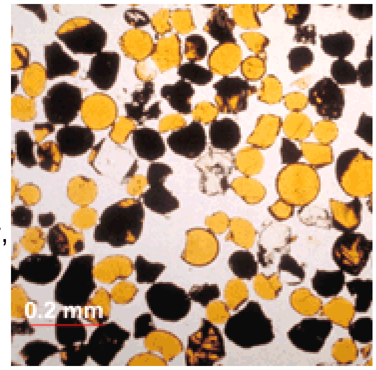
Hot Idea September 22, 2008



The Bone-Dry Moon Might be Damp

--- Cosmochemists have written in stone that the Moon is almost totally devoid of water, but new analyses of volcanic glasses suggest that they need to do some editing.

Written by G. Jeffrey Taylor
Hawai'i Institute of Geophysics and Planetology

Detailed analysis of the first lunar samples collected by Apollo 11 astronauts in 1969 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.

But is it really completely dry? Recent analyses of lunar volcanic glasses suggest that a smidgeon, maybe even a mega-smidgeon, of water is present. Alberto Saal and his colleagues at Brown University, the Carnegie Institution of Washington, and Case Western Reserve University have measured volatile elements in lunar volcanic glass beads, using ion microprobe capabilities not available until a few years ago. They measured OH^- (hydroxyl) anions (which are fragments of the H_2O) molecule). All the measurements (of OH^-, sulfur, fluorine, and chlorine) had higher concentrations in the center of the 276-micrometer beads, and decreased progressively towards the surface. This is a classic diffusion profile, suggesting that these elements were present in the droplets of magma when erupted, but began to be lost to the surrounding volcanic gases. Saal and his colleagues calculated how much of these volatiles were present upon eruption. They concluded that the lunar magmas contained about 745 parts per million of water, similar to the amount in magmas produced at mid-ocean ridges on Earth. The results imply that the region of the lunar interior that melted to make the magmas contained about the same amount as in the Earth's depleted upper mantle, which is way more than a smidgeon. This may have implications for the origin of the Moon. It certainly will spark new research on lunar volatiles--and lots of arguments!

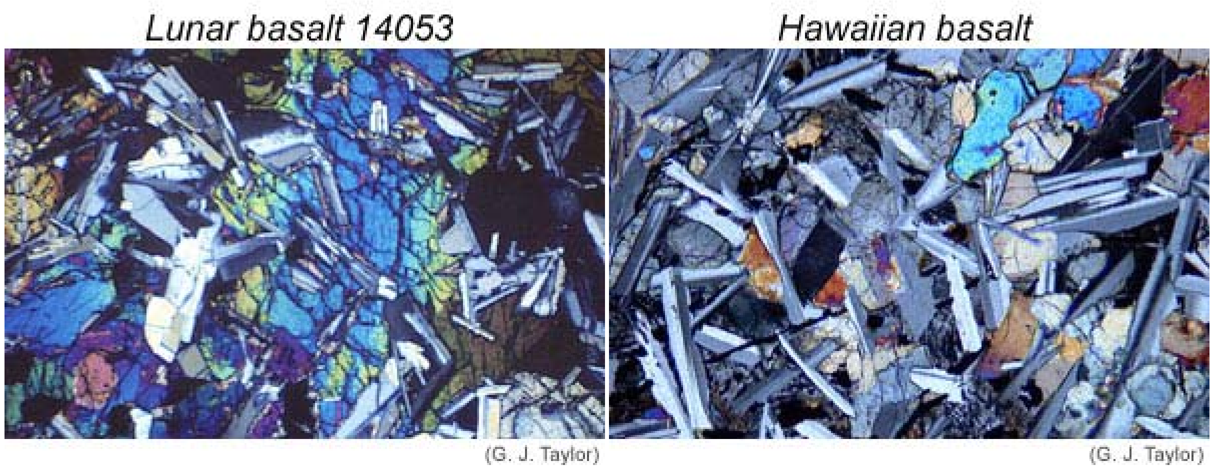
Reference:

- Saal, Alberto E., Hauri, Erik H., Lo Cascio, Mauro, Van Orman, James A., Rutherford, Malcolm C., and Cooper, Reid 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.

PSRDpresents: The Bone-Dry Moon Might be Damp --Short Slide Summary (with accompanying notes).

