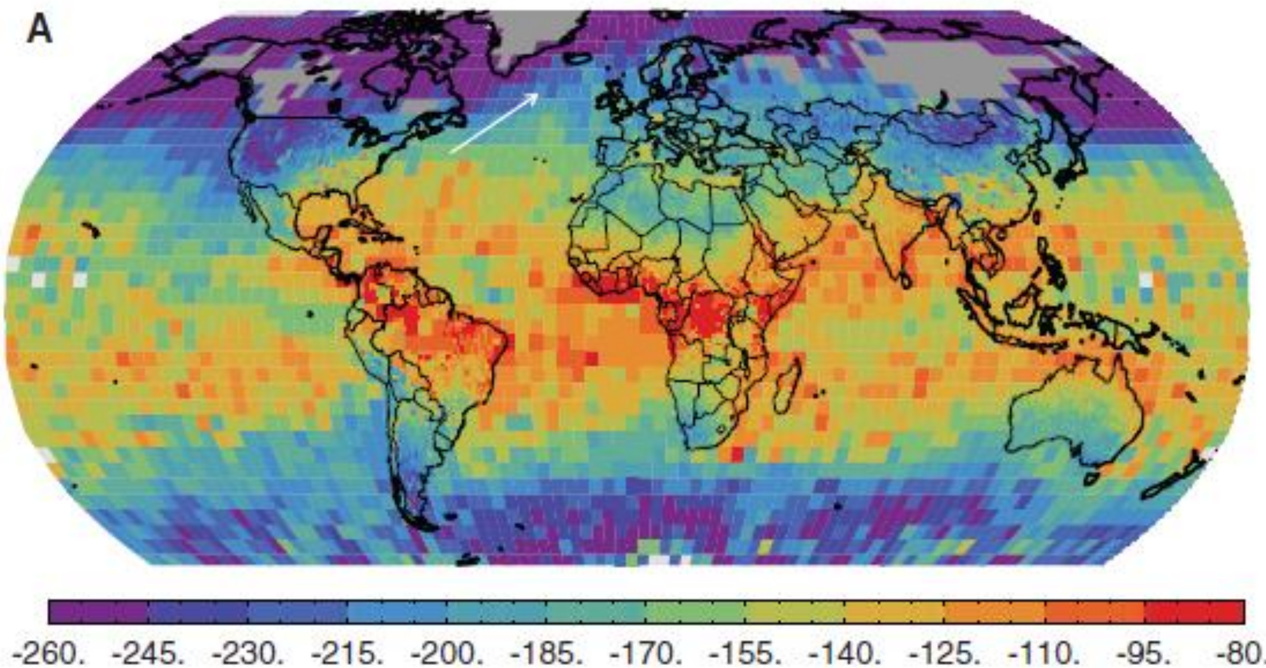
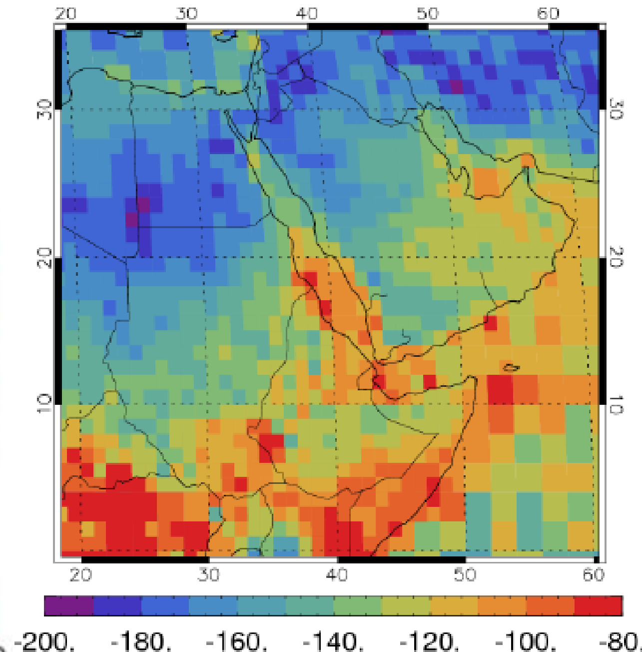


Fig. 3. Arrhenius plot (logarithm of rate constant versus inverse temperature) for the reactions $O + H_2 \rightarrow OH + H$ (open circles), $O + HD \rightarrow OH + D$, $OD + H$ (open triangles), and $O + D_2 \rightarrow OD + D$ (open squares), taken from the data of *Presser and Gordon* [1985].

反応速度定数における同位体分別：O + H2 → OH + H の例．[Kaye, 1987]

導入：地球では





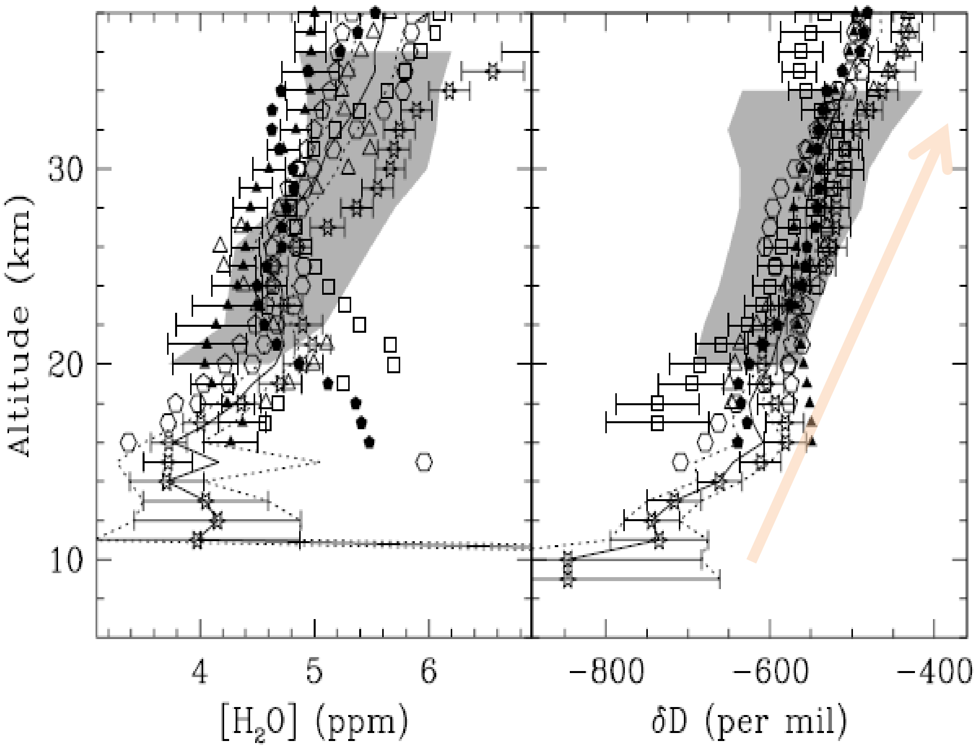
$$\delta D = 1000 \times \{ ([HDO]/[H_2O]) / SMOW - 1 \} \quad [‰]$$

ENVISAT衛星SCIAMACHY によるH_2O & HDO同時観測（2.35-2.37μm）から導出された対流圏カラム平均δDの全球分布(2003–2005年平均) [Frankenberg et al., 2009].
SMOW = Standard Mean Ocean Water; HDO/H_2O = 3.11E-4

