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Review article

Constraints on early Earth's water budget from the evolution of the lunar hydrogen cycle

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A B S T R A C T

During the Hadean, Earth recovered from the Moon-forming giant impact, became covered with liquid water oceans, and witnessed the onset of plate tectonics and life. Quantifying the abundances, distribution, and chemical states of water in the atmosphere, on the surface, and in the interior of the early Earth is essential to constrain the early evolution of System Earth. Assessing these parameters is hampered by the general dearth of early Earth samples, the difficulty of distinguishing primary signatures from later alteration processes in such samples, leading to large uncertainties on the influx and outflux of water to and from the early Earth. Given the close proximity of Earth and Moon, constraints on the early hydrogen cycle in the Moon may reflect coeval aspects of the water cycle on early Earth. Here, we assess constraints on the lunar water cycle from the time the Moon formed until the end of late accretion at ~3.8 Ga, and implications of these constraints for the early Earth water budget. Dynamic accretion models suggest the Moon initially contained ~455 ppm of water. Recent experimental studies of lunar magma ocean crystallization suggest similarly substantial initial lunar water contents. Hydrogen concentration measurements in lunar plagioclase crystals derived from the magma ocean illustrate that the Moon experienced significant degassing during the solidification of the lunar magma ocean (thought to have occurred between 4.5 and ~ 4.3 Ga). Hydrogen and chlorine systematics in lunar magmatic apatite grains formed between ~4.1 Ga and ~ 3 Ga indicate that lunar hydrogen reservoirs were replenished by volatile delivery during late accretion (~4.1–3.8 Ga), after which the water abundance of the Moon stabilized. Using this knowledge of the lunar water cycle to model Earth's early water budget leads to two scenarios that are consistent with the observed present-day terrestrial water content of 1000–3000 ppm: (1) Earth contained significantly more water than the Moon-forming material immediately after the giant impact, suggesting hydrogen heterogeneity in the initial Earth-Moon system; (2) Earth did not experience significant degassing in the aftermath of the giant impact, and the late accretion mass added to Earth was large and water-rich

1. Introduction

Liquid water plays an important role in the origin of life on the Earth. Key aspects of the early evolution of Earth's water cycle, including its origin, timing of its accretion, and abundances in the main reservoirs on and in the Earth, are remain an unsolved mystery (e.g., Marty and Yokochi, 2006; O'Brien et al., 2018; Wu et al., 2018), mainly due to the limited availability of atmosphere, water, and rock samples from the early Earth (>4 billion years (Ga) ago). Here, we argue that the Moon, which has accompanied our planet as a satellite since ~4.5 Ga (e.g., Barboni et al., 2017), can provide some unique clues about Earth's early water evolution.

Classically, the Moon was thought to be completely dry from its origin, due to the extreme temperatures that would result from the giant impact that is thought to have led to its formation (e.g., Canup, 2012; Ćuk and Stewart, 2012). Over the past decade, the unambiguous identification of hydrogen and other volatile elements on the lunar surface, in lunar minerals (apatite and plagioclase), melt inclusions within lunar minerals, and in lunar volcanic glass beads, has led to a rapidly increasing number of sample-based (e.g., Tartèse and Anand, 2013; Boyce et al., 2010, 2015; McCubbin et al., 2010; Sharp et al., 2010; Greenwood et al., 2011; Barnes et al., 2016; Robinson and Taylor, 2014; Hui et al., 2013, 2017; Wang et al., 2019; see review in Lin and van Westrenen, 2019), experimental (e.g., McCubbin et al., 2015; Lin et al., 2017a; Lin et al., 2019; Lin et al., 2020), modeling (e.g., Sharp et al., 2013; Pahlevan et al., 2016; Nakajima and Hauri, 2017), and remote sensing efforts (e.g., Klima et al., 2013; Li and Milliken, 2017; Li et al., 2018; Flahaut et al., 2020) to constrain the temporal evolution of the lunar hydrogen budget. The aim of this paper is to provide a brief review of current knowledge about the early lunar water cycle (lunar interior water evolution) and illustrate how models of this cycle can be used to test and improve constraints on the history of water during the

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early evolution of our own planet.

