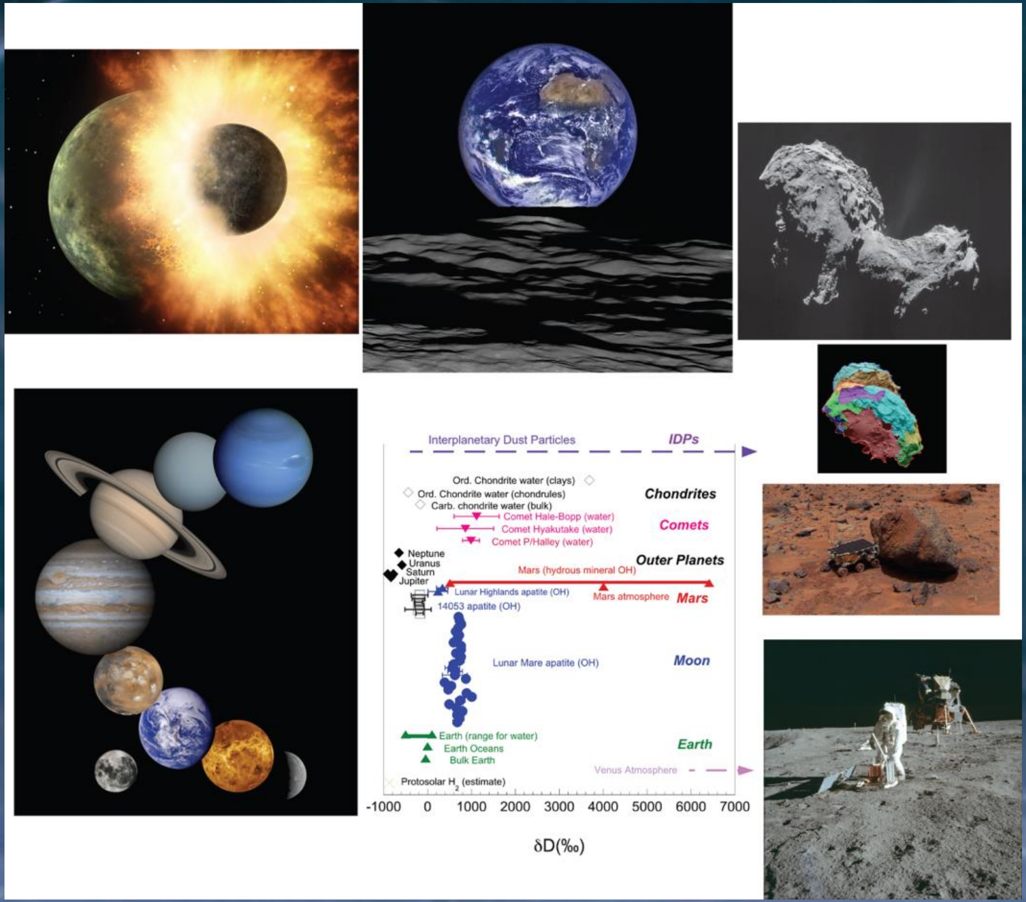
Volatiles of
Inner Solar System Bodies



James Greenwood

E&ES
&
Planetary Sciences

Wesleyan University, Connecticut USA

Origin of Volatiles in Habitable Planets: The Solar System and Beyond
University of Michigan, October 16-17, 2017

Volatiles of Inner Solar System Bodies

- Cosmochemistry 101
- Volatiles of
  - Mercury
  - Venus
  - Moon
  - Mars
- New Model for origin of inner solar system hydrogen, oxygen, and nitrogen

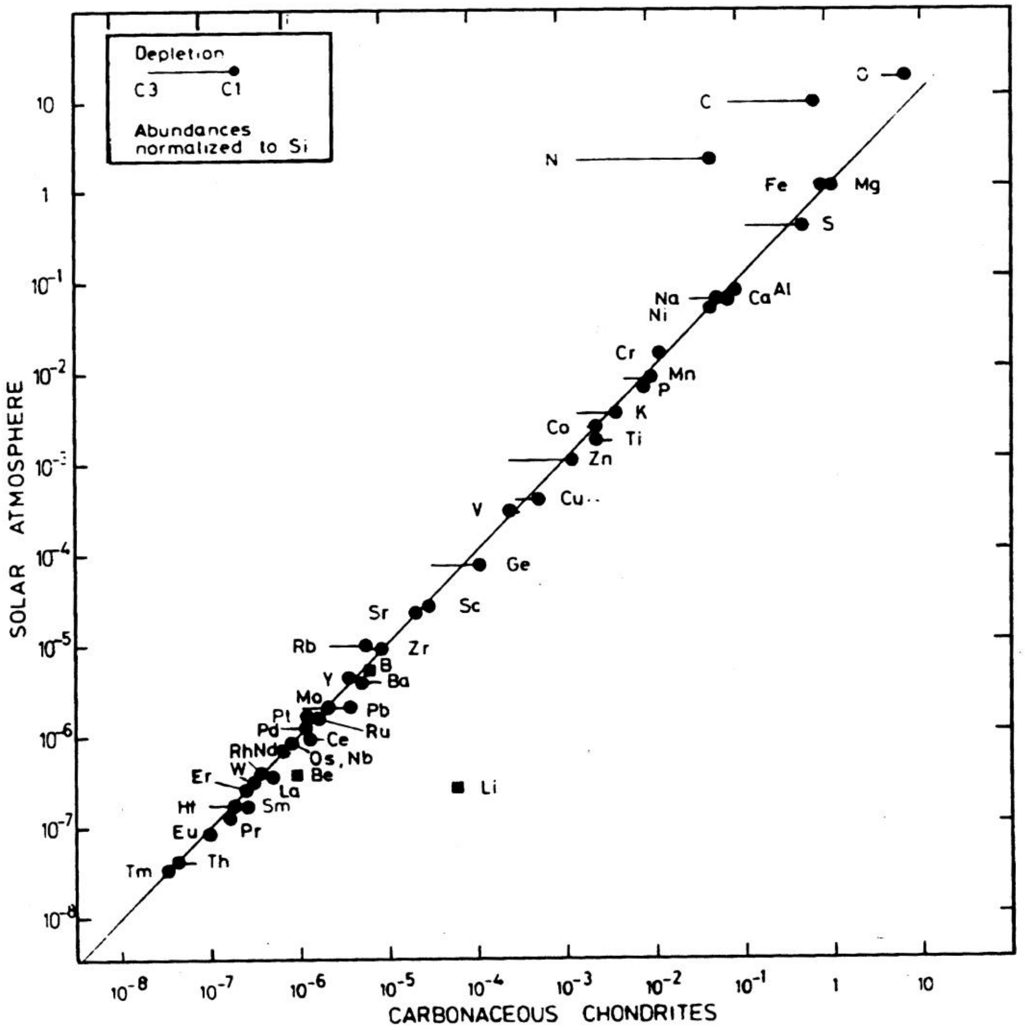


Figure 7.7. Abundances in the Solar Atmosphere Compared with those in C1 and C3 Carbonaceous Chondrites. Courtesy H. Holweger and International Astronomical Union.

1:1 correlation between Sun and CI chondrite

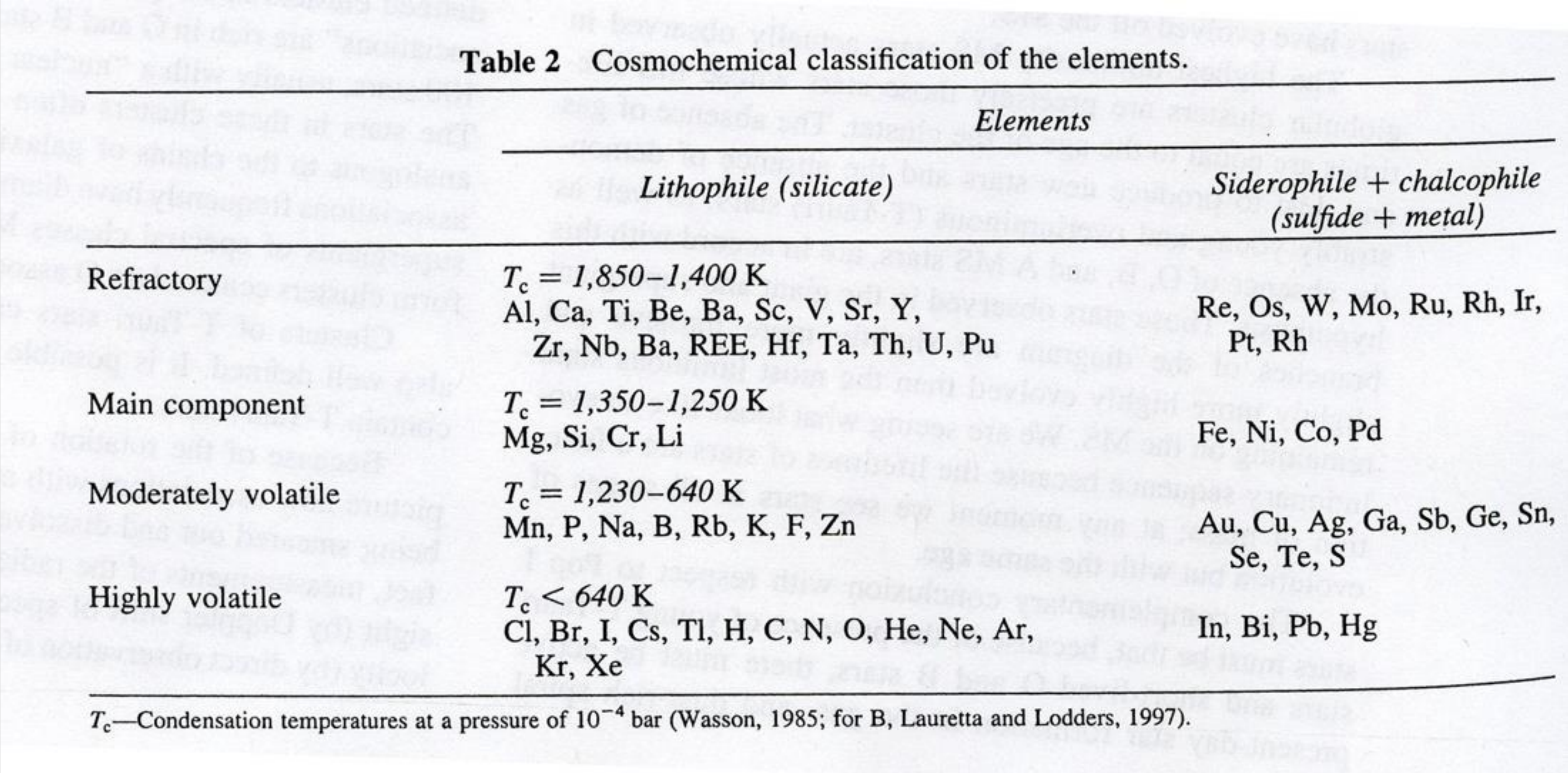


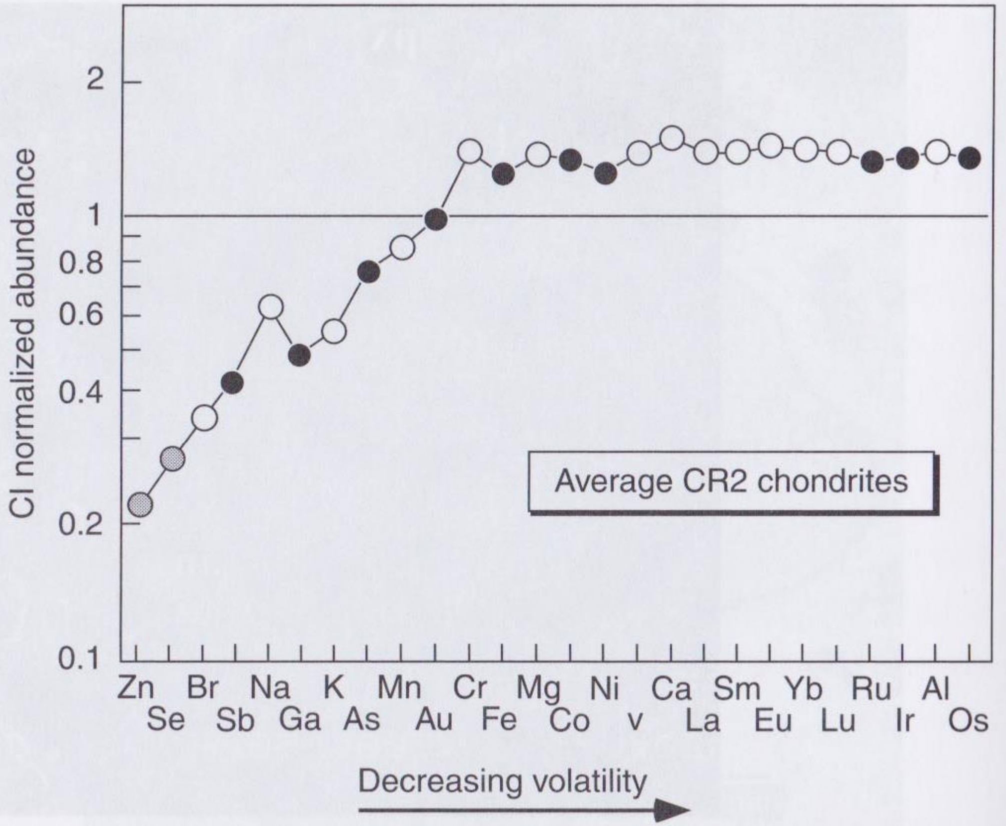
Table 2 Cosmochemical classification of the elements.

	Elements	
	Lithophile (silicate)	*Siderophile + chalcophile (sulfide + metal)*
Refractory	$T_c = 1{,}850$–$1{,}400$ K Al, Ca, Ti, Be, Ba, Sc, V, Sr, Y, Zr, Nb, Ba, REE, Hf, Ta, Th, U, Pu	Re, Os, W, Mo, Ru, Rh, Ir, Pt, Rh
Main component	$T_c = 1{,}350$–$1{,}250$ K Mg, Si, Cr, Li	Fe, Ni, Co, Pd
Moderately volatile	$T_c = 1{,}230$–640 K Mn, P, Na, B, Rb, K, F, Zn	Au, Cu, Ag, Ga, Sb, Ge, Sn, Se, Te, S
Highly volatile	$T_c < 640$ K Cl, Br, I, Cs, Tl, H, C, N, O, He, Ne, Ar, Kr, Xe	In, Bi, Pb, Hg

T_c—Condensation temperatures at a pressure of 10^{-4} bar (Wasson, 1985; for B, Lauretta and Lodders, 1997).

Cosmochemical fractionations

- The elements are fractionated in meteorites and planets based on these basic properties
  - Physical and chemical processes lead to fractionations
  - Gas-solid: Evaporation: condensation processes
  - Also gas-liquid (evaporation-condensation)
  - Physical fractionations (sorting by size)
  - Oxidation/reduction
  - Planetary differentiation
  - Igneous fractionations (geochemical fractionations)



Elemental abundances in CR2 chondrites normalized to the CI composition and plotted in order of decreasing volatility from left to right. Lithophile elements are shown with open circles, siderophile elements with black circles, and chalcophile elements with gray circles. CR2 data from Kallemeyn *et al.* (1994).

Elemental abundances in CR2 chondrites normalized to CI-no difference between siderophile, chalcophile, or lithophile

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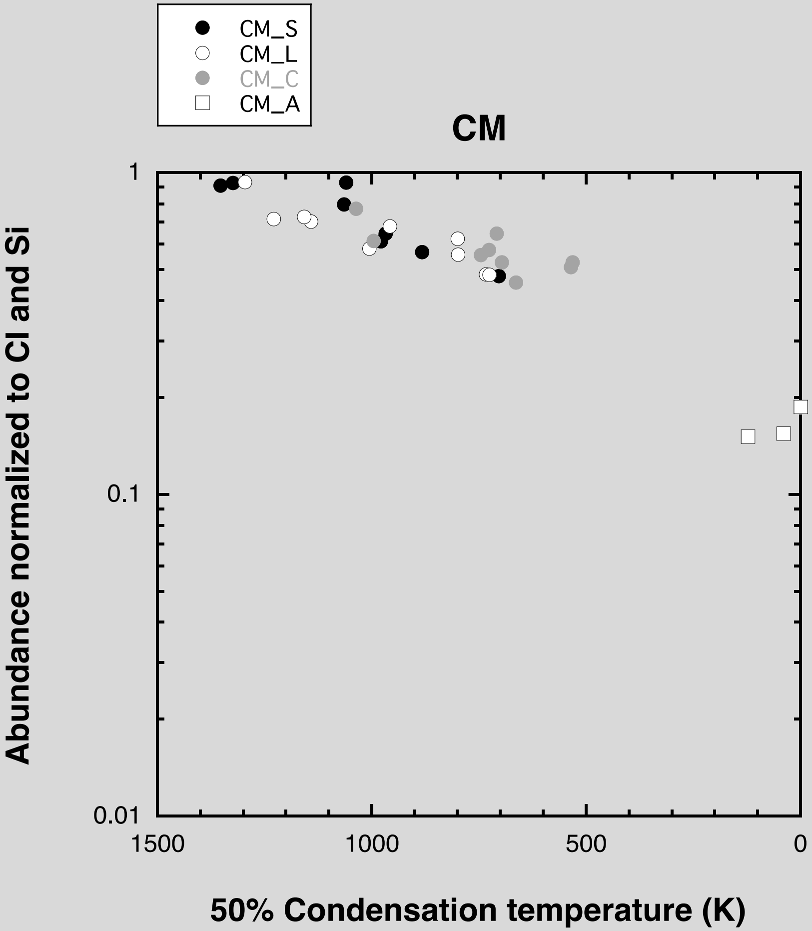
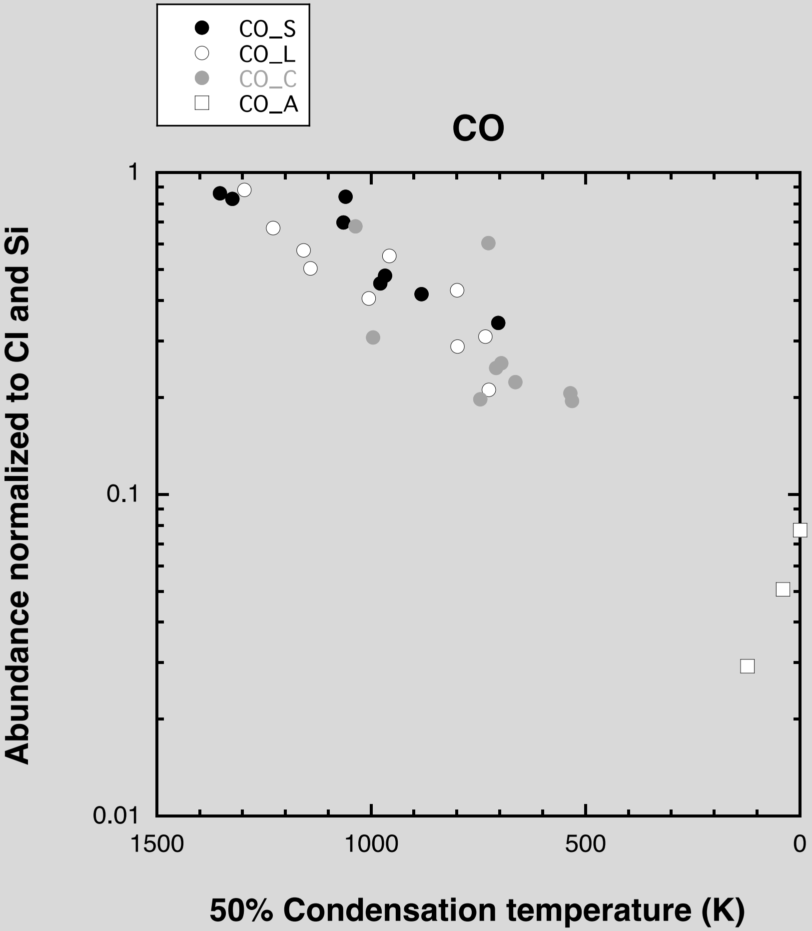
Carbonaceous Chondrites normalized to CI and Si





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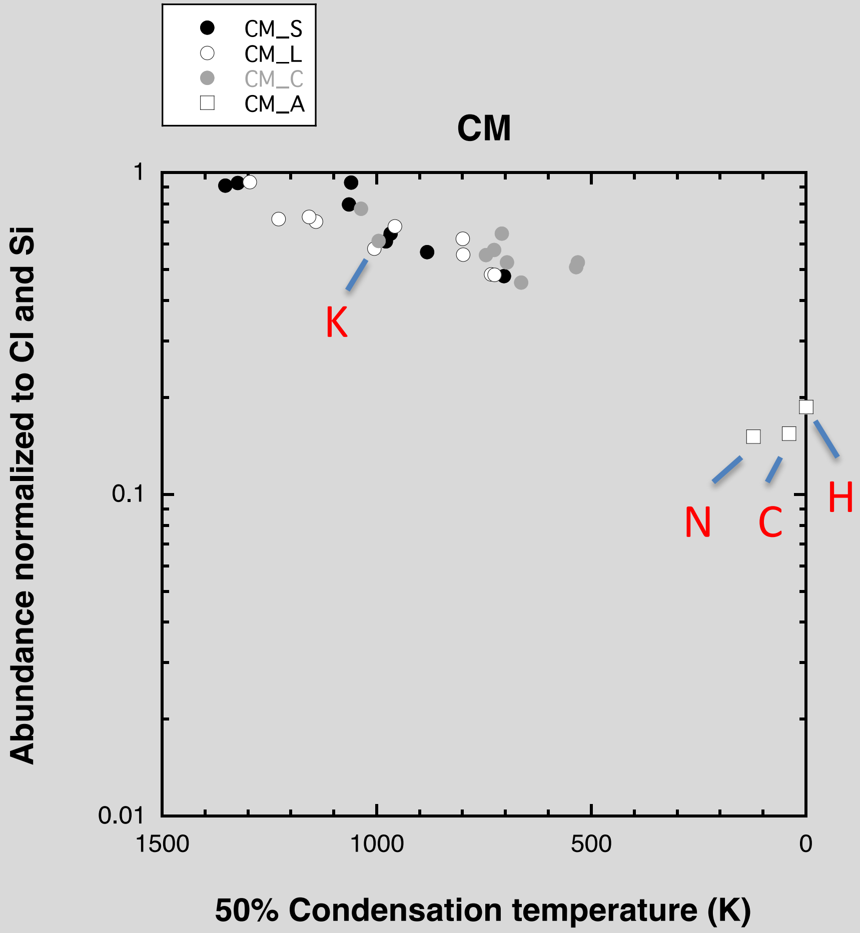
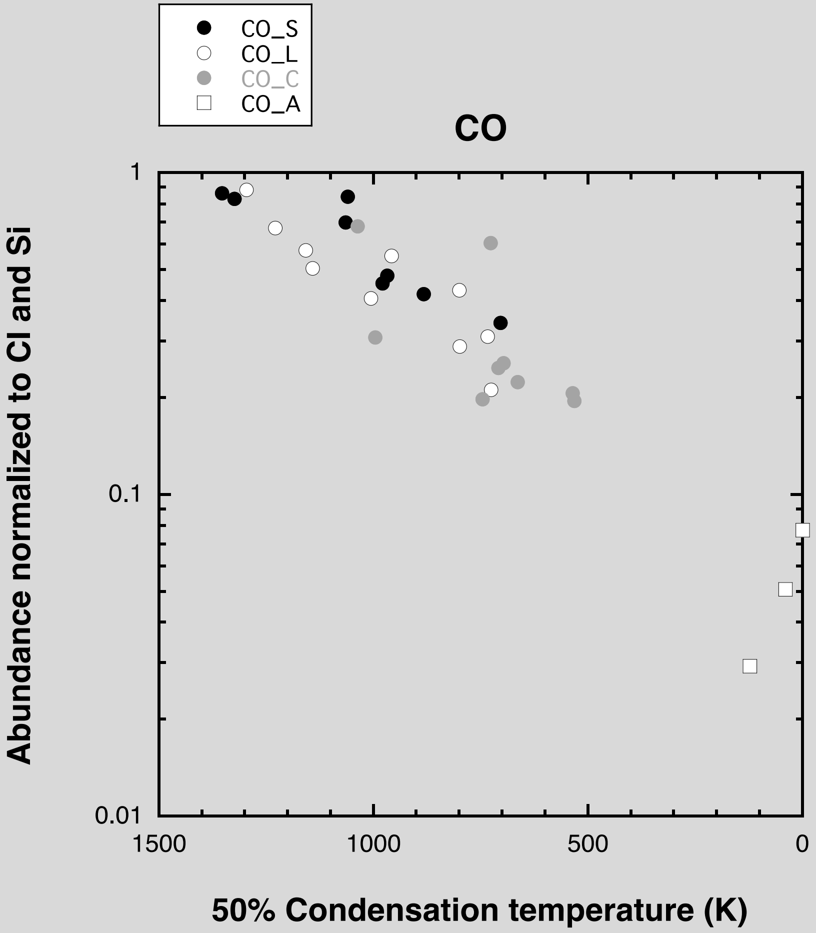
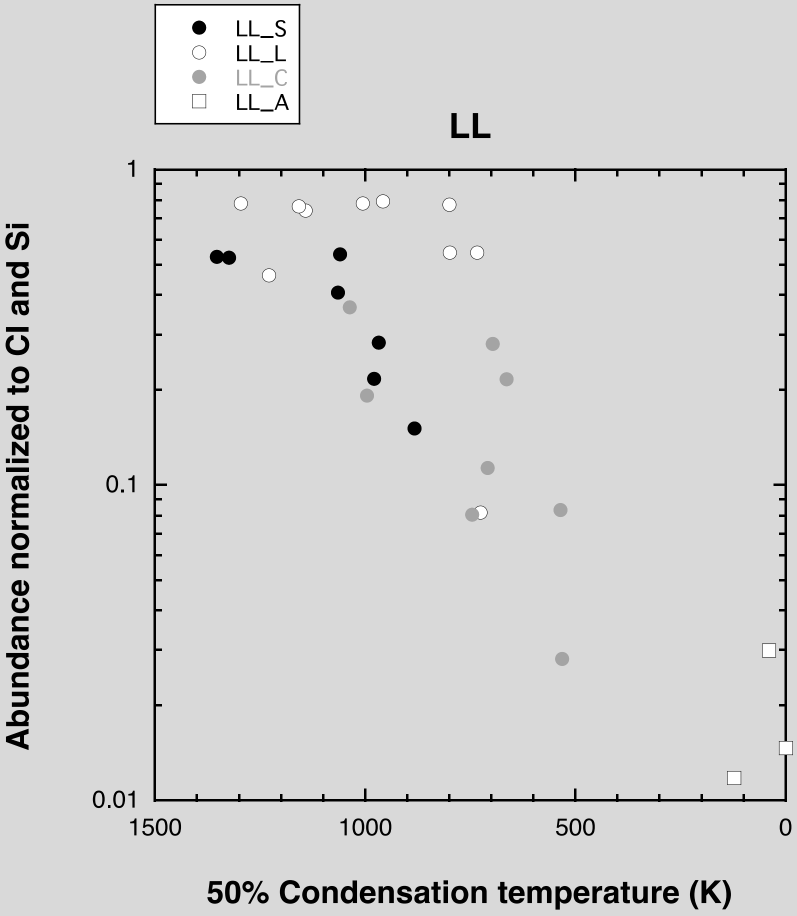
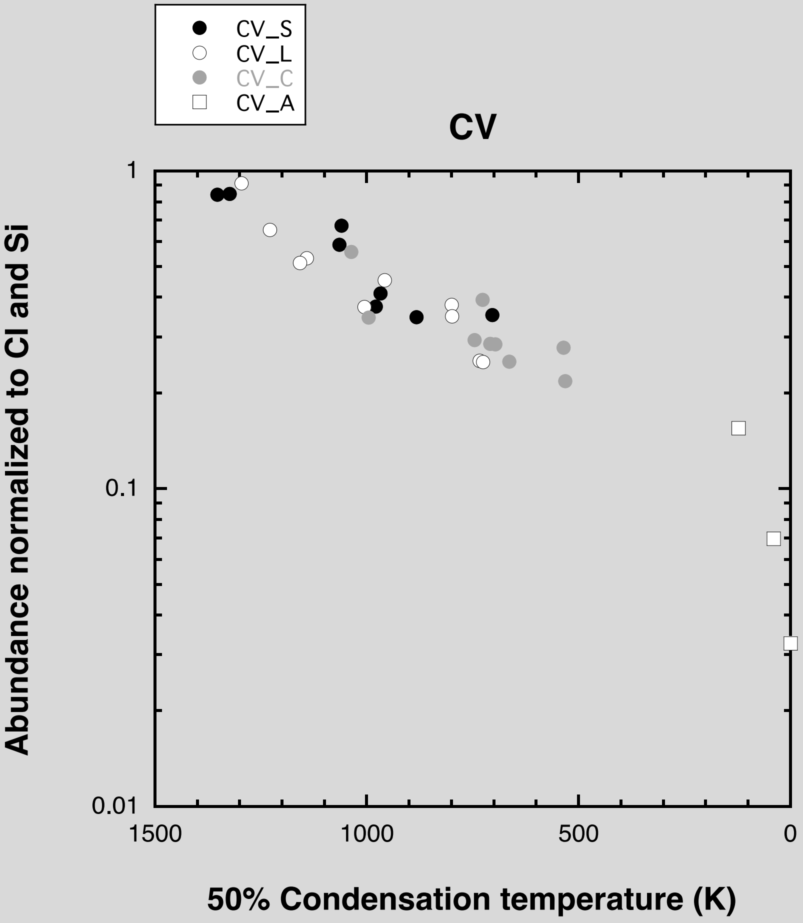
Carbonaceous Chondrites normalized to CI and Si





