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### Supplementary Materials

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# Hydrogen Isotopes in Lunar Volcanic Glasses and Melt Inclusions Reveal a Carbonaceous Chondrite Heritage

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Water is perhaps the most important molecule in the solar system, and determining its origin and distribution in planetary interiors has important implications for understanding the evolution of planetary bodies. Here we report in situ measurements of the isotopic composition of hydrogen dissolved in primitive volcanic glass and olivine-hosted melt inclusions recovered from the Moon by the Apollo 15 and 17 missions. After consideration of cosmic-ray spallation and degassing processes, our results demonstrate that lunar magmatic water has an isotopic composition that is indistinguishable from that of the bulk water in carbonaceous chondrites and similar to that of terrestrial water, implying a common origin for the water contained in the interiors of Earth and the Moon.

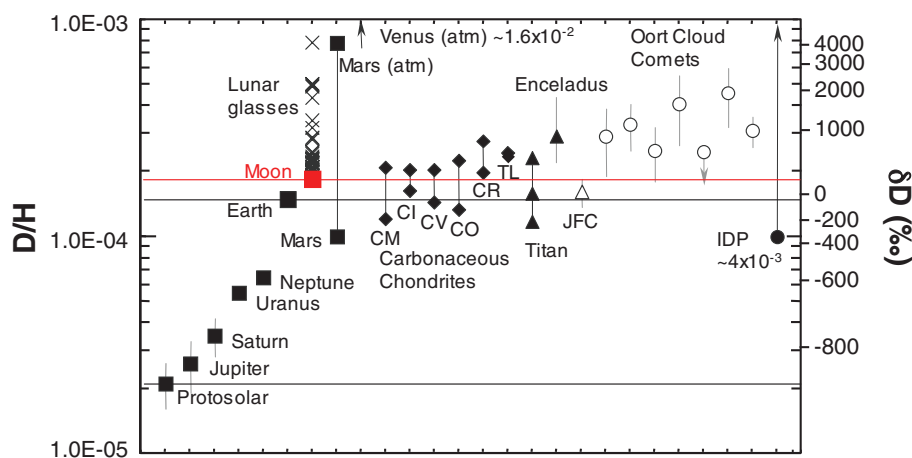
During the solar system's early stages, the solar nebula was cold enough to allow the condensation of water into ice only beyond a distance of ~1 to 5 astronomical units (AU), termed the snowline (where 1 AU is the Earth-Sun distance). Planetesimals accreted beyond this distance grew into water-rich bodies, whereas those accreted closer to the Sun were devoid of water, resulting in relatively H<sub>2</sub>O-depleted terrestrial planets and H<sub>2</sub>O-enriched giant planets (1). Dynamical models suggest that water and other volatiles in the terrestrial planets have been the result of the accretion of volatile-rich asteroids coming from two different source regions at two distinct times: one from inside the Jupiter-formation region and the other between and beyond the giant planets, 5 to 100 million years (My) and >300 to 500 My after the formation of the first solids, respectively (1, 2).

Hydrogen isotopes (deuterium, D; and hydrogen, H) provide unique insight into the origin of water in planetary bodies (3–7). The solar sys-

tem consists of reservoirs containing water with an extremely wide range of D/H ratios (8). The variation in D/H ratios partly reflects the primordial gradient of water and other volatiles through the solar system as a function of distance from the

Sun (Fig. 1). Deuterium depletion is characteristic of the protosolar nebula (7), whereas the water ice from the outer solar system, such as in the Oort cloud comets, is enriched in D/H ratios by a factor of 2 or more over terrestrial water (3–7). The bulk water in carbonaceous chondrite meteorites (3) has a D/H ratio similar to that of Earth's water (9), suggesting that these meteorites might be responsible for bringing water to the terrestrial planets. However, a terrestrial-like D/H ratio has recently been measured on a Jupiter-family comet (JFC), raising the possibility that Earth's water could have originated from cometary material (10). The similar D/H ratios among CI-CM carbonaceous chondrite meteorites, JFCs, and Earth may support the hypothesis of a common source region for the water of these celestial objects (3, 10, 11).