2. The lunar water cycle

A summary of current knowledge of the evolution of the lunar water cycle through time is provided in Fig. 1. The Moon is thought to have formed around 4.51 Ga ago (e.g., Barboni et al., 2017) in a giant impact between a Mercury- to Earth-sized object and an early-formed proto-Earth (Ćuk and Stewart, 2012; Canup, 2012). This impact led to a hot (>4000 K; Nakajima and Stevenson, 2014) and partially vaporized Moon-forming disk. These temperatures did not lead to complete water loss from the Moon-forming material. Water vapor present in the hot Moon-forming disk orbiting the Earth may not have hydrodynamically escaped, with the escape suppressed by heavy elements dominating the disk vapor composition (Nakajima and Stevenson, 2018). Nakajima and Hauri (2017) modeled the evolution of a Moon-forming silicate-vapor disk and propose an average value of ~465 ppm as the initial water abundance in the Bulk Silicate Moon (BSM). This is equivalent to ~455 ppm water in the Moon as a whole, as pressures in the small lunar core (~2 wt% of the lunar mass; Hood et al., 1999; Weber et al., 2011), estimated to be <5.5 GPa, were too low for any hydrogen to be incorporated.

This core formed through the first major differentiation event in lunar evolution (metal-silicate segregation). Our knowledge of the size, physical state, and chemical composition of the lunar core has grown substantially over the past decade (e.g., Hood et al., 1999; Weber et al., 2011; Garcia et al., 2011; Antonangeli et al., 2015; Rai and van Westrenen, 2014; Steenstra et al., 2016, 2017a, 2017b; Righter, 2019). To date, it has not been possible to derive information about the evolution of the water content of the Moon during core formation. This is mainly due to the absence of appropriate models for metal-silicate partitioning of trace elements as a function of silicate hydrogen content. Pioneering initial work in this area (Righter and Drake, 1999) suggests there is no significant effect of water on metal-silicate partitioning, but the database of water-bearing metal-silicate partitioning experiments remains very limited. If water were to leave a measurable imprint on the geochemistry of the silicate Moon during core formation, this would provide additional information on the overall lunar water budget in the first several millions of years after Moon formation.

The next lunar evolution stage for which constraints on water availability have been developed recently is primitive crust formation. A combination of experiments and measurements of the water content of plagioclase crystals from the primitive crust provides estimates of the evolution of the lunar water cycle during this period (Lin et al., 2017a; Hui et al., 2013, 2017; Lin et al., 2019; Lin et al., 2020). Although the precise timing and duration of lunar crust formation are debated (e.g., Borg et al., 2011, 2019; Elkins Tanton et al., 2011; Nemchin et al., 2009; Barboni et al., 2017), current thinking is that this episode may have lasted anywhere from 100 to 200 million years (~4.5 Ga to ~4.4–4.3 Ga). During this period, a global silicate magma ocean, referred to as the lunar magma ocean (LMO) (e.g., Smith et al., 1970; Wood et al., 1970; Warren, 1985), with an estimated initial depth ranging from 400 km based on Snyder et al. (1992), to 1350 km (equivalent to whole Moon melting; e.g., Rai and van Westrenen, 2014; Steenstra et al., 2016), started crystalizing. Eventually, plagioclase crystals started forming and floated to the surface of the Moon due to their low density, forming the highland crust.

The initial abundance of water in the LMO has been estimated by comparing the average thickness of the highland crust of the Moon consistent with observations from the GRAIL gravity field mission to the Moon (34–43 km, Wieczorek et al., 2013), with thicknesses derived from experimental LMO solidification studies under dry and wet conditions (Lin et al., 2017a, 2020). This comparison suggests that the LMO contained at least 45–354 ppm water when the anorthitic crust started forming, with the lower minimum linked to a shallow (400 km) magma ocean and the higher minimum corresponding to a deep (1000 km) initial magma ocean). This range is close to the independently derived initial water content of the Moon of ~455 ppm derived from numerical modeling of the evolution of the Moon-forming disk (Nakajima and Hauri, 2017) (Fig. 1).

The water contents in lunar anorthosites thought to compose the primary crust were determined by secondary ion mass spectrometry (SIMS) to be about 4 ± 0.5 ppm for Apollo sample 15,415, 5 ± 0.5 ppm for Apollo sample 76,535 (with an age of 4.306 ± 0.010 Ga; Borg et al., 2015), and 5 ± 0.5 ppm for Apollo sample 60,015 (Hui et al., 2017). Using new constraints on the partitioning of water between plagioclase and melt under lunar conditions (Lin et al., 2019), this translates to water levels remaining in the Moon when these samples were formed of only 12.1 ± 1.5, 5.1 ± 0.5, 2.0 ± 0.2 ppm water, respectively. The average Mg# (molar MgO/[MgO + FeO]x100) of anorthosites from the three Apollo samples 15,415 (Hansen et al., 1979; Papike et al., 1997), 76,535 (James and Flohr, 1983) and 60,015 (Dixon and Papike, 1975) are approximately 54, 43 and 37, respectively. Compared with the evolved Mg# of mafic minerals in anorthosite during progressive LMO crystallization (Lin et al., 2017b), the plagioclases from 15,415, 76,535, and 60,015 were estimated to form when the LMO had solidified by

