

## Headline Article

July 1, 2010

# Damp Moon Rising

--- Cosmochemists find more evidence for water inside the Moon, showing that it is not the bone-dry place we thought.

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The discovery in 2008 by Alberto Saal (Brown University) and colleagues that lunar volcanic glasses contain water surprised lunar scientists: the Moon could no longer be viewed as being practically waterless. Francis McCubbin (Carnegie Institute of Washington) and coworkers there, at the Stony Brook University (New York), and Okayama University in Japan have confirmed the presence of water in the lunar interior and show that it is present in other types of igneous rocks, not just in those forming glassy volcanic deposits. McCubbin and colleagues measured the concentrations of fluorine, chlorine, and hydroxyl ion (OH<sup>-</sup>) in apatite (calcium phosphate) crystals in a lunar mare basalt sample and an igneous rock from the highlands. They found abundant water in the apatite crystals (hundreds to thousands of parts per million), which translates to at least 0.6 to 5 parts per million of H<sub>2</sub>O in the lunar interior. While less than that estimated by Alberto Saal and coworkers from volcanic glasses (tens of parts per million), it is still vastly larger than the next-to-nothing (less than one part per billion) of previous estimates. The higher water content has implications for the origin of the Moon and may shed light on how the inner planets acquired their water.

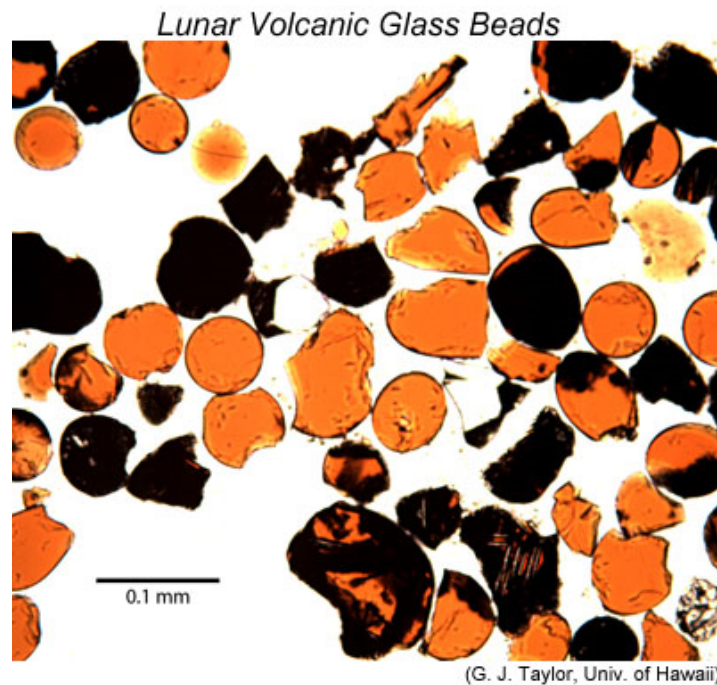
### Reference:

- McCubbin, F. M., Steele, A., Hauri, E. H., Necvasil, H., Yamashita, S., and Hemley, R. J. (2010) Nominally Hydrous Magmatism on the Moon. *Proceedings of the National Academy of Sciences*, [www.pnas.org/cgi/doi/10.1073/pnas.1006677107](http://www.pnas.org/cgi/doi/10.1073/pnas.1006677107).
- **PSRD presents:** Damp Moon Rising --**Short Slide Summary** (with accompanying notes).

## A Wet Blanket on the Bone-Dry Moon

Cosmochemists searched thoroughly (or so we thought) for water in the first lunar samples returned to Earth by the Apollo 11 mission. Detailed analysis of those first lunar materials revealed no evidence that lunar magmas contained even a smidgeon of water. Analysis of samples returned by subsequent missions did not contradict this important observation. It became a tenant of lunar science that the Moon is bone dry. A complete discussion of the evidence for the Moon containing at most micro-smidgeons of water is given in the **PSRD** article, **The Bone-Dry Moon Might be Damp**.

