Commentary: Spectrum Misreading - Most of the Lunar Water Detected by M3 Might Actually Be Lunar Methanol

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Abstract

We have to face an important and urgent problem: even though according to spectral detection, we cannot conclude that there is much water ice on the Moon as the prevailing theory claims. We might have overlooked the widespread presence of methanol on the Moon. After the interstellar methanol ice fell onto the Moon, the methanol in it was retained due to the strong adsorption of methanol in the carbon-rich lunar regolith and the water in it could be divided into two situations: one involved in catalytic reactions with methanol on lunar surface and another one escaped to the deep space because of harsh environment. The rest of methanol might still be widespread on lunar surface. M3 is unable to distinguish between hydroxyl radicals from water ice and hydroxyl groups from methanol because the absorption strengths of the two are all 2.9 μm, and there are no established methods to distinguish them using the 2.9μm band. Thus, most of the lunar water detected by M3 might be lunar methanol. Attention should be paid to previous misreading of the spectrum. The so-called surficial water illogically appeared at lunar equator, seriously shaking the credibility of M3 spectra data analysis. The vast quantities of hydrogen found in lunar polar craters should be hydrogen ice, which easy to confuse with water ice. The author has also made a preliminary study of the physical / chemical process chains on lunar surface. It is necessary to conduct in-depth research in this field in the future.

Commentary: Spectrum Misreading - Most of the Lunar Water Detected by M^3 Might Actually Be Lunar Methanol

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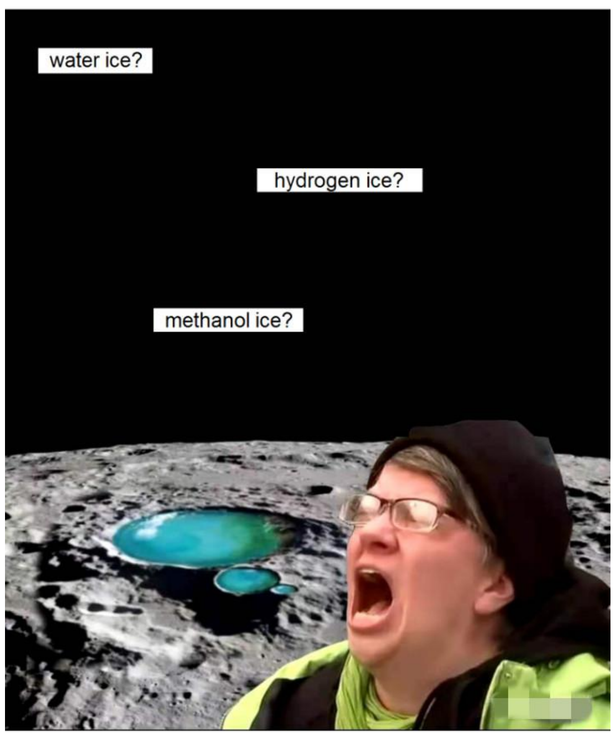
Key Points:

- M^3 is unable to distinguish between hydroxyl radicals and hydroxyl groups because the absorption strengths of the two are all 2.9 μm
- The so-called surficial water appeared at lunar equator based on M^3 spectral detection, shaking the credibility of M^3 spectra data analysis
- The vast quantities of hydrogen found in lunar polar craters should be hydrogen ice, which easy to confuse with water ice

Graphical Abstract:



Key Words: Moon; Water ice; Lunar methanol; Hydroxyl radicals; Hydroxyl groups; Hydrogen ice.

Abstract

We have to face an important and urgent problem: even though according to spectral detection, we cannot conclude that there is much water ice on the Moon as the prevailing theory claims. We might have overlooked the widespread presence of methanol on the Moon. After the interstellar methanol ice fell onto the Moon, the methanol in it was retained due to the strong adsorption of methanol in the carbon-rich lunar regolith and the water in it could be divided into two situations: one involved in catalytic reactions with methanol on lunar surface and another one escaped to the deep space because of harsh environment. The rest of methanol might still be widespread on lunar surface. M^3 is unable to distinguish between hydroxyl radicals from water ice and hydroxyl groups from methanol because the absorption strengths of the two are all 2.9 µm, and there are no established methods to distinguish them using the 2.9 µm band. Thus, most of the lunar water detected by M^3 might be lunar methanol. Attention should be paid to previous misreading of the spectrum. The so-called surficial water illogically appeared at lunar equator, seriously shaking the credibility of M^3 spectra data analysis. The vast quantities of hydrogen found in lunar polar craters should be hydrogen ice, which easy to confuse with water ice. The author has also made a preliminary study of the physical / chemical process chains on lunar surface. It is necessary to conduct in-depth research in this field in the future.

