The Water Isotope (D/H) History in the Strata of The North Polar Cap : Inferences About the Water Cycle.

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Abstract

A time varying stable isotope model for the D/H history of Mars water cycle is developed with variable atmosphere, space loss rate , ground and ice cap flux rates. It considers coupled ground reservoirs and traces D/H in the air and reservoirs secularly and over obliquity cycles. The various flux rates are prescribed time variables that simulate surface flux, and solar driven space loss rates. Predicted bulk averages for the ice cap , ground ice reservoirs and atmosphere span the observed ranges reported by Mumma et al. (2003). When the dominant obliquity cycle variations are scaled so that the model delivers present seasonal variations , the present long term bulk D/H average for the ice cap is ~ +2.7 (equivalent to +1700 o/oo in $\delta(D)$ wrt SMOW) . The obliquity driven D/H cycle in the ice caps layer varies between 3 and 6. The smaller more accessible reservoirs have larger bulk averages with the smallest being able to reach D/H values over 9 within ~ 10^5 years. Small hypothetical solar activity driven variations in the escape rate to space and in the fractionation constant (Krasnopolsky and Feldman 2001) for the escape process can produce a "solar wiggle" whose D/H amplitude can reach 0.1 ($\delta(D)$ amplitude of 100 o/oo). Because of the temporal variability, a single modern measured atmospheric D/H ratio at a particular Ls can not tell very much about the total water inventory of Mars. A bulk average for the Northern Ice Cap and better still a dated vertical profile of D/H from the ice cap would , however, go a long way towards illuminating the "modern" water history of Mars . The age and stability of the Northern Ice Cap and the D/H history locked in the layering is discussed . An ice cap that is very young and exchanges its mass through the atmosphere often will necessarily have a large D/H .

Key Words: Mars; Water Cycle ; Stable Isotope Model; Ice Cap; D/H; Obliquity Cycle; Solar Cycle.

Introduction and Some of the Problems

The D/H ratio has been measured remotely in Mars atmosphere and is related to its water cycle. Its long term variation and seasonal cycle depends on several processes and on the sizes and time scales of the accessible ice-water reservoirs.

D/H in Earth's ocean (Standard Mean Ocean Water, or SMOW) in absolute terms is : 155.8 x 10^{-6} . A value close to SMOW's is taken as the start for ancient mixed water in the solar system, Mars included, (Yung et al., 1988). The SMOW ratio will be denoted $(D/H)_{SMOW}$ and much of what subsequently follows Mars ratios are relative to the SMOW ratio ie $(D/H)_{Mars}/(D/H)_{SMOW}$. Typically on this relative scale atmospheric D/H has been measured remotely to be between 2.7 and 9.9 (eg see Mumma et al.,2003;Novak et al.,2005) ; Krasnopolsky and Feldman,2001)) . The most extreme ratios on Earth are 0.5 in East Antarctic Snow, (using the more standard terrestrial measure $\delta(D)=((D/H)_{sample}/(D/H)_{SMOW} - 1)*1000$, Antarctica's D/H = 0.5 is equivalent to $\delta(D)$=-500 o/oo , while Mars atmospheric values range from +1700 to +8900 o/oo). The D/H notation will be continued , because the theoretical expressions are simpler , but the equivalent $\delta(D)$ notation is often included, because it is used in geophysics.

Prior to the observational results of Mumma and Novak (2003) , observed D/H in the range 5.5 to 8 combined with models lead to a range of estimates of Mars total initial water inventory from an early global cover of 0.2m (Yung et al.,1988) ;through 30-80m (Jakosky et al.,1991) to 65-120 m(Krasnopolsky and Feldman, 2001). Mumma and Novak have shown that there is a strong seasonal cycle in D/H . Fig. 1a shows a version of their data of D/H plotted against the precipitable water column height "Pr" for different Ls . Their observations are at present limited by 'footprint' and season to the maximum equivalent Pr of 49µm obtained for Northern hemisphere summer water. They have not yet managed to 'capture' the D/H ratio for the peak of the seasonal water (Pr=~80 µm) "dome" that forms over the North Cap at Ls~118.Extrapolating their data in Fig. 1a with an exponential puts the Pr=80µm with a D/H of 0.75 , which is very earth-like. As later modeling here shows , the average D/H given off by the present ice cap is a

good estimate of the cap's bulk average and is likely to be in the 2-3.5 range . What Mumma and Novak data have indicated is that a single representation of D/H for Mars atmospheric water might not indicate much about the total reservoir size. Different source reservoirs might have different values of D/H depending on their size , accessibility and 'age' and these different reservoirs might be getting activated/deactivated at different times of the Mars year.

The main process that drives the D/H on Mars to such large values is the preferential loss of the lighter isotope to space after a complex set of atmospheric photochemical reactions , (see eg. Yung et al., 1988; Cheng et al., 1999). If this was simply the only set of processes, one might expect that vertical profile of D/H would show an increase of D/H with elevation. The Yung photochemical model predicts that the ratio $(HD/H_2)_{upper\ air}/(HDO/H_2O)_{near\ surface}$ is 1.6, ie the D/H at high (>100 km) elevation should be higher than at the surface . But HST spectral measurements made by Krasnopolsky et al. (1998) on the limb (during cold atmospheric conditions (T=180K)) at aphelion during a period of solar minimum showed that instead of 1.6 as predicted they found 0.09 , which suggests D/H at height is 11 times smaller than at the surface. Krasnopolsky et al. (1998) pointed out that Yung et al.'s thermodynamic process alone (1988) would give the observed ratio , but this switch in process would require rate constants for it that are 10 orders of magnitude outside lab measured values ! The puzzle of processes producing D/H ratios measured on Mars and their meaning in terms of the initial and present sizes of water inventories has been encapsulated by Yung and Kass (1998) as " Deuteronomy ? : A puzzle of Deuterium and Oxygen on Mars".

Two new processes have been added to help decrease the D/H ratio at high elevation and alleviate the apparent "Deuteronomy problem". Cheng et al.,(1999) added a photochemical process to Yungs' suite that will reduce the photochemically predicted ratio to about 0.64 . Bertaux and Montmessin (2001) Further reduced (by a factor of 3.5) the D/H at higher elevations by using a Rayleigh condensation model approach much as described by Fouchet and Lellouch, (2000). As pointed out by Fouchet and Lellouch , the assumptions made about the cloud model ,(vertical temperature gradient , water vapor content and the equilibrium fractionation coefficient (α)) can change the fractionation effect by a factor of 5 . When Krasnoplosky et al. (1998) made their observations in the cold part of the winter hemisphere the water content in the air is already next to zero , certainly well below the range of conditions examined by Fouchet and Lellouch.

Jakosky (1991) suggested a line of reasoning that possibly helps untie some of the knot of deuteronomy. Since the scale time to change D/H in a closed atmosphere is shorter than the major obliquity cycle, (Yung et at.,1988) (which has a 1.2 x 10^5 year period) , the D/H observed at present is probably less to do with the long term average outflux rates of water and initial global reservoir sizes than with the time varying nature of these rates combined with the fact that over the last few million years of Mars history, the insolation cycle has been rather weak, (Toon et al.,1980). Thus the D/H observed could just be a reflection of atmospheric water that has been weakly replenished by climate change. He also suggests that reservoirs of different sizes and accessabilities could contribute water at different scale times and that all these time varying aspects of the water flux taken together with the relatively short scale time the D/H process will determine the present observed value(s). This view seems to resonate with the Mumma et al.(2003) and Novak et al. (2005) results and determines the approach explored here . The approach will include multiple reservoirs of varying sizes, that gain and loose water to the atmosphere as functions of time . Loss rates to space are also variable as is the fractionation factor (F), which Krasnopolsky and Feldman (2001) have shown varies with solar activity. The long term average losses to space are taken to be offset by the long term average losses from the reservoirs. All the time variability here is prescribed , so process sensitivities can be explored but only rough simulations can be attempted. The space loss variability is kept rather low whilst there are large periodic swings in the ground losses to the atmosphere so that the atmospheric water content can change by as much as a factor of 1000 .