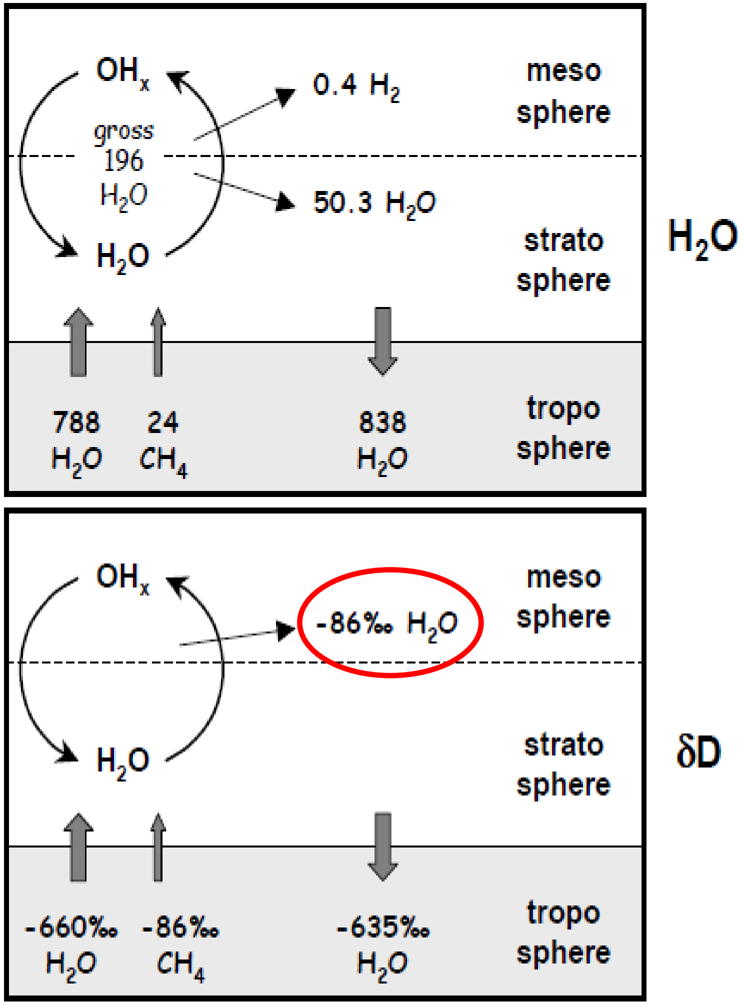
大きな緯度依存性 ＝ 凝結によるHDOの除去
熱帯大陸上での高δD ＝ 活発な蒸発散活動
白矢印 ＝ メキシコ湾流（暖流）による蒸発大，etc.

導入：地球では

成層圏でのδDは化学反応を強く反映



気球観測(FIRS-2)で得られたHDO/H2O比の高度分布. [Johnson et al., *JGR*, 2001]



[Bechtel & Zahn, ACPD, 2003]

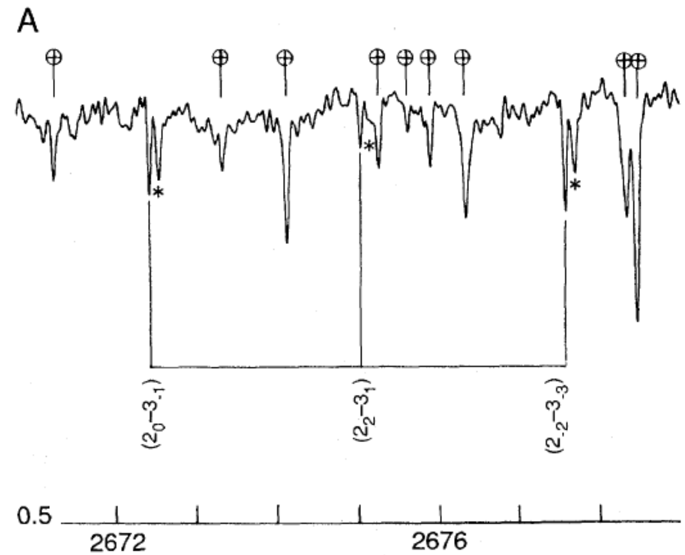
成層圏におけるメタンの酸化によりH2Oが生成する際に, δD が増加する.
（成層圏に流入してくるHDOの量にも注目）

火星では（ここからBertaux & Montmessin論文の内容）

- 地上望遠鏡観測による HDO の検出 [Owen et al., Science, 1988]

  → 火星下層大気中の HDO/H2O は 6±3 SMOW もの大きな値に！

  … 昔は今よりも6 倍も多い水が存在？（火星全球を 55 mの深さで覆うほど）



近赤外の火星HDOスペクトル．＊は地球HDO，〇十字はH2O以外の地球吸収．[Owen et al., 1988]

- 大気散逸でどれほどHが逃げていくかを知るには，上層大気中でのD/Hが重要 → ハッブル望遠鏡による観測：HD/H2 = 1.5±0.6 E-4

  ＝ 下層大気の HDO/H2O ～ 1.7E-3 と比較して 11倍も小さい．

- Partitioning：火星大気中では D は HDO or HD として存在していると思われる．R = (HD/H2)/(HDO/H2O) を求めると，観測値 ＝ 0.09 となり，光化学モデルによる予想 1.6 [Yung et al. 1988] と大きく異なる．
- Krasnopolsky らは H2 と H2O間の熱力学平衡で説明する（R = 0.14）が，Yung & Kass [Science, 1988] で「平衡定数に無理がある」と反論．

Krasnopolsky et al. [1998, Sciene] による火星上層大気（z > 100 km）のLy-alpha 観測.

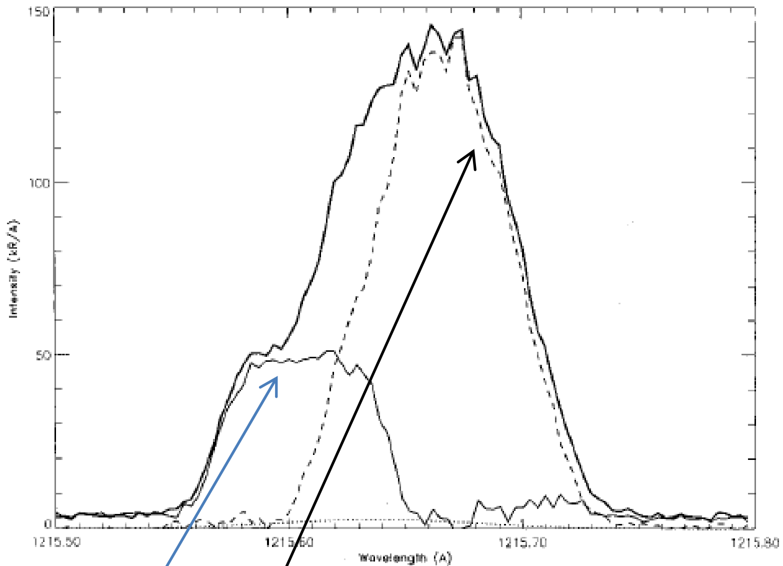


Fig. 1. Fragment of the HST spectrum (thick solid line) near the H Ly α line of the martian upper atmosphere. Geocoronal H (dashed line) and interplanetary H (dotted line) emissions are also shown. Their subtraction results in the martian hydrogen line (thin solid line). The geocoronal line is the difference of spectra recorded in the illuminated and shaded parts of the HST orbit.

火星 H Ly-α

地球 H Ly-α

観測データ（× 10） →

観測データ →

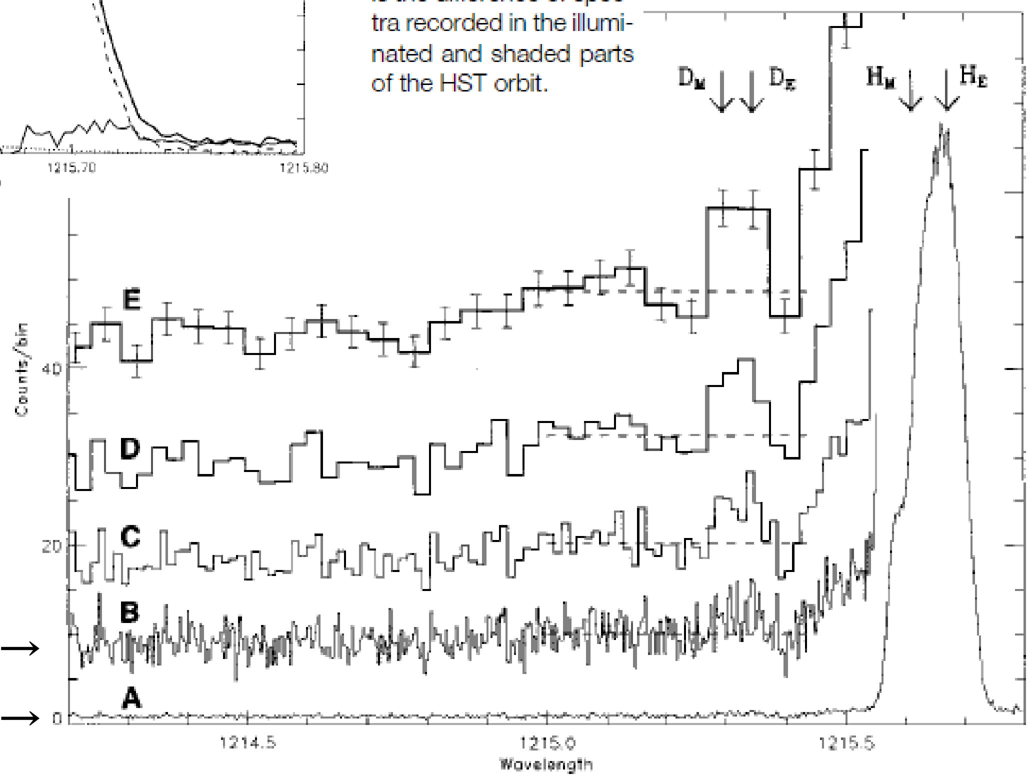


Fig. 2. Fragment of the HST spectrum that shows the martian and telluric D Ly α lines at 1215.29 and 1215.34 Å, respectively. A is the initial weighted mean spectrum, B is that spectrum scaled by a factor of 10, C is binned to 4 pixels and scaled by a factor of 5, D is binned to 8 pixels and scaled by a factor of 4, and E is binned to 16 pixels and scaled by a factor of 3. Dashed horizontal lines indicate the local background baselines. The positions of the martian and telluric D and H lines are shown; subscript M and E refer to Mars and Earth, respectively.