Traditional View: An Ultra-Arid Moon

A surprise to most cosmochemists looking at the Apollo samples was that no minerals that contain water (either as OH^- ions or as H_2O) appeared to be present. We found no mica, clay minerals, or hydrous iron oxides. Such hydrous minerals are common in earth rocks. The older the rocks, the more altered by reactions with water solutions they tend to be, and the first lunar basalts brought back from the Moon were about 3.5 billion years old, yet unaltered. Young terrestrial igneous rocks that erupt onto land, such as those in Hawaii, are also extremely fresh. Bulk chemical analyses indicate the presence of some H_2O (probably present as the OH^- ion), but hydrous minerals are rare and we do not know where most of the water resides in the rocks. Indeed, most recently-erupted basalts on Earth look as fresh as lunar basalts. This does not mean that terrestrial basalt magmas did not contain water when they approached the surface and erupted. They lost the water as the pressure dropped as they ascended (water is more soluble at higher pressure).



Photomicrographs in polarized light of thin sections of lunar basalt 14053 **(left)** and a basalt from Hawaii **(right)**. Both photos are 3 mm across. Neither rock shows evidence for alteration by water. The Hawaiian basalt shown here was only a year old when collected. Older basalts tend to have hydrous weathering products in them.

Lunar rocks formed in large underground magma bodies (geologists call such rocks "plutonic") also appear to lack water-bearing minerals. In this case the water does not escape to the surroundings because the pressure is high. On Earth, crystallization eventually leads to formation of hydrous minerals. Hydrous minerals have not been positively identified in the lunar plutonic rocks.

Many lunar igneous rocks contain small grains of metallic iron, which would have rusted rapidly if water were present. It appeared to all studying the samples returned by the Apollo missions that the magmas contained no significant amounts of water and that the rocks were not subsequently altered by water vapor escaping from the interior or by water flowing across or raining onto the stark lunar landscape. Everyone studying the Moon concluded that it was bone dry. (Some hydrous minerals such as mica were reported early in the lunar rock program, but these were probably contaminants. One lab, for example, also found carbonate minerals and brass.)

Chemical analyses of lunar igneous rocks are consistent with the mineralogical observations. H_2O concentrations in typical basalts on Earth erupted on land (rather than on the sea floor) contain 0.2 to 1 wt% H_2O (wt% means the concentration by weight in percent). In contrast, lunar basalts contain on the order of 0.01 wt.%, an unknown amount of which is terrestrial contamination. On the other hand, my University of Hawaii colleague Mike Garcia, an expert in Hawaiian volcanic rocks, thinks that it is likely that freshly-erupted basalts contain much less than 0.1 wt% H_2O. Those with a few tenths of a percent water have been exposed enough to have been weathered slightly.

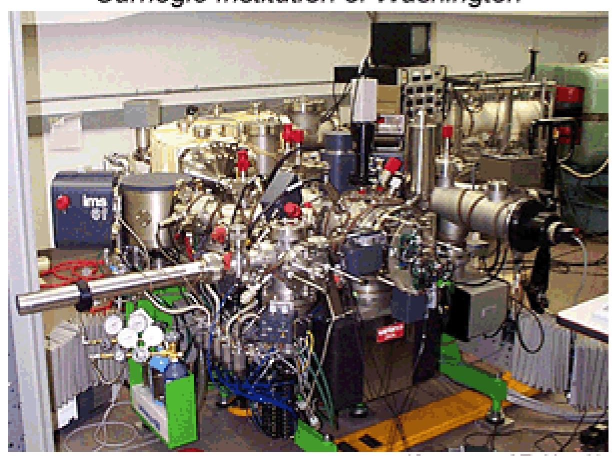
Rock evidence was supported by the way the Moon transmitted seismic waves in its outer several kilometers. The first strong signal was generated by the Apollo 12 seismometer when the spent Apollo 12 Lunar Module, the vehicle used by the Apollo 12 crew to land on the Moon, was sent crashing into the Moon after delivering the crew safely to the Command Module in orbit. The signal was different from terrestrial seismic signals. The waves bounced around for a few hours, making the Moon ring like a bell. Water-bearing rocks and wet soil layers attenuate seismic waves on Earth. The continued seismic ringing of the Moon was consistent with a bone-dry little planet.

But how dry is bone dry? Is there really none? That's unlikely, although papers addressing water on the Moon suggested that the amount was vanishingly small. There were hints of lunar water from measurements on basalts and samples of the volcanic orange glass, though the amount was only 0.1 wt%. Small, but not none. Samples of lunar regolith appear to contain more water than do igneous rocks. Detailed studies of the gases released from lunar dust indicated that the water released is mostly terrestrial contamination, though perhaps combined with solar wind hydrogen that reacted with oxygen in mineral grains. So, how dry is the Moon?