The Moon is thought to have formed in a giant collision between a planet and an early formed proto-Earth (12, 13). Although it has long been considered that this event removed essentially all hydrogen from the Moon (14), recent measurements on lunar volcanic glasses, melt inclusions, lunar apatites [Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,Cl,OH)], and



**Fig. 1. The range of hydrogen isotopic composition in solar system objects.** X symbols are the  $\delta D$  values of individual glass beads and melt inclusions corrected for cosmogenic contributions of H and D (see table S1). The glasses with errors  $\pm 1000\%$  after spallation correction were not considered. The value for the lunar mantle (red square) represents the lowest  $\delta D$  and the highest water content measured in lunar melt inclusions. IDP, interplanetary dust particles; JFC, Jupiter-family comet. See (21) for references.

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plagioclase from ferroan anorthosites have demonstrated that the Moon's interior is not devoid of water (15–20). To the contrary, some of these reports showed that volatile depletion in the lunar lavas is the result of magmatic degassing, and that some of the lunar melts originally contained as much water as terrestrial mid-ocean ridge magmas (15, 19).

Here we present the isotopic composition of hydrogen dissolved in lunar volcanic glasses and in their olivine-hosted melt inclusions to establish the source of the lunar magmatic water. These volcanic glasses, returned by the Apollo 15 and 17 missions, represent some of the best-studied and most primitive magmas generated within the Moon (14, 21). We measured the D/H ratios and H<sub>2</sub>O contents simultaneously in the center of the exposed interiors of individual lunar volcanic glass beads and olivine-hosted melt inclusions using a Cameca NanoSIMS 50L multicollector ion microprobe (21). We examined very-low-Ti and low-Ti glasses from Apollo 15 15426/27 and high-Ti glasses from Apollo 17 74220. The Apollo 17 high-Ti glasses contain olivine-hosted melt inclusions, small samples of magma trapped within the olivine that grew in the magma before eruption. By virtue of their enclosure within their host crystals, melt inclusions are protected from loss of volatiles by degassing during eruption. Thus, melt inclusions have the highest concentrations of water, up to 1200 parts per million (ppm) (19). The matrix glasses surrounding the olivines with melt inclusions contain 6 to 32 ppm H<sub>2</sub>O, and other Apollo 17 high-Ti glasses contain 3 to 9 ppm water. Apollo 15 low-Ti and very-low-Ti glasses range from 16 to 69 ppm and 4 to 34 ppm water, respectively. All of the glass beads and melt inclusions are enriched in deuterium compared with terrestrial ocean water, with  $\delta D$  values ranging from +189 per mil (‰) up to +5023‰ (table S1).

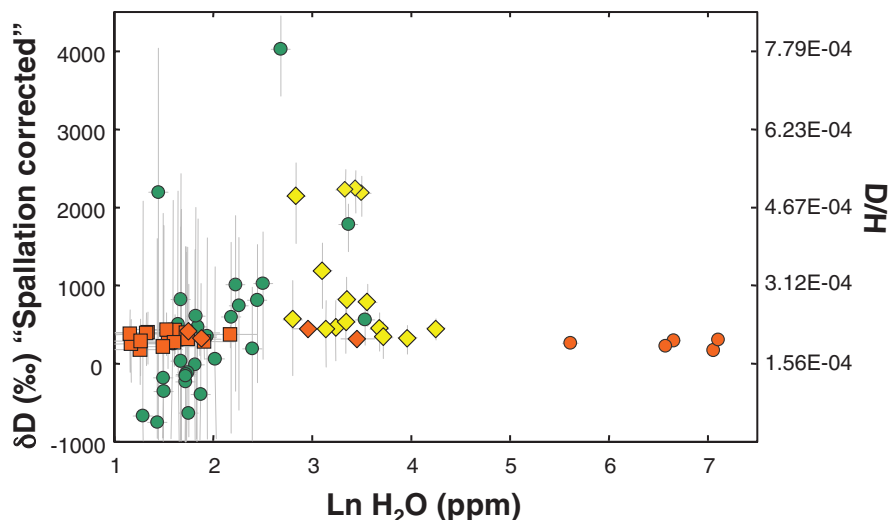
Care must be taken when interpreting variations in the D/H ratios of planetary volcanic rocks in order to distinguish process-related D/H variations from source-related D/H composition. Thus, before the D/H ratio can be used as a source indicator for planetary water, it is important to consider secondary processes that can change this ratio (21). Our data exhibit a negative correlation of D/H ratio with water content (fig. S1), a feature of the entire data set independent of the compositional type of glass measured. This correlation points to a set of processes that have modified the original magmatic water present in these lunar magmas during and/or after their eruption. Solar wind implantation, cosmic-ray spallation, and magmatic degassing can all potentially modify the water content and D/H ratios. Although the effect of solar wind implantation is negligible in the samples studied here (21), cosmic-ray spallation and degassing processes have significantly affected the water and D/H ratios of the lunar glasses. However, as demonstrated in the following sections, these processes are inferred to have had minimal effect on the D/H ratio for the melt inclusions with high water content (21). The