Plain Language Summary

I lean towards there being far less water on the Moon than is generally stated in the news. Moreover, I believe we all agree that many possibilities other than water ice (solid H_2O) exist that can explain many of the observations that are often described as "water on the Moon" by various publications (especially newspapers/websites). Another place I see the data misinterpreted and/or misquoted is when people are trying to sell something --- especially people who want to use lunar water as a resource. Well, it's time to take a fresh look at whether the Moon has lots of water ice.

1 Introduction

The Albert Einstein once said, "The formulation of a problem is often more essential than its solution."(Einstein, **1938**).

The author finds a problem that we might have not paid attention to before: the absorption strengths of hydroxyl radicals from water and hydroxyl groups from methanol are all 2.9µm. Therefore, it is easy to confuse hydroxyl radicals and hydroxyl groups when interpreting M^3 spectra data(Sun, **2020**).

It must be noted that a fundamental vibration of molecular water can produce a spectral signature at 6 µm that is not shared by other hydroxyl compounds(Starukhina, **2001**). SOFIA claimed to find "molecular water" based on "a 6 µm emission feature at high lunar latitudes"(Honniball, et al., **2020**). In fact however, what SOFIA found at 6 µm spectral signature is water molecules stored within glasses or in voids between grains(Honniball, et al., **2020**), or "water molecules locked in mineral grains on the surface of the Moon -- magmatic water, or water that originates from deep in the Moon's interior"(Siddiqi, **2018**; NASA, **2019**), not water ice.

However, crystalline water normally cannot be separated easily from minerals and is not the water resources we crave. Thus, lunar crystalline water is meaningless when discussing whether the Moon has water.

S. Li et al.(**2018**) once said that "There are a number of strong indications of the presence of water ice in similar cold traps at the lunar poles, but none are unambiguously diagnostic of surface-exposed water ice, and inferred locations of water ice from different methods are not always correlated."(Li, et al., **2018**)

Moreover, an unprecedented upper limit of the OH (MgI) content in the lunar exosphere was obtained from the in-situ measurements carried out by LUT of China Chang'E-3 Mission. "The upper limit of <10^4/cm^3 derived for the OH radicals is lower than that derived from the HST low-resolution spectroscopy by about two orders of magnitude, and is lower than that inferred from the mass spectra taken by the Chandrayaan-1 mission by about 6 orders of magnitude"(Wang et al., **2015**). The lower the actual measurement of the OH (MgI) content in the lunar exosphere, the less likely it is that lunar exosphere will deliver enough water to lunar cold traps.

The high temperature caused by large and small objects hitting the Moon's surface, coupled with the lack of lunar atmosphere and low gravity, as well as lunar water's consuming by reacting with lunar methanol(in detail below), making lunar surface difficult to preserve water. Therefore, no matter how much water that brought by comets and asteroids or the one caused by solar wind, the lunar water will be almost lost out.

As to water from lunar exosphere to lunar cold traps, the in-situ measurement values derived by LUT of China Chang'E-3 Mission above(Wang et al., **2015**) have seriously shaken this unproven hypothesis of lunar cold trapped water. Schörghofer, N. et al. (**2021**) also considered that "Exospheres can transport water to cold traps, but the efficiency of this process remains uncertain"; "no part of this process has yet been confirmed."(Schörghofer et al., **2021**)

In fact, no water was involved in the formation of the Moon:

(1) The main lunar rocks are anorthitite, basalt and breccia, and no aqueous rocks such as sandstone, shale and limestone which are very common on the Earth(Ouyang, **2005**);

(2) Lunar minerals are generally devoid of water. Elements in lunar minerals are all low-valence, for example, divalent or zero valences for iron. This shows that lunar minerals were formed in a strict reducing environment with no water. The main lunar minerals are pyroxene [$(Ca,Fe,Mg)_2Si_2O_6$], anorthite [$(Ca,Na)(Al,Si)_4O_8$], olivine [$(Mg,Fe)_2SiO_4$], ilmenite ($FeTiO_3$) and spinel ($MgAl_2O_4$); No primary and secondary hydrated minerals (such as clay, mica and amphibole) were found(Ouyang, **2005**).