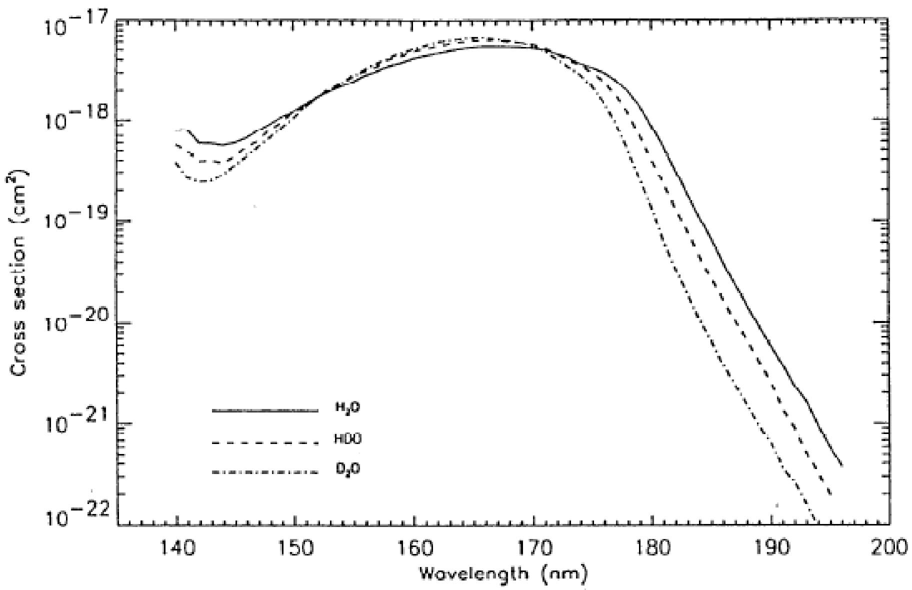
PHIFE

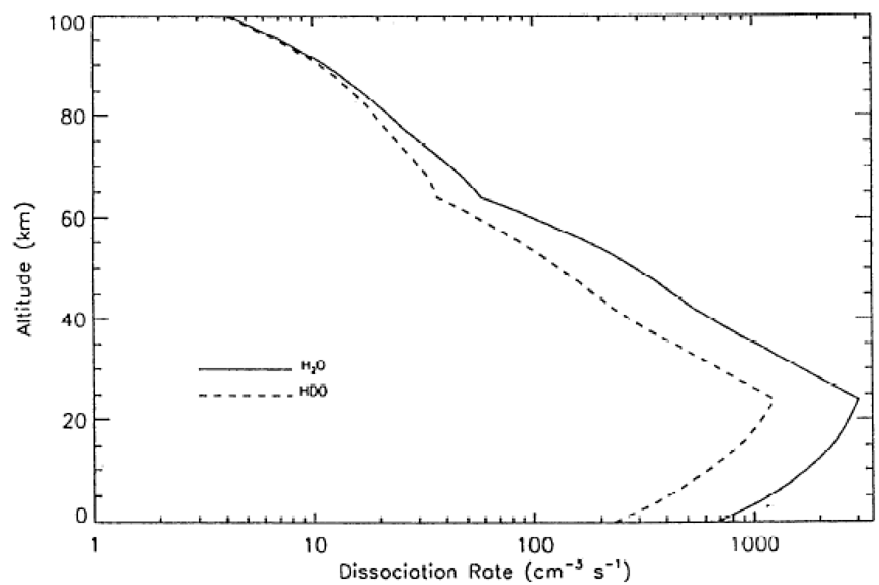
GEOPHYSICAL RESEARCH LETTERS, VOL. 26, NO. 24, PAGES 3657-3660, DECEMBER 15, 1999

Photo-Induced Fractionation of Water Isotopomers in the Martian Atmosphere

Cheng, et al. (1999)

- HDO と H2O の光解離吸収断面積を測定.
- HDO（下左図点線）の断面積波長特性は短波長側にずれる.
- 一方で，火星大気に於いては，波長の長い（λ ～ 190 nm）紫外線ほど CO2による吸収を免れて下層大気深くまで入ってくる.
- 結果として，下層大気では H2O（下右図実線）の方が相対的により多く解離.

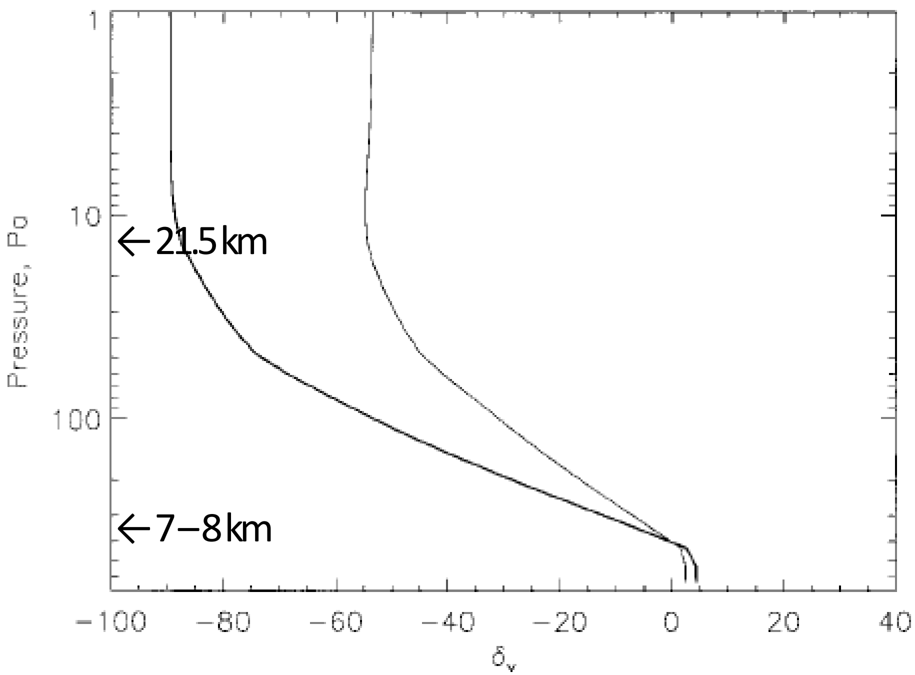




光乖離率

CEFE

- 本論文の目的：PHIFEの影響によるHDO/H2O の上層/下層差の説明（2-3倍）では説明し切れない分を 相変化による影響で説明しようという試み.
- HDOの方が凝結し易い（H2Oの方が気体で居やすい）. 上層で水蒸気が凝結し，それが重力沈降し，下層大気で再昇華. → H2やHDが生成する上層大気中での気相HDO を減らす効果.



$\delta v = 100 \times \{(R/R\_ref) - 1\}$;

R = (HDO/H2O)v,　R_ref = 1.7E-3

Figure 1. Vertical profile of the depletion factor δ_v of HDO with respect to H_2O due to preferential condensation of HDO on icy grains. The thin curve is for a fractionation factor α constant below 230 K, while the thick curve (more realistic) is for a value of α extrapolated for temperatures lower than 230 K, the lowest-temperature laboratory measurements. Note that HDO is depleted by a factor of 10 above 10 pascal pressure level and slightly enriched near the surface (below 300 pascal).

← 火星GCM（Montmessin et al., 2001）数値実験による計算結果.
太い実線の方がより現実的な同位体分別定数を使用した結果.

