

Magmatic Degassing and the Volatile Budget of the Moon

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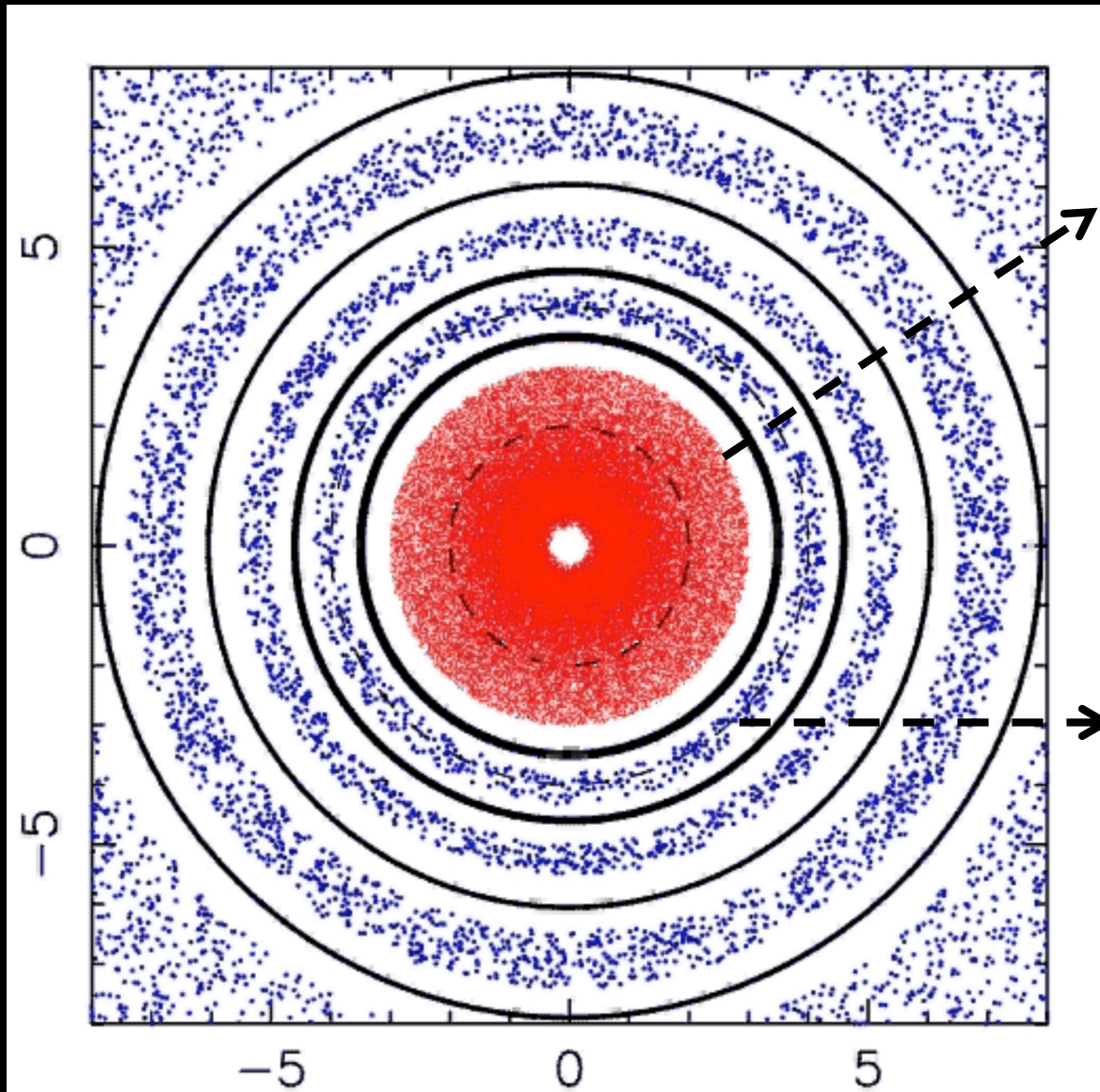
Collaborators: Erik Hauri, Mac Rutherford and James van Orman



Outline

- Motivation
- Rational for studying the Moon and volatiles
- The “consensus” on the Moon’s Volatile Budget
- Our results and explanation
- Conclusions

The Snow Line (150-175 °K)



Asteroids type S

Asteroids type C

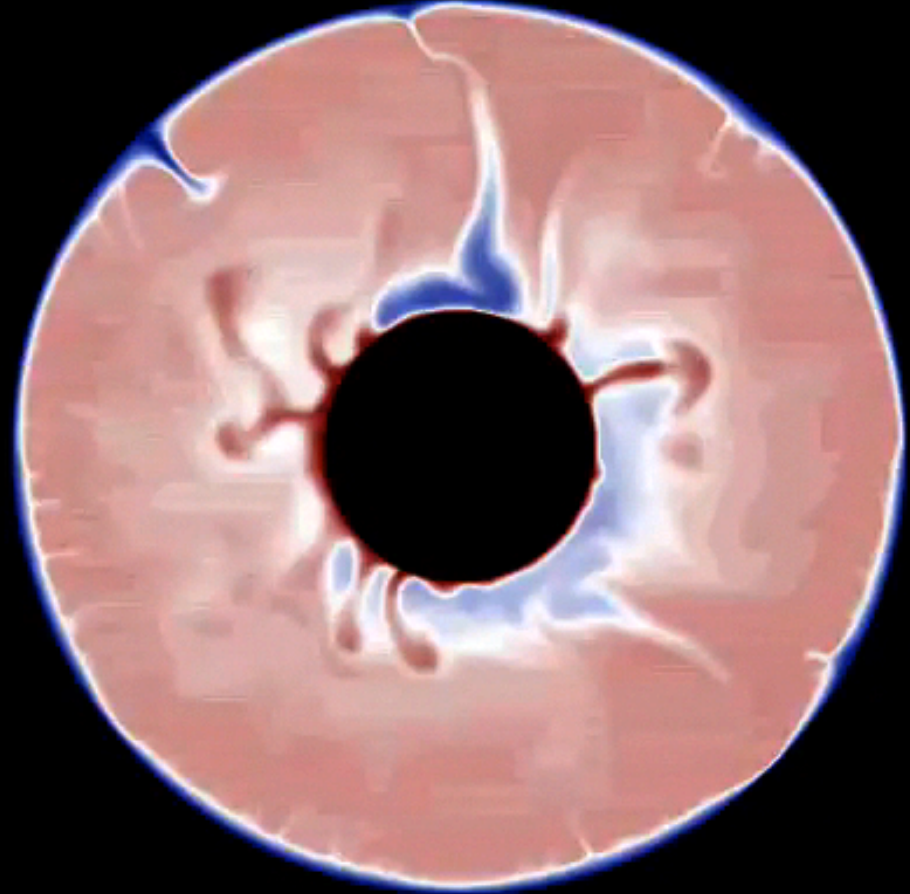
Walsh et al., (2011)

But we know the Earth has water



when, how and from where volatiles came to the Earth-Moon system?

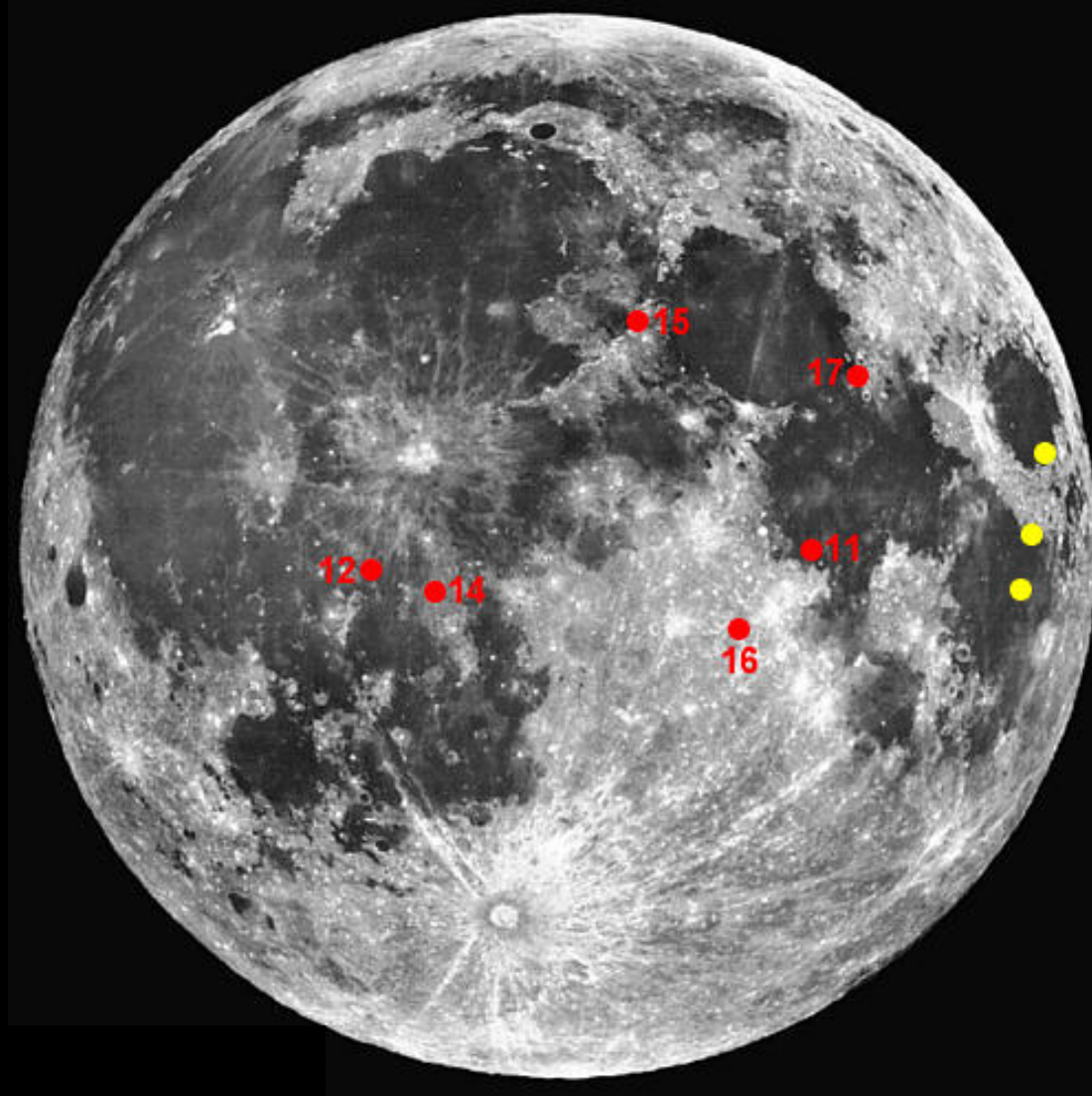
The Dynamic Earth



Cannot provide the answer

Peter van Keken

Why to study the Moon?



The Moon provides a frozen record of the first 200 Ma of Solar System formation.

Why is it important to determine the volatile (H-C) contents of planets?

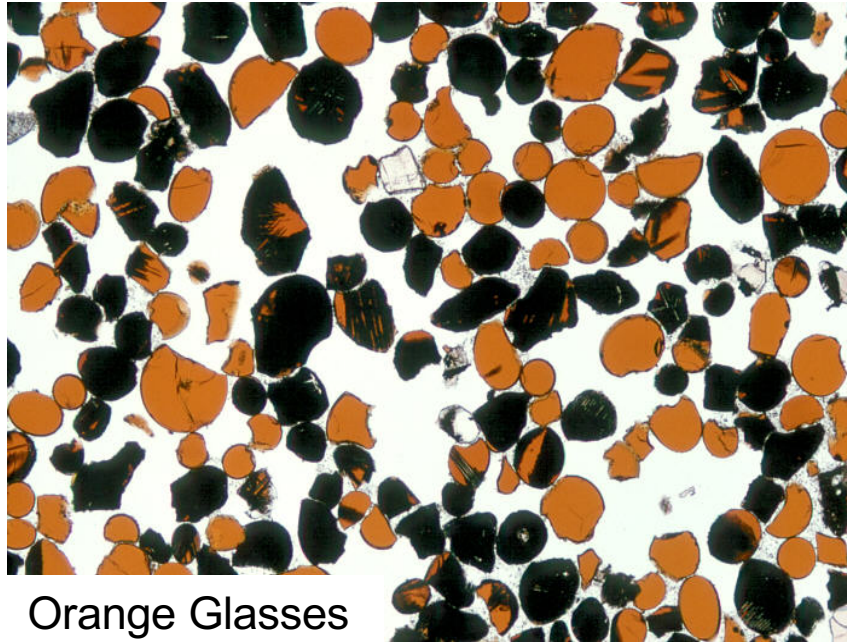
- 1) Provides information on the conditions of planet formation.
- 2) Affects the dynamics of planetary interiors (modifying the mantle and melts viscosities, influencing core segregation and longevity).
- 3) Decreases the melting point of solids.
- 4) Affects the mechanism of lava eruption.
- 5) It is fundamental for the origin of life.

An indirect approach:
the chemistry of mantle melts

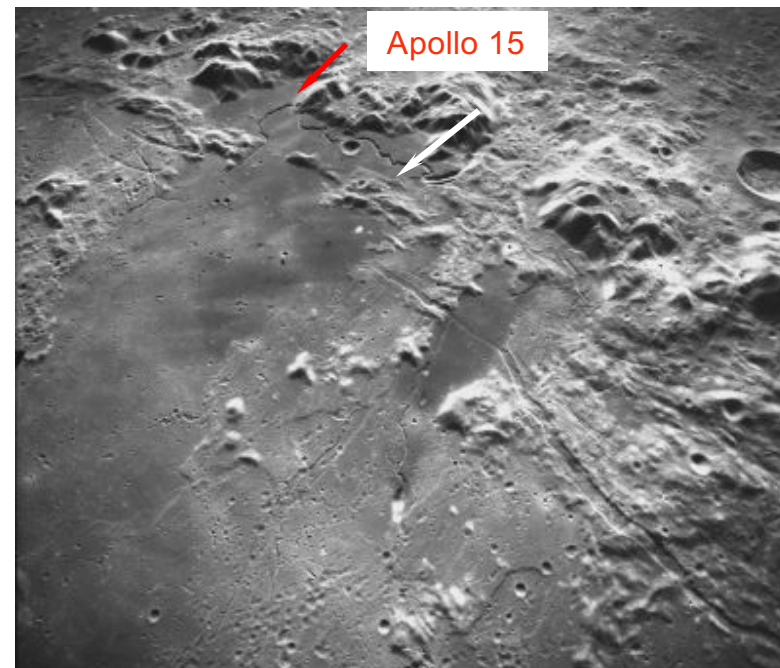
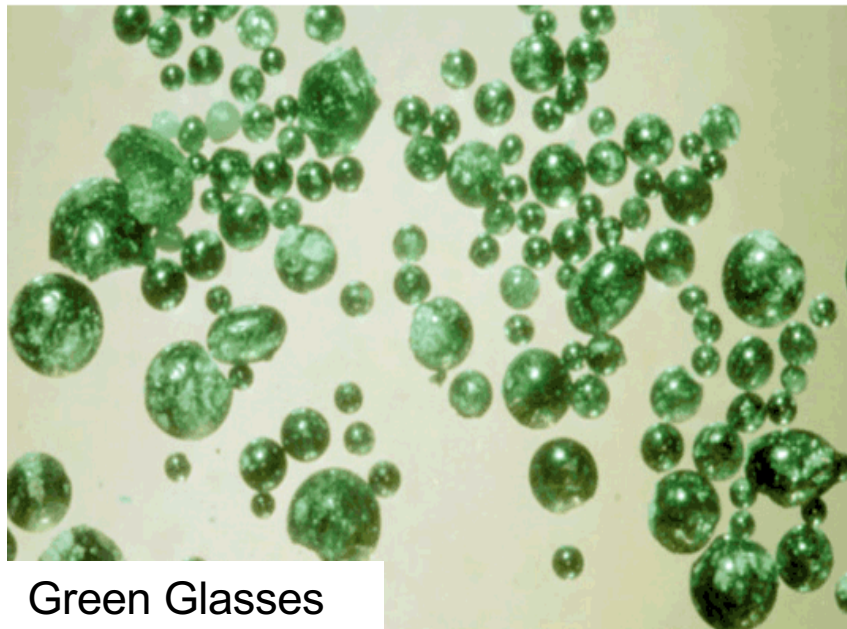
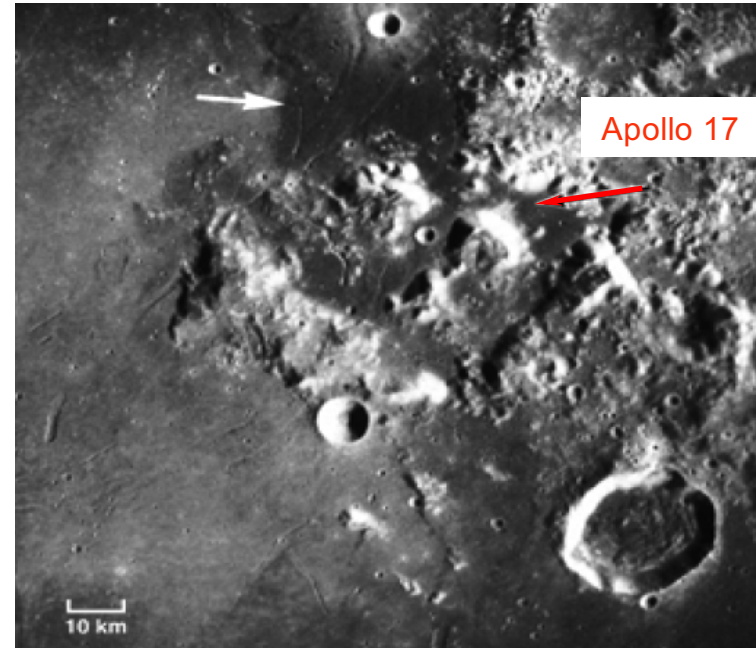