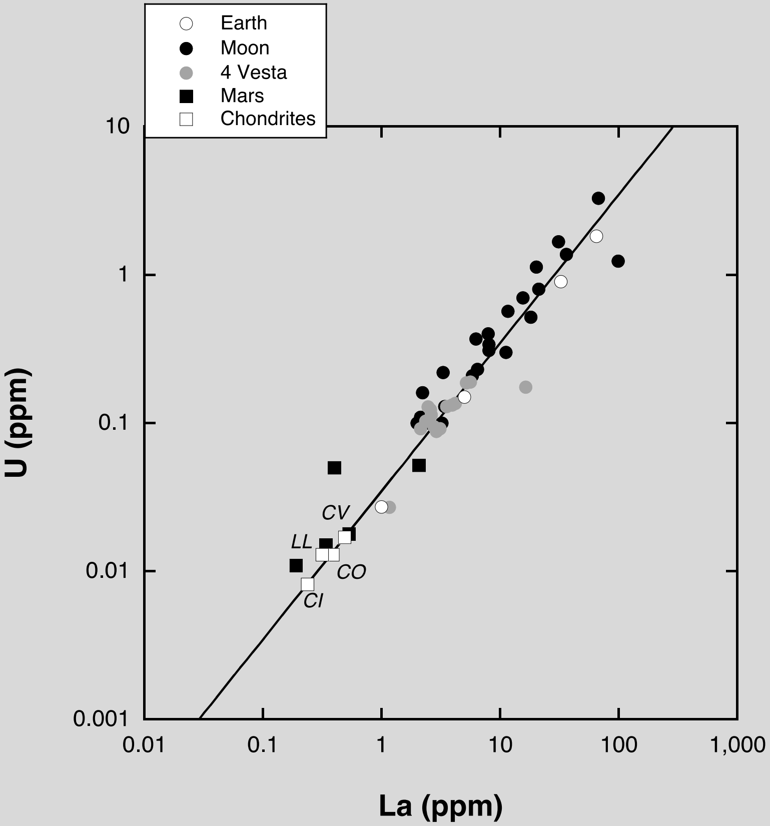
Ordinary and CV chondrites



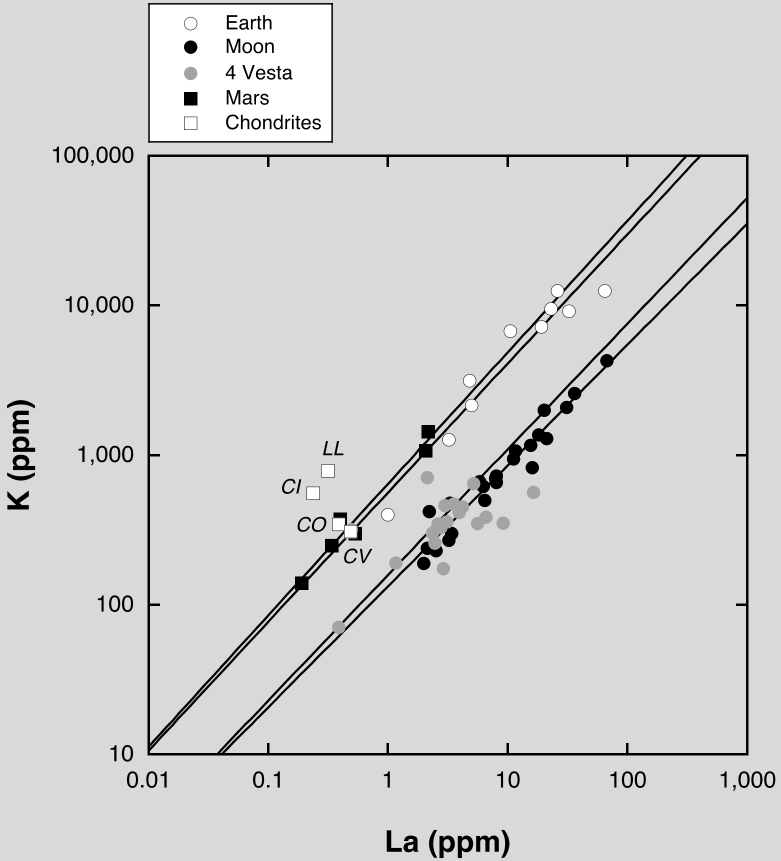


Loss of volatiles during planetary formation

Refractory vs. Refractory for inner solar system



Volatile vs. Refractory for inner solar system



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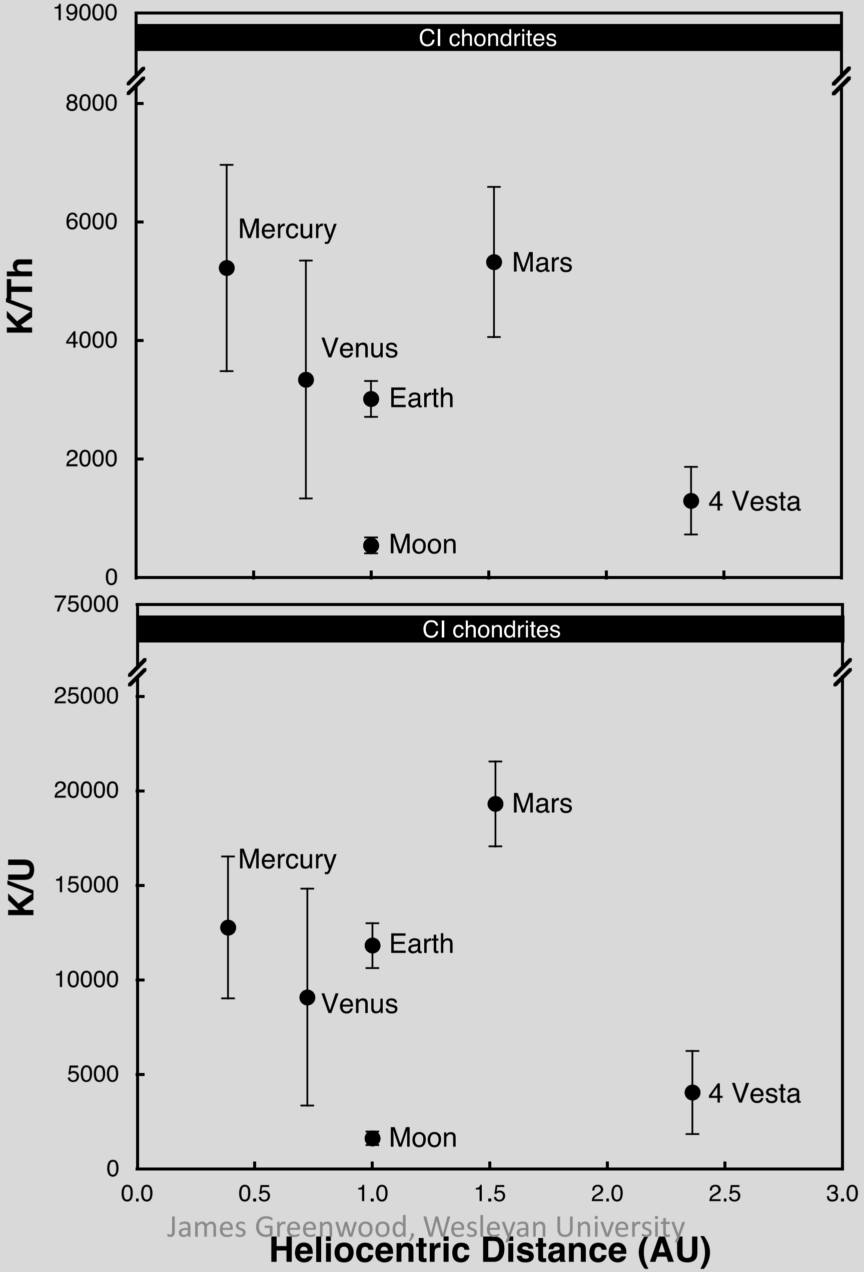
McCubbin
et al. (2012)
GRL
L09202,
doi:10.1029
/2012GL05
1711, 2012



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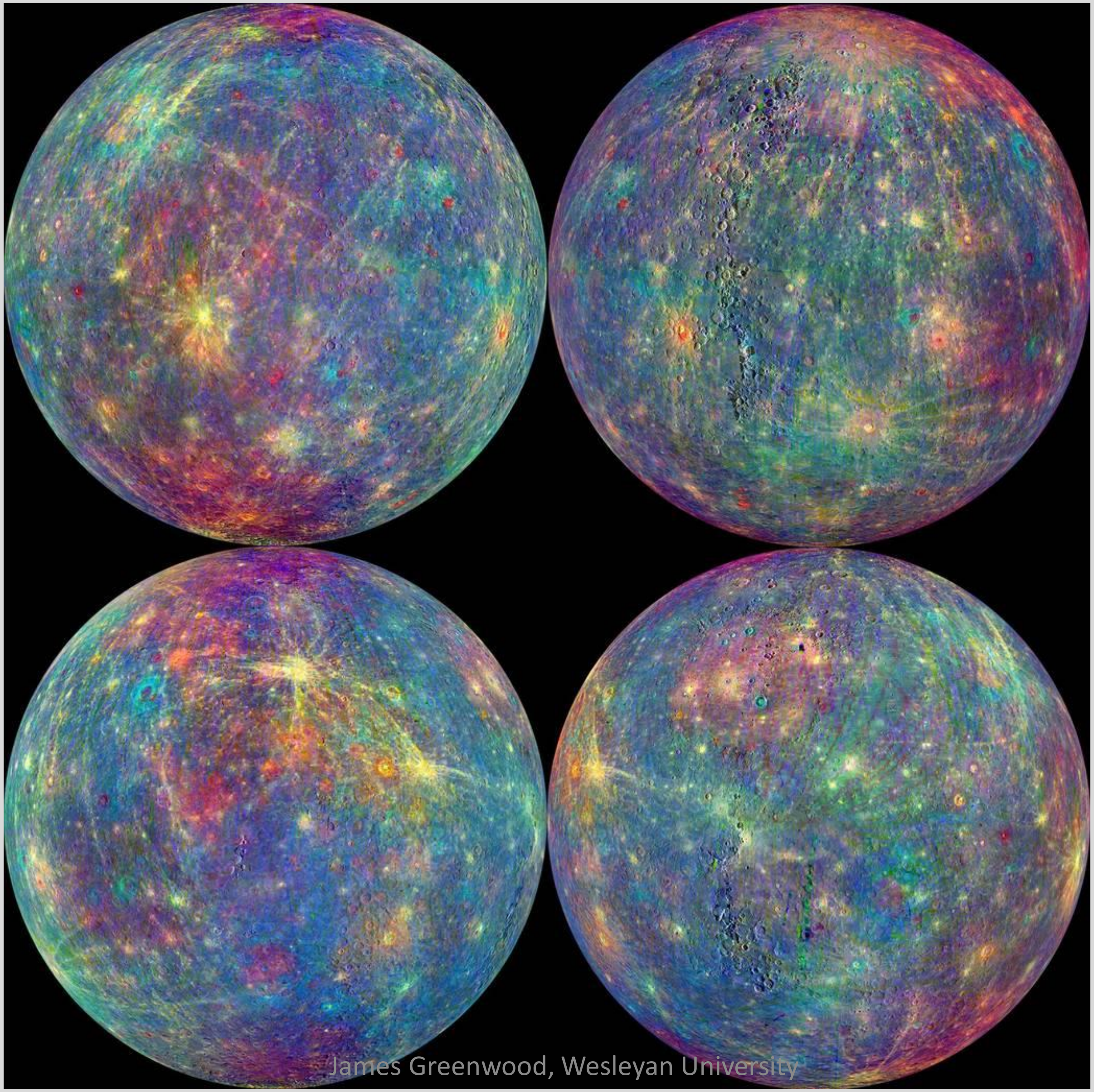
Mercury- A volatile-rich planet



Cl vs. K

Evans et al. (2015) Icarus 257, 417-427

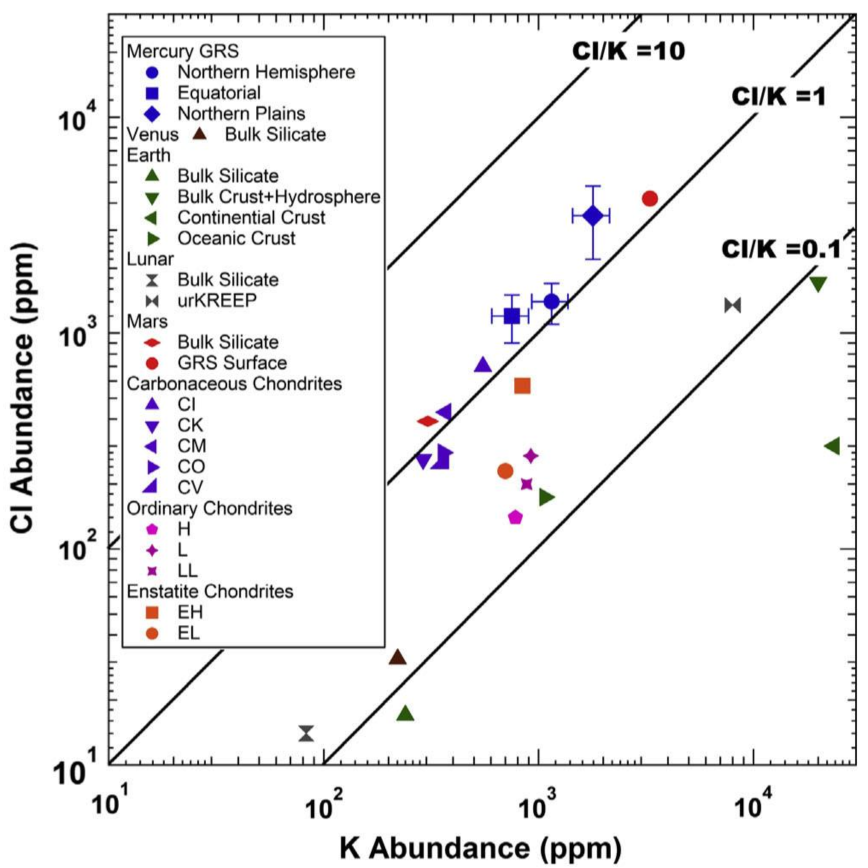
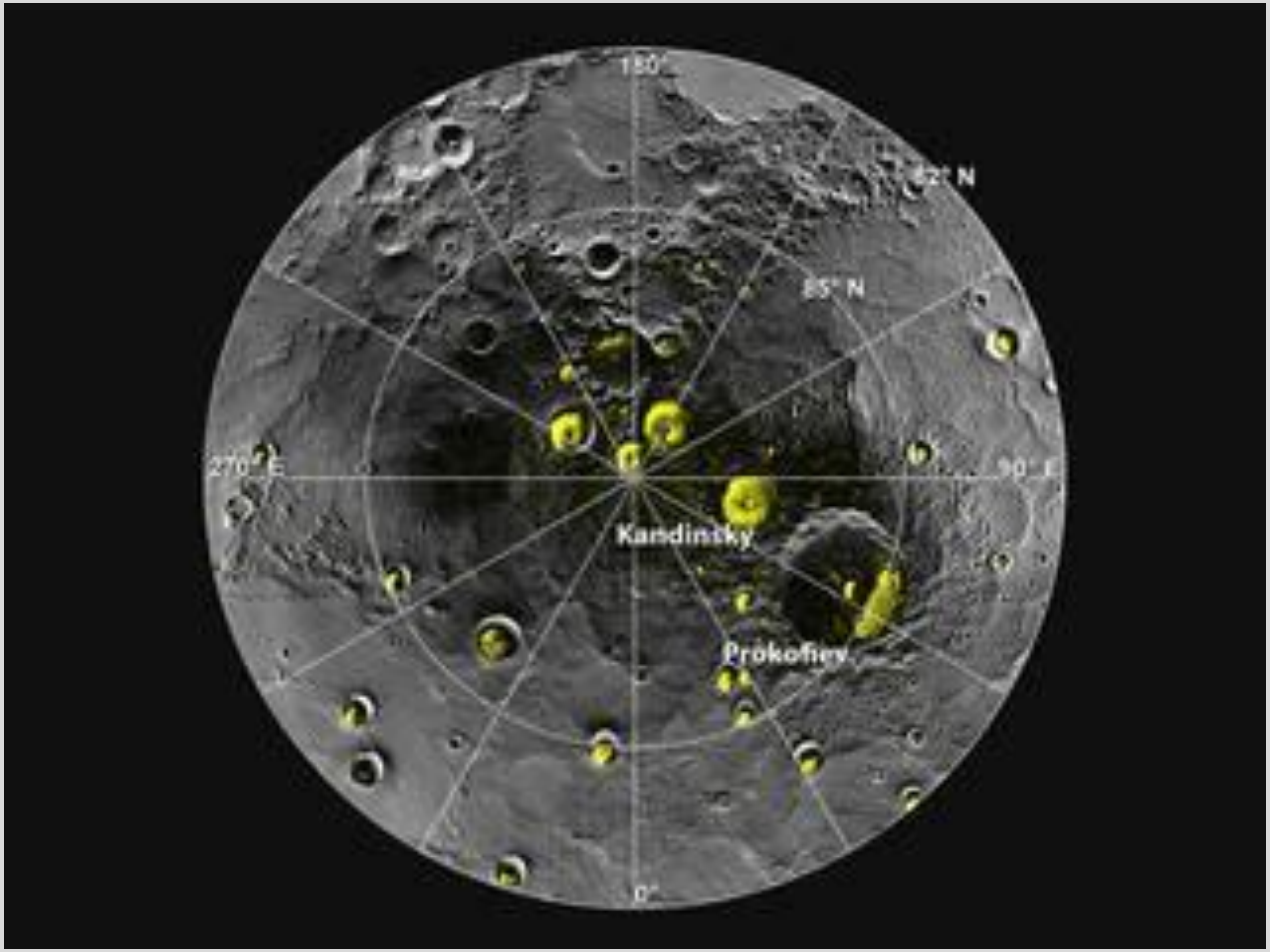
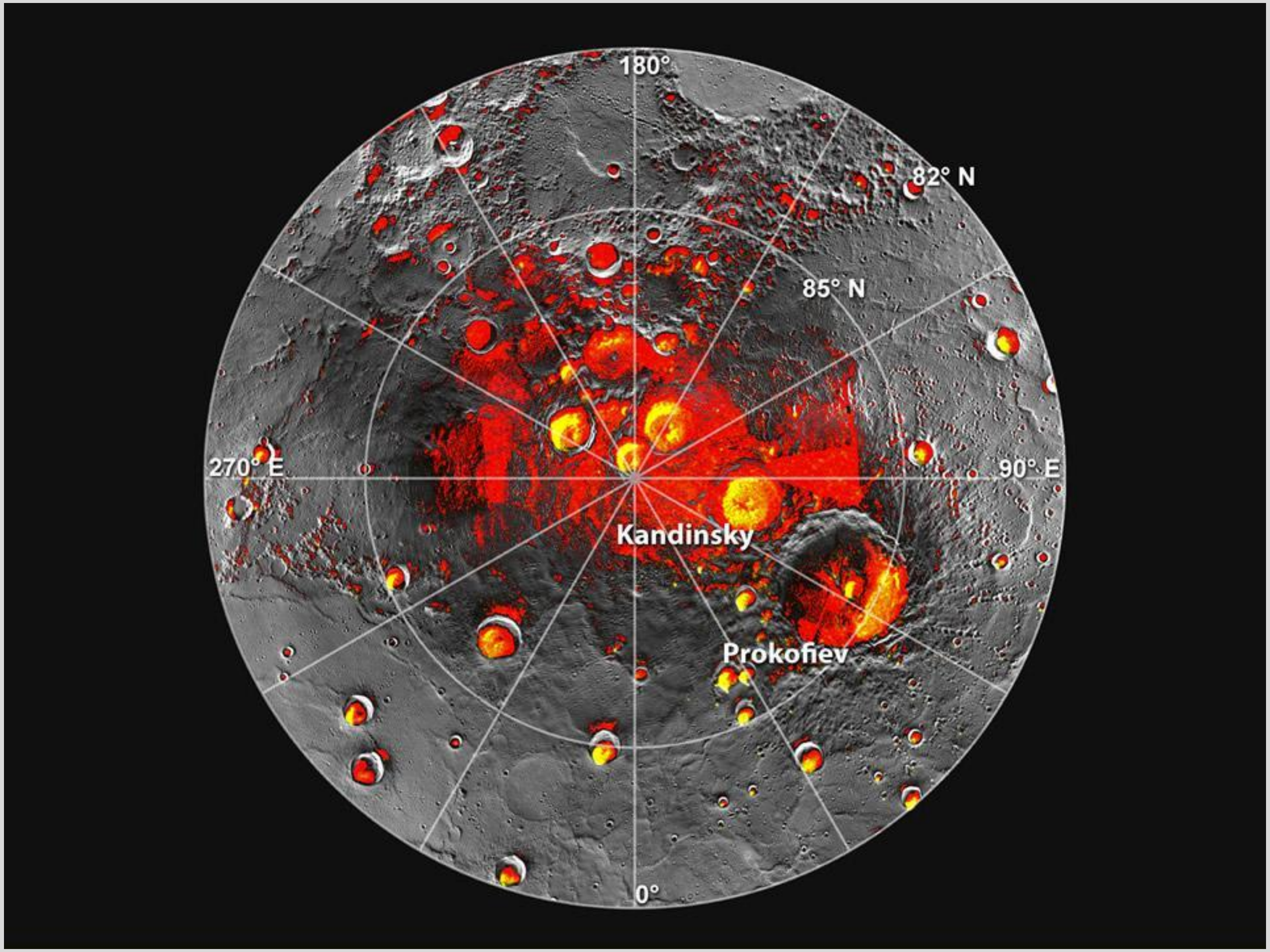


Fig. 4. Relationship between Cl and K for Mercury (dark blue symbols) and other Solar System objects. Values are shown for Venus in brown, Earth in green, Mars in red, carbonaceous chondrites in purple, ordinary chondrites in pink, and enstatite chondrites in orange. Data for this figure for Venus are from Morgan and Anders (1980); Earth, McDonough and Sun (1995) and Lodders and Fegley (1998); the Moon, Taylor (1982), Warren (1988), and McCubbin et al. (in press); Mars, Boynton et al. (2007) and Taylor et al. (2010); chondrites Lodders and Fegley (1998); and Mercury, Peplowski et al. (2011). Lines of constant Cl/K are shown for reference.