The North Polar Cap and the buried ground ices are both assumed to loose water with the reservoir's D/H value in the summer and gain it mostly back in fall at the atmospheric D/H (altered by some fractionation) so that average D/H for the whole reservoir changes slowly with time. For the North Cap the losses are from the finely layered ablation scarps whose layers span the full time history of the Cap so that the D/H of the water lost is an average for the Cap. The whiter areas are the accumulating zones that take that years' D/H value back , see Fig 1b showing a cartoon of the seasonal gain/loss from the ice cap and from the ground ice . The history of the polar atmospheric D/H is thus contained in the water in the layers. For a summary of the issues related to the North Cap's layers see (Fisher 1993,2000; Hvidberg,2003). Every Mars year, the ground ice reservoirs are also assumed to be able to loose ice that has its average

D/H and gain ice with the atmospheric value of D/H . This is probable for the adsorbed water in the "desiccated" surface layer over the ground ice and conceivable for the buried ground ice that is porous even if its pores are saturated with ice (Fisher ,2005).

Given the relatively large size of the seasonal water vapor variation and this re-cycling process to and from the reservoirs a given water molecule spends much longer under the surface than in the air. Depending on the age of the ice cap and whether it flows or not (Fisher, 1993;Hvidberg 2003) the water molecule could spend 10 to 100 million years under the surface for every year spent in the air . This 'storage time' is unknown but has an important effect on the evolution of D/H of the air and of the changing D/H of the ice cap. The smaller ground ice reservoirs are not so slowly cycled through the air but the effects of the storage time are similar. The adsorbed water reservoir no doubt has the shortest storage time and gets 'aired' most often. This geographically wide spread adsorbed reservoir must then have its D/H relatively quickly moved to the large end point values (~10 if the start value was 1) and probably provides the high D/H values observed when the water column heights are small.At low latitudes where the ice table is deeper the adsorbed water is probably the major seasonal reservoir.

   The North Ice Cap presently feeds itself, with the moisture coming off the (mobile) ablation scarps to form the water vapor dome in the summer (75<Ls<130) re-sublimating higher up on one of the horizontal whiter areas, (Howard et al.,1982). It is presently its own major source of moisture and if the rate of ablation were to increase , the rate of accumulation would also no doubt increase. The issue of whether the ice cap flows as a result of the mass movement through the air is still open (Fisher,2002; Greve and Mahajan,2005; Ivanov and Muhlman,2000) , and its resolution will partly determine the age of the oldest ice in the layer column(s) of that ice cap. Another open issue is whether the ice cap water system is closed or exports water to lower latitudes, (ie how much mixing is there between latitude zones).

 Reservoir Sizes and Variables
        The formulation will follow a combination of Yung et al. (1988) and Dansgaard (1961) . Each of two reservoir/atmosphere bins is treated separately and at each step of the integration there is some mass mixing between their atmosphere's at some specified level that can be defined for each run. On an annual basis , the water bins are probably presently rather isolated,

eg. (Haberle and Jakosky 1990). The debate about substantial export of water from the North Cap towards the south is at present still active (Mischna et al., 2003; Head et al.,2003). Here the inter-latitudinal interaction is a free parameter called the mixing factor that can be interpreted as a mixing time for the zonal bins. The debate about the vigor of the pole to pole water see-saw is one of the issues that the North caps D/H history could illuminate.

The specific size of the atmospheric reservoir is denoted q_v with units (number of H atoms/cm^2) and the D/H ratio is denoted a_v and is either an absolute ratio or relative to earth's ocean ($a_{SMOW} = 1.5576$ x 10^{-4},Hageman et al.,1970)) depending on context. Only two surface or subsurface reservoirs are considered , one being the ice cap (i=1) and the other is subsurface ground ice (i=2) or adsorbed water. Both q(i,t) and a(i,t) are time (t) variables and different between the two reservoirs denoted "i". The important size of the sub-surface reservoir and their attendant average D/H value are q_g (1,t) and a_g(1,t) for the ice cap and q_g(2,t) and a_g(2,t) for the ground ice . q_g has (number of H atoms/cm^2) as units.

The relationship between the reservoir size q_g and equivalent ice thickness, Z, is just: $Z(cm) = (q_g * \mu)/(2 * Avogadro * \rho_{ice})$, where μ the gm molecular wt of water (18) , Avogadro is 6.023 x 10^{23} molecules/ (gm mole wt) and ρ_{ice} is ice density (0.917 gm cm^3).   In the integrations of the model the initial reservoir sizes q_{v0} and q_{go} values are taken as estimates of present sizes and the start values for the D/H ratio is typically taken as 1 wrt SMOW. The initial reservoir sizes are given in Table 1.

Table 1:   **Initial Reservoir Sizes and D/H values**

Name N Latitude	**Area** 10^6**km**^{2}	**Reference**	q_o **Size (H atoms cm**$^{-2}$**)**	**Z equivalent ice thickness meters**	a_o **1=earth SMOW** **
Atmosphere 0-90N	72	Yung et al. 1988	5 x 10^{19}	8.1 x 10^{-6}	1
Ice Cap 75N-90N	2.5	Zuber et al. 1998	4.6 x 10^{27}	750 m * half the present	1

near surface ground ice 60N-75N	7.2	Boynton et al 2002	2×10^{26}	32 m #	1
..	..	..	6.2×10^{25}	10 m #	1
..	..	..	1.54×10^{25}	2.5 m #	1
Adsorbed regolith seasonal water 0-75N	69.6	Haberle & Jakosky,1990 ; Smith,2002	5.7×10^{19}	9.2×10^{-6} m	1
deeper ground ice 0-60N	62	Clifford 1993	6.1×10^{25} - 6.1×10^{26} ?	10 - 100 m ?	1

* the actual average thickness is 1500 m , the half is used here to allow for dust and to be conservative.

Boynton et al. (2002) have measured estimates of the ice content in the upper meter of polar regolith but these ground ice thicknesses do not contain any knowledge about how deep the lower boundary of this ice could be and the "estimates" are for the sake of calculation only.

** 1 is used here for the sake of argument but estimates from range from 1.2 to 1.6 for Mars initial water inventory ,(Lammer et al.,2005).

 Mass Loss Rates

   Space Losses; atmosphere to space

   The long term average space loss rate for H atoms Φ_1 is taken as a constant in time and geographically (Yung et al.,1988) as is the space loss rate for D atoms, Φ_2. An important fractionation factor R in Mars isotope studies is determined by a set of related photo-chemical reactions tempered possibly with some other still debated reactions , see introduction. R is defined ;

$$R = \frac{\Phi_2/\Phi_1}{[HDO]_o/2*[H_2O]_o} = \frac{\Phi_2/\Phi_1}{a_v(t)} \ldots \ldots (1)$$

where $[HDO]_o/2[H_2O]_o$ is the near surface water D/H ratio in the air. Φ_1 is about 1.6×10^8 [H atoms cm^{-2} sec^{-1}] and Φ_2 about 8.3×10^3 [D atoms cm^{-2} sec^{-1}](Yung et al.,1988) . R was thought to be about 0.32, but Krasnopolsky and Feldman (2001) have found that it is related to solar activity with and average value of 0.115, Table 2.