光乖離が起きるのは，25 km程度：その高度より下で HDO が既に大きく減少.
＝ HDO-cold trap，Deuteropause

CEFE

- HDOとH2Oで別々の鉛直分布を考慮した上で光乖離率を計算すると…

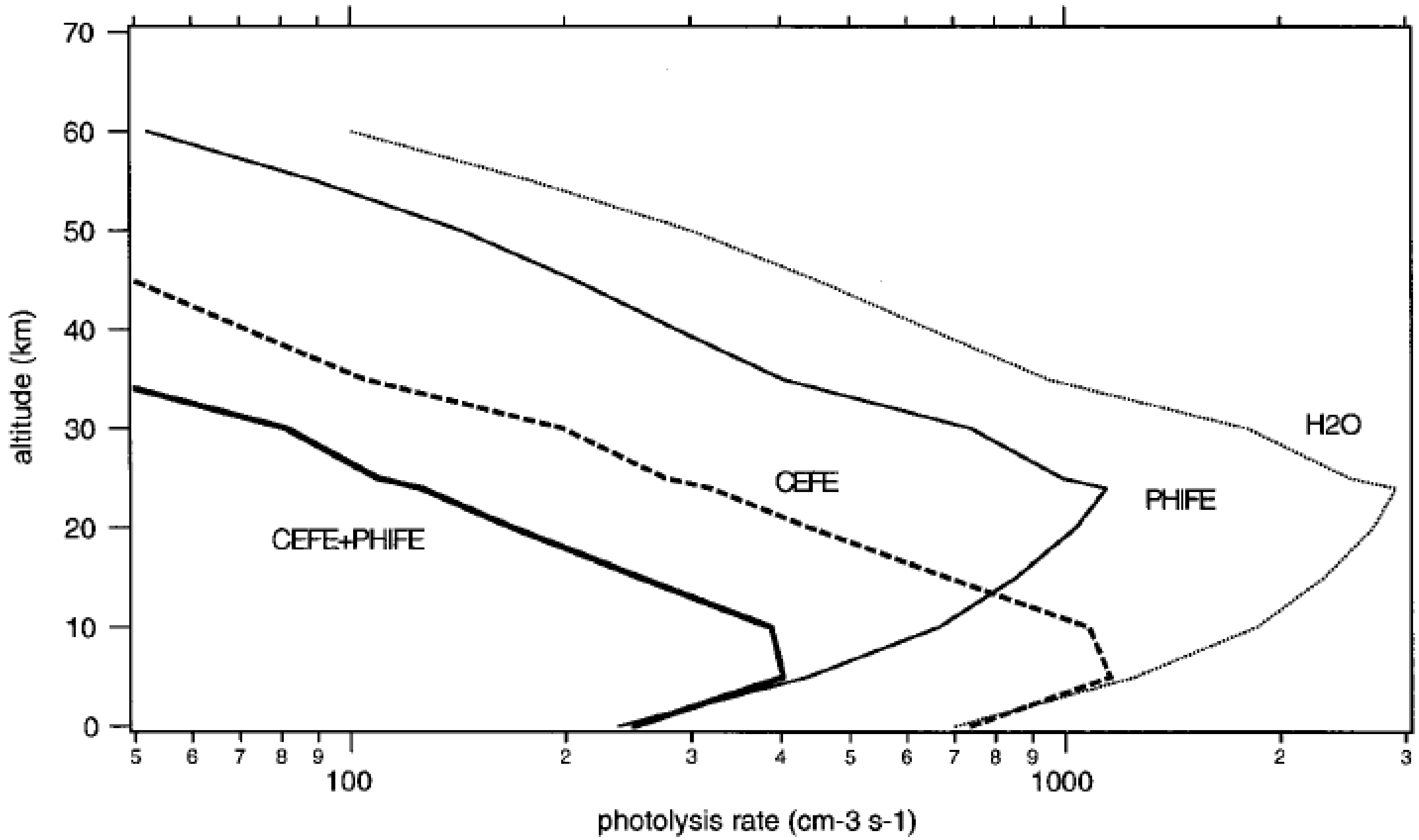


Figure 2. The dotted line is the photolysis rate of H_2O in the atmosphere of Mars (in molecules cm^{-3} s^{-1}) as taken from *Cheng et al*. [1999] as a function of altitude. The curve labeled PHIFE (also from *Cheng et al*. [1999]) is the photolysis rate of HDO, if its mixing ratio were equal to the mixing ratio of H_2O. It illustrates the effect of a lower photodissociation cross section of HDO. The dashed curve labeled CEFE illustrates the effect of the HDO depletion of Figure 1. The thick curve labeled CEFE+PHIFE indicates their combined effect. The integrated photolysis rate of this last curve is 9.5 times lower than for H_2O, which explains why there are so few deuterium atoms in the upper atmosphere of Mars.

Discussion

- CEFEの度合いは，気温分布（低温ほど雲が出来る）や雲微物理モデルの妥当性に強く依存する．PHIFEと合わせ技で Krasonopolsky et al. の観測値を説明しようとした場合，PHIFEは当然 太陽天頂角に依存する．

  → 今回の論文では一例（遠日点，Ls～60）しか示しておらず，モデル信頼性等の誤差解析もしてはいない…

  が，今回示した例の遠日点のケースは，雲生成に向いている時期では無く，その時期でも大きなCEFEの効果が出たということは，仮に火星1年で平均をしたとしても CEFEの効果が大きく下方修正されることはないであろう．

- 今回の論文で示した CEFE + PHIFE の効果は，上層大気でDが著しく減っていることを明瞭に説明できる．（Krasnopolskyらによって導出された R = 0.09 から示唆されるHDO光乖離率のdepletion ～ 1.6/0.09 = 18 という結果は，R = 0.09 を求める際の渦拡散係数の精度にもよる）

- 大事なのは，CEFEによって「HDOの存在上限高度」Deuteropauseが出来ること．これによって上層大気へのDの供給が大きく減少し，Dの大気散逸率も（11倍）小さくなる． **＝ 過去から現在にかけて，Dは殆ど逃げていないと考えられる．**

Discussion

- 現在のH2Oリザーバー量に対して，過去のリザーバー量を求めると，6.22倍に.
- 現在のリザーバー量を 9 m [Zuber et al., 1988] と仮定すると，昔は 9 × 6.22 = 55 m のH2Oリザーバーが有った．55 – 9 = 46 m相当 が宇宙空間に散逸した.
- この散逸量は Kass and Yung, 1995 のモデル計算値（散逸可能な最大値） 80 m の半分くらいだが，この 80 m の見積もりはかなり極端な場合.
- 46 m分が極冠以外のところにゴッソリ残っているとは考えにくい.

- 今回の論文での話は，HDO-cold trapよりも上空では H2OとHDOの大半が光乖離すると想定している．しかし，実際の火星の場合はそうとは限らない（HDO-cold trapが30 km付近になりうることもある）.
- この辺りの議論は 3次元GCMを使った今後の課題.

- おまけ：地球大気では，上層大気中のD/Hは海洋中の値と大差ない．対流圏圏界面で HDO-cold trap があるにも関わらず，何故？ → CH3D（対流圏圏界面で凝結しない）が成層圏にDを運んでる.
- 火星上層大気中の D/H が極めて小さいのは，CH4 が無いから？？？

Montmessin et al. 2005

Modeling the annual cycle of HDO in the Martian atmosphere

F. Montmessin[1]
NASA Ames Research Center, Moffett Field, California, USA
T. Fouchet
LESIA, Observatoire de Paris, Paris, France
F. Forget
Laboratoire de Météorologie Dynamique, Institut Pierre Simon Laplace, Paris, France

*JGR **110**, (2005)*

tion of ozone on Mars by *Lefèvre et al.* [2004]). It includes the major processes affecting water vapor in the Martian atmosphere (except regolith adsorption); e.g. transport by winds, exchanges with the surface, atmospheric condensation and sublimation as well as sedimentation of icy particles. Water can either sublime (if ice is present on the ground) or condense onto the surface depending on the difference in mixing ratios between the vapor in the first layer and that in contact with the surface. Water ice clouds are supposed to form whenever water gets supersaturated with respects to ice. In that

Montmessin et al. 2005

Modeling the annual cycle of HDO in the Martian atmosphere

F. Montmessin[1]
NASA Ames Research Center, Moffett Field, California, USA
T. Fouchet
LESIA, Observatoire de Paris, Paris, France

