

WHERE HAS ALL THE LUNAR WATER GONE? Lawrence A. Taylor¹, George R. Rossman², and Qu Qi¹; 1 = Planetary Geosciences Institute, Department of Geological Sciences, University of Tennessee, Knoxville, TN 37996; 2 = Div. of Geol. & Planet. Sci., Calif. Institute of Technology, Pasadena, CA 91125.

One of the first significant findings from study of the lunar rocks was the apparent absence of any minerals containing water. Apatite and amphibole were reported, but the hydroxyl sites were occupied by chlorine and fluorine. Estep et al. [1] studied various lunar minerals, basalts, and glasses by infrared and raman vibrational spectroscopy and found no evidence for hydroxyl (= water), further verifying the anhydrous nature of lunar samples. Subsequently, the mineral akaganeite, FeOOH, was found in many lunar rocks, especially 66095 and other Apollo 16 rocks [2-3]. But this was conclusively shown to be due to terrestrial contamination [2-4]. Effectively, the extremely deliquescent mineral lawrencite, FeCl₂, underwent oxyhydration to form the "rust" when exposed to the Earth's atmosphere. However, water has been observed to evolve from all samples of lunar soil upon heating, even up to 400 °C. This water is largely a contaminant; however, some of it is possibly lunar. Friedman et al. [5], Zeller et al. [6], Gibson and Moore [7], and others felt that small amounts of water could be synthesized on the outer few 100 Å of soil particles from solar-wind protons. [Note: protons are effectively hydrogen nuclei.] This still remains the general consensus (E.Gibson, pers. comm.). But this remains only a theory without positive proof.

Agglutinates in the lunar soil are a likely place to find water. Agglutinates are effectively aggregates of lithic fragments, minerals, and glasses welded together by impact-produced, vesicular glass. The unique aspect of this agglutinitic glass is the presence of billions of minute native Fe grains (i.e., Fe⁰) [review by 8]. The majority of these tiny grains are "single-domain" Fe⁰ less than 200 Å in diameter. Tsay et al. [9] were the first to explain this apparent phenomena. It is generally accepted that the lunar soil is saturated with solar-wind implanted particles, notably protons and carbon nuclei. When a portion of the soil is melted by micrometeorite impact, these elements impose an extreme reducing environment upon the melt such that Fe²⁺ in the silicate melt is effectively reduced to Fe⁰ which forces nucleation and growth of this myriad of tiny Fe⁰ spheres. The reaction can be simply written as FeO_(l) + H₂ = Fe⁰ + H₂O. The vesicular nature of the agglutinitic glass is probably due to escaping water, as well as any remaining solar wind. However, because of the extremely rapid quenching of the agglutinitic glass, as witnessed by the fine-grain size of the native Fe, some of this water is probably still contained in the glass. With this thesis in mind, we decided to search for evidence of this water.

One of the best methods for observing water (= OH) in solid materials is using FTIR spectroscopy. This has been demonstrated by the finding of hydroxyl in normally anhydrous terrestrial minerals such as olivine, ortho- and clinopyroxene, quartz, rutile, zircon, etc. [10-11]. Indeed, the water budget of the Earth's mantle may be largely explained by small amounts (up to 2000 ppm) of OH in olivine and pyroxene and their polymorphs [12]. Using this same sensitive method, we have attempted to investigate the possible presence of water in certain lunar minerals and agglutinitic glasses.

EXPERIMENTAL METHOD - Infrared spectra were obtained with a Nicolet 60SX FTIR and a NicPlan IR microscope. Samples were run both as doubly polished self-supporting slabs and as polished slabs mounted on fused silica slides. Sample thickness typically was in the range of 125-160 µm. Sample areas for examination depended upon the sample and were defined by mechanical apertures in the range of 50 to 175 µm in width. Limits of detection were estimated using a representative molar absorption coefficient of 80 for water in glass. When samples were glued to a supporting slide, strong absorption bands from the adhesive occur in the region of the spectrum where the signal from OH and water is expected. Such interferences were minimized by correcting the spectra by computer-subtracting the spectrum of the adhesive until the C-H bands of the adhesive were minimized. In general, such corrections are never exact, and the limits of detection are significantly worse than those with the unmounted samples.

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Table 1. Lunar phases examined for OH⁻ by FTIR.

Phase	Sample
Clinopyroxene	15555, 869
"	70035, 107
Agglut. Glass	70019, 143
"	70182, 5
"	71502, 10
"	75122, 3

OBSERVATIONS - With the aid of the Lunar Curatorial Staff, we obtained several samples for examination for the possible presence of water. These are listed in Table 1. Specifically, sample 77019 is an agglutinate breccia and several portions of the agglutinitic glass directly in contact with poorly indurated soil were examined. With the 1-2 mm soils, 70182, 71502, and 75122, several typical agglutinates were selected through examination with a binocular microscope.

The results of our examination of all the lunar samples listed in Table 1 is that **any OH⁻, if present, is below the detectability limit of the FTIR measurements.** A conservative estimate of the detectability limit is in the range of 50 ppm.

DISCUSSION - *Where has all the water gone??* The absence of any OH⁻ in lunar clinopyroxene is obviously a result of the anhydrous nature of the igneous systems on the Moon. But the results on the agglutinitic glass are surprising. Let's analyze this situation more. A typical lunar rock contains 14-20 wt% FeO. If these rocks are comminuted to soil and melted by micrometeorite impact, the melt contains 15% FeO, for example. A conservative estimate would have that about 1/3rd of this FeO is reduced by reaction with solar wind. This would produce over 1 wt% H₂O. Even accounting for volatile loss in the formation of vesicles, it would be expected that the glass should retain several 1000 ppm H₂O.

Factors to be Considered: The temperatures in normal igneous systems seldom reach higher than the liquidus. However, with impact melts, the temperatures can reach > 2000°C, well above the melt liquidus. Couple this with the nature of the atmosphere on the surface of the Moon, which is an effective "very hard" vacuum of 10⁻¹² to 10⁻¹⁴ torr (mm Hg). Diffusion rates of chemical species in melts at such temperatures are extreme. As a first approximation, the diffusion of H₂O or OH⁻ in a silicate melt at 1200 °C would appear to be sufficient for the H₂O to escape to the vacuum in < 1 second. However, perhaps the thesis that the agglutinates ever contained lots of water is wrong. This would necessitate that the single-domain Fe must have formed by another reduction mechanism, possibly involving carbon. It is possible that the protons (i.e., hydrogen) are so loosely bound that they would be scavenged by the vacuum before reacting with the melt, whereas the solid carbon particles would be retained to cause the reduction.

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