melt inclusions therefore provide the most direct constraints on the isotopic composition of juvenile lunar water.

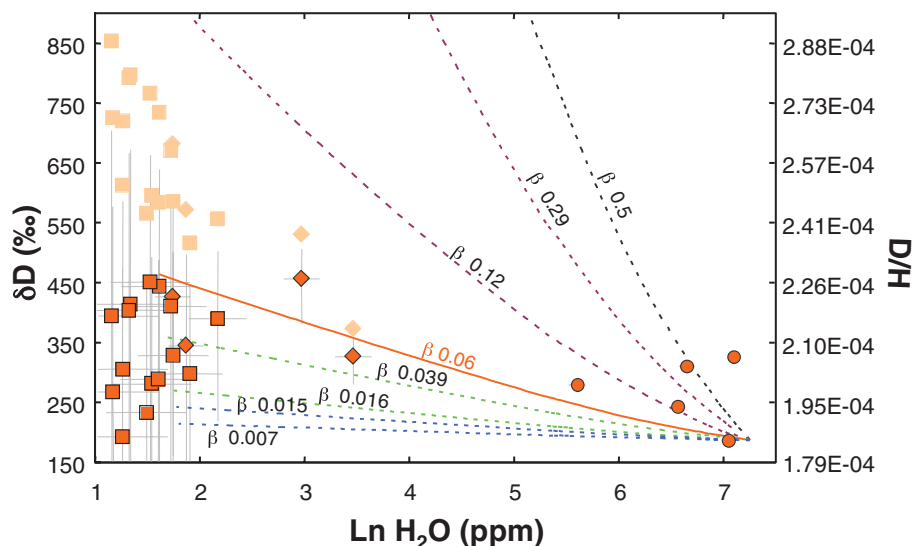
We calculate the cosmogenic contributions of D and H using the known H and D production rates (22, 23) and the average cosmic-ray exposure ages  $284 \pm 51$  My and  $30 \pm 10$  My for Apollo 15 and 17 glasses, respectively (24, 25). Once corrected for cosmogenic production (21), the total variation in D/H ratios among the lunar glasses is greatly reduced (Fig. 2). However, the

data, excluding glasses with water  $\leq 10$  ppm because of their large associated uncertainties, still define a slightly negative correlation of D/H ratio with water content, suggesting that degassing has also affected the isotopic composition (Fig. 3 and fig. S2).

It has been demonstrated that single lunar glass beads have core-rim diffusion profiles for H<sub>2</sub>O and other volatiles, which is evidence for diffusion-limited kinetic degassing in a low-pressure environment after fragmentation of the magma



**Fig. 2. Water contents and hydrogen isotope compositions of lunar volcanic glasses and melt inclusions corrected for spallation processes.** Green circles: very-low-Ti glasses; yellow diamond: low-Ti glasses; orange circles, diamonds, and squares: high-Ti melt inclusions, matrix glass, and glass beads, respectively. The error bars represent propagation of errors in the analyses, exposure ages, and D and H production rates. See fig. S1 for measured values before correction (21).