JGR ***110***, *(2005)*

極冠に凍りつく際にはHDOが減少

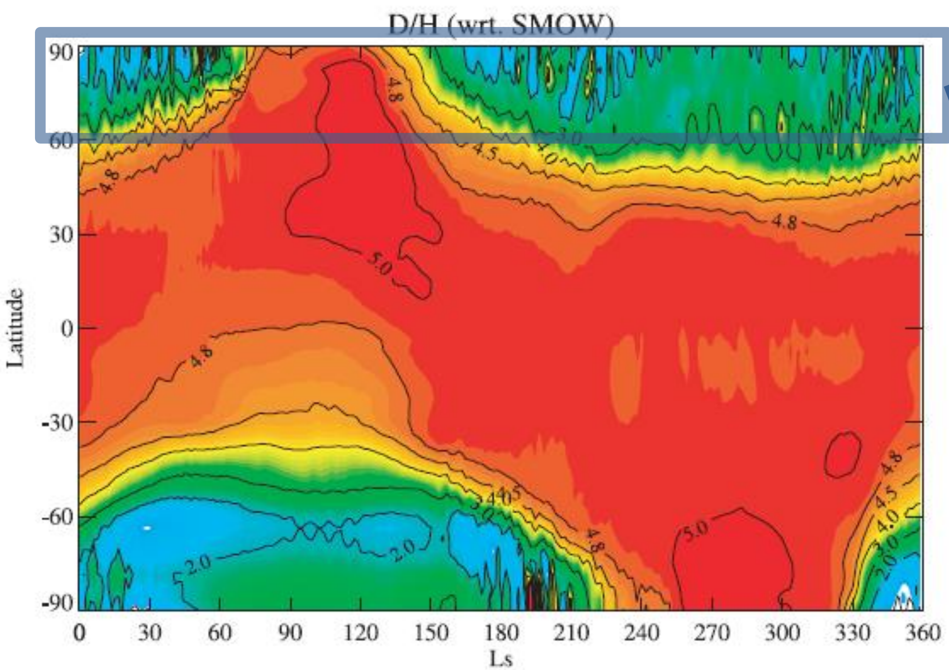


Figure 2. (top) Latitudinal and seasonal distribution of the zonally averaged abundances of HDO vapor in the Martian atmosphere as predicted by the model. (bottom) Corresponding values of the D/H ratio in the vapor phase.

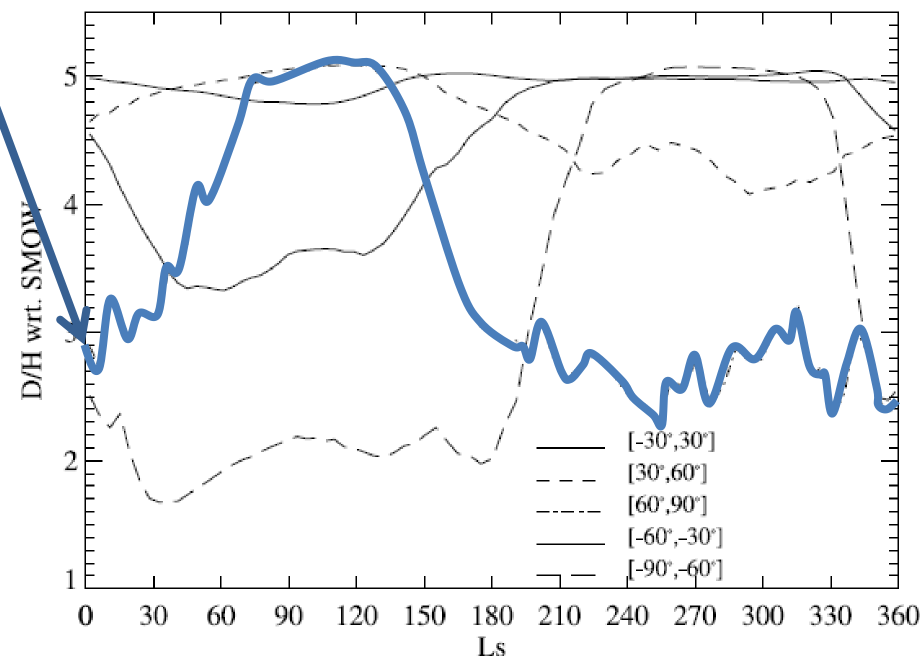


Figure 5. Seasonal evolution of D/H in different latitudinal bands as obtained by the model.

Montmessin et al. 2005

Modeling the annual cycle of HDO in the Martian atmosphere

F. Montmessin[1]
NASA Ames Research Center, Moffett Field, California, USA
T. Fouchet
LESIA, Observatoire de Paris, Paris, France

JGR ***110****, (2005)*

北半球の夏に生成するEquatorial Cloud Belt によるHDO除去

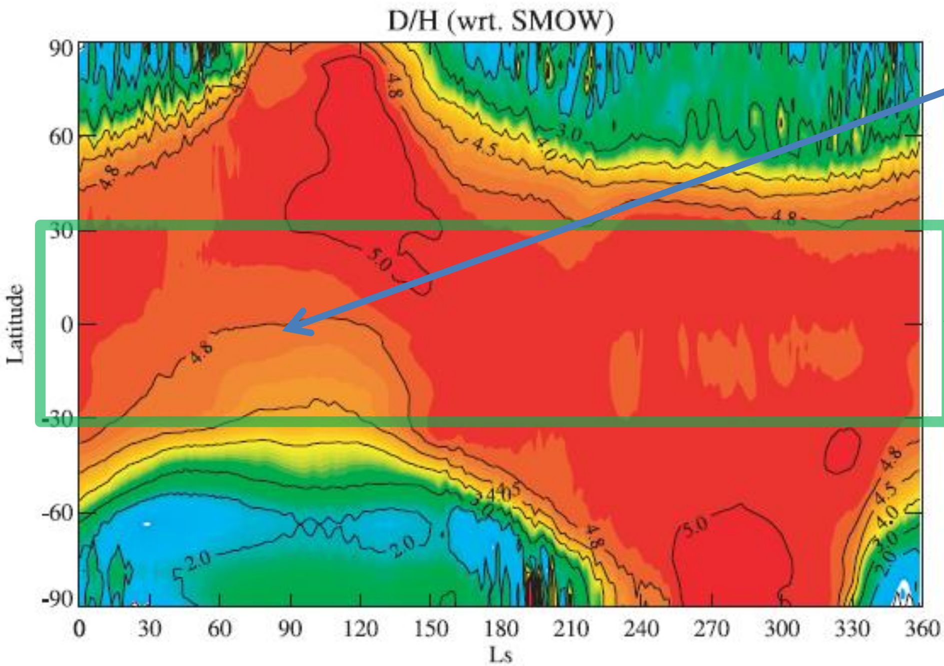


Figure 2. (top) Latitudinal and seasonal distribution of the zonally averaged abundances of HDO vapor in the Martian atmosphere as predicted by the model. (bottom) Corresponding values of the D/H ratio in the vapor phase.

