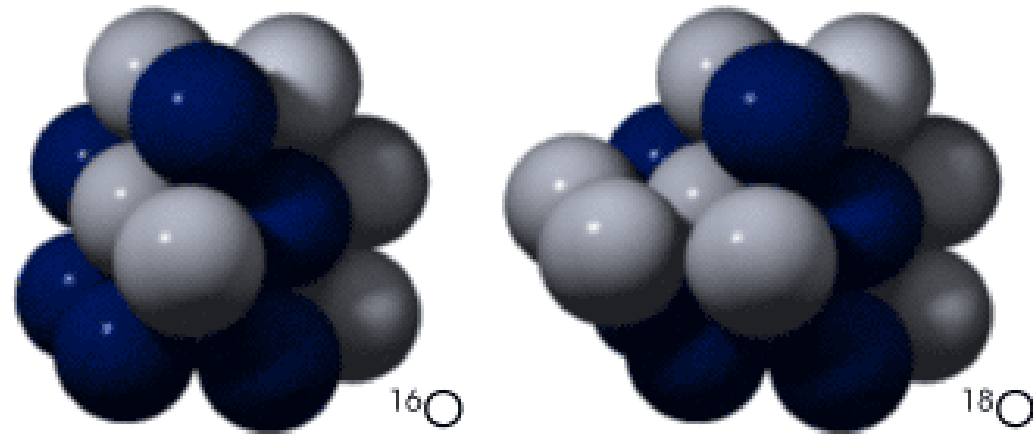
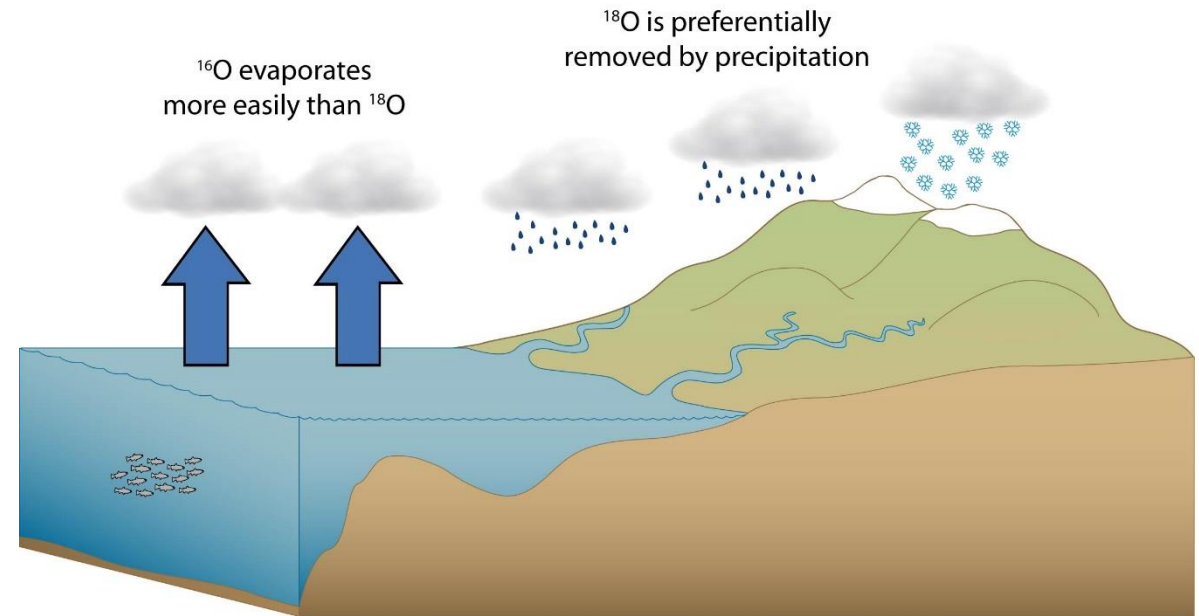
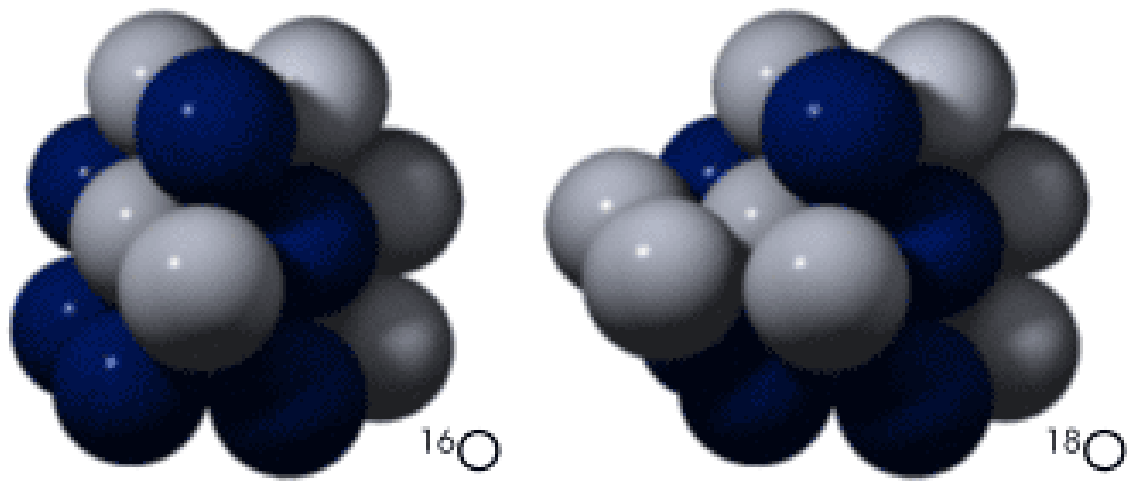


Isotopic measurements for the Mars Ice Cap

-Matt Siegler PSI/SMU KISS workshop

- 1) Temperature dependent fractionation of stable isotopes ($^{18}\text{O}/^{16}\text{O}$, D/H)
- 2) Cosmogenic Nuclides (^{10}Be , 1.4 Myr half-life)





^{16}O , ^{17}O and ^{18}O oxygen isotopes are stable and occur naturally in various proportions (99.76, 0.035 and 0.20 %, respectively)

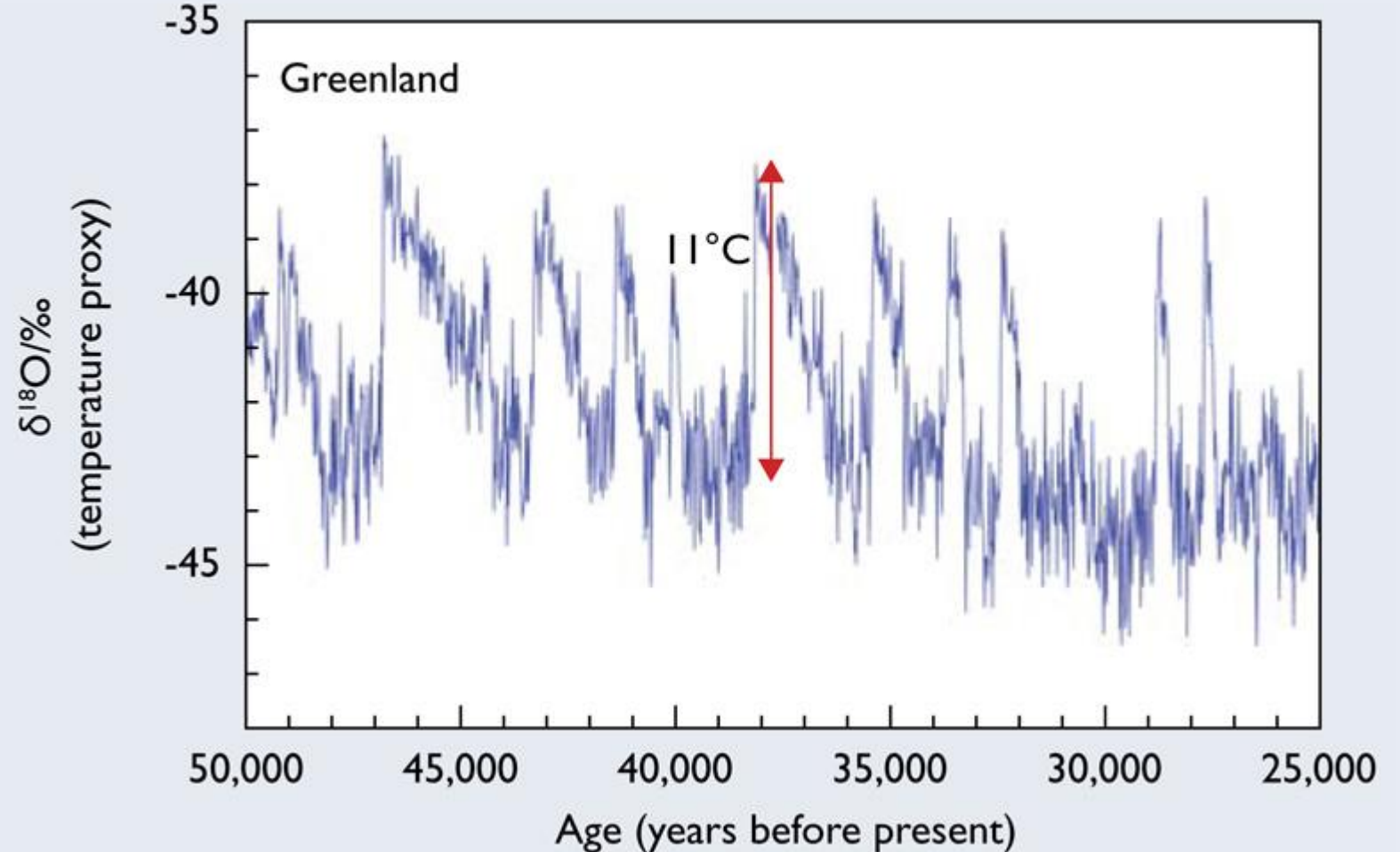
When clouds form over the ocean, **fewer of the heavy isotopes will evaporate, resulting in clouds that are depleted in ^{18}O** . When these clouds then move over land and start to produce rain, **the molecules containing the heavy isotope will rain out first. This results in rain containing less and less ^{18}O , the further you go land inwards.**

This is used regularly and a temperature proxy for global (really ocean reservoir) temperature variation.

This does not necessarily record the temperature at the ice cap, but really the temperature at the reservoir from which the source water evaporate.

What would this reservoir on Mars be and what would its initial $\delta^{18}\text{O}$ be?