Alberto Saal (Brown University) and his coworkers showed that the conventional wisdom of a dry Moon was all wet. He and his colleagues measured volatile elements in lunar volcanic glass beads, using ion microprobe capabilities not available until a few years ago. All the molecules measured (H<sub>2</sub>O, sulfur, fluorine, and chlorine) had higher concentrations in the center of 100-micrometer beads, and decreased progressively towards the surface. This is a classic diffusion profile, suggesting that these molecules were present in the droplets of magma when erupted, but began to be lost upon eruption. Saal and his colleagues calculated how much of these volatiles were present in the magmas initially. They concluded that the lunar magmas contained between 260 and 745 parts per million of water, only a bit lower than the amount in magmas produced at mid-ocean ridges on Earth.



(G. J. Taylor, Univ. of Hawaii)

Thin (30 micrometers) slice of the orange glass deposit at the Apollo 17 landing site. Dark spheres are of the same composition, but have crystallized ilmenite, which is opaque, even in thin sections, so does not allow light to pass through. Alberto Saal discovered small amounts of water in the orange glass beads and in green glass beads from the Apollo 15 landing site.

The work on volcanic glasses shows that at least some parts of the lunar interior contain water, but how widespread is it? Perhaps some unusual conditions led to a tiny amount of lunar water concentrating in the portions of the mantle that melted to form volatile-laden magmas that erupted explosively. Thus, it seemed sensible to Francis McCubbin to search for water in other types of lunar rocks besides pyroclastic glasses. In fact, he suspected that water was present in phosphate minerals from the amounts of chlorine and fluorine in apatite crystals in a suite of lunar rocks, and reported the results at the Lunar and Planetary Science Conference in 2008. The only problem was that water (actually the OH molecule) was only inferred to be present. Now it has been measured directly.

## KREEPy Samples

A good place to look for lunar water is in rocks that might have a lot of it. Samples with high abundances of potassium, rare earth elements, and phosphorus (so-called KREEP samples) are ideal because the KREEPy component formed as a late-stage product formed by crystallization of the ocean of magma surrounding the Moon when it formed. H<sub>2</sub>O is quite soluble in molten silicate and is not readily incorporated into the anhydrous minerals that crystallize from the magma ocean. It builds up, along with potassium (K), rare earth elements (REE), phosphorus (P), and other trace elements. McCubbin and his colleagues discuss two lunar rocks, one from the Apollo collection and the other a lunar meteorite.

Lunar sample 15404,51 is a rock fragment in the 4-10 millimeter sieve fraction of a soil found on top of a rock at the Apollo 15 landing site. The boulder, about 3 meters long, rested on the lower slopes of the Apennine Mountains, which form part of the prominent ring of the Imbrium impact basin. This sampling locale was at the highest point on the Apennine Front, located about 130 meters above the mare plains on which the Apollo 15 lunar module landed. A pile of debris rests against the up-slope side of the rock, and some of that debris is on top of the rock. The material on top was sampled by astronauts Dave Scott and Jim Irvin. It is not clear whether the debris is directly related to the boulder or slid down slope. The boulder itself was sampled in the form of rock 15405, an impact melt breccia that may have been tossed to the site by the impact that formed the 55-kilometer crater Aristillus.



NASA Apollo 15 photograph AS15-90-12187.)

Sample 15404,51 was collected as part of the soil that is piled up in this photograph of the boulder at Station 6a, Apollo 15. The boulder is about three meters long. Note the pile of debris on the up-slope side of the boulder. Some of that material also resides on top and was sampled by Apollo 15 astronauts. Rock 15405 was collected from the knobby area of the boulder to the right of the loose material. The prominent peak in the background is Mount Hadley; lower region in the middle of the photograph is local mare.

Little rock 15404,51 consists of pyroxene, plagioclase, and potassium feldspar, with smaller amounts of silica, apatite, merrillite (another phosphate mineral that does not contain water), and other minor minerals. The compositions of pyroxene and plagioclase are consistent with the rock being a member of the alkali suite of lunar rocks, which means it is also related to KREEP, hence a good candidate for a water search.