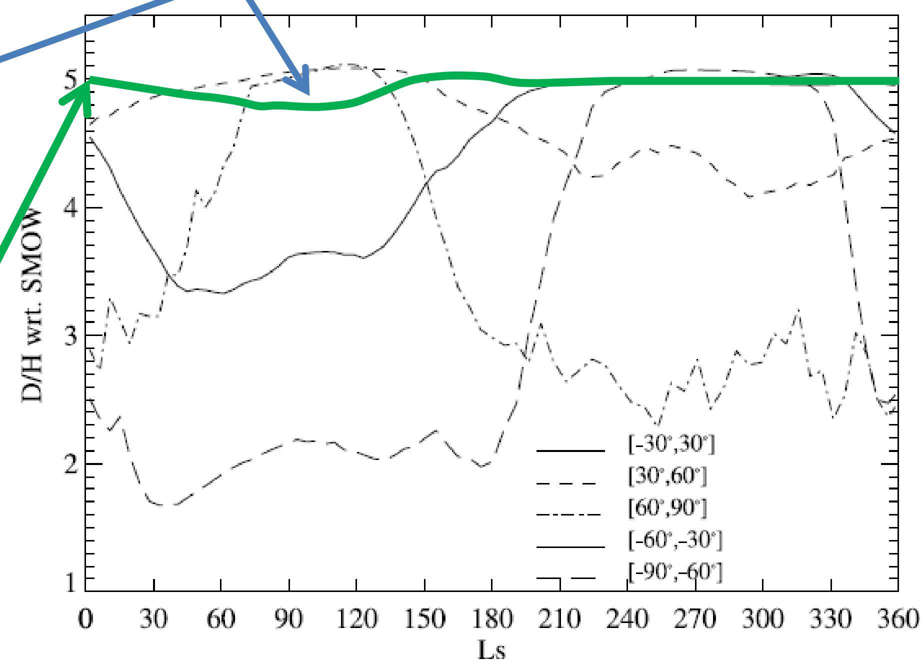
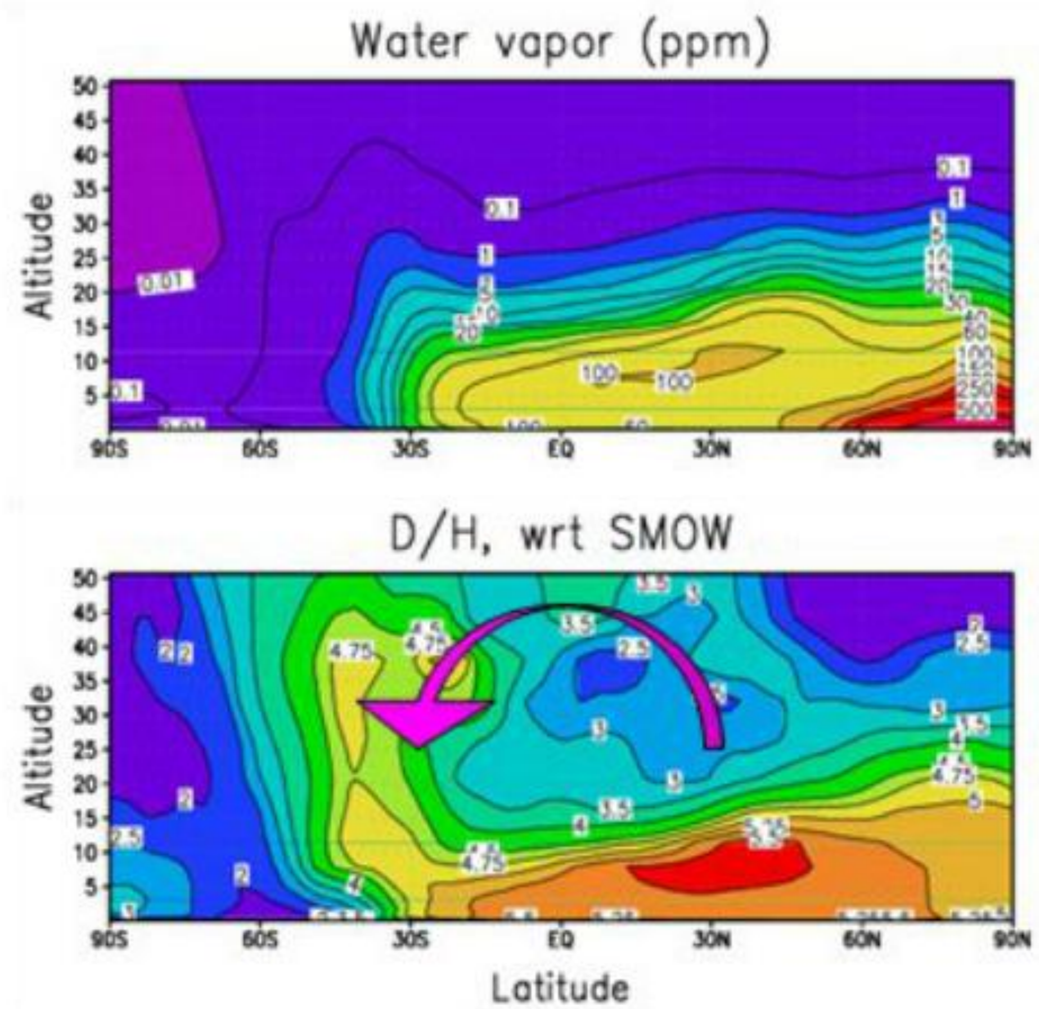


Figure 5. Seasonal evolution of D/H in different latitudinal bands as obtained by the model.

Montmessin et al. 2005

Modeling the annual cycle of HDO in the Martian atmosphere

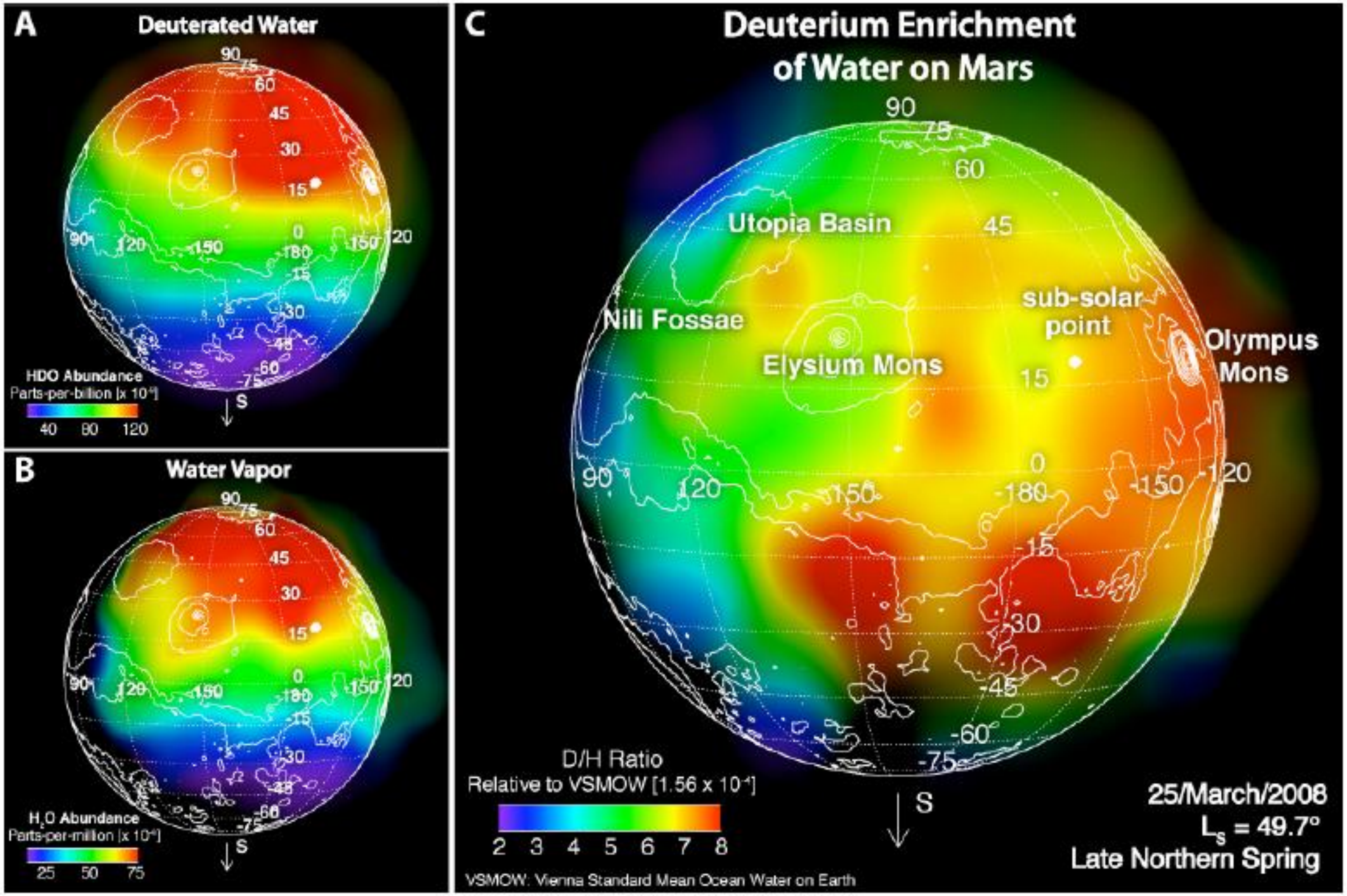
JGR ***110**, (2005)*



Ls = 90（北半球の夏）での
HDO/H2Oの鉛直 vs 緯度断面図.

南半球中緯度の比較的高い高度
でHDO/H2Oが大きくなる:
赤道域低高度で生成したECB がハ
ドレー循環で南半球に輸送される.
その下降流では，断熱圧縮により，
ECB（HDOをより多く含む）が昇華.
そもそもの背景水蒸気量が少ない
ことも有り，HDO/H2O比が一気に
高くなる…という考察.

