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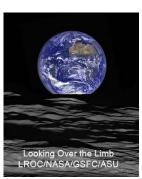
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March 24, 2020

Hydrogen Isotopes in Small Lunar Samples Provide Clues to the Origin of the Earth and Moon



--- Small samples of igneous rocks from the Moon have low deuterium/hydrogen ratios, indicating that some planetary bodies involved in the formation of the Earth and Moon trapped gas from the solar nebula.

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A prominent difference between Earth and the Moon is that one of them has lots of water, making it look like a pale blue dot when viewed from space, and the other is a gray, dusty place. The difference is almost certainly due to how the two bodies formed. Steven Desch (Arizona State University) and Katharine Robinson (Lunar and Planetary Institute, TX) used the abundances of hydrogen isotopes (hydrogen and deuterium) to probe the sources of water in the Moon and Earth. Most of the hydrogen in both bodies has a deuterium/hydrogen ratio of about 150 parts per million (not much deuterium). Most, but not all. Slowly-cooled igneous rocks (called quartz monzodiorites, OMDs for short) from the Apollo 15 landing site on the Moon have D/H of 40 parts per million, much lower than Earth and carbonaceous chondrites (about 140 parts per million). Desch and Robinson suggest that the low D/H in the QMDs indicate that low D/H regions exist inside the Moon, perhaps reflecting batches of lunar raw materials that had acquired hydrogen from the inner solar nebula (the disk of gas and dust surrounding the infant Sun), which had D/H of about 20 parts per million. This acquisition of solar nebula hydrogen could have taken place in planetary bodies large enough (about 40% of the final mass of the Earth) to form an atmosphere of nebula gas, some of which dissolved into the molten body. This scenario has implications for the nature of the giant impact that formed the Moon.

Reference:

- Desch, Steven J. and Robinson, Katharine L. (2019) A Unified Model for Hydrogen in the Earth and Moon: No One Expects the Theia Contribution, Geochemistry, v. 79, doi: 10.1016/j.chemer.2019.125546. [article]
- PSRDpresents: Hydrogen Isotopes in Small Lunar Samples Provide Clues to the Origin of the Earth and Moon -- Short **Slide Summary** (with accompanying notes).

Water Water Everywhere, But Where Did it Come From?

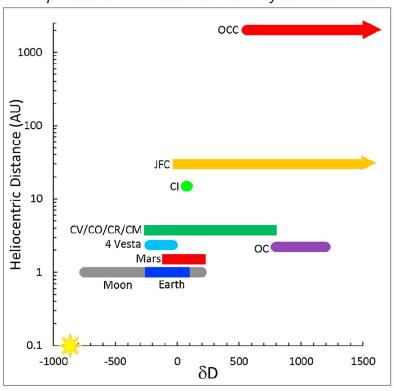
Water in the Earth's oceans absorbs the orange and red of the visible electromagnetic spectrum, reflecting the blue, causing the Earth to be a pale blue dot when viewed from space. The oceans contain 1.4×10^{21} kilograms of water, but far from all the water in the Earth. The interior contains about seven oceans' worth, tied up in rocks in the mantle and in the metallic core. Where did this water come from? Based on the similarity in hydrogen isotopic composition in Earth and carbonaceous chondrite meteorites, a promising idea is that most water was delivered by impacting planetesimals similar to carbonaceous chondrites. (See PSRD CosmoSparks report: Water, Carbonaceous Chondrites, and Earth.) The crucial data are the deuterium/hydrogen ratios (D/H). Deuterium is an isotope of hydrogen. Its nucleus contains a proton and a neutron; hydrogen's nucleus contains only a proton. As a reference, the measured D/H in Earth's standard mean ocean water (SMOW) is 156 x 10⁻⁶ (0.000156, or 156 parts per million). D/H in the water that is bound inside hydrous minerals, averages 140 parts per million. Estimates of D/H in the bulk Earth and

Moon are about 150 parts per million.