Fig. 5: Oxygen isotope ratio (temperature proxy) from the NorthGRIP (Greenland) ice core showing a sequence of rapid temperature jumps⁽⁸⁾

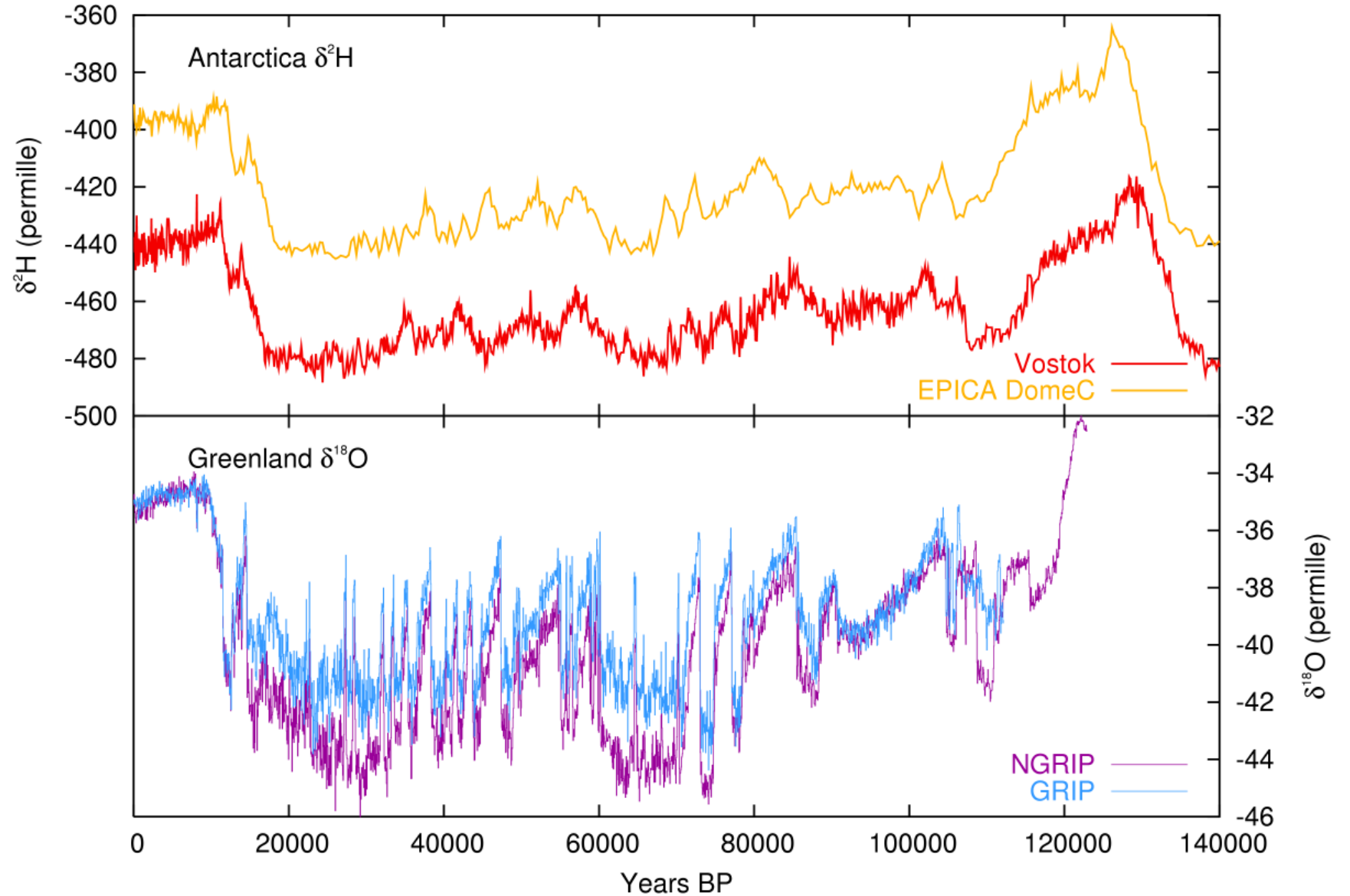


Likewise, making the water more massive by adding a neutron to the H instead of the O.

So on Earth, we have two clear temperature proxy isotopes-

But again, what would this variation look like on Mars and what would our reservoir be?

Isotope data for Antarctic and Greenland ice cores



Stable isotope measurements have to be in reference to something. On Earth, we have a mixed reservoir of the oceans and have settled on “SMOW” (Standard Mean Ocean Water) as a D/H $^{18}\text{O}/^{16}\text{O}$ ratios.

People have tried to make models of Mars mixing based on assumed initial sources (e.g. Fisher, 2005) which show there should be D/H modulation around “SMOW”.

As H is lost, Mars “SMOW” will get higher D/H over time, but at different rates at each source.



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Icarus 187 (2007) 430–441

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Mars’ water isotope (D/H) history in the strata of the North Polar Cap: Inferences about the water cycle

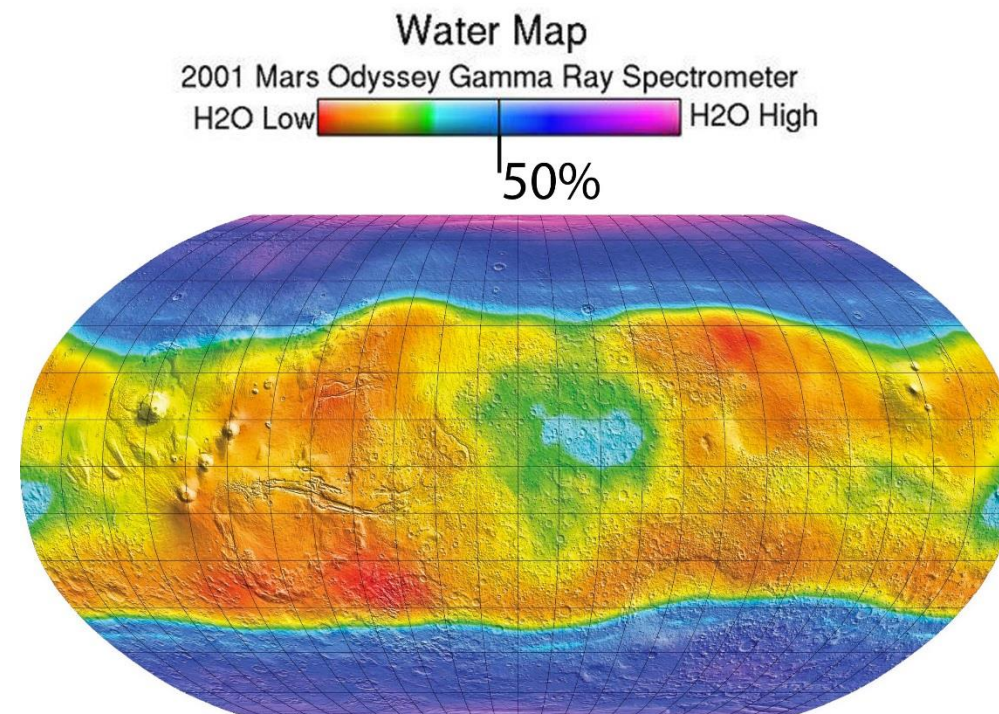
David Andrew Fisher *

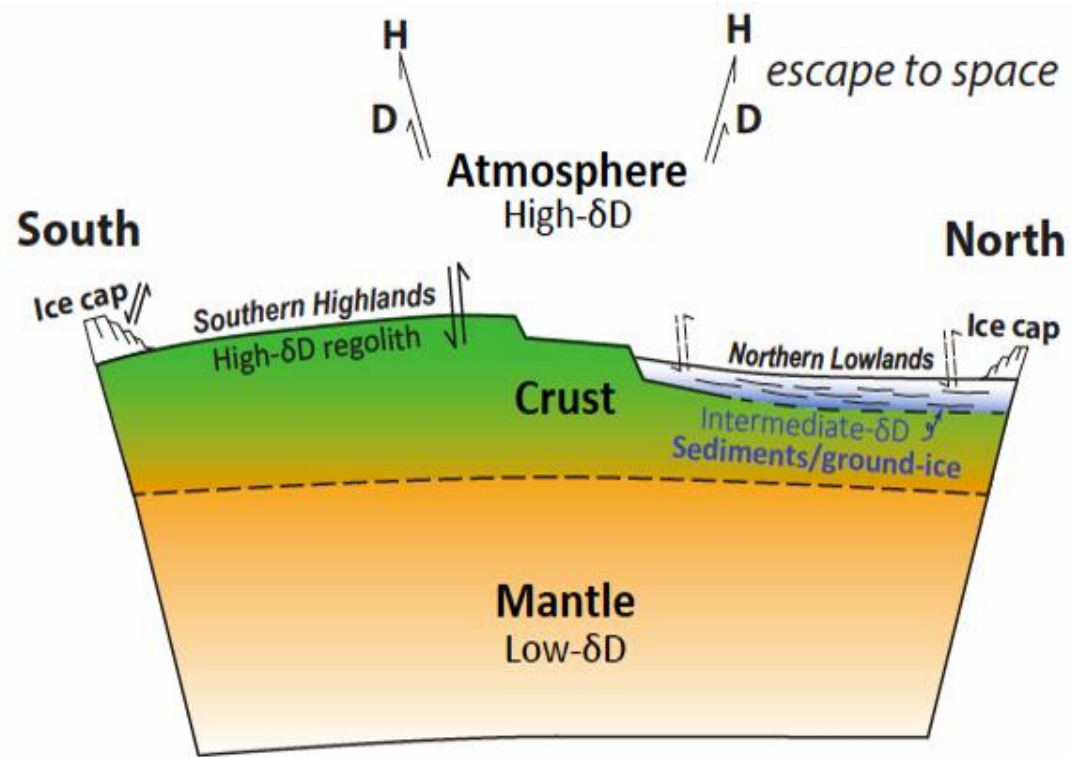
Glaciology Section, Geological Survey of Canada, NRCan, 601 Booth Street, Ottawa, Ontario K1A 0E8, Canada

Received 8 May 2006; revised 22 September 2006

Available online 19 December 2006

Name N latitude	Area 10^6 km^2	Reference	q_0 size (H atoms cm^{-2})	Z equivalent ice thickness meters	a_0 1 = Earth SMOW ^c
Atmosphere 0–90 N	72	Yung et al. (1988)	5×10^{19}	8.1×10^{-6}	1
Ice cap 75–90 N	2.5	Zuber et al. (1998)	4.6×10^{27}	750 m ^a half the present	1
Near surface ground ice 60–75 N	7.2	Boynton et al. (2002)	2×10^{26}	32 m ^b	1
–	–	–	6.2×10^{25}	10 m ^b	1
–	–	–	1.54×10^{25}	2.5 m ^b	1
Adsorbed regolith seasonal water 0–75 N	69.6	Haberle and Jakosky (1990); Smith (2002)	0.6×10^{15}	1 m	1
Deeper ground ice 0–60 N	62	Clifford (1993)	6.1×10^{25} – 6.1×10^{26} ?	10–100 m?	1





Martian Meteorite measurements have constrained this D/H evolution. This illustration depicts Martian water reservoirs. Recent research provides evidence for the existence of a third reservoir that is intermediate in isotopic composition between the Red Planet's mantle and its current atmosphere. These results support the hypothesis that a buried cryosphere accounts for a large part of the initial water budget of Mars.

Meteoritic evidence for a previously unrecognized hydrogen reservoir on Mars Usui et.al Volume 410, EPSL, 15 January 2015, Pages 140-151

Based on *in situ* hydrogen isotope (D/H) analyses of quenched and impact glasses in Martian meteorites, we provide evidence for the existence of a distinct but ubiquitous water/ice reservoir (D/H= \sim 2–3 times Earth's ocean water) that lasted from at least the time when the meteorites crystallized (173–472 million years ago) to the time they were ejected by impacts (0.7–3.3 million years ago), but possibly much longer. The origin of this reservoir appears to predate the current Martian atmospheric water (D/H= \sim 5–6 times Earth's ocean water) and is unlikely to be a simple mixture of atmospheric and primordial water retained in the Martian mantle (D/H \approx Earth's ocean water). This reservoir could represent hydrated crust and/or ground ice interbedded within sediments. Our results corroborate the hypothesis that a buried cryosphere accounts for a large part of the initial water budget of Mars.

