LIGHT HYDROGEN IN THE LUNAR INTERIOR: NO ONE EXPECTS THE THEIA CONTRIBUTION!

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Introduction. The Moon is thought to have formed after a planetary embryo, known as Theia, collided with the proto-Earth over 4.5 billion years ago. The size and composition of Theia have a profound effect on the composition of Earth and the Moon, and therefore are important to constrain. In the canonical model [1-3], Theia was Mars-sized (0.1 Earth masses, M_E). Other successful lunar formation models include Theia with mass ~ 0.3 M_E [4] or even as large as 0.4 – 0.45 M_E [5]. Compositionally, it is important to constrain whether Theia resembled Earth and enstatite chondrite material, or contained significant carbonaceous chondrite material. An isotopic dichotomy in the solar nebula has been recently recognized, showing that carbonaceous chondrite material originated beyond Jupiter [6]. Constraining Theia's composition constrains its place of origin and the circumstances of its collision with proto-Earth.

For the first time, we use H isotopes to help constrain the composition of Theia. We conclude the Moon incorporated very low-D/H (δD ≈ -750‰) hydrogen derived from solar nebula H_2 ingassed into the magma ocean of a large (~0.4 M_E), enstatite chondrite-like Theia that was largely devoid of chondritic water. These new constraints have profound implications for the Moon-forming impact and the evolution of the Earth-Moon system.

Hydrogen from the Lunar Interior: Apatite [$Ca_5(PO_4)_3(OH,F,Cl)$] is the only water-bearing mineral found in lunar samples. Hydrogen isotopic measurements of apatite in lunar rocks show that there seem to be multiple H reservoirs within the lunar interior [7]. Intriguingly, apatite in the KREEP-rich Apollo 15 quartz monzodiorites (QMDs) exhibit δD as low as -750‰ (**Figure 1**), which is almost as low in D as protosolar H or solar wind. Their unique formation environment deep in the lunar crust makes it unlikely they incorporated solar wind, and instead they seem to sample H indigenous to the lunar interior [7]. We propose [8] a new hypothesis for Theia's composition to explain this ultralow D reservoir (**Figure 2**).

Ingassed Solar Nebula Hydrogen: How is D depleted nebular H incorporated into planetary interiors? Wu et al. [9] proposed that Earth's mantle contains solar nebula hydrogen and ^{3}He and ^{22}Ne, ingassed into the magma ocean of its largest embryo due to a ~1 bar H_2 atmosphere in contact with solar nebula gas. This requires a large embryo, > 0.3 – 0.4 M_E [10], to have existed during the first few Myr of the solar nebula. Wu et al. [9] argued that ~0.14 oceans (1 ocean = 1.5 × 10^{21} kg) solar nebula hydrogen with D/H = 21 × 10^{-6}, combined with ~8 oceans of chondritic water with D/H = 140 × 10^{-6}, leading to some materials with D/H = 120 × 10^{-6} (δD ≈ -230‰) that should reside at the Earth's core-mantle boundary. The discovery of materials with δD ≈ -218‰ in terrestrial lavas sampling deep-mantle plumes [11] may support this hypothesis.

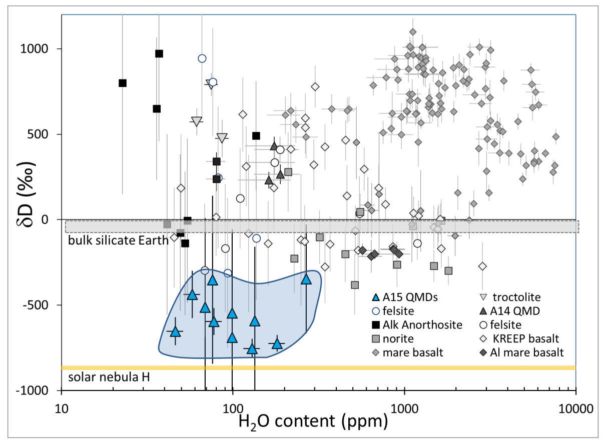

Figure 1: D/H ratios in lunar samples (data from [7], references therein). The Apollo 15 QMDs are outlined in blue and extend to very low D/H (δD≈-750‰), with diverse D/H ratios within the lunar interior, e.g. [7].

Nebular H in the Moon? The Moon formed too late to ingas nebular H directly into its magma ocean. It also could not have inherited its lowest δD material from Earth [9]. This leaves ingassing into the magma ocean of Theia (the impactor) as the only plausible source of D-depleted nebular hydrogen. Ingassing into Theia's mantle could yield materials with δD ≈ -750‰, but requires it to be large enough to attract a significant atmosphere (> 0.3–0.4 M_E) [10], and to contain little (< 200 ppm) chondritic water, as to not dilute the nebular signature. Such a massive Theia is consistent with both the merger model [5] and some iterations of the hit-and-run model [4]. Enstatite chondrites (ECs) are extremely dry, with oxygen fugacity 5 log units below the iron-wüstite buffer (ΔIW = -5), and are consistent with this dry composition [11, references therein].

We model proto-Earth's mantle with ~1800 ppm H_2O and bulk δD ≈ +25‰, before core formation, and Theia's mantle with ~180 ppm H_2O and bulk δD ≈

-610‰, before core formation, and ~100 ppm H_2O after core formation (**Figure 2**).