(3) There have not existed any trace of flowing water on the Moon. On the contrary, there are a lot of traces of flowing water on the Mars.

Recently, China Chang'E-5 revealed a dry lunar mantle(Hu et al., **2021**; Lin et al., **2022**).

The existing M^3 data are best interpreted as representing the presence and distribution of OH and provide no unambiguous evidence for the presence of H_2O(Li & Milliken, **2017**). A very important question is whether this "OH" is hydroxyl radicals of lunar water or hydroxyl groups from Moon's methanol?

So that, the presence of much water on our Moon is worthy of renewed scrutiny.

In this article, only spectral misreading of M^3 lunar water detection will be discussed.

2 There is much methanol on our Moon

2.1 Source of lunar methanol

Methanol (CH_3OH) is an important interstellar molecule. Solid methanol is an important constituent of ice in the interstellar medium(Dawes et al., **2016**). CH_3OH has been observed in comets and on the surfaces of trans-Neptunian objects(Dalle et al., **2014**). In dense molecular clouds, CH_3OH is observed to be one of the most abundant constituents of ice after H_2O and CO(Pontoppidan, **2004**).

2.2 Presence evidences of methanol on the Moon

● "Carbon dioxide, methane, ethylene, and methanol were all found to be part of the LCROSS plume"(Colaprete et al., **2010**). Please note that Carbon dioxide(CO_2), methane(CH_4) and ethylene(C_2H_4) are OH free except for methanol(CH_3OH). So, only methanol(CH_3OH) is eligible to participate in the spectroscopic debate with water(H_2O) in this article. In the same way, carbon monoxide(CO) is not considered either, although CO is much more common in comets than CH_3OH.

● It is necessary to point out that Qasim D. et al.(**2018**) studied the formation of interstellar methanol ice prior to the heavy CO freeze-out stage, and got an important result: CH_3OH formation is shown to be possible by the sequential surface reaction chain, $CH_4 + OH \rightarrow CH_3 + H_2O$ and $CH_3 + OH \rightarrow CH_3OH$ at 10–20 K. The end products of various chemical reactions above are methanol (CH_3OH) and water (H_2O).

After the interstellar methanol ice fell onto the Moon, the methanol in it was retained due to the strong adsorption of methanol in the carbon-rich lunar regolith and the water in methanol ice would divided into two situations: one involved in catalytic reactions with methanol absorbed in the carbon-rich regolith using Pt/C catalysts(please see Section **3.1** in detail) and another one would escape out to the deep space because of the harsh lunar environment.

Does Carbon(C) exist widespread on the Moon? The answer is yes. The evidences are as follows:

● "Lava associated with lunar fire fountains contained significant amounts of carbon"(Saal et al., **2015**).

● "There would appear to be 1.72% carbon from carbonaceous condrites"(Krahenbuhl et al., **1972**).

● Carbon may also be directly implanted in the lunar regolith from the solar wind(Bibring et al., **1974**; Pillinger & Eglinton, **1977;** Haskin & Warren, **1991**).

In fact, the abundance of carbon in lunar regolith alone is enough to absorb large amounts of methanol(Carrott et al., **2001**).

Furthermore, "CH_3OH, NH_3 and complex organic species survive during low-speed comet impacts as products of disequilibrium processes"(Berezhnoy et al., **2012**).

Therefore, methanol should be widespread on the surface of the Moon.

2.3 It is easy to confuse hydroxyl radicals and hydroxyl groups when interpreting M^3 data

The "absorption strengths" of hydroxyl radicals and hydroxyl groups are all ~2.9 μm.

● "The absorption strength of hydroxyl radicals is ~2.9 μm"(Li & Milliken, **2017**).

● "A broadband absorption at 2.9 μm due to the presence of the hydroxyl groups"(Zhao et al., **2015**).

● The Moon Mineralogy Mapper (M^3) on Chandrayaan-1 has recently detected absorption features near 2.8 to 3.0 micrometers on the surface of the Moon. "For silicate bodies, such features are typically attributed to hydroxyl- and/or water- bearing materials"(Pieters, **2009**).