The lunar meteorite is Northwest Africa (NWA) 2977, which has been paired with NWA 773. ("Paired" means that cosmochemists have determined from chemical compositions and mineralogy that the two stones, though found separately, likely belonged to the same meteoroid before it entered Earth's atmosphere.) NWA 2977 is an impact melt breccia that contains a prominent clast of an igneous rock. The igneous rock consists of more than 50% olivine, with lesser amounts of pyroxene and plagioclase, and small amounts of potassium feldspar, silica, and phosphate minerals. Previous studies of the clast in NWA 773 concluded that it is similar to mare basalts, but with KREEP trace element concentrations, making it another good candidate for the water search. In spite of being found, not observed to fall, NWA 2977 does not appear to have been significantly affected by terrestrial weathering by water. This is substantiated by the fresh condition of its fusion crust (see photo below left) and the presence of metallic iron (common in lunar samples), which would readily alter to iron oxides if substantial water had permeated the meteorite after it fell.

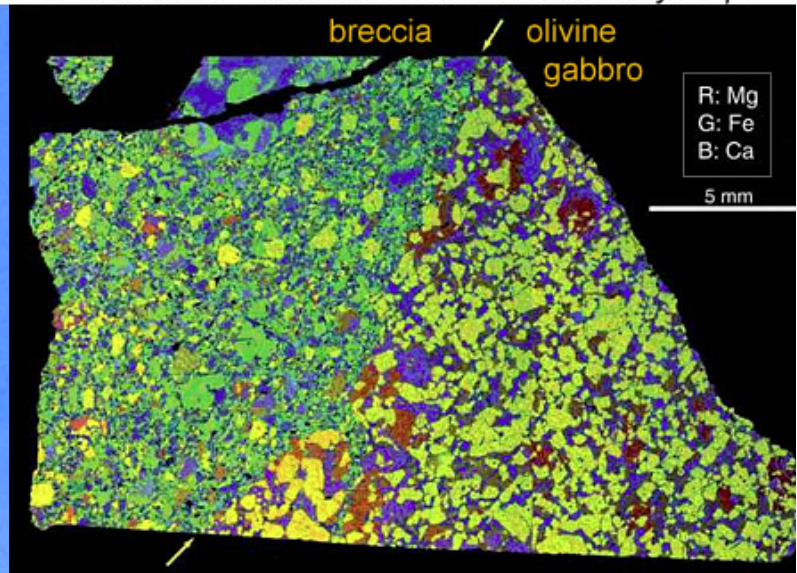


Lunar Meteorite NWA 2977



Photograph © Michael Farmer (<http://www.meteoritehunter.com>)

Lunar Meteorite NWA 773 Elemental X-ray Map



(From Fagan *et al.*, 2003, *Meteor. Planet. Sci.*, v. 38, p. 529-554.)

**Left:** Sample of NWA 2977 that can fit in the palm of your hand. Note the fresh, black fusion crust, which indicates little alteration by water after it landed on Earth. Image courtesy of Michael Farmer (<http://www.meteoritehunter.com>). **Right:** Elemental X-ray map of a thin section of NWA 773, which has been paired with NWA 2977. In this map red = Mg; green = Fe; and blue = Ca. Note the sharp boundary (indicated by arrows) dividing the breccia matrix from the olivine gabbro lithology. The olivine gabbro contains olivine (yellow), pigeonite (low-calcium pyroxene, orange), augite (high-calcium pyroxene, purple), and feldspars (blue).

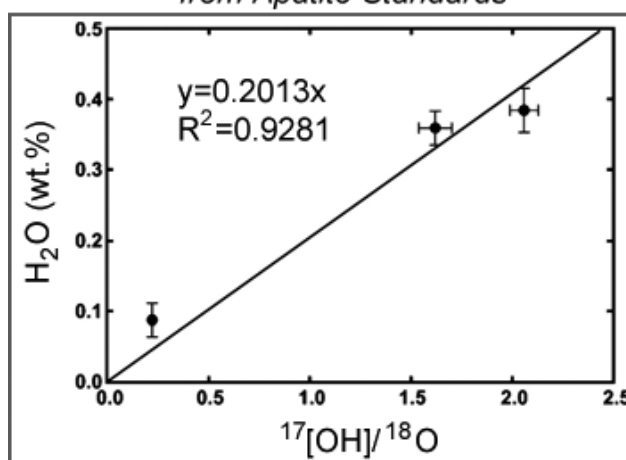
McCubbin and his colleagues also studied lunar basalt 14053, and in fact found water in apatite in it, but decided that the rock was not suitable for water measurements. Basalt 14053 is decorated with unusual mineralogical features that formed after crystallization, including a striking amount of reduction of iron-rich olivine ( $\text{Fe}_2\text{SiO}_4$ ) to iron metal. The phosphate minerals were affected by this process. To play it safe, McCubbin and his colleagues do not consider this rock in their estimates of water in the lunar interior.