Analytical Improvements

Saal and his colleagues have cast some doubt on the desert-Moon concept. They did this by analyzing H_2O and other typical volcanic gases (sulfur, chlorine, and fluorine) in lunar volcanic glass beads. For this work, they used a secondary ion mass spectrometer (SIMS, or ion microprobe for short). [For more information on this instrument, see **PSRD** article: Ion Microprobe.] Analyses of small amounts of water and the volatile elements have been difficult in the past, but Saal's collaborator Erik Hauri (Department of Terrestrial Magnetism, Carnegie Institution of Washington) has developed the techniques necessary to measure concentrations much smaller than previously possible.

Ion Microprobe
Department of Terrestrial Magnetism, Carnegie Institution of Washington



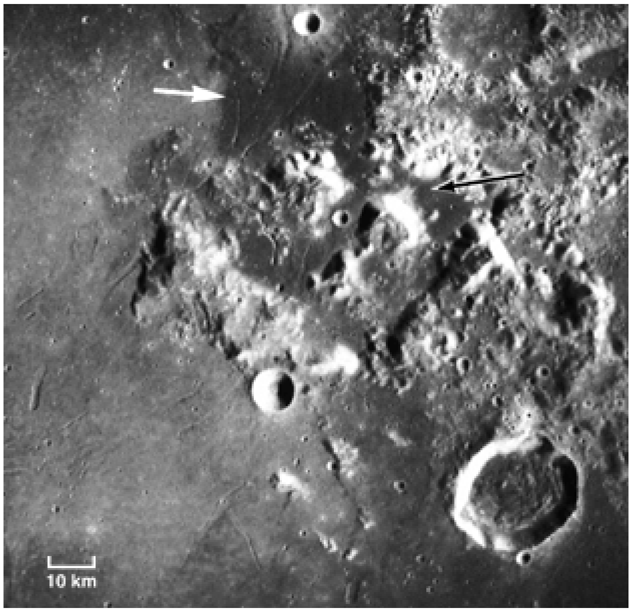
(Courtesy of E. Hauri.)

Photo of the Cameca IMS 6f used to analyze water and other volatiles in lunar volcanic glasses.

Hauri and his colleagues are experts in analyzing terrestrial volcanic glasses to understand how water cycles through the Earth and volcanic systems. They also study the water contents in minerals that are nominally anhydrous, such as pyroxene, garnet, and olivine in rocks from the Earth's mantle. They have found that the water measurements require driving down the background for hydrogen. Backgrounds are always present in instruments and even adsorbed on samples, and the amount of the element of interest has to be larger than the background in the machine and generated by the analysis. Hauri and his colleagues used three main tricks to decrease the background for hydrogen (which works for sulfur, chlorine, and fluorine, too). First, they used procedures to ensure that the vacuum in the instrument was very good, less than 1 trillionth of atmospheric pressure. Second, they used a primary beam consisting of positively-charged cesium ions, which are much more efficient at producing OH^- ions from the sample than the negatively-charged oxygen ions that are usually used. Third, they used an aperture to mask the region outside the center of the crater sputtered by the primary ion beam, thereby decreasing contamination from the walls of the crater and the polished sample surface. The result is that water can be analyzed if present at more than a few parts per million, and F, S, and Cl at even lower levels (0.1 parts per million).

Lunar Volcanic Glasses

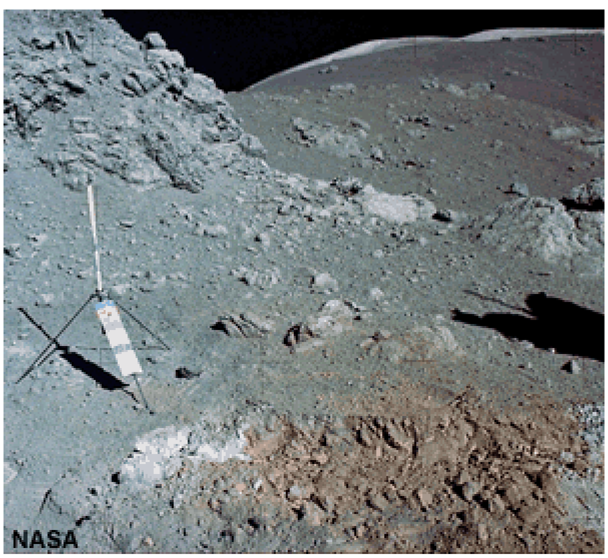
Alberto Saal has been interested in processes in the Earth's mantle, including how water migrates through it, so it was natural for him to become interested in lunar magmas, too. No doubt his colleague at Brown, Macolm Rutherford, spiked his interest. Rutherford has decades of experience in lunar science, with a focus on laboratory experiments on magma production and modification, including volcanic glasses. Lunar volcanic glasses contain a huge amount of information about the lunar interior, in part because of the wide range in their chemical compositions. This compositional difference shows up in the colors of the glasses--red have the highest titanium (about 15 wt% TiO_2) and green the lowest (less than 1 wt% TiO_2). One puzzle is to understand the source of the gas that drove the eruptions that deposited billions of little glass spheres. For more information about lunar volcanic glasses, see **PSRD** article: Explosive Volcanic Eruptions on the Moon.