**Fig. 3. Water contents and hydrogen isotope compositions of high-Ti glasses and melt inclusions.** Errors and symbols as in Fig. 2. Light orange points represent measured data uncorrected for spallation. Curves represent 1D diffusive degassing model; full line encompasses the data with an empirical  $\beta \leq 0.06$ . Colored dashed lines indicate diffusive degassing of H<sub>2</sub>, H<sub>2</sub>O, and OH<sup>-</sup> with their values of  $\beta$ . See fig. S2 for comparison of all the data with degassing model; see also text and (21) for details.

during eruption (15). Therefore, it is important to consider how kinetic degassing might affect the D/H ratios of the magmatic water contained in lunar volcanic glasses. The mass dependence of diffusion of hydrogen isotopes can be represented as

$$\frac{D_H}{D_D} = \left( \frac{m_D}{m_H} \right)^{\beta_{H/D}} \quad (1)$$

where  $D$  is the diffusion coefficient,  $m$  is the atomic mass, and  $\beta$  is an empirical exponent that likely depends on hydrogen speciation (21). Under the reducing conditions relevant to lunar magmas, hydrogen may exist in several different molecular species— $H_2$ ,  $H_2O$ , and  $OH^-$ —in proportions that depend on the total concentration of H, oxygen fugacity ( $f_{O_2}$ ), pressure, and temperature (26, 27). The diffusivities of these species in silicate liquids and glasses are very different, with  $D_{H_2} > D_{H_2O} \gg D_{OH^-}$  (26). The mass dependence of hydrogen isotope diffusion is also expected to be different for each of these species because of their different molecular masses and their different mechanisms of diffusive transport, with  $\beta$  values that could range from as high as 0.5 to as low as  $\sim 0.01$  (21). From comparison of the D/H ratios and water contents of Apollo 17 high-Ti glasses and melt inclusions to the results of a simple one-dimensional (1D) spherical diffusive degassing model (Fig. 3), we obtain an empirical  $\beta$  that depends on the initial and final  $\delta D$  considered, but is constrained to be  $\leq 0.06$ . This  $\beta$  value is intermediate between those estimated for diffusion of  $OH^-$  and  $H_2$  (21), the hydrogen species expected at the conditions of the lunar magmas (27). In the simple model presented here, H diffusivity and  $\beta$  are assumed to be constant during degassing. It is instead likely that  $\beta$  changed with progressive degassing, from initial values of 0.29

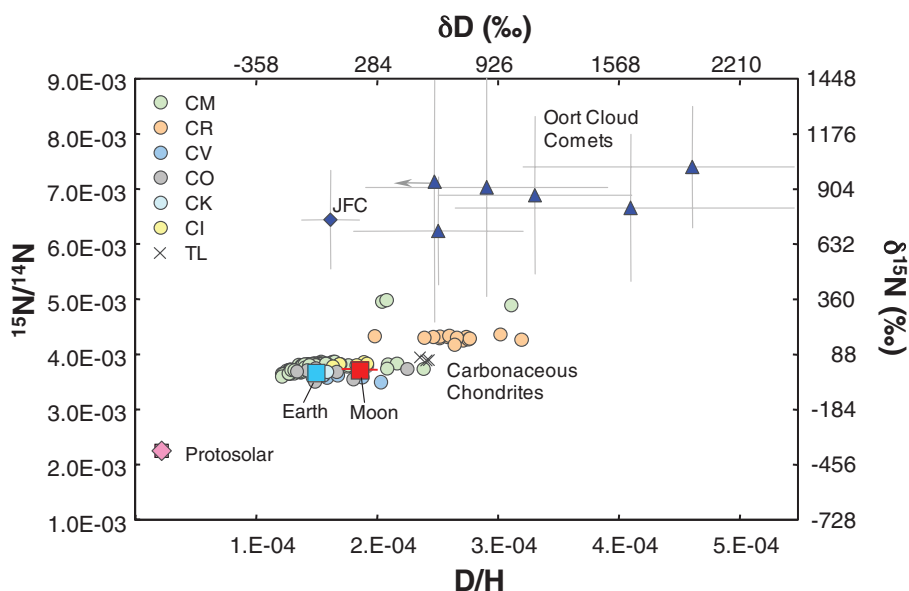
to 0.12, representing  $H_2$  diffusion, to values as low as 0.015 to 0.007 in the later stages of degassing, where diffusion is expected to be predominantly as  $OH^-$  (21). A more complex modeling of the data considering these changes is unwarranted, however, given the large uncertainties in D/H ratios of glasses with water content lower than 10 ppm and the lack of experimental data on the diffusivities of the relevant hydrogen species in melts at variable hydrogen concentration, temperature, and  $f_{O_2}$ .