● "The overlapping of observed CH_3OH vibrational absorption bands with H_2O and silicate absorption features"(Dawes et al., **2016**).

● Widespread hydration was detected on the lunar surface through observations of a characteristic absorption feature at 3 μm by three independent spacecraft. "Whether the hydration is molecular water (H_2O) or other hydroxyl (OH) compounds is unknown and there are no established methods to distinguish the two using the 3 μm band"(Honniball et al., **2020**).

● "Some of the measurement techniques do not distinguish between water (H_2O) and hydroxyl (OH), so 'water group' (OH or H_2O) is a frequently used term"(Schörghofer et al., **2021**).

Therefore, it is easy to confuse hydroxyl radicals and hydroxyl groups when interpreting M^3 data.

Considering the confusion caused by the spectral properties of lunar water with lunar methanol, how did some scientists get such viewpoint that methanol in lunar polar craters as a substantially smaller fraction of the ice than water?

It must note that hydroxyl radicals and hydroxyl groups are two different concepts: hydroxyl radicals belong to the ion, whereas hydroxyl groups are the type of functional groups in organic matter, at least exist in methanol(Gracia et al., **2008**).

The so-called surficial water illogically appeared at the lunar equator based on M^3 spectral detection("equatorial latitudes may contain some amount of surficial water during early morning and late afternoon, consistent with the Deep Impact observations")(Sunshine et al., **2009**; Li & Milliken, **2017**), seriously shaking the credibility of M^3 spectra data analysis. Please note that the lunar equator, where the extremely high temperature is up to 150℃(Ouyang, **2005**).

3 What kind of ice is in the lunar polar craters? Water ice? Hydrogen ice or methanol ice?

3.1 Catalytic reactions of producing hydrogen

On our Earth, methanol can react with water to produce molecular hydrogen, with a very high efficiency of low-temperature hydrogen production using Pt/α-MoC catalysts. These reacts form large amount of hydrogen (Lin et al., **2017**).

In fact, besides the Pt/α-MoC catalysts, there is a better Pt/C catalyst. Pt/C catalyst is the most active Hydrogen Evolution Reaction catalyst. Hydrogen Evolution Reaction can be realized at a voltage very close to the electromotive force of the thermodynamic reaction(Tang et al., **2002**; Zhou et al., **2018**). Since Pt(Platinum)(Shieber, **2018**) and C(Carbon)(Saal et al., **2015**; Krahenbuhl et al., **1972**; Bibring et al., **1974**; Pillinger & Eglinton, **1977**; Haskin & Warren, **1991**) are very abundant in the carbon-rich lunar regolith, this catalysis can be easily realized.

3.2 The origin of molecular hydrogen in the lunar exosphere

In situ experiments from the Apollo missions confirmed the presence of a tenuous exosphere on the Moon comprised of atoms and light molecular species(Crandall et al., **2019**).

As the most prominent volatiles found in the exosphere, molecular hydrogen (H_2) has drawn considerable attention. And where did the molecular hydrogen come from?

Except the proton bombardment of silicate minerals from the solar wind(Crandall et al., **2019**) and protons from the Earth's magnetotail plasma(Starukhina & Shkuratov, **2000**), the author suggests that the escaping of molecular hydrogen, which the result of water reacting with methanol in the carbon-rich lunar regolith, should be main origin of molecular hydrogen in the Moon's exosphere.

3.3 The leading actor within lunar exosphere should be hydrogen rather than water

As pointed out above(please see Section Introduction in detail), there is almost no water in lunar exosphere (The upper limit of $<10^4/cm^3$ derived for the OH radicals is lower than that inferred from the mass spectra taken by the Chandrayaan-1 mission by about 6 orders of magnitude)(Wang et al., **2015**).

Thus, the lunar cold traps hypothesis also holds if we change the water for hydrogen: exospheres can transport molecular hydrogen to lunar cold traps, thus clarifying a question NASA raised that "Scientists have long speculated about the source of vast quantities of hydrogen that have been observed at the lunar poles."(NASA Content Administrator, **2017**)

3.4 What is the state of the vast quantities of hydrogen in lunar polar craters now?

It found mid-winter, night-time surface temperatures inside the coldest craters—the south western edge of the floor of Hermite crater, the southern edges of the floors of Peary and Bosch craters in the northern polar region—can dip as low as minus 249°C (26K)(NASA Lunar Science Institute, **2009**), very close to the boiling point of hydrogen (minus 252.88°C) and the melting point of hydrogen (minus 259.35°C) on our Earth(Abe, **2007**).