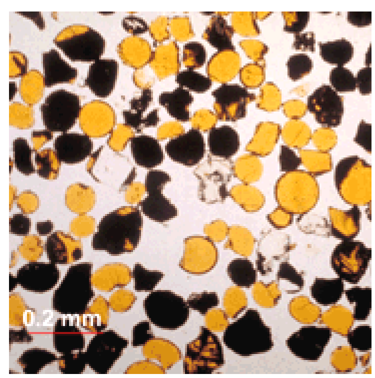


NASA photo, Apollo 17 frame M-5000

(Photo courtesy of the National Park Service.)

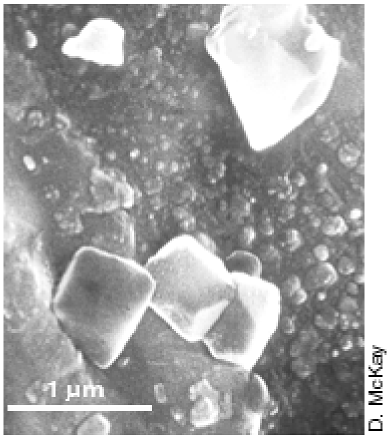
Photo on the **(left)** shows a dark deposit (white arrow) surrounding the Apollo 17 landing site (black arrow). Field work and samples revealed that the deposit, and probably others like it elsewhere on the Moon, is composed of volcanic glass beads formed in explosive eruptions like the one shown at **right** at Kilauea Volcano, Hawai'i.





Astronauts Jack Schmitt and Gene Cernan sampled this orange deposit **(left)** at the Apollo 17 landing site. The deposit is composed of numerous glass spheres, averaging about 80 micrometers in diameter, as shown on the **right** in a photomicrograph of a thin section of the sample (by Graham Ryder, Lunar and Planetary Institute.) The sample was mounted in epoxy and ground down to 30 micrometers thick. 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.

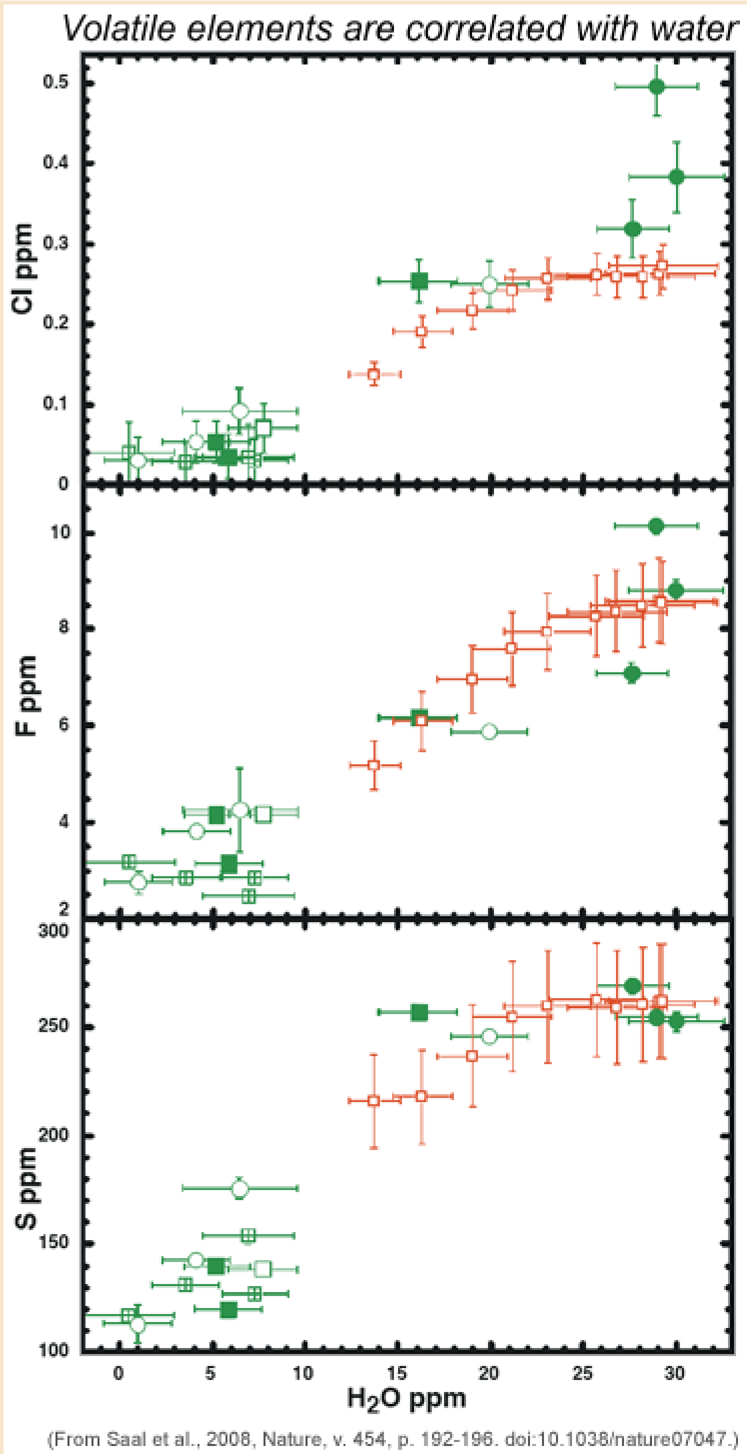
The pyroclastic glasses are notable for their elevated concentrations of relatively volatile elements, such as chlorine, fluorine, sulfur, lead, and several elements that behave geochemically like lead. It thus seems logical to search the volcanic glasses for even more volatile species, such as H_2O, which Saal and colleagues did.