Table 2 Relationship between R and Solar Activity

Solar Activity	Low	Medium	High	Average
R	0.055	0.082	0.167	0.115

Here, the long term average space loss rate Φ_1 is held constant and made equal to the long term loss rate from the ice cap and regolith (surface to atmosphere) , but on shorter term the loss rate to space is allowed to vary arbitrarily using :

$$\Phi_1(t) = \overline{\Phi_1} + f_\Phi (\frac{q_{vo}}{P_\Phi}) \sin(\frac{2\pi t}{P_\Phi} + ph_\Phi) \ldots \ldots (2)$$

where P_Φ is a period in years q_{vo} is the present atmosphere's water content (see table 1) and f_Φ is an adjustable factor. (q_{vo}/P_Φ) sets the rate scale and $\Phi_1(t)$ is always positive. P_Φ could plausibly be a period found in production rates of C^{14} and Be^{10} . From terrestrial ice cores,(Beer et al. (1996; Lean,1996) have found that Be^{10} various with the 11 year solar cycle and also has a 2500 year 'periodicity' thought to be also related to solar activity. So Φ_1 was allowed to vary up to 9% around its mean. Also R was allowed to vary between the values suggested by Table 2 ,Eq.(3), both with a 2500 year period .

$$R(t) = 0.115 + 0.055 \sin(\frac{2\pi t}{P_\Phi}) \ldots \ldots (3)$$

Where P_Φ is a hypothetical 2500 year solar activity periodicity.

The total H loss to space by time t is denoted q_s and total D loss is Q_s .With the help of Eq.(1) :

$$dQ_s = \Phi_2 dt = R(t)\Phi_1(t)a_v(i,t)dt .... (4)$$

Using Eq.(4), and the assumption that the long term average ground loss rate ave(ε) equals the average space loss rate ave(Φ_1) , Yung et al.(1988) show that a_v will reach an asymptote of $a_v = a_{vo}/R$ in an e-folding time of $q_{vo}/(R\ \Phi_1)$; (for atmospheric water vapor of size $q_{io} = 5\text{x}10^{19}$ [H atoms cm^{-2}]) starting at a D/H of a_{vo} and being replenished at the constant rate $\varepsilon = \Phi_1$ with regolith reservoir vapor at with a D/H of a_{vo}). Using Yung's result and Krasnopolsky and Feldman's (2001) recommended average R=0.115, an a_{vo}=1 and with $\Phi_1 = 1.6\ \text{x}\ 10^8$ [H atoms cm^{-2} sec^{-1}] , one sees that the atmospheric value "quickly" reaches a stable value of $a_v = 8.69$ in about 8.6 x 10^4 a, ie less than an obliquity cycle.

Losses from Ground Reservoirs to the Atmosphere

The *net loss* from a reservoir i to the atmosphere is a function of time and denoted $\varepsilon(i,t)$. It is positive when the reservoir loses water to the atmosphere. The long term time average of $\varepsilon(i,t)$ is assumed to be equal to the long term average of the space loss flux , ie.

$$\overline{\varepsilon}(i) = \overline{\Phi}(i)$$

$\varepsilon(i,t)$, however is taken here to be periodic about the long term mean so that the net mass flux out or into the reservoir i is:

$$\varepsilon(i,t) = \overline{\varepsilon} + f_\varepsilon(i)(\frac{q_{vo}}{P_\varepsilon})\sin(\frac{2\pi t}{P_\varepsilon}) .... (5)$$

where the period is P_ε and f_ε is a factor to set the rate amplitude. The periodicity looked at here is the main obliquity period ~ 1.2 x 10^5 years. $\varepsilon(i,t)$ can be positive such that the atmospheric

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water content in i grows or negative and it shrinks. The two main 'ground' reservoirs are of course the North Polar Cap and the buried ground ice (see Table 1). The much smaller adsorbed water reservoir is probably periodically re-charged from these two larger reservoirs.

Although the net flux $\varepsilon(i,t)$ adequately represents the overall net mass balance from the ground to atmosphere , the seasonal gains and losses from the ground and ice cap within each year should be addressed because they no doubt have different D/H ratios and these changes effect the average D/H of the reservoir . For example water gained by the regolith or the ice cap during the cooling off part of the year will reflect the atmospheric D/H ratio ,ie. α $a_v(i,t)$, (where α is the vapor-solid fractionation coefficient for D/H (Yung et al. 1988), which will be discussed later) and water going from the regolith or ice cap into the atmosphere in the warming part of the year will carry the reservoir average D/H = $ave(a_g(i,t))$ which is an integration of the reservoir's history. This difference will be allowed for in the following manner. The summer loss rate (averaged over a year) is :

$$\varepsilon_l(i,t)=\overline{\varepsilon}+N(i)f_\varepsilon(i)(\frac{q_{vo}}{P_\varepsilon})(1+\sin(\frac{2\pi t}{P_\varepsilon}))........(6)$$

and the fall-winter gain rate (averaged over a year) is :

$$\varepsilon_g(i,t)=f_\varepsilon(i)(\frac{q_{vo}}{P_\varepsilon})[\sin(\frac{2\pi t}{P_\varepsilon})(1-N(i))-N(i)]........(7)$$

where $N(i)$ is an adjustable parameter that allows one to change the amplitude of the gain and loss functions while maintaining the net mass balance , Eq.(5) , ie $\varepsilon(i,t) = \varepsilon_l(i,t) + \varepsilon_g(i,t)$. What are the ranges of $\varepsilon_l(i,t)$ and $\varepsilon_g(i,t)$ for the ice cap i=1 and for the ground ice i=2 ? Fig. 1b shows in cartoon form the various fluxes.

The ranges are necessarily estimates . Presently the maximum polar precipitable water is about 75 x 10^{-6} meters, which is raised in 1/6 of a Mars year so the Mars year average loss rate is ~12 x 10^{-6} m/mars-year or ~ 7 x 10^{-6} m/a. Here it is considered a BIG seasonal loss/gain if $\varepsilon_l(i,t)$ >> 7 μ m/a , MEDIUM if $\varepsilon_l(i,t)$ ~7 μ m/a and a SMALL if $\varepsilon_l(i,t)$ <<<7 μ m/a.

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Table 3 gives the sizes of f_ε and $N(i)$ that are used in the VERY-HIGH, HIGH, MEDIUM and SMALL run cases reported later. The present maximum summer water content, annually averaged summer loss rate and the range of annual atmospheric water content q_v/q_{vo} (over the oblquity cycle) are given, for each case in Table 3. The ice cap zone, $i=1$, uses larger values than the ground ice ,$i=2$, zone.

Table 3, Low, Medium and Big cases of ground water flux to Atmosphere

Case i=1 ice cap i=2 ground ice	Secular flux factor for obliquity cycle $f_e(i)$	Seasonal factor for flux N	Ave summer water loss rate for ε_i $(t*2\pi/P_\varepsilon)=45$ μm/a	Approx Summer Max Precipitable water microns	q_v/q_{vo} Range of atmospheric water content for oblquity cycle
Small i=1	110	2	0.023	.25	1-36
Small i=2	24	2	.005	.05	1-9
Medium i=1	600	42	3	32	1-192
Medium i=2	120	42	.54	6	1-39
High i=1	2828	84	25	270	1-901
High i=2	707	28	2.1	23	1-226
Very High i=1	7070	210	125	1350	1-2300
Very High i=2	1768	70	12	125	1-570

The ground ice is arbitrarily assumed to have about 1/4 the secular amplitude and 1/3 the seasonal amplitude because its losses and gains are modulated by a lag of regolith.

