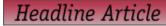


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# The Tarnished Moon

--- Remote sensing observations reveal the presence of ferric iron in the form of the mineral hematite at high latitudes on the Moon, possibly the product of reaction of ferrous iron on the Moon with oxygen from the Earth's upper atmosphere.



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 $\mathbf{F}$  erric iron (Fe<sup>3+</sup>) is rare in lunar samples and when found it has been ascribed to contamination after arrival on our oxygenrich planet. However, using data obtained by the Moon Mineralogy Mapper (nicknamed M<sup>3</sup>) on the Indian Space Research Organization's Chandrayaan-1 lunar orbiter, Shuai Li (University of Hawai'i) and colleagues at U. Hawai'i, Jet Propulsion Laboratory, University of California at Berkeley, Applied Physics Lab at Johns Hopkins University, and Brown University show that the mineral hematite (Fe<sub>2</sub>O<sub>3</sub>) is present at latitudes above 60 North and South on the Moon. The reddish mineral is

particularly abundant on the Earth-facing side of the Moon. Using radiative transfer modeling and M<sup>3</sup> data, Li and coworkers estimate that the hematite occurs as grains at least 1 micrometer across and ranges in abundance (where detected) from a few weight percent to 10 weight percent. Considering that lunar rocks are inherently too reducing to form ferric iron, the presence of highly oxidized iron is surprising. Li and coworkers suggest that the source of the oxygen could be the upper atmosphere of the Earth. They hypothesize that oxygen is ripped from the upper atmosphere and deposited on the lunar surface when Earth passes between the Sun and the Moon. If correct, it shows an interesting cosmic linkage between the Earth and the Moon.

#### Reference:

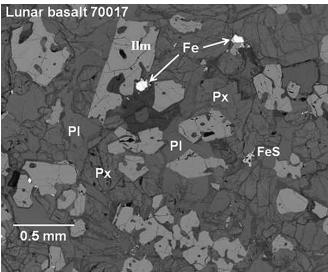
- Li, S., Lucey, P. G., Fraeman, A. A., Poppe, A. R., Sun, V. Z., Hurley, D. M., and Schultz, P. H. (2020) Widespread hematite at high latitudes on the Moon, Science Advances, v. 6, eaba1940, doi: 10.1126/sciadv.aba1940. [article]
- PSRDpresents: The Tarnished Moon --Slide Summary (with accompanying notes).

## The Reduced Moon

One of the countless fascinating differences between Earth and Moon is the Moon's much more reduced state. This is seen clearly in lunar rocks, in which essentially all the iron is in the 2+ oxidation state (Fe<sup>2+</sup>), rather than 3+. In fact, many samples collected by the Apollo missions contain tiny grains of metallic iron (Fe<sup>0</sup>). For example, lunar basaltic lava flows precipitate small grains of metallic iron late in their solidification whereas terrestrial basalts precipitate magnetite (Fe<sub>3</sub>O<sub>4</sub>), in which half the iron is in the 3+ oxidation state. In both cases, most of the iron is in the 2+ oxidation state and resides in minerals such as pyroxene, olivine, and ilmenite. Although oxygen makes up about half the Moon (and the rocky portions of the terrestrial planets), free oxygen available to react with other elements is not very abundant on the Moon. The amount of available oxygen in any rocky system can be viewed as related to the partial pressure of oxygen gas available to react with the components in the rock. The concept is captured by the term **fugacity**, which is a partial pressure corrected for the nonideal behavior of the gas. It is as if the oxygen were in an atmosphere that permeates a magma or rock. In fact, the fugacity is measured in terms of

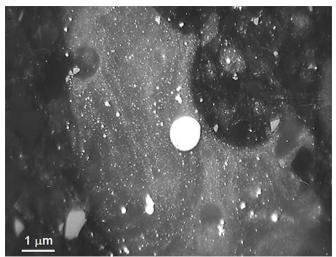
atmospheric pressure. This atmosphere is rather tenuous: In most magmas, oxygen fugacity ranges from  $10^{-10}$  to  $10^{-18}$  atmospheres of pressure. ( $10^{-10}$  means that the oxygen partial pressure is one ten-billionth of the pressure at the surface of Earth.)