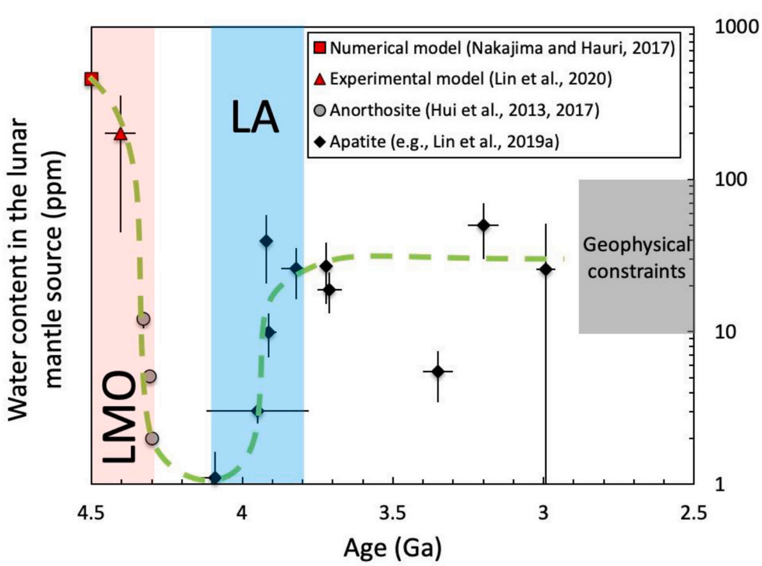

Fig. 1. Variation in calculated water (H_2O) content in the lunar mantle source as a function of age (in billions of years). Gray bar shows water concentration of ~10 to 100 ppm in the lunar mantle by geophysical constraints based on the observed tidal dissipation and electrical conductivity (Karato, 2013). Anorthosite ages are not absolute, except for sample 76,535 (4.306 ± 0.010 Ga, Borg et al., 2015) crystallized at ~95% solid (PCS), but 15,415 and 60,015 were estimated to ~4.33 Ga at ~85 PCS and ~ 4.30 Ga at ~98 PCS, respectively, based on a simplified linear LMO crystallization model discussed in the main text.

~85, ~95 and ~ 98%, respectively (Fig. 2). Although samples 15,415 and 60,015 have not been dated precisely, their ages can be roughly approximated by assuming a linear rate of magma ocean crystallization. Starting at a presumed age of the Moon of 4.51 Ma (Barboni et al., 2017), and anchored by the age of 76,535, these plagioclase crystals would correspond to snapshots of the lunar water cycle at ~4.33, 4.31 and ~ 4.30 Ga. These age estimates are highly uncertain, but the absolute ages are not the key issue here. The main point of Fig. 1 is that the chemical composition of the anorthosites suggests a clear relative age sequence from one sample to the next that can be linked to progressive LMO crystallization. The decreasing lunar water content during this relative age sequence is consistent with significant water loss through degassing from the Moon during LMO crystallization (Fig. 1).

Magmatic activity in the Moon continued far beyond LMO solidification, producing a wide range of basaltic melts and intrusive rocks, including the Mg-suite rocks, high-Ti and low-Ti mare basalts (e.g., Neal and Taylor, 1992; Shearer et al., 2006). During the later stages of their solidification, apatite crystals formed in many of these rocks, once their melt chemistries had evolved from mafic to more evolved compositions (e.g., Potts et al., 2016). Apatite from lunar basalts has played an important role in estimating lunar interior water contents for the post-LMO Moon (e.g., McCubbin et al., 2015; Lin and van Westrenen, 2019. Many studies have reported high-precision volatile abundance measurements of apatite and from both lunar meteorites and Apollo samples (e.g., Tartèse and Anand, 2013; Boyce et al., 2010, 2015; McCubbin et al., 2010; Sharp et al., 2010; Greenwood et al., 2011; Barnes et al., 2016; Robinson and Taylor, 2014; Hui et al., 2013, 2017; Wang et al., 2019). Assuming the apatites in lunar rocks have the same age as the bulk crystallization age of the magmatic rocks they are found in, apatite data cover ages ranging from ~4.1 Ga to ~3.0 Ga. Apatite hydrogen and chlorine abundance and isotope data were recently reviewed in Lin and van Westrenen (2019).

