



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.

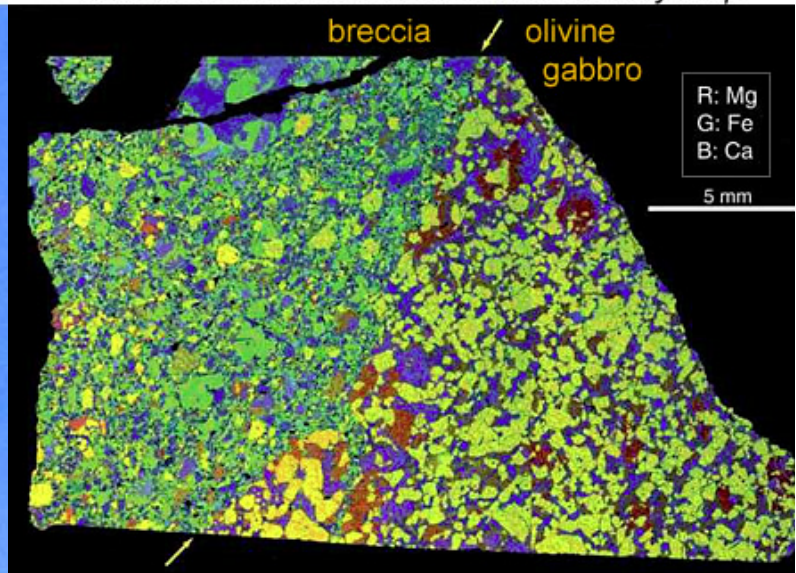
The lunar meteorite is Northwest Africa (NWA) 2977, which has been paired with NWA 773. ("Paired" means that cosmochemists have determined from chemical compositions and mineralogy that the two stones, though found separately, likely belonged to the same meteoroid before it entered Earth's atmosphere.) 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).

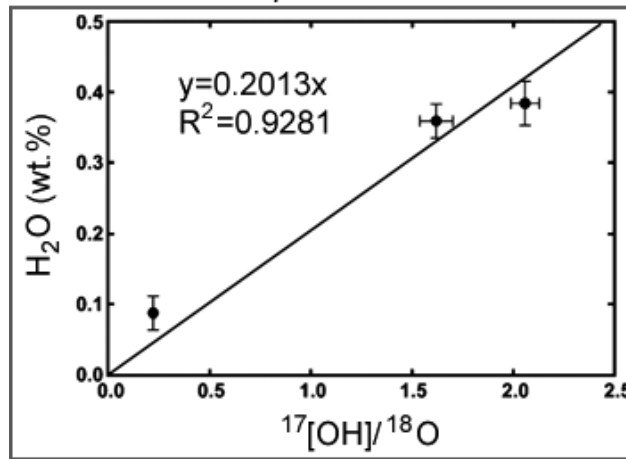
McCubbin and his colleagues also studied lunar basalt 14053, and in fact found water in apatite in it, but decided that the rock was not suitable for water measurements. Basalt 14053 is decorated with unusual mineralogical features that formed after crystallization, including a striking amount of reduction of iron-rich olivine (Fe_2SiO_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 H_2O), 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 H_2O . 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.)