最近の火星HDO/H2O観測



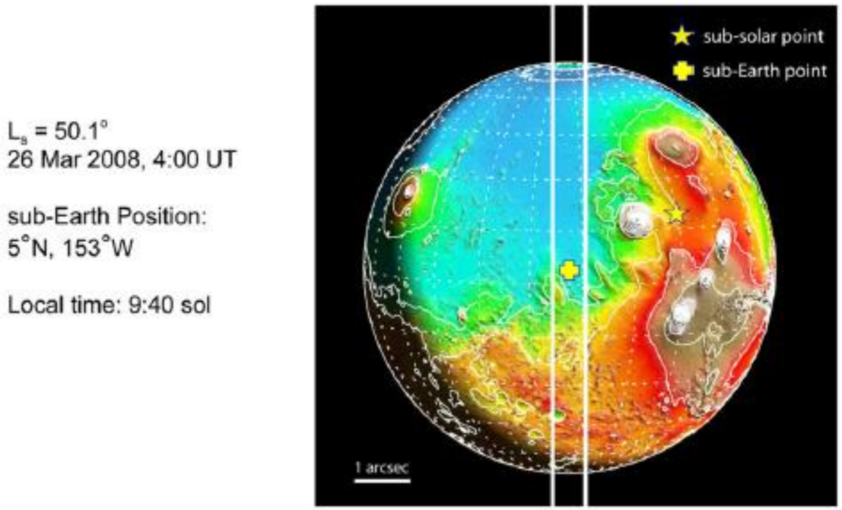
IRTF望遠鏡 近赤外分光器で観測された火星HDO/H2Oマップ [Villanueva et al. 2008 (Conf. Proc.)]

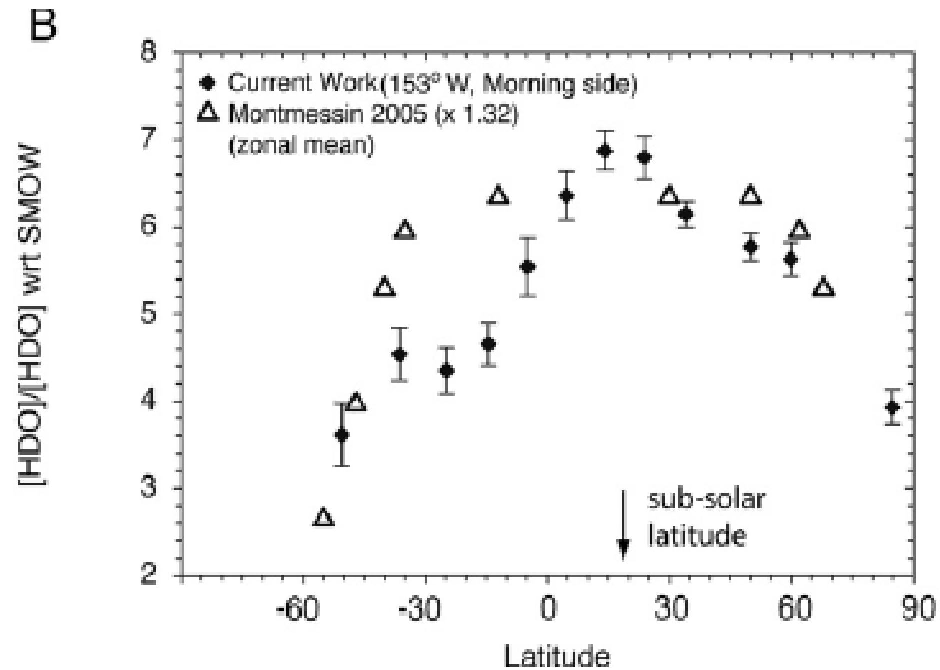
最近の火星HDO/H2O観測

Measurement of the isotopic signatures of water on Mars; Implications for studying methane

Icarus, 2011

R.E. Novak [a,*], M.J. Mumma [b], G.L. Villanueva [b,c]





HDO/H2Oに大きな緯度依存性.
気温分布との関係で説明.

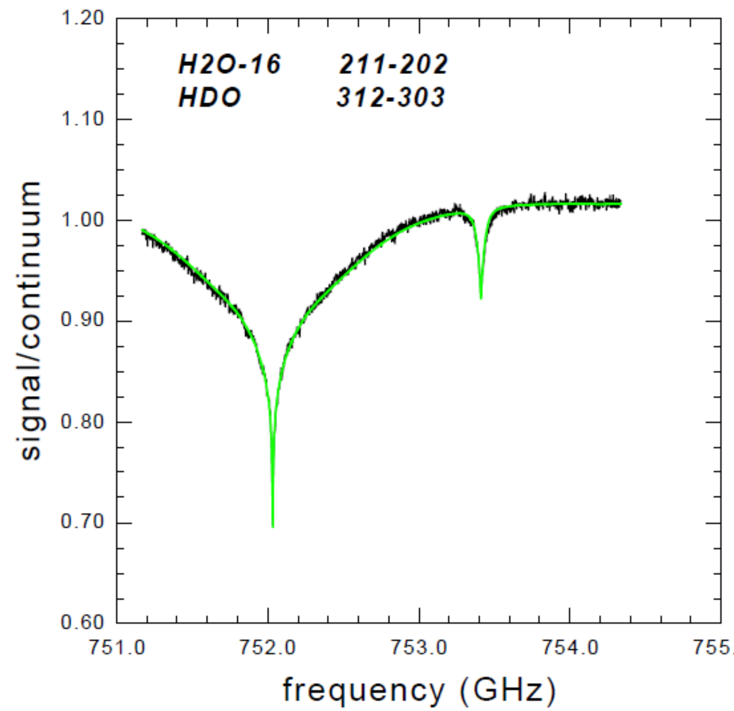
Fig. 2. (A) Column densities of HDO and H_2O measured with spectral extracts at three row intervals (0.6 arcsec) along the north–south meridian. (B) Ratio between HDO and H_2O compared to their ratio on Earth. Our results for $L_s = 50°$ are presented along with predictions of Montmessin et al. (2005) (multiplied by 1.32) for the same season (mid-spring in Mars' northern hemisphere).

経度方向にも変化しているであろう（…でも 前頁の様なマッピングを出していないのは何故？）

最近の火星HDO/H2O観測

Herschel/HIFI サブミリ波受信機による H2O，HDO，$H2^{18}O$，$H2^{17}O$の観測.
Hartogh, Jarchow et al. を中心にデータ解析中.

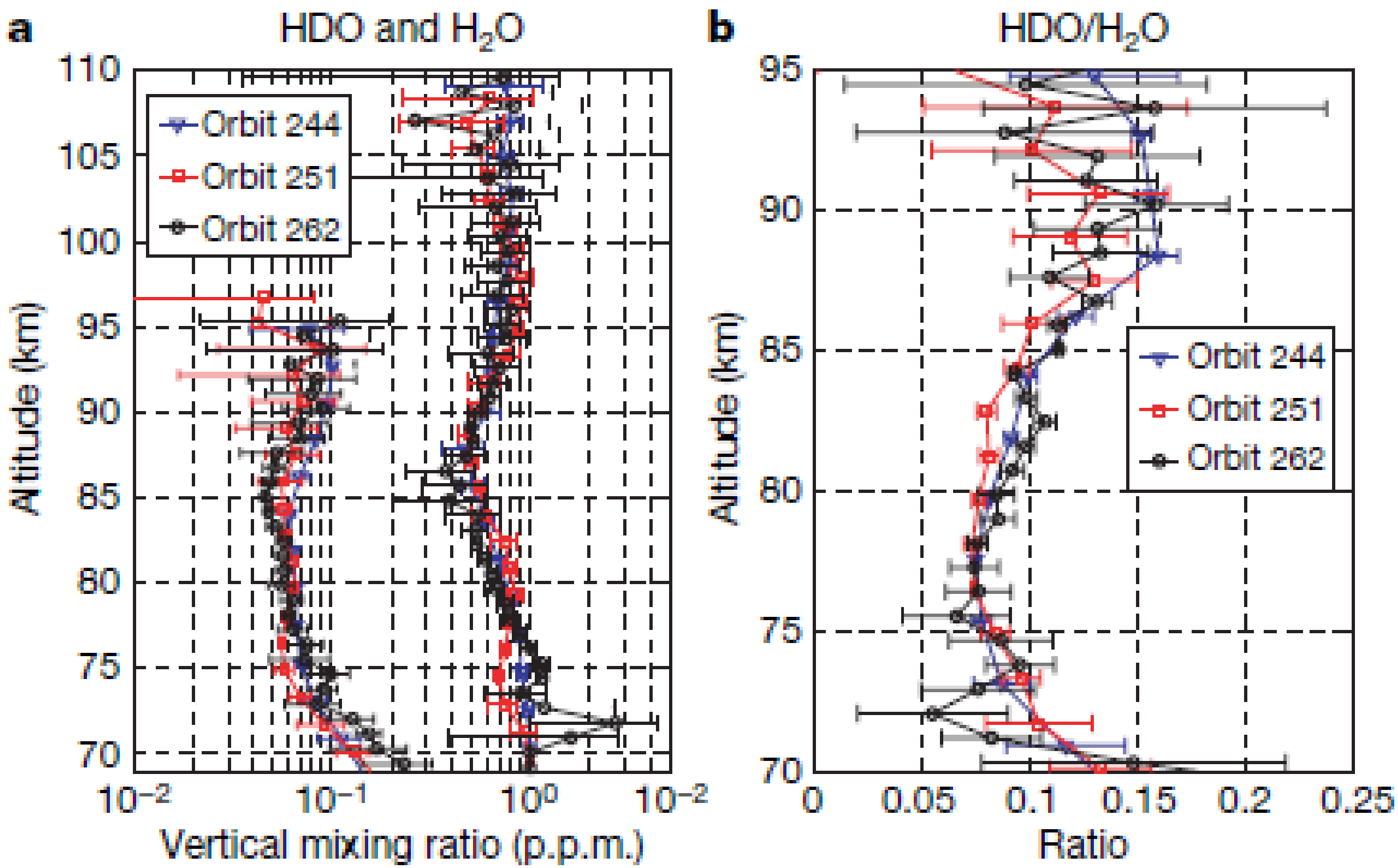
速報値では，HDO/H2O = 5.1 VSMOW.
それい以外の同位体比は，地球と同じ.