Strong water isotopic anomalies in the martian atmosphere: Probing current and ancient reservoirs

G. L. Villanueva,^{1,2*} M. J. Mumma,¹ R. E. Novak,³ H. U. Käufel,⁴ P. Hartogh,⁵
T. Encrenaz,⁶ A. Tokunaga,⁷ A. Khayat,⁷ M. D. Smith,¹
Science 10 APRIL 2015 • VOL 348

We measured maps of atmospheric water (H₂O) and its deuterated form (HDO) across the martian globe, showing strong isotopic anomalies and a significant high deuterium/hydrogen (D/H) enrichment indicative of great water loss. The maps sample the evolution of sublimation from the north polar cap, revealing that the released water has a representative D/H value enriched by a factor of about 7 relative to Earth's ocean [Vienna standard mean ocean water (VSMOW)]. Certain basins and orographic depressions show even higher enrichment, whereas high-altitude regions show much lower values (1 to 3 VSMOW). **Our atmospheric maps indicate that water ice in the polar reservoirs is enriched in deuterium to at least 8 VSMOW, which would mean that early Mars (4.5 billion years ago) had a global equivalent water layer at least 137 meters deep.**

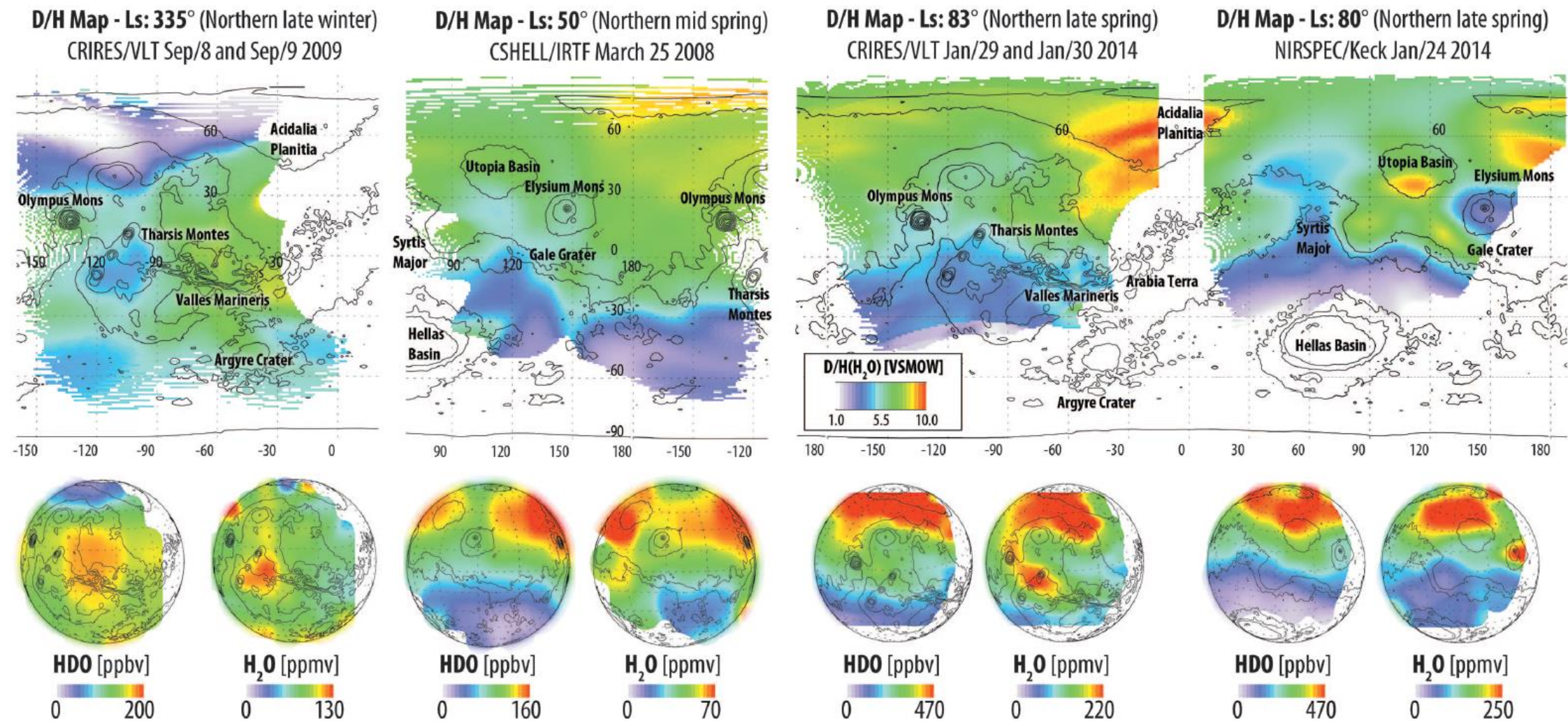


Fig. 2. Maps of HDO and H₂O and their ratio on Mars, obtained at four different seasons (from late northern winter to late northern spring). D/H maps (upper row) were obtained by calculating the ratio of the measured abundance of HDO and H₂O extracted from maps of the individual species (lower row) and are presented relative to the D/H value in Earth's ocean water (VSMOW). The ratio maps (upper row) show the progressive enrichment of

D/H in the northern hemisphere as the polar cap sublimates during northern spring. The isotopologue maps (HDO and H₂O) also reveal strong local enhancements and variability but with significant differences between them, associated with global and local climatology. In particular, low D/H values are observed at regions of low temperature and/or high altitude, with high values observed at orographic depressions (e.g., Acidalia Planitia and Utopia Basin).

- Current water reservoir**
- ~21 m (North + South PLD)
- Ancient water reservoir (4.5 Gyr)**
- ~137 m, 20% of surface

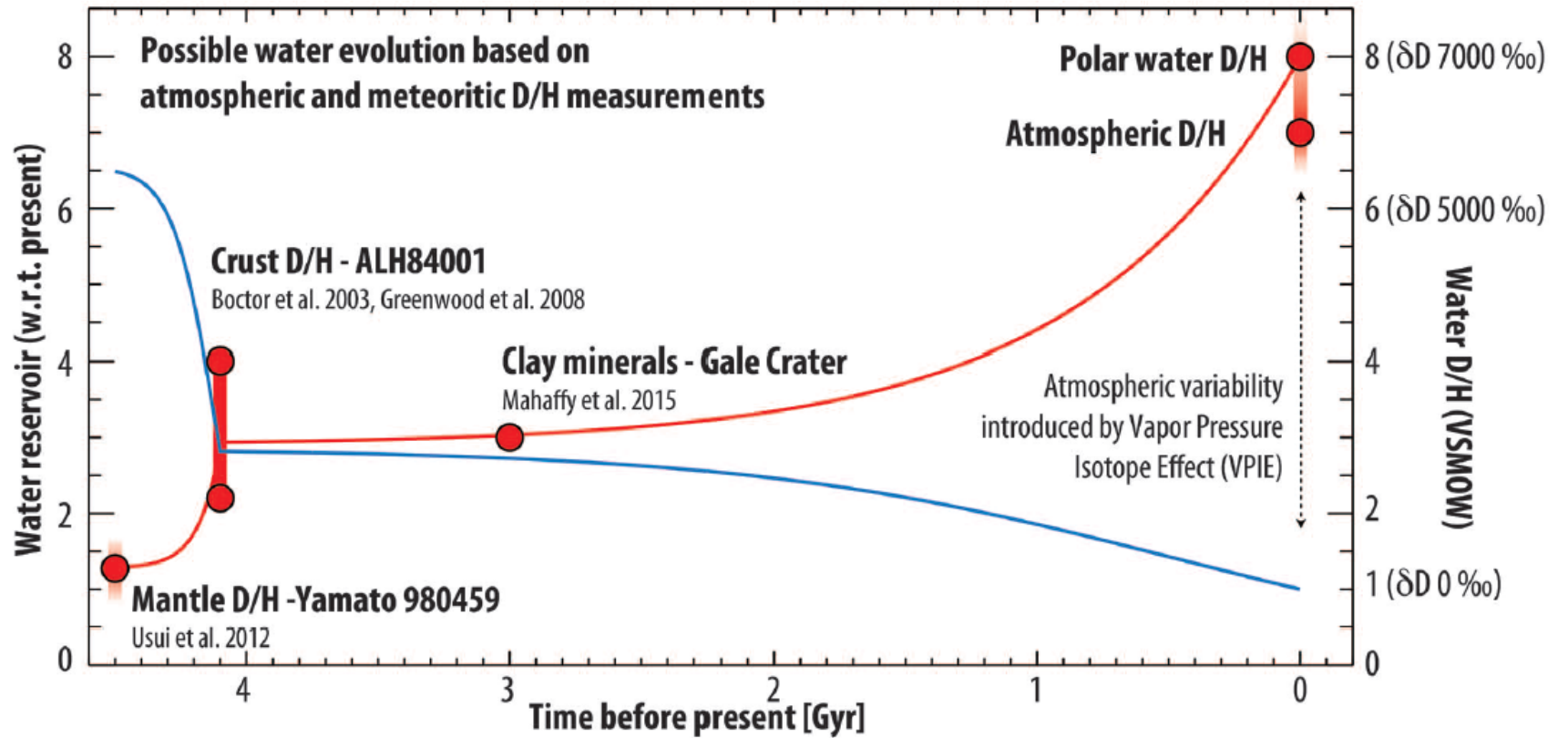
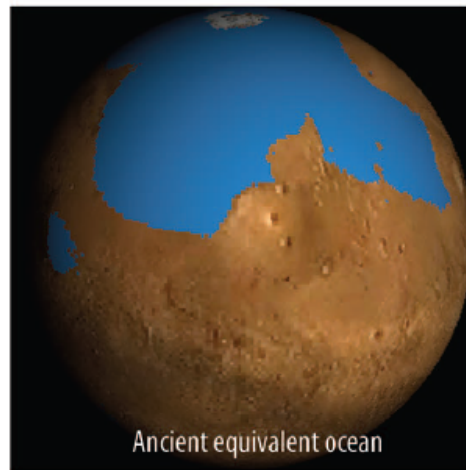