With time , a ground or surface reservoir "i" loses or gains mass so that at time t :

$$q_g(i,t)=q_{go}(i,0)-\int_0^t \varepsilon(i,x)dx.......(8)$$

And the heavy isotope ,D, concentration in [atoms cm^{-2}] is $Q_g(i,t)$ and is:

$$Q_g(i,t)=\overline{a}_g(i,t)q_g(i,t)..........(9)$$

where $a_g(i,t)$ is the average D/H ratio for whole reservoir i at time t in absolute D/H . Since the ice cap is losing mass primarily from the dark scarps whose many layers are thought to represent ancient surfaces (isochrones) (see eg Toon et al.,1980; Howard et al.,1982; Fisher 1993) the

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water vapor lost can reasonably be assumed to have the temporal average a_g. For the ground ice, the assumption that exit flux's isotopic ratio is equal to the reservoir average is weaker, but gains some credence from the non-zero porosity of massive ground ice within 10s of meters of the surface (Fisher,2005). An simple estimate of the temporal average a_g for a reservoir i is :

$$\overline{a}_g(i,t) = \frac{\overline{a}_g(i,0)q_g(i,0) - \sum_0^{t-\Delta t} [\varepsilon_l(i,t)\overline{a}_g(i,t-1) + \alpha(t)\varepsilon_g(i,t)a_v(i,t-1)]\Delta t}{q_g(i,t)} \quad .....(10)$$

where the temporal average above attempts to take account of water vapor being lost ,$(\varepsilon_l(i,t))$, and gained $(\varepsilon_g(i,t))$ each season from the reservoir and the net balance $\varepsilon(i,t)=\varepsilon_l(i,t)+\varepsilon_g(i,t)$. Eqs. (6) and (7) and Table 3 define and specify the seasonal rates based on the arbitrarily specified net rate $\varepsilon(i,t)$, given by Eq.(5).

If the reservoir is (on net) losing mass so that $\varepsilon(i,t)>0$ then using Eq.(8) and Eq.(9) the change in heavy isotope concentration is :

$$dQ_g(i,t) = \overline{a}_g(i,t)dq_g(i,t) = -\overline{a}_g(i,t)\varepsilon(i,t)dt .....(11)$$

where the $(q_g da_g)$ term is a much smaller and has not been included. If each year the ice in reservoir is gaining on net , ie if $\varepsilon(i,t)<0$ then

$$dQ_g(i,t) = -\overline{a}_v(i,t)\alpha(t)\varepsilon(i,t)dt ......(12)$$

where $\alpha(t)$ is a (D/H) fractionation coefficient that applies to the phase change that brings the vapor into or onto the ice cap. If it were purely an equilibrium vapor to solid sublimation then α would be estimated by a function given by (Merlivat and Nief, 1967),

$$\ln\alpha = \frac{16.288}{T^2}x10^3 - 9.34x10^{-2}$$

The measurements behind this expression spanned only the temperature range   230<T<360 so much of Mars temperature range is missed. Extrapolating gives $\alpha = 1.43$ at T=190K . But authors have tended to be conservative in extrapolating α and instead use a constant for T below the known range. Yung for example just uses $\alpha=1.3$ for T=200 (Yung et al., 1988) . Fouchet and Lellouch (2000) use either extrapolated values or a constant α of 1.24 beyond the measured range. In any case α is probably a maximum and some authors (Jakosky,1991;McElroy and Yung, 1976) maintain that seasonal water vapor - ice transfers to and from the ice cap are complete and involve virtually no phase change fractionation, ie.$\alpha=1$.

Over the ice cap the water vapor 'dome' is mostly removed by Ls=180 (Smith 2002), before the CO_2 begins to accumulate there (Smith et al., 2001). In the northern spring and early summer the water dome does not start growing until after most of the CO_2 seasonal cover has departed. Thus there does not seem to be any significant water ice accumulation by precipitation on the North Cap. This is probably true everywhere.

Any water vapor that gets trapped within the regolith before subliming would take all its isotopes with it and effectively undergo little free air to regolith   fractionation. But there would be some isotopic fractionation caused by molecular diffusion , whereby the lighter water species has a slightly larger diffusivity coefficient. Since even ice saturated regolith and presumably the surface of the cap itself have non-zero porosity due to thermal cracking (Fisher ,2005) , vapor penetration and limited fractionation are probable. So for the phase change fractionation of Eqs. (10,12) α is in the range $1 <\alpha <1.35$. If water is sublimated from the air onto a surface or if ice crystal clouds form and fall then α should be at the high end of the range.

The Atmospheric Balance

The atmosphere loses water to space everywhere at rate $\Phi_1(t)$ and either gains it or losses it from reservoir i at net rate $\varepsilon (i,t)$. At any time t the atmosphere's water content is $q_v(i,t)$ and is:

$$q_v(i,t)=q_v(i,0) - \int_0^t \Phi_1(x)dx + \int_0^t \varepsilon_1(x)dx.......(13)$$

and the D concentration is : $Q_v(i,t)=a_v(i,t)q_v(i,t)$ so that :

$$dQ_v(i,t)=a_v dq_v+q_v da_v=a_v(i,t)[\varepsilon(i,t)-\Phi_1(t)]dt+q_v(i,t)da_v(i,t)....(14)$$

The Overall Balance for D in The Atmosphere, Ground and Space

If there is no mixing between types of zone , then at each time step:

$$dQ_s(i)+dQ_v(i)+dQ_g(i)=0........(15)$$

When the expressions for the above differentials given in Eqs.(4,11,12 and 14) are substituted into Eq.(15) and the terms gathered then :

$$\frac{da_v(i,t)}{dt}=-[\frac{a_v(i,t)(R(t)-1)\Phi_1(t)+\varepsilon(i,t))-E(i,t)}{q_v(i,t)}].....(16)$$

where :   If $\varepsilon(i,t) \geq 0$ then :

$$E(i,t)=\overline{a}_g(i,t)\varepsilon(i,t)$$

and if $\varepsilon(i,t) < 0$ then :

$$E(i,t)=\alpha\varepsilon(i,t)a_v(i,t)$$

Eq.(16) can be solved for a given single zone , using a fourth order Runge Kutta procedure (Press et al.,1986) when the above defined arbitrary functions for vapor fluxes and resultant reservoir averages are used , ie Eqs.(2,3,5,6,7 and 10). For example with a single zone and a constant flux assumption, the Yung et al. (1988) result described earlier can be obtained.

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Mixing

On earth the non-condensing gases of the atmosphere mix completely in a year (Brook et al.,1996) but volcanic aerosols take about 3 years to flush out of the air (Clausen and Hammer,1988) and very fine solid dust particles have about the same lifetime , (Junge, 1963). The airborne lifetime for a typical water molecule is about 10-20 days (from evaporation to re-precipitation) during which , it can travel about 1000 to 5000 kms (Fisher,1990). If it gets captured by an ice cap it then can reside under the surface for a very long time (10^5 to 10^6 years ; Greenland and East Antarctica respectively). Capture in the Earth's permafrost system also results in similar retention times . If the water molecule ends up in the deep ocean , it could remain there for a few thousand years and in the ocean's active layer (upper ~100m) a few centuries (Broecker,1982) . So a terrestrial mixing time for earth's non-ice cap and non-ground ice water is the range 100 - 2000 years .