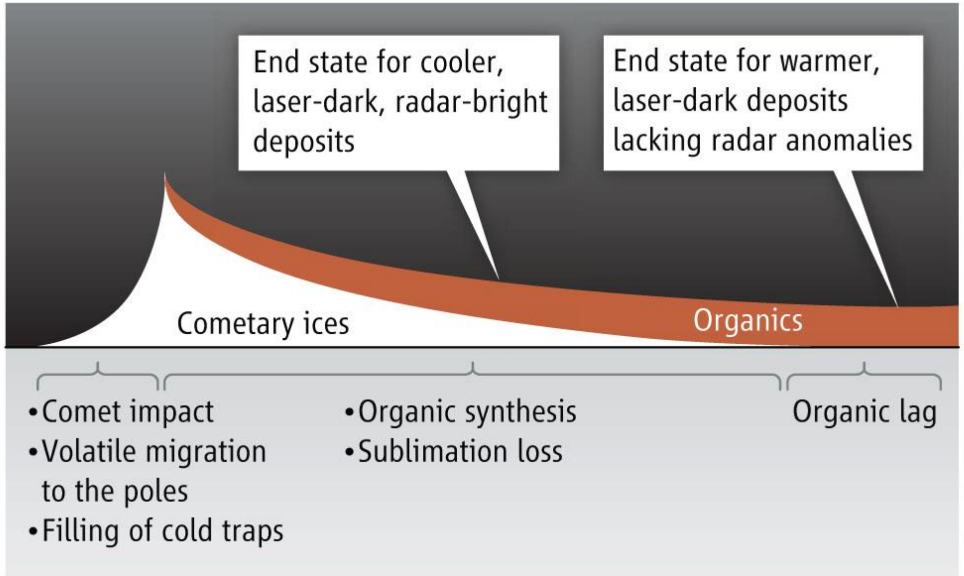
Arecibo radar anomalies at Mercury pole



Messenger at Mercury Topographic lows

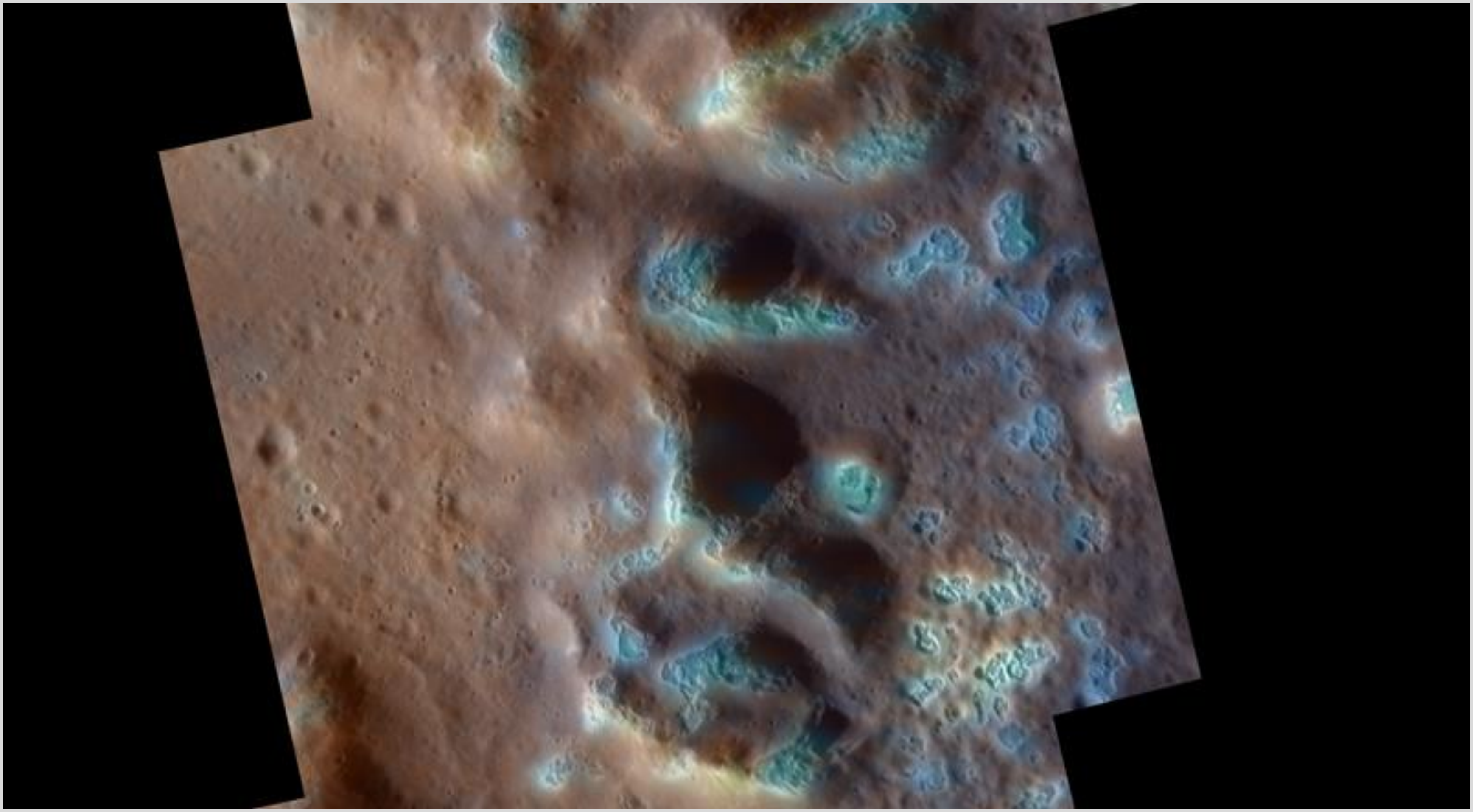


Lucey (2013) Science 339 282-283



Atmosphere dynamics. Mercury's polar cold traps appear to have been filled by one or more comet impacts that introduced massive quantities of water and other volatile vapors in the tenuous atmosphere that promptly migrated to the polar cold traps. Ices began to immediately sublimate, and to acquire organic lag deposits, probably from radiation-induced chemical synthesis. The colder parts of the poles now exhibiting radar anomalies retained water ice below the lag deposit, while in warmer portions the ice entirely sublimed away, leaving the low-reflectance organic residue. Not depicted are the rare very-high-reflectance spots that are confined to the coldest portions of the pole. These may indicate a slow continuous production of water from small wet meteorites, solar wind proton interactions with oxygen in Mercury's surface, or inhibition by the very low temperatures of the organic synthesis occurring elsewhere.

Hollows on Mercury



Paige et al. (2013) Science 339, 300-303

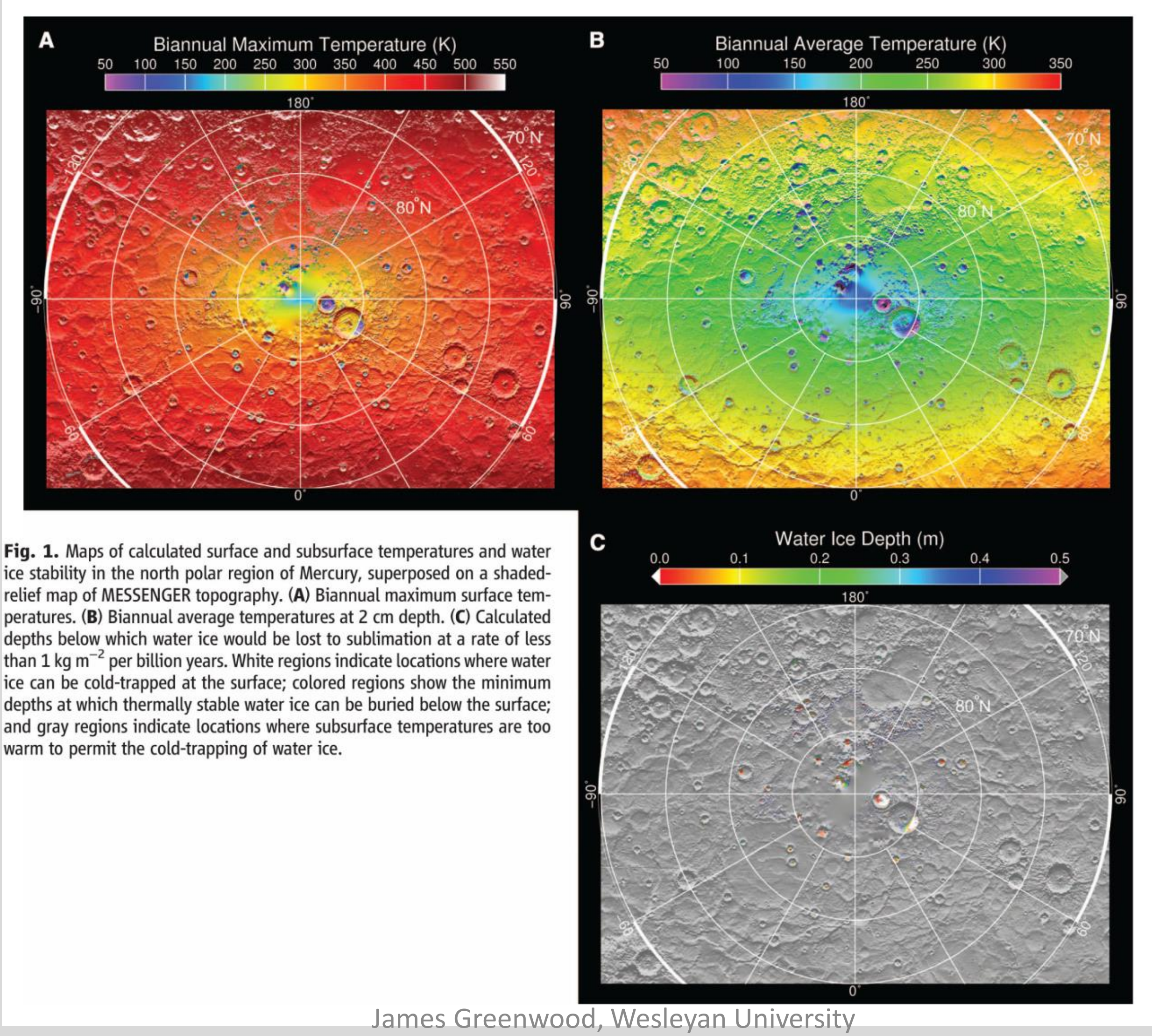
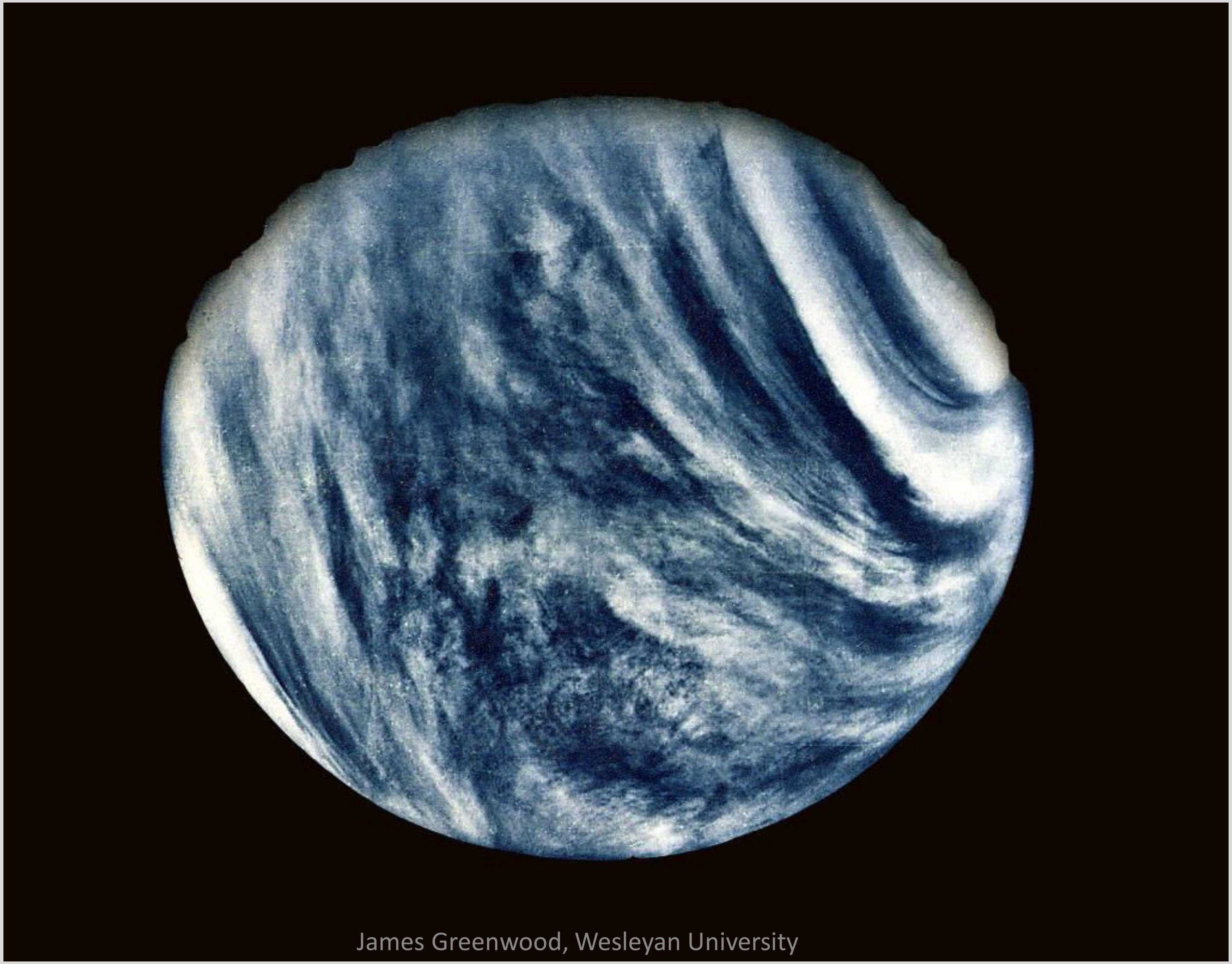


Fig. 1. Maps of calculated surface and subsurface temperatures and water ice stability in the north polar region of Mercury, superposed on a shaded-relief map of MESSENGER topography. (**A**) Biannual maximum surface temperatures. (**B**) Biannual average temperatures at 2 cm depth. (**C**) Calculated depths below which water ice would be lost to sublimation at a rate of less than 1 kg m^{-2} per billion years. White regions indicate locations where water ice can be cold-trapped at the surface; colored regions show the minimum depths at which thermally stable water ice can be buried below the surface; and gray regions indicate locations where subsurface temperatures are too warm to permit the cold-trapping of water ice.

Mercury-summary

- Mercury has high intrinsic levels of volatile elements (K, Cl, S)
- Cl-rich volcanic terrains
- Graphite ‘anti-crust’ suggests no shortage of Carbon
- Hollows point to recent volatile loss in craters
- Mercury has water ice in permanently shadowed craters in north polar region
- The ice is apparently covered with an organic-rich lag deposit that protects the water ice from sublimating away
- Ice and organics may be cometary derived in recent times, or…

Venus first look-Mariner 10



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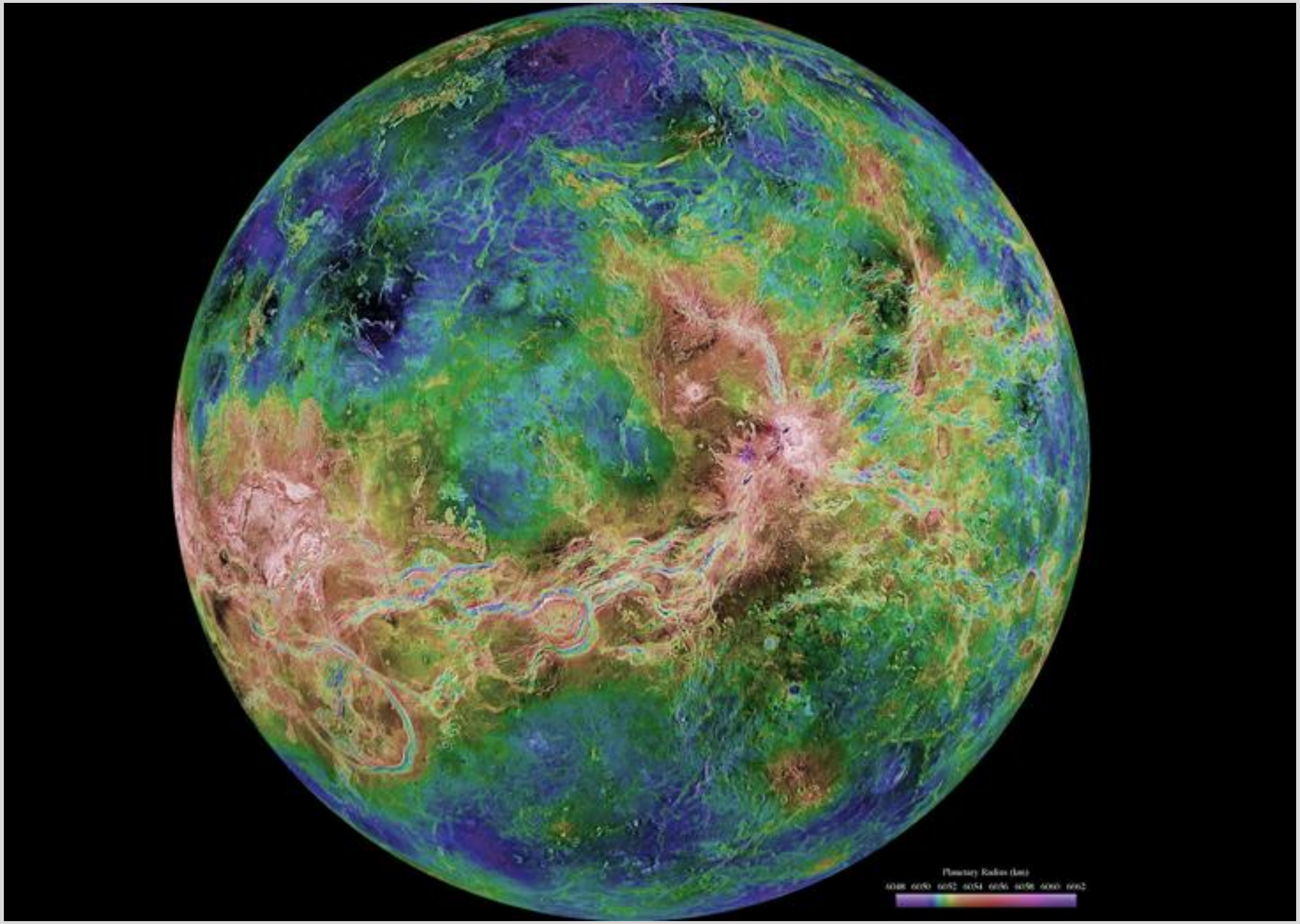
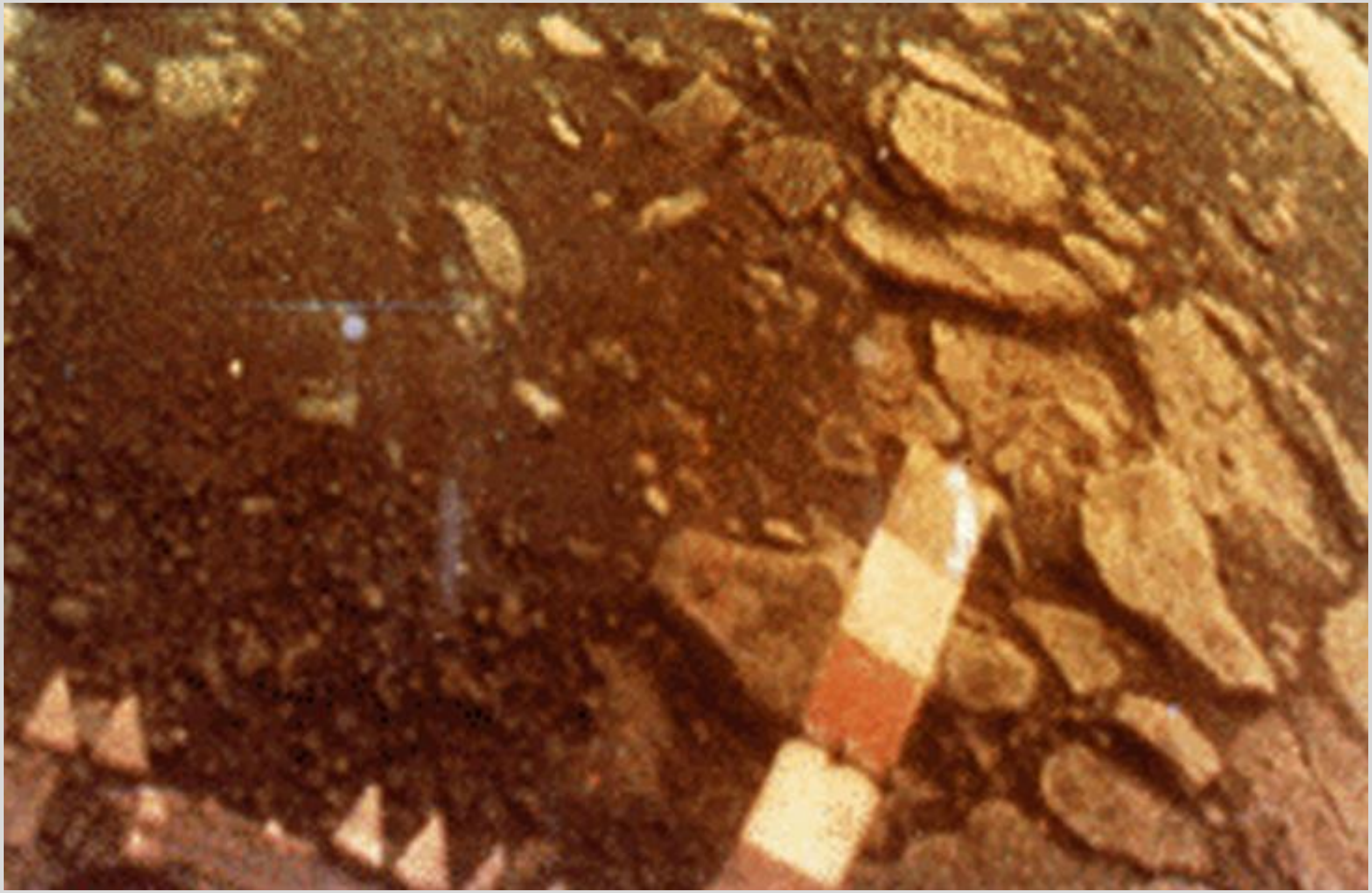
Venus topography



Venusian surface



Venus-summary

- Highly fractionated D/H (120 x Earth) suggests almost complete loss of water from the current atmosphere
- Venus likely received as many volatiles as Earth (why not?)
- C and N of Venus atmosphere similar to Earth abundances
- Means early Venus could have been similar to Early Earth in atmosphere and surface conditions (conducive to life too?)
- Venusian tesserae likely preserve evidence of previous volatile-rich weathering environment

Gilmore et al. (2017) Space Sci. Rev.

DOI 10.1007/s11214-017-0370-8

M. Gilmore et al.

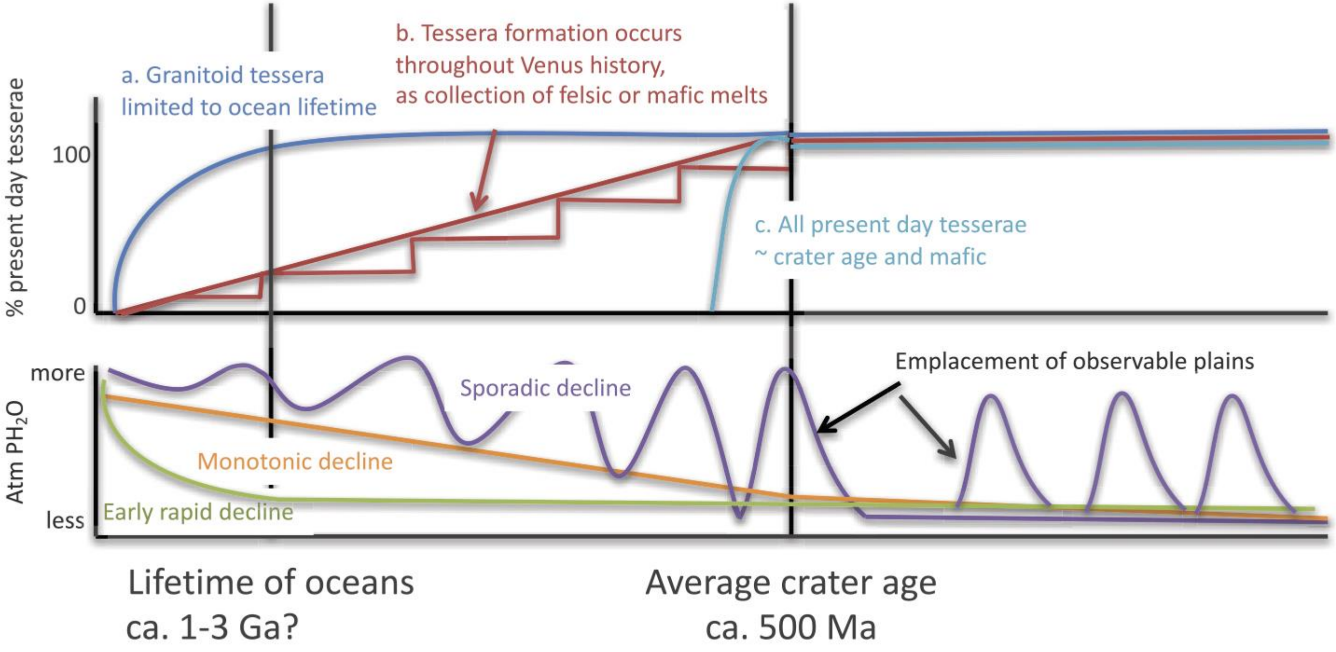


Fig. 6 Schematic diagram of tessera formation (*upper panel*) and atmospheric H_2O (*bottom panel*). Several models of water loss can be envisioned including early, rapid loss (e.g., Kasting and Pollack 1983), monotonic decline (e.g., Grinspoon 1993), or sporadic decline such as that predicted in catastrophic overturn models (e.g., Grinspoon and Bullock 2007). (**a**) The formation of continents' worth of felsic tesserae terrain is limited to the lifetime of oceans on Venus. (**b**) Tessera terrain could be produced by the aggregation of small volumes of felsic melt or weathering of mafic melts. (**c**) Tesserae formed just prior to plains emplacement. Recent volcanism may contribute to steady or sporadic influx of volatiles into the atmosphere resulting in changing weathering regimes

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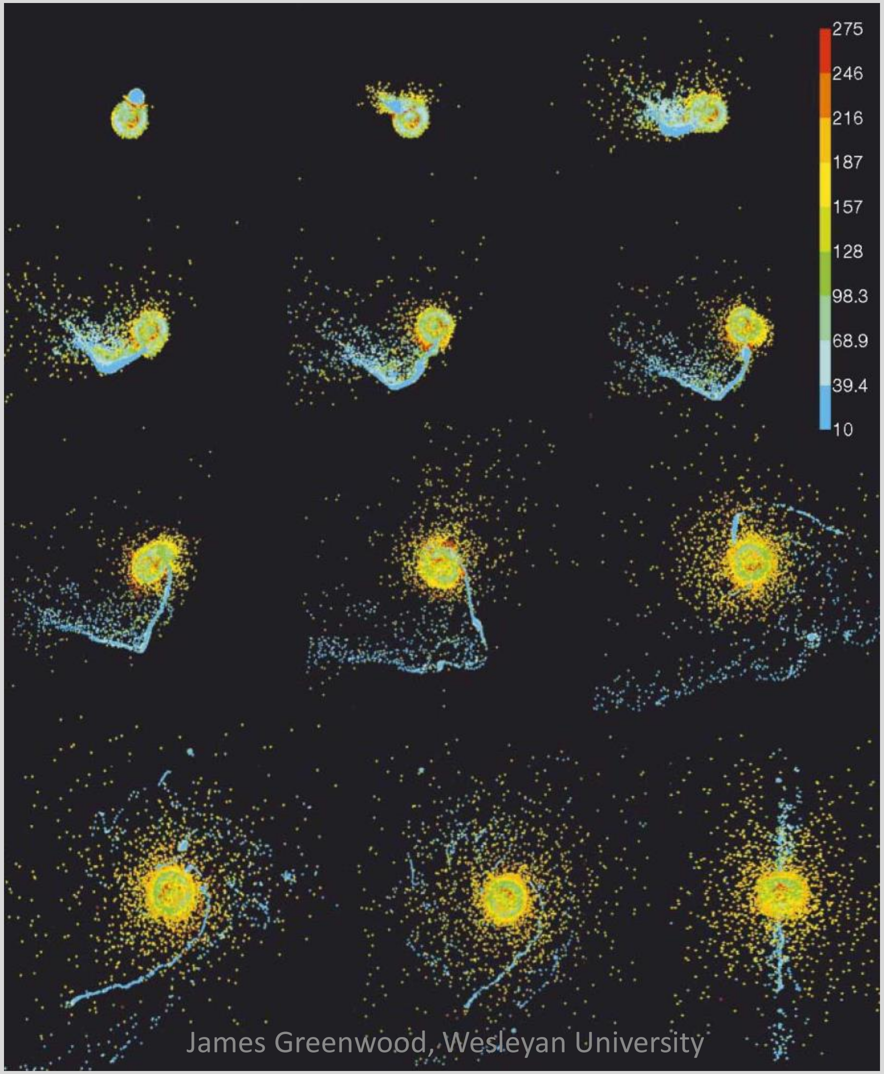
Moon

- Formed in giant impact with Mars-sized body
- Had giant magma ocean
- Youngest lavas ~ 1 Ga
- What happened to volatiles in this process?

