Slide Bank for Lightning Talk on Isotopes

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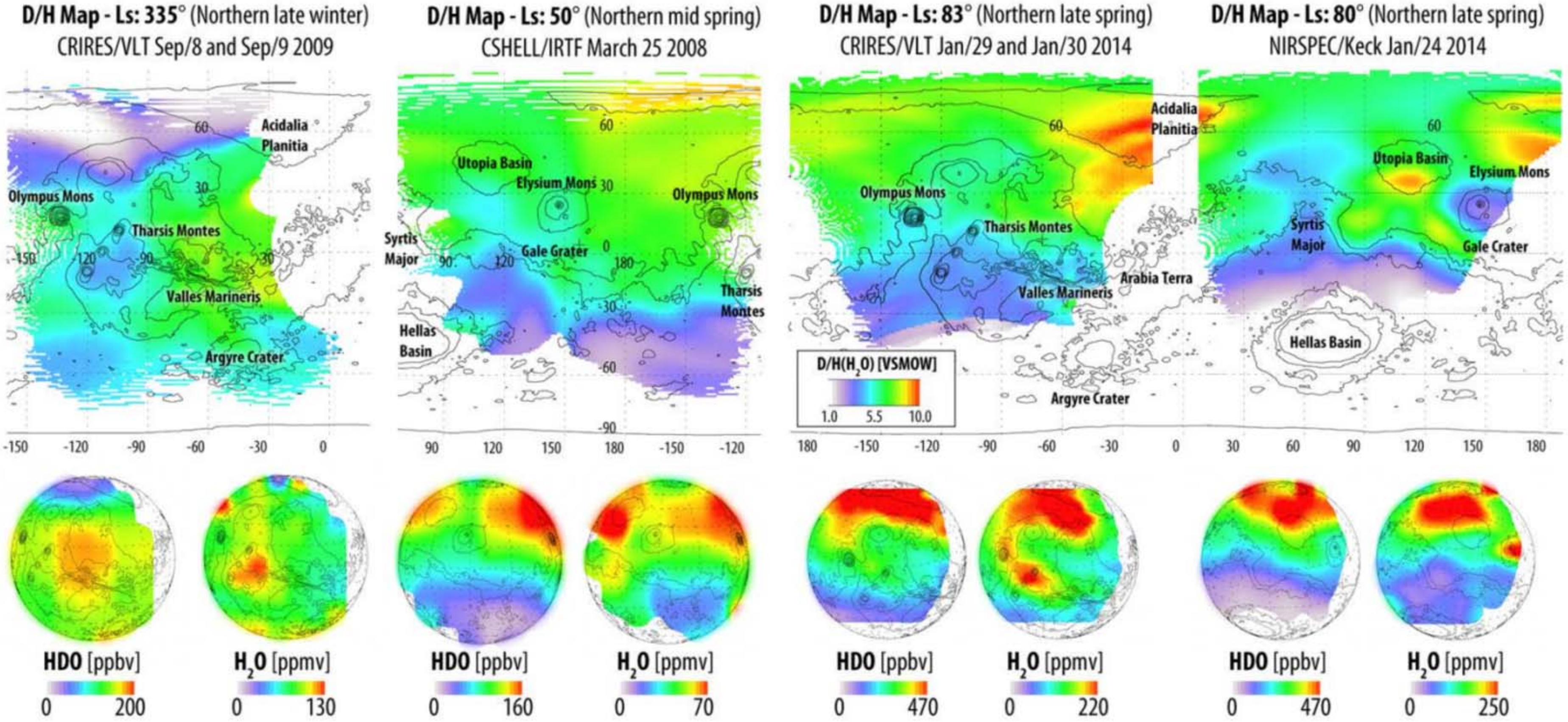
9 August 2017