Eruption of Kilauea 1959

Volcanic Glasses

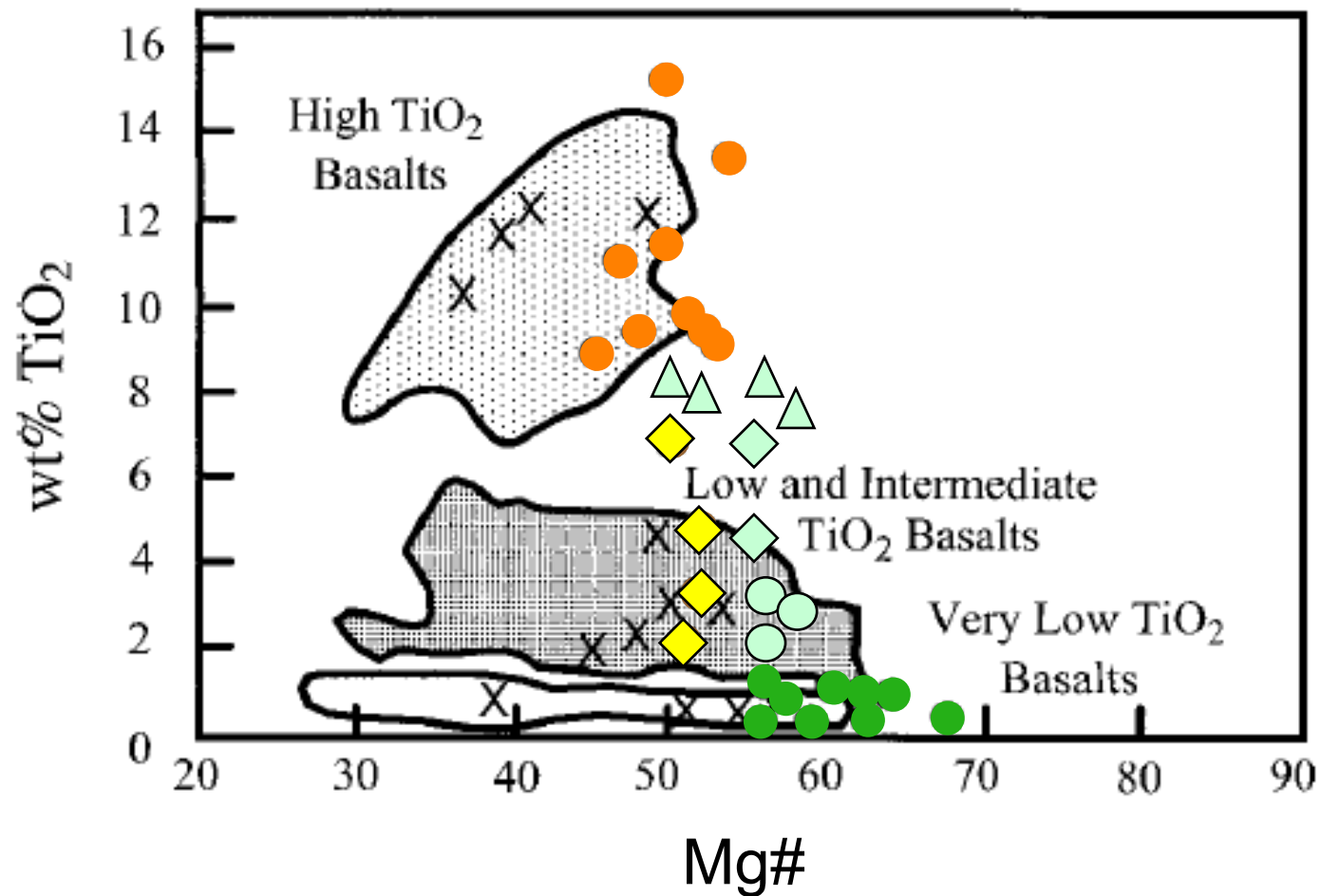


Dark Mantle Deposits



(NASA Apollo 15, S79-32188.)

The primitive composition of the lunar volcanic glasses



Shearer et al., 2006

(Delano, 1980; 1986; Shearer and Papike, 1993; 1999; Shearer et al., 2006)

Previous studies on the volatile contents of lunar samples

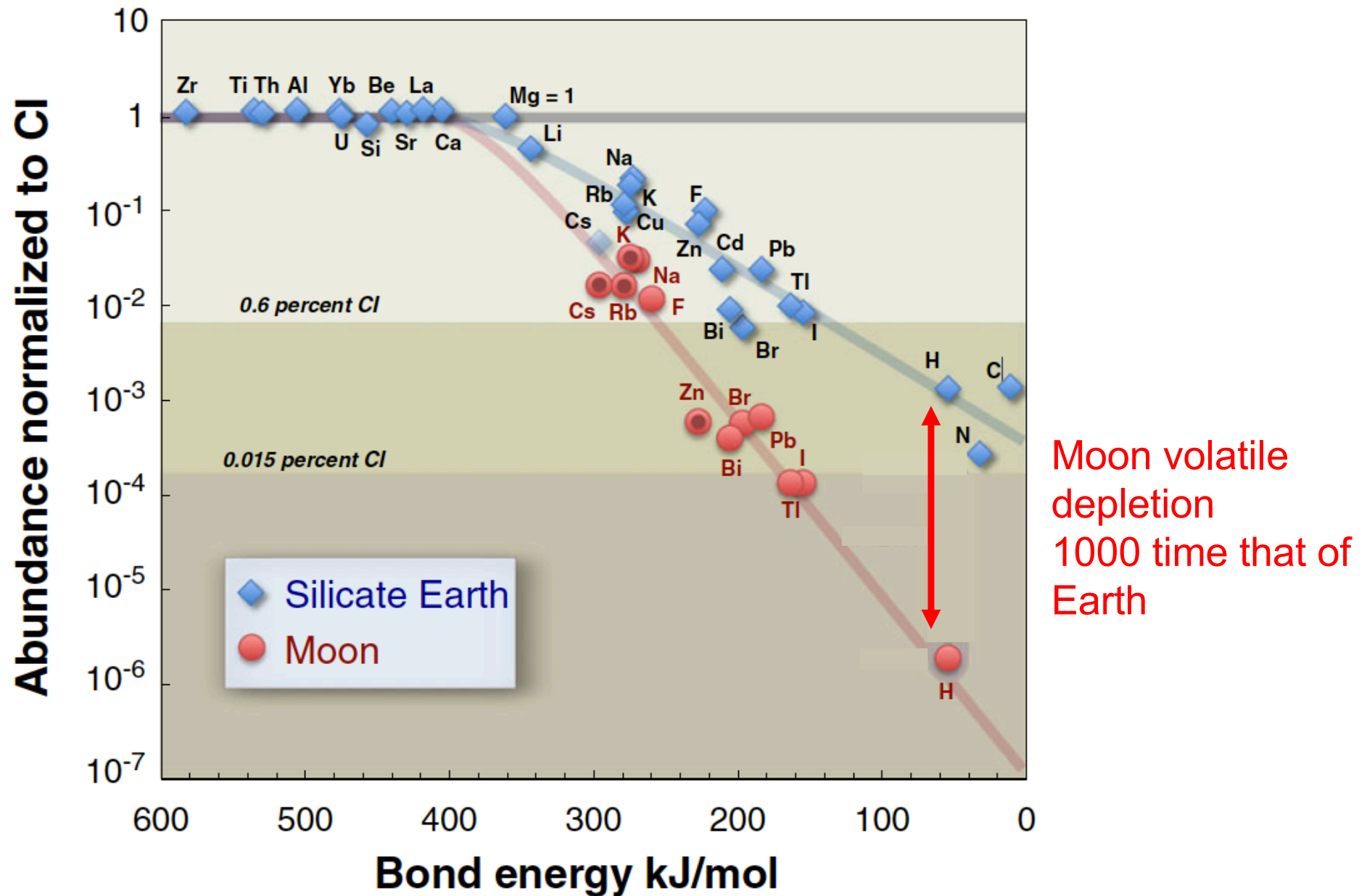
- 1) The hydrogen was produced by implantation of solar wind on the surface of the samples.
- 2) The measured molecular H_2O probably represented terrestrial contamination.
- 3) The conclusion was that the Moon was “bone dry”
Epstein and Taylor, 1973 and reference therein

For ~ 40 years the evidence for the presence of H_2O in the Moon interior remained elusive. Consistent with the general consensus that the Moon was “bone dry” due to its origin by a Giant impact between the Earth and a Mars-size planet ~ 4.5 Ga.

Simulation of a collision between the Earth and a planet of Mars size (Canup 2004)



The Consensus

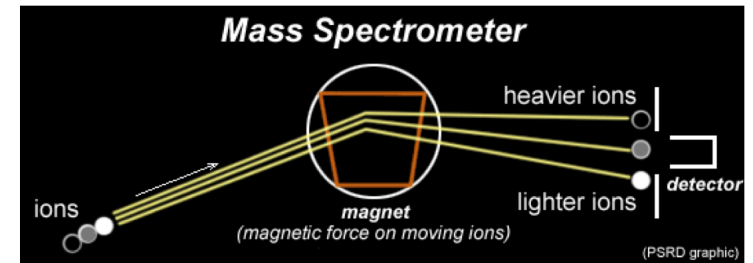
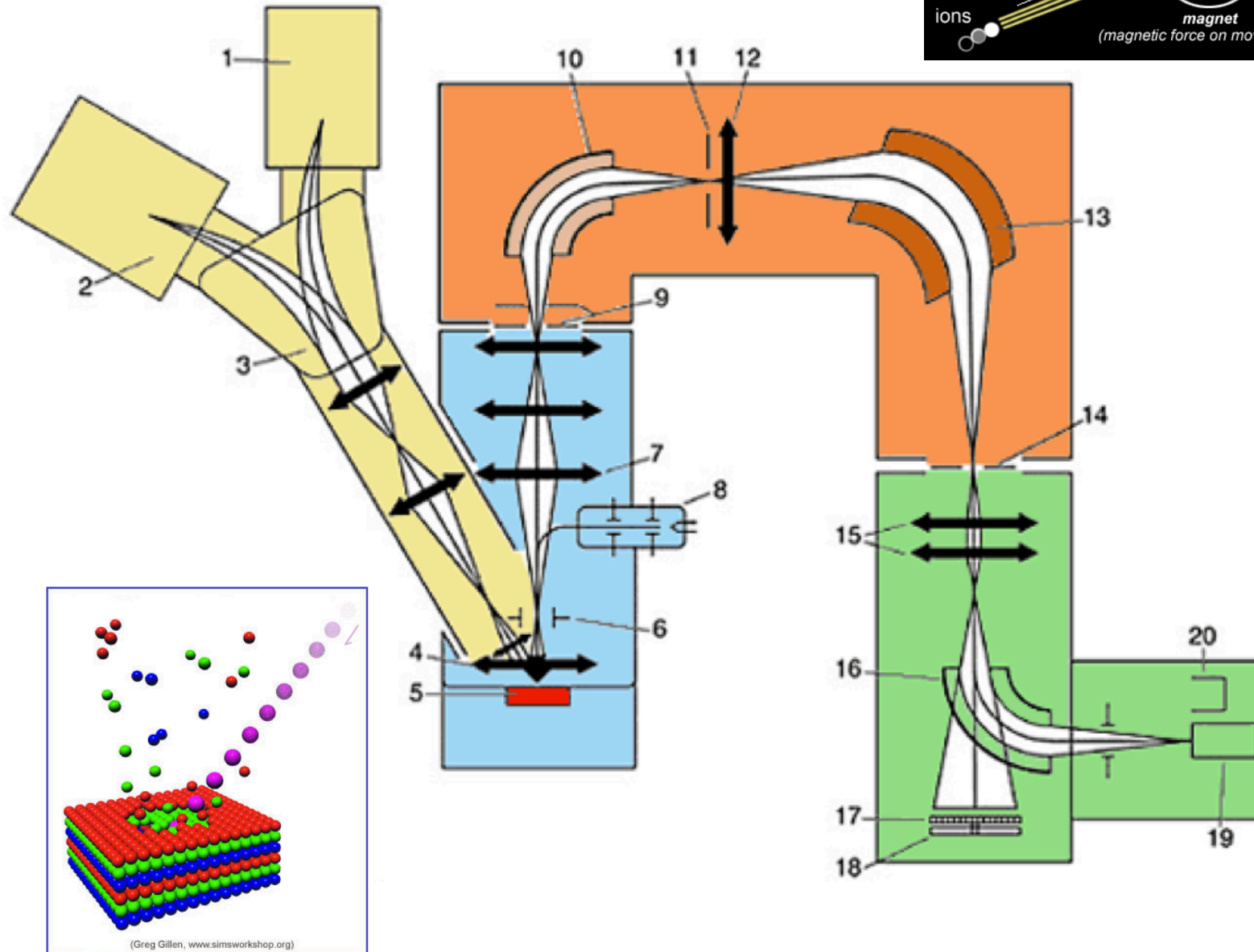


Albarede et al., 2014

Our work

- 1.- A little bit of the Analytical Techniques
- 2.- Present the first unequivocal evidence for indigenous lunar water carbon content and confirmation of F, Cl and S in volcanic glasses and melt inclusions.
- 3.- Our Moon volatile budget
- 4.- Reasons for the discrepancy between our and the consensus Moon's volatile budget.
- 5.- From where, how and when the volatile budget were set in the Earth-Moon system

The new SIMS (Secondary Ion Mass Spectrometer)