Presentation by Jarchow et al.
in EPSC/DPS-2011

サブミリ波のヘテロダイン観測では，
非常に高い周波数分解能を実現.
分子吸収線の圧力広がりを検出可能.
→ 観測分子の高度プロファイルを導出.
火星周回軌道からのサブミリ波観測に期待.

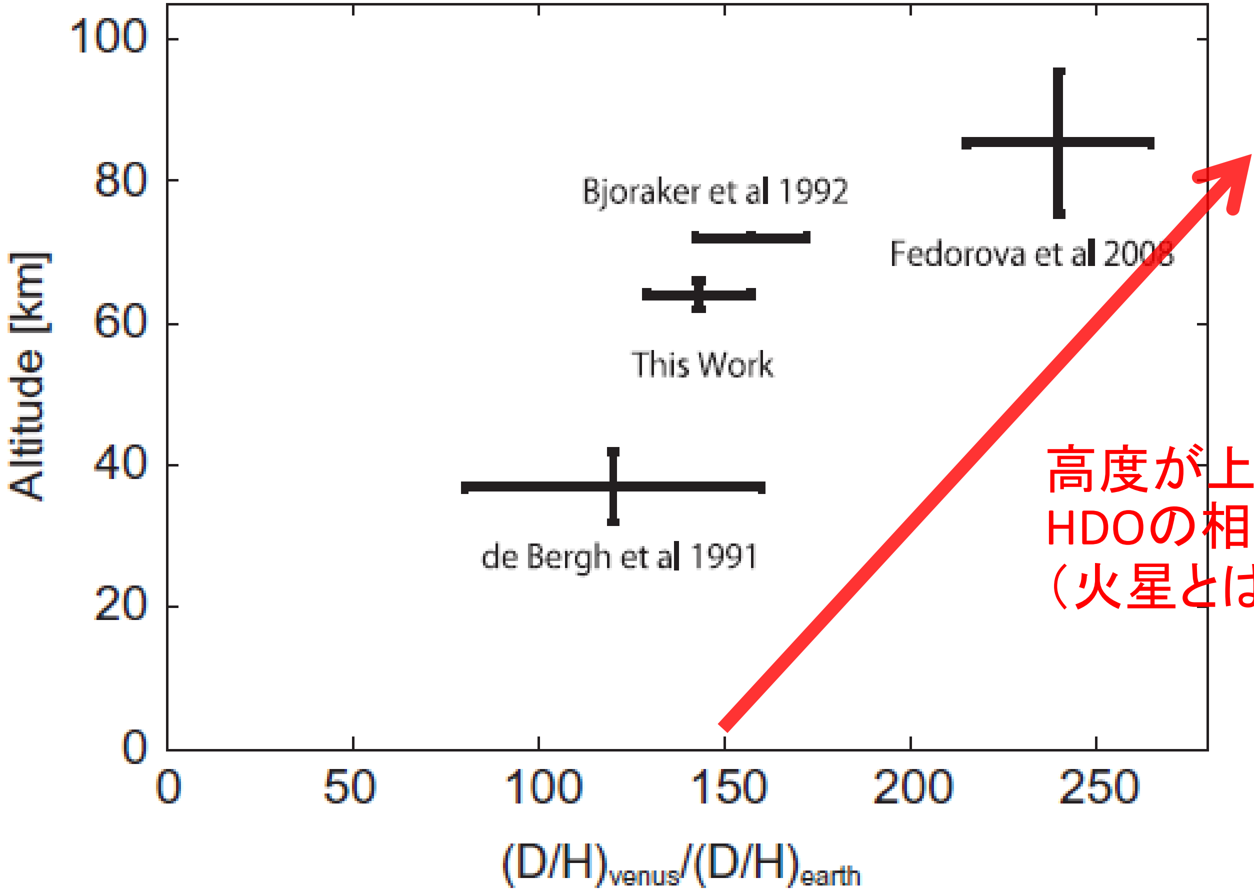
最近の金星HDO/H2O観測



Venus Express/SPICAVによる掩蔽観測の結果 [Bertaux et al., Nature, 2007].
HDO/H2O VSMOW = 3.11E-4 と比較すると，～250 VSMOW もの値に！

最近の金星HDO/H2O観測

IRTFを利用した地上観測の結果を含む金星HDO/H2Oの
高度分布 [Matsui et al. 2011]



高度が上がるにつれて,
HDOの相対量が増加
（火星とは逆のセンス）

Fig. 7. Comparison of estimated D/H ratios in Venus $(D/H)_{Venus}$ in units of the terrestrial ratio $(D/H)_{Earth}$.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 114, E00B28, doi:10.1029/2008JE003095, 2009

Modeling the distribution of H_2O and HDO in the upper atmosphere of Venus

Mao-Chang Liang[1,2] and Yuk L. Yung[3]

A new mechanism, the photo-induced isotopic fractionation effect (PHIFE) of H_2O and HCl, is incorporated into our model. The observed enhancement of HDO could be attributed to (1) preferential destruction of H_2O relative to HDO via PHIFE and (2) escape of hydrogen that enhances the abundance of D and hence its parent molecule HDO. Over a wide range of the sensitivity of the results to the changes of the two mechanisms, we find that the observed profiles of HDO and H_2O profiles cannot be explained satisfactorily by current knowledge of chemical and dynamical processes in this region of the atmosphere. Several conjectures to tackle the problems are discussed.

PHIFE では説明できない（実線，点線がモデル計算のHDO/H2O．線種はH2O鉛直分布計算条件の違い）.

CEFEで説明できるか？
[岩上先生＋はしもとさん他が研究中]

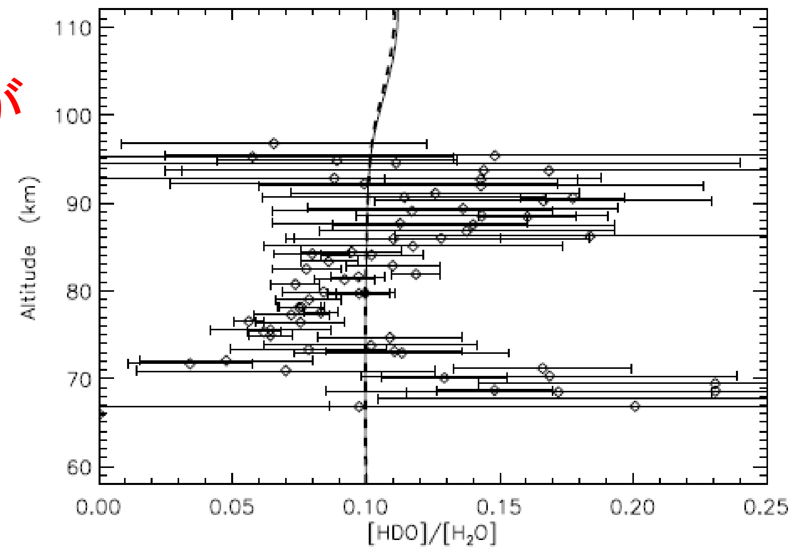


Figure 4. Model HDO/H_2O corresponding to cases in Figure 1. Data are from *Bertaux et al.* [2007]. The two curves are indistinguishable below ~100 km. Line designation is the same as that in Figure 1.