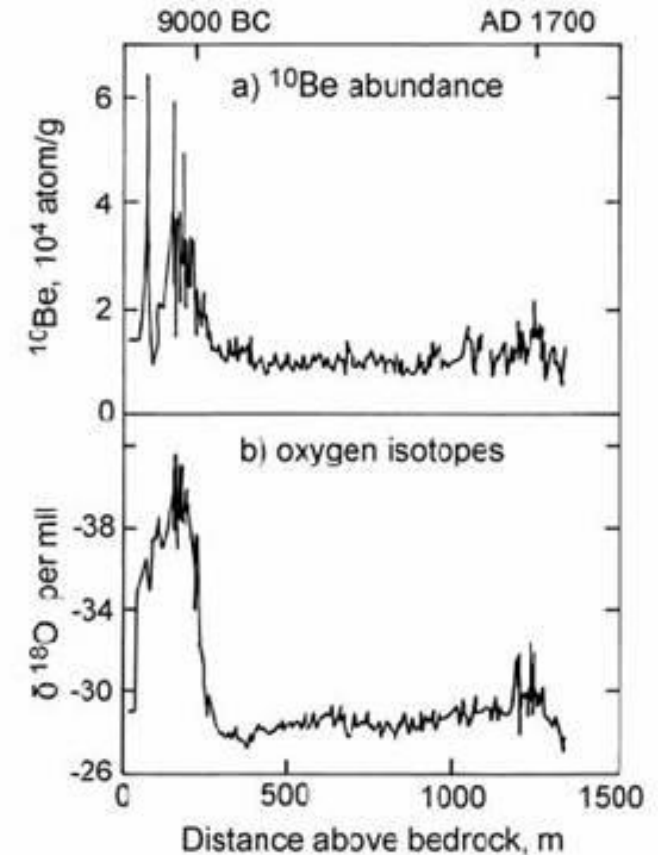
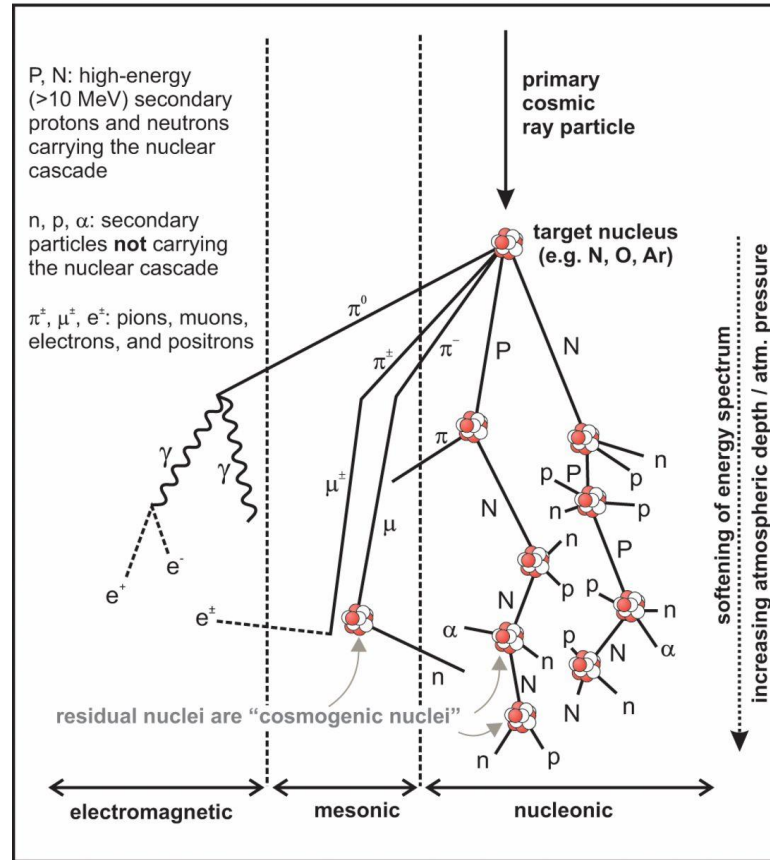
Fig. 3. Isotopic enrichment as evidence for global loss of water on Mars. After correcting for local climatological fractionation of the measured D/H ratio (Fig. 2), the current ratio for D/H in atmospheric water on Mars is at least 7 VSMOW, implying a D/H ratio of 8 VSMOW in the north polar reservoir (red curve and right axis). Assuming a fractionation factor f of 0.02, the D/H ratios obtained from water in Mars meteorites (Yamato 980459, 4.5 billion years old) imply that Mars's initial water reservoir was larger than the current water available on Mars by a factor of at least 6.5 (blue curve and left axis). When considering the current PLD content of 21 m of water, this would imply that at least 137 m GEL of water was present on Mars 4.5 billion years ago, covering 20% of the planet's surface.

Cosmogenic Nuclides

Isotopes formed by the action of cosmic rays

Isotope	half life	Isotope	half life
³ H (tritium)	12.3 y	³² P	14.3 d
⁷ Be	53.2 d	^{34m} Cl	34 m
¹⁰ Be	1,387,000 y	³⁵ S	87.5 d
¹¹ C	20.3 m	³⁶ Cl	301,000 y
¹⁴ C	5,700 y	³⁷ Ar	35 d
¹⁸ F	110 m	³⁸ Cl	37 m
²² Na	2.6 y	³⁹ Ar	269 y
²⁴ Na	15 h	³⁹ Cl	56 m
²⁸ Mg	20.9 h	⁴¹ Ar	110 m
²⁶ Al	717,000 y	⁴¹ Ca	102,000 y
³¹ Si	157 m	⁸¹ Kr	229,000 y
³² Si	153 y	¹²⁹ I	15,700,000 y

THE ATMOSPHERIC NUCLEAR CASCADE



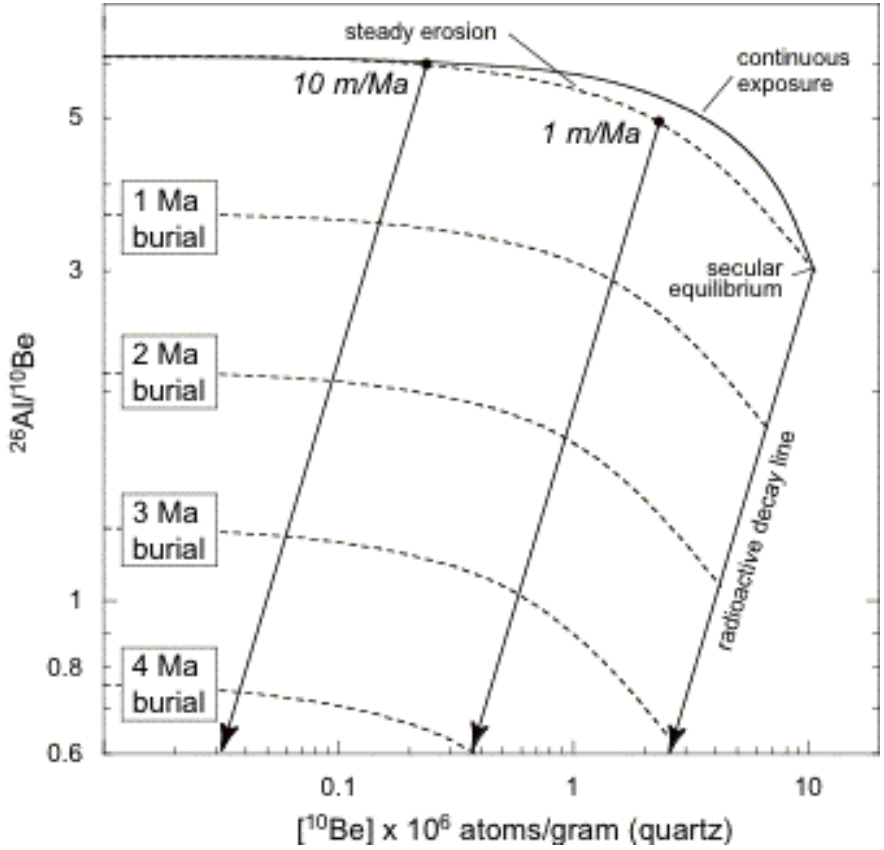
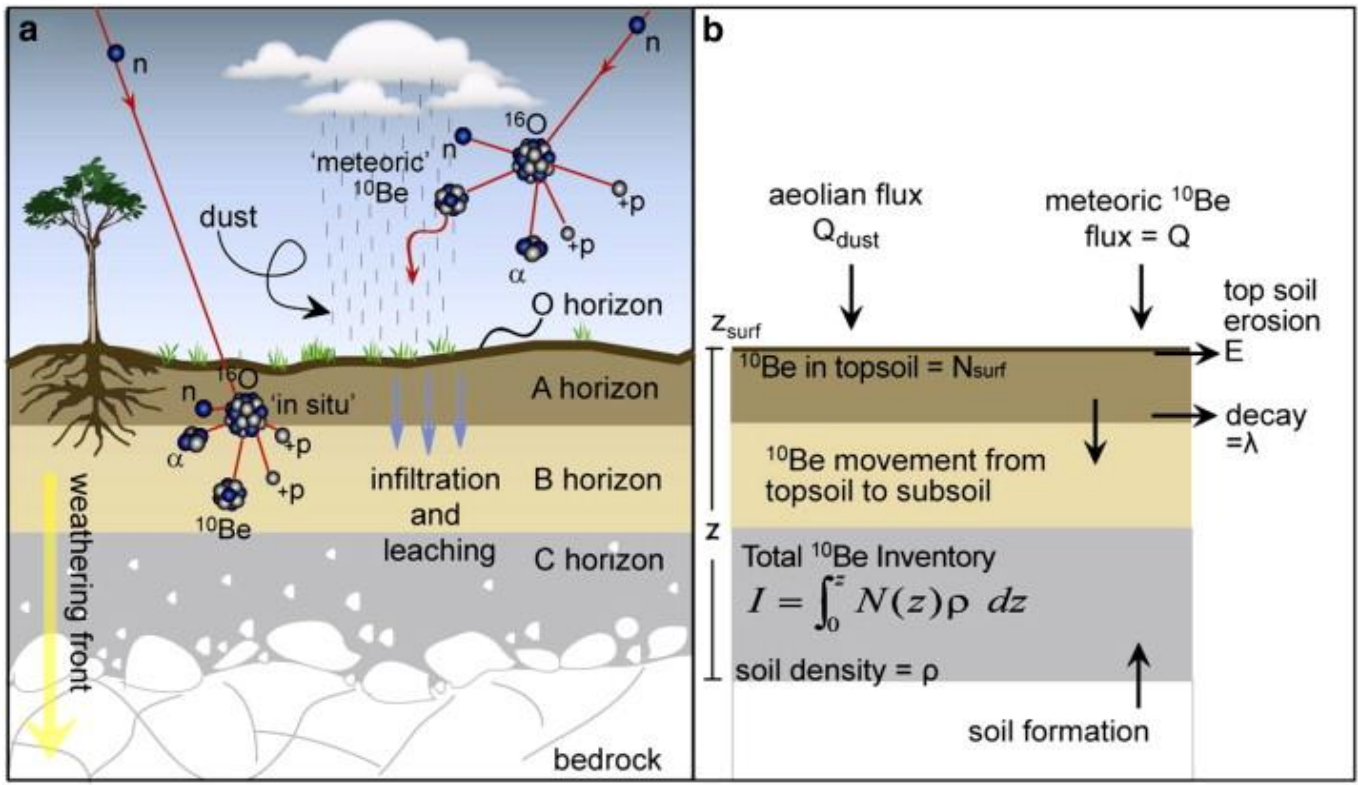
Beryllium-10 (¹⁰Be) is a radioactive isotope of beryllium. It is formed mainly by the cosmic ray spallation of oxygen. Beryllium-10 has a half-life of 1.39×10^6 years

It can be used for surface age exposure (very similar to Carbon-14 dating), but also holds a record of cosmic ray flux rate.

10Be correlates well with O isotopes in ice cores.

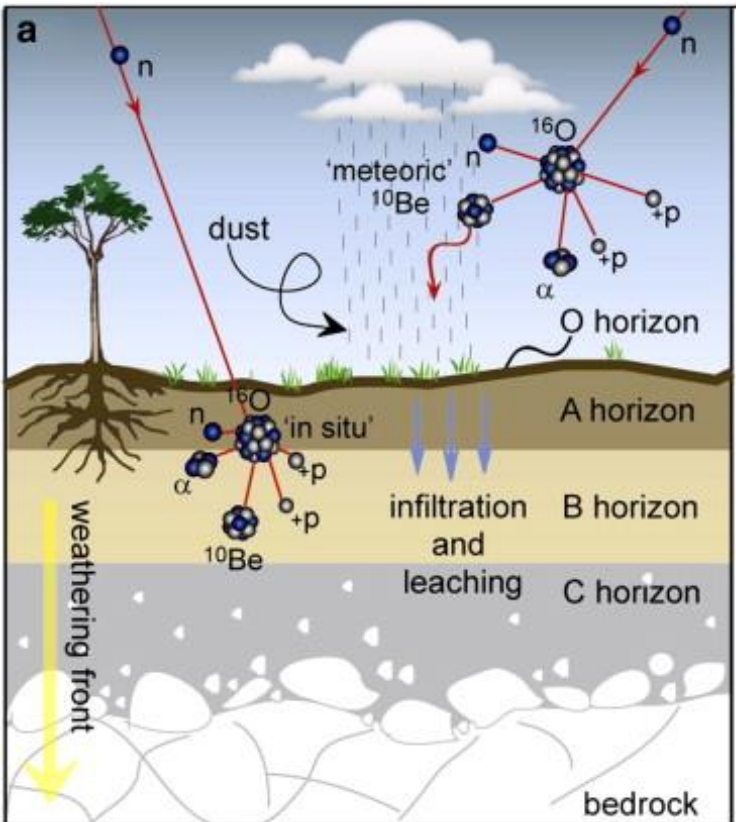
Are we seeing a climate variation in 10Be, or is it recording deposition rate?