Measured hydrogen contents in lunar apatites can be used to estimate hydrogen contents of the lunar mantle source from which the magmatic rocks containing the apatites were formed at partially melting a mantle source to a melt fraction of 15%, using a model outlined in Lin and van Westrenen (2019). This analysis constrains the water content of the lunar mantle to be 1.1 ± 0.2 ppm at 4.09 ± 0.05 Ga (KREEP sample 72,275), 3.0 ± 0.2 ppm at 3.95 ± 0.17 Ga (Mg-Suite sample 14,305), 39.4 ± 18.7 ppm at 3.92 ± 0.01 Ga (lunar meteorite SaU169), 10.0 ± 1.1 ppm at 3.91 ± 0.03 Ga (KREEP sample 15,386), 26 ± 9.6 ppm at 3.82 ± 0.05 Ga (high-Ti basalt 75,055), 26.8 ± 11.7 ppm at 3.72 ± 0.01 Ga (high-Ti basalt 10,044), 18.8 ± 5.6 ppm at 3.71 ± 0.04 Ga (high-Ti basalt 10,058), 5.5 ± 2.0 ppm at 3.35 ± 0.05 Ga (low-Ti sample 15,555), 49.9 ± 20.0 ppm at 3.2 ± 0.05 Ga (low-Ti basalt 12,039), and 25.6 ± 14.3 ppm at 2.99 ± 0.03 Ga (lunar meteorite NWA773) (Fig. 1).

These calculated mantle source water abundances based on apatite hydrogen contents and apatite hydrogen isotope measurements suggest the abundance of water in the Moon increased significantly at ~4.1–3.8 Ga (Fig. 1, Lin and van Westrenen, 2019), with impacts of water-bearing materials (meteorites and/or comets) as the likely water source. This period is variously referred to as the Late Heavy Bombardment (LHB) period, the final episode or Terminal Cataclysm at the end of the LHB, Late Veneer (mainly cited for Earth) or the final stage of Late Accretion (LA) (e.g., Bottke and Norman, 2017; Cohen et al., 2000; Kring and Cohen, 2002; Morbidelli and Wood, 2015). Here, we refer to this period as LA. Water from impactors was likely added to the source of the apatite-forming magmas in the lunar mantle, requiring crust-breaching impacts (e.g., Barnes et al., 2016).

After LA, from ~3.9 Ga onwards, the lunar interior water abundance in the source region of apatites stabilized at ~25 ± 15 ppm. This is lower than the lunar mantle water concentration of 79 to 409 ppm estimated from melt inclusions in olivine (Hauri et al., 2011), but in excellent agreement with the lunar mantle water concentration of ~10 to 100 ppm yielded by geophysical constraints based on the observed tidal dissipation and electrical conductivity (Karato, 2013) in the present-day Moon (Fig. 1).

3. Implications for the early Earth's water budget

In the Moon, water degassing was an essential feature of early water cycle evolution. From an initial concentration of ~455 ppm water, the Moon degassed so that its water content just prior to Late Accretion was down to only ~1 ppm. Most of this degassing seems to have occurred before ~4.3–4.4 Ga. As discussed in section 2 above, models based on lunar crustal thickness suggest the Moon contained at least 45–354 ppm water during the initial LMO stages (Lin et al., 2017a, 2020), already down slightly from the initial value of ~455 ppm. Plagioclase crystals grown from the LMO towards the end of LMO crystallization (~4.3 Ga) imply that >97% of this water had been lost at this point (Fig. 1).