Jun Wu and colleagues at Arizona State University have investigated potential sources of Earth's water. (See **PSRD** article: **The Complicated Origin of Earth's Water**).) Through detailed modeling they show that a minor but important component came via "ingassing" from a proto-atmosphere surrounding Earth. This primitive atmosphere would have formed by accretion of **solar nebula** gas, which has a small D/H ratio, about 20 parts per million. It would not take much dissolution of hydrogen from this atmosphere to modify the hydrogen isotopic composition of the originally accreted Earth to account for the overall hydrogen isotopic composition (given by D/H) of the planet. The model also considers dissolution of hydrogen into the metallic core of Earth and its effect on D/H.

The value of the D/H ratio as a tracer of potential water sources is shown in the diagram below. The D/H is expressed by a derived parameter called *delta* D, δ D. This parameter uses the D/H ratio in a planetary sample compared to standard mean ocean water (SMOW): δ D = [(D/H)_{planet}/(D/H)_{SMOW} - 1] x 1000. This results in a useful measure of variations in D/H in parts per thousand and gives geochemists an excuse for using a Greek letter. Note the large range in δ D across the Solar System, giving plenty of possible contributors to the Earth and Moon. However, the Moon is the only body that contains a low δ D component, extending down close to the δ D determined for the solar nebula.

Comparison of D/H Ratios for Solar System Materials



(From Desch and Robinson, 2019, *Geochemistry*, v. 79, doi: 10.1016/j.chemer.2019.125546.)

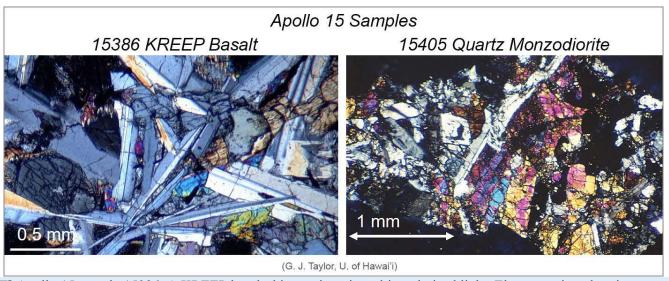
Plot showing the variation in δD in planetary materials throughout our Solar System. In addition to the yellow Sun symbol, **OCC**: Oort cloud comets, which reside in the outer solar system beyond Pluto. **JFC**: Jupiter family comets, which hang out in the vicinity of Jupiter. **CI**: Ivuna class of carbonaceous chondrites, whose chemical compositions are close to that of the Sun. **CV**, **CO**, **CR**, **CM**: Other carbonaceous chondrites. **OC**: Ordinary chondrites. Notice the large variation in δD overall and within some groups. **Asteroid 4 Vesta** (represented by numerous meteorites in the Howardite-Eucrite-Diogenite family), **Earth**, and **Mars** have relatively narrow ranges. The **Moon** is quite variable, with a low end not greatly different from the solar nebula.

Small samples of igneous rocks from the Apollo 15 landing site have exceptionally low D/H ratios, indicating that a distinctive region of the lunar mantle might contain materials from planetary bodies large enough to trap gas from the solar nebula. Desch and Robinson investigate whether ingassing of the solar nebula hydrogen could be involved and explore the consequences for processes operating during the formation of the Moon by a giant impact between two planetary bodies.

KREEPy Igneous Rocks formed in Magma Chambers

In a paper published in 2016, Katharine Robinson and colleagues from the University of Hawai'i and the Open University in the United Kingdom investigated hydrogen concentrations and the D/H ratio in a variety of lunar samples related to **KREEP** basalts from the Apollo 15 landing site. KREEP is an acronym describing the chemical characteristics of some lunar samples, namely their enrichment compared to most samples in potassium (K), rare earth elements (REE), and phosphorous (P). At Apollo 15, the samples consist of **basalts** erupted as lava flows and as slowly-cooled samples that crystallized in magma chambers below the lunar surface. The magma in the chambers was of similar composition as the erupted basalts but produced a variety of different rocks as it slowly crystallized (a process called **fractional crystallization**). The most abundant magma chamber product at Apollo 15 is called "quartz monzodiorite" and is nicknamed QMD.