D/H Map - Ls: 335° (Northern late winter)
CRIRES/VLT Sep/8 and Sep/9 2009

D/H Map - Ls: 50° (Northern mid spring)
CSHELL/IRTF March 25 2008

D/H Map - Ls: 83° (Northern late spring)
CRIRES/VLT Jan/29 and Jan/30 2014

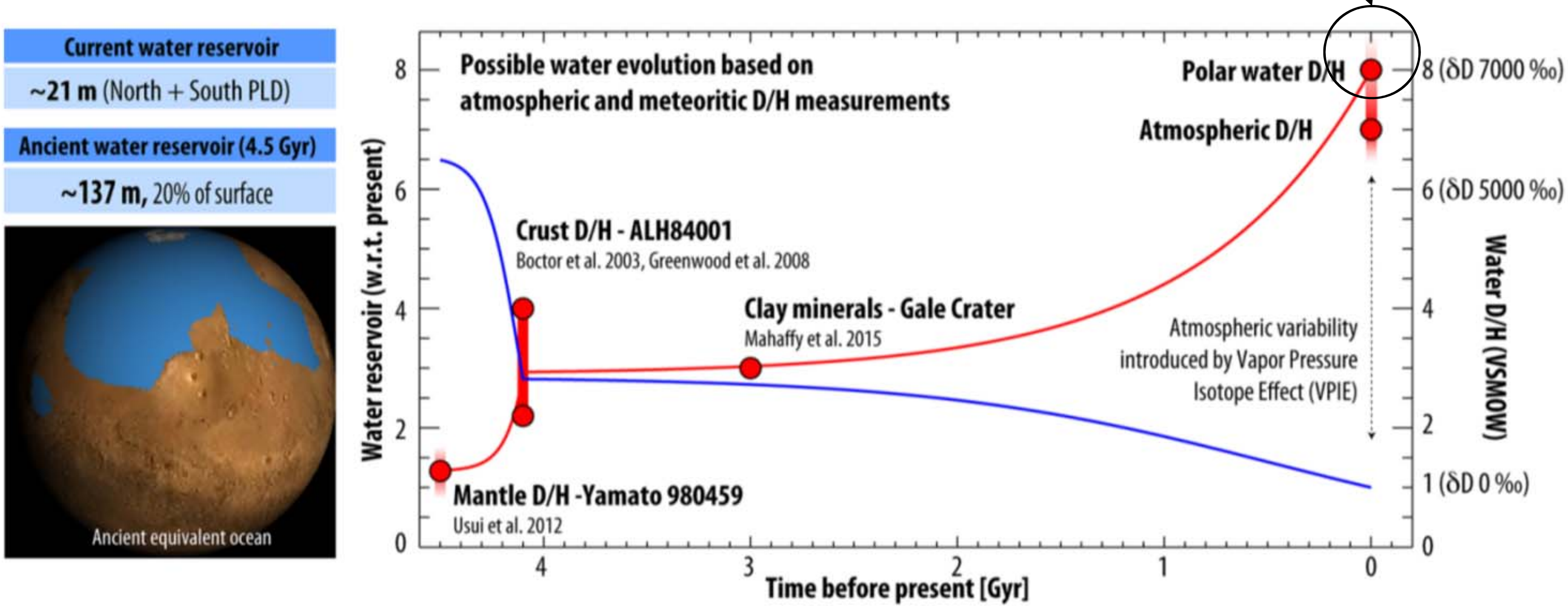
D/H Map - Ls: 80° (Northern late spring)
NIRSPEC/Keck Jan/24 2014

Villanueva et al., Science, 2015

Fig. 2. Maps of deuterated water (HDO) and water (H_2O) 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 H_2O 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 H_2O data show the progressive enrichment of D/H in the northern hemisphere as the polar cap sublimes during northern spring. The isotopologue disk maps (HDO, H_2O) 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).