Mars-sized impact into proto-Earth to form Moon-U.S. version



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Moon’s volatile depletion

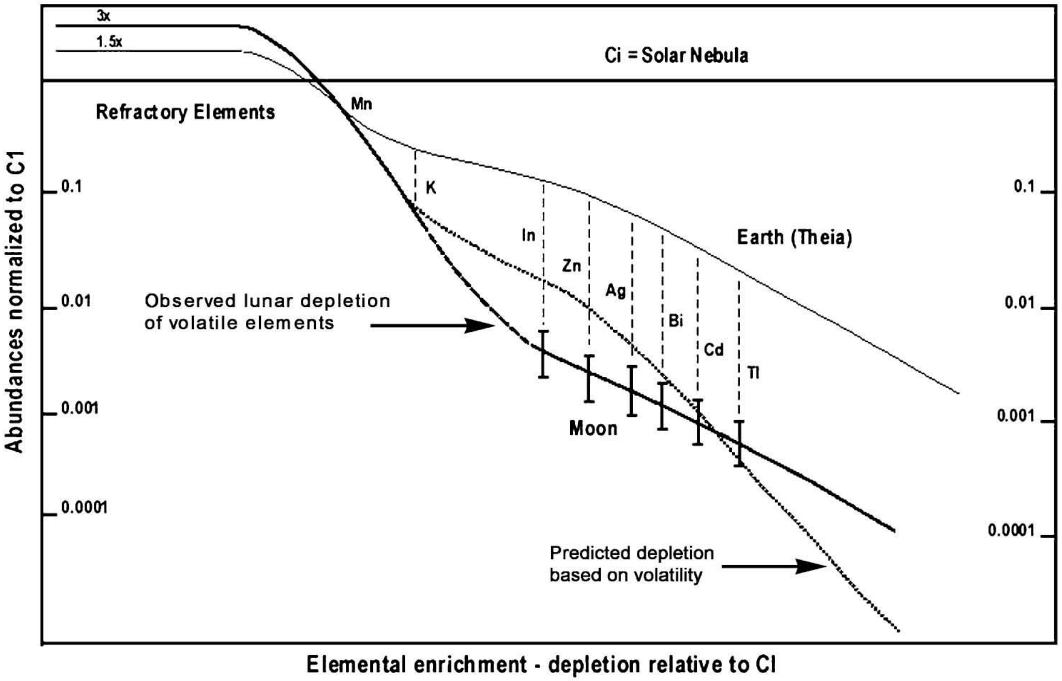
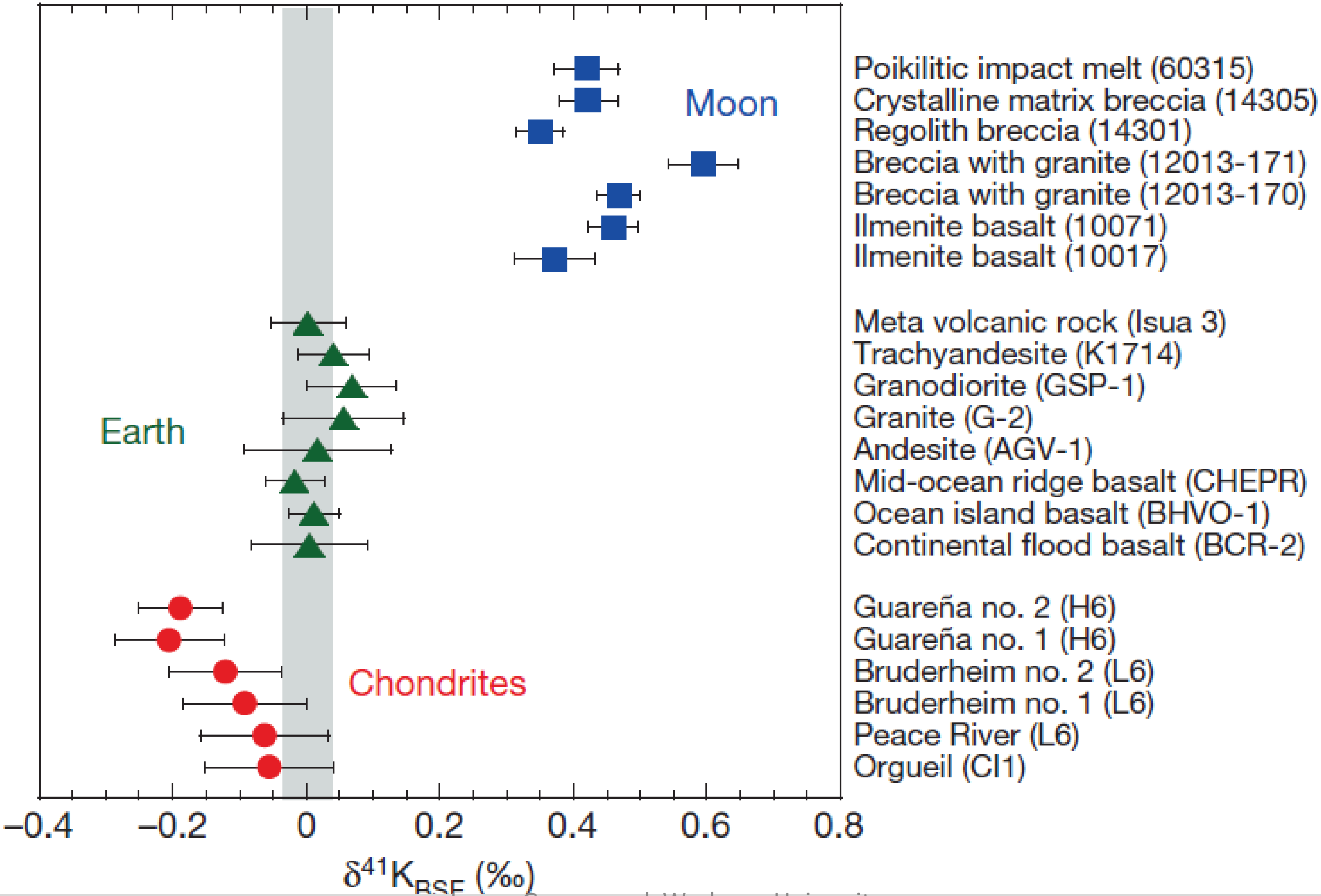


Fig. 1. The composition of the Moon compared with that of the Earth, both normalized to CI carbonaceous chondrites (dry basis). The abundance curve for the Earth is principally derived from Wänke et al. (1984), Taylor and McLennan (1985), and other sources. The refractory elements in the Earth are 1.5 times CI, and for the Moon, are set at three times CI (see text). We interpret the figure to indicate that the material in the impactor mantle (Theia), from which the Moon was derived, was inner solar-system material already depleted in volatile elements at To and that the abundances in the Earth provide an analogue for its composition. Mn and K provide fixed points for the Moon curve. Mn has the same abundance in the Earth and Moon. Potassium abundances are derived from K/U values (Earth 12,500; Moon 2500). The volatile-element data for the Moon are derived from Wolf and Anders (1980), who recorded a uniform depletion of 0.026 ± 0.013 for the elements listed, in lunar low-Ti basalts compared to terrestrial oceanic basalts. In the absence of more recent data for both bodies, we adopt their study as recording the Moon-Earth depletion. The significant point is that the lunar depletion is uniform and not related to volatility, which would produce a much steeper depletion pattern (lower dotted line). Thus, the lunar pattern is interpreted as resulting from a single-stage condensation from vapor (>2500 K) that effectively cut-off around 1000 K.



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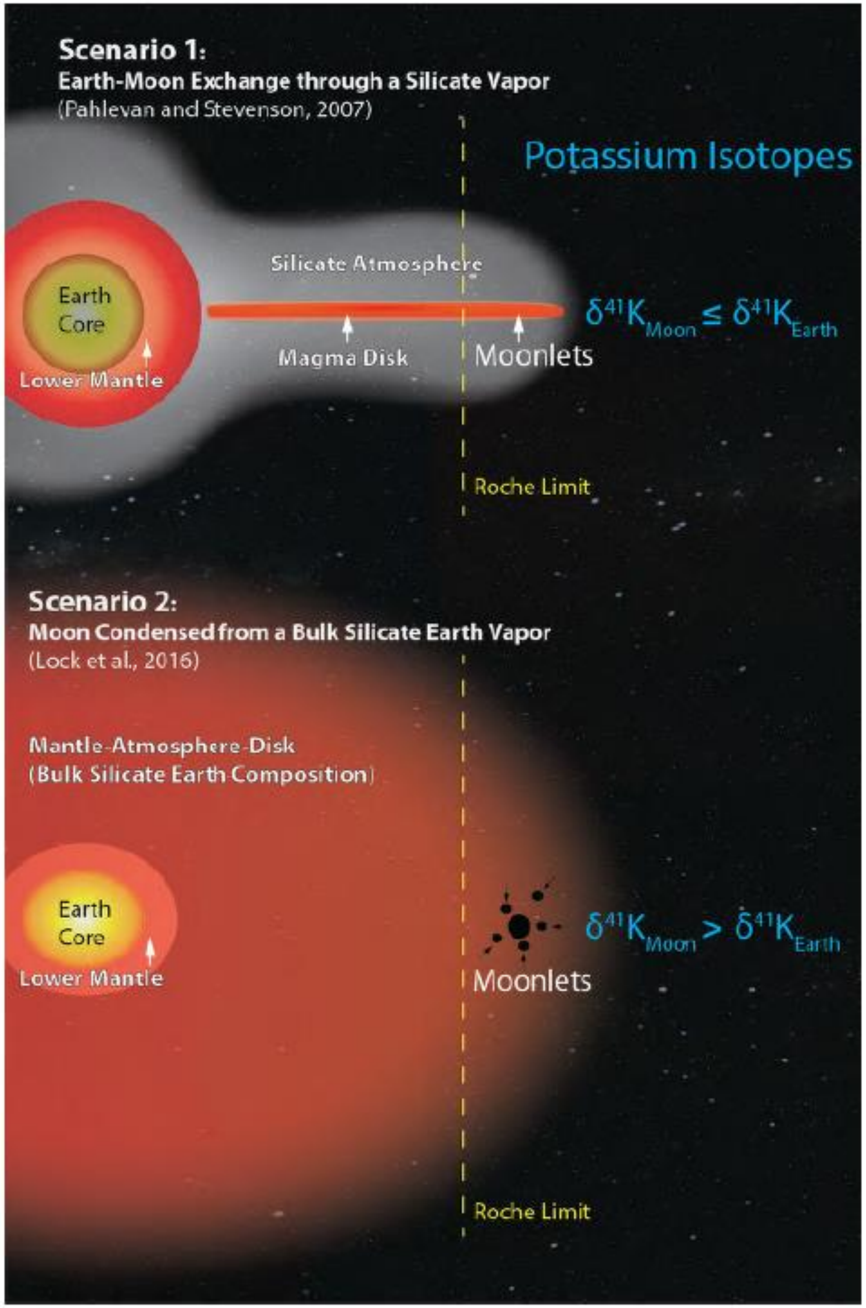
Scenario 1:

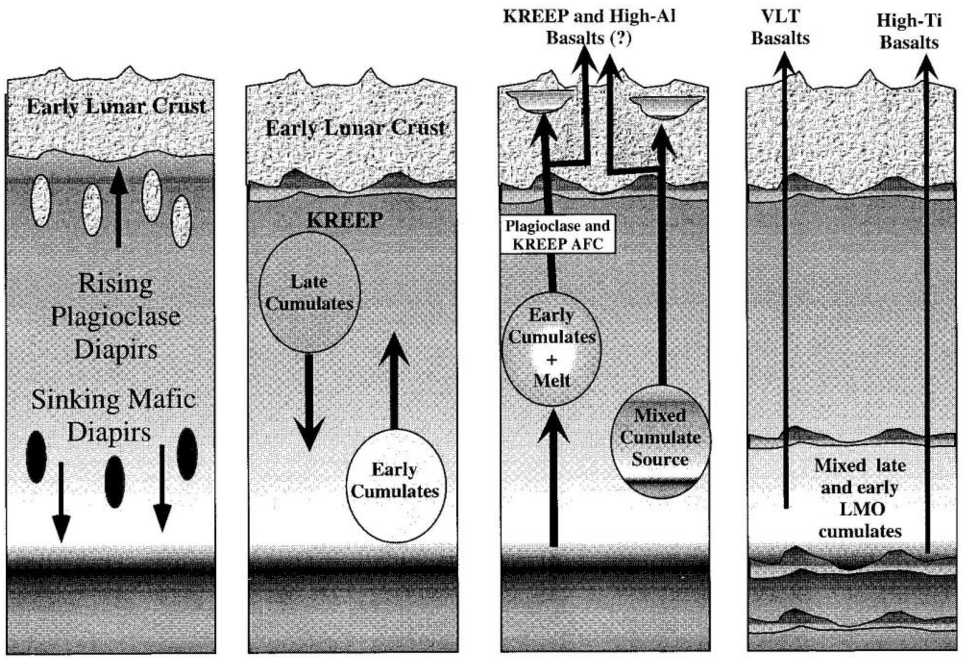
T = 2500K
δ^{41}K moon <= δ^{41}K earth
P ~10 bar
Silicate atmosphere around magma disk

Scenario 2:
T = 3700K
δ^{41}K moon> δ^{41}K earth
P = 20bar



Extended Data Figure 2 | An artist's rendering of the two recent models of the origin of the Moon and their implications for K isotopes. Scenario 1 is from ref. 7; scenario 2 is from ref. 8.

Lunar magmatic evolution



a. Lunar differentiation through magma ocean

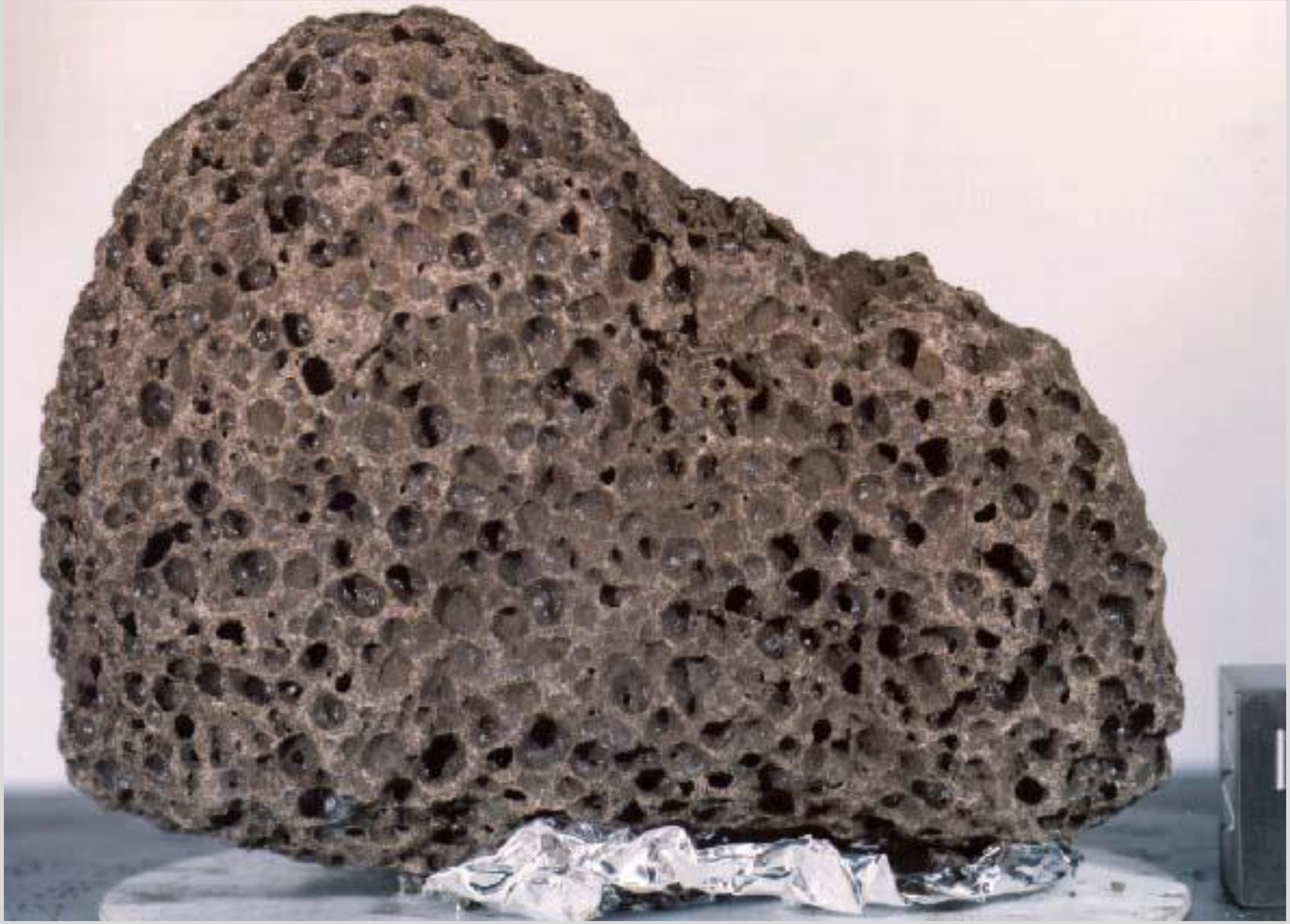
b. Cumulate pile disruption and cumulate mixing

c. Generation of highland plutonic and volcanic basaltic magmas

d. Generation of mare basaltic magmas

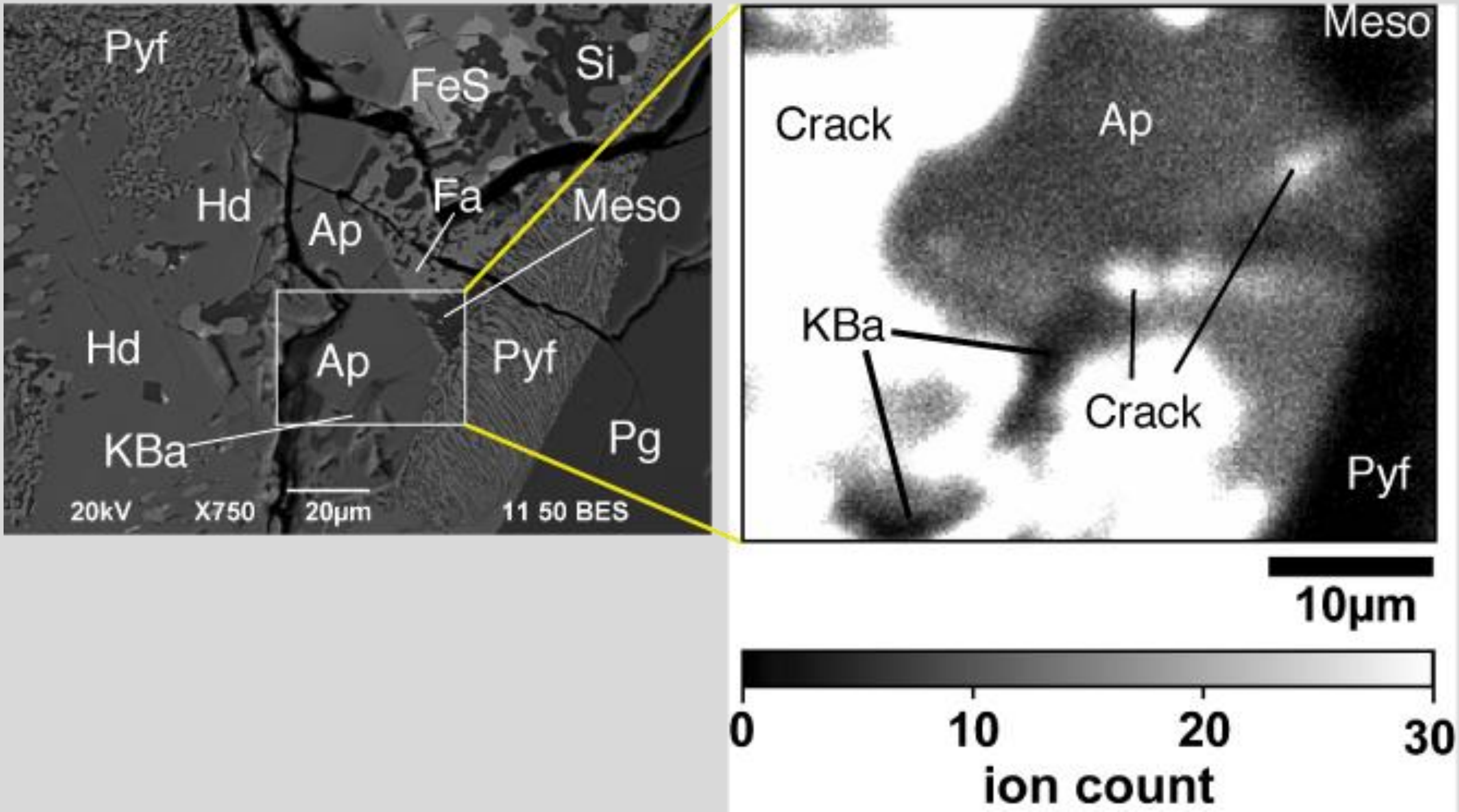
FIGURE 15. Summary models for the evolution of the lunar mantle and magmatism. **(a)** Early lunar crust formation and lunar mantle differentiation through magma ocean development and crystallization. **(b)** Disruption of cumulate products of magma ocean crystallization due to gravitational destabilization. **(c)** Generation of parental highland basaltic magmas through pressure release melting. The high Mg' and incompatible-element signature of the Mg suite rock types are a result of either assimilation of KREEP and early crust by the parental magmas followed by fractional crystallization or partial melting of hybrid cumulate sources and assimilation of KREEP. The alkali suite and highland volcanics may be related to Mg suite magmas through fractional crystallization and crystal accumulation or are simply contemporaneous magmas produced through partial melting of distinctively different sources. **(d)** Generation of mare basalts through small to moderate degrees of partial melting of mineralogically chemically varied hybrid cumulates. Melting to produce these magmas was initiated in the deep lunar mantle.