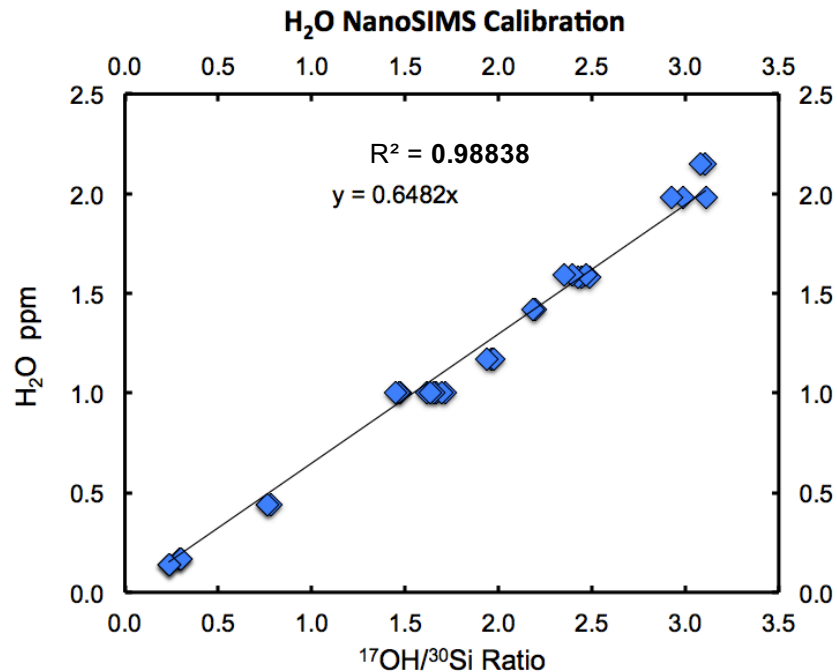
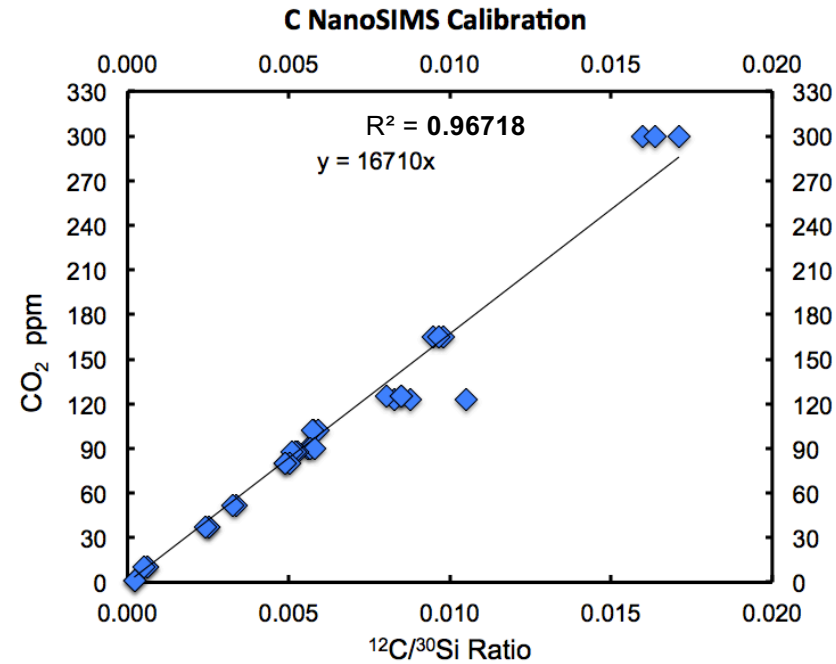


SIMS data at DTM

NanoSims : Cs⁺ beam
 3.7 μ of 10 μ or 11 μ of 30 μ
 Pre-sputter time 6 min

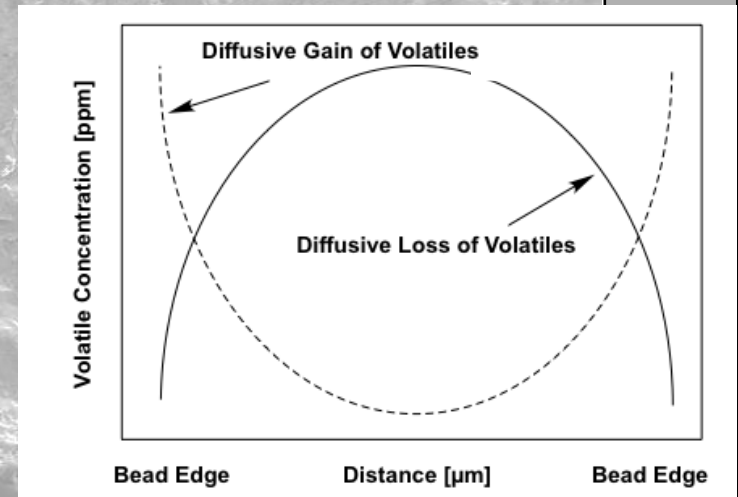
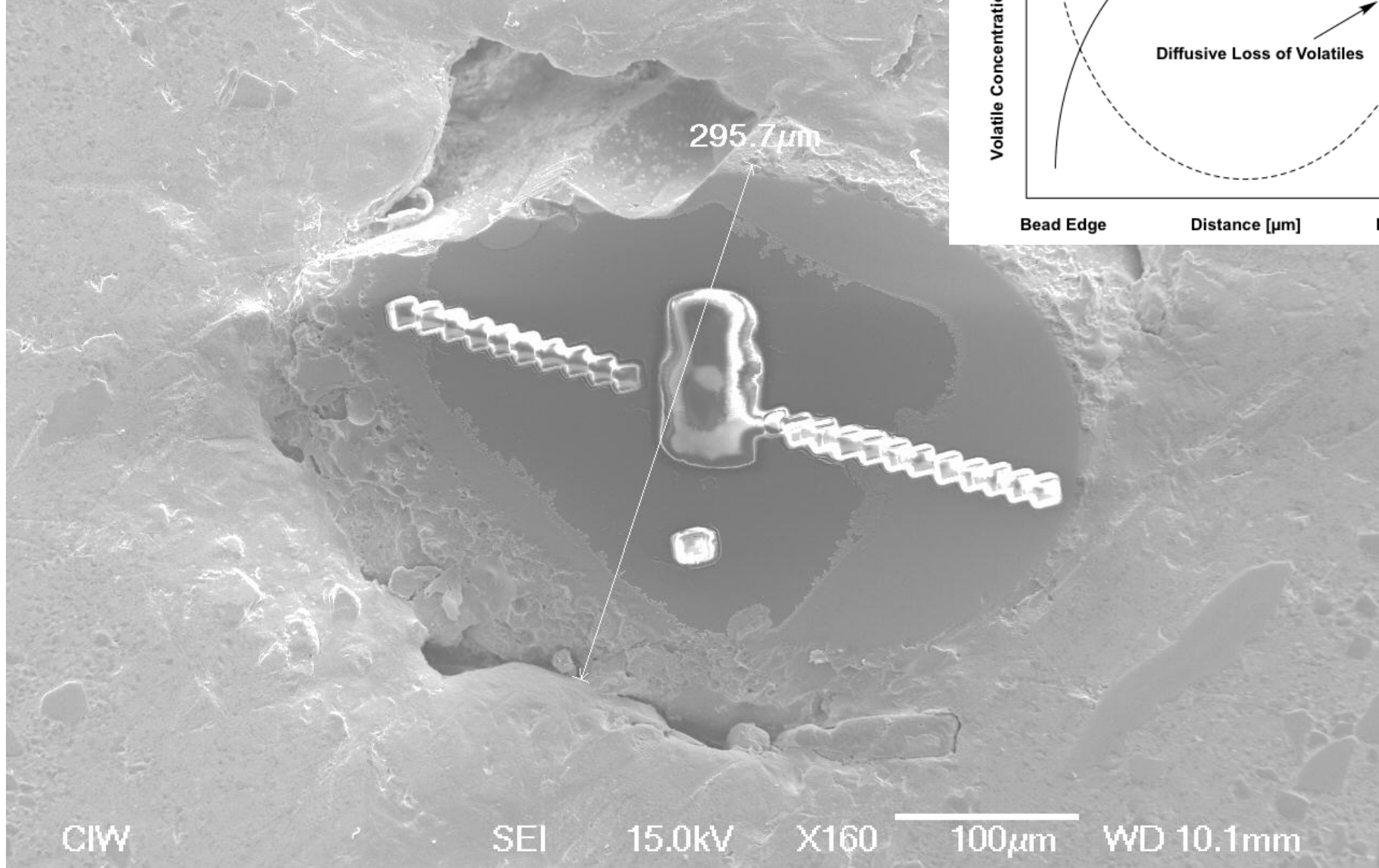
Detection Limits: C 0.068 ppm and H₂O 0.99 ppm;
 F 0.046 ppm; S 0.064; Cl 0.08 ppm

Combined accuracy and reproducibility is 17% for C, 9.3% for H₂O, 13% for F, 6.4% for S, and 29% for Cl.

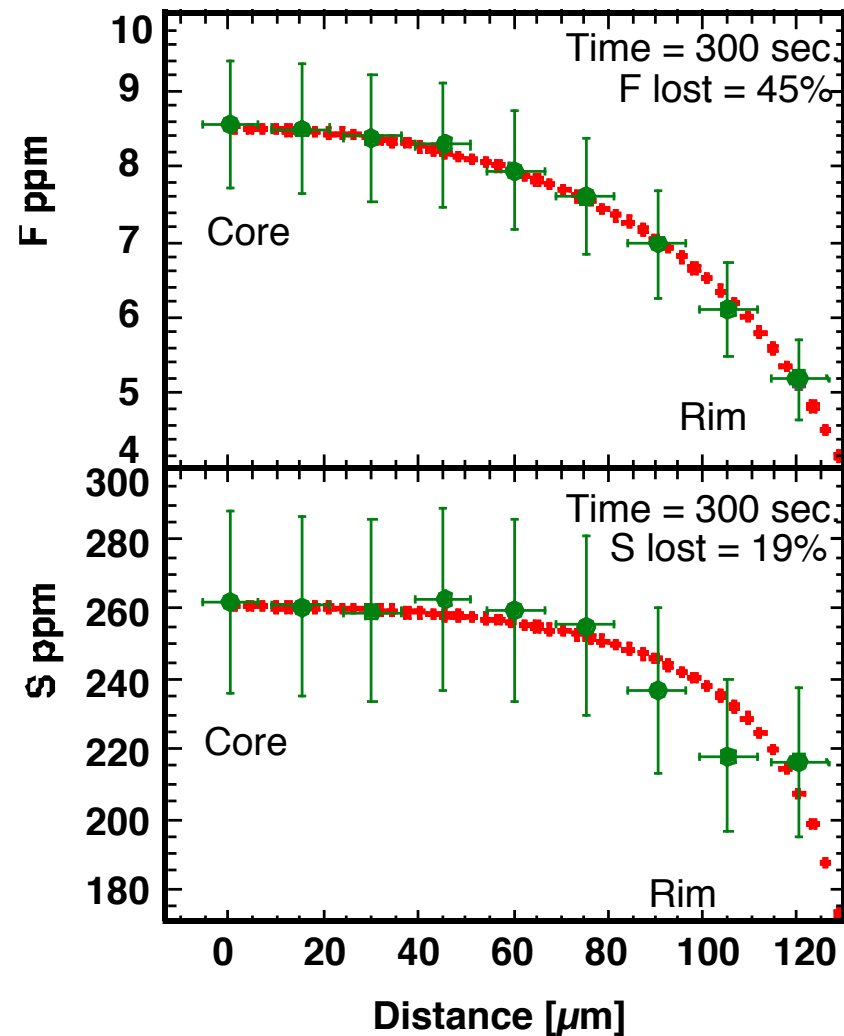
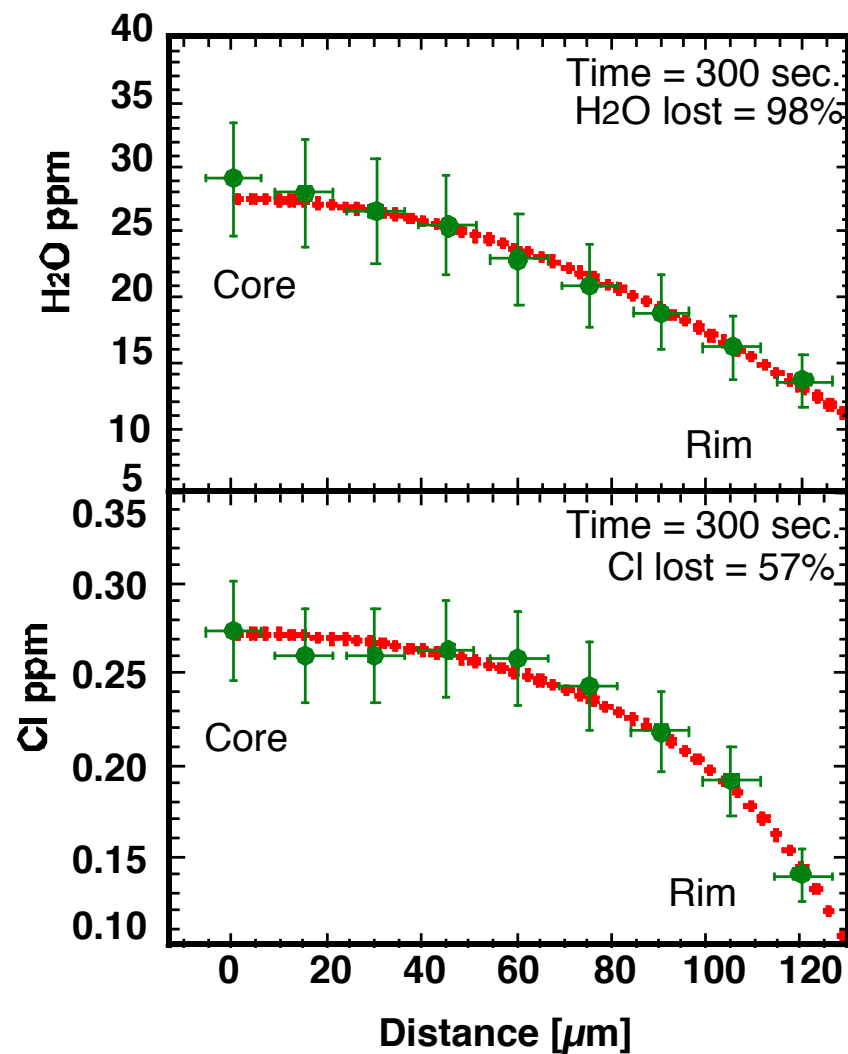


Hauri et al., unpublished; 2002; 2006; 2011
 Koga et al., 2003; Aubaud et al., 2004