Surface exposure dating is a collection of geochronological techniques for estimating the length of time that a rock has been exposed at or near Earth's surface. Surface exposure dating is used to date glacial advances and retreats, erosion history, lava flows, meteorite impacts, rock slides, fault scarps, and other geological events. It is most useful for rocks which have been exposed for between 10 years and 30,000,000 years.



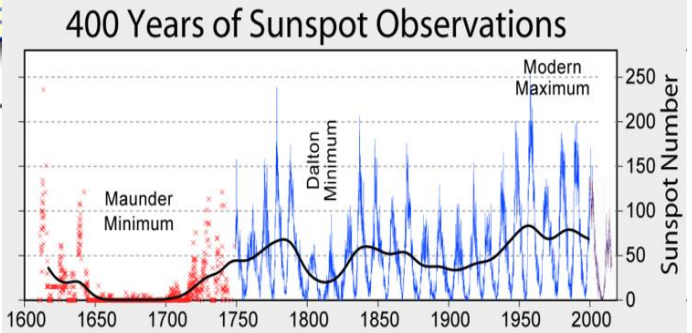
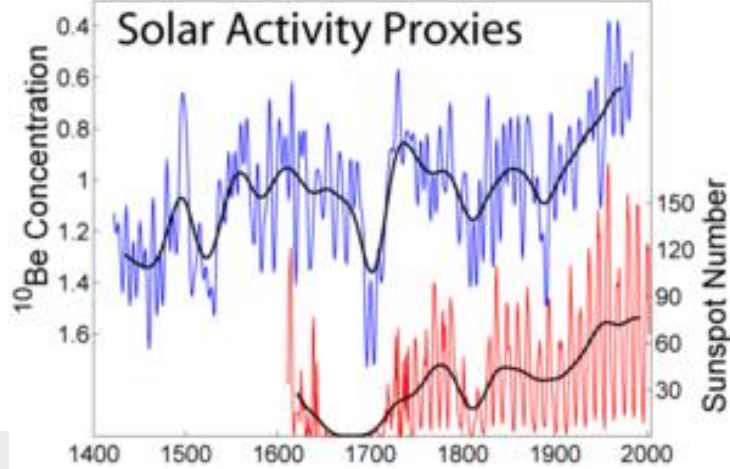
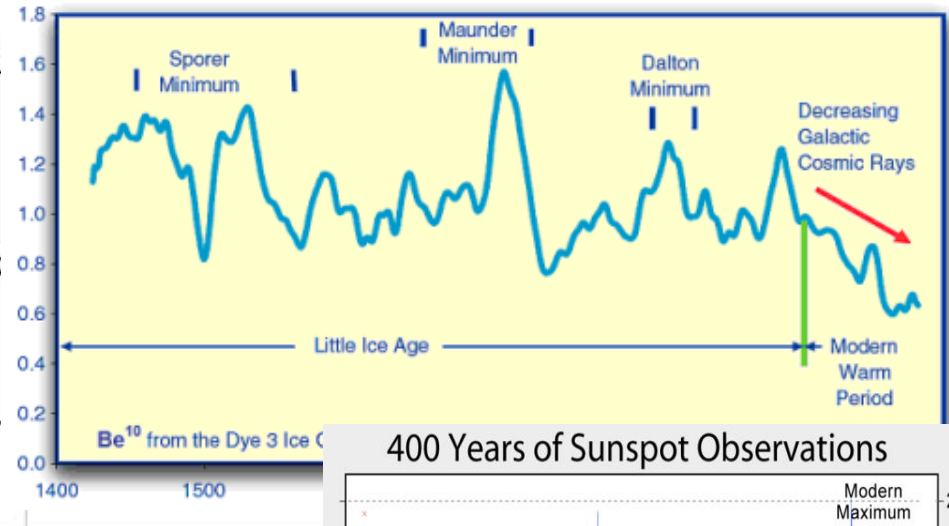
^{10}Be concentration give us a burial rate (deposition vs erosion)— If we can identify when a surface was last exposed (incorporating ^{10}Be from snowfall or from direct implantation) we can see how that concentration decays with time, giving an age. That is generally done by comparing it to another reference isotope, like ^{26}Al or ^{21}Ne ... but can be model based to some accuracy.

Surface exposure dating is a collection of geochronological techniques for estimating the length of time that a rock has been exposed at or near Earth's surface. Surface exposure dating is used to date glacial advances and retreats, erosion history, lava flows, meteorite impacts, rock slides, fault scarps, and other geological events. It is most useful for rocks which have been exposed for between 10 years and 30,000,000 years.



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When the Sun is active (has lots of Sunspots), the magnetic field protects the Earth, and presumably Mars, from galactic cosmic rays. This modulates the Berillium-10 production.

The cosmic ray flux has also been suggested (but not really proven) to cause more clouds to form (the cosmic rays are suggested to help form condensation nuclei).

Berillium isotopes in Mars icecap should therefore be modulated by solar variability, and allow for some possibility of exposure age. Perhaps (especially as Mars doesn't have its own magnetic field) this will also modulate cloud formation and deposition rate, or at least test this theory (e.g. did Mars also get colder during the Maunder Minimum?)

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H. Miyahara, Y. Yokoyama, & Y. T. Yamaguchi

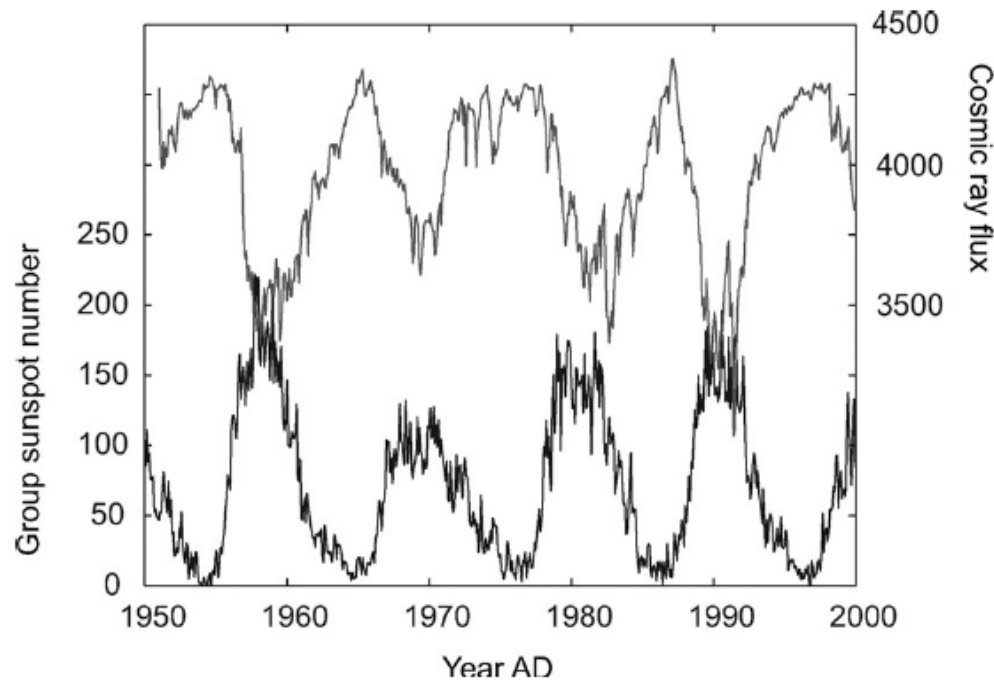
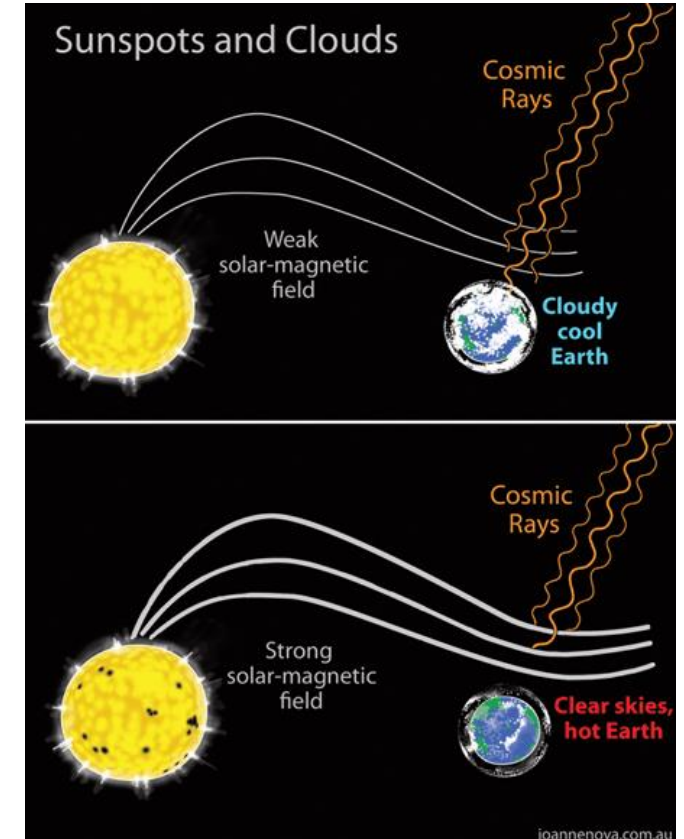


Figure 1. Monthly variation of the cosmic ray intensity observed by the Climax neutron monitor (upper gray line) and the group sunspot numbers (Hoyt & Schatten, 1998) (lower black line).



Conclusions

- ^{10}Be , with a 1.4 Myr half life, might be our best way to “date” but we may want a reference reference (e.g. ^{26}Al) to constrain flux rate. (is this detectable by TLS).

-It should also record deposition rate.