Orange glass spheres contain deposits of volatile substances. The faceted ones, in this black and white view using a scanning electron microscope, are sodium chloride (table salt). The bumpy surface layer is composed of other elements, including sulfur, fluorine, and chlorine. These deposits are typical of lunar volcanic glasses and their volatile-rich nature shows that such glasses are logical places to use for searching for more volatile compounds, such as H_2O.

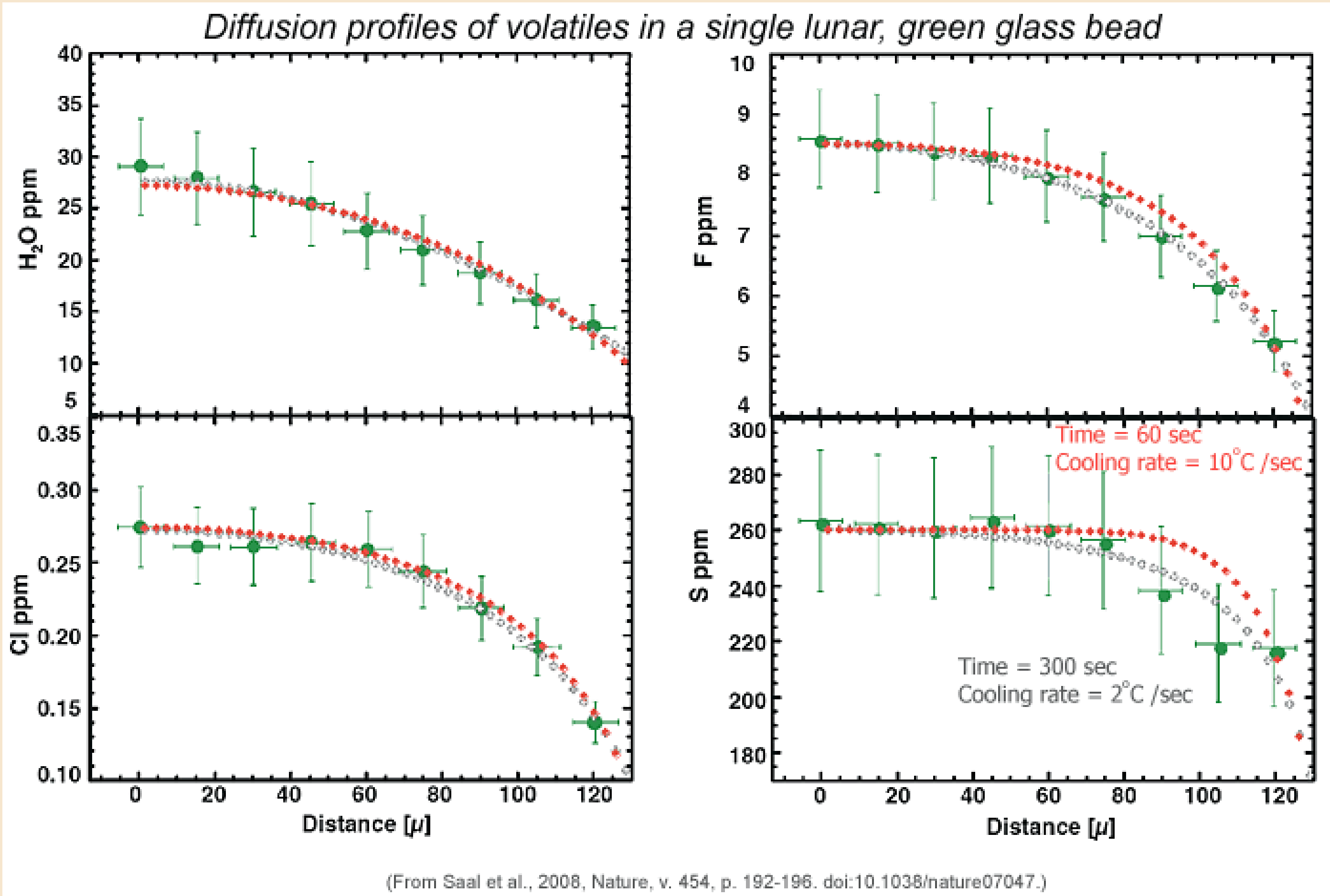
Possible New View: A Damp Moon

The new analyses of lunar volcanic glass beads by Saal and co-workers seem to show conclusively that at least some water is present in the beads and, hence, in the magma when it erupted. It might be possible that the hydrogen is not from water but instead originated by solar wind implantation. However, Saal and his coworkers argue convincingly that this is highly unlikely. For one thing, the hydrogen concentration is higher inside the beads. If implanted by the solar wind after eruption, hydrogen (measured by the OH^- anions sputtered from the glass) should be higher near the surface of each bead. Furthermore, the measured H_2O correlates with the concentrations of chlorine (Cl), fluorine (F), and sulfur (S), as shown in the diagrams below, but the solar wind contains only small amounts of those elements. It seems clear that there is H_2O in the volcanic glasses.



Volatile elements are correlated with H2O concentration in volcanic glass beads. The very-low-Ti green glasses are plotted in green symbols, and high-Ti orange glasses are plotted in orange symbols. Different symbols represent samples. The trend of increasing H2O with increasing Cl, F, and S supports the idea that all were present in the magma, but were lost to the surroundings after eruption and dispersion of the magma into small droplets. The differences in volatile concentrations between glass compositional types indicate variations in the amount of volatile elements inside the Moon.