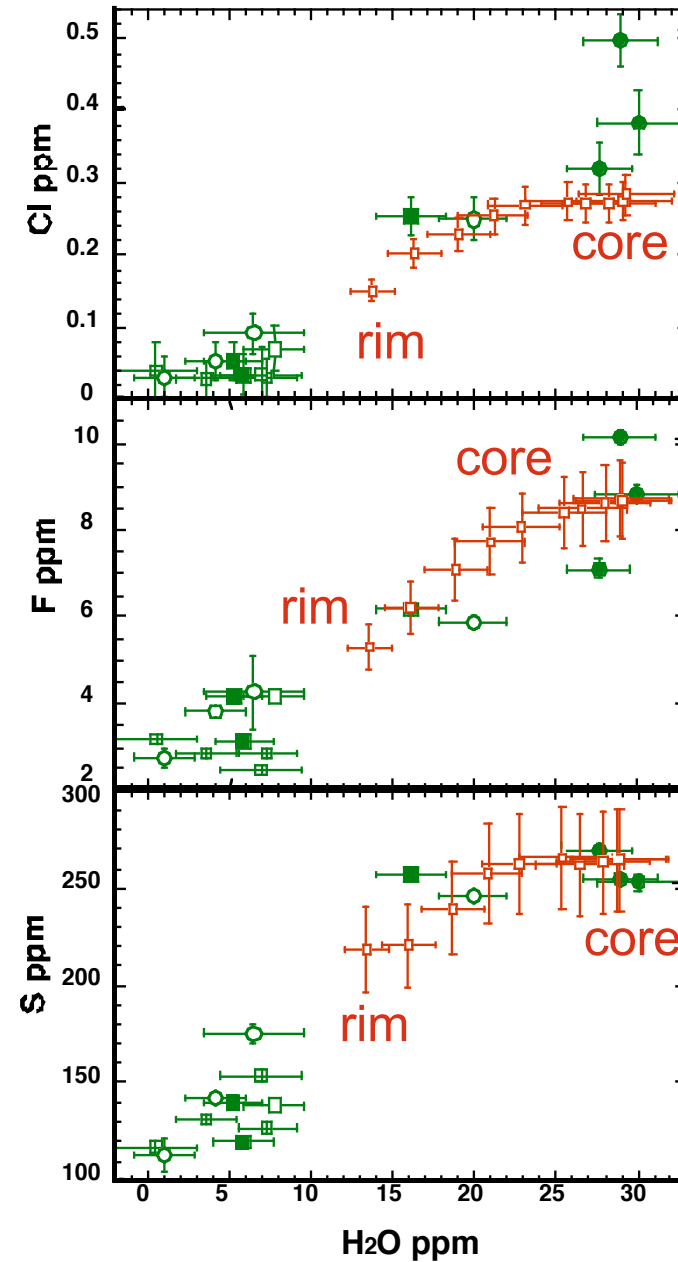
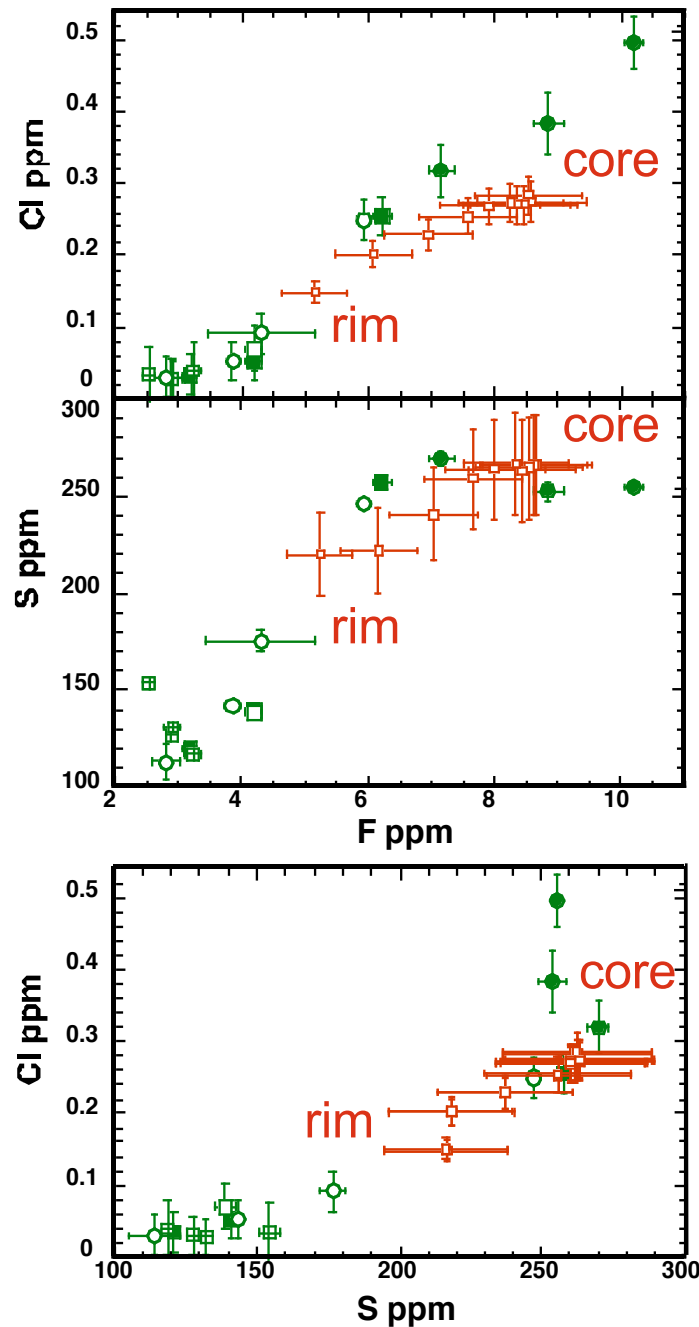
In 2008 we presented the first report of Lunar water (H_2O , F, S, Cl) in single lunar glass beads and concentration profiles across beads of very-low-Ti glasses.



Degassing models with cooling rates of 2°C/sec and 300 sec until the bead is quenched, suggest that the initial water concentration was ~ 750 ppm, with a minimum of 260 ppm at the 95% confidence level.



Concentration profiles in a single bead reproduced the trends defined by all the glasses suggesting the volatile variation is due to degassing processes.



two issues were raised:

what is the primitive (pre-degassing) volatile contents of lunar magmas?

(How much water was in the primitive magmas?)

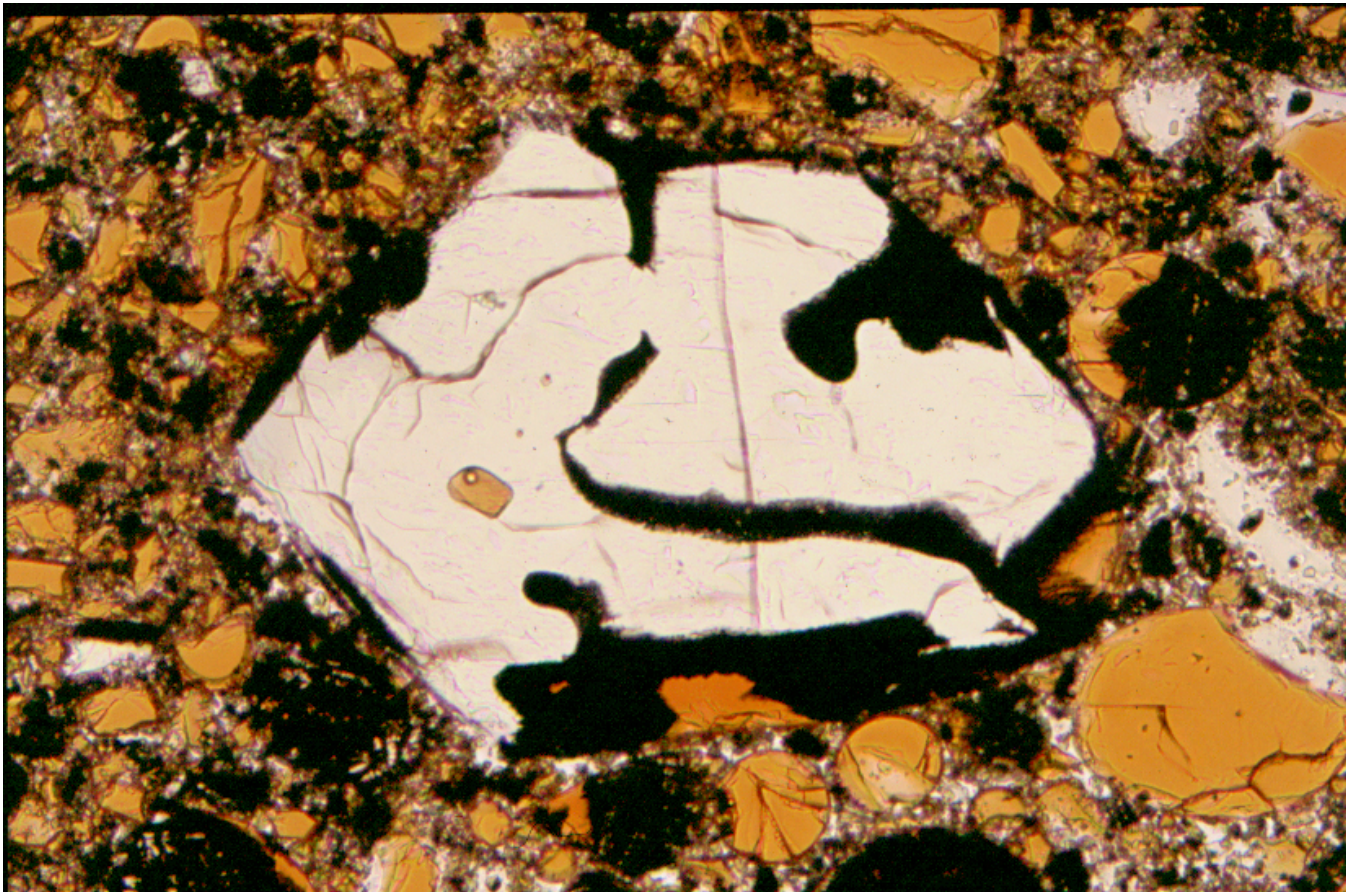
The surface pressure prevailing during eruption of lunar magmas is on the order of 10^{-10} to 10^{-15} bars, ~ one-trillionth the pressure prevailing on Earth's surface (Stern, 1999)

What is the distribution of the volatiles within the Moon (reservoirs)

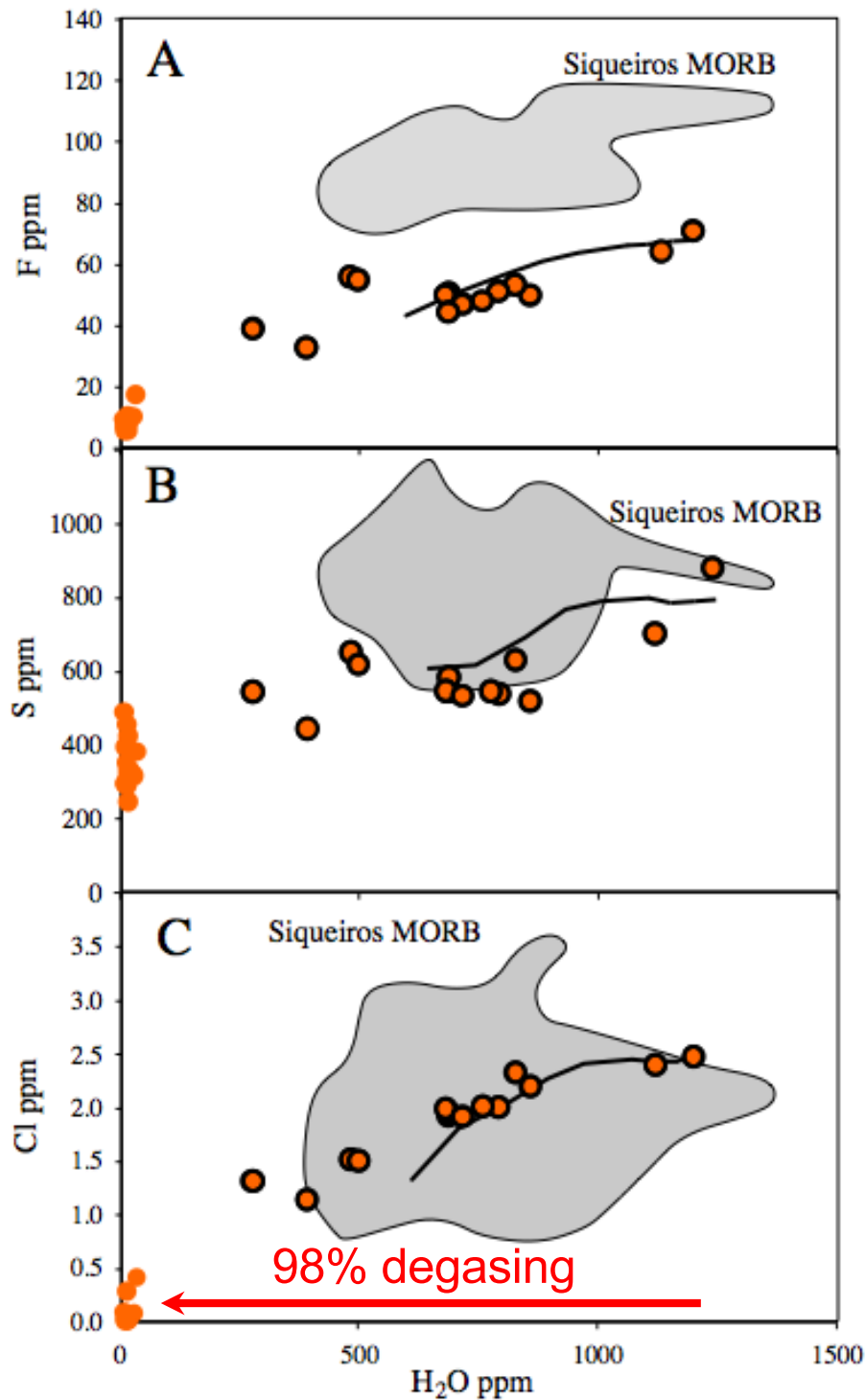
(How representative is our estimation?)