With higher oxygen fugacity, there is more  $Fe^{3+}$  (ferric iron) and less  $Fe^{2+}$  (ferrous iron) in the iron-bearing minerals in a rock. In some cases, the oxygen fugacity is so low that iron occurs as  $Fe^{2+}$  and uncharged (metallic) iron. Moon rocks are like that: They contain tiny bits of metallic iron.



Photograph of a lunar basalt taken in reflected light using an optical microscope. Lunar basalt 70017, collected during the Apollo 17 mission in December 1972, contains two sizable grains of metallic iron (labeled "Fe" on the photo). As in all basalts, most of the rock consists of pyroxene (Px) and plagioclase (Pl). This high-titanium basalt contains a lot of ilmenite (FeTiO<sub>3</sub>), reflecting the high titanium concentration in the magma. The sample also contains iron sulfide (FeS). (Image from A. G. Tindle and M. Anand, *Moon Minerals: A Visual Guide*, p. 92, Open University, UK. See the **iBook** from The Open University for more information.)

Metallic iron is also abundant in the lunar **regolith**, where it has formed by reduction of Fe<sup>2+</sup> by hydrogen from the **solar wind**. This often creates striking distributions of minuscule metallic iron grains in glasses produced by impact melting of the rubbly lunar surface. This abundant metal shows that in general the lunar surface is highly reducing because of the presence of hydrogen derived from the Sun via the solar wind. It is not a welcoming environment for making hematite, in which all the iron is Fe<sup>3+</sup>.



This scanning electron microscope photograph of a lunar regolith particle shows countless microscopic grains of metallic iron formed by reduction of iron oxide present in the glass, which

makes up most of the particle. Most spherules of iron are substantially submicron in size, but a few have coalesced to form larger spheres up to a micrometer in diameter. (Image courtesy of David S. McKay, NASA Johnson Space Center.)

## **Hematite on the Reduced Lunar Surface**

So, the lunar surface seems to be the last place to look for a ferric-iron-bearing mineral like hematite. But Shuai Li and colleagues point out in their paper that minerals containing ferric iron are present in some lunar samples, one of which, Apollo 16 impact melt breccia 66095, was nicknamed "rusty rock." The reddish color comes from the presence of ferric iron oxide-hydroxide minerals such as goethite and akageneite. Both have the approximate formula Fe<sup>3+</sup>O(OH). At the time of their discovery their presence was ascribed to the effects of cometary impacts into the Moon (comets have lots of water) or to contamination of water-free salts with terrestrial water, perhaps even the moist Pacific Ocean air that filled the command module after splashdown.

Apollo 16 Lunar Surface Photo of Sample 66095 Collection



Laboratory Photo of a Rusty Area in Sample 66095



NASA image S72-48424. (above) NASA photo AS16-107-17523. (left)

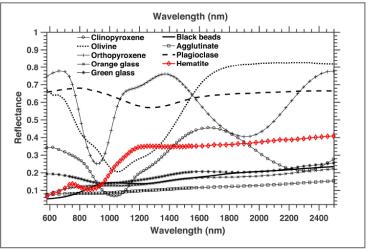
[LEFT] Photograph from the Apollo 16 Image Library showing the rock on the lunar surface that Astronaut John W. Young hit with a hammer to collect a piece (seen lying on the surface at right center) that would be named sample 66095. [RIGHT] Close up photograph of a rusty area in Apollo 16 sample 66095, taken in the Lunar Curatorial Facility at NASA's Johnson Space Center. The image is about 1 cm wide.