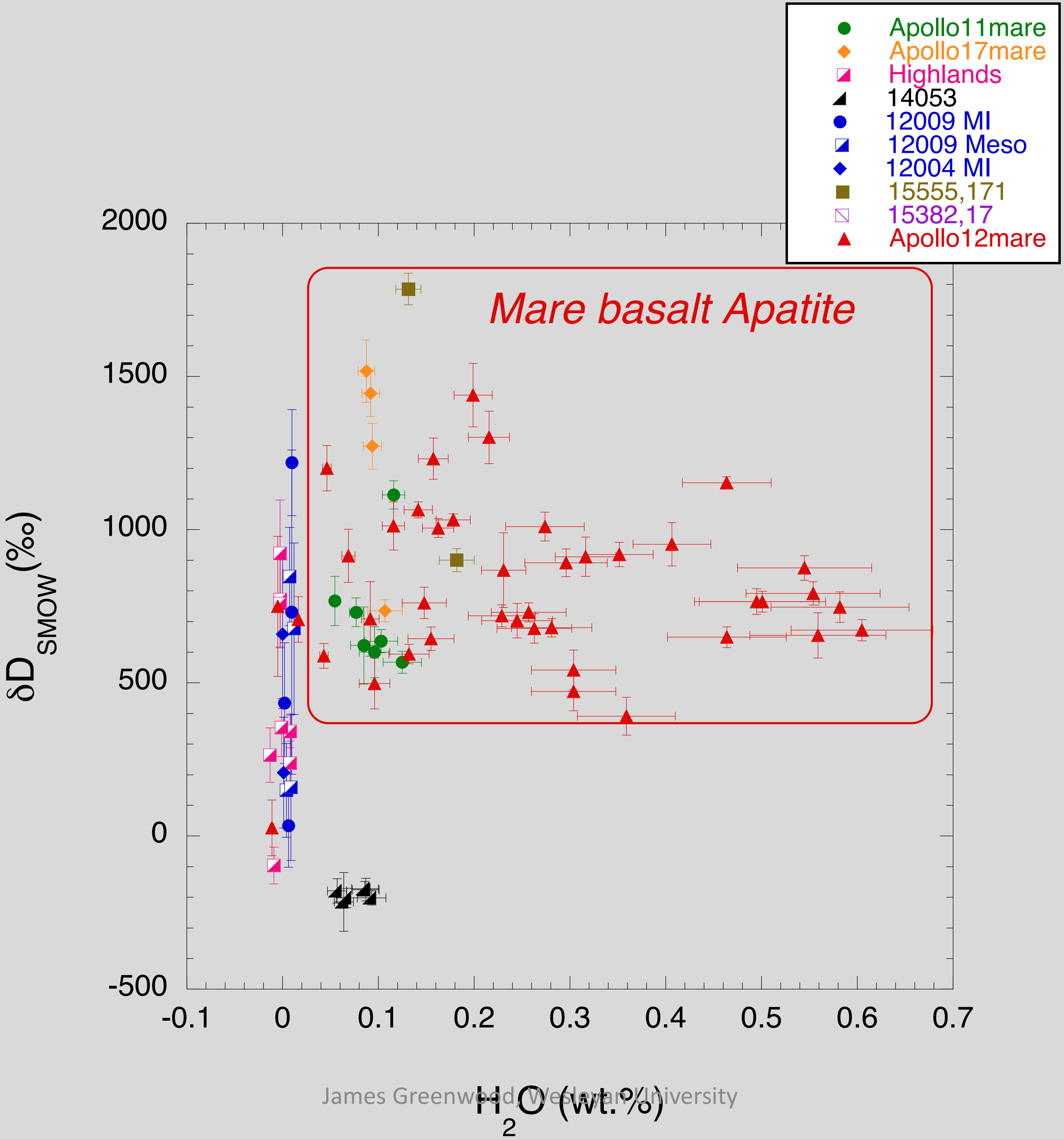
Vesiculated basalt from Apollo 15



Cameca ims 1270 SIMS Hokkaido University

^{1}H SCAPS of 10044 apatite





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Moon-Summary

- Likely less water than Earth
- But still plenty of volatiles (?)
- High Cl and Zn isotope signatures likely due to magma ocean degassing
- Overall high D/H may be partial result of magma ocean degassing
- Low D/H of lunar samples likely solar wind contamination of near-surface magmas

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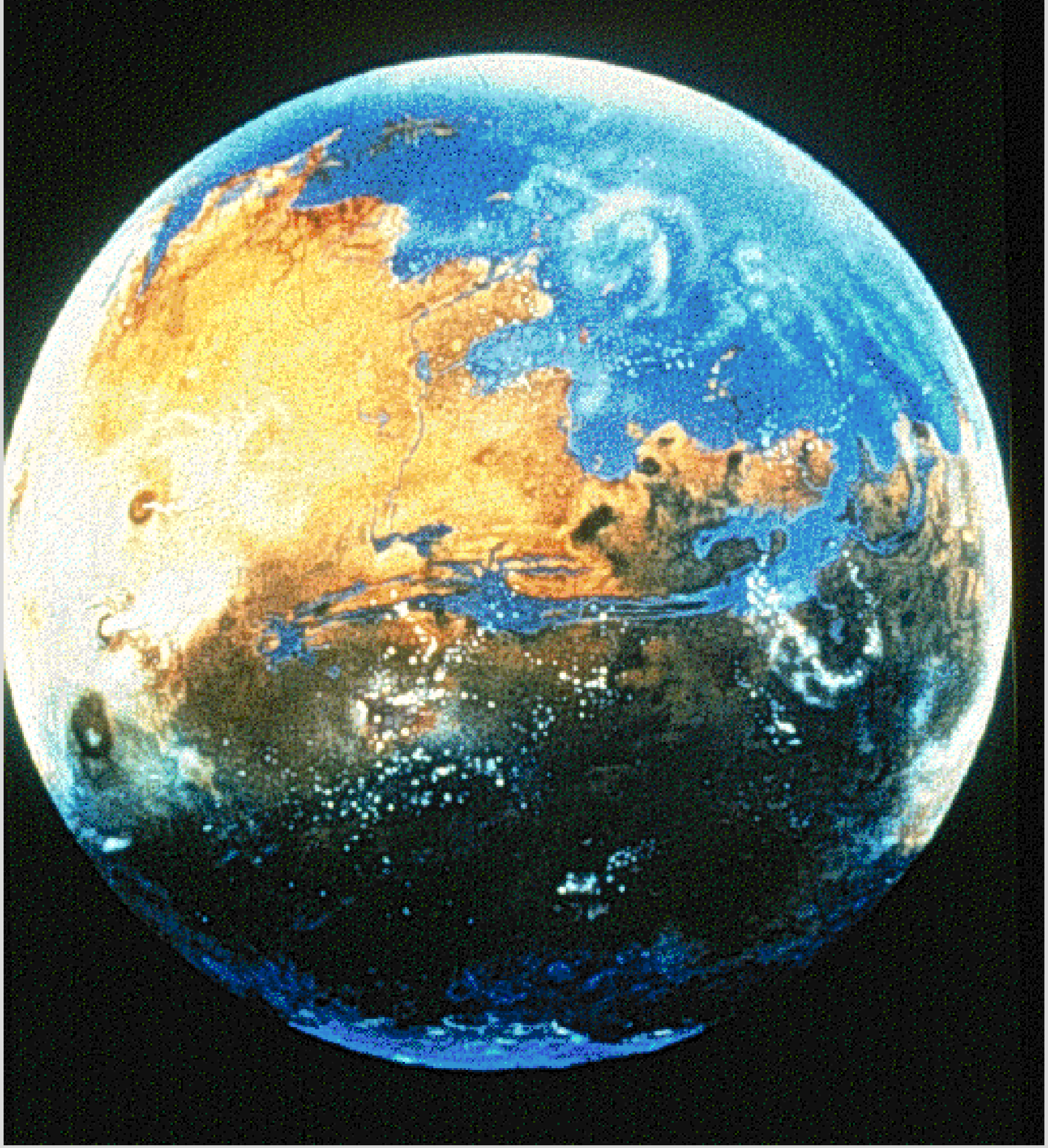

Past oceans on Mars?

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What about Mars?

- Had early, aqueous environment near surface or at surface
- Conditions on Mars surface ~4.0-4.4 Ga may have been similar to Earth at this same time
- But how much water? Was there running water on the surface for millions of years, or just short wet episodes (thousands of years)
- Conditions on early Mars same as on early Earth
  - Early Earth saw the origin of life, why not Mars?
  - Did life come from Mars on a meteorite? Or did Earth seed early Mars??

What the Curiosity Rover sees

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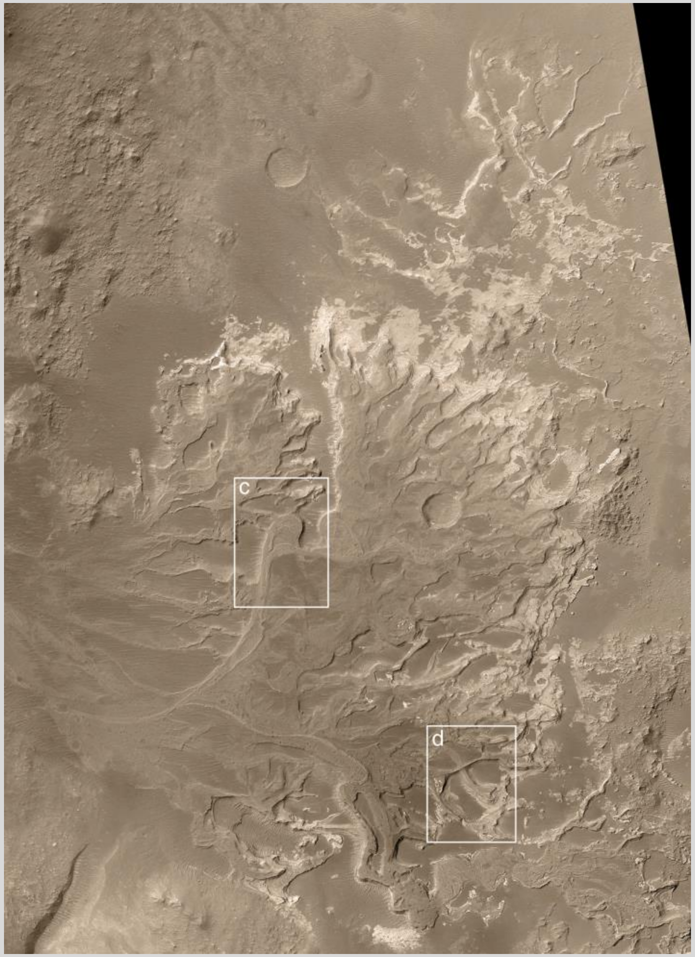
Sedimentary layers at Mars

Martian hydrologic landforms



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Mars Topography 65˚N-65˚S

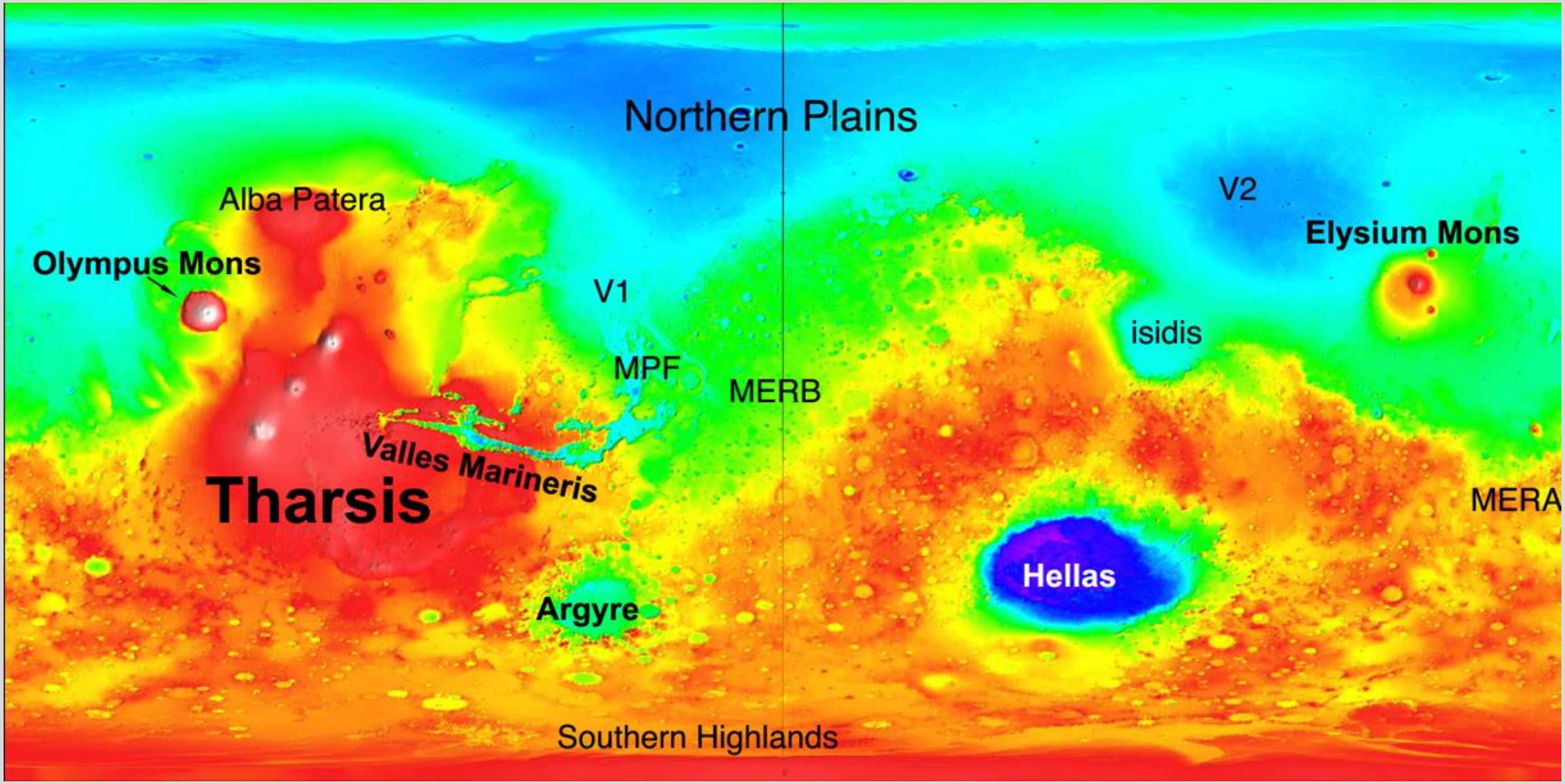
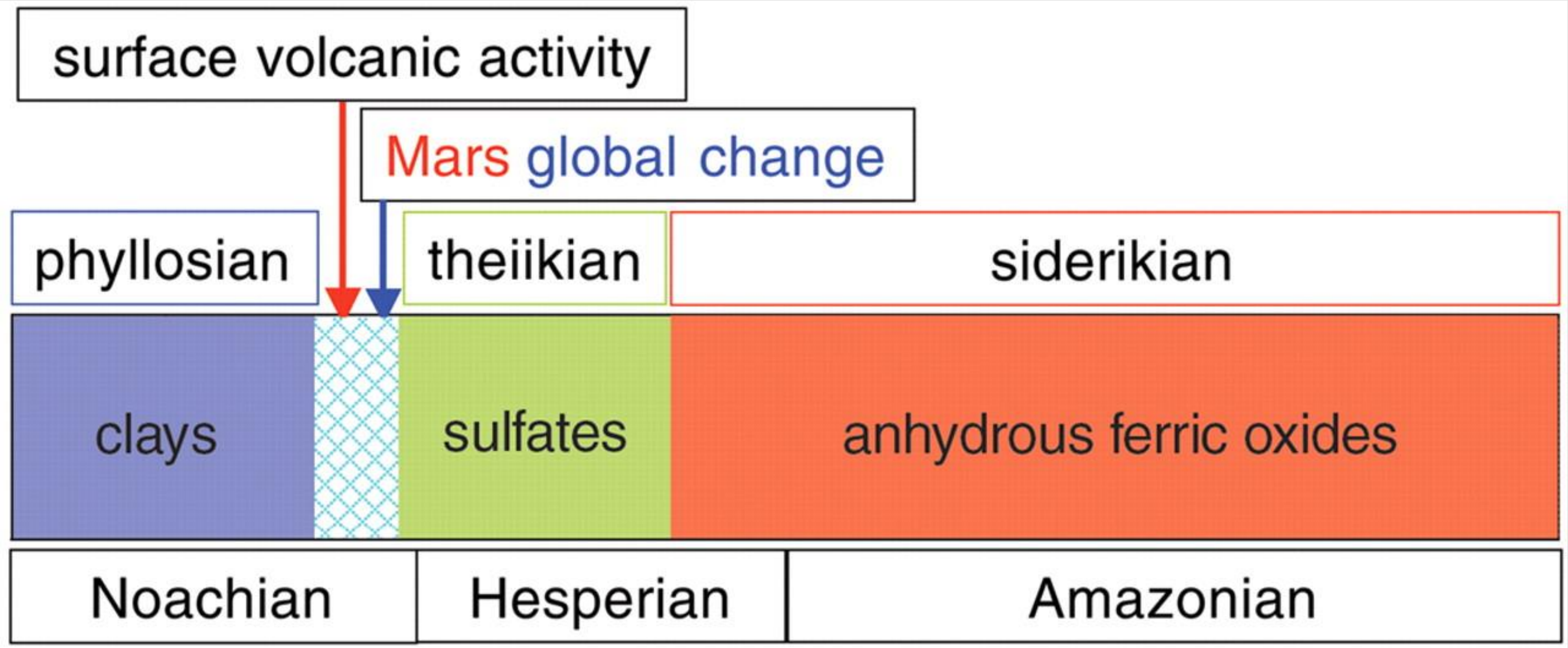


Fig. 5. Sketch of the alteration history of Mars, with phyllosilicates formed first, then sulfates, then anhydrous ferric oxides.



J Bibring et al. Science 2006;312:400-404

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Published by AAAS

Villanueva et al. (2015) Science, 348 218-221

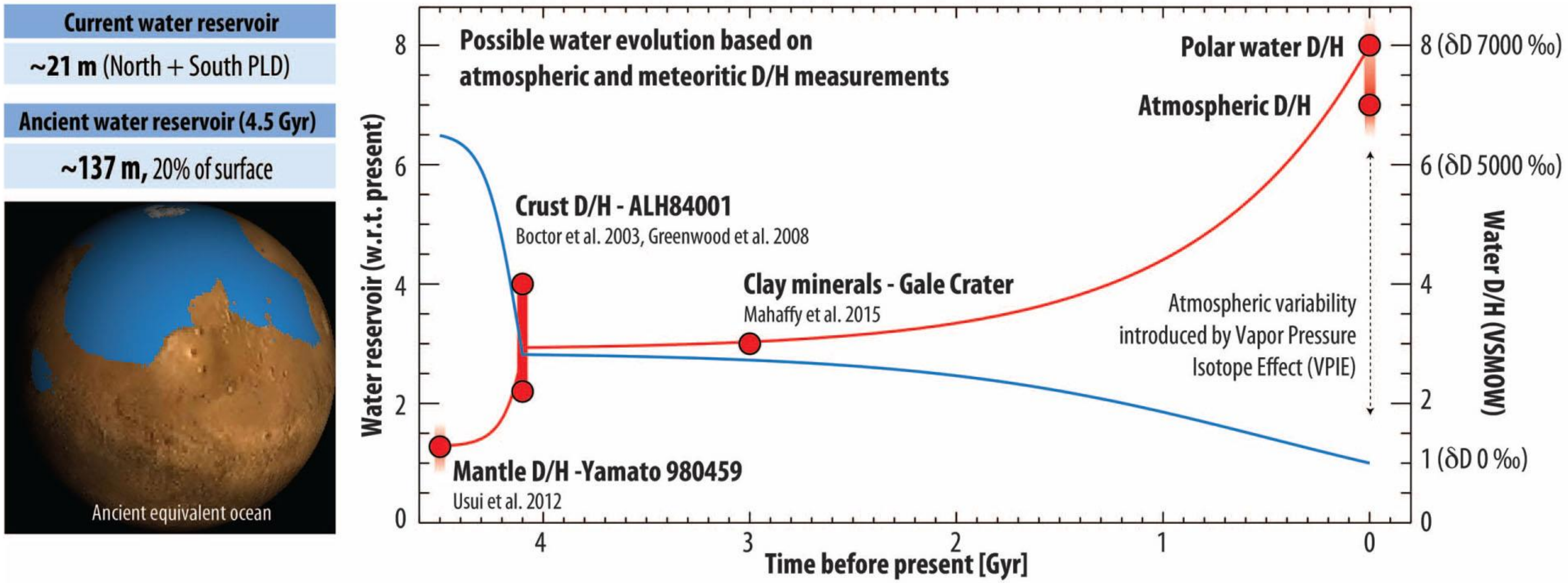


Fig. 3. Isotopic enrichment as evidence for global loss of water on Mars. After correcting for local climatological fractionation of the measured D/H ratio (Fig. 2), the current ratio for D/H in atmospheric water on Mars is at least 7 VSMOW, implying a D/H ratio of 8 VSMOW in the north polar reservoir (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.

Hydrodynamic Escape

- Elevated levels of heavy isotopes of hydrogen, nitrogen, carbon, oxygen, and noble gases
- Classic example of hydrodynamic escape due to early blow-off of hydrogen that carries all the other atmospheric gases away, which can cause mass-dependent isotope fractionation ***if*** the conditions are right (Hunten et al., 1987)
- If loss is at too high a rate, or the event is too rapid, the loss of the atmosphere does not lead to isotopic fractionation

Watson et al., (1994)
Science, 265 86-90

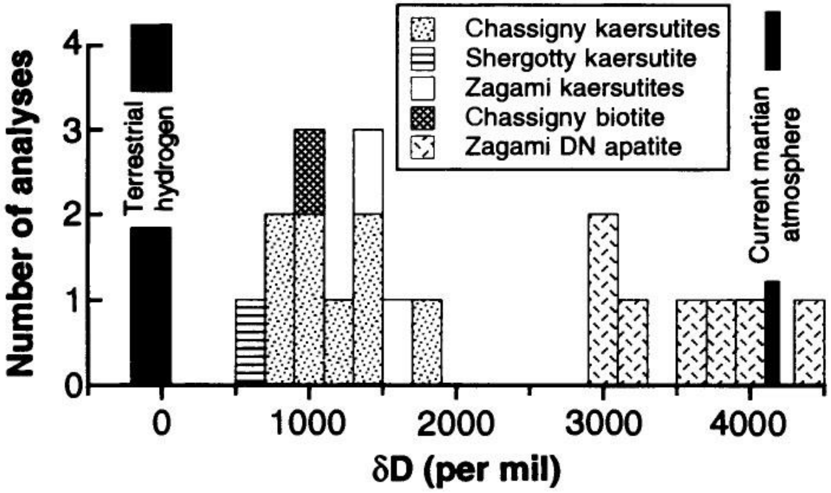
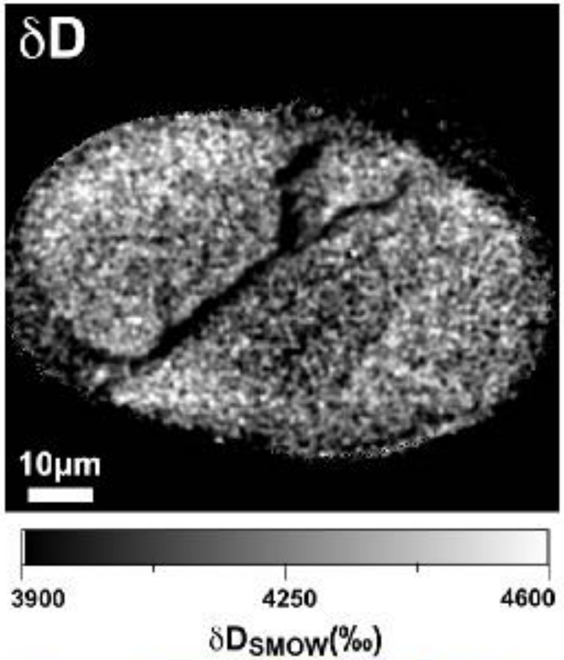
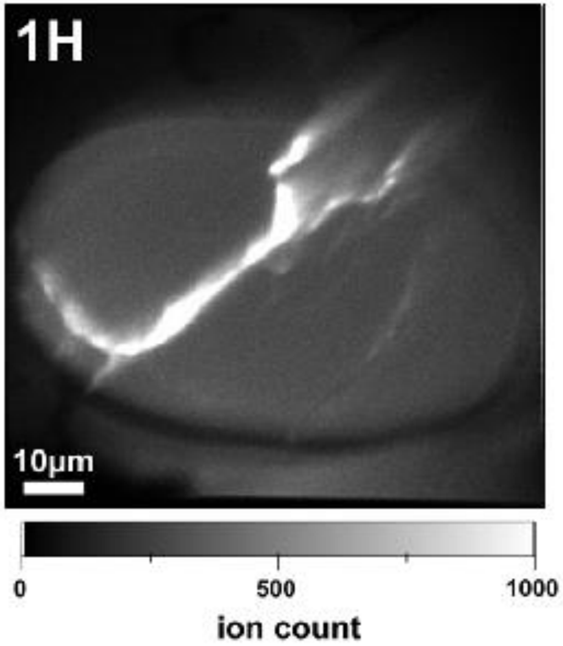
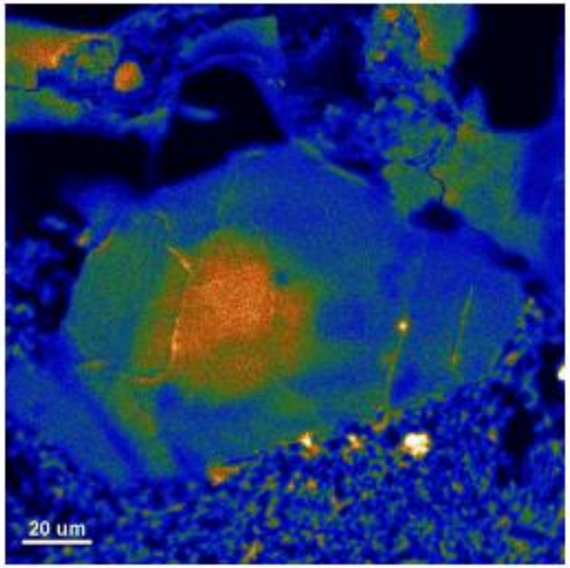
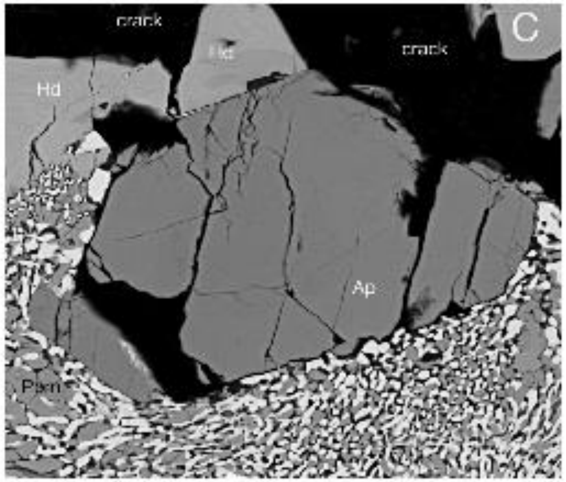


Fig. 2. Histogram of the δD values reported in this work. The bin size is 200 per mil. Uncertainties for each measurement are given in Table 1 and average ±68 per mil for the kaersutites and ±158 per mil for the apatite. The uncertainty on the biotite measurement is ±40 per mil. The range of δD values of terrestrial hydrogen and the most recent measurement of the δD value of the current martian atmosphere (*1*) are shown in black.