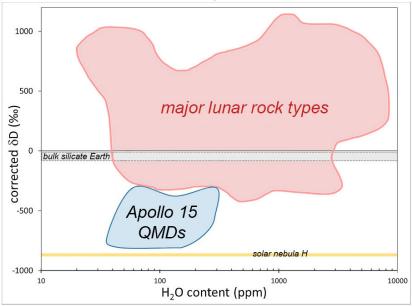
An important feature of the QMDs is that they formed at higher pressure than did the basalts. Because the solubility of water increases as pressure increases, water is retained as a magma crystallizes below the surface. In contrast, lava flows lose most of their water as they crystallize on a planetary surface, which causes an increase in the D/H ratio because hydrogen is lost much more efficiently due to its lower atomic mass. Formation in a magma chamber also shields the rocks from the **solar wind**, preventing contamination with solar hydrogen, whose D/H is about 20 parts per million (δD of -865 parts per thousand).



[LEFT] Apollo 15 sample 15386. A KREEP basalt thin-section viewed in polarized light. Elongate mineral grains are plagioclase feldspar, blocky gray and yellowish ones are low-calcium pyroxene crystals. The mineral shapes and how they are intergrown is characteristic of crystallization of basaltic lava. [RIGHT] Apollo 15 sample 15405. Photograph of thin-section of a fragment of quartz monzodiorite viewed in polarized light. Gray is plagioclase, red and orange crystals are pyroxene. The mineral grains are larger than in the KREEP basalt, indicating slower cooling. Textures and chemical compositions indicate that a rock like the 15405 quartz monzodiorite could have formed by fractional crystallization of a magma with a chemical composition like that of KREEP basalt.

Katie Robinson determined the total H_2O concentrations and D/H ratios in the mineral apatite in several QMDs. Most lunar D/H measurements have been made in apatite because it has a site in its crystal structure that can contain the hydroxyl molecule (OH). Results are shown in the blue-shaded area in the simplified graph below, along with a red-shaded area representing numerous other measurements of different lunar samples (by Robinson and several other investigators). The data show variation of D/H inside the Moon (and for basalts from the lunar **maria**, variation caused by preferential loss of H as water spewed out of lava flows). The QMDs stand out in the sea of data. They are distinctly lower than other samples, almost as low as the δD value of the solar nebula (shown by yellow-shaded band). The lowest measurement records δD of -750 parts per thousand. This exceptionally low value sparked Robinson and Desch to think about how solar nebula water could have been trapped inside the Moon.

Comparison of Measurements of Hydrogen Isotopes and Water Content in Apatite in Lunar Rocks



(Simplified from Desch and Robinson, 2019, Geochemistry, v. 79, fig. 2, doi: 10.1016/j.chemer.2019.125546.)

Plot of δD versus the hydrogen content (expressed as the equivalent amount of H_2O) in apatite crystals in lunar rocks. The QMD samples (blue-shaded area) form a distinct region on the diagram, characterized by low δD . The lowest values approach that of the solar nebula (yellow band). The red-shaded area shows the spread of data from other types of lunar rocks. The bulk Earth is shown by the gray band. The big spread among lunar samples is caused by variations in δD in the interior and in the case of mare basalts and KREEP basalts loss of hydrogen during eruption onto the lunar surface.

The D/H ratio in the Moon certainly seems variable, but broadly speaking, it is not greatly different from carbonaceous chondrites, except for these unusual QMD rocks from Apollo 15. (There might be other rocks on the Moon with ultra-low D/H, but we have not collected them yet.) How was this unusual hydrogen component added to the Moon? Desch and Robinson suggest that it was delivered by the collision between the proto-Earth and the Moon-forming impactor, often called Theia.

Origin of the Moon by a Giant Impact

The original fully-formulated giant-impact hypothesis for the origin of the Moon emerged in 1984. (Read my reminisces about the conference.) The hypothesis depicted a collision between the proto-Earth with about 90% of its final mass and a Mars-sized impactor. The impact was a bit off-center, causing the Earth to spin the way it does. The metallic core of the impactor (the body was assumed to have differentiated into metallic core and silicate mantle) merged with that of the proto-Earth, thus explaining why the Moon has a tiny core—almost all of the impactor's metal is in the Earth. Calculations indicated that most of the Moon formed from the impactor's silicate mantle. The hypothesis involved complicated physics-based computer modeling, made possible by the availability of high-speed computers in the 1980s.