Besides rusty rock, hints of ferric iron came from remote sensing data acquired when NASA's Galileo spacecraft flew past the Earth-Moon system in 1990 and 1992 on its way to Jupiter. Galileo carried an instrument called the Solid State Imager (SSI), with wavelengths from 0.35 to 1.1 micrometers (the visible to near-infrared range). There was a weak **spectral** feature around 0.7 micrometers at high latitudes of the Moon (north and south of 58 degrees), but investigators could not determine what caused the spectral feature. A ferric iron mineral was one possibility, but so was ilmenite and even phyllosilicates (clay minerals containing H<sub>2</sub>O or OH molecules). Nevertheless, it showed that further study would be worth the effort.

Li and colleagues note that hematite detection using reflectance spectral observations is feasible because hematite has spectral properties quite different from major lunar minerals (see diagram below). The presence of Fe<sup>3+</sup> in hematite causes an absorption near 0.85 micrometers, a region that is not shared by the common lunar minerals or by other ferric oxides. The deep

absorption centered near 0.85 micrometers is diagnostic and quite strong. It is like a DNA profile, except that nobody goes to jail. Shuai Li used data from the Moon Mineralogy Mapper (M<sup>3</sup>) on the Indian Space Research Organization's Chandrayaan-1 lunar orbiter.

# Reflectance Spectra of Lunar Surface Minerals

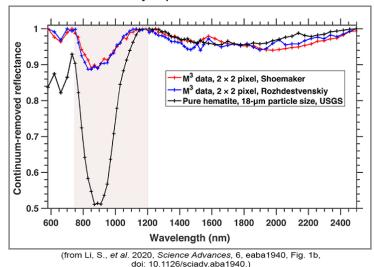


(Li, S., et al., 2020, Science Advances, 6, eaba1940, fig. S1b, doi: 10.1126/sciadv.aba1940.)

Reflectance spectra obtained in the laboratory of typical lunar surface minerals, orange and green volcanic glasses, and impact glasses (agglutinates), compared to a hematite standard (red diamonds). The valley around 0.85 micrometers (850 nanometers) is not matched by other materials common on the lunar surface.

The hematite spectrum stands out like a sore thumb. In the remote observations with the continuum (the overall background spectrum) removed, the reddish, swollen thumb is even easier to see (see graph below), as the absorption band descends like the Grand Canyon from the surrounding plateau. Two spectra are shown for craters near the lunar poles, Shoemaker (51 km in diameter) near the South Pole and Rozhdestvenskiy (42 km in diameter) near the North Pole. The hematite feature is clearly seen in the spectra from both craters.

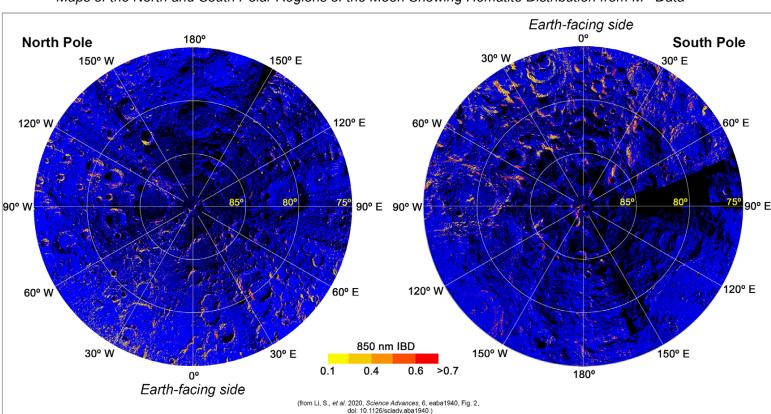
# Comparison of Hematite-rich M<sup>3</sup>Spectra with Laboratory Spectra of Pure Hematite



Examples of reflectance spectra obtained with the M<sup>3</sup> instrument onboard the Chandrayaan-1 lunar orbiter. The black is a laboratory spectrum of pure hematite (USGS is United States Geological Survey) and the other two spectra are large craters near the North (Rozhdestvenskiy) and South (Shoemaker) poles of the Moon. The background spectrum (called the continuum) has been removed

to emphasize the features of the absorption bands. To allow for mapping the hematite distribution on the Moon, the researchers added the band depths of all the points in the valley from 750 to 1200 nanometers (shaded area) and named this parameter the *Integrated Band Depth* (IBD); see map below.