To determine the primitive (pre-degassing) volatile contents

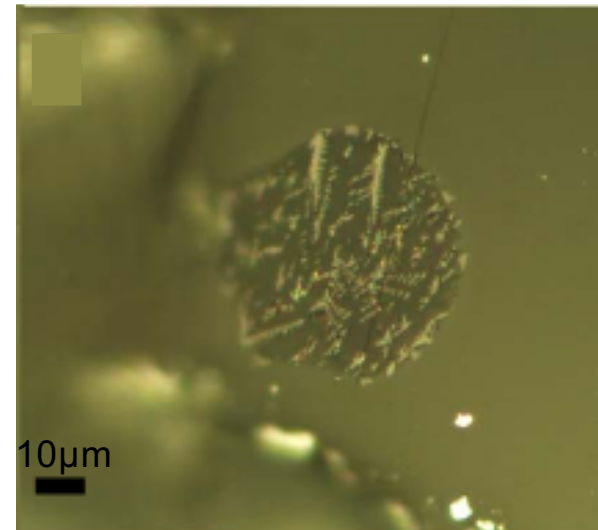
We used melt inclusions



Weitz et al 1999

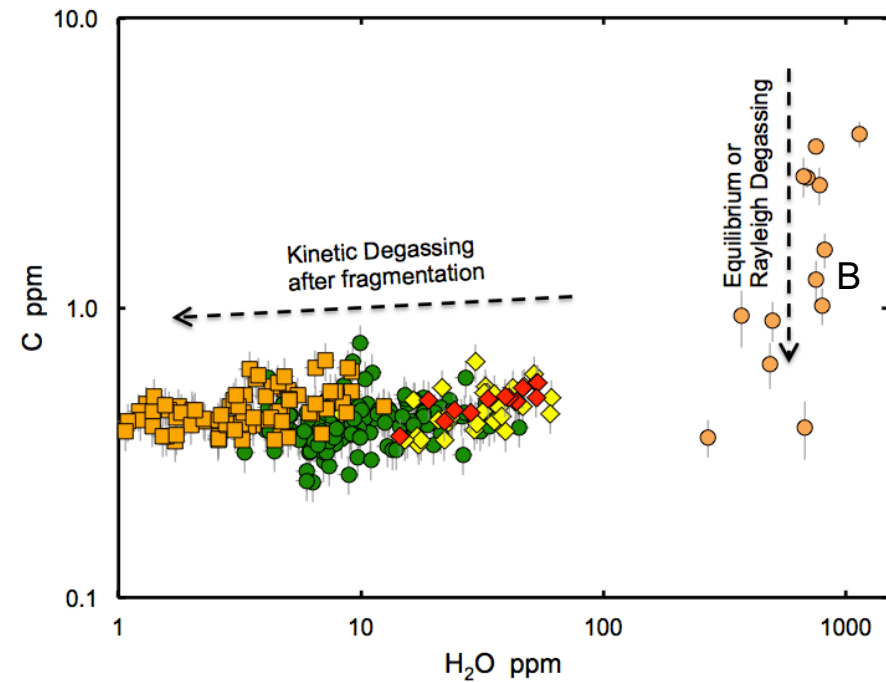
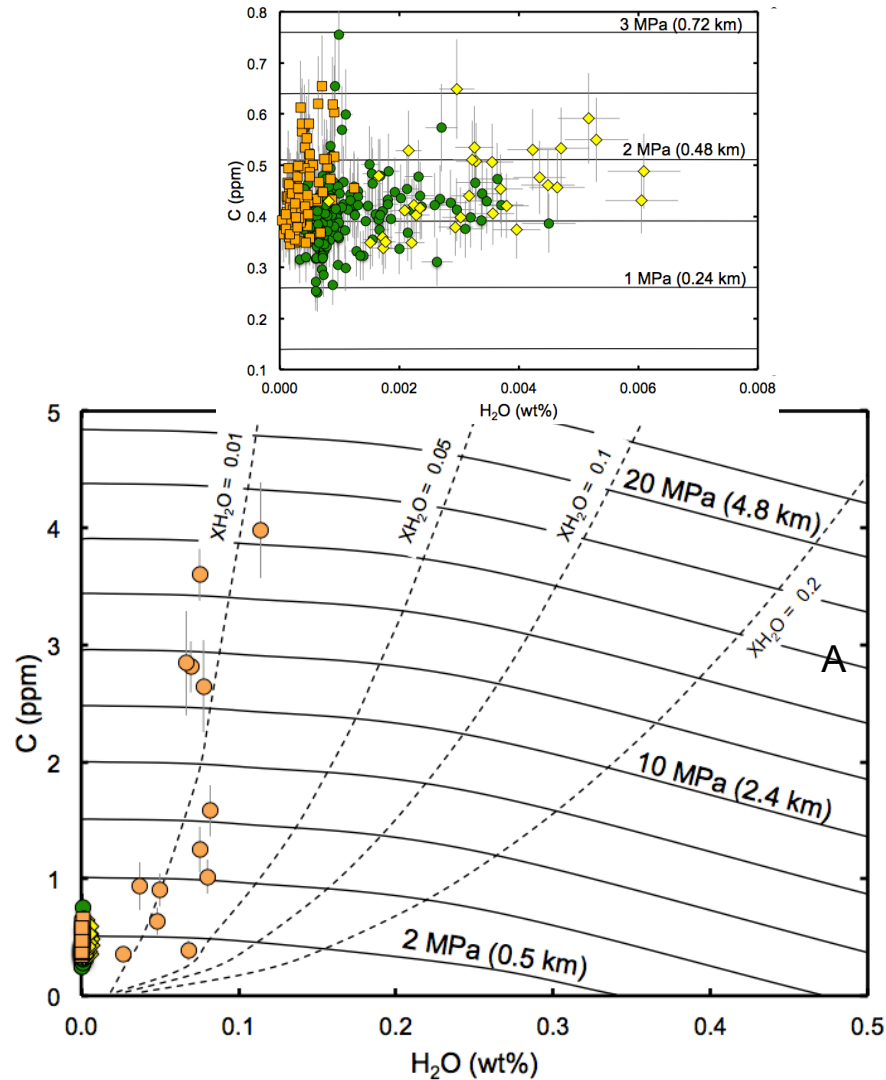


We used olivine-hosted melt inclusions in glass beads from A17 sample.



The new melt inclusion study confirmed our predictions that the volatile contents of the lunar volcanic glasses were equivalent to those found in MORB

The Carbon Content and Magmatic Degassing



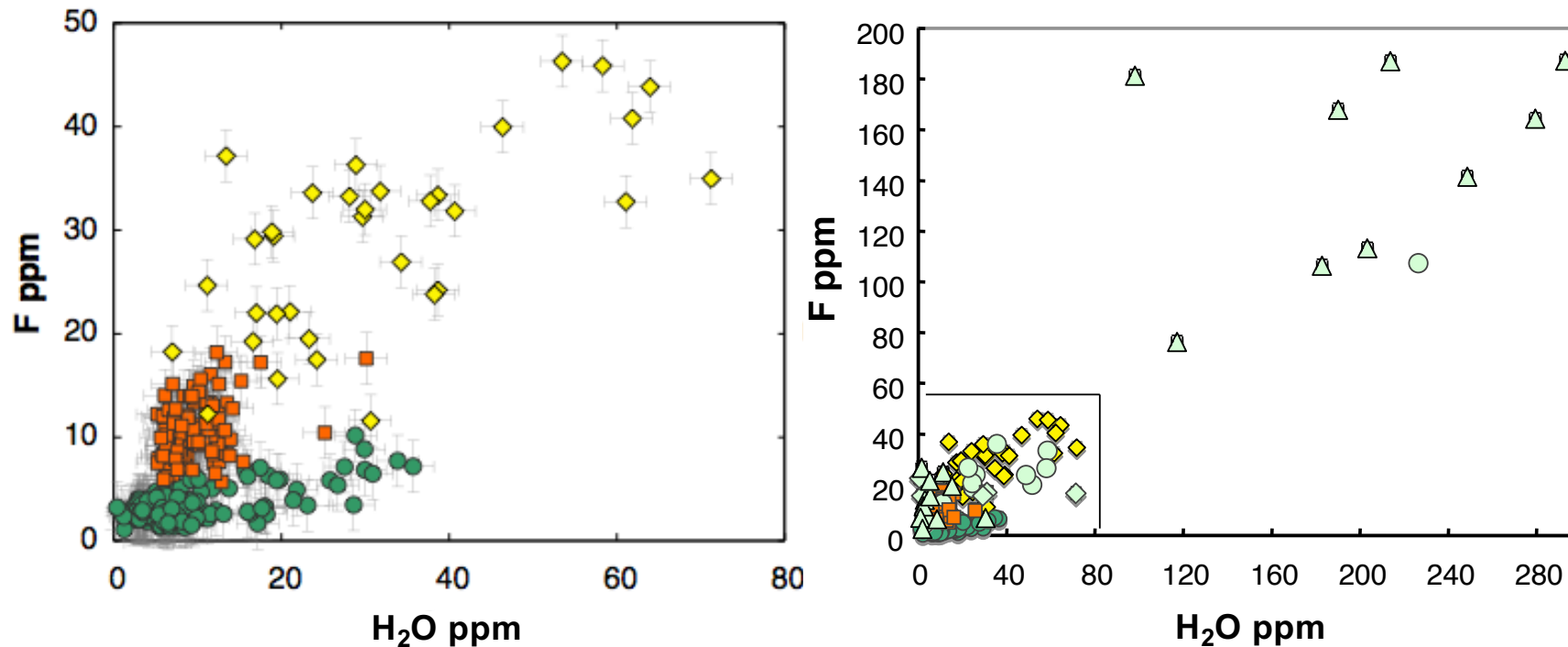
Wetzel et al., 2015

The H/C ratios of the lunar magmas range between 2 and 3, similar to ratios for undegassed terrestrial MORB. And the $\delta^{13}\text{C}$ of orange glasses is -7.3‰ , similar to that of MORB ($6.9 \pm 0.9\text{‰}$).

To determine the distribution of the volatiles contents within the Moon

We performed new volatile analyses for more than 360 individual volcanic glasses from A-15, A-17 and A-14 .

F vs H₂O



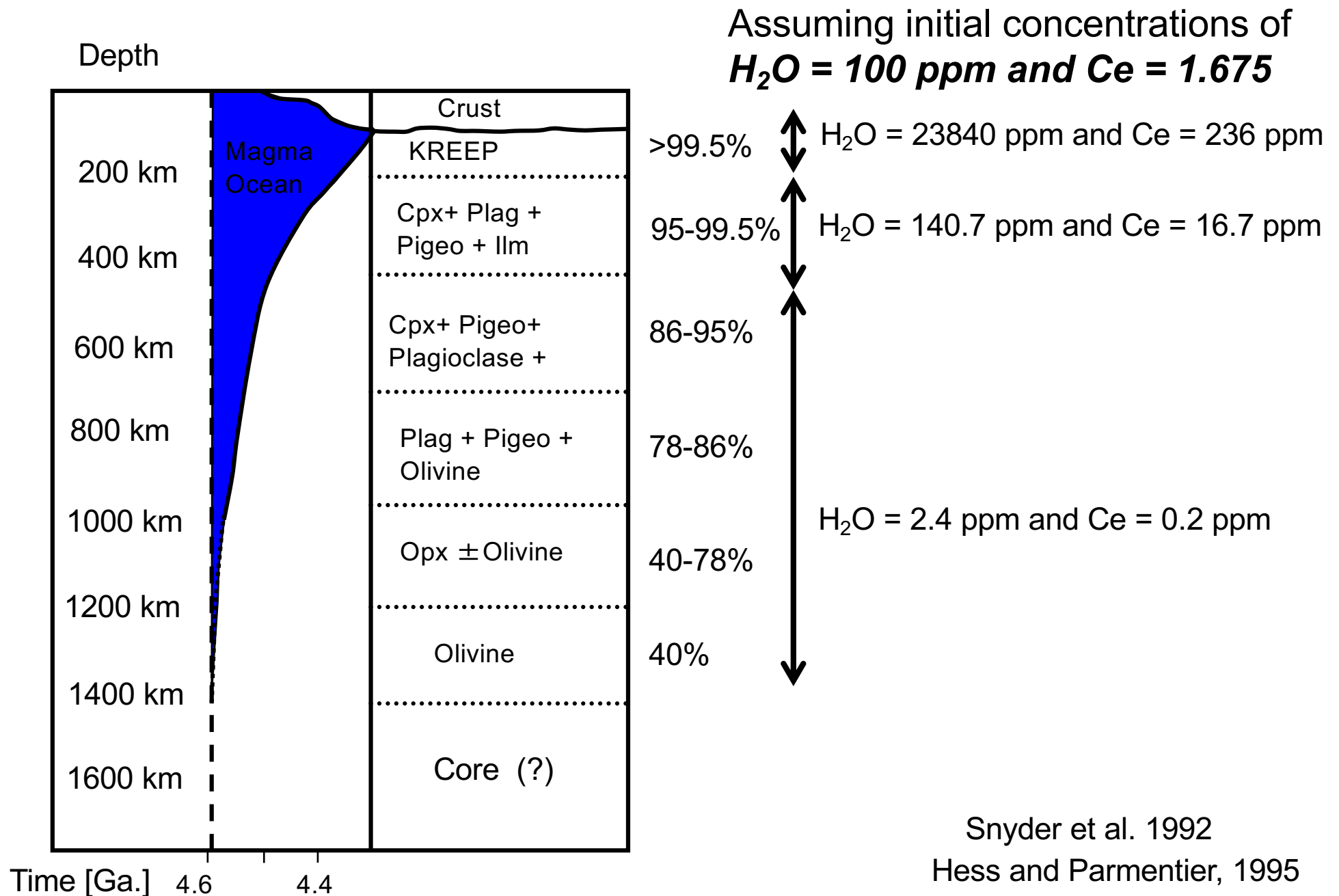
● A-15 VLT

■ A-17 HT

◆ A-15 LT

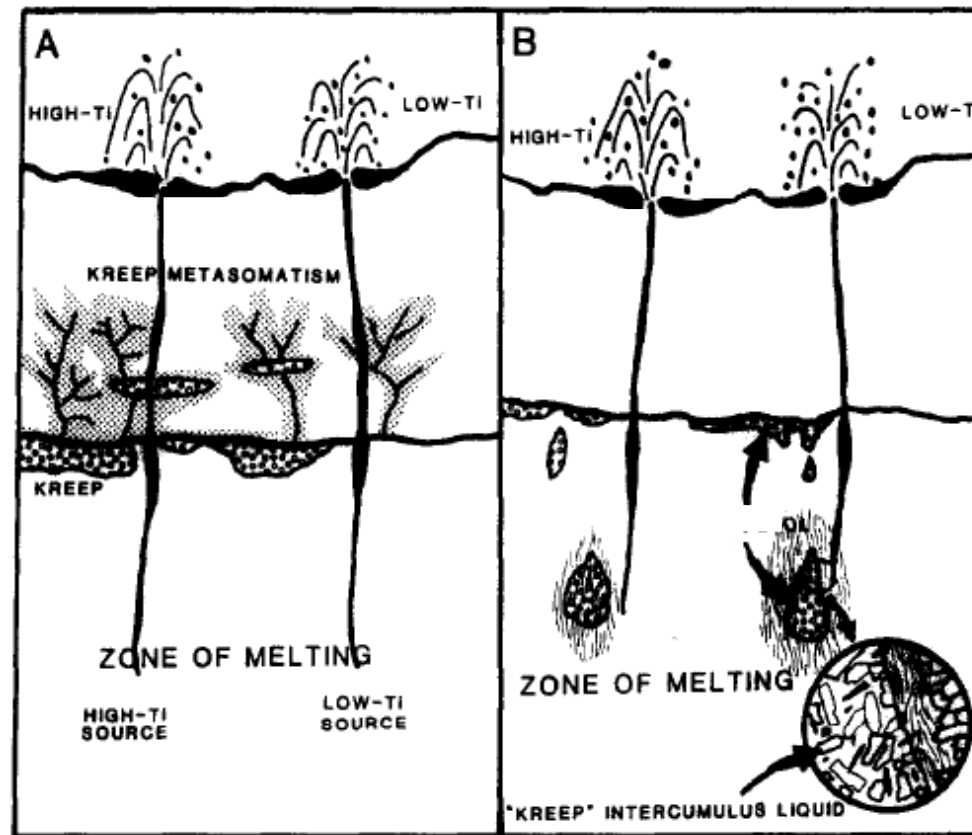
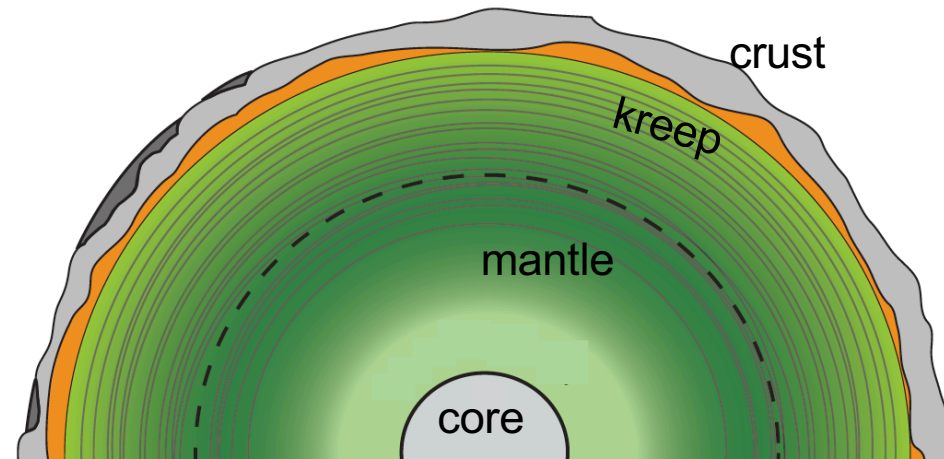
△ ◇ ○ A-14