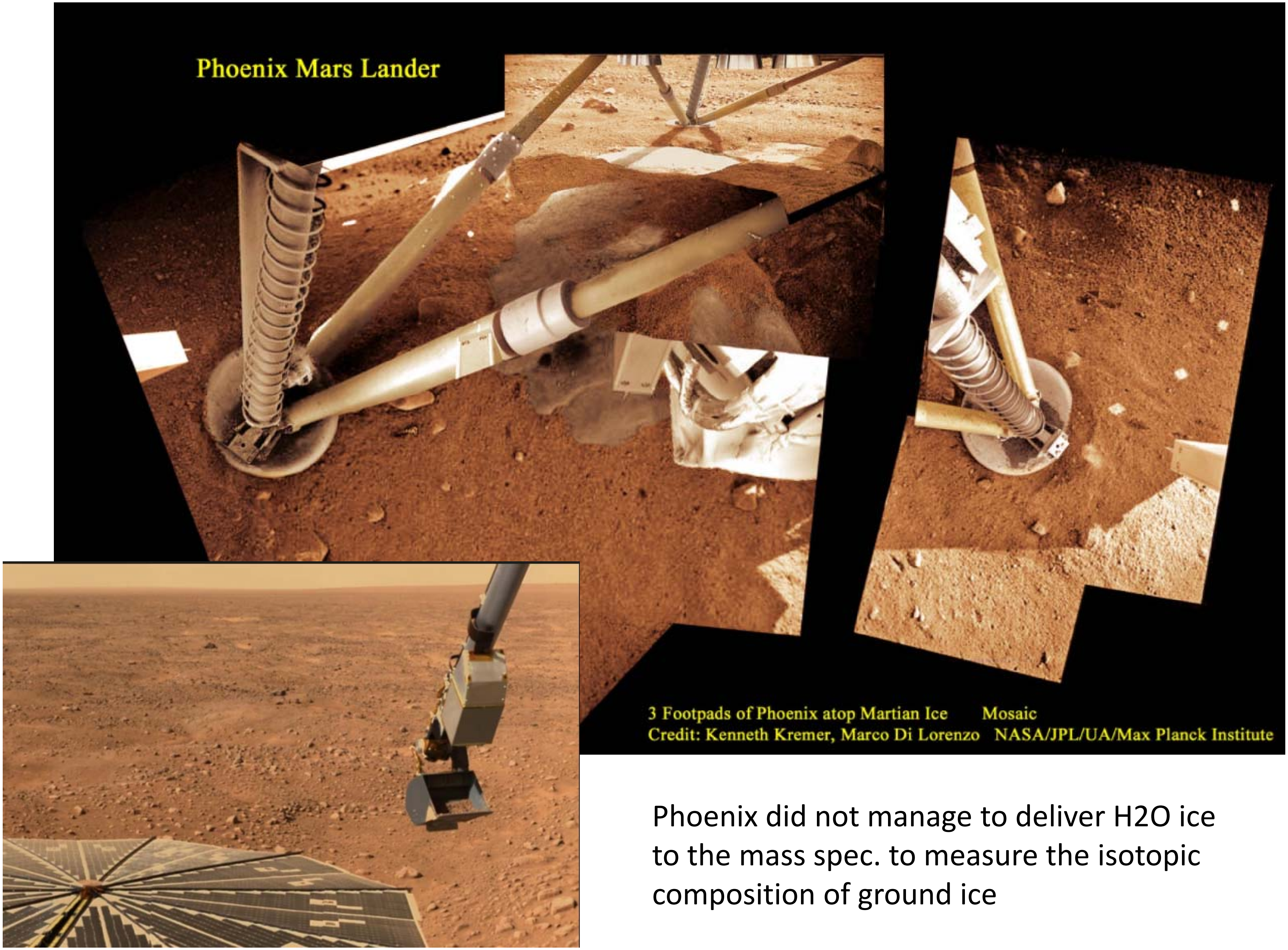
Atmospheric history of Mars from D/H

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



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)