To visualize the hematite distribution on the Moon, Li and coworkers developed a parameter to characterize the intensity of the hematite valley in the spectra obtained by the M³ spectrometer on Chandrayaan-1. They added up the spectra points between 750 and 1200 nanometers (from the rim to the floor of the hematite valley), giving one number per spectrum. They call this value the *Integrated Band Depth* (IBD). Each spectrum (hence, its mapped IBD), has a spatial resolution on the lunar surface of between 140 and 280 meters per pixel. Maps of the North and South Polar regions of the Moon (at latitudes of 75 degrees and higher) are shown below. The conclusion is obvious: Hematite is present on the lunar surface. The maps show the hematite occurrences at latitudes greater than 75 degrees but in fact, almost all the hematite detections occur at latitudes greater than 60 degrees. Furthermore, an asymmetry exists in the distribution of hematite: In both polar regions, most of the hematite detections are on the Earth-facing hemisphere (the Earth direction is 0 degrees on each map). Finally, the floors of craters (visible as shaded relief beneath the colors on the maps) rarely contain hematite signals; flat places do not have much hematite. So, hematite is associated with the Earth-facing directions of the lunar polar regions.



Maps of the North and South Polar Regions of the Moon Showing Hematite Distribution from M<sup>3</sup> Data

Map derived from M<sup>3</sup> data showing hematite detections (shown in yellow, orange, and red), as revealed by the IBD parameter. Most of the mapped areas are simply blue, indicating no detectable hematite. Black spots are places with no M<sup>3</sup> data of sufficient quality to use; these are mostly places in shadow or where the solar illumination angle was too low. Above all, these maps show clearly that hematite is present on the lunar surface, but also note that the hematite occurrences are on the Earthfacing sides (the Earth direction is 0 degrees on each polar view). Finally, crater floors rarely contain hematite.

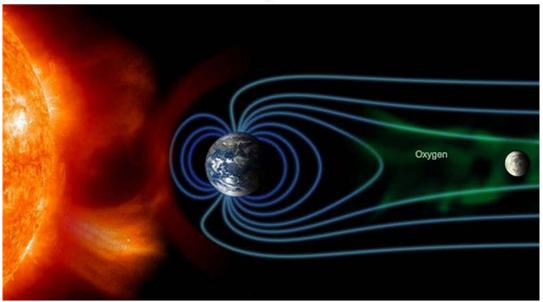
Shuai Li and co-authors estimate the amount of hematite detected. To do this they used the spectral data and calculations involving how light is transferred in the surface materials. This lab- and theory-based process, called radiative transfer modeling is well established, though not without uncertainties. They estimate that the detected hematite on the lunar surface is larger than one micron and ranges in abundance from a few weight percent to about 10 wt%. Much of the lunar surface has hematite abundances lower than the detection limits of the measurements.

## Source of the Oxygen

**T**o produce the observed hematite on the generally reducing lunar surface it is essential to add oxygen. Li and colleagues outline the possibilities, pointing out the complex set of processes involved in the environment at the lunar surface: There is no air, solar wind bathes the surface and implants hydrogen (a reductant, opposite of an oxidizer), and micrometeorite impacts add considerable heat and in most cases water. None of these add oxygen in a form that would change iron from the 2+ to the 3+ oxidation state.