The evolution of the lunar magma ocean might provide a starting point



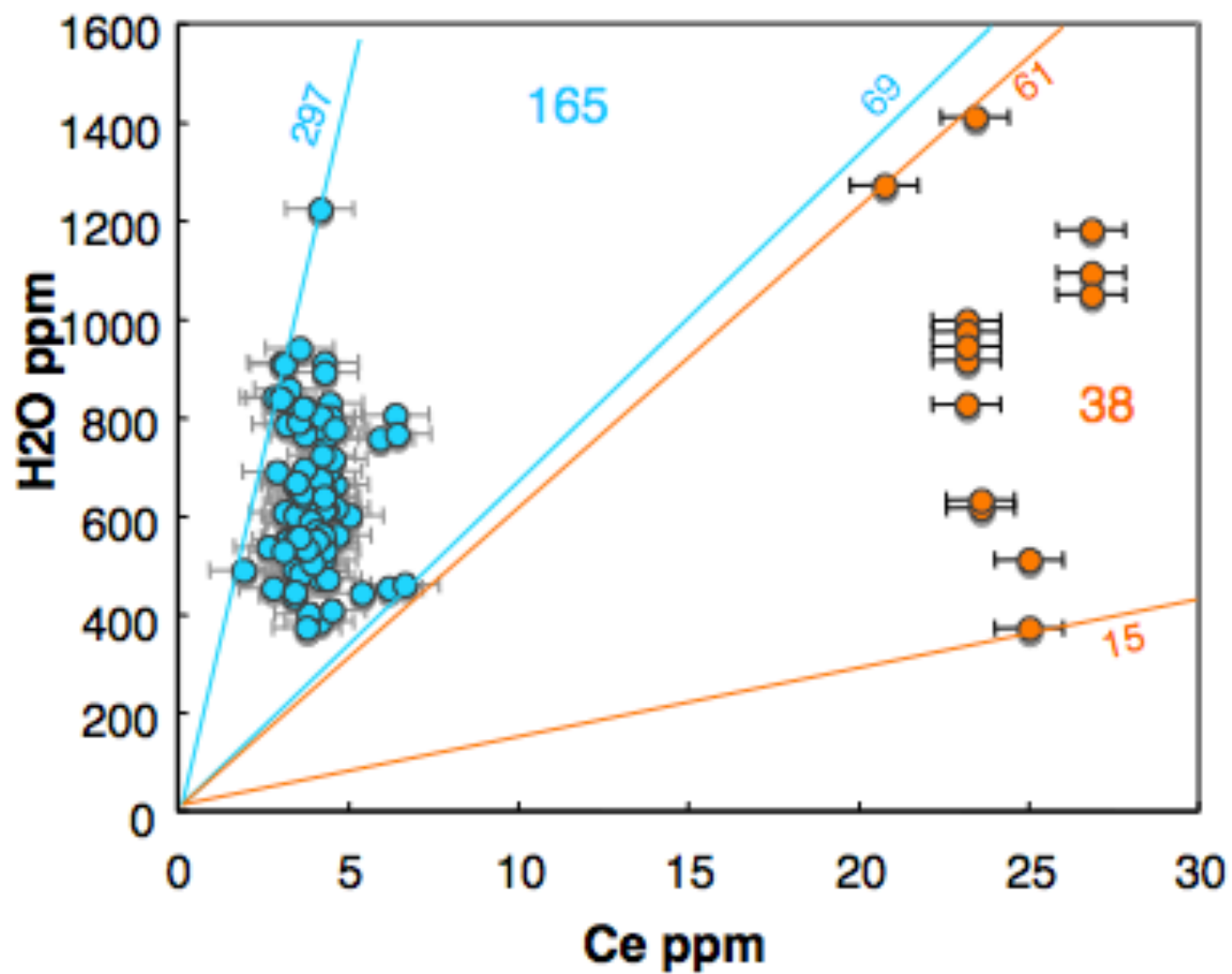
Two possible scenarios

- A) Shallow assimilation of KREEP into primitive melt
- B) Deep hybridization of the lunar mantle source during LMO cumulate overturn



Grove and Krawczynski (2009) Shearer et al. (1990)

Volatile-refractory element ratios in melt inclusions from the Moon and MORB



Volatile/non-volatile ratios for lunar glasses and MORB suggest a factor of <10 rather than 1000 volatile depletion

| | CO₂/Nb | H₂O/Ce | F/Nd | S/Dy | Cl/Nb |
|------------------------------|--------------------------|--------------------------|-------------|-------------|--------------|
| A15green VLT ¹ | | 169-60 | 3.700 | 129 | 0.231 |
| A17orange 74220 ² | 223-132 | 62.4 | 4.350 | 94.5 | 0.385 |
| depleted MORB ³ | 239±46 | 168 ± 95 | 16 ± 1 | 225 ± 50 | 3.0 ± 0.8 |

¹ estimated from diffusion modeling, Saal et al. (2008)

² highest ratios measured in 74220 melt inclusions, Hauri et al. (2011), this study.

³ depleted MORB averages from Saal et al. (2002)

The presence of surface coatings has been widely attributed to their deposition onto bead exteriors during cooling of clouds of volcanic gas

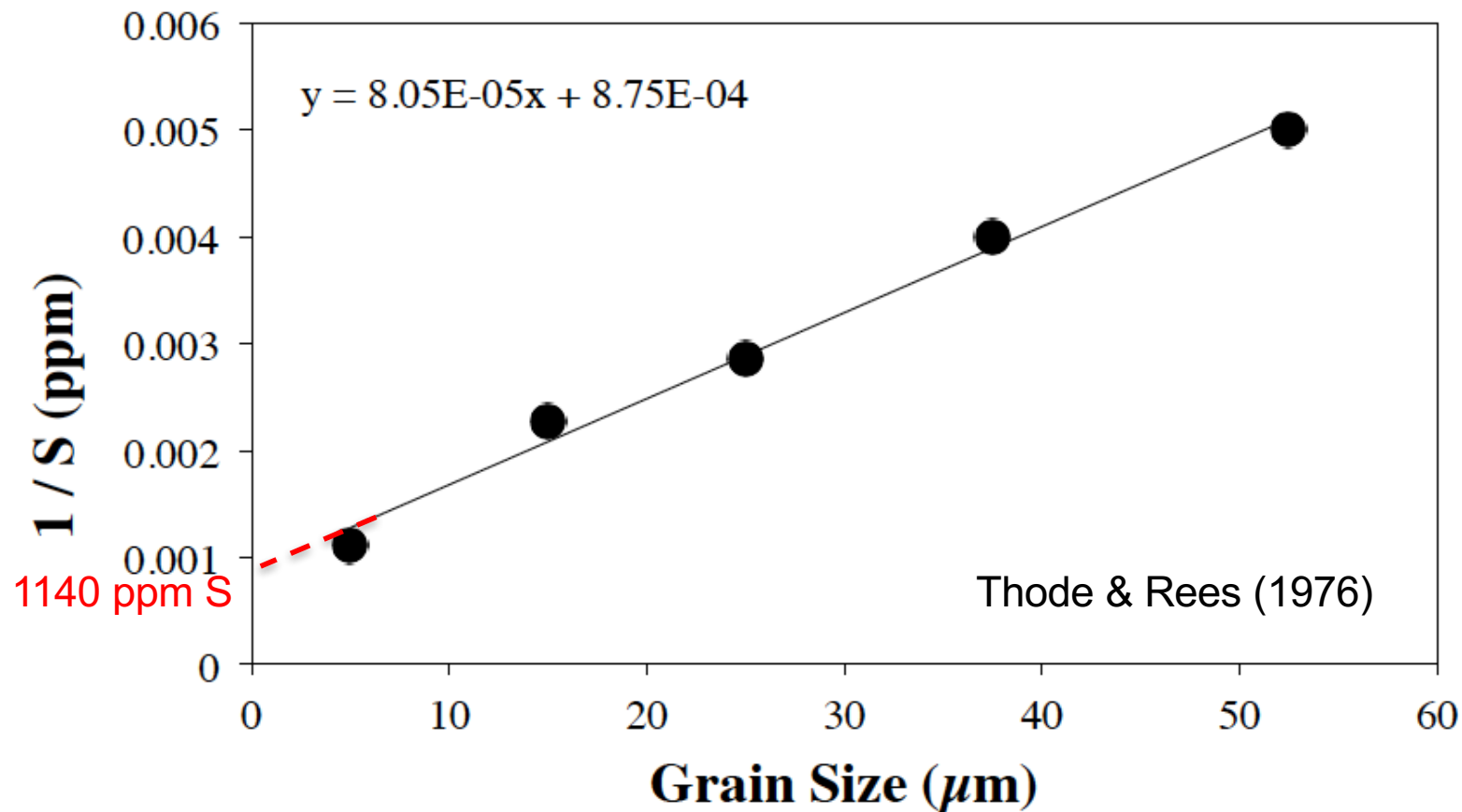


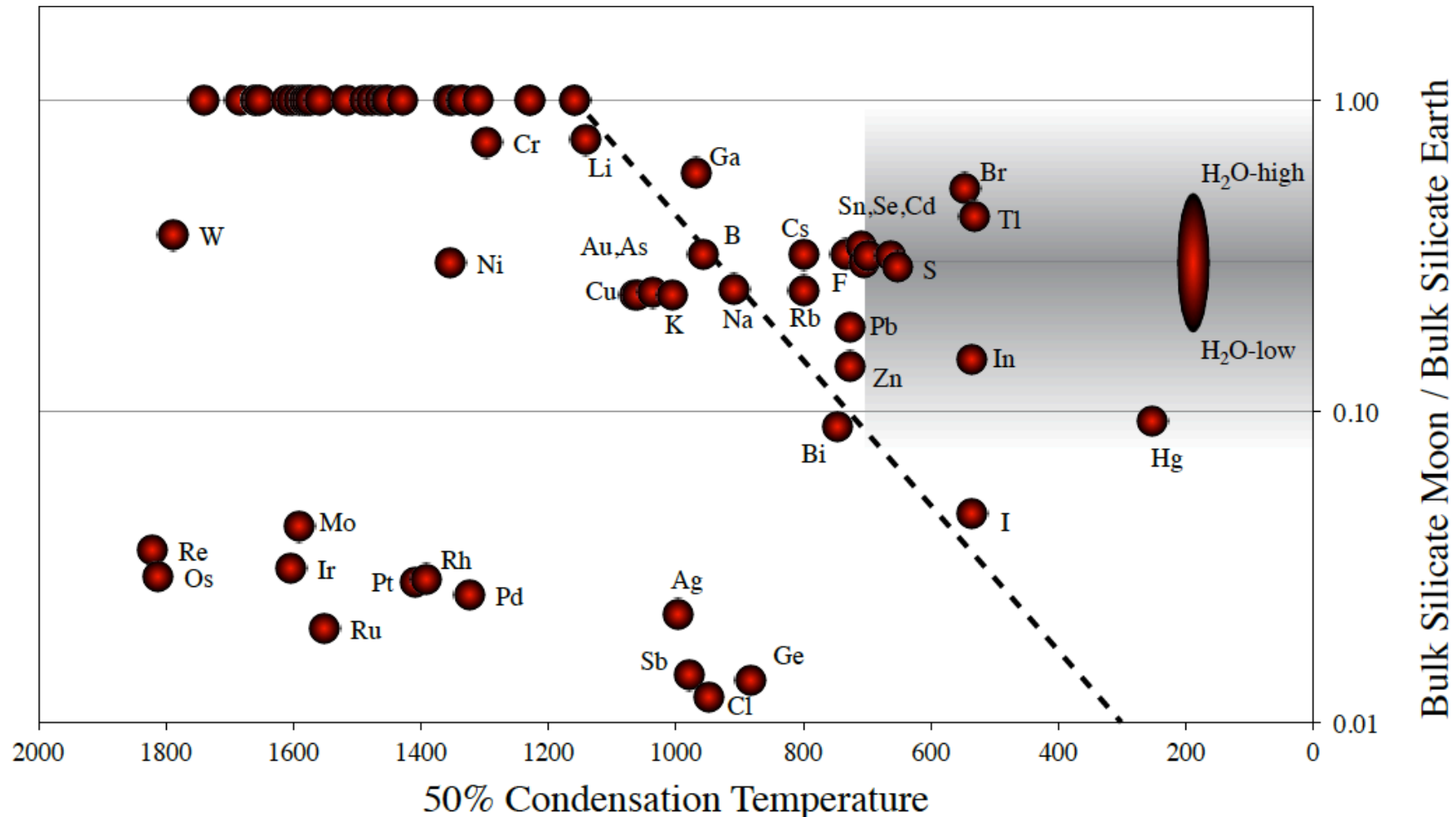
Table 2. Composition of volatile elements in 74220 glass bead coatings, glass bead interiors, and reconstituted pre-eruptive composition (see text).

| | S ppm | Na ppm | Zn ppm | Ga ppm | Ge ppb | Cd ppb | In ppb | Te ppb | Hg ppb | Pb ppm |
|---------------------------------------|-------|--------|--------|--------|--------|-------------|-------------|-------------|-------------|--------|
| A17orange coating composition | 1143 | 3181 | 252 | 19.5 | 344 | 267 | 37.1 | 93.5 | 21.3 | 8.13 |
| A17 orange glass interior composition | 325 | 2137 | 3.97 | 16.7 | 0.19 | <i>n.d.</i> | <i>n.d.</i> | <i>n.d.</i> | <i>n.d.</i> | 0.305 |
| A17orange glass reconstituted | 884 | 3692 | 127 | 26.3 | 168 | 131 | 18 | 46 | 10 | 4.28 |
| % degassed | 63% | 42% | 97% | 36% | 100% | <i>n.d.</i> | <i>n.d.</i> | <i>n.d.</i> | <i>n.d.</i> | 93% |

Chou et al. (1975), Wasson et al. (1976), Cirlin et al. (1978) and Krahanbuhl (1980).

The lunar mantle $^{87}\text{Rb}/^{86}\text{Sr}$ from Sr isotopes in anorthosites and Mg-suite samples is 0.035 (Carlson et al., 2014) and from a lunar meteorite is 0.044 (Borg et al., 2009), 1/3 and 1/2 of that in the BSE (0.089).

The lunar mantle $^{238}\text{U}/^{204}\text{Pb}$ (μ) from Pb isotopes was estimated ~ 30 (Tera and Wasserburg, 1976), 21 (Kita et al., 1995), 18 (Terada et al., 2008), and 10 (Misawa et al., 1993) compared with the BSE value of 8.5. Thus the abundances of Rb (0.245x BSE) and Pb (0.187x BSE) in the BSM

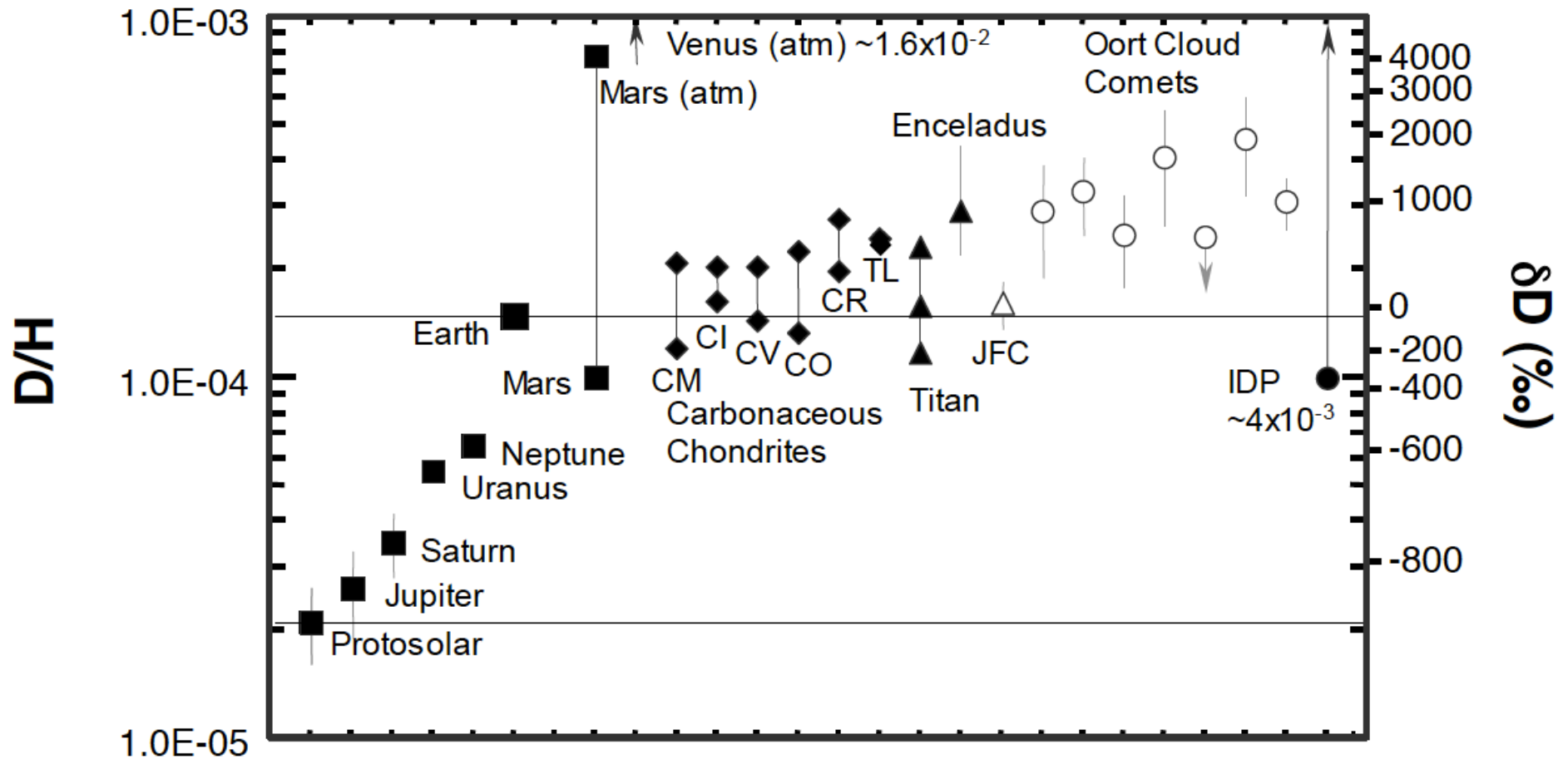


two new issues were raised:

Where did the water come from?