Suppose plausibly that the Northern ice cap and major ground ice reservoirs are confined respectively to the latitude zones 75-90N and 60-75N degrees of latitude. There is readily accessible near-surface adsorbed water at all latitudes.

Since the parameters, such as mixing time in the modern Mars climate are uncertain and since in the distant past they are unknown completely , the simplest possible scheme is used to couple the two main zones together . Then the coupled zone runs for many mixing times will be reported in an effort to establish sensitivities and a few fixed points independent of these sensitivities.

The simplest change to the balance Eq. (15) is :

$$dQ_s(1)+dQ_v(1)+dQ_g(1)=a_v(2,t)dq_{vex}(2,t)(S(2)/S(1))-a_v(1,t)dq_{vex}(1,t)(S(1)/S(1))........(17)$$

$$dQ_s(2)+dQ_v(2)+dQ_g(2)=a_v(1,t)dq_{vex}(2,t)(S(1)/S(2))-a_v(2,t)dq_{vex}(2,t)(S(2)/S(2))........(18)$$

where dq_{vex} is the amount of water transported from one zone to the other in dt and S(1),S(2) is

the area of the ice cap zone and the total area of the ground ice zone. Since the ice cap zone is presently 1/3 the area of the ground ice zone and since atmospheric water content in the ice cap zone is always set at 3 times that of the ground ice zone eqn is simplified by having (assuming $dq_{vex}(i,t) \propto q_v(i,t)$) :

$dq_{vex}(2,t)[S(2)/S(1)] = dq_{vex}(1,t)[S(1)/S(2)] = dq_{vm}$ so that Eq.(17) & similarly Eq.(18) becomes:

$$dQ_s(1) + dQ_v(1) + Q_g(1) = [a_v(2,t) - a_v(1,t)]dq_{vm}........(19)$$

where dq_{vm} is the exchanged q between zones 1 and 2 in time interval dt and is positive definite . With the exchange term in the balance Eq.(19) , Eq.(16) becomes for zone 1 :

$$\frac{da_v(1,t)}{dt} = -[\frac{a_v(1,t)(R(t)-1)\Phi_1(t)+\varepsilon(1,t))-E(1,t)}{q_v(1,t)}] + [\frac{(a_v(2,t)-a_v(1,t))}{q_v(1,t)}]\frac{dq_{vm}}{dt}.....(20)$$

There is a similar equation for zone 2 and they are solved together using the fourth order Runge Kutta procedure, (Press et al.,1986). Estimating dq_{vm}/dt could in principal come from a GCM or other type of physical model that included an atmosphere , an icy regolith and an ice cap with a protective surface lag feed back but no such model exists yet and the run times to get to interesting model elapsed times would be prohibitive. Also the accurate model constants and many of the boundary conditions are unknown. So a very rough method will be used to include this mixing term and a range of mixing strengths are tried and the results reported. So dq_{vm}/dt is estimated simply by:

$$\frac{dq_{vm}}{dt} = f_m.\frac{Min[q_v(1,t),q_v(2,t)]}{P_\varepsilon}.....(21)$$

where "Min" selects the minimum of the functions in the argument , P_ε is the periodicity of the ground flux forcing function for both reservoirs and f_m is a constant scaling factor $0 \le f_m \le \infty$. The relationship between the order of magnitude the time needed to mix the isotopic values for

the two zones would be : P_ε / f_m . So if an $f_m = 10$ and $P_\varepsilon = 1.2 \times 10^5$ years the mixing time is of order 1×10^4 years. The real mixing time is unknown but a range can be tried by picking f_m and this is done and presented over a range from 500 to 10^5 years.

Results and Discussion

The results are meant to underline the sensitivity that this very simple model has to reservoir size, accessibility, solar activity and the rate of exchange between the ice caps, polar ground ice and lower latitude ices. The case will be made that the modern atmospheric D/H average could be explained with a host of possible water ice reservoir histories. An argument is also made that a good way to start to start to unravel the Mars water reservoir sizes and histories is to get a depth (time) profile of D/H from the North Cap. The average value and the sizes of the D/H "Milankovic" obliquity cycles in the North Cap should offer a window into many aspects of the water cycle.

Fig. 2 shows what happens when the model is driven by a constant obliquity cycle . It presents the long term evolution of the model's ice cap average a_g and the range of obliquity driven atmospheric a_v values for the 4 cases . Fig.2 uses runs in which the ice cap zone is coupled with a polar ground ice zone that contains 4 m of ice and with the effective atmosphere the mixing parameter $f_m = 2.5$ corresponding to 48×10^3 years. The runs all assume the average a_g and a_v start at 1. For the SMALL case the flux rates to the atmosphere are so slow that the average a_g stays close to its start value of 1. The ice in the ice cap does not even exchange with the atmosphere once during the nominal 3×10^9 years. But the MEDIUM, HIGH and V-HIGH cases h the ice cap a_g ends up at 3.1, 5.4 and >50 respectively. The size of the obliquity D/H variation decreases at the higher exchange rates and the number of times the complete ice cap mass goes through the atmosphere is 6.8 , 64 and 403 for MED, HIGH, V-HIGH cases, see table 4.

TABLE 4 North Caps bulk D/H and stability

Case	Bulk D/H ice cap average	Number of turnovers of ice cap mass	3×10^9 yrs/number of turnovers , years
SMALL	1.1	0.06	NA
MEDIUM	3.1	7	4×10^8
HIGH	5.4	65	5×10^7

VERY HIGH	> 20	400	7×10^6

 The model cycles the ice cap through the atmosphere so many times because of the $N(i)$ factor (that 'simulates' the seasonal ablation rate) is much greater than the net rate . Of course the real ice cap - ground ice pair have not been in their present locations for such a long time but the model is in fact so simple one could imagine that the model does not require a fixed location for the zones, only   that the water vapor follows the seasonal and net flux rates set by the model constants . So these runs could set lower limits for a migrating ice- cap-ground ice couple .What is not captured in using this model to "migrate" the zones is the zones relative areas and mixing constraints. If an ice cap and ground ice reservoirs were really moving as suggested for example by (Head   et al.,2003;Mischna et al.,2003) then the inter-zone mixing would be greater and the areas would be time variable. Both effects one would expect would drive the bulk average D/H to values higher than suggested by these model runs. The longer time the water spends in the air the bigger gets D/H .The V-HIGH case would seem to be excluded because it cycles the entire ice cap mass so many times through the atmosphere (>400 times) that very high D/H are produced exceed ~50 !.

    In an observational sense, the 4 cases at any given age could be separated by the average a_g for the ice cap and the amplitude of the obliquity cycle in D/H.   Being able to get the D/H obliquity amplitude from layer to layer is presently beyond remote methods resolution . If the average D/H at maximum Pr is between 2 and 4 the extreme V-HIGH case would be very unlikely and point rather at the MEDIUM or HIGH cases for the water exchange rates between ice cap and ground ice reservoirs , at least for this simple model. The age of the oldest ice in the cap is of course unknown and depends partly on whether it flows or not, which is still debated.