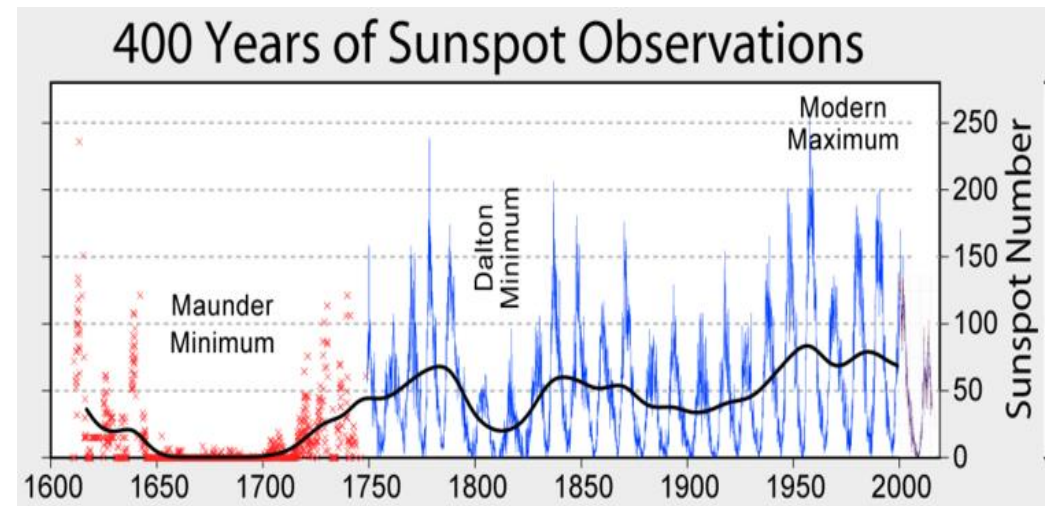
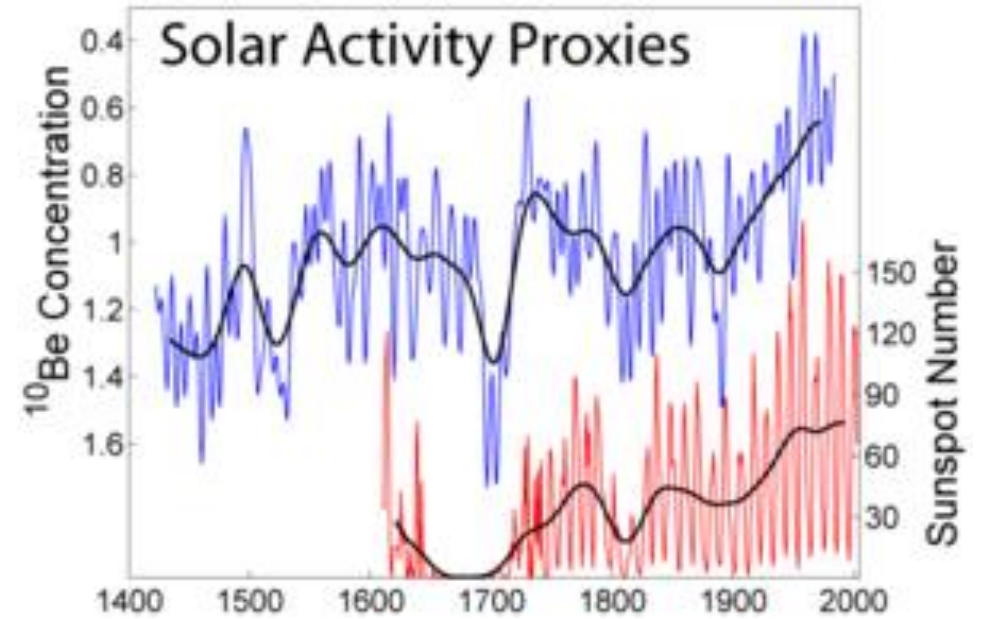
-It might provide a hugely import and record of solar activity.

-It should be a cleaner record than we can get on Earth due to the lack of a magnetic field on Mars (a 4 million year record of sunspots?).

-D/H should also be measureable and should both variations due to temperature, but Mars “SMOW” has many sources with different D/H that have also changed with time.

- $^{18}\text{O}/^{16}\text{O}$ might be measureable, and show similar info to D/H but a little trickier due to higher mass.

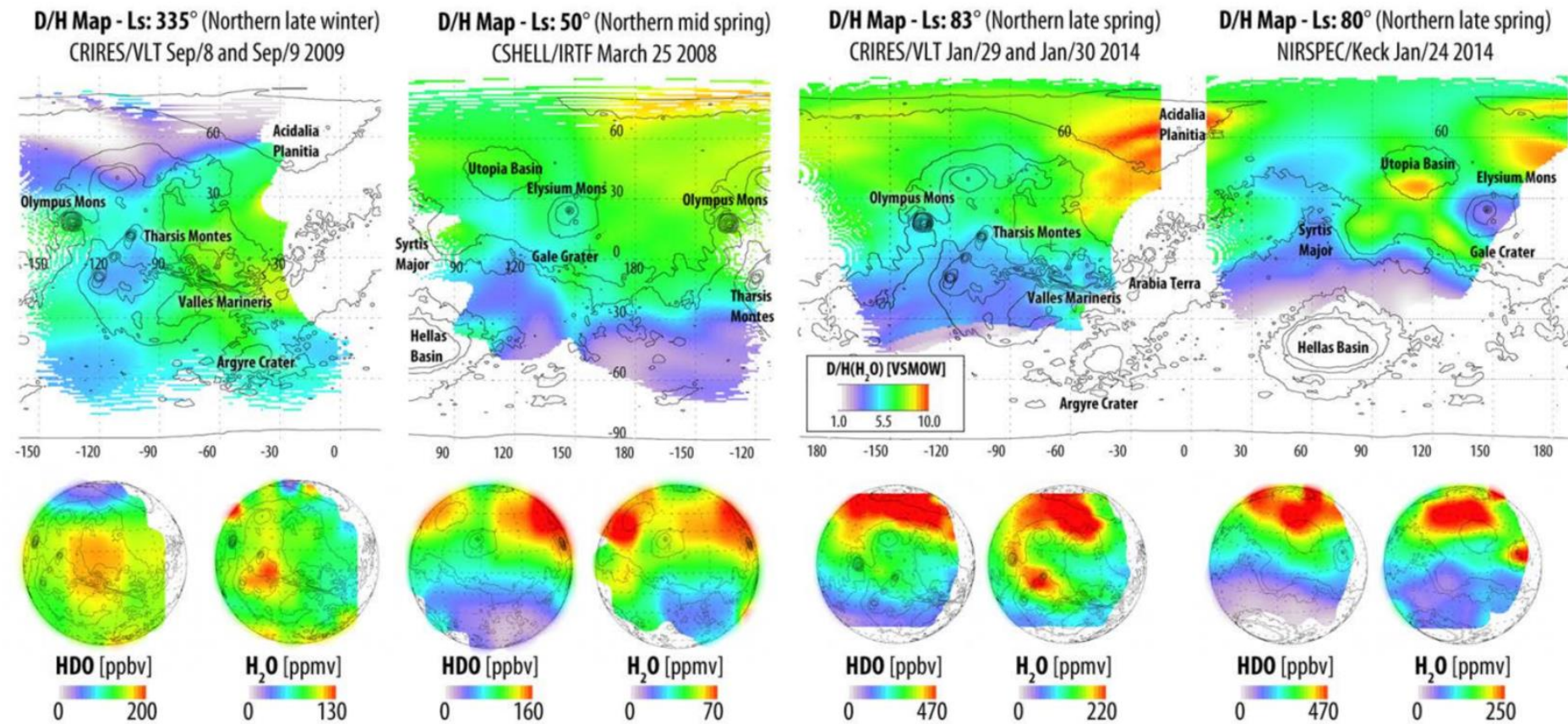
Since O is lost more slowly lost, Mars SM“O”W might not change as much with time



Slide Bank for Lightning Talk on Isotopes

Bethany Ehlmann

9 August 2017

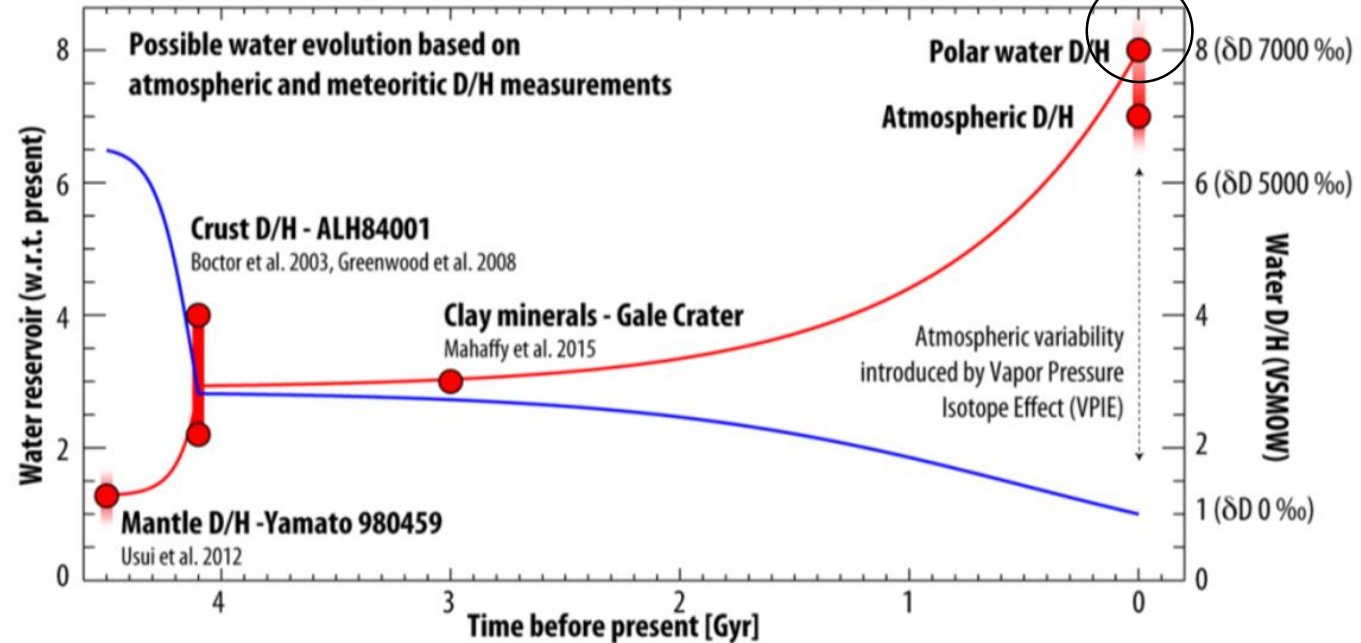
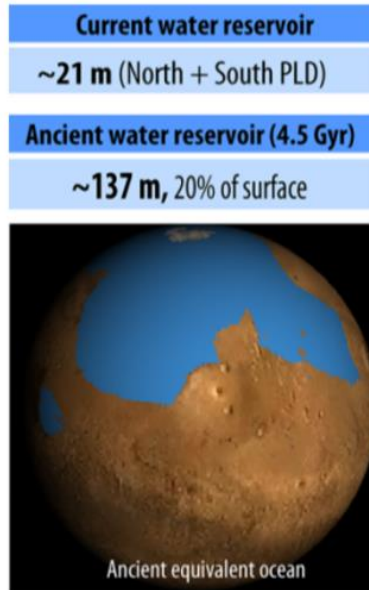


Villanueva et al., Science, 2015

Fig. 2. Maps of deuterated water (HDO) and water (H₂O) and their ratio on Mars, obtained at four different seasons (from late northern winter to late northern spring). D/H maps (upper row) were obtained by ratioing the measured abundance of HDO and H₂O extracted from maps of the individual species (lower row), and are presented relative to the D/H value in Earth's ocean water (VSMOW). The HDO and H₂O data show the progressive enrichment of D/H in the northern hemisphere as the polar cap sublimates during northern spring. The isotopologue disk maps (HDO, H₂O) also reveal strong local enhancements and variability but with significant differences between them, associated with global and local climatology. In particular, low D/H values are observed at regions of low temperature and/or high-altitude, with high values observed at orographic depressions (e.g., Acidalia Planitia, Utopia Basin).