Enstatite Chondrite Theia: The similarity in multiple stable isotopes (ε^{48}Ca, ε^{64}Ni, ε^{92}Mo, Δ^{17}O, ε^{50}Ti, ε^{54}Cr, ε^{96}Zr, ε^{182}W; [12, references therein]) between the Earth and Moon is a long-standing mystery. If Theia is made of EC material, and the mixing parameter $|f_{PM}/f_{PE} - 1| \leq 40\%$ (f_{PM}=fraction of Moon that is proto-Earth, f_{PE}= fraction of Earth that is proto-Earth), work by Meier et al. [12] demonstrates that all these similarities are explained.

Despite this evidence for a Theia with EC composition, as pointed out by Meier et al. [12], ECs are FeO-poor, and yet the Earth's mantle has 7.8wt.% FeO and the Moon's mantle is 10.6wt.% FeO [13]. It is likely that the Moon incorporated proportionally more material from Theia than Earth, implying Theia was FeO-rich. This appears inconsistent with a reduced composition, but [12] show that sequestration of Si in Theia's core could oxidize Theia's mantle by reactions similar to 3 Fe + $SiO_2 \rightarrow$ FeSi + 2 FeO [14] a process only efficient in a reduced body.

Using the formulism of Meier et al.[12], we show [8] that sequestration of 12% of Theia's Si in its core (consistent with equilibration at < 20 GPa, 1800 K and ΔIW = -5) would lead to its mantle being 15 wt.% FeO, and would increase δ^{30}Si by 0.27‰. Equilibration in proto-Earth (~25 GPa, 2800 K, ΔIW = -2) would sequester only 3% of its Si, leading to its mantle being < 5 wt.% FeO, and increasing δ^{30}Si by 0.03‰. For reasonable starting compositions, both proto-Earth and Theia (and therefore Earth and Moon) could have δ^{30}Si ≈ -0.28‰ after core formation. In a collision with f_{PM} = 36%, f_{PE} = 60%, $|f_{PM}/f_{PE} - 1|$ = 40%, consistent with either merger [5] or possibly hit-and-run[4] impacts, Earth and Moon's mantles achieve their observed FeO, and Earth's core (the two merged cores) is 3.1wt.% Si.

Conclusions: A massive (~0.3 – 0.4 M_E), EC-like Theia is consistent with many stable isotope similarities between the Earth and Moon [12], including, we show, D/H ratios. For reasonable initial conditions [8], our model is also consistent with the mantle FeO content and δ^{30}Si values for the Earth and Moon, and Earth's core Si mass fraction, provided Si is sequestered in proto-Earth's and especially Theia's core, consistent with Theia's large and reduced nature. Because it apparently accreted no carbonaceous chondrite material, Theia likely originated interior to Earth's orbit.

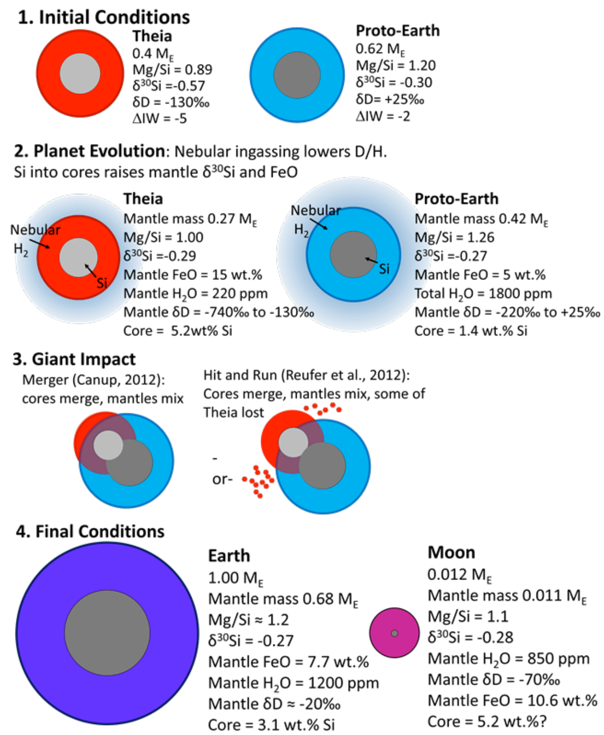

Figure 2: Our hypothesized sequence of events leading to the Moon's formation, starting with a massive and chemically reduced Theia impacting a proto-Earth that already had accreted carbonaceous chondrite material.

References: [1] Cameron A.G.W. and Ward W.R., (1976) *7th LPSC* , 120-122. [2] Cameron A.G.W. and Benz W.,(1991), *Icarus 92*, 204-216. [3] Canup R.M. and Asphaug E. (2001) *Nature 412*, 708-712. [4] Reufer A. et al. (2012) *Icarus 221*, 296-299. [5] Canup R.M. (2012) *Science 338*, 1052-1055. [6] Kruijer T.S. et al. (2017) *PNAS 114*, 6712-6716. [7] Robinson K.L. et al. (2016) *GCA 188*, 244-260. [8] Desch S.J. and Robinson K.L. (2019) *Chemie der Erde 79*, 125546. [9] Wu J. et al. (2018) *JGR 123*, 2691-2712. [10] Stökl A, et al. (2015) *A&A 576*, A87. [11] Hallis L.J. et al. (2015) *Science 350*, 795-797. [12] Meier M.M.M. et al. (2014) *Icarus 242*, 316-328. [13] Warren P.H. and Dauphas N. (2014) *45th LPSC* abs.#2298. [14] Javoy M.(1995) *GRL 22*, 2219–2222.