The concentration of H_2O and the other volatiles decreases from the centers of the beads to the edges, indicating that they were lost to the surrounding tenuous, temporary volcanic atmosphere as the erupted magma disrupted into tiny droplets. The loss of water makes it tricky to calculate the amount present originally in the magma, a crucial number to determine. Clearly, there was at least the amount of water now present in the glasses, the largest value of which is 46 parts per million. However, Saal and his co-workers thought they could do better than that. They noted that the concentration of all the volatiles they measured varies smoothly from the center to the edge, suggesting that they were lost by diffusion out of the glass beads. If they knew how fast each volatile diffused through the glass and how long the diffusion time was, they could calculate how much of each volatile there was in each glass.



Variation in the concentrations of volatiles in a single green glass bead. The green data points show the concentrations in the glass, from center (left) to edge. The red diamonds and gray crosses show the variation predicted by two calculations of cooling time and cooling rate. To fit the measured compositional profiles, the initial concentration of water would have to be 70 parts per million for the fast-cooling case and 745 parts per million for the slower-cooling case. Looking at how close the calculated and measured data fit for all four volatiles, it appears that the best agreement is for the slowly-cooled (gray) case, suggesting that the water content might be as high as 745 parts per million before eruption.

To calculate the diffusive loss of volatiles, Saal and his colleagues followed the procedures used in a paper about lunar volcanic glasses by Bobby Fogel (now managing research programs at NASA Headquarters) and Mac Rutherford. This takes into account variation in the rates of diffusion with temperature, important because the spheres are cooling, and assumes evaporation from the surface of the spheres.