Atmospheric history of Mars from D/H

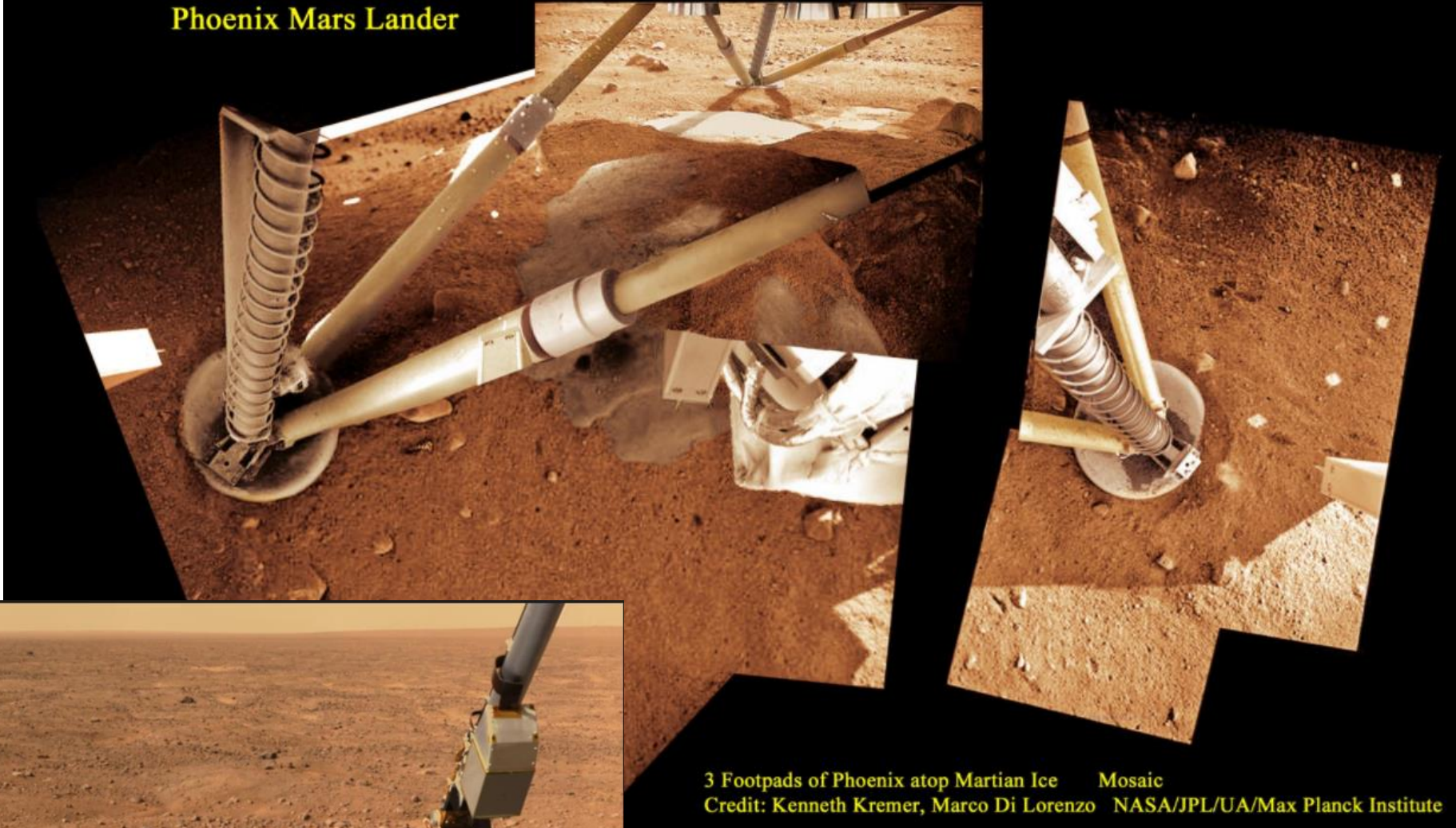
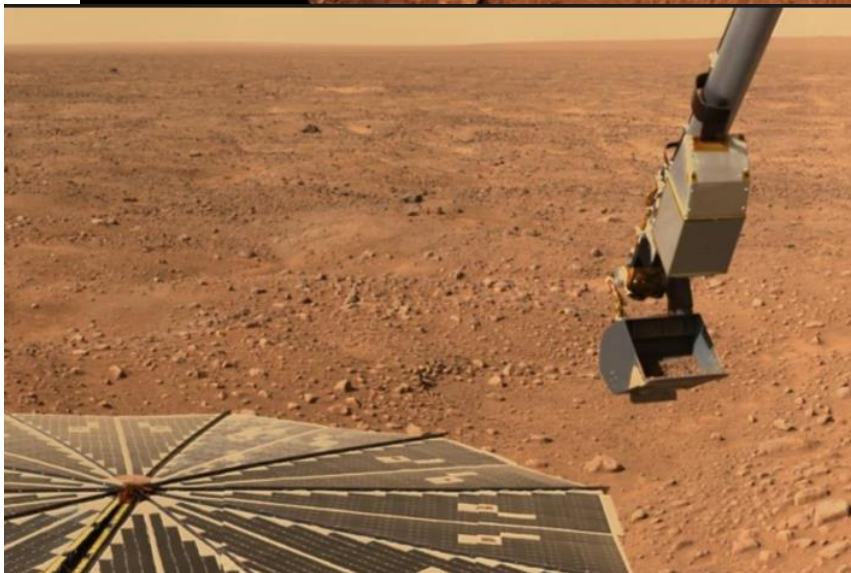
Not ever actually measured. Merely inferred



Villanueva et al., Science, 2015

Secular isotopic change in other volatiles (in ices or soils) that may be in the poles is also important for understanding Mars' volatile history and constraining geochemical cycles: e.g., d13C, d18O, d34S, d15N

Phoenix Mars Lander



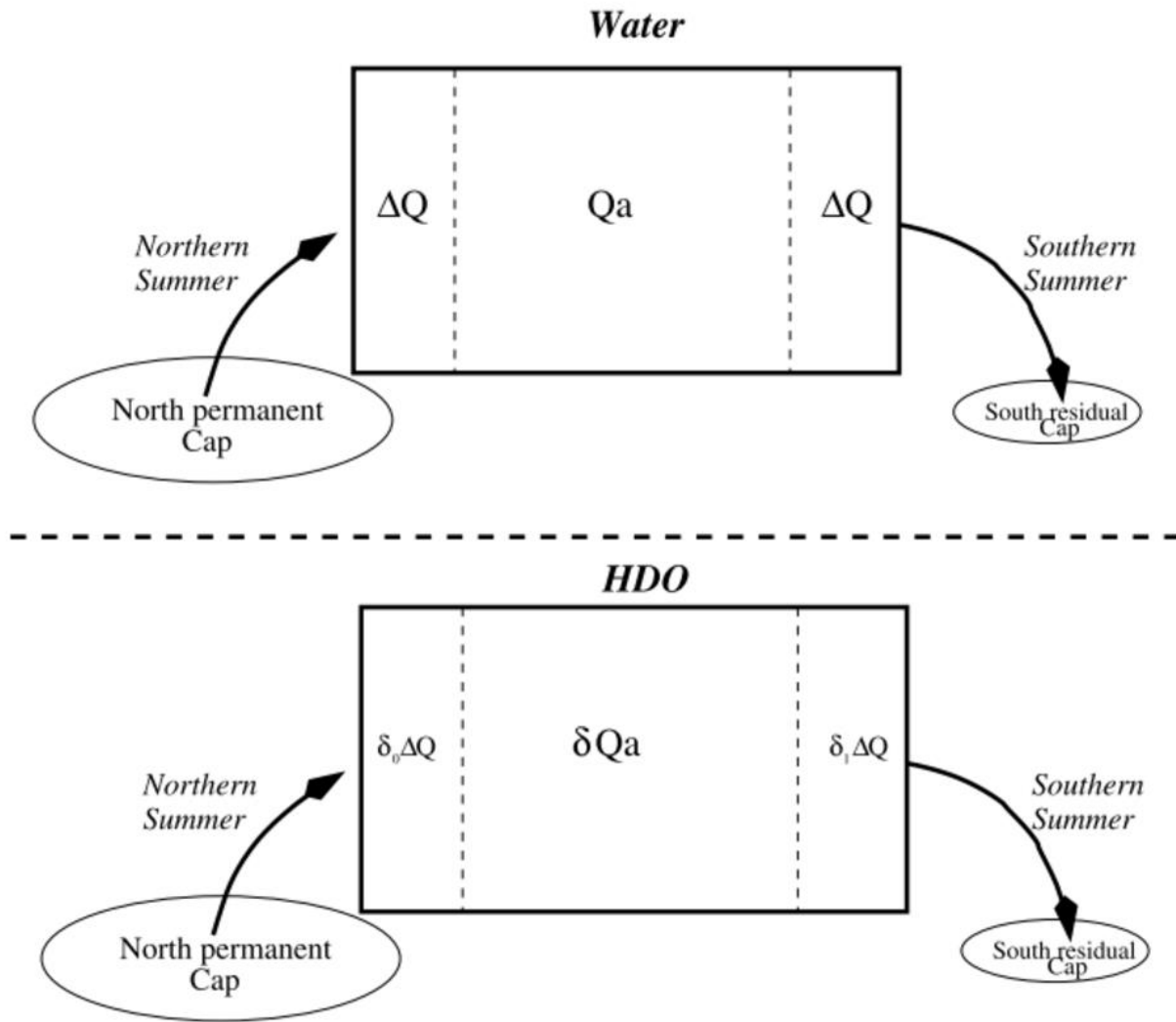
3 Footpads of Phoenix atop Martian Ice Mosaic
Credit: Kenneth Kremer, Marco Di Lorenzo NASA/JPL/UA/Max Planck Institute

Phoenix did not manage to deliver H₂O ice to the mass spec. to measure the isotopic composition of ground ice

Ge194, 2015, Week 1: D/H evolution

Villanueva et al., 2015; Mahaffey et al., 2015; Usui et al., 2015

- There exists a plausible process for producing large (1000s per mil) D/H variations on short timescale (vapor pressure isotope effect)
- Atmospheric variability of 1000s per mil seasonally and spatially may exist on Mars (but see Villanueva SM for potentially challenging aerosol and column depth scattering corrections)
 - if this variability exists, it has HUGE implications for interpreting the geologic record because the D/H of minerals formed will reflect local water at some particular point in time/space that is not reflective of any meaningful global average
 - Problematic is the manuscript is not showing residual spectra so model fits to abundance are impossible to evaluate
- The Martian polar ice cap D/H may be 8*SMOW(terrestrial) based on atmospheric observations and VPIE effects (but see methods caveat above)
- The MSL value of D/H=3 for YKB clays is likely an upper bound on clay D/H (actual would be lower as there could be some modern mixed in)
- An distinct endmember “intermediate” D/H reservoir (2000-4000 per mil) does exist on Mars, supported by meteorite analyses. Could be ground ice, hydrated crust.
 - We don't know modern ground ice D/H



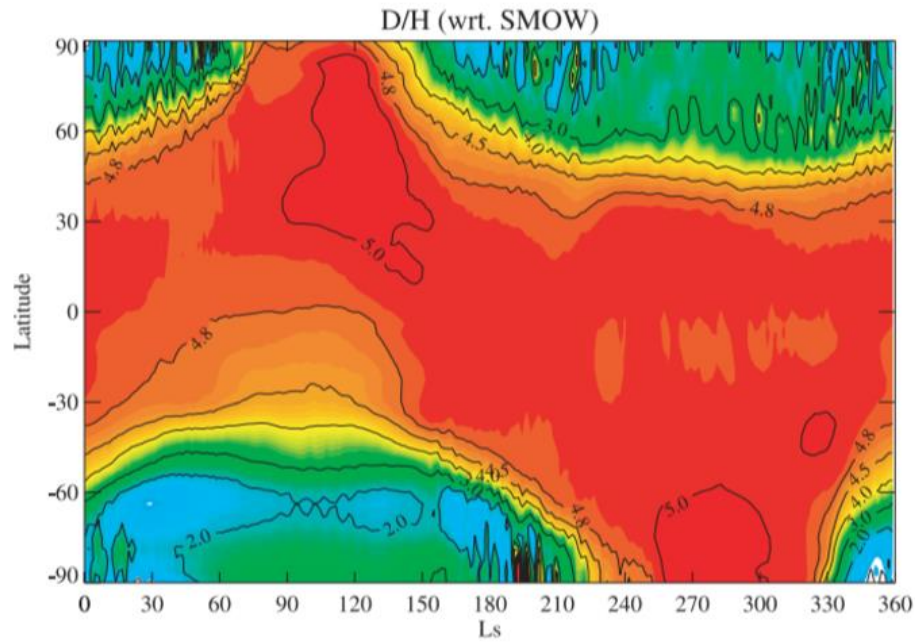
**Atmosphere-
Polar Cap
Exchange
Seasonally
(ground ice is
likely also
involved)**