## The Apatite Water Depository

Apatite has the chemical formula  $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ . Each part of the formula represents a site inside the crystal structure where the listed elements occur. F (fluorine), Cl (chlorine), and OH (hydroxyl ion) add up to 1.0 (in atomic proportions) if the analysis and the mineral are both perfect. Apatite can have any amount of F, Cl, and OH. Francis McCubbin had already found strong hints of OH in apatite in lunar basalts from literature data and by making careful measurements of the compositions, especially the F, Cl, and OH concentrations, in apatite in lunar basalts. In one case, mare basalt 15058, he and his colleagues showed that OH was definitely present, but the analyses were not quantitative.

Rock 15404,51 and meteorite NWA 2977 both contain good phosphate grains to analyze. McCubbin and colleagues used three terrestrial apatite samples as standards for the ion microprobe analyses they made of F, Cl, and OH. This required that they determine the OH content of the apatite standards, which had not been measured previously. They could not make this measurement by ion microprobe because, well, they did not have a standard. Other techniques available, such as the electron microprobe, do not measure hydrogen or water directly. They chose to collaborate with Shigeru Yamashita of the Institute for the Study of the Earth's Interior at Okayama University in Japan. Yamashita used a technique called "hydrogen manometry," which determines the amount of hydrogen by measuring the pressure of the hydrogen gas given off. This sounds easier than it actually is. The measurement required ensuring that no adsorbed gases were present on the samples (which were powdered) or the apparatus, heating the samples in platinum crucibles to drive off bound water (the OH comes off as  $\text{H}_2\text{O}$ ), collecting the water, reducing it to hydrogen, transferring the hydrogen to calibrated volumes, measuring the pressure of hydrogen in those volumes, calculating the amount of hydrogen that corresponds to, and finally converting that amount of hydrogen to  $\text{H}_2\text{O}$ . Cosmochemists go to a lot of effort to calibrate standards! The results allowed McCubbin and colleagues to quantify their OH measurements by creating a calibration curve.

### Calibration Curve Constructed from Apatite Standards



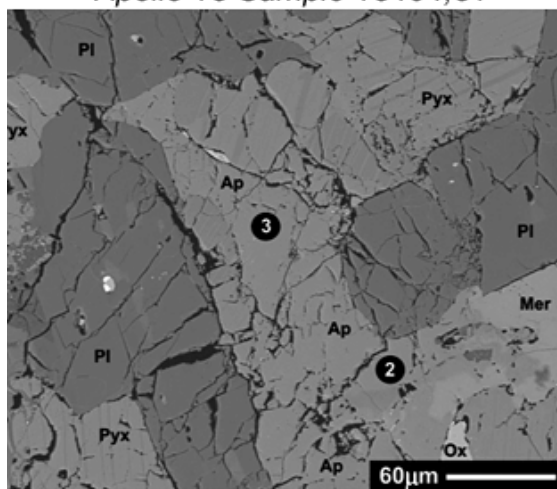
(From McCubbin *et al.*, 2010, *PNAS*, doi:10.1073/pnas.1006677107.)

Calibration curve showing water content in three apatite standards (y-axis, determined by hydrogen manometry) versus the ratio of OH (made from oxygen-16) to oxygen-18 as determined by ion microprobe. Deviations from a straight line define the uncertainty in the analysis, which is 17% of the amount present.