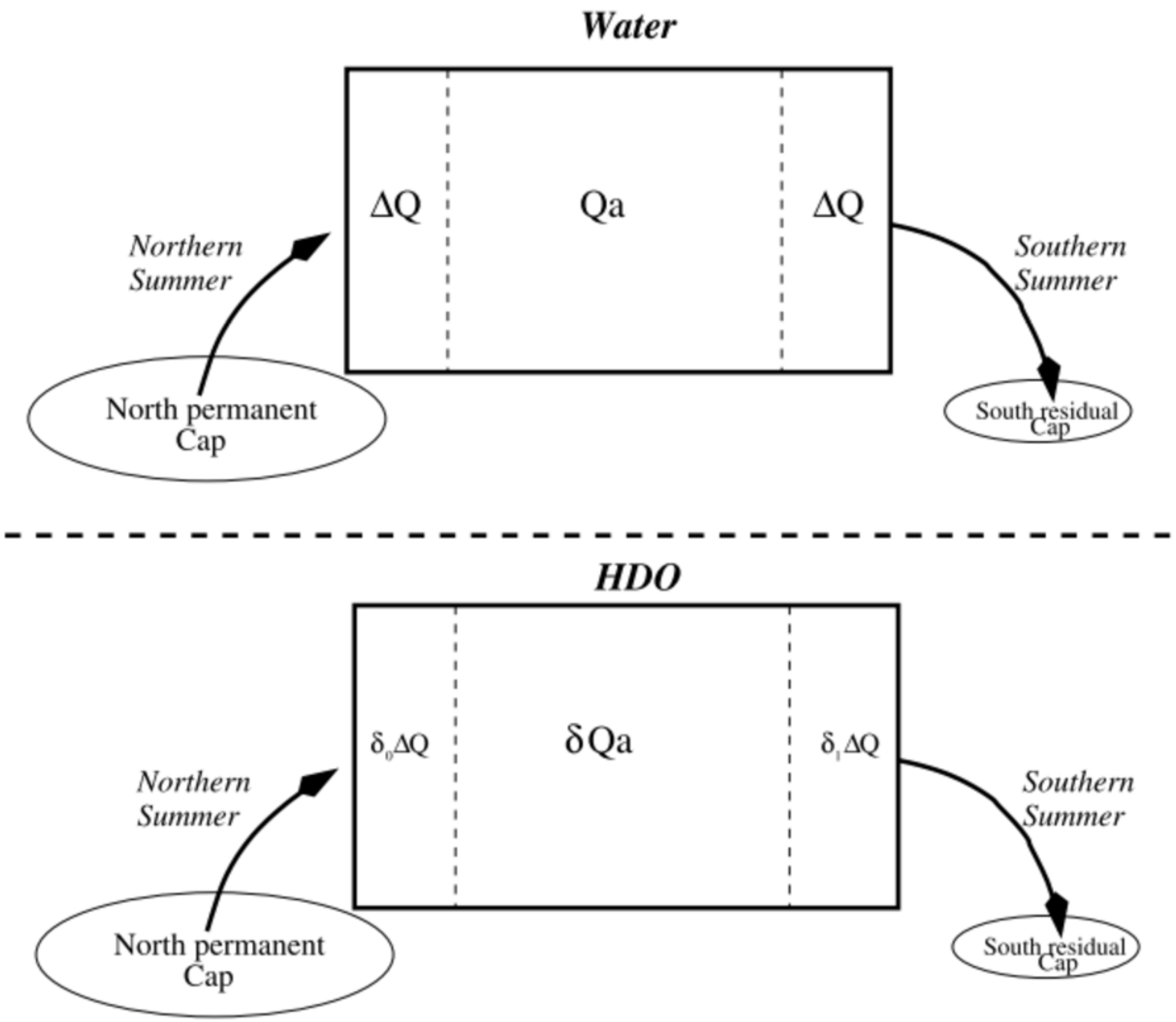
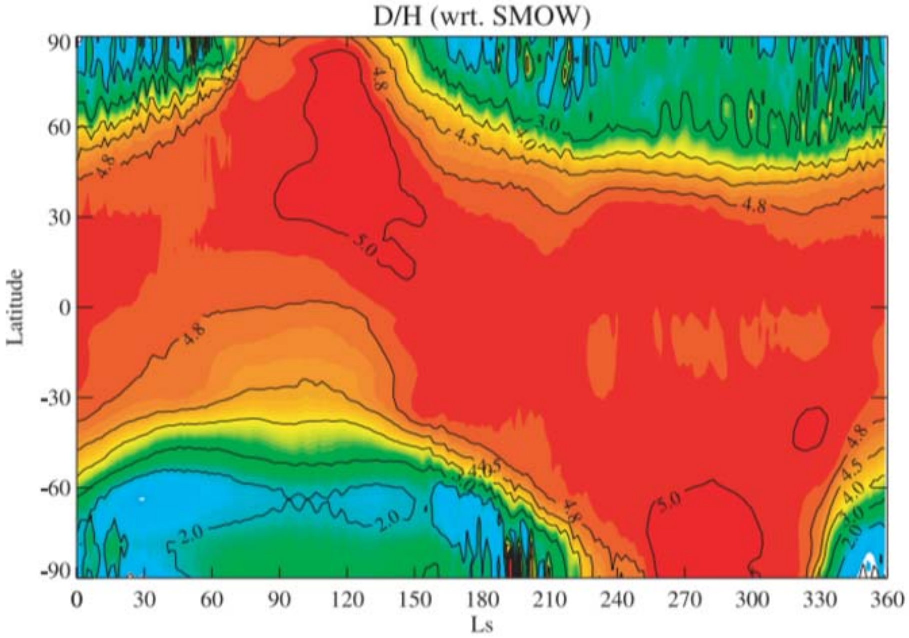


Figure 12. Chart describing the exchanges of water between the three major components of the water cycle: the north permanent cap, the seasonal reservoir (atmosphere and ground frost), and the south residual cap. In the upper part, we show the corresponding exchanges in HDO.