    During the 3×10^9 years there have been episodic losses and gains in water (Clifford,1993) that has been left accessible to the surface. It is assumed the losses in Mars' early life left the remaining inventory with an average D/H of 1 . The deep sequestration of water in a ground water system (Clifford,1993) of unknown quantity with an uncertain flux rate means that the model assumption of no long term constant out-flux of "new" D/H water need not be right. The simplest deviation form this assumption is to set the second zone (i=2) to have a constant flux from the very deep regolith to the atmosphere equal to the space loss rate as before, but have the

flux completely constant and from a reservoir ten times larger than the ice caps with a_g=1.0 (Earth's ratio) and covering the 60-75 latitude zone. If this hypothetical very large subsurface reservoir was alone on the planet, its atmospheric D/H would be at Yung's asymptote of 8.67. If there was a sudden doubling of the exit rate (through sustained hydrothermal events say, (Neukum et al.,2005)) that lasted a few tens of thousands of years then the atmospheric D/H over this hypothetical very large subsurface reservoir would drop from 8.67 to about 2 relatively quickly , shown in Fig. 2c.

But if instead of being isolated, this very large reservoir shared Mars with a surface ice cap reacting to obliquity cycles (HIGH case) then the D/H of the atmosphere would be somewhat different. Depending on the model's adopted mixing factor f_m this results in an average ice cap $a_g(1)$ that converges with the atmospheric value over the ground ice zone $a_v(2)$ as shown in Fig. 2b. In this mixed case , if a sudden introduction of 'old' a_g =1 water , (say from the volcanoes thought to active in recent times very near the North Cap (Neukum et al., 2005)) would cause a sudden and time limited reduction in the $a_v(i,t)$ at a time which would have corresponding depth in the ice cap. For example in Fig. 2b for f_m=50 , a sudden doubling in the exit flux from hypothetical deep large reservoir would drive the ice caps overall average a_g from the 1.7 (of Fig. 2b) to 1.5 and show up within a few 10s of thousand years *in the atmospheric value of a_v* and thus in the ice cap layer's D/H , (Fig. 2c) . These sorts of changes in the average D/H of the layers would be readily picked up in an ice core record from the ice cap. Especially if it was accompanied by an increase in net accumulation and other climate related variables (eg dust).

The ice cap interacting with a very large subsurface reservoir is the end case of what is examined and shown in Fig. 3 , which shows for 3 surface flux amplitudes cases (SMALL, MEDIUM,HIGH) the bulk D/H averages for an ice cap interacting with reservoirs of various start sizes. The run times are 3×10^9 years (the mixing factor f_m used is 2.5) but the result that is illustrated would be the same for shorter runs and other f_m 's, namely that the smaller the "other" reservoir the larger becomes the ice cap's bulk D/H= $a_g(1,t)$.In Fig. 3b, the heavy gray line shows how much of the non-ice-cap reservoir is left after the run. The smallest survivable reservoir size is about 2.5 m . Of course the bulk average D/H of these reservoirs also changes and average $a_g(2,t)$, for the ground ice, is shown in Fig. 3b. The smallest reservoirs end up with the largest bulk average D/H. They can of course greatly exceed the 8.67 Yung asymptote ,

because the ice gets recycled many time gaining in D/H each time. The most accessible of the reservoirs, the adsorbed water in the lower latitudes probably has very high D/H for this reason. Mumma et al. (2003) seasonal measurements of D/H suggest that the further away from the polar regions and the colder the season , the larger the D/H value. This is probably because the smallest reservoirs especially in the lower latitudes are every year the first out and the last back into the ground. This could also contribute to an "up-side-down" vertical structure of D/H in the atmosphere that is observed in at least some seasons (Krasnopolsky and Feldman,2001 . The effects of changing f_m for the MEDIUM case of the ice cap and a   4m reservoir is pictured in Fig. 4. Larger f_m means faster mixing times. The ice caps bulk average D/H at 3×10^9 years is between 2.5 and 3.5 and is only weakly dependent on the size of f_m, see lower solid line in Fig. 4. This is good because f_m is poorly constrained. The maximum-minimum difference of the atmospheric D/H over the ice cap over an obliquity cycle depends somewhat on f_m, the vertical bars in Fig. 4c The effects of f_m are considerably larger on the bulk D/H of the the 4 m reservoir , which is intuitively expected for a smaller reservoir that can get completely run through the atmosphere many more times than the larger ice cap.

So the average bulk ice cap D/H depends on the size of the other reservoirs and on the vigor of the various forced changes (obliquity , solar cycles etc). Fig. 5 shows an example of what might be found in an ice cap vertical profile. It shows the results of obliquity (and solar) forcing on the atmospheric D/H over the large ice cap reservoir coupled to a   4m polar ground ice reservoir. Fig. 5a plots the obliquity driven changes in D/H for the atmosphere over the ice cap and over the 4m reservoir, at $t=3 \times 10^9$ years . The former would essentially be the values found in the layers of the ice cap. In Fig. 5a atmospheric D/H over the ice cap has a small wiggle, which is expanded in the inset of Fig.5a .This wiggle is due to the small forcing provided by the (Krasnoplosky and Feldman,2001) change in R(t) and in a small (9%) prescribed periodicity about the mean for the space loss rate Φ , both assumed to be in phase and having period periods of $P_\Phi = 2500$ years. The size of the "solar wiggle" increases as D/H increases and the air water content goes down. The wiggle amplitude here varies between 0.002 and 0.1 (peak to trough) on the D/H scale for high and low accumulation rate , which would be 2 and 100 o/oo respectively on the $\delta(D)$ scale wrt   SMOW.

Fig. 5b plots the model atmospheric D/H over the ice cap and polar ground ice reservoirs

versus the relative water content over these zones (using the MEDIUM case and f_m=2.5). All the D/H vs relative water content curves have a hysteresis form .Also plotted is the Mumma et al. (2003) observed atmospheric D/H vs precipitable water column height in microns for Northern summer. It is assumed here that the sub surface reservoirs have smaller ground loss amplitudes around the common mean than the ice cap , see Table 3. This is arbitrary but conforms to the present North cap polar ground situation as suggested by Pr vs Ls measurements for different latitude bands (Smith,2002 ; Haberle and Jakosky,1990). It would seem that the observed range and general shape of the Mumma et al. (2003) seasonal data follows the space mapped out by the hysterisis loops. The low latitude adsorbed water is probably a relatively small reservoir that has get re-charged often from one of the ground ice reservoirs and as a result it would have a large D/H as discussed above. It could provide the larger D/H values at all phases of the water cycle when most other reservoir water had departed the atmosphere .

Speculations : What might be found by coring the North Cap

On the basis of these simple model results, a vertical core or profile in the North Cap would be expected to show variations in D/H with various periodicities and amplitudes. The obliquity cycle (1.2×10^5 years) would show up as spiky Milankovitch type variations with a peak to trough amplitude of 1 to 2 (1000 to 2000 o/oo in δ(D)) and possibly riding on top of them a smaller solar wiggle (2500 year period) with peak to trough Δ(D/H) of 0.002 to 0.1 (2 to 100 o/oo on δ(D) scale) in intervals of high and low accumulation rate (low and high D/H).

Any large sustained injections of low D/H water from a hypothetical very deep large reservoir would show up within a few thousand years in the ice cap as a trend in the D/H averaged over obliquity cycles.