The primitive major-element compositions, the high water contents, and the minimal effect of spallation and degassing on the D/H ratios of Apollo 17 olivine-hosted melt inclusions indicate that they are ideal samples to determine the primitive  $\delta D$  of the lunar juvenile water. Melt inclusions provide an advantage over erupted lunar glasses because they are commonly trapped at pressures exceeding the pressure of eruption, and they are protected from eruptive degassing by their host crystal (28). However, there is no way of knowing how extensively lunar magmas have degassed before the melt inclusions formed. It is likely that these magmas underwent some degree of degassing before or during the formation of the melt inclusions. The presence of metal blebs trapped in olivine phenocrysts of Apollo 17 high-Ti glasses have been interpreted as evidence for magmatic degassing before olivine crystallization and melt inclusion formation (29). Therefore, it is expected that the original preeruptive  $\delta D$  value of these lunar magmas was lower, and that kinetic D/H fractionation has resulted in preferential loss of H during magmatic degassing before entrapment (28). Hence, our melt inclusion data (1200 ppm  $H_2O$  and  $\delta D +187\%$  for the less degassed inclusion) indicate a lower limit on the water content and an upper limit on the primary  $\delta D$  of these

magmas. This  $\delta D$  value is similar to that measured in apatite (+238%) from a 3.9-billion-year-old alkali anorthosite adcumulate, 14305 (18). If this cumulate crystallized as a closed system, then its  $\delta D$  may be comparable to the primitive D/H ratio of a reservoir in the lunar interior (21), supporting our assertion that the  $\delta D$  of the melt inclusions represent most closely the isotopic composition of the primitive lunar magmatic water.

The  $\delta D$  of lunar juvenile water ( $\sim +187\%$ ) is within the range of carbonaceous chondrites (3), slightly heavier than that estimated for bulk Earth ( $\sim -43\%$ ) (6), significantly lighter (by a factor of  $\sim 2$ ) than those of the Oort cloud comets (5), but similar to the  $\delta D$  measured in the JFCs (10). However, when we combine our D/H results with the previously reported  $^{15}N/^{14}N$  ratios for the Moon (30), the values for the lunar indigenous volatiles are within the range measured for carbonaceous chondrites, but quite distinct from those in comets, greatly limiting the possible cometary contribution to the lunar juvenile water and nitrogen budgets (Fig. 4). The lunar N and H isotopic compositions suggest that the volatile elements in the Moon originated from the same reservoir as the parent bodies of primitive meteorites, contrary to previous interpretation of  $\delta D$  of lunar apatites (18). Our results on lunar volatiles are consistent with a recent evaluation of the origin of Earth's volatile budget (3–5) and suggest a common origin for the water in Earth and Moon.

The similarity of both preeruptive  $H_2O$  content (19) and magmatic D/H ratios (this study) of the lunar glasses to terrestrial magmas supports the notion that the water from Earth and the Moon have a common origin. The Moon must have received its water during or shortly after its accretion, before the formation of a robust lunar lithosphere  $\leq 100$  My after the generation of the satellite. Data for highly siderophile elements (31) suggest that a late veneer of meteoritic material delivered to the Moon was too small to be responsible for the lunar volatile budget (15–20). Moreover, no quantitative model has been presented yet that convincingly explains the volatile and siderophile elements budget and isotopic composition for Earth and Moon by a late veneer (4, 5). Therefore, the simplest scenario consistent with our observations is that Earth was wet at the time of the Moon-forming impact, as predicted by dynamic models (1, 2), and that the water was not completely lost during this event. Furthermore, our results provide evidence that Earth's water budget and isotopic composition at the time of the giant impact were broadly similar to what they are today. The hydrogen isotopic similarity suggests that chemical exchange of even the most volatile elements between the molten Earth and the proto-lunar disc could have been pervasive and extensive, even at the very high temperatures expected after a giant impact. This could have been aided by the presence of a high-temperature convective atmospheric envelope