Planetary dynamicists found modeling lunar origin by a giant impact an enticing problem to work on, with lots of free parameters to test. The list includes the relative sizes of the proto-Earth and impactor (which received the name Theia), impact velocity, the angle of impact (the offset of the objects' centers relative to the directions they were moving), glancing blows, and assorted compositional variations. Some highly energetic models formed a completely vaporized object called a synestia from which both Earth and Moon formed. Other models depicted lots of smaller impactors that were large enough to lift material into orbit around the proto-Earth.

Most computer simulations ended up with a partly molten, partly vaporized disk around the Earth, and considerable attention has been paid to the extent to which this disk and the primitive terrestrial atmosphere chemically equilibrated. This work was driven by measurements of the oxygen isotopic compositions of rocks from the Moon and Earth, which suggested that they were the same within analytical uncertainty. Other isotope systems such as titanium, silicon, and magnesium also seem to be the same in the Earth and Moon, suggesting either formation of the proto-Earth and Theia from the same reservoir of materials in the solar nebula, or

post-formation processes that evened out original differences (see **PSRD** article: **Compositional Balancing before Moon Formation**). The idea of total or partial equilibration between the proto-Earth and the proto-lunar disk has played a role in modeling element distributions between the two bodies, such as volatile elements that concentrate in metallic iron. (See **PSRD** article: **Volatile Elements Test Models for the Origin of the Moon**.)

The integration of computer modeling of the origin of the Moon with chemical compositions of both bodies shows that it is in principle possible to use compositions to test models for lunar origin. This is what Steve Desch and Katie Robinson are trying to do with their exploration of how water with ultra-low D/H occurs in pockets inside the Moon. (The paper by Desch and Robinson also models the silicon isotopic compositions and FeO concentrations in the Earth and Moon. For simplicity I discuss only the hydrogen isotopic compositions.)

Scarfing up Hydrogen from the Solar Nebula

The only ancient source of hydrogen with very low D/H is the solar nebula, the cloud of gas and dust surrounding the infant Sun. Its hydrogen came from the interstellar cloud from with our Solar System formed. The hydrogen accreting to the solar nebula was elevated in D/H, but isotopic exchange reactions among hydrogen-bearing species in the gas (H_2 , H_2O , HD, HDO) in the hot regions of the nebula (within about 2 AU of the Sun) greatly decreased the D/H ratio in the gas. This led to a hydrogen-rich inner nebula with D/H of about 20 parts per million, or a δD of -865 parts per thousand. Desch and Robinson propose that Theia had a magma ocean (i.e., was essentially completely molten with a metallic core) and was large enough (larger than about 0.4 times the mass of the Earth) to capture nebula gas with low δD into an atmosphere. The hydrogen in this atmosphere would dissolve into the magma ocean. They also propose that Theia had a composition like that of enstatite **chondrites**, which are notable for their highly reduced nature (essentially no iron in silicates). Their comprehensive analysis uses the isotopic composition of hydrogen as a tracer of the sources of water and its processing during planetary formation and subsequent differentiation. (As noted above, they also considered the changes in FeO and silicon isotopic composition, which we ignore in this article.) Below is an overview of their model in four stages.



Theia
Mass = 0.4 of final Earth
H₂O = 180 parts per million
D = -300 %

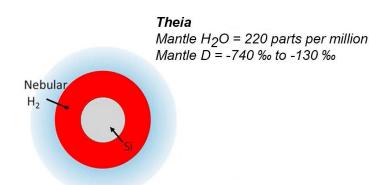


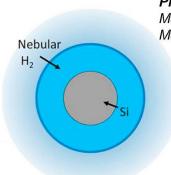
Proto-EarthMass = 0.62 of final Earth $H_2O = 1800$ parts per million D = +25 %

(From Desch and Robinson, 2019, Geochemistry, v. 79, doi: 10.1016/j.chemer.2019.125546.)