*Montmessin et al.,
2005, JGR*

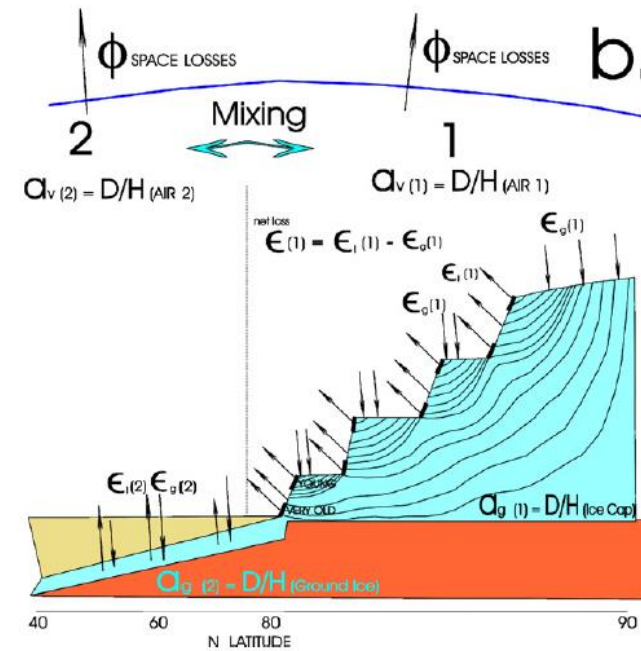
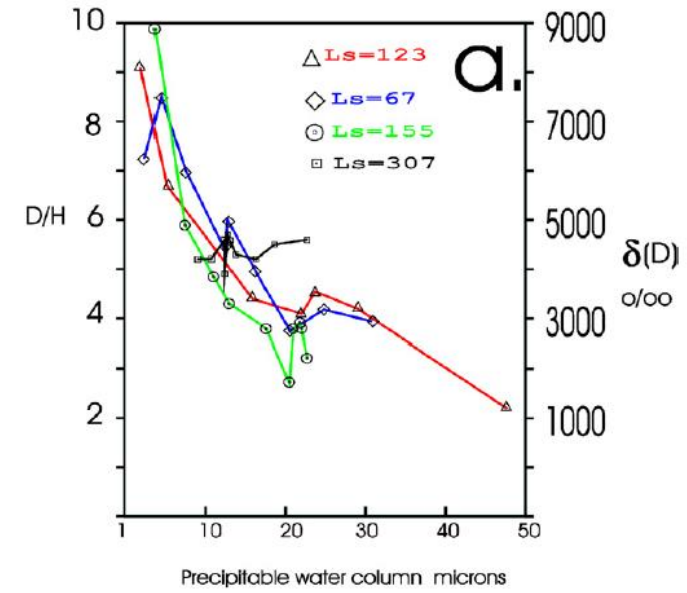
Figure 12. Chart describing the exchanges of water between the three major components of the water cycle: the north permanent cap, the seasonal reservoir (atmosphere and ground frost), and the south residual cap. In the upper part, we show the corresponding exchanges in HDO.

Predictions for D/H as a function of latitude and L_s

Different depending on the model



Montmessin et al.,
2005, JGR



Fisher, 2007; Fisher et al., 2008

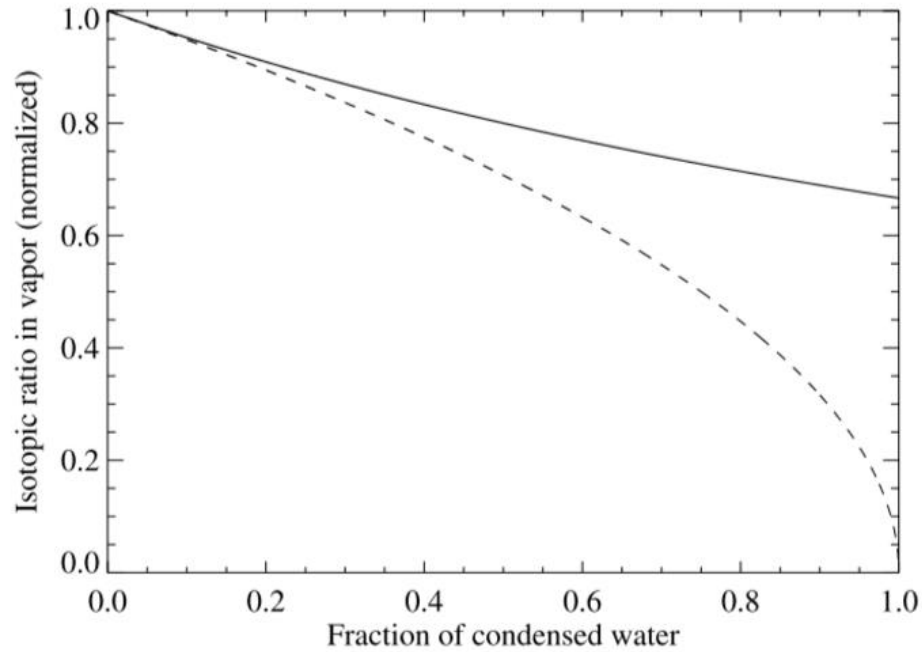


Figure 1. Evolution of the water isotopic ratio in a gaseous sample brought to condensation at a temperature of 180 K. Two different fractionation processes are plotted here. The dashed line represents the case where only the instantaneous flux of condensation is at isotopic equilibrium with the gaseous phase. The solid line is for the case of an isotopic equilibrium between the whole condensed phase and the surrounding gas.

Montmessin et al., 2005, JGR

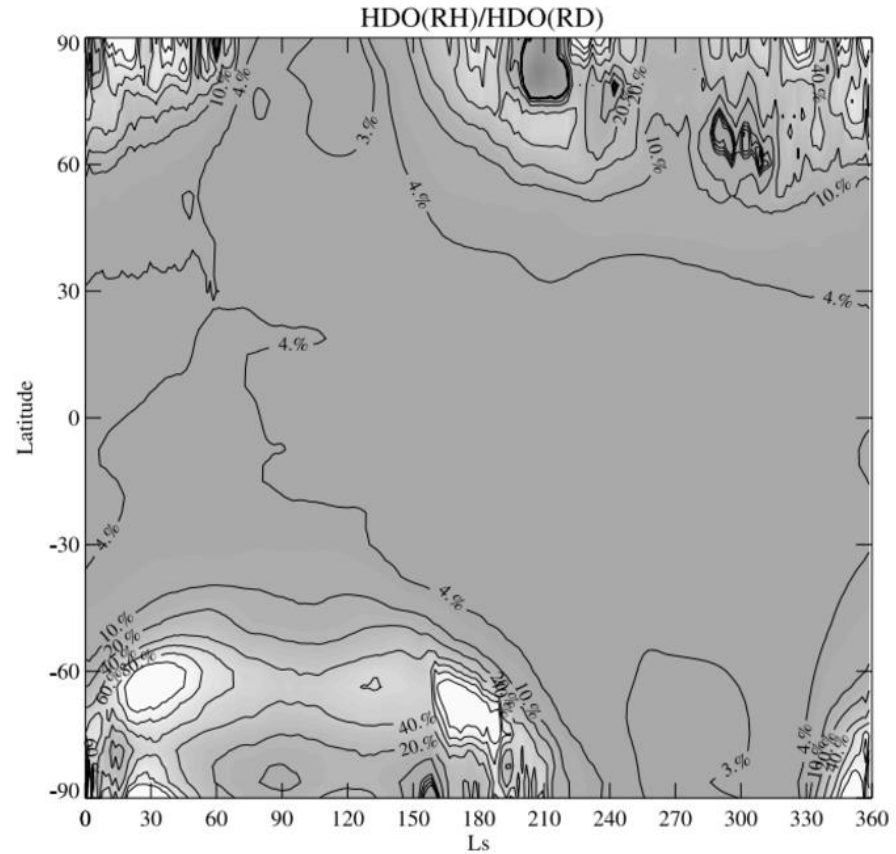


Figure 14. Seasonal and geographical variations of the HDO abundances predicted by the Rapid Homogenization model (RH) onto those predicted by the Rayleigh Distillation model (RD).

The composition of the ice (and thus polar cap H₂O_v release to atmosphere) also depends on the nature of how to model the ice condensation process

Ge194, 2015, Week 2: Modern cycling of water
Montmessin et al., 2005; Fisher et al., 2007

- The Villanueva et al 2015 observed magnitude of D/H seasonal variability is predicted by climate physical models + VPIE, albeit with some caveats
 - there is observed and should be (based on models) an isotopically light D/H in the north in northern winter by a factor of ~2-3x
 - the efficient N-->S transport of spring high D/H subliming polar cap predicted by Montmessin is not observed by Villanueva over near equatorial lats
 - QUESTION: is this difference due to the physics of the atmosphere, an unmodeled process like adsorption by regolith, or a problem with the data behind the observation?
- Our knowledge of N Polar ice reservoir D/H poorly constrained (the constraint is the spring D/H atmosphere measured in the North; the unknown is the ice-atmosphere isotope fractionation factor)
- Our knowledge of the South polar ice D/H or ground ice D/H (if different from poles) is not yet constrained by observation; these secondary modern reservoirs may need to be considered
- The modern Mars ice-atmosphere system must mostly/fully(?) exchange on Myr timescales, driven by obliquity. Thus there is a “reset” to the ice D/H

Does CO₂ ice isotopically fractionate?

- One lab study



Articles

Experimental constraints on the stable-isotope systematics of CO₂ ice/vapor systems and relevance to the study of Mars

John M Eiler^a, Nami Kitchen^a, Thom A Rahn^a

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[https://doi.org/10.1016/S0016-7037\(99\)00327-0](https://doi.org/10.1016/S0016-7037(99)00327-0)

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Oxygen-isotope fractionation between ice and vapor ($\Delta_{\text{ice-vapor}} = 1000 \cdot \ln ([^{18}\text{O}_{\text{ice}}/^{16}\text{O}_{\text{ice}}] / [^{18}\text{O}_{\text{vapor}}/^{16}\text{O}_{\text{vapor}}])$) varies approximately linearly vs. $1/T$ between temperatures of 150 and 130 K (from 4.2 and 7.5 ‰, respectively). Carbon isotopes are unfractionated ($\Delta^{13}\text{C}_{\text{ice-vapor}} \leq 0.2\text{‰}$) at temperatures ≥ 135 K and only modestly fractionated ($\Delta^{13}\text{C}_{\text{ice-vapor}} \leq 0.4\text{‰}$) at temperatures between 135 and 130 K. Martian atmospheric volumes that are residual to high extents of condensation (i.e., at high latitudes during the winter) may vary in $\delta^{18}\text{O}$ by up to tens of per mil, depending on the scales and mechanisms of ice/vapor interaction and atmospheric mixing.

Precise (i.e., per mil level) examination of the Martian atmosphere or ices could be used as a tool for examining the Martian climate; at present such precision is only likely to be had from laboratory study of returned samples or substantial advances in the performance of mass spectrometers on landers and/or orbital spacecraft. **Oxygen-isotope fractionations accompanying the CO₂ condensation/sublimation cycle may play a significant role in the oxygen-isotope geochemistry of secondary phases formed in SNC meteorites, in particular as a means of generating ¹⁸O-depleted volatile reservoirs**