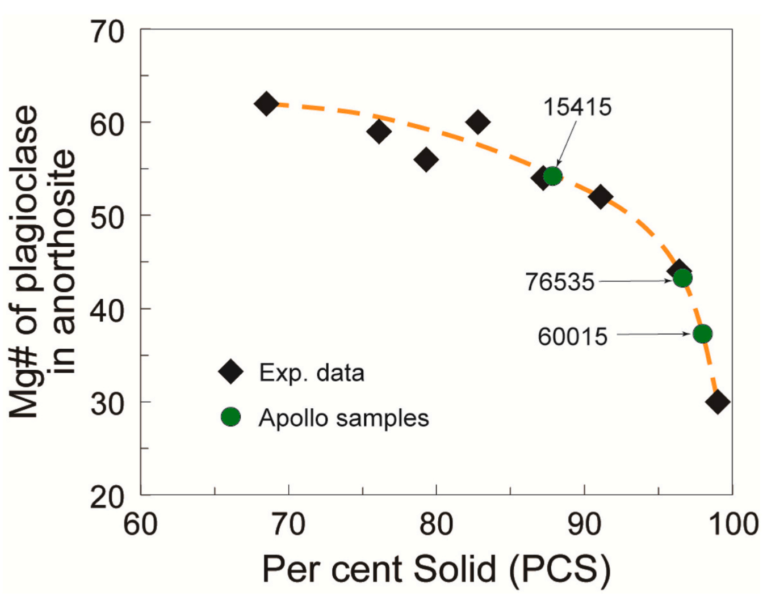

Fig. 2. Evolution of Mg# of plagioclase in anorthosite during progressive LMO solidification. The black diamonds represent experimental data from Lin et al. (2017b); the green circles represent Apollo samples from Dixon and Papike (1975), Hansen et al. (1979), James and Flohr (1983), Papike et al. (1997). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In contrast, the relatively smaller extent of outgassing from ~2 ppm at ~4.3 Ga to ~1 ppm based on apatites formed at ~4.09 Ga (coinciding with the start of Late Accretion) indicates that the thickened highland crust may have played a role in slowing down water loss by degassing. Late Accretion led to a replenishment of hydrogen (as well as other volatiles) in the lunar mantle (requiring crust-breaching impacts) after which values stabilized, not changing significantly over the past ~3 Ga. In the following paragraphs, we assess what the lunar evolution summarized in Fig. 1 can tell us about the early Earth.

It is tempting to assume that the estimated initial water content of the Moon ~455 ppm based on numerical modeling (Fig. 1) provides a best estimate for the water content of the bulk silicate Earth in the aftermath of the giant impact. After all, the bulk silicate Earth and the Moon are geochemically indistinguishable for a range of elements and isotopes, including oxygen, silicon, titanium, and tungsten (summarized by De Meijer et al., 2013). Whether that similarity is due to highly efficient mixing of materials directly after the giant impact (e.g., Pahlevan and Stevenson, 2007), or due to chemical similarity between the Earth and the giant impactor (e.g., Belbruno and Gott III, 2005) does not really matter here.

To estimate the Bulk Earth water content at this time, the possible presence of hydrogen in the Earth's core has to be assessed. At the extreme conditions in Earth's core, hydrogen can be incorporated into iron-rich metal by forming iron hydride ($FeH_{X(\leq 5)}$; Okuchi, 1997; Shibazaki et al., 2009; Mao et al., 2017; Pépin et al., 2017; Wu et al., 2018). If the temperatures in the Earth due to the giant impact led to full-Earth melting, up to 60% of its hydrogen could reside in Earth's core if it equilibrated fully with the mantle, equivalent to a core molar ratio Fe:H $\approx$ 1:0.02, see Wu et al., 2018). If the core was in equilibrium with a mantle containing 455 ppm water, the water concentration in the core could be 683 ppm, with a corresponding Bulk Earth water concentration of 529 ppm. On the other hand, if no hydrogen was present in the core, the Bulk Earth water concentration assuming a 455 ppm water abundance in the mantle would be ~307 ppm. If we assume the experiment-based minimum values of water in the Moon during initial LMO crystallization (45–354 ppm, Lin et al., 2017a, 2020) are more representative of the earliest Moon than the Nakajima and Hauri (2017) value derived from Moon-forming disk models, these values would be even lower.

This range of possible abundances of water in the Earth in the aftermath of the giant impact (~307–529 ppm) is significantly lower than estimates of Earth's present-day water budget in all cases (1000–3000 ppm according to Marty, 2012). Any degassing of the BSE after the giant impact would further increase this discrepancy, whereas late accretion of water to the BSE would decrease this discrepancy. The amount of water added to the BSE during late accretion (LA) can be estimated in two different ways: (1) scaling the addition of water during LA the lunar case (Fig. 1) to Earth; (2) using estimates of the LA mass added to Earth based on the highly siderophile element content of the bulk silicate Earth.