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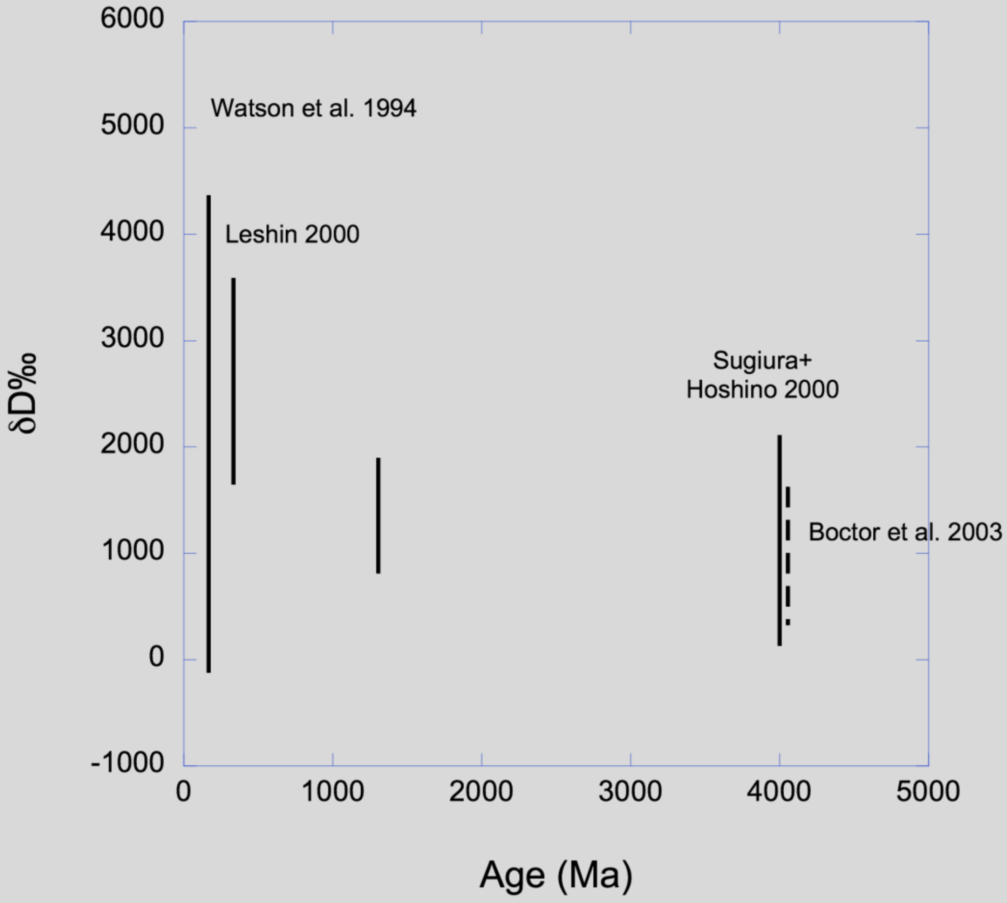
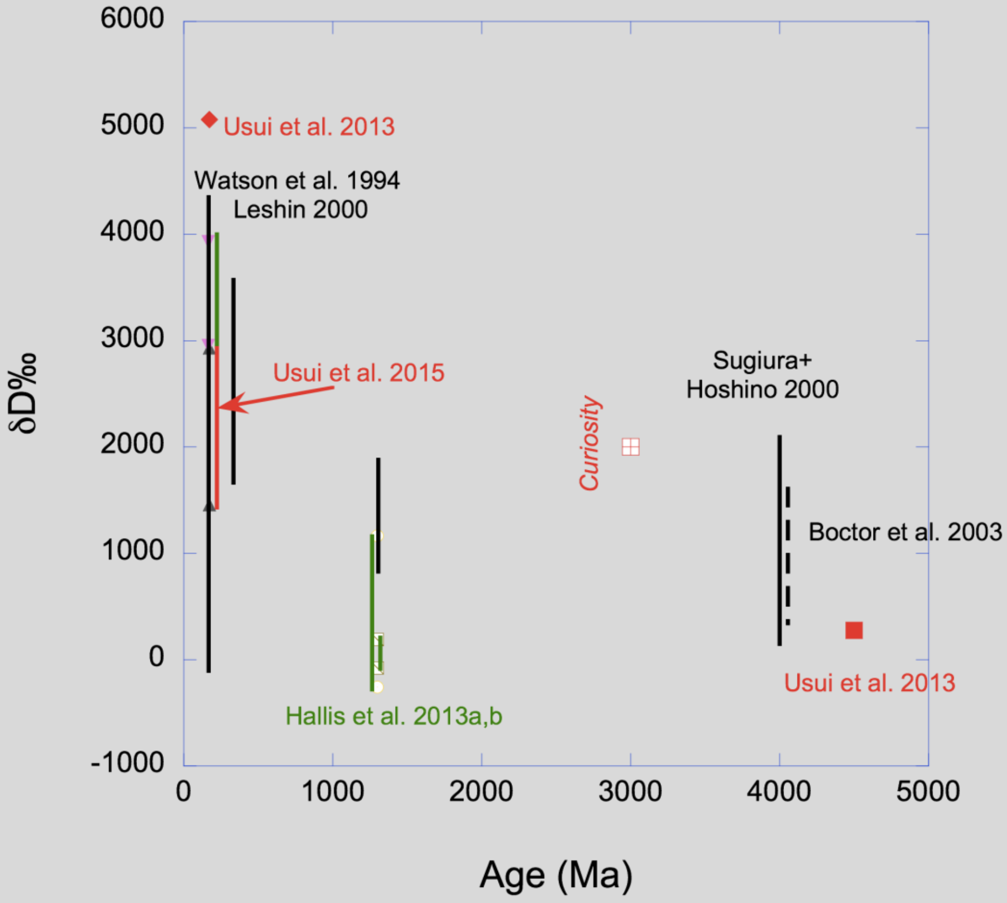
2003


Watson et al. 1994
Leshin 2000
Sugiura+
Hoshino 2000
Boctor et al. 2003
δD‰
6000
5000
4000
3000
2000
1000
0
-1000
0
1000
2000
3000
4000
5000
Age (Ma)

2015



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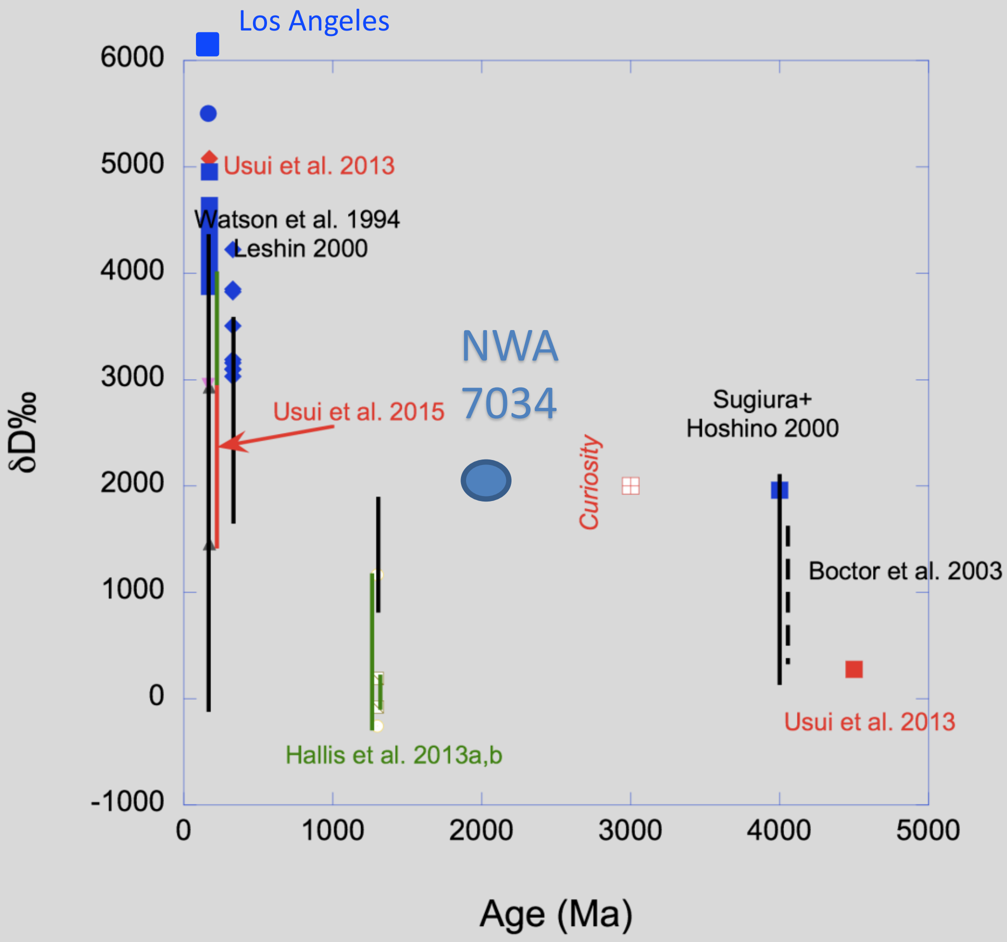
2017



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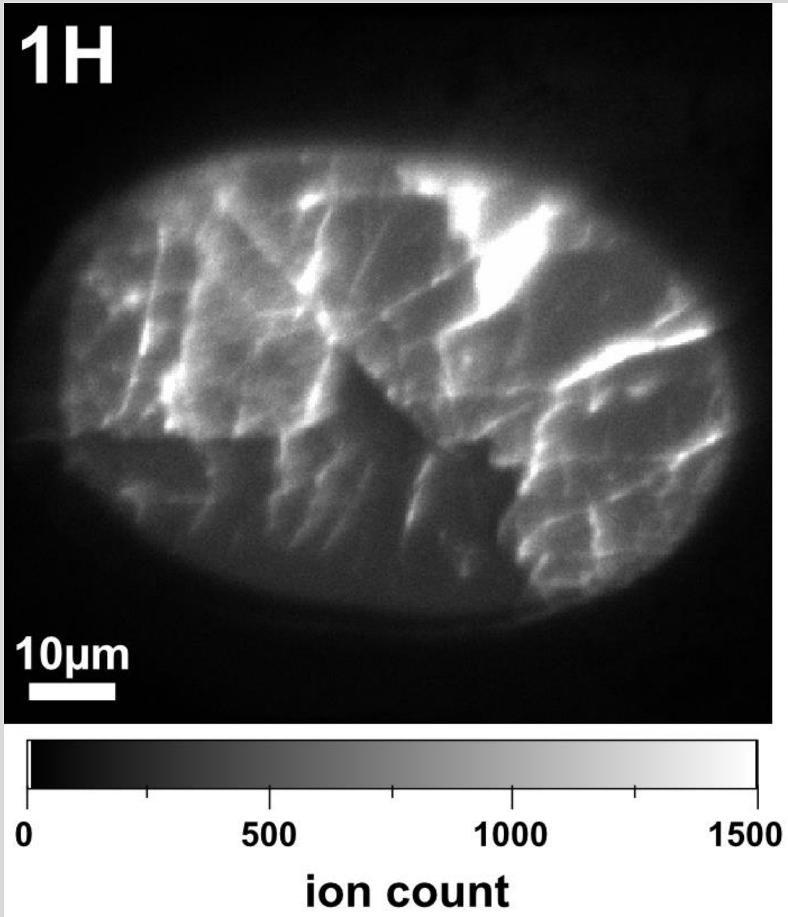
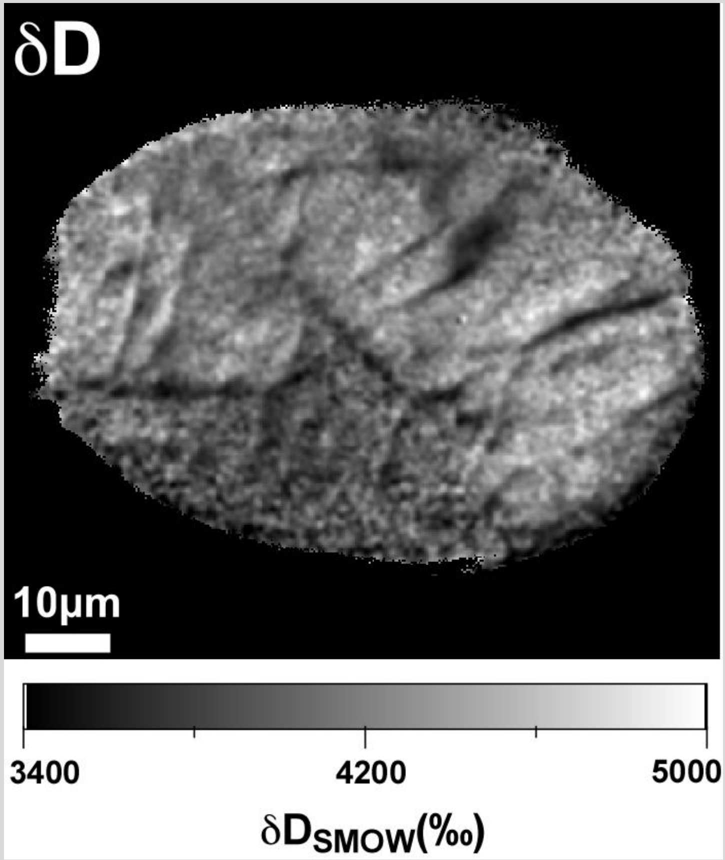
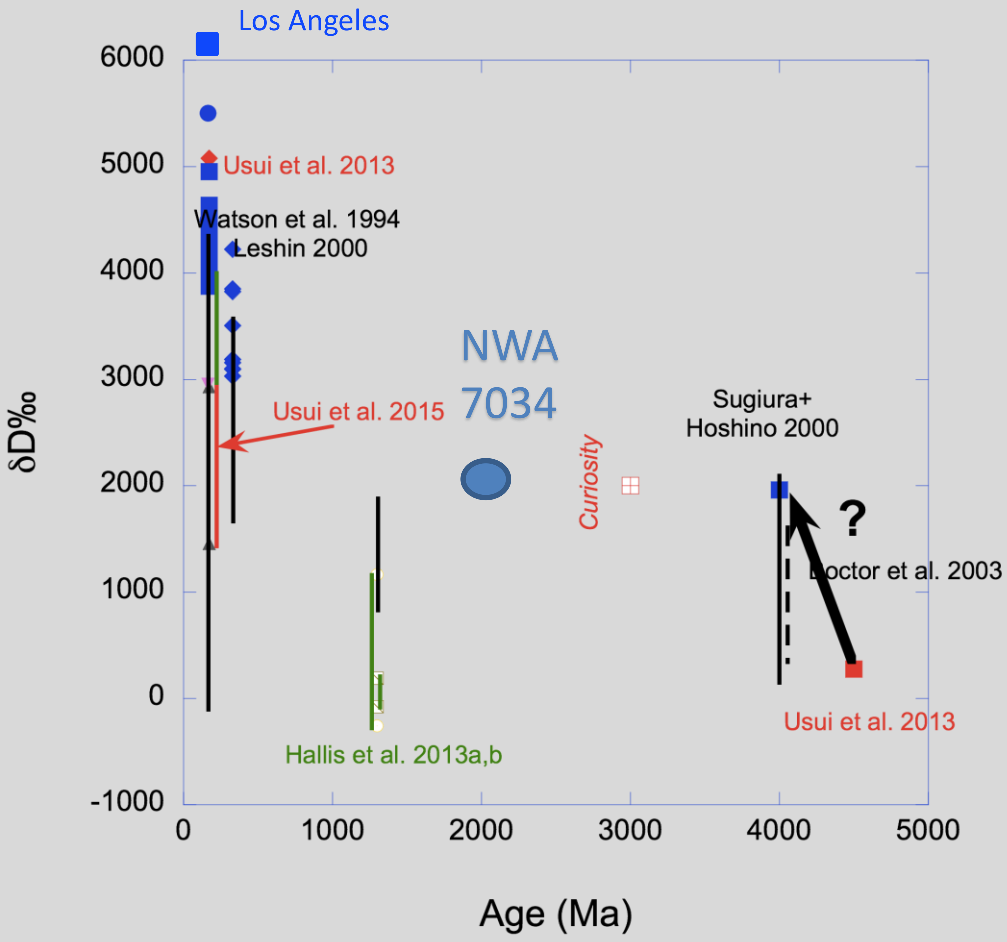
Shergotty


1H
10µm
0
500
1000
1500
ion count


δD
10µm
3400
4200
5000
δD$_{SMOW}$(‰)

Hydrodynamic escape?



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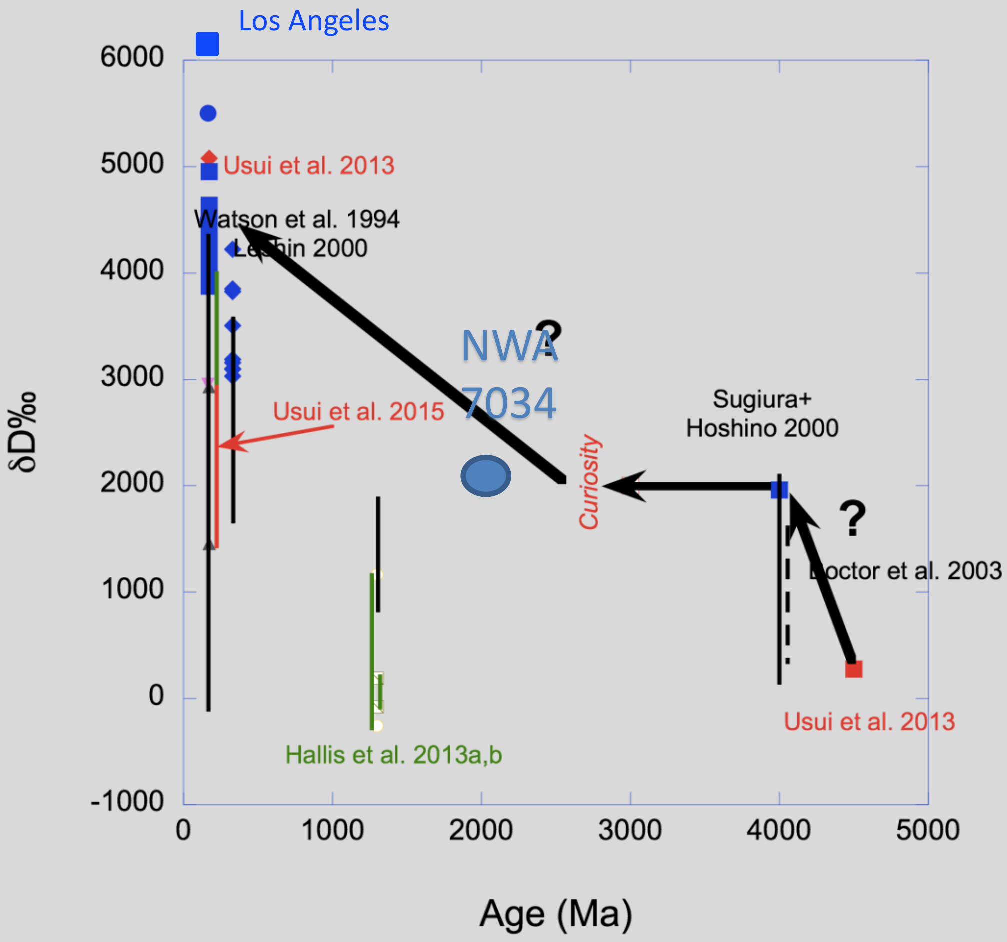
Then from 4.0 to 2.0 Ga a homogeneous, well-mixed water reservoir, then atmospheric escape?



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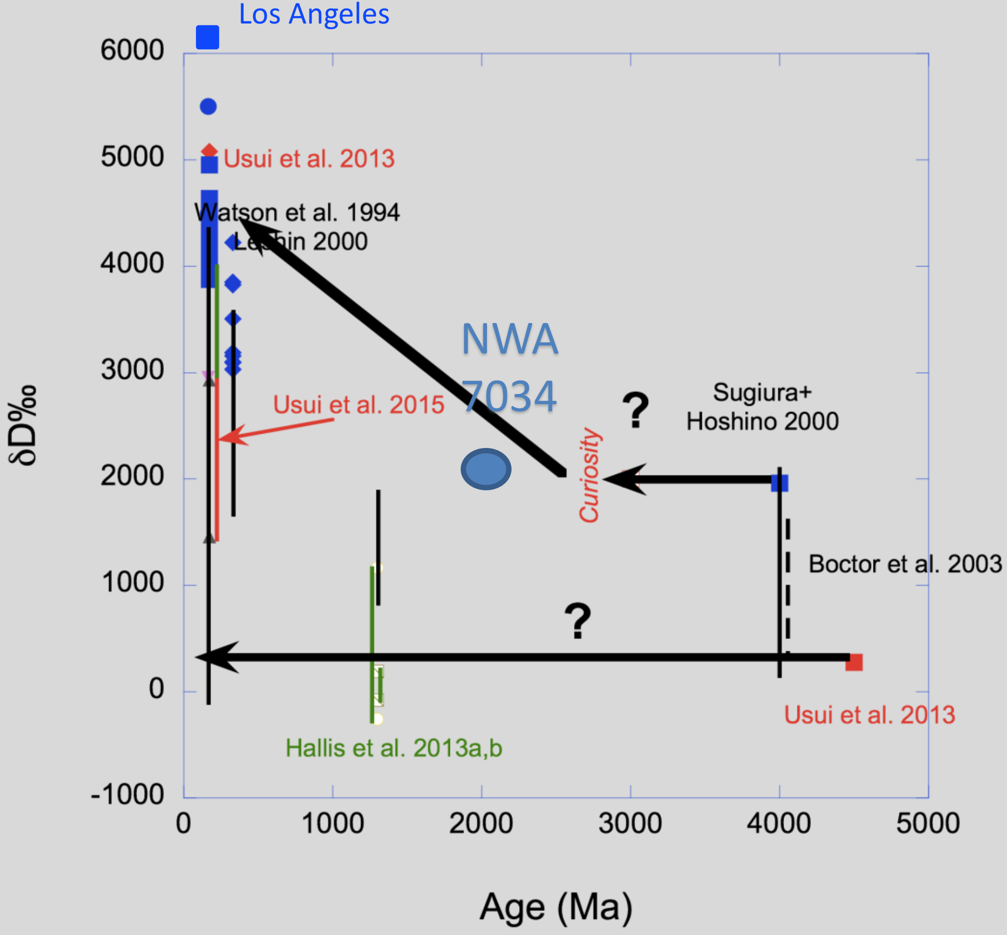
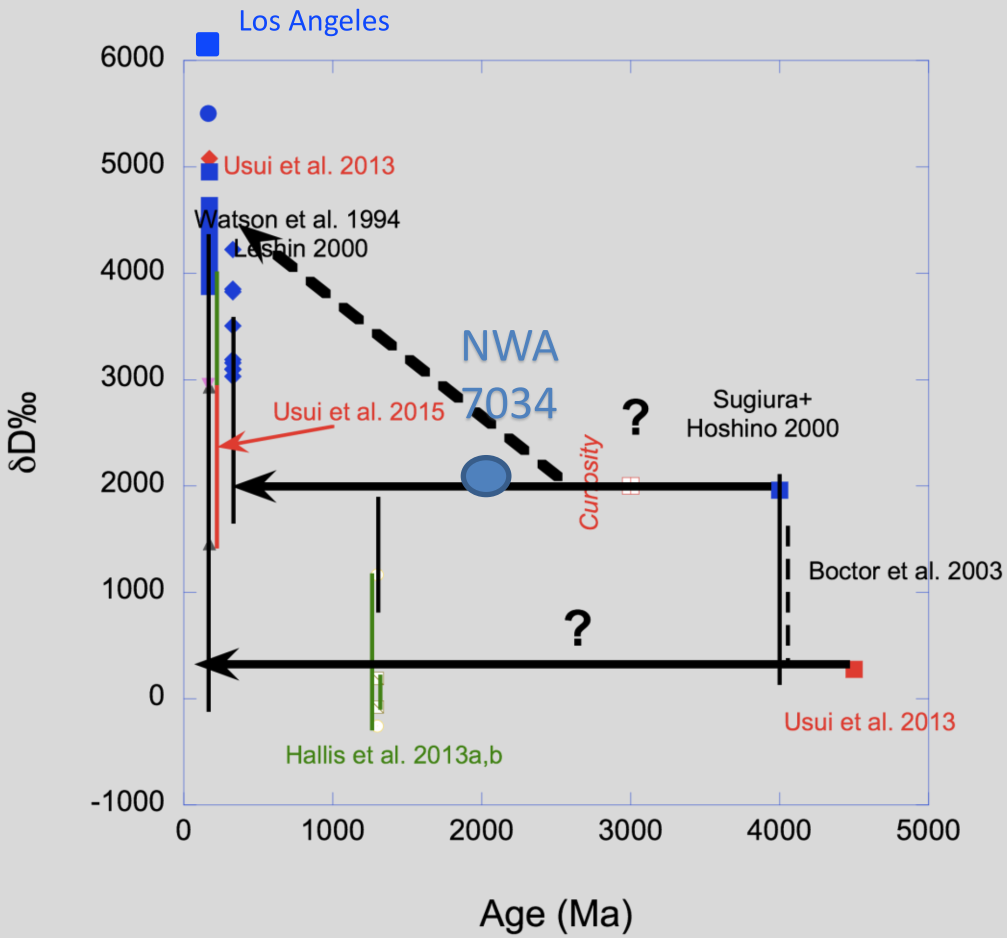
OR, early chondritic delivery of water, followed by cometary delivery, leaving mantle and crustal reservoirs unmixed, due to no plate tectonics on Mars



Intermediate D/H crustal reservoir is frozen and can only contribute small amounts to atmosphere during obliquity cycles-is this the intermediate reservoir of Usui et al. (2015), also sampled by NWA 7034 (McCubbin et al., Goldschmidt Yokohama)??