We cannot exclude the presence of lower temperatures in the much deeper locations of these lunar craters at North Pole, not to mention those at the bottom of lunar craters in the southern polar region where the sunlight never reached. If the temperature in those lunar polar craters mentioned above would be measured to further reduced by only 3.88°C, it would have reached the boiling point of hydrogen (minus 252.88°C, if on the Earth), forming liquid hydrogen(Abe, **2007**); and on this basis, if the temperature be further reduced by 6.47°C, it would have reached the melting point of hydrogen (minus 259.35°C, if on the Earth)(Abe, **2007**), forming brown~black solid molecular hydrogen that appeared in snowflake patterns(Anon, **2019**).

Given that atmospheric pressure on the lunar surface is 10,000 times smaller than that on the Earth and lunar atmospheric density is 14 orders of magnitude smaller than that of the Earth(Ouyang, **2005**), what are the boiling point and the melting point of hydrogen on the lunar surface respectively? Moreover, the catalytic temperature required for the catalytic reaction of producing hydrogen on the Moon should be very different from the catalytic temperature on Earth. Is it necessary for the scientific community to conduct some relevant simulation experiments?

The pressure on the Moon is much lower than the triple point of hydrogen. So that, the liquid hydrogen on the Moon is not stable, it will be either gas or solid. The gas hydrogen will rise up to lunar exosphere and the solid one will become into hydrogen ice.

The existence of the solid molecular hydrogen(hydrogen ice) in lunar polar craters could consistent with phenomena observed as follows:

1. Total internal reflections;
2. Increase in the same sense polarization;
3. Planar surface;
4. Maximum hydrogen abundance.

Therefore, hydrogen ice in lunar polar craters would be easy to confuse with water ice.

3.5 Physical / chemical process chains on lunar surface

The interstellar methanol ice fell onto the Moon(physical) → the methanol in it was retained due to the strong adsorption of methanol in the carbon-rich lunar regolith(physical) and → the water in it could be divided into two situations: one reacted with methanol absorbed in the carbon-rich regolith to produce massive molecular hydrogen using Pt/C catalyst(Chemical); and another one would escape out to the deep space because of the harsh lunar environment(physical) → The rest of methanol might still be widespread on lunar surface(physical/chemical) → molecular hydrogen produced by the catalytic reaction mentioned above rose up into lunar exosphere(physical) → exospheres transported molecular hydrogen to lunar cold traps(physical)

→ forming brown~black solid molecular hydrogen (hydrogen ice) that appeared in snowflake patterns under extremely low temperature within lunar polar craters (physical/chemical).

4 Discussion

As everyone knows that the essence of science is its falsifiability.

Stephen W. Hawking also once said, ”you can disprove a theory by finding even a single observation that disagrees with the prediction of the theory. ”(Hawking, 2017)

Now, we all find such “a single observation”, i.e., the so-called surficial lunar water appeared at the lunar equator, thus showing that the analysis of M^3 spectral data could be seriously problematic.

5 Conclusions

We have to face an important and urgent problem: even though according to spectral detection, we cannot conclude that there is much water ice on our Moon as the prevailing theory claims.

We might have overlooked the widespread presence of methanol on the Moon. The real situation might be: After the interstellar methanol ice fell onto the Moon, the methanol in it was retained due to the strong adsorption of methanol in the carbon-rich lunar regolith and the water in it could be divided into two situations: one involved in catalytic reactions with methanol on lunar surface using Pt/C catalysts and another one would escaped out to the deep space because of the harsh lunar environment. The rest of methanol might still be widespread presence on the lunar surface.

M^3 is unable to distinguish between hydroxyl radicals from water and hydroxyl groups from methanol because the absorption strengths of the two are all 2.9 μm, and there are no established methods to distinguish them using the 2.9 μm band. Thus, most of the lunar water detected by M^3 might actually be lunar methanol.

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Conflicts of interest

There are no conflicts to declare.

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