The above issues are all related and further related to the massive ice found by Odyssey (Boynton et al.2002) north of latitude 60 in the upper few meters (and maybe deeper). The ice contents that they found in the higher latitudes suggest lower limits for the upper meter of regolith of up to 85% by volume of ice , which can not be reasonably produced by simply filling soils' dry void space with ice. One of the explanations of its formation is coupled to the migrating North Cap idea, namely that a layer of snow and ice is laid down using ablated water ice from the ice during warm periods in the obliquity cycle then covered over by soil and dust (Head et al., 2003). An alternative process for generating the massive ice layers relies on the water vapor-ice back

filling of thermal cracks produced by the downward moving seasonal temperature wave. The cracking wave process can produce massive ice in situ over a few million years using a more gentle diffusion of water from above or below. So the massive ice does not in theory necessarily need a major migrating ice cap reservoir. Would the D/H of the massive ice layers contain any residue of the process that produced them ? As Fig. 5 shows the average D/H of any given reservoir depends on its size . Unlike in the case of the ice cap , there is presently no thickness for these massive ice layers are known .Their average D/H ,could suggested by the "rising Pr" branch of a Mumma et al. type D/H vs Pr curve . Their furthest north latitude measurement for D/H is near the maximum Pr at Ls=123 is for a latitude of ~45 wrt the sub-solar point or in other words for real latitude ~68 N, which is in the middle of the massive ice zone. Here Mumma at al.(2003) Have measured D/H at 2.3 ! Since this is virtually at the maximum Pr for this latitude, there is no re-condensation fractionation so this value should be close to that seeping out of the ground. This value can hopefully be checked by the D/H measurements that the Phoenix Polar Mission will provide both for the atmospheric water and the top of the ice table at latitude ~65 N. If this max (lat 68.Ls=123) D/H= 2.3, is confirmed in the air and the ice , then this strongly suggests that the ice in the massive ice layer is forming in situ from diffusion vapor derived probably from an North Cap which is fairly stable geographically and whose bulk D/H average is a little higher than 2.5 ,(because Ls=123 is slightly after the actual peak Pr that occurs at Ls=118). Time and data will tell.

But what of the most interesting question left unanswered; " how large was the original water inventory and how much is left ?" All that this simple model work suggests is that the previous use of single values for atmospheric D/H to infer initial water reservoir size seems doomed to error , because D/H varies seasonally , geographically , over obliquity cycles , through possible migration episodes and secularly. Bulk average D/H for the ice cap, $a_g(1,t)$, would be a better number to use (ie the minimum D/H for Pr=100 microns,Ls=118) but between that figure and a good estimate of total initial water reservoir size stands the need to have the sizes and accessibility scale times for all the various sub-reservoirs. Having a long time series of D/H from the ice cap with all its possibly rich texture of variation and secular trends would provide a much better platform for making the estimate .

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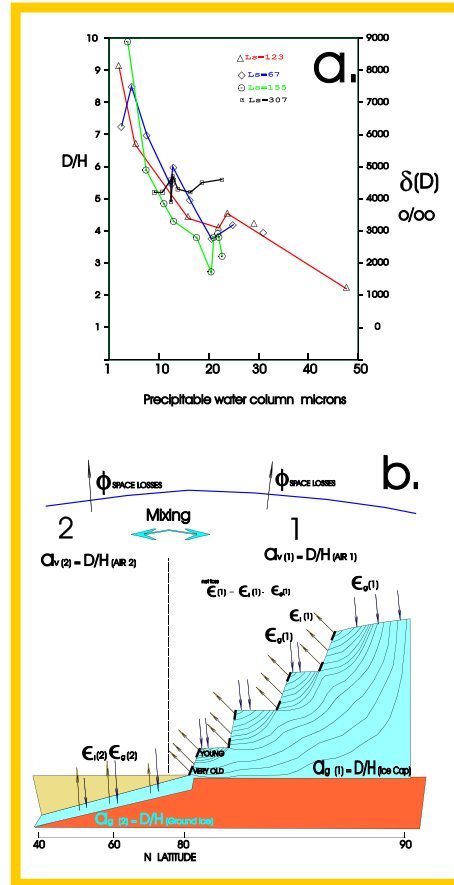
Figures:

Fig. 1 a) reproduces the Mumma et al., (2003) D/H vs Pr the precipitatble water content .
b) Shows the main reservoirs (1=ice cap; 2= ground ice) and the flux between the reservoirs and the atmosphere. In a given Mars year the annual average gain on the ice cap is ε_g (1,t) in [H atoms] cm^{-2} a^{-1} and the year averaged loss is ε_l (1,t) so that the net mass balance over the whole ice cap is $\varepsilon(1,t) = \varepsilon_l(1,t) - \varepsilon_g(1,t)$. $\varepsilon(1,t)$ is a prescribed function in the model (eg varies with obliquity). For the ground ice zone there are similarly defined averaged gain ,loss and net balance functions, but with different amplitudes etc. The flux loss to space, Φ_1 is the same for all zones but is also prescribable in time. The average D/H for the air in zone 1 is $a_v(1,t)$ and for the ice reservoir is $a_g(1,t)$. Between the zones 1 and 2 is some mixing , with a scale time for completely mixing the zones prescribed in the model .
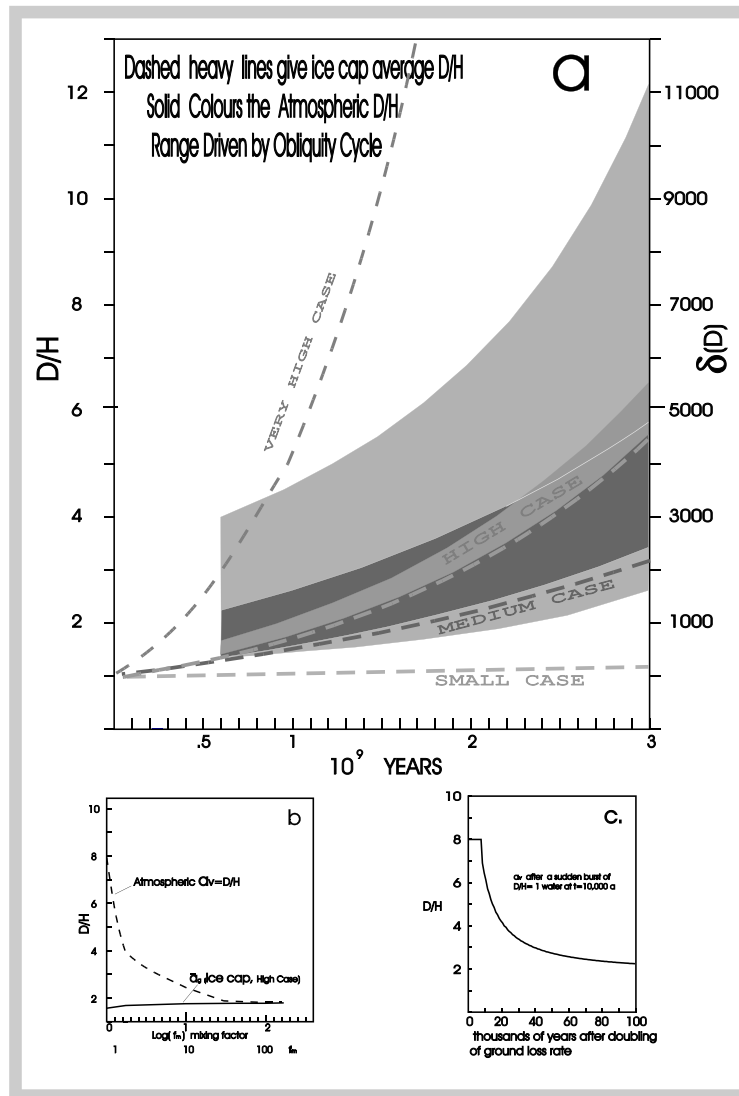
31

Fig. 2. a)   Evolution of D/H of the ice cap over 3×10^9 years starting with atmospheric and ice reservoirs with D/H=1. The ice cap exchanges with a ground ice reservoir which is initially 4 m thick. The evolution of the ice caps bulk average D/H are the thick dashed lines ; High , Medium , Small and very High Cases   assume a fixed 120000 year obliquity period. The gray regions denote the amplitude of the atmospheric D/H variations over the pole due to the obliquity cycle changes .It is assumed here that the atmospheric water mixing factor is $f_m = 2.5$. 2b) If the ground ice reservoir is 10 times larger than the ice cap and has D/H=1 throughout and if

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the water leaks slowly out from this reservoir at a constant rate equal to the loss rate to space, then after 1 Ga the ice cap's bulk average moves from its start value,1, to about 1.7 almost regardless of the atmospheric mixing factor (Time).