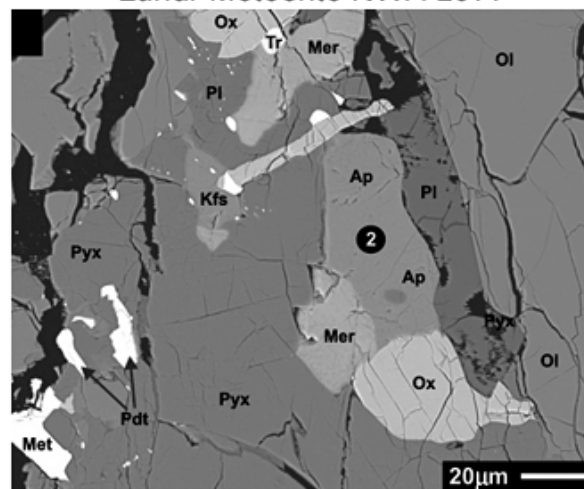
Once good apatite standards were available, McCubbin and associates measured the chlorine, fluorine, and OH amounts in apatite crystals in 15404,51 and NWA 2977. Both samples have good apatite grains to analyze. The measurements were made on an ion microprobe at Carnegie Institute of Washington, using the same instrument and Eric Hauri's expertise as used in the analyses of lunar volcanic glasses.

### Back-Scattered Electron Images

#### Apollo 15 Sample 15404,51



#### Lunar Meteorite NWA 2977



(From McCubbin *et al.*, 2010, *PNAS*, doi:10.1073/pnas.1006677107.)

Back-scattered electron images of Apollo 15 grain 15404,51 and lunar meteorite NWA 2977. **Left: 15404,51.** Minerals identified by abbreviations are Ap (apatite), Pyx (pyroxene), Pl (plagioclase). The numbers inside black circles show the locations of ion microprobe analyses (point number 1 is in a different location). **Right: NWA 2977.** Minerals are Ap (apatite), Pyx (pyroxene), Pl (plagioclase), Ol (olivine), Ox (iron-titanium oxide), Mer (merrillite), kfs (potassium feldspar), Met (metallic iron-nickel), and Pdt (pendlandite, an iron sulfide), and Tr (another type of iron sulfide). An ion microprobe analytical point is shown by the numbered circle.

### Confirmation of More Damp Rocks

The apatite crystals in both 15404,51 and NWA 2977 contain 2.5 to 2.7 wt% fluorine, making them "fluorapatite." The concentration of chlorine in apatite is about 1 wt% in 15404,51 and 0.03 to 0.2 wt% in NWA 2977. The big news, of course, is that both contain significant OH, well above detection limits. 15404,51 apatite contains 0.02 to 0.1 wt% (200 to 1000 parts per million) and NWQ 2977 contains 0.4 to 0.7 wt% (4000 to 7000 parts per million). These data imply

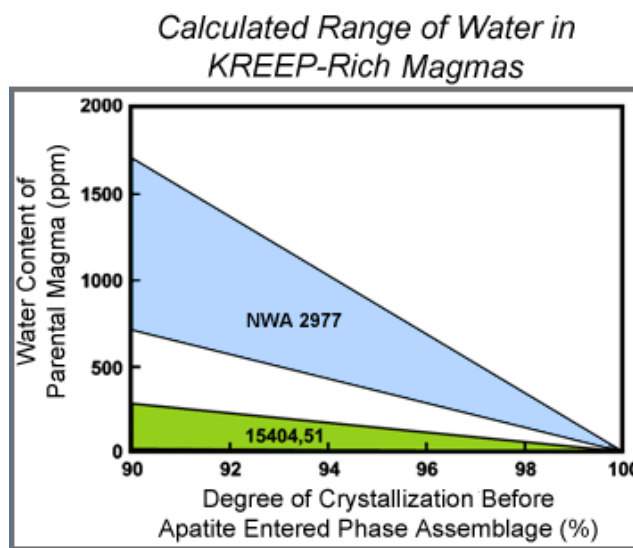
significant water inside the Moon. But how much?