Stage 1 — Initial Conditions

The story starts with two planetary bodies, called Theia and Proto-Earth, destined to crash into each other, each having formed a metallic core. They would have grown from smaller planetesimals, with the proto-Earth's water-budget dominated by water like that in carbonaceous chondrites and Theia's water dominated by water like that in enstatite chondrites. Measurements of water contents and D/H in enstatite chondrites vary widely, so there is some uncertainty in these initial values. The planetary bodies had to have formed rapidly in order to reach sizes large enough to accumulate an atmosphere while the solar nebula was still present. The nebula dissipated within about 3 million years of the formation of our Solar System.





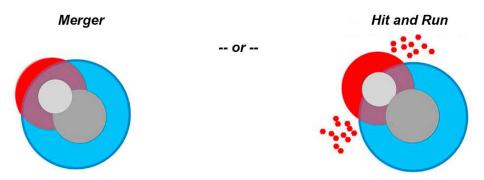
Proto-EarthMantle H₂O = 1800 parts per million
Mantle D = -220 % to +220 %

(From Desch and Robinson, 2019, Geochemistry, v. 79, doi: 10.1016/j.chemer.2019.125546.)

Stage 2 — Planet Evolution

Solar nebula gas is captured by both Theia and Proto-Earth. The gas is composed mostly of hydrogen, which dissolved in the molten silicate mantle, a process that cosmochemists call ingassing. Because the hydrogen has a very low D/H, dissolution of the nebula hydrogen lowers the δD in the mantles of both bodies, but more so in Theia because of its smaller initial amount of H₂O.

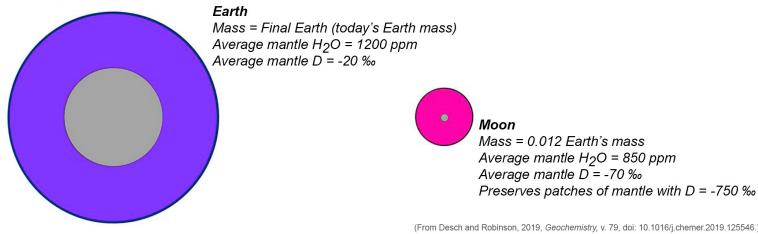
An interesting additional effect is that considerable silicon (Si) is reduced in Theia because the enstatite chondrite starting material is so reducing and hydrogen (also a reductant) was added to it. This also raises the amount of iron left in the silicate mantle. The δD in parts of the Earth could have been as low as -220 parts per thousand, not unlike regions identified by work on basaltic lavas derived from the deep mantle (see **PSRD** article: **Primeval Water in the Earth**).



(From Desch and Robinson, 2019, Geochemistry, v. 79, doi: 10.1016/j.chemer.2019.125546.)

Stage 3 — Giant Impact

Desch and Robinson considered two cases of the Giant Impact model. In one case, called merger (developed by Robin Canup, Southwest Research Institute, Boulder), the metallic cores merge and the mantles mix substantially. In the other case nicknamed hit and run (developed by Andreas Reufer, University of Bern, Switzerland, and colleagues), the mantles mix and the cores merge, but some of Theia is lost.



Stage 4 — Final Products

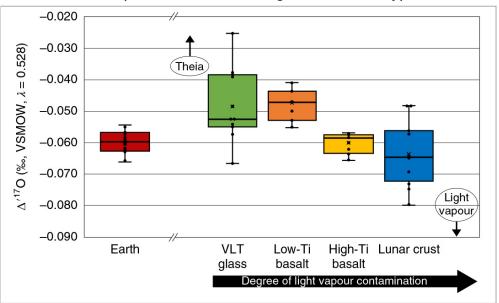
In both scenarios for the giant impact, the Moon ends up with less H_2O and lower average δD than does the Earth because the hypothesis assumes that Theia is large enough to ingas substantial amounts of nebula hydrogen that is almost devoid of deuterium. There must be some source of Earth building blocks that have such low δD , and a large Theia as suggested by Desch and Robinson fills the bill. The average δD in the lunar mantle is much higher than that in the regions of the lunar interior sampled by the quartz monzodiorites (QMDs), indicating that mixing of the mantles was not complete.