The mathematics of diffusion is complicated and many solutions to the diffusion equations need to be done numerically. Fortunately, a famous book by John Crank (The Mathematics of Diffusion) has worked almost all of it out, and Fogel and Rutherford, and Saal and coworkers, use the solution for diffusion in a sphere with simultaneous evaporation from the surface. Thus, as water molecules reach the surface, they are lost to the surrounding gas, thereby decreasing the concentration in the underlying glass. They are replaced by water molecules diffusing from the interior, which produces a characteristic curve on a plot of distance from the center versus concentration, as shown in the graph above. (Crank's book is one of those invaluable resources for those of us who have done diffusion calculations. The solution to the diffusion equation can be found for numerous practical cases, including different shapes (spheres, rectangular solids, and cylinders), varying surface compositions and constant surface compositions, constant diffusion rates and variable rates, and more. You have to know some math, though!)

Using published data for diffusion rates of H_2O, Cl, F, and S, Saal and his colleagues calculated the diffusion profiles by assuming different starting concentrations, and then compared the calculated concentration-distance profiles to those measured in the glass beads. If the assumed initial concentration is too low, the resulting concentration profile is too flat. Conversely, if the assumed initial concentration is too high, the profile is too steep. As shown in the graphs above, the best fits to the measured compositional profiles were the cases where the initial concentration of water was between 70 and 745 parts per million. Looking at how close the calculated and measured data fit for all four volatiles, the best agreement is for the slowly-cooled (gray symbols in the diagrams) case, suggesting that the water content might be as high as 745 parts per million before eruption.

Typical terrestrial mid-ocean-ridge basalt glasses (which do not lose their volatiles because they cool so fast and are surrounded by water at high confining pressure) have H_2O concentrations between 750 and 2000 parts per million. This implies that the lunar glasses might have had almost as much water as do terrestrial basalts. In turn, this implies that the parts of the lunar mantle that melted to form the pyroclastic glass magmas might have contained as much H_2O as does the Earth's mantle. This is a surprising result that is bound to spark new research.

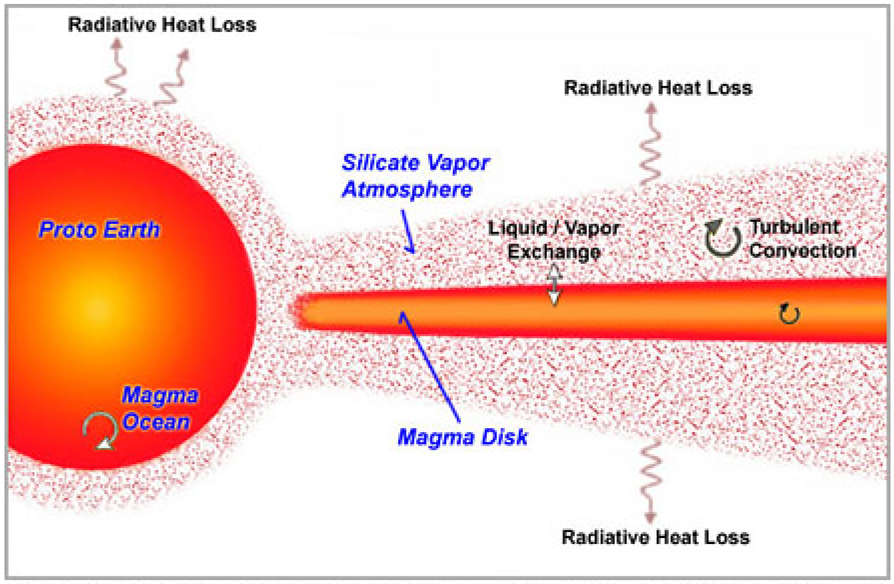
Other Hints of Water in the Moon

Francis McCubbin and colleagues at the State University of New York, Stony Brook, and Washington University in St. Louis have reported that the mineral apatite in some lunar samples might contain significant amounts of OH^-. Apatite has the ideal formula $Ca_5(PO_4)_3$ (F,Cl,OH). McCubbin and his colleagues measured the concentrations of all the pertinent elements, using an electron microprobe at Washington University and procedures developed for the accurate determination of Cl and F. If the elements are measured accurately, the mineral has a composition reflecting its ideal formula, and no other elements occur in the F-Cl-OH site in the crystal, then by measuring F and Cl alone we can assess whether OH^- is also present. The results suggest that for samples with high abundances of potassium, rare earth elements, and phosphorus (so-called KREEP samples), there seems to be a deficiency in the F-Cl-OH site, suggesting the presence of the OH^- molecule, hence the presence of water in the magma that produced the samples. The team plans to measure hydrogen by ion microprobe to measure its concentration directly. This research is just beginning.