## How Much Water Inside the Moon?

The important number is the concentration of water in the bulk Moon. That is what will help us understand water delivery to the inner planets and the details of lunar formation. The first step is to determine the amount of water in the magmas in which 15404,51 and NWA 2977 formed. McCubbin used published experimentally-determined data for how H<sub>2</sub>O partitions into apatite compared to how much stays in the remaining silicate melt. The values range from 0.1 to 0.25, which means that the ratio of water in apatite to that in the associated magma is between 0.1 and 0.25; that is, the magma contains more water than does the apatite.

As always, the situation is complicated. For one thing, the value of the partition coefficient (the values between 0.1 and 0.25) varies with the composition of the silicate melt. McCubbin avoids that problem by using the value of 0.25 because that results in a smaller estimate of water in the magma than does using the smaller (0.1) value, hence tends to lead to a minimum concentration of water in the lunar interior. Using the measured water in apatite from the two samples, this leads to an estimate of 0.7 to 1.7 weight percent water in the magma.

That's quite a bit of water, but it indicates the water concentration when apatite crystallized. However, except in rare cases, magmas do not suddenly crystallize all their minerals at once. Instead, minerals crystallize sequentially. In most basaltic magmas, minerals such as apatite crystallize late in the sequence. This surely is the case for the 15404,51 and NWA 2977 magmas because apatite occurs along with other late minerals and between big crystals of olivine, plagioclase, or pyroxene. Because the major minerals do not incorporate any water into their structures, their formation results in the residual magma becoming progressively richer in H<sub>2</sub>O. McCubbin calculated the amount of water in the original (totally liquid) magma as a function of the amount of crystallization before apatite formed, using the reasonable assumption that this would not happen before 90% of the magma had crystallized. The calculations indicate that for apatite formation at 95% crystallization the original magmas contained between 360 and 850 parts per million H<sub>2</sub>O (for NWA 2977) and between 10 and 140 parts per million (for 15404,51). These values are not much different from those estimated for volcanic glasses, 70 to 745 parts per million (see PSRD article, [The Bone-Dry Moon Might be Damp](#)).



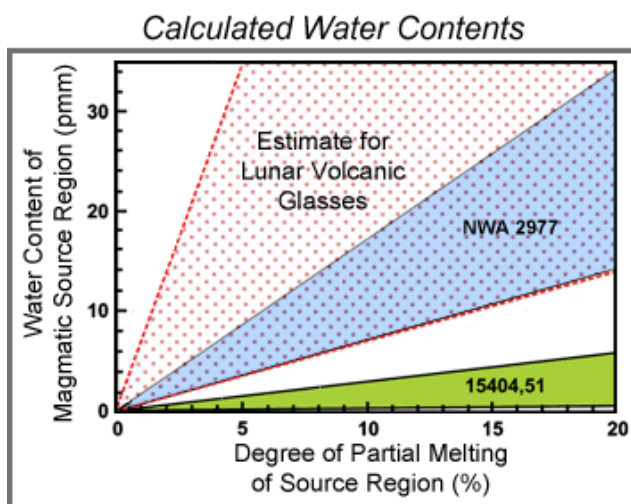
(From McCubbin *et al.*, 2010, *PNAS*, doi:10.1073/pnas.1006677107.)

Calculated range of water in the original magmas for NWA 2977 (blue area) and 15404,51 (green area). The amount of water depends on how much crystallization had taken place before apatite began to form. For KREEP-rich samples like these, values in the range of 95 to 99% are reasonable. The ranges for each sample represent the range of measured OH values in the analyzed apatite crystals.

The calculations give us an estimate of the amount of water in the magmas, but what does this imply about the amount in the lunar interior, where the magmas formed by partial melting? (As for crystallization, the minerals making up rocks do not melt all at once. They partially melt over a range of temperature.) As rocks heat up and begin to melt, any water in the rock concentrates in the melted portion. For a given amount of water in a magma, such as McCubbin's estimate for the two lunar rocks, the inferred amount of water in the interior is related to the amount of partial melting, as shown in the diagram



below. (The calculations assume that apatite formed after 99% of the magma had crystallized.) If the amount of melting was only 3% (that is, the lunar mantle source consisted of 97% solid rock mingled with 3% molten material), then the rock 15404,51 source would have contained 0.06 to 0.08 parts per million of water and the NWA 2977 source would have contained between 2 and 5 parts per million. For comparison, the same calculations for volcanic glasses indicates that the source rocks deep inside the Moon contained between 2 and 21 parts per million  $\text{H}_2\text{O}$ . The amount of melting was likely higher. At 10% partial melting, the inferred interior source regions would have contained 0.2 to 3 parts per million  $\text{H}_2\text{O}$  (for 15404,51) and between 7 and 17 parts per million (for NWA 2977).