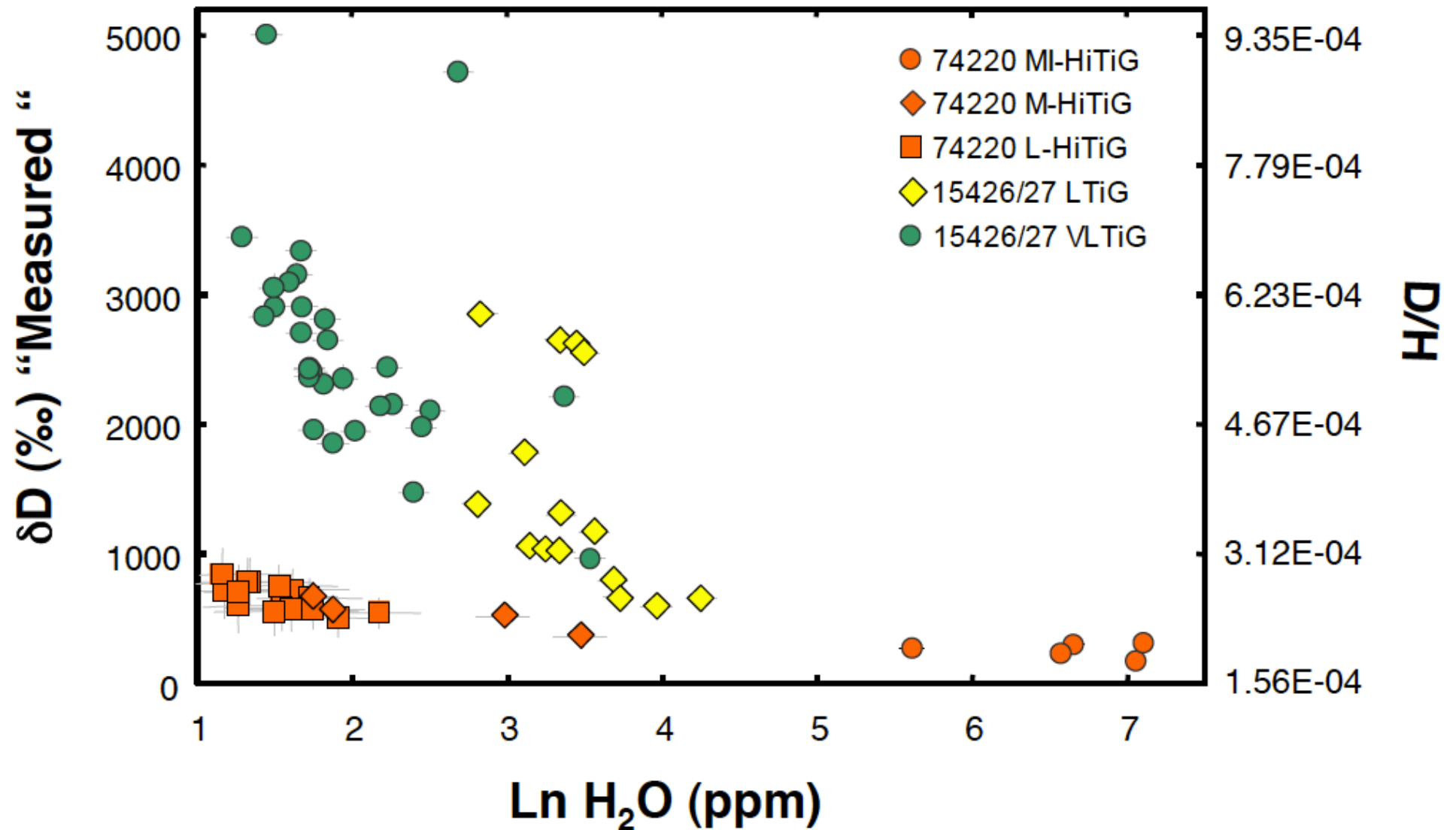
When did the water come to the Moon ?

D/H ratios as a fingerprint for the origin of the lunar water



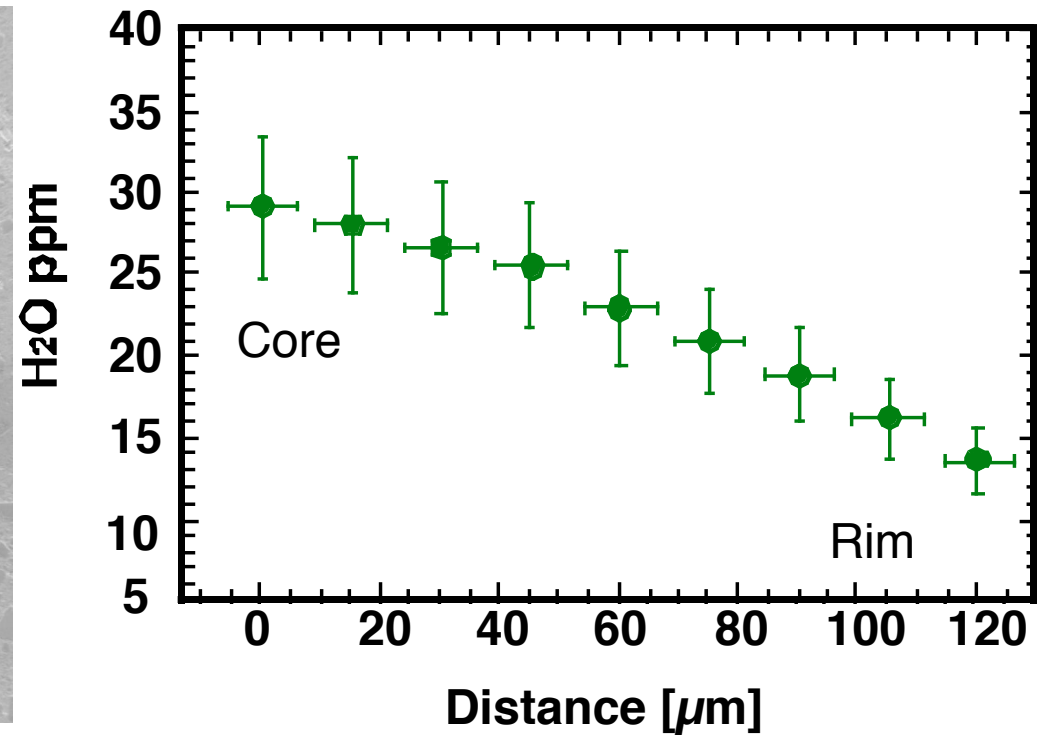
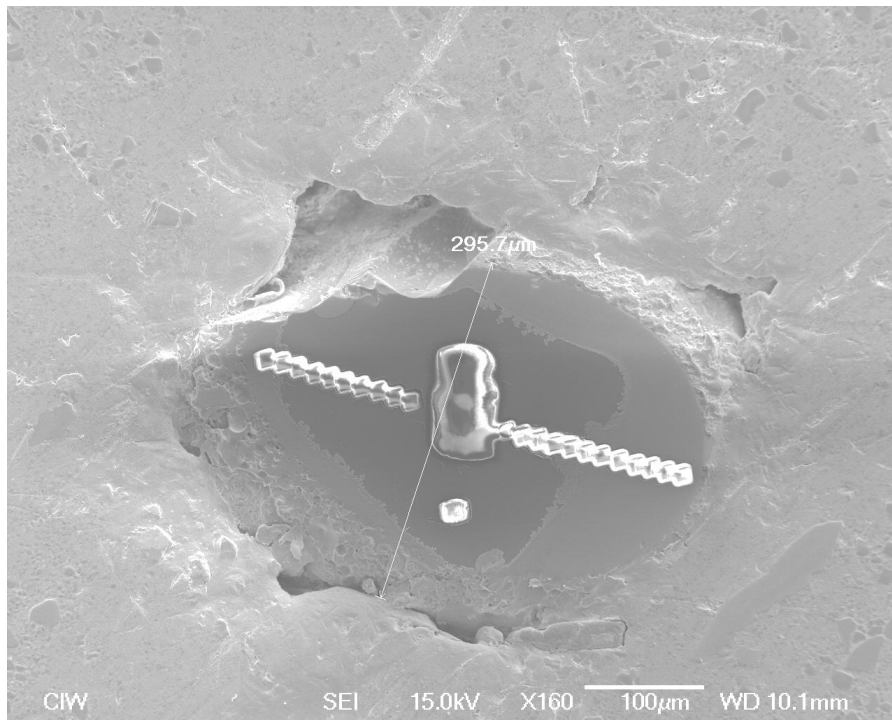
$$\delta D = [(D/H_{sam} / D/H_{SMOW} - 1) * 1000]$$

δD measured versus H_2O content in the lunar glasses



We have to consider degassing processes

Equilibrium or Rayleigh Fractionation cannot be applied to the lunar volcanic glasses



Diffusive Degassing:

The mass dependence of diffusion of hydrogen isotopes can be represented as:

$$\frac{D_H}{D_D} = \left(\frac{m_D}{m_H} \right)^{\beta_{H/D}} \quad \text{where } \beta \text{ is an empirical exponent that likely depends on hydrogen speciation}$$

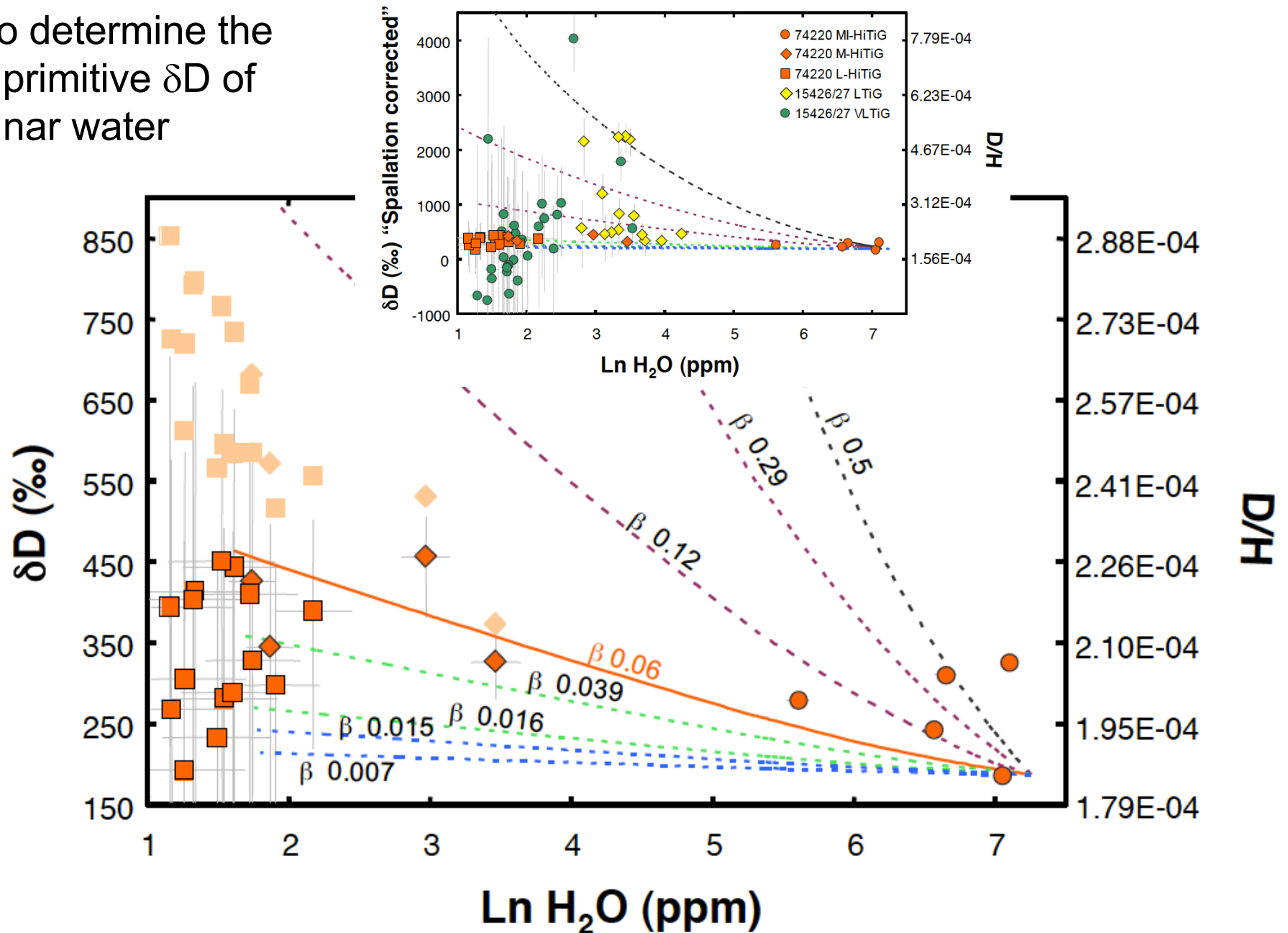
Approximate solution of the 1D spherical diffusion equation

$$\begin{aligned} 0.85 \leq f \leq 1 \quad f &\simeq 1 - (6/\pi^2) \exp(-\pi^2 Dt/a^2) \\ 0 \leq f \leq 0.85 \quad f &\simeq (6/\pi^{3/2})(\pi^2 Dt/a^2)^{1/2} - (3/\pi^2)(\pi^2 Dt/a^2) \end{aligned}$$