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Villanueva et al. (2015) Science, 348 218-221

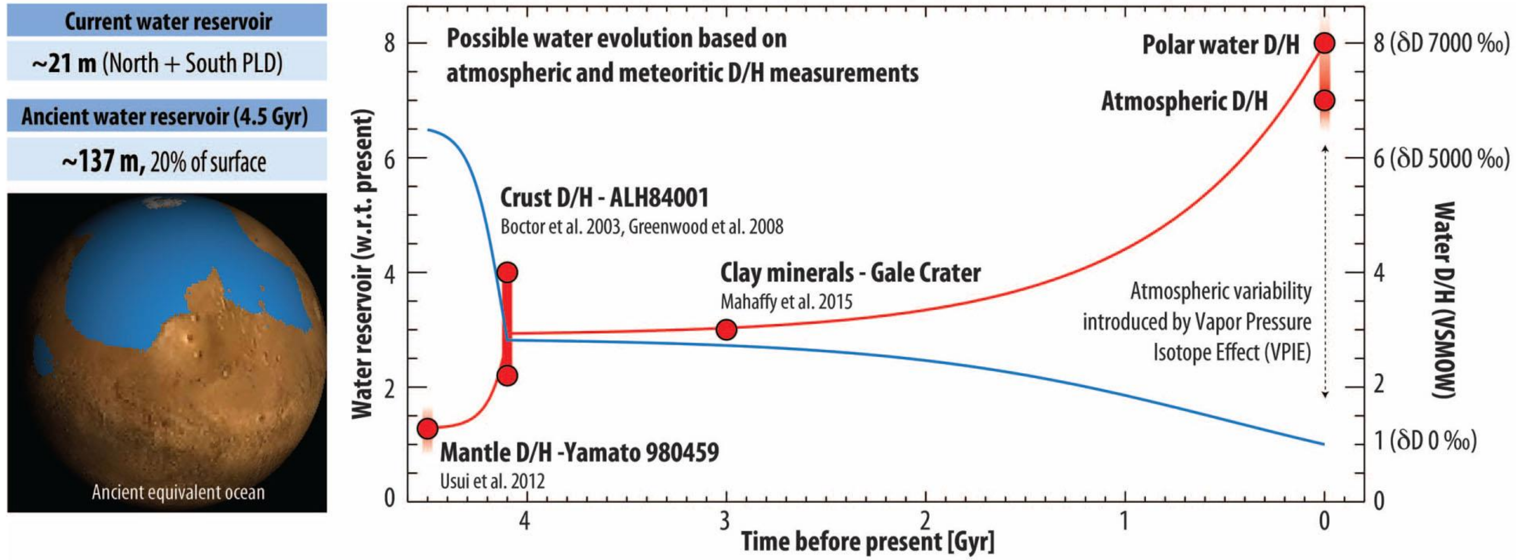


Fig. 3. Isotopic enrichment as evidence for global loss of water on Mars. After correcting for local climatological fractionation of the measured D/H ratio (Fig. 2), the current ratio for D/H in atmospheric water on Mars is at least 7 VSMOW, implying a D/H ratio of 8 VSMOW in the north polar reservoir (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.

Kurokawa et al. (2014) EPSL 394 179-185
Water loss in two episodes to reflect the dichotomy at ALH 84001.

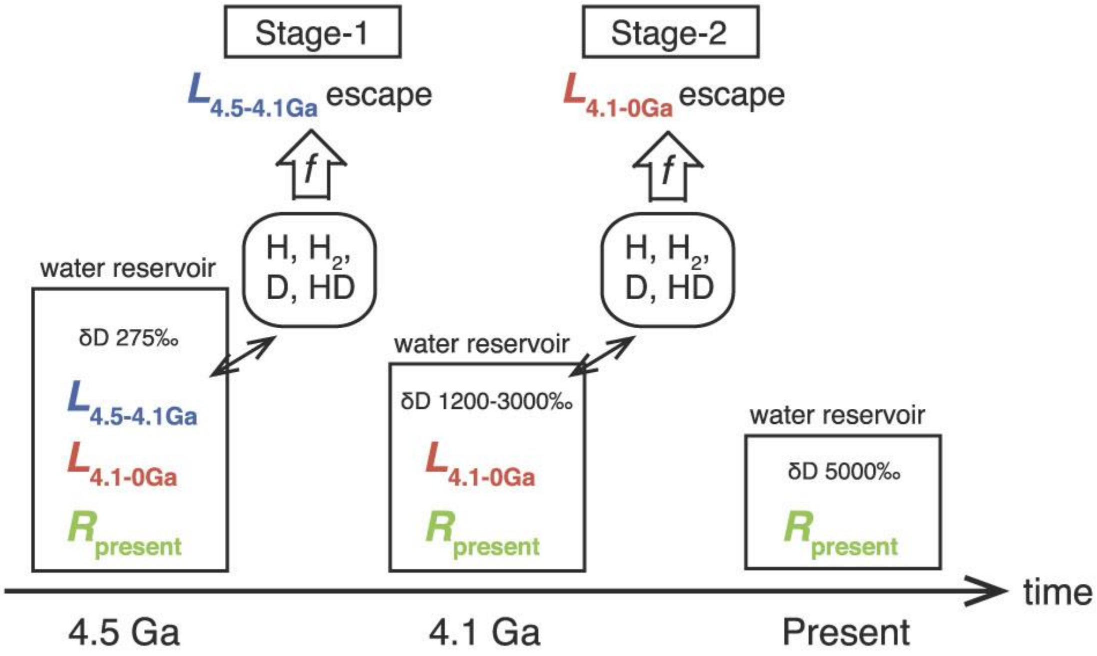
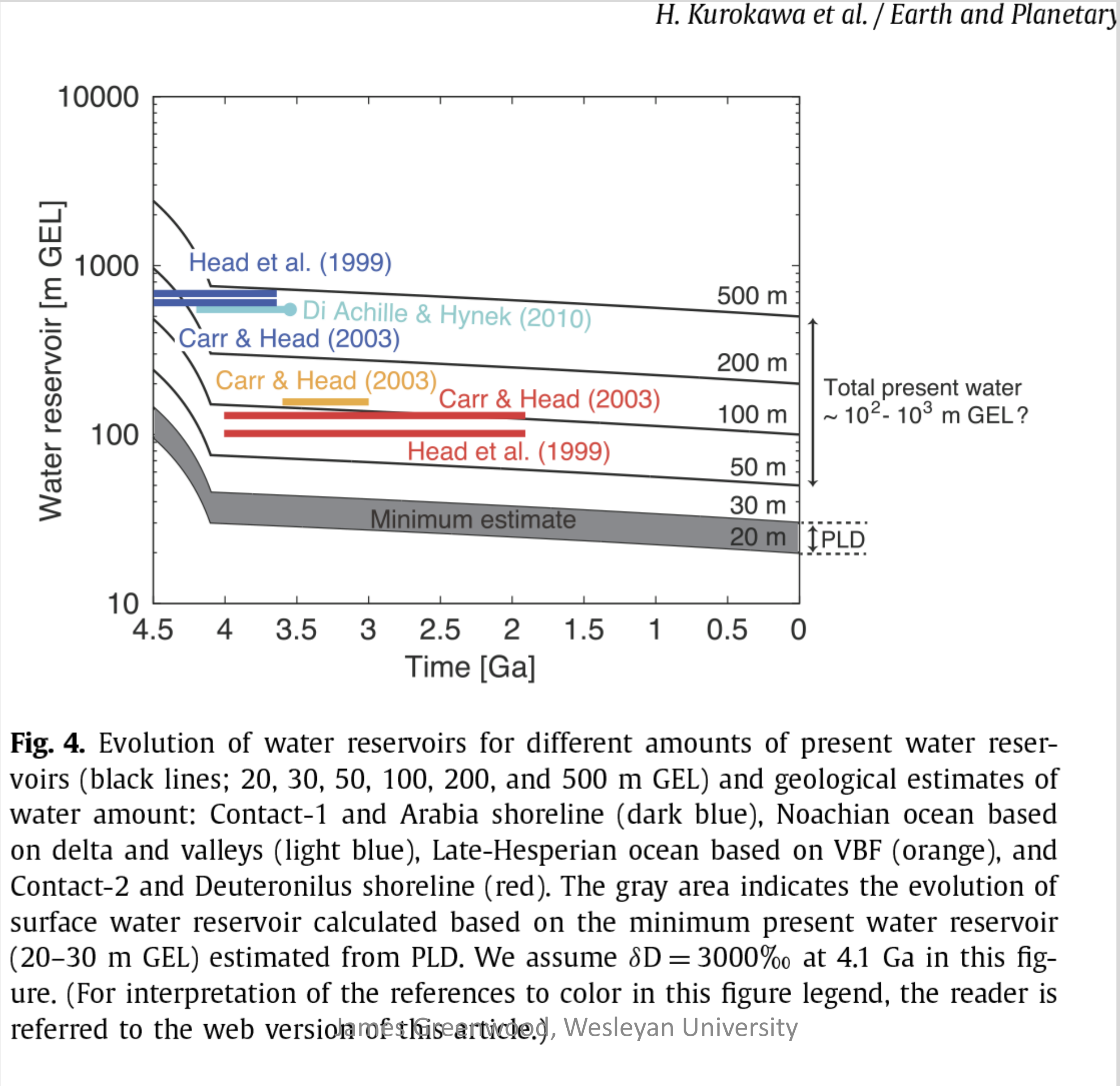


Fig. 1. Schematic illustration of the two-stage model for the evolution of the global surface water reservoir on Mars. R_{present} is the size of the present water reservoir, $L_{4.5-4.1\,\mathrm{Ga}}$ and $L_{4.1-0\,\mathrm{Ga}}$ are the water loss during Stage-1 and -2, and f is the fractionation factor (see text).

Kurokawa et al. (2014) EPSL 394 179-185.



H. Kurokawa et al. / Earth and Planetary

Fig. 4. Evolution of water reservoirs for different amounts of present water reservoirs (black lines; 20, 30, 50, 100, 200, and 500 m GEL) and geological estimates of water amount: Contact-1 and Arabia shoreline (dark blue), Noachian ocean based on delta and valleys (light blue), Late-Hesperian ocean based on VBF (orange), and Contact-2 and Deuteronilus shoreline (red). The gray area indicates the evolution of surface water reservoir calculated based on the minimum present water reservoir (20–30 m GEL) estimated from PLD. We assume $\delta D = 3000‰$ at 4.1 Ga in this figure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Estimates of water on Mars for ALH 84001 δD=+1960‰

- After Kurokawa et al. 2014:
- $\frac{Mp}{Mc} = (\frac{Ic}{Ip})^{1/_{1-f}}$
- Where *Mp*=GEL of past water reservoir (in m), *Mc* is the current water inventory, *Ic* is the D/H of the current water inventory, and *Ip* the D/H of the past water inventory

Present water reservoir depends on the size of past reservoir, its D/H, and how it was lost (fractionation factor, f)

- If ***Mc= 21 m*** (current water in the PLD), *Ic*: δD=+6412‰ (Los Angeles apatite), then we estimate ***Mp*=54 m**
- 54 m is much lower than estimates based on geology (Carr and Head (2003) estimate 130 m minimum GEL to 1500 m GEL)
- If Carr and Head are correct, then we are missing ~75 m of water, which could be buried ice (3x the current PLD?!)
- This estimate assumes no early loss of water due to hydrodynamic escape or early EUV induced loss of atmosphere (e.g. Lammer et al., 2013)

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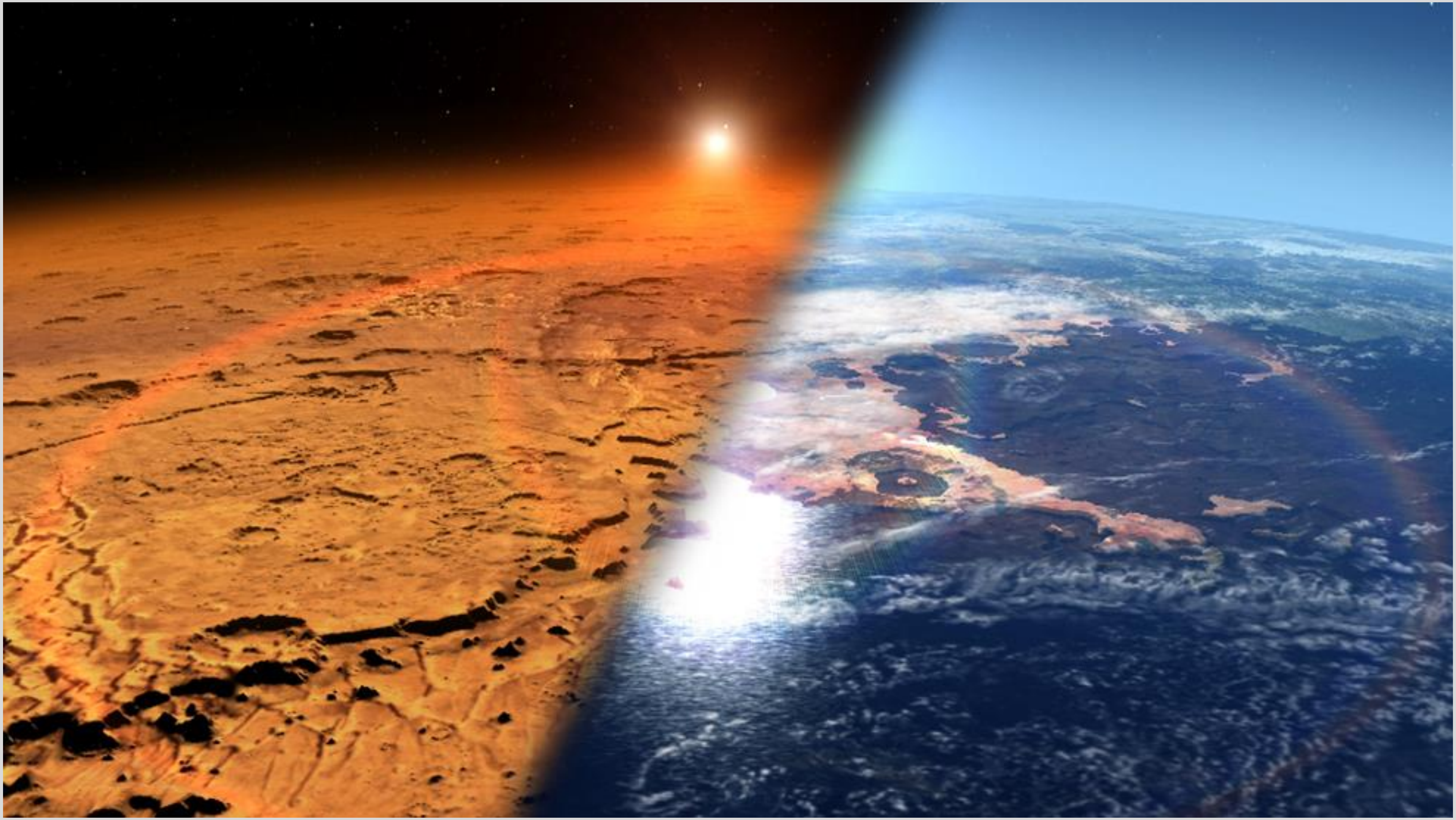
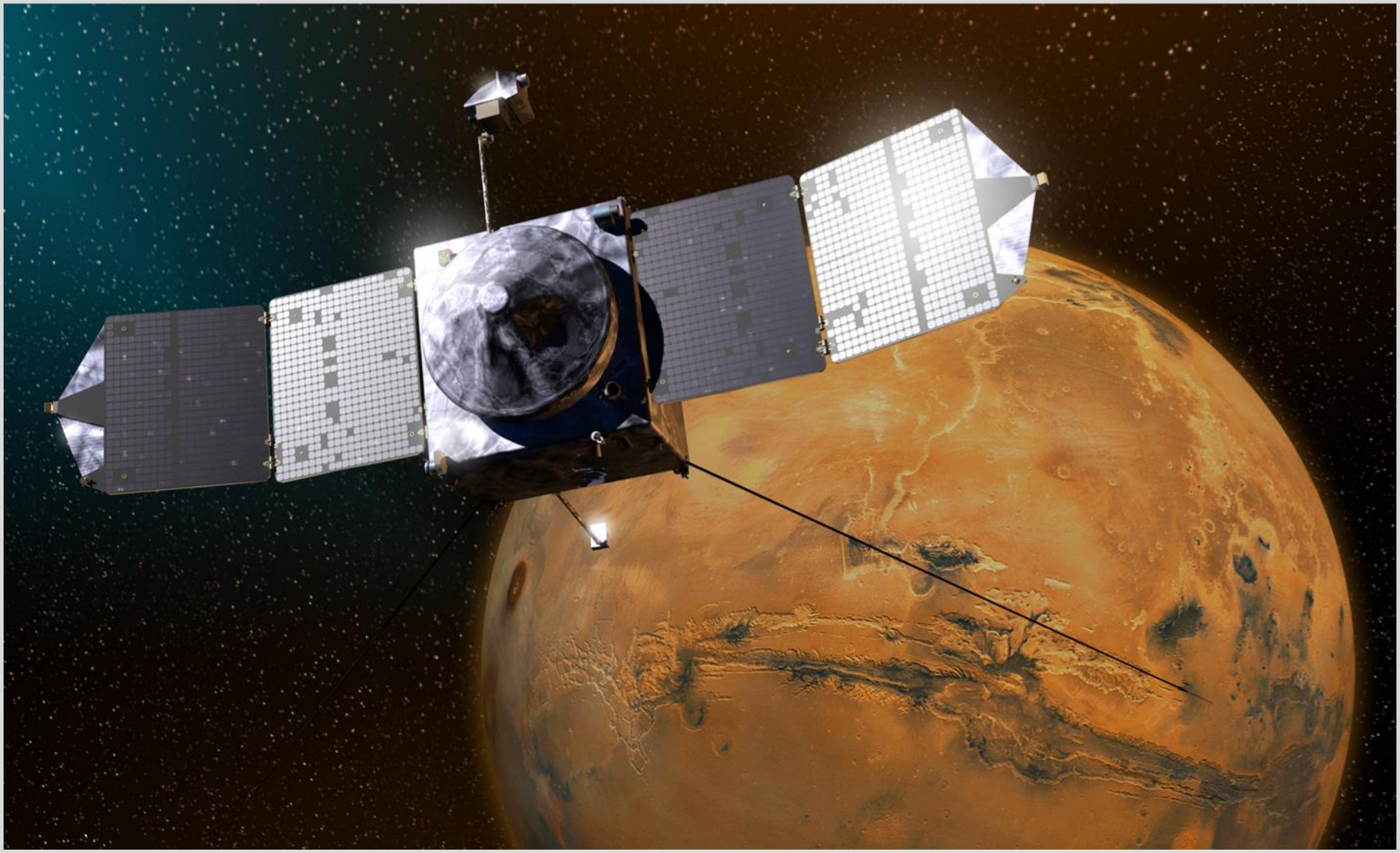
63% loss of water

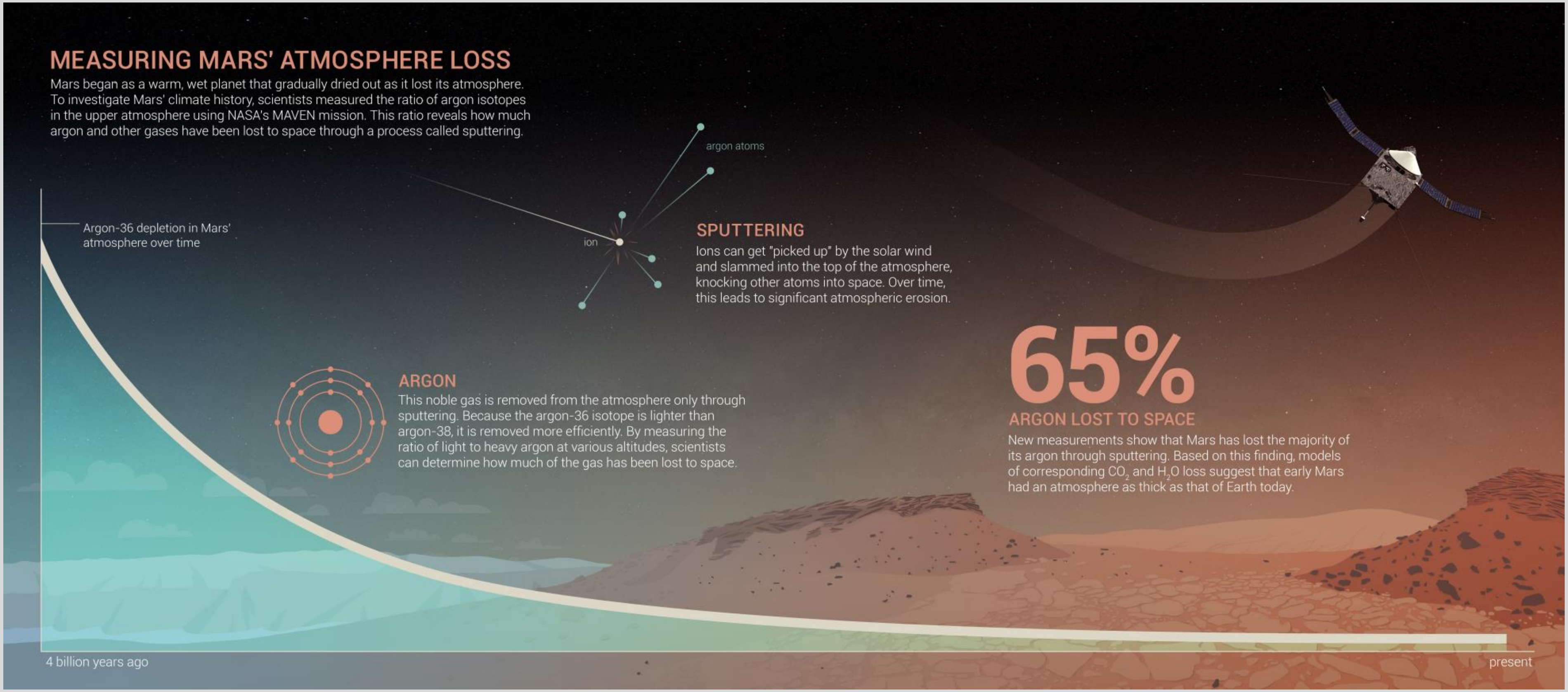
Mars-what MAVEN sees



MAVEN-Mars Atmosphere Volatile EvolutioN Mission



At least 65% of the atmosphere has been lost to space over time



MEASURING MARS' ATMOSPHERE LOSS

Mars began as a warm, wet planet that gradually dried out as it lost its atmosphere. To investigate Mars' climate history, scientists measured the ratio of argon isotopes in the upper atmosphere using NASA's MAVEN mission. This ratio reveals how much argon and other gases have been lost to space through a process called sputtering.

SPUTTERING

Ions can get "picked up" by the solar wind and slammed into the top of the atmosphere, knocking other atoms into space. Over time, this leads to significant atmospheric erosion.

ARGON

This noble gas is removed from the atmosphere only through sputtering. Because the argon-36 isotope is lighter than argon-38, it is removed more efficiently. By measuring the ratio of light to heavy argon at various altitudes, scientists can determine how much of the gas has been lost to space.

65%

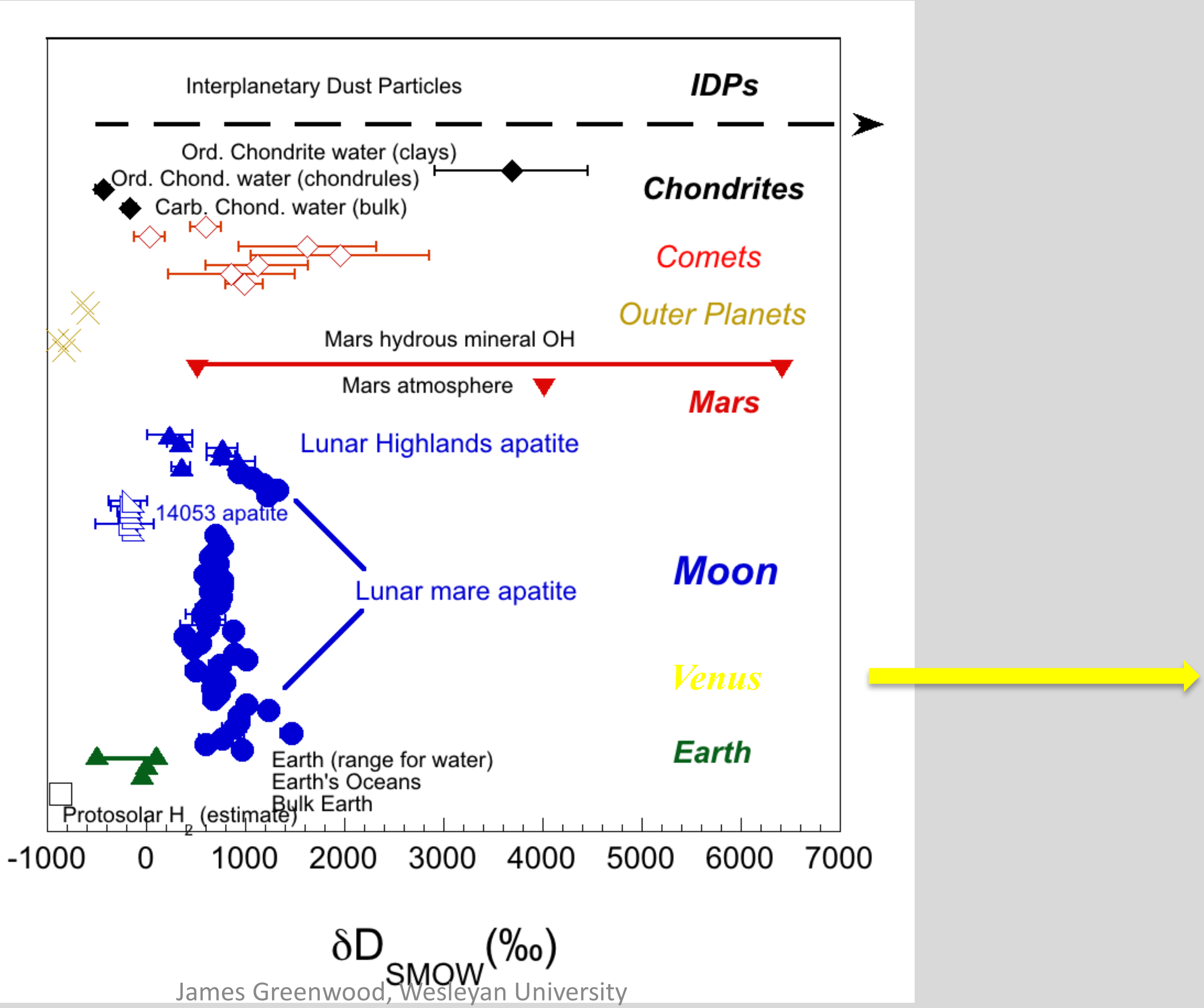
ARGON LOST TO SPACE

New measurements show that Mars has lost the majority of its argon through sputtering. Based on this finding, models of corresponding CO$_2$ and H$_2$O loss suggest that early Mars had an atmosphere as thick as that of Earth today.

Mars Summary

- Still not sure of mantle volatile content and total abundance of Martian volatiles
- Mars could be best preserved example of cometary delivery of water and volatiles to inner solar system due to lack of plate tectonics.
- (WARNING: Highly controversial idea!)