So where does the oxygen come from? Shuai Li and team suggest it comes from Earth's upper atmosphere. They follow up on the intriguing suggestion of Kentaro Terado (Osaka University, Japan) and colleagues at Nagoya University and the Japanese Aerospace Exploration Agency that oxygen from Earth's uppermost atmosphere is transported to the Moon. (See PSRD CosmoSparks Report: Flux of O+ Ions from Earth to the Moon.) Terado and colleagues draw attention to the detection of surges in the concentration of oxygen ions in the lunar exosphere by the Kaguya spacecraft when the Moon passes through the central portion of Earth's magnetotail (the region known as the Earth's plasma sheet, see diagram below). Shuai Li and colleagues point out that not only is oxygen added to the lunar surface, but during this short (a few days) time each month, most of the solar wind (hence most of the reducing gas hydrogen) is blocked from the Moon. The result is that the stage is set for oxygen to react with ferrous iron oxide to form ferric iron oxide-hematite. The effect would be strongest on the Moon's Earth-facing hemisphere, consistent with the distribution determined by Li and colleagues using M<sup>3</sup> data.

# Illustration of Earth's Magnetic Field and the Moon



(from Osaka University)

Earth's magnetic field protects us from the solar wind and the more energetic solar flares. Downwind (meaning down solar wind) from the Earth, the terrestrial magnetic field is stretched out into the magnetotail, the central portion of which is a region called the plasma sheet. Atoms can be torn from Earth's upper atmosphere (which has a high concentration of oxygen) and incorporated into the plasma sheet. When the Moon passes through this region, which it does once a month when the Moon is full, it is shielded from the hydrogen-rich (and reducing) solar wind and is showered by oxygen ions from Earth's upper atmosphere. It is this combination of lower hydrogen implantation and much higher oxygen addition to the lunar regolith that might have made conditions just right for the formation of hematite.

Li and colleagues go into detail about the precise mechanisms involved in lunar oxidation, suggesting that it may involve not only straight oxidation, but also reactions involving H<sub>2</sub>O and/or OH molecules to produce FeOOH, which subsequently decomposes to hematite. The precise set of reactions will not really be known until we collect samples from known hematite occurrences and examine them with optical and electron microscopes in labs on Earth. Whatever the details turn out to be, oxidation occurs on the Moon, despite its generally highly reducing environment. That pretty orb in the sky is filled with

surprises.

### **Planet Interactions**

**T** ransport of oxygen ions from Earth's uppermost atmosphere to the Moon may seem surprising, but it is just one of numerous interactions among the bodies in our Solar System. Energy from the Sun drives all surface geologic processes, including weathering, erosion, and deposition of sediments. Large solar events called solar flares can disrupt space-based communication networks. Impact of asteroids or comets may have caused periodic extinctions of most of life on Earth, including dinosaurs due to an impact 65 million years ago. Our knowledge of the history of our Solar System derives from study of meteorites, chips of asteroids and even planets (Martian meteorites) that are liberated by impacts onto their parent bodies and then travel for millions of years to land on Earth. And don't forget those footprints on the Moon, left by Earthlings driven by their sense of exploration.

## Additional Resources

Links open in a new window.

- **PSRDpresents:** The Tarnished Moon -- **Slide Summary** (with accompanying notes).
- Li, S., Lucey, P. G., Fraeman, A. A., Poppe, A. R., Sun, V. Z., Hurley, D. M., and Schultz, P. H. (2020) Widespread hematite at high latitudes on the Moon, *Science Advances*, v. 6, eaba1940, doi: 10.1126/sciadv.aba1940. [article]
- Martel, L. (May 2017) Flux of O+ Ions from Earth to the Moon, *Planetary Science Research Discoveries*, www.psrd.hawaii.edu/CosmoSparks/May17/magnetospheric-oxygen.html.
- Terada, K., *et al.* (2017) Biogenic oxygen from Earth transported to the Moon by a wind of magnetospheric ions, *Nat Astron.*, v. 1, 0026, doi: 10.1038/s41550-016-0026. [article]
- Tindle, A. G. and Anand, M. (2019), *Moon Minerals: A Visual Guide*, iBook, p. 92. Open University, UK. [iBook link (pdf) from The Open University]



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