Lin and van Westrenen (2019) show that the addition of ~0.06–0.11 wt% lunar mass equivalent of ordinary chondrite (OC; containing ~1.1 wt% H_2O; Alexander et al., 2012) is required to explain the significant changes in both the abundance and isotopic compositions of hydrogen and chlorine of lunar apatites during the LA. Taking into account the ratio of gravitational cross section between Earth and Moon, this suggests that ~0.01–0.02 wt% Earth's mass equivalent of OC should have accreted to the Earth at the same time. Adding this mass of OC would be equivalent to adding only ~1.6–3 ppm water to the bulk silicate Earth (BSE) over the 4.1–3.8 Ga timeframe, assuming 100% efficient addition of water. Clearly this is insufficient to bridge the gap between an initially Moon-like water concentration in the BSE and present-day bulk Earth estimates.

A significantly larger estimate of ~0.5 wt% Earth's mass delivered to the Earth during Late Accretion has been derived from the observed abundance patterns of highly siderophile elements (HSEs) in the BSE (Walker, 2009; Jacobson et al., 2014; Wang and Becker, 2013). An OC Late Accretion of this size would add ~55 ppm to the Earth, giving bulk Earth abundances in the region ~362–584 ppm, far below present-day values. Adding more water-rich CI chondrites (~14 wt%; Alexander et al., 2012) would lead to a Bulk Earth water content after Late Accretion of ~1007–1229 ppm, just overlapping the lower range of the present-day estimates.

Several caveats apply to this scenario. First, we note that although the relatively high late veneer mass deduced from HSE abundances could overestimate the actual mass accreted, (because of the uncertain effects of inefficient metal-silicate differentiation during core formation on pre-LA mantle abundances (Morbidelli and Wood, 2015), this overestimation can only be minimal for the resulting Bulk Earth water content after late accretion to remain within the bounds of present-day estimates. Second, it is important to note that the substantial HSE-based late accretion to Earth is not consistent with the much smaller late accretion to the Moon, even after accounting for their different cross-sections. This scenario therefore requires stochastic late accretion (e.g., Bottke et al., 2010).

Finally, we also note that this whole analysis assumes no degassing of water from Earth at any time after the giant impact. Any significant degassing from Earth after the giant impact would worsen the disagreement between observed and modeled terrestrial water contents. If we assume, as an end member case, that the extent of degassing from the BSE in a terrestrial magma ocean stage was as large as the extent of degassing from the silicate Moon in the LMO stage (Fig. 1), the concentration of water in the Earth at the start of the late accretion stage (~4.1 Ga) would be as low as ~9–16 ppm. There is no realistic late accretion scenario that could make the Earth return to present-day water concentration values in this scenario.

An alternative route leading to the present-day water inventory of the Earth has to assume that the Bulk Silicate Earth right after the giant impact must have had a significantly higher water abundance than the 455 ppm characterizing the Bulk Moon at this time. To reach current Earth's water budgets, between ~945–2945 ppm water (in the absence of later degassing), and ~ 3.15–9.82 wt% water (including later Moon-like degassing levels) had to have been present in the bulk Earth directly after Moon formation. This scenario indicates that in the direct aftermath of the giant impact, the water abundance of the silicate Earth must have been higher than the water abundance in the Moon-forming disk, suggesting at least some chemical heterogeneity as a function of location in the initial Earth-Moon system.

Such high initial water contents are not unrealistic. Hydrogen isotopic measurements suggest that the main hydrogen reservoir on Earth and the other inner solar system planets could come from carbonaceous chondritic material (e.g., Sarafian et al., 2014). CI chondrites are extremely water-rich (~14 wt% water; Alexander et al., 2012). If the initial inner solar system bodies including Earth contained such large amounts of water, some degassing occurred on Earth and on the giant impactor before the giant impact.

4. Conclusion

The main point of our analysis is reviewing the lunar interior water cycle, we can test and constrain models of the terrestrial early water budget. The initially substantial water content of the Moon decreased significantly by up to >97% between the start of the LMO and the formation of the lunar crust, after which a clear increase in water content occurred during LA. Using this knowledge of the lunar water cycle to model Earth's water cycle leads to two possible scenarios leading to a present-day water content of the Earth of 1000–3000 ppm: (1) The Earth contained significantly more water than the Moon-forming material immediately after the giant impact, suggesting heterogeneity in the initial Earth-Moon system; (2) Earth did not experience any significant degassing in the aftermath of the giant impact and the Late Accretion mass to Earth was large and caused by water-rich impactors.

Declaration of Competing Interest

The authors declare no conflict of interests.

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