Graph showing the calculated water contents in the source regions in the lunar interior for NWA 2977 (blue area) and 15404,51 (green area), with lunar volcanic glasses shown for comparison (red stippled area). The inferred water contents vary with the amount of melting because water concentrates in the melted portion. The bottom line is that the measurements of water in lunar rocks and these inferred concentrations in the portions of the interior where they formed show that the Moon must contain considerably more water than the traditional value of almost none (less than one part per billion).

These new data show that the Moon, though not soggy, is certainly damper than we thought. The interior seems to contain between one and a few tens of parts per million of water. The total Moon might contain less because crystallization of the lunar magma ocean would have created vast volumes with essentially no water. However, even taking that into account, the bulk Moon appears to contain at least 1000 times the 1 part per billion given by our conventional wisdom. What a huge difference in our view of the Moon!

## The Water Delivery and Retention System

The leading theory for lunar origin pictures the Moon forming as the result of a Mars-sized object hitting Earth near the end of its construction. In fact, the event was an important one in the accretion of our planet. Knowing that the Moon contains some water in its interior raises some important questions about the dynamics of how planets formed. Dynamical calculations indicate that most of the Moon was formed from material that resided in the impactor. Did the impactor contain water? If so, how much? Was some of it lost as the result of the large impact? Was a lot or a little lost? Did some react with silicates in the proto-lunar disk? Or was the water added later, to both Earth and Moon? Why does the Moon contain a few parts per million to a few tens of parts per million water while the Earth contains much more, 500 to 1000 parts per million?

These are important questions bearing on how the inner planets formed, and the work reported by McCubbin and his colleagues provides us with important information about accretion. Pinning down the amount of water in the lunar interior and understanding how it got there is an area of research that is just beginning. More studies of lunar rocks (Apollo samples, meteorites, and future sampling missions) will help elucidate the total amount of water in the Moon and its distribution and its relation to KREEP and to magma ocean crystallization. Research will be done on the extent of water loss during planetary accretion. The results will lead to an improved understanding of how water was delivered to Earth and other inner planets.

The Moon, a treasure of cosmochemical information, still graces the night sky . . . only it's a bit damper than we thought.

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## Additional Resources

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Links open in a new window.

- **PSRD presents:** Damp Moon Rising --**Short Slide Summary** (with accompanying notes).
- Fagan, T. J., Taylor, G. J., Keil, K., Hicks, T. L., Killgore, M., Bunch, T. E., Wittke, J. H., Mittlefehldt, D. W., Clayton, R. N., Mayeda, T. K., Eugster, O., Lorenzetti, S., and Norman, M. D. (2003) Northwest Africa 773: Lunar Origin and Iron-enrichment Trend. *Meteoritics and Planetary Science*, v. 38, p. 529-554.
- McCubbin, F. M., Steele, A., Hauri, E. H., Necvasil, H., Yamashita, S., and Hemley, R. J. (2010) Nominally Hydrous Magmatism on the Moon. *Proceedings of the National Academy of Sciences*, [www.pnas.org/cgi/doi/10.1073/pnas.1006677107](http://www.pnas.org/cgi/doi/10.1073/pnas.1006677107).
- McCubbin in Am Mineralogist (article is in the folder)
- Saal, A. E., Hauri, E. H., Lo Cascio, M., Van Orman, J. A., Rutherford, M. C., and Cooper, R. F. (2008) Volatile Content of Lunar Volcanic Glasses and the Presence of Water in the Moon's Interior. *Nature*, v. 454, p. 192-196. doi:10.1038/nature07047.
- Taylor, G. J. (2008) The Bone-Dry Moon Might be Damp. *Planetary Science Research Discoveries*. <http://www.psrh.hawaii.edu/Sept08/MoonWater.html>.



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