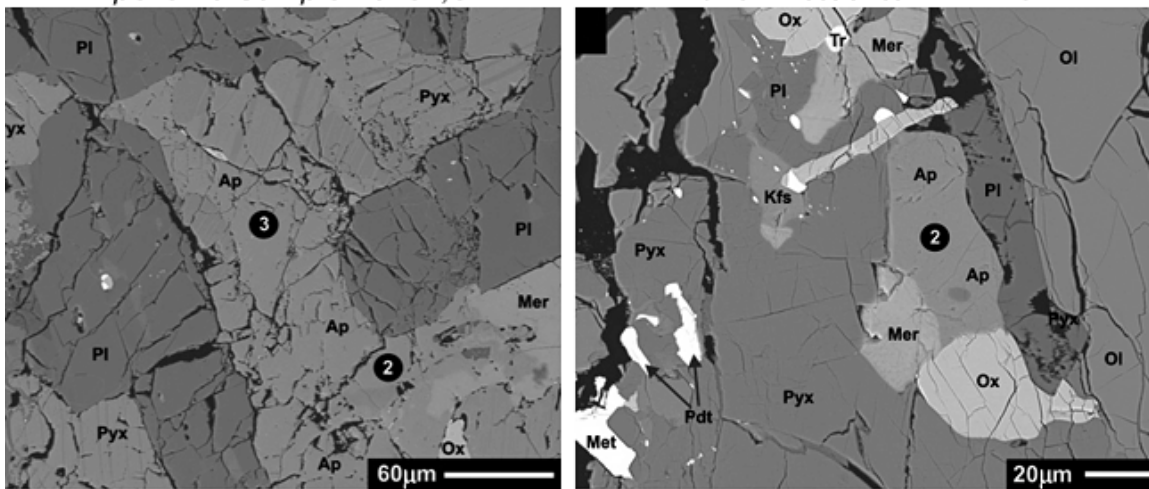
Calibration curve showing water content in three apatite standards (y-axis, determined by hydrogen manometry) versus the ratio of OH (made from oxygen-16) to oxygen-18 as determined by ion microprobe. Deviations from a straight line define the uncertainty in the analysis, which is 17% of the amount present.

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 NWA 2977 contains 0.4 to 0.7 wt% (4000 to 7000 parts per million). These data imply

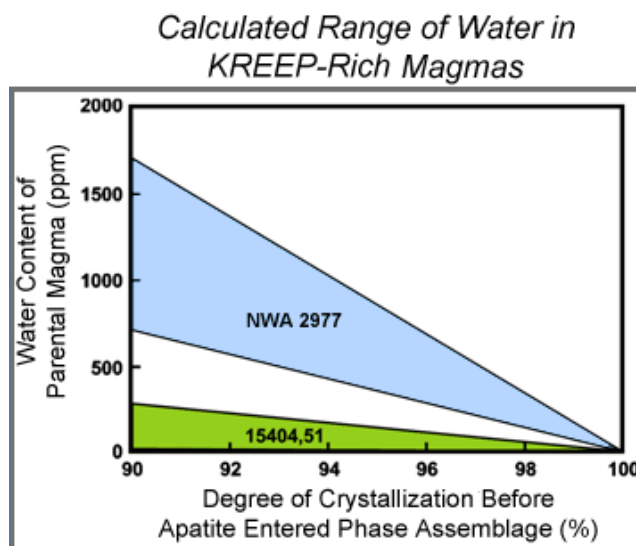
significant water inside the Moon. But how much?

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 H₂O 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 H₂O. 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 H₂O (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](#)).

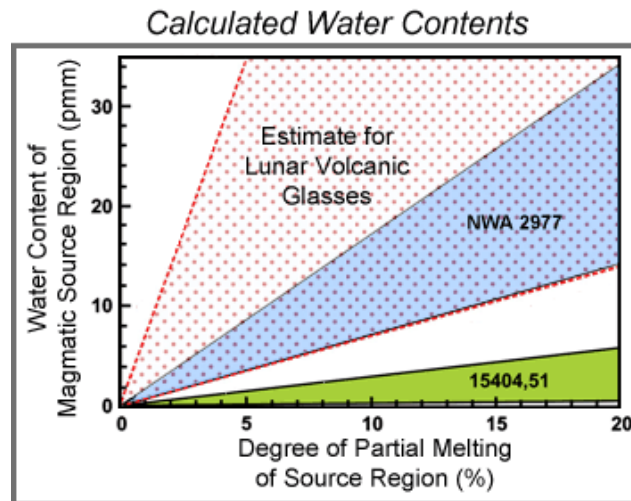


(From McCubbin *et al.*, 2010, *PNAS*, doi:10.1073/pnas.1006677107.)

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 H₂O. 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 H₂O (for 15404,51) and between 7 and 17 parts per million (for NWA 2977).



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

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.

Additional Resources

Links open in a new window.

- **PSRDpresents:** 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.
- 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.psrд.hawaii.edu/Sept08/MoonWater.html>.



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