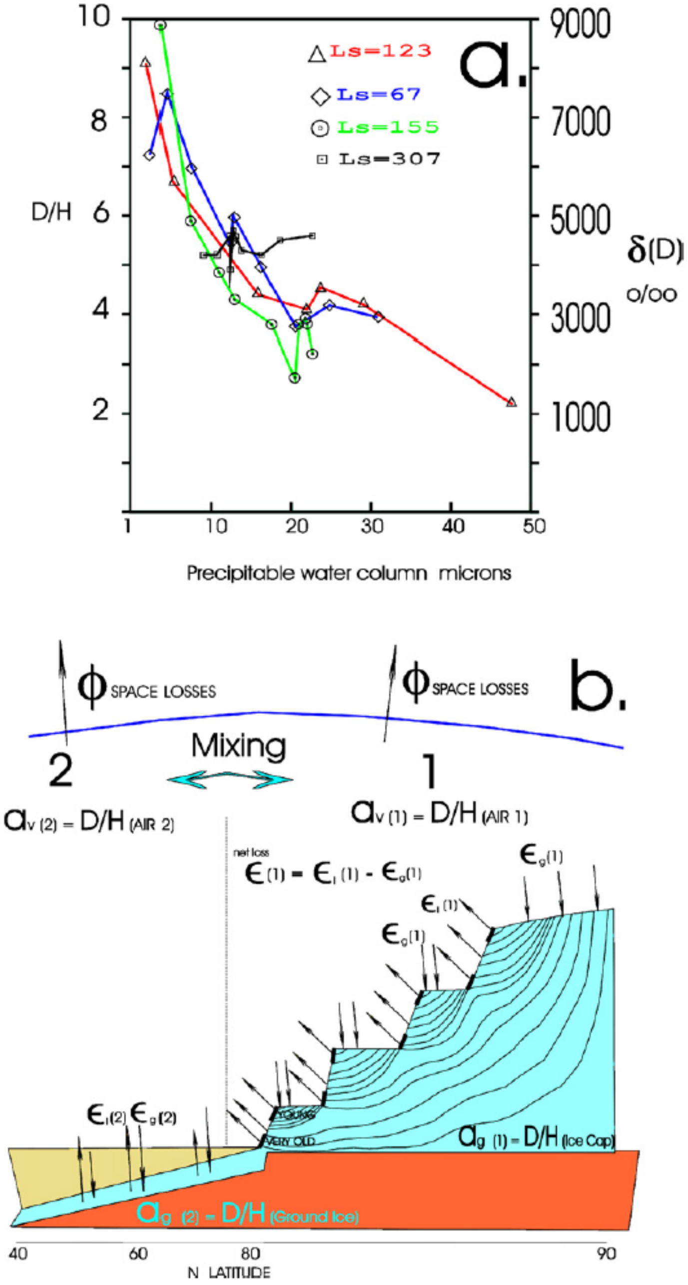
Montmessin et al., 2005, JGR

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

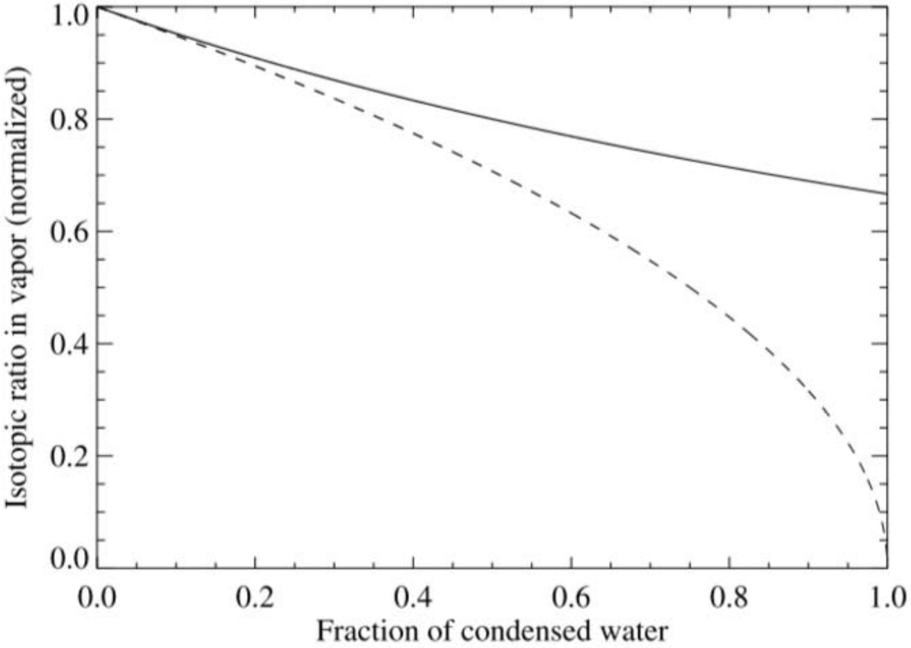


Figure 1. Evolution of the water isotopic ratio in a gaseous sample brought to condensation at a temperature of 180 K. Two different fractionation processes are plotted here. The dashed line represents the case where only the instantaneous flux of condensation is at isotopic equilibrium with the gaseous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

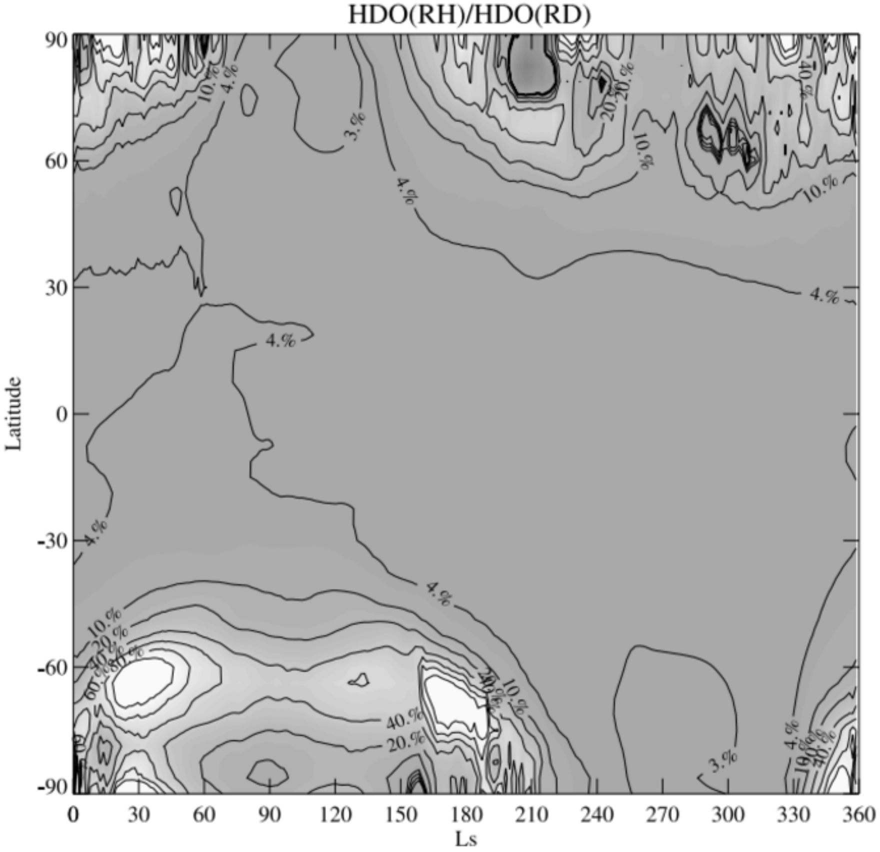


Figure 14. Seasonal and geographical variations of the HDO abundances predicted by the Rapid Homogenization model (RH) onto those predicted by the Rayleigh Distillation model (RD).

Montmessin et al., 2005, JGR

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

Geochimica et Cosmochimica Acta

Volume 64, Issue 4, February 2000, Pages 733–746

Articles

Experimental constraints on the stable-isotope systematics of CO_2 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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Oxygen-isotope fractionation between ice and vapor ($\Delta_{ice\text{-}vapor} = 1000 \cdot \ln([^{18}O_{ice}/^{16}O_{ice}] / [^{18}O_{vapor}/^{16}O_{vapor}])$ varies approximately linearly vs. 1/T between temperatures of 150 and 130 K (from 4.2 and 7.5 ‰, respectively). Carbon isotopes are unfractionated ($\Delta^{13}C_{ice\text{-}vapor} \leq 0.2‰$) at temperatures ≥ 135 K and only modestly fractionated ($\Delta^{13}C_{ice\text{-}vapor} \leq 0.4‰$) 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 $\delta^{18}O$ 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 CO_2 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 ^{18}O-depleted volatile reservoirs**