Solar System D/H



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Interplanetary Dust Particles (IDPs)

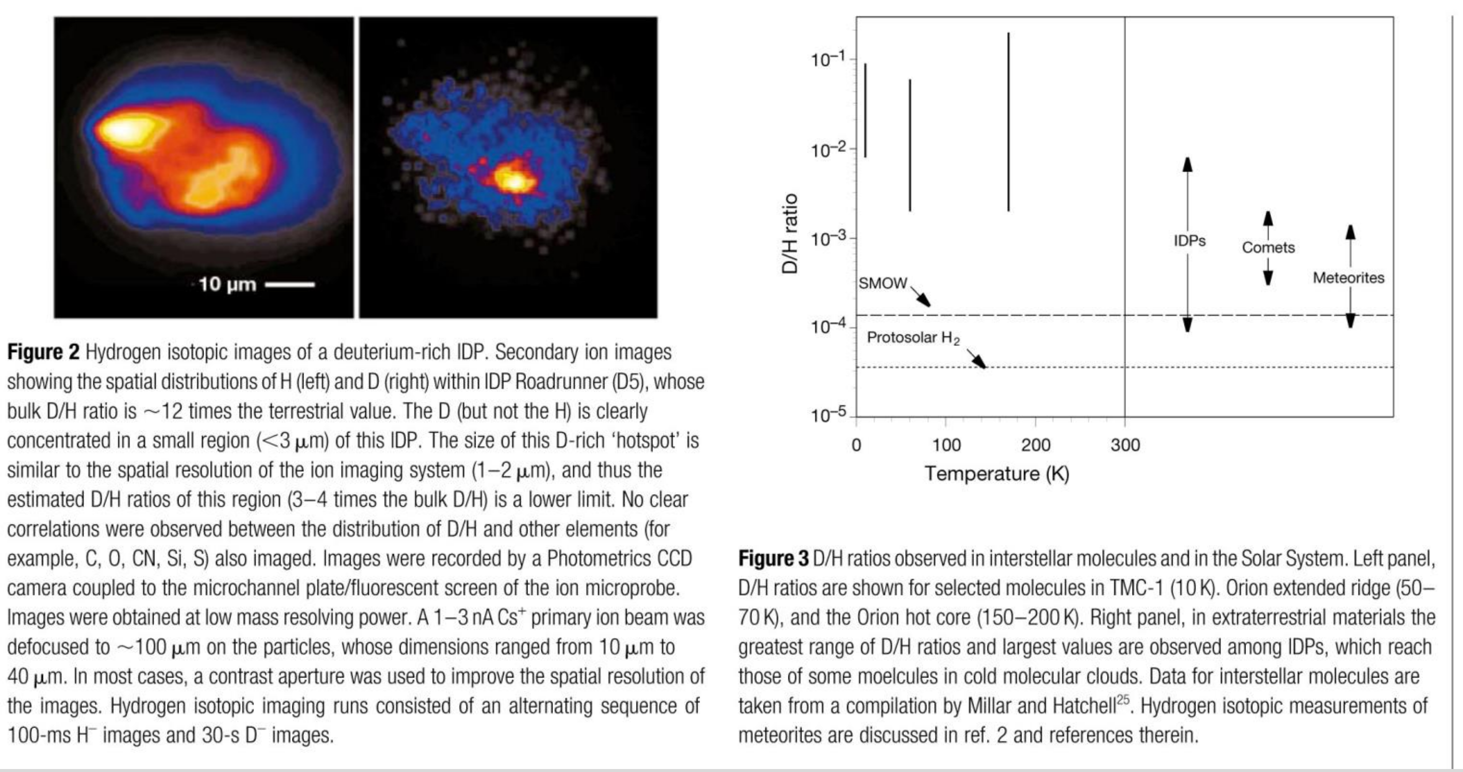


Figure 2 Hydrogen isotopic images of a deuterium-rich IDP. Secondary ion images showing the spatial distributions of H (left) and D (right) within IDP Roadrunner (D5), whose bulk D/H ratio is ~12 times the terrestrial value. The D (but not the H) is clearly concentrated in a small region (<3 μm) of this IDP. The size of this D-rich 'hotspot' is similar to the spatial resolution of the ion imaging system (1–2 μm), and thus the estimated D/H ratios of this region (3–4 times the bulk D/H) is a lower limit. No clear correlations were observed between the distribution of D/H and other elements (for example, C, O, CN, Si, S) also imaged. Images were recorded by a Photometrics CCD camera coupled to the microchannel plate/fluorescent screen of the ion microprobe. Images were obtained at low mass resolving power. A 1–3 nA Cs^+ primary ion beam was defocused to ~100 μm on the particles, whose dimensions ranged from 10 μm to 40 μm. In most cases, a contrast aperture was used to improve the spatial resolution of the images. Hydrogen isotopic imaging runs consisted of an alternating sequence of 100-ms H^- images and 30-s D^- images.

Figure 3 D/H ratios observed in interstellar molecules and in the Solar System. Left panel, D/H ratios are shown for selected molecules in TMC-1 (10 K). Orion extended ridge (50–70 K), and the Orion hot core (150–200 K). Right panel, in extraterrestrial materials the greatest range of D/H ratios and largest values are observed among IDPs, which reach those of some moelcules in cold molecular clouds. Data for interstellar molecules are taken from a compilation by Millar and Hatchell[25]. Hydrogen isotopic measurements of meteorites are discussed in ref. 2 and references therein.

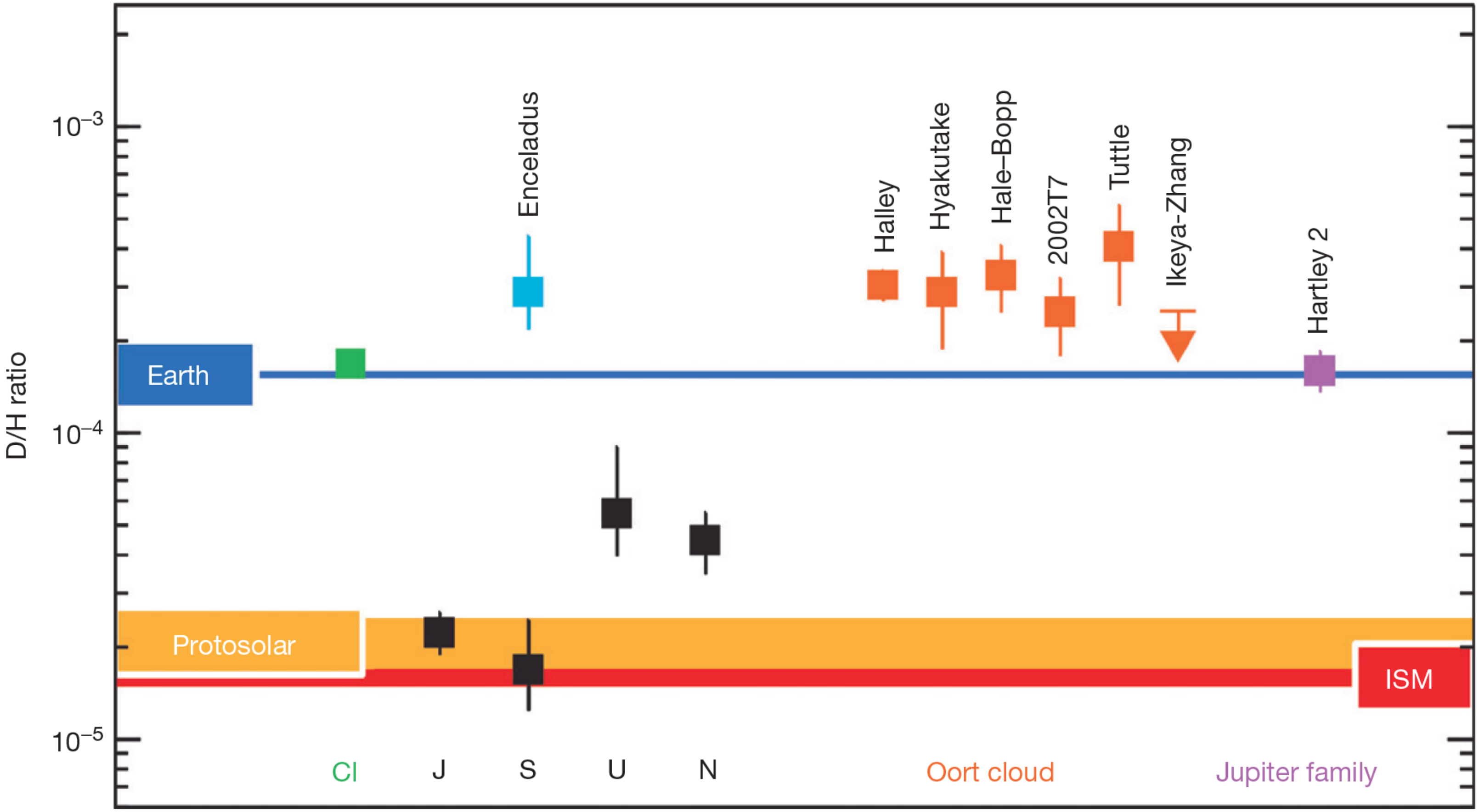


Figure 24 D/H ratios of several seven comets compared with Earth, planets, interstellar medium (ISM), Enceladus, and CI chondrites. Reproduced from Hartogh P, Lis DC, Bockelée-Morvan D, et al. (2011) Ocean-like water in the Jupiter-family comet 103P/Hartley 2. *Nature* 478: 218–220.

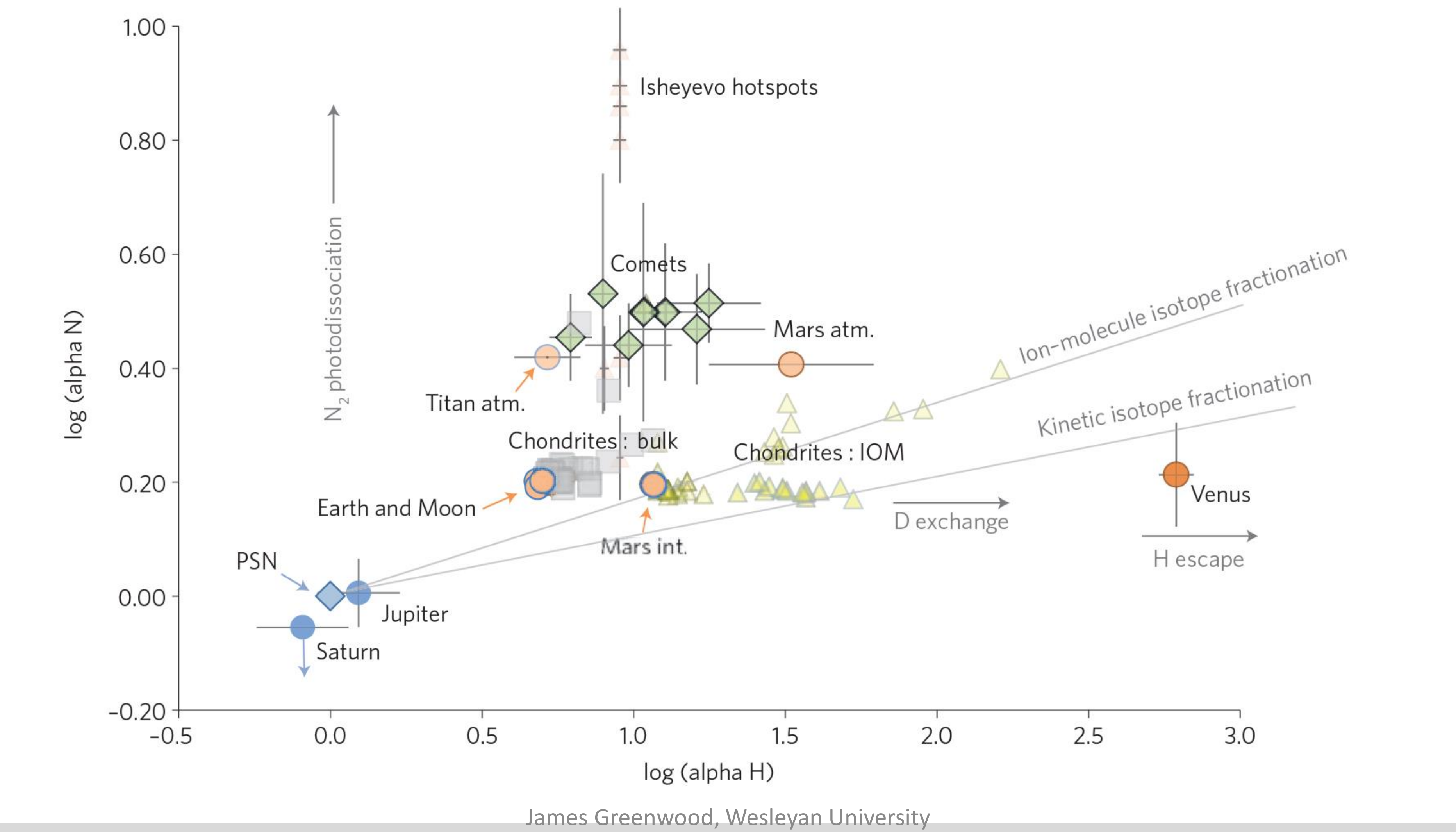
D/H in the solar system

- Sun is D-depleted object (low D/H), and also similar to ISM (interstellar medium)
- Hotspots in IDP’s have very high D/H, similar to molecular clouds
- Everything else in solar system is in between these two endmembers
- Is it a mixing line between solar H and D-rich materials, like hotspots in IDP’s?

Sources of water for the inner solar system

- Extreme enriched D and ^{15}N organic matter in chondrites similar to enrichment of these isotopes in interstellar molecules
- Nitrogen and Oxygen isotopes seem to require mixing of isotopically distinct sources

Furi and Marty (2015) Nat. Geosci.



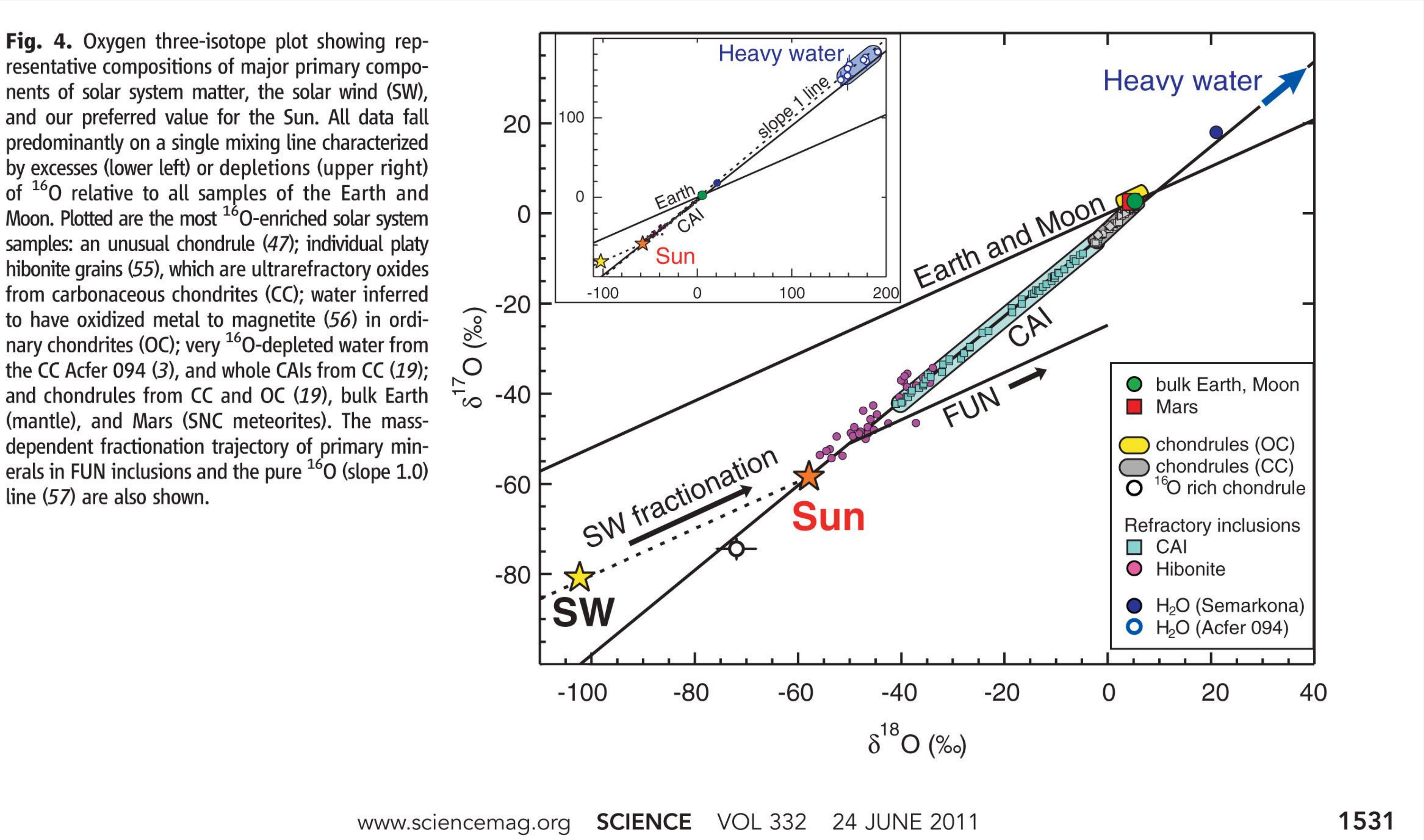


Fig. 4. Oxygen three-isotope plot showing representative compositions of major primary components of solar system matter, the solar wind (SW), and our preferred value for the Sun. All data fall predominantly on a single mixing line characterized by excesses (lower left) or depletions (upper right) of ^{16}O relative to all samples of the Earth and Moon. Plotted are the most ^{16}O-enriched solar system samples: an unusual chondrule (*47*); individual platy hibonite grains (*55*), which are ultrarefractory oxides from carbonaceous chondrites (CC); water inferred to have oxidized metal to magnetite (*56*) in ordinary chondrites (OC); very ^{16}O-depleted water from the CC Acfer 094 (*3*), and whole CAIs from CC (*19*); and chondrules from CC and OC (*19*), bulk Earth (mantle), and Mars (SNC meteorites). The mass-dependent fractionation trajectory of primary minerals in FUN inclusions and the pure ^{16}O (slope 1.0) line (*57*) are also shown.

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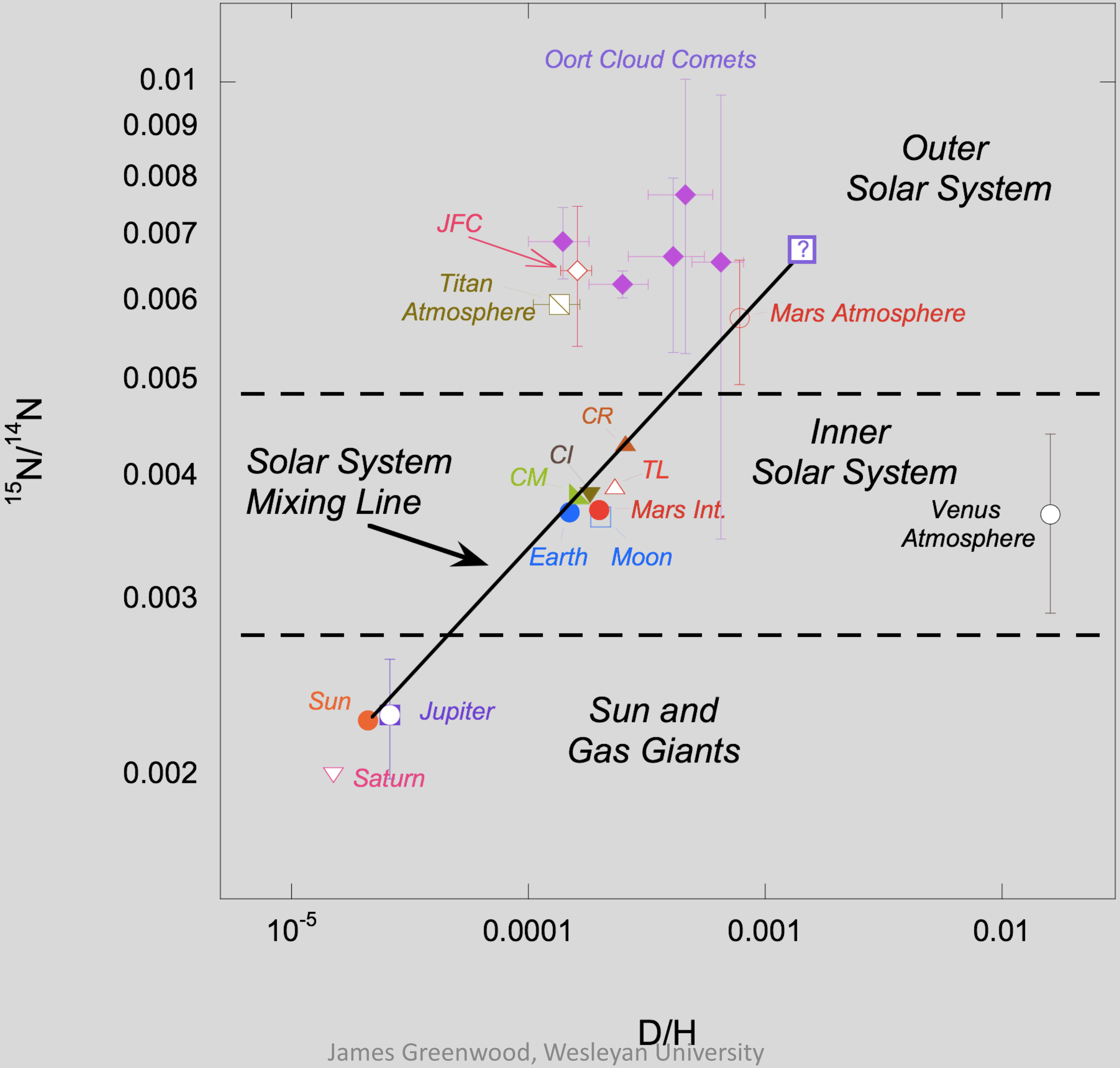
Oxygen isotopes of the solar system
June 2011

James Greenwood, Wesleyan University



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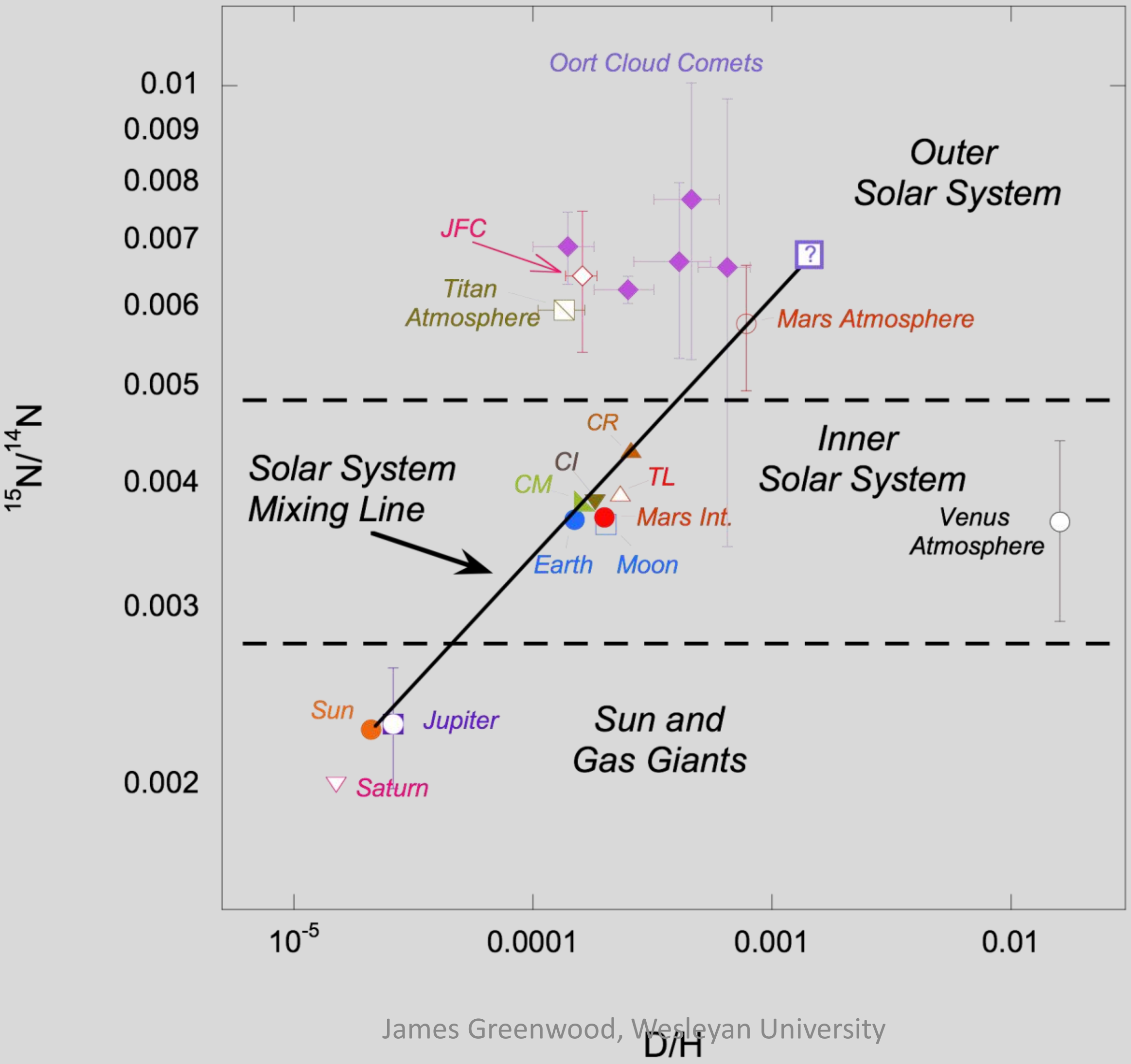
New model: Mixing of Outer Solar System Ices and Protosolar Gas



Water and Volatile Delivery to the Inner Solar System

- D/H can be simply explained as mixing of protosolar nebula hydrogen and outer solar system ice
  - Can also explain nitrogen and oxygen isotopes of inner solar system materials
  - Timing would suggest very early to explain the oxygen isotopes of planetary materials
- This model would suggest only minor additions of volatiles after initial accretion
- WARNING: Highly controversial new idea!

Questions?

Acknowledgements: This talk is based on work for the chapter “Delivery of water and volatiles to the inner solar system” for the ISSI Book “The delivery of water to proto-planets, planets, and satellites”
Authors: James P. Greenwood, Shun Karato, Kathleen Vander Kaaden, Kaveh Pahlevan, and Tomohiro Usui