The Importance of Water in the Moon

Besides possibly overturning a long-held tenant of lunar science that proclaims that the Moon is bone dry, the discovery of water in lunar samples has implications for the conditions existing during lunar formation. It is particularly important for understanding how and when Earth obtained its water. Understanding how much water there was initially in the Moon is pertinent to understanding delivery of water to the inner Solar System and to unraveling the details of lunar formation. The amount of water in the Moon also would have affected the compositions, movement, eruption, and crystallization of lunar magmas, depending on how much water resided in the Moon.

Most planetary scientists think that the Moon formed as the result of the impact of a Mars-sized impactor with the primitive Earth. There is nothing gentle about such an impact and the result is an atmosphere of vaporized rock surrounding the primitive Earth, connected to which is a disk of molten rock and silicate vapor, as depicted in the diagram on the right. In this story of planet formation, the Moon forms from the surrounding disk, called the "proto-lunar disk." Kaveh Pahlevan and David Stevenson (Caltech) have studied some of the chemical processes that would operate in this short-lived disk, and suggest that there was considerable chemical equilibration between the proto-lunar disk and the primitive, molten Earth, facilitated by the continuous silicate atmosphere.



(PSRD graphic based on Pahlevan and Stevenson, 2007, *EPSL*, v. 262, p.438-449, Fig. 3.)

The proto-Earth and the proto-lunar disk immediately after the giant impact, as depicted by Pahlevan and Stevenson. Rapid loss of heat into space causes convection in the Earth, the magma disk, and the silicate atmosphere, all of which facilitate exchange of material to even out differences in isotopic and chemical compositions. Cosmochemists will investigate the fate of water contained in the impactor and the growing Earth in this hot environment, assuming that the Earth and the impactor had significant water when the impact took place.[Click for enlargement.]

If the Earth and the impactor had water in them, what happened to it? If the Moon is bone dry, either the Earth and the impactor had none, or processes in the proto-lunar disk caused the complete loss of water. This might have happened by water molecules being transported to the surface of the silicate atmosphere, where it could be split into hydrogen and oxygen, with preferential loss of the very light hydrogen. Or, chemical reaction between water molecules and other chemical species, especially metallic iron, might cause the formation of iron oxide and hydrogen, followed by loss of hydrogen. Alberto Saal and his colleagues suggest that this process was not 100% efficient and that water, if present, was not completely lost.

The Moon is also depleted in other volatile elements and compounds, even those we do not think of as being volatile, such as potassium and sodium. David Stevenson pointed out in a summary paper in 1987 that the proto-lunar disk is likely to be a closed system, a system from which little is lost, except possibly for hydrogen. It turns out that in spite of the huge amount of energy involved in a giant impact, the vaporization of lots of silicate rock, and the high temperature of the proto-lunar disk and its silicate atmosphere, the thermal energy is smaller than the amount of energy needed to escape from the system, so there is little loss of volatiles.

If volatiles were not lost during the giant impact, why is the Moon so depleted in them? Or is it? In particular, how depleted was it initially in the highly volatile substances such as water? Saal and his coworkers have starting us thinking about this, and their paper will stimulate a lot of work. Other cosmochemists are skeptical about the results, especially the high concentrations of water inferred from the diffusion calculations. The water fight has just begun!

Additional Resources

LINKS OPEN IN A NEW WINDOW.

- **PSRDpresents:** The Bone-Dry Moon Might be Damp --Short Slide Summary (with accompanying notes).

- Hauri, E., Wang, J., Dixon, J. E., King, P. L., Mandeville, C., and Newman, S. (2002) SIMS analysis of volatiles in silicate glasses 1. Calibration, matrix effects and comparisons with FTIR. *Chemical Geology*,

v. 183, p. 99-114.

- Martel, L. and Taylor, G. J. (2006) Ion Microprobe. *Planetary Science Research Discoveries.* http://www.psrd.hawaii.edu/Feb06/PSRD-ion-microprobe.html
- McCubbin, F. M., Nekvasil, H., Jolliff, B. L., Carpenter, P. K., and Zigler, R. A. (2008) A survey of lunar apatite volatile contents for determining bulk lunar water: How dry is "bone dry"? *Lunar and Planetary Science XXXIX,* abstract #1788. Lunar and Planetary Institute, Houston.
- Moon Water Discovered: Dampens Moon-formation Theory from Carnegie Institution for Science.
- 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.
- Weitz, C. M. (1997) Explosive Volcanic Eruptions on the Moon. *Planetary Science Research Discoveries.* http://www.psrd.hawaii.edu/Feb97/MoonVolcanics.html

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