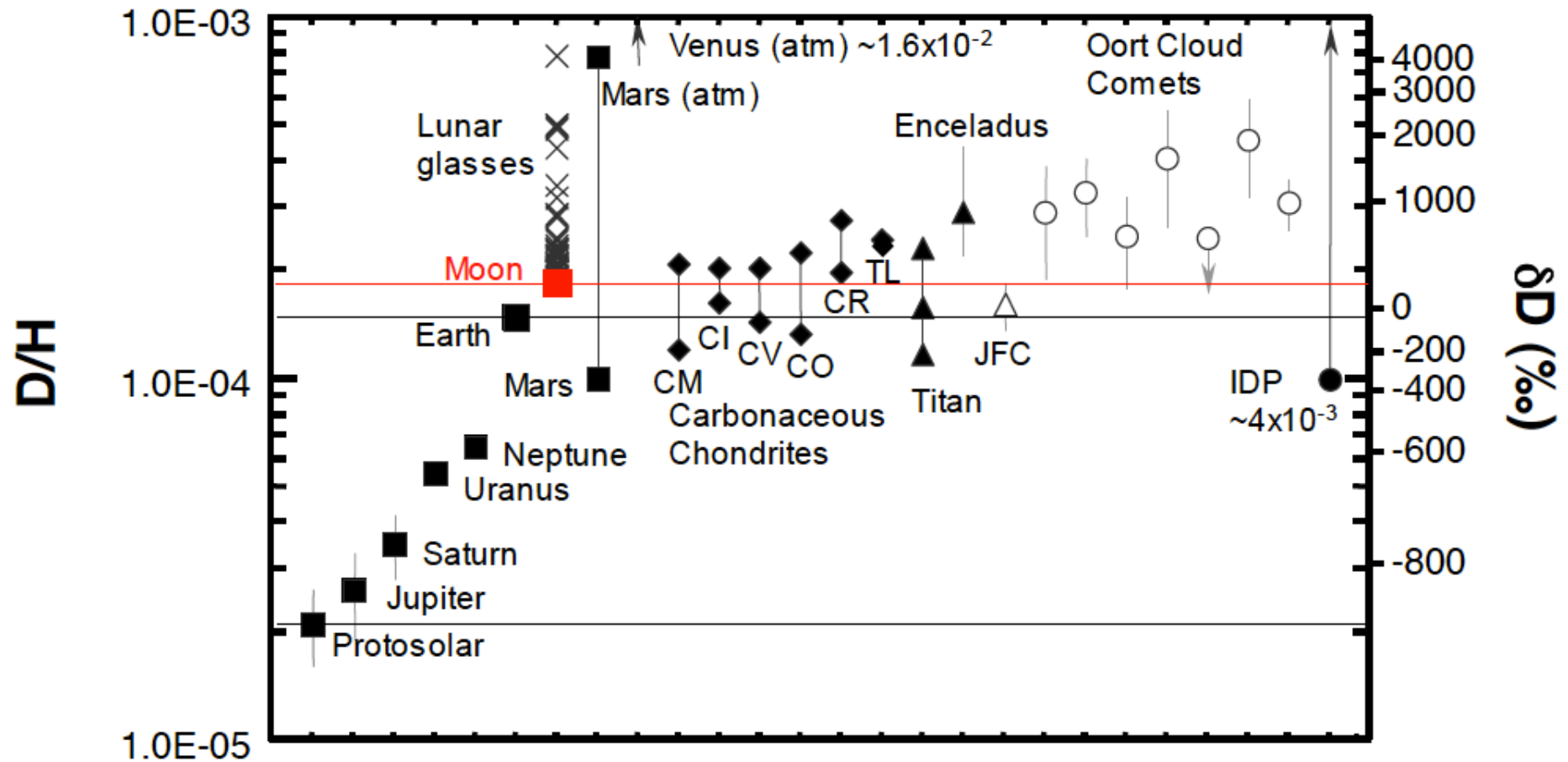
Where “f” is the fraction of H or D lost

McDougall and Harrison (1988)

A17 Melt Inclusions:
Key to determine the
most primitive δD of
the lunar water



The D/H ratios of the lunar melt inclusions indicate that the water in Earth and Moon came from carbonaceous chondrites rather than comets



Halliday (2013), Marty (2012)

Nitrogen isotope confirms the carbonaceous chondrite origin of the volatiles

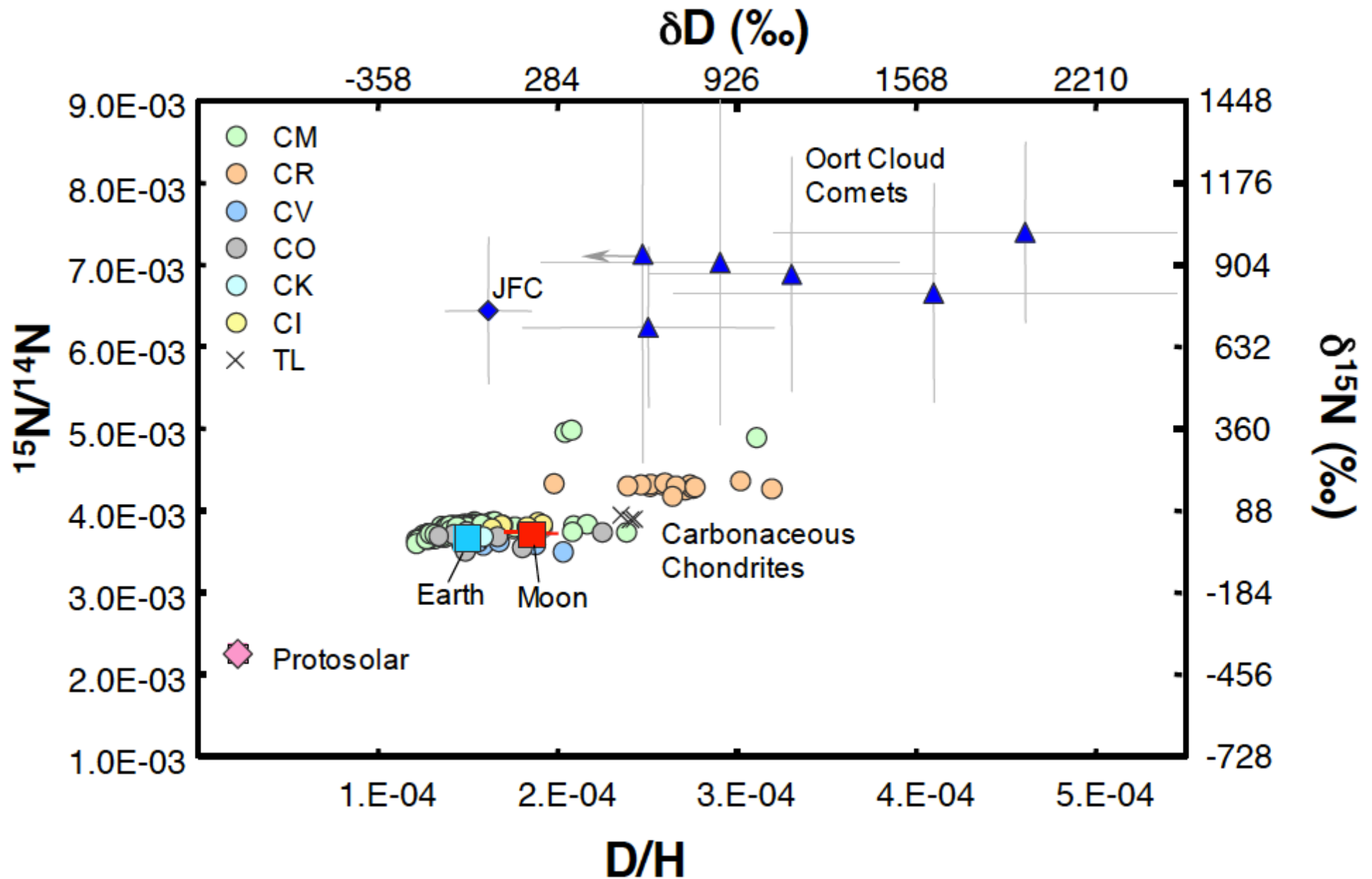


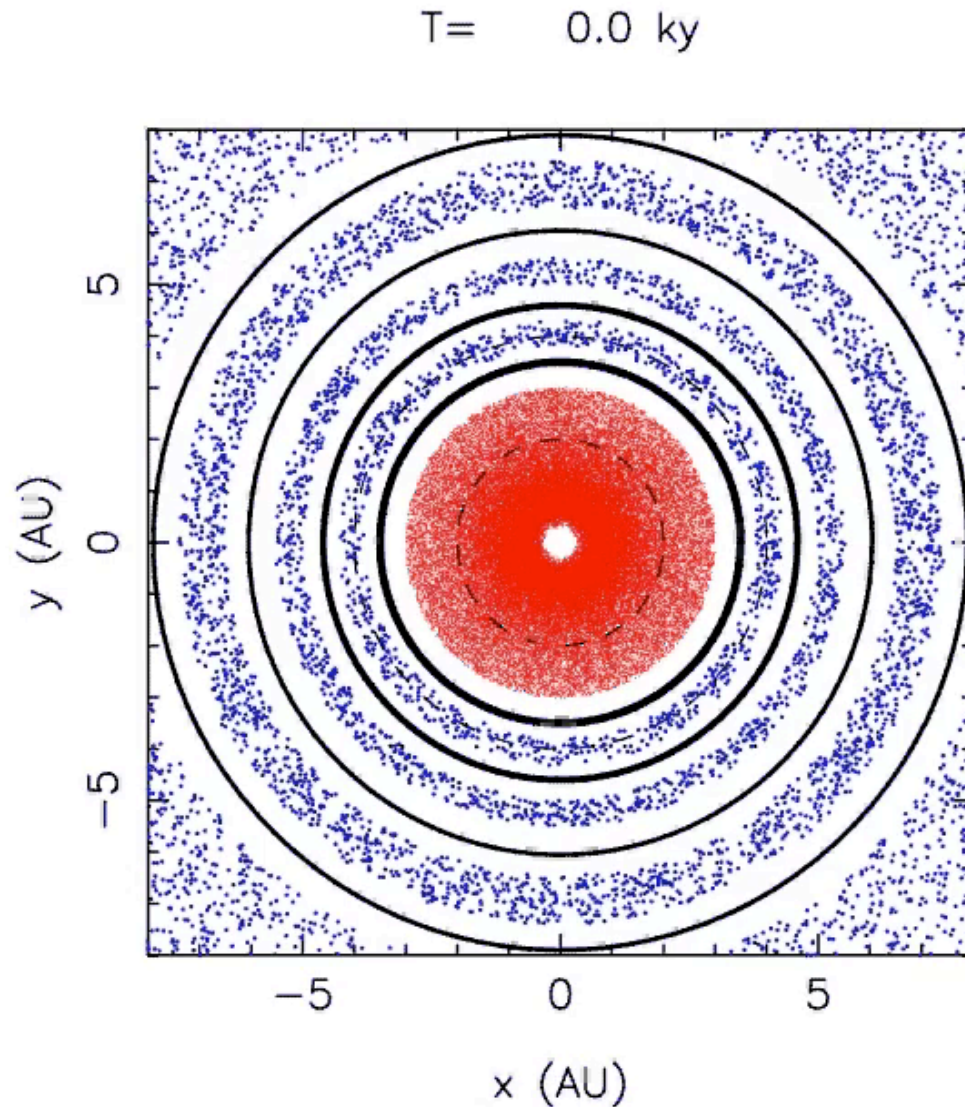
Figure modified from Marty (2012), Marty et al. (2002), Alexander et al.,(2012)

How the volatiles reached the Moon?

The presence of volatiles in lunar volcanic glasses and their δD , $\delta^{15}N$ suggest that either

- 1) The volatile were added ~ 50 - 100 Ma after the formation of the Moon during the final stages of accretion: “late veneer of carbonaceous chondrites”.
- 2) The Earth formed with volatiles and the Giant Impact event did not evaporate all the volatiles away.

The effect of Jupiter migration and Jupiter-Saturn orbital resonance

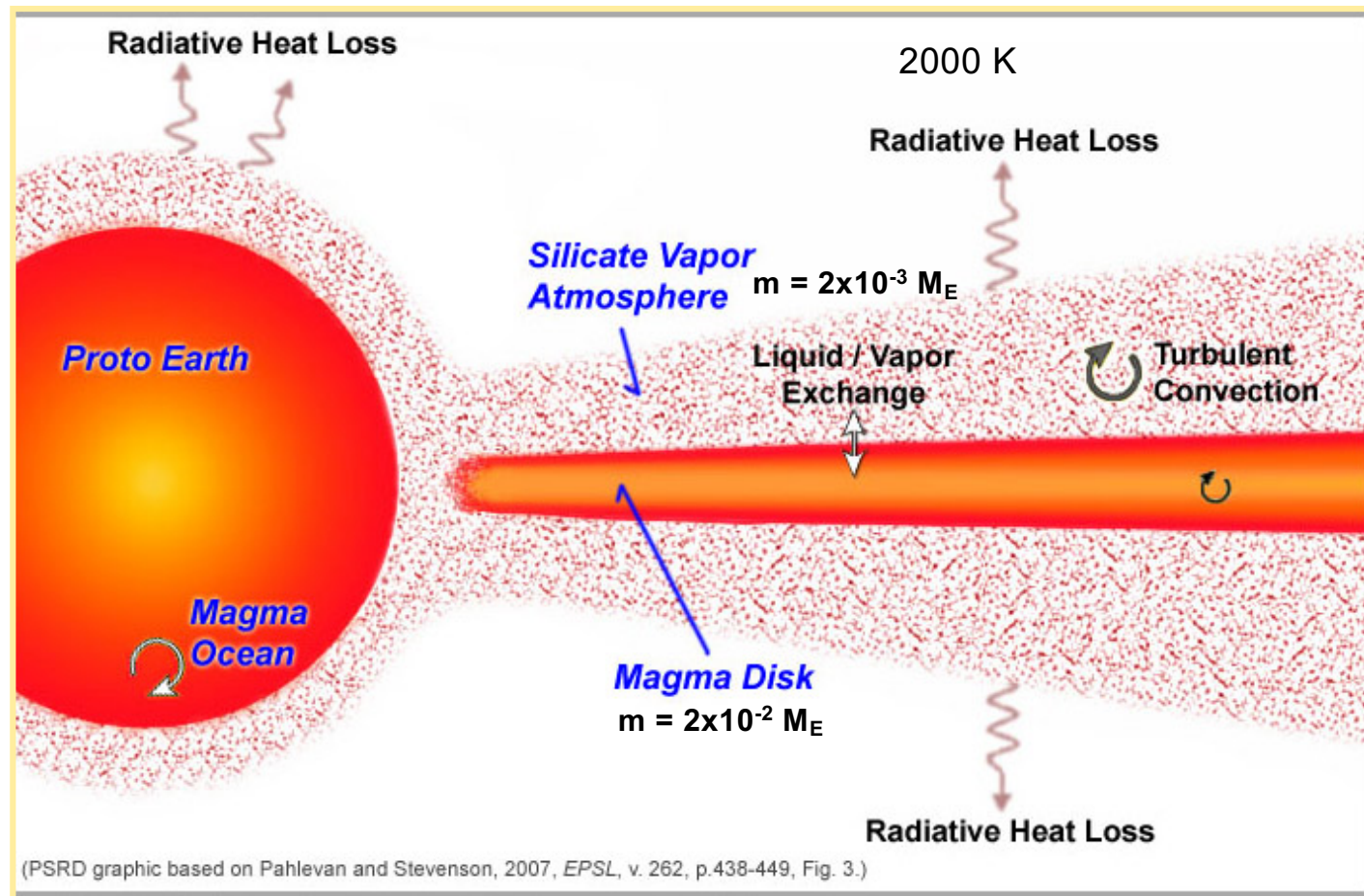


Hydrodynamic simulations provide an explanation for the origin of volatile elements in the Terrestrial Planets

Walsh et al., 2011

How did part of the Hydrogen survive the Giant Impact?

Pahlevan and Stevenson (2007) proposed diffusive equilibration of the silicate vapor atmosphere between the proto-Earth and proto-lunar disk after the giant impact.



Conclusions

1.- We estimated that amount of H, C, F, S and Cl in the lunar volcanic glasses was equivalent to that of MORB.

2.- Volatile/refractory element ratios in the glasses and melt inclusions suggest that the Moon's volatile budget is < 10 times (rather than 1000 times) more depleted than Earth. The reason for the discrepancy is that previous work did not consider magmatic degassing

3.- We showed that the lunar volatiles, as Earth's volatiles, originated from carbonaceous chondrites. The simplest explanation is that Earth had volatiles from its birth (consistent with dynamic models), and either during the giant impact that formed the Moon they were not completely lost or more volatiles were added during the late veneer.