2c.) If a very large isolated ground reservoir for which the bulk average D/H= 1 suddenly doubles its loss rate to the atmosphere , then the atmospheric D/H changes from ~8 to 2 in only 30 ka.
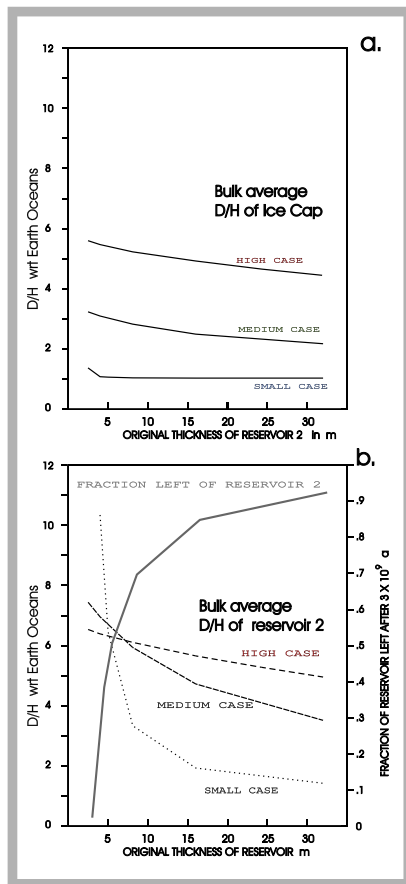
Fig. 3 a).The bulk average D/H for the North Cap for High, Medium and Small water flux (reservoir<->air) cases vs the initial size of the ground ice reservoir that interacts with the North Cap with an atmospheric mixing set at f_m=2.5.

b) Same thing as above except it gives the average D/H for the ground ice reservoirs of different sizes after 3 billion years. The thick gray line shows what fraction of the original ground ice reservoir is left after 3 billion years
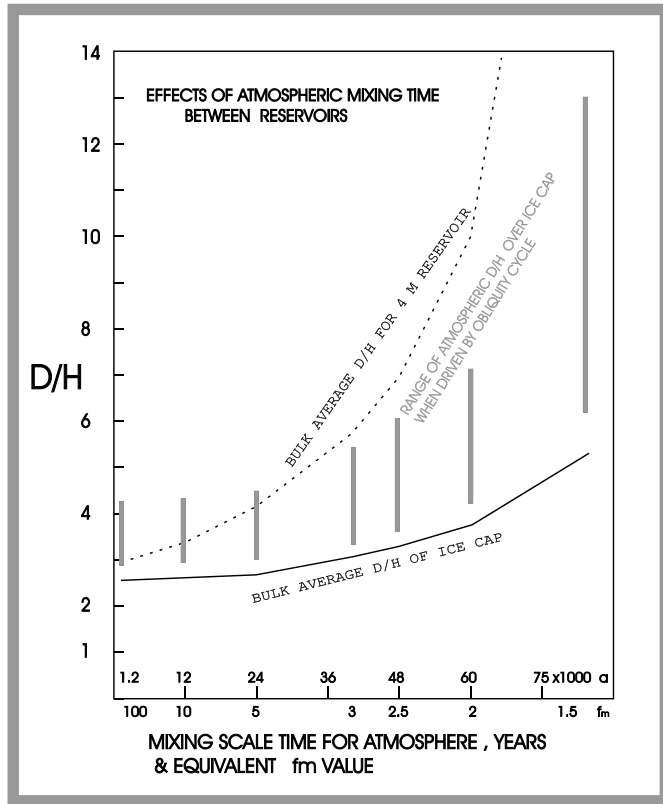
Fig. 4 . The effect of mixing time of water in the atmosphere on the evolved bulk average D/H after 3 billion years. The black solid line is for the bulk average D/H for the North Polar Cap and the dashed is for a ground ice reservoir that starts out 4 m thick. The water vapor from the ice cap and the ground ice zones intermingle completely mixed over the number of years given on the bottom axis. The gray bars give the range of atmospheric D/H over an obliquity cycle over the North Cap.
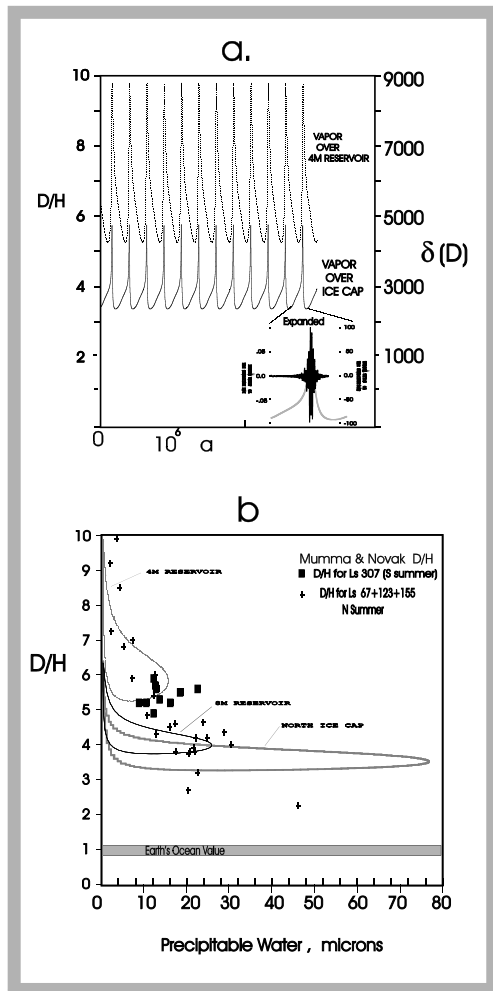
Fig. 5 a) Model Time Series of D/H over the North Ice Cap (solid black) and over the Northern ground ice zone (dashed) assuming a MEDIUM case atmospheric water vapor amplitude (spans about 2 orders of magnitude in water content), f_m=2.5 mixing factor for the atmosphere and assuming a constant obliquity amplitude of period 120,000 years. One of the main drivers of D/H in Mars water cycle is R the fractionation factor that arises from preferred loss of lighter species at the top of the atmosphere.   This figure shows the residuals from the smoothed obliquity. This "solar wiggle" has the highest amplitude when the net accumulation rates (water content) are the lowest .The peak to trough D/H wiggle amplitude ranges from 0.002 to o.100 (corresponding to 2 to 100 o/oo in the δ(D) scale.

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b). The hysteresis loops of D/H vs water content for atmospheric water over the polar cap and over the 4m ground ice zone and 8 m ground ice . The crosses and squaress are measured data D/H vs precipitable water column (Mumma et al.,2003;Novak et al.,2005).