**Fig. 4.** D/H and  $^{15}N/^{14}N$  ratios of the Moon compared to carbonaceous chondrites, Earth, and comets. The  $\delta D$  value for the lunar mantle (red square) represents the lowest value measured in lunar melt inclusions and the  $\delta^{15}N$  from (30). Figure modified from (5). See (21) for details and references.

surrounding Earth and the proto-lunar disc as the Moon solidified (32). Alternatively, it is conceivable that a portion of the lunar interior escaped the widespread melting and degassing expected in the aftermath of a giant impact and simply inherited water from the proto-Earth. The latter alternative is consistent with the hypothesis that the Moon began with a 200- to 300-km-thick outer shell near melting conditions and a relatively cold interior (33). This hypothesis has received support from recent gravity gradiometry observations by the Gravity Recovery and Interior Laboratory (GRAIL) (34). Any dynamic model proposed for the formation of the Earth-Moon system must meet the constraints imposed by the presence of H<sub>2</sub>O with an isotopic composition similar to that of terrestrial water in the lunar interior.

Our findings also have implications for the origin of water ice in permanently shadowed lunar craters, which has been attributed to solar wind implantation and to cometary and meteoritic impacts (21). It is conceivable that at least part of this water could have originated from magmatic degassing during lunar volcanic eruptions.

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#### Supplementary Materials

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## Clarifying the Dominant Sources and Mechanisms of Cirrus Cloud Formation

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Formation of cirrus clouds depends on the availability of ice nuclei to begin condensation of atmospheric water vapor. Although it is known that only a small fraction of atmospheric aerosols are efficient ice nuclei, the critical ingredients that make those aerosols so effective have not been established. We have determined in situ the composition of the residual particles within cirrus crystals after the ice was sublimated. Our results demonstrate that mineral dust and metallic particles are the dominant source of residual particles, whereas sulfate and organic particles are underrepresented, and elemental carbon and biological materials are essentially absent. Further, composition analysis combined with relative humidity measurements suggests that heterogeneous freezing was the dominant formation mechanism of these clouds.

The effect of clouds on the climate system is more uncertain than the influence of heat-trapping greenhouse gases (1). Clouds can cool by reflection of solar radiation and warm by trapping terrestrial heat with the balance of effects depending on cloud properties such as altitude, thickness, phase, and droplet or crystal size (2). Cirrus clouds are of particular importance because they have extensive global coverage and occur high in the atmosphere, at altitudes of 8 to 17 km (2). Global modeling suggests that human effects on ice clouds may rival the radiative effect of all anthropogenic aerosol particles that do not participate in cloud formation (3).

Due to the temperature at their altitude of formation, cirrus clouds are composed exclusively of ice crystals (2). Ice nucleation does not take place directly from water vapor but instead requires a preexisting particle (4). Ice forms via two pathways, termed homogeneous and heterogeneous freezing. Homogeneous freezing, the spontaneous nucleation of ice within a sufficiently cooled solution, is better understood. A simple theoretical framework for this process has been developed for use in model studies (5). Because the vast majority of atmospheric aerosol particles are aqueous solutions of sulfates and organic molecules (6), homogeneous freezing has been as-

sumed the dominant process (7). However, one drawback to homogeneous freezing is that relative humidity must be strongly supersaturated with respect to ice ( $RH_i = 150$  to  $170\%$ ) (4, 8). In contrast, heterogeneous freezing can start just below  $0^\circ\text{C}$  and at  $RH_i \sim 100\%$  (2, 8). Heterogeneous freezing remains poorly understood, however, because it can take several subpathways, among which are depositional freezing of water vapor onto a particle surface and immersion freezing from within an aqueous coating (4). Many materials have been shown to act as ice nuclei (IN) in laboratory experiments, including mineral dust, metallic particles, some biological materials, low-temperature glasses, and anhydrous salts (4, 9–11). Despite this variety, only a small fraction of atmospheric particles at ground level (as few as  $\sim 1$  in  $10^5$ ) have been shown to act as IN (4, 8).

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