Mixing and Matching

The interesting Desch-Robinson model is an excellent illustration of how measured geochemical data can be combined with models of planet formation and the chemistry inferred for the solar nebula to test ideas for how the Moon formed. It is, almost certainly, not the last word on the subject of why the Moon has regions of exceptionally low δD . Similar approaches from different angles illuminate the processes and materials going into the Moon during its formation and subsequent differentiation. They are explained in the **PSRD** article highlighting Kevin Righter's work, **Volatile Elements Test Models for the Origin of the Moon**. These theoretical models have the virtue of being tied to geochemical data for the Earth and Moon, so are testable, and show us where there are gaps in our database. Gaps that can be filled by obtaining additional samples of the Moon.

The idea that two different large planetary bodies combined (violently) to make the Moon—but that subtle isotopic differences were preserved in regions of the lunar interior—is reinforced by new oxygen isotopic analyses of lunar samples. The measurements were made by Erick Cano, Zachary Sharp, and Charles Shearer (University of New Mexico). For a long time, oxygen isotopic analyses suggested the Earth and Moon formed from the same batch of Solar System stuff, as it appeared that both Earth and Moon had the same oxygen isotopic compositions, within analytical uncertainties. Cano and colleagues show that the Earth and Moon differ in oxygen isotopic compositions. Most importantly, their data show that oxygen isotopic compositions vary with rock type, as shown in the diagram below.

Isotopic Variations Among Lunar Rock Types



(From Cano, E. J., et al., 2020, Nature Geoscience, doi: 10.1038/s41561-020-0550-0.)

Oxygen isotopic compositions in lunar basaltic rocks from the maria and nonmare rocks from the lunar **highlands** crust. The delta notation is explained in a **PSRD** research note: **Oxygen Isotope Plot**. The rocks from the nonmare crust were affected by magma ocean processes. Erick Cano and colleagues suggest that oxygen with a low delta-O mixed with a vapor phase generated during the giant impact. This phase mixed in differing amounts with non-vaporized material from Theia, forming the range observed.

The data for lunar **highlands** rocks show that they are depleted in oxygen-17 compared to the heavier oxygen-18. In contrast, mare basalts and volcanic glasses, which formed deep in the Moon, have more oxygen-17. Cano and colleagues argue that there was a component that experienced vaporization, losing lighter oxygen-17 compared to oxygen-18. This light component could have mixed with heavier oxygen as the Moon was assembled. They also suggest that the oxygen with higher delta oxygen-17 might have come from Theia.

The important point for our story of D/H in the Moon is that somehow during its formation, distinctive regions of the Moon preserved the distinctive isotopic characteristics of hydrogen and oxygen. They are not necessarily the same regions, but the research gives us hope that we can use isotopic compositions and element concentrations, things we can measure, to trace processes that operated during formation of the Earth-Moon system.

Additional Resources

Links open in a new window.

- **PSRDpresents:** Hydrogen Isotopes in Small Lunar Samples Provide Clues to the Origin of the Earth and Moon -- **Short Slide Summary** (with accompanying notes).
- Cano, E. J., Sharp, Z. D., and Shearer, C. K. (2020) Distinct Ocygen Isotope Compositions of the Earth and Moon, *Nature Geoscience*, doi: 10.1038/s41561-020-0550-0. [abstract]
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- Desch, S. J. and Robinson, K. L. (2019) A Unified Model for Hydrogen in the Earth and Moon: No One Expects the Theia Contribution, *Geochemistry*, v. 79, doi: 10.1016/j.chemer.2019.125546. [article]
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- Righter, K. (2019) Volatile Element Depletion of the Moon–The Roles of Precursors, Post-impact Disk Dynamics, and Core Formation, *Science Advances*, v. 5(1), doi: 10.1126/sciadv.aau7658. [article]



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