Water in Lunar Materials

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I. THEORY

Two lines of evidence, as follows, suggest independently that materials which formed the Moon were not anhydrous:

1. Meteorites, our only sample of extraterrestrial material, contain water in varying amounts. Chondrites average about 0.25% water by weight. Carbonaceous chondrites, however, contain up to 20% water; and, although much of this water may be adsorbed atmospheric and surface water, the abundance of silicate hydrates in these objects indicates that considerable water existed in these meteorites before Earth impact.
2. The gas emission from Alphonsus observed by Kosyrev (Ref. 1) indicates that volatiles are diffusing out of the Moon. The observed emission was a C_2 band. Analyses of presumably juvenile gases reaching the Earth's surface show that water generally composes 95% or more of the gas. By analogy, it is suggested that water must be reaching the lunar surface.

Consequently, it is reasonable to conclude that water existed in the materials which formed the Moon as well as those which formed the Earth or meteorites (or their source object). An estimate of the water content of the primordial Earth is 0.03% (Ref. 2).

Water originally uniformly distributed throughout an accreted Moon would diffuse radially outward until a chemical potential gradient was established with lunar pressure and temperature gradients under which further flow of water would cease. This zero flow gradient may be expressed by

$$\frac{d\mu_{H_2O}}{dz} = \mathbf{M}_{H_2O}g - \left(S_{H_2O} + \frac{Q^*}{T}\right)\frac{dT}{dz}$$

where lateral gradients are zero and M is the mass of a mole of water, g is gravitational acceleration, z is depth, S is molar entropy of water, and $Q^* \equiv Q - H_1$; Q is the energy transported per mole of H_2O, H_1 is the partial molar enthalpy of water, and μ_{H_2O} is the chemical potential of water. This problem is extended by a number of possible complicating factors: i.e., convection of rock masses in the Moon, fusion in the lunar interior, strength of lunar interior and depth of fracture, and degree of nonideality of diffusing fluids.

Diffusion of water radially outward in the Moon should continue until a zone is reached in which hydration and absorption can occur. Neglecting the latter, it can be estimated that hydrous silicates are unstable below 250–300 km depth in the Moon where pressure is around 12–14 kbar. The temperature at this level would be around 1000°C if the Moon is assumed to have a uniform distribution of a chondritic abundance of K^{40}, U^{238}, U^{235}, and Th^{232}. The upper surface of this hydration zone will be either the lunar surface or, in the case of some hydrous silicates which partially to totally dehydrate in vacuum, some shallow depth down to 20 m, where the load pressure has increased to 1 bar. Greater depths would be required if water is completely mobile in the surface materials. Within the zone of hydration, assemblages of hydrous silicates will change vertically in accordance with the temperature, pressure, rock composition, and water diffusivity gradients in the zone. In

general, however, successive silicate assemblages should be progressively more hydrous as the exterior of the hydration zone is approached. As water enters this zone, a partition will occur between hydration and continued diffusion to the surface. If very deep fissures are absent in the Moon, it seems unlikely that much water could have reached the surface, considering the great thickness of the hydration zone through which the diffusing water had to pass, unless the Moon contained an unusually large amount of primeval water. It should be emphasized that, because of the complete uncertainty of flow rates, it is not clear whether all water over the equilibrium amount has reached the zone of hydration in 4.5×10^9 years. Table 1 shows bulk water contents of the hydration zone as a function of original lunar water content, assuming complete degassing of the interior and no loss of water at the surface.

Table 1. Bulk water contents of the hydration zone

Bulk lunar water wt. %	Hydration-zone water wt. %
0.03	0.067
0.3	0.67
3.0	6.7

II. OCCURRENCES OF WATER

Possible occurrences of water on the Moon are as follows:

a. Crystalline Hydrates. Table 2 lists crystalline hydrates and their water contents by the most prominent natural chemical systems. The temperatures of dehydration given in the Table were obtained by differential thermal analysis (Fig. 1), and the temperatures so derived depend upon the rate of heating and environmental gas pressure. This is not a reversible process, and the temperatures are not equilibrium dehydration temperatures. Heating rates for most of these runs were 5–10°/min. For lower heating rates, dehydration temperatures would be a little lower.

Heat requirements H for dehydration of these phases are given by

$$H = \int_0^{T_D} C_{PdT} + \Delta H_D$$

where the subscript D = dehydration. Calculated results specified in calories per gram of H_2O derived are given in the last column of Table 2 for phases in which heat capacity as a function of temperature and heat of dehydration data are known. For phases in which data do not exist, energy requirements are guessed, and categorized on the basis of other mineralogical considerations. As a result, it is clear that energy requirements for water extraction from minerals are widely varied. Consequently, the need for exploration for hydrous mineral assemblages with lowest dehydration energy requirements is indicated.

b. Glasses. Volcanic glasses on Earth contain up to 0.5% by weight juvenile water. Secondary water, the source of which is chiefly groundwater, occurs in partly to wholly devitrified glasses in amounts from 2–6%. Dehydration temperatures for water in volcanic glasses are generally less than 300°C.

c. Adsorbed Water. Adsorbed water occurs in rocks with widely different adsorption bond strengths. The amount of adsorbed water will differ greatly with composition of the adsorber. For instance, powdered olivine and SiO_2 glass were both exposed to the atmosphere for several days. Adsorbed water was not detected on the olivine, whereas the SiO_2 glass adsorbed 4% water.

Table 2. Prominent hydrous phases, temperatures of their dehydration peaks, and energy requirements for dehydration

Mineral	Composition	H_2O wt. %	T (at 1 atm) °C	H_2O* cal/g
	$MgO\text{-}SiO_2\text{-}H_2O$			
Brucite	$Mg(OH)_2$	31.0	410	1075
Chrysolite and lizardite	$Mg_6Si_4O_{10}(OH)_8$	13.0	637–715	~ 2200
Antigorite	$Mg_6Si_4O_{10}(OH)_8$	13.0	790–802	2550
Anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	3.4	1020	> 700
Sepiolite	$Mg_3Si_4O_{11} \cdot 5(H_2O)$	12.0	775	B
Talc	$Mg_3Si_4O_{10} \cdot (OH)_2$	4.5	970	7000
Stevensite	$2xM \pm Mg_{3-x}Si_4O_{10}(OH)_2 \cdot nH_2O$	17.5	830	B
	$MgO(FeO)\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$			
Chlorite	$Mg_4Al_2(Al_2Si_2)O_{10}(OH)_8$	12.9	680, 840	~ 3100
	$Fe_4Al_2(Al_2Si_2)O_{10}(OH)_8$	11.4		
	$Al_2O_3\text{-}SiO_2\text{-}H_2O$			
Gibbsite	$Al(OH)_3$	34.6	350, 500	832
Montmorillonite	$X_4(Al, Si)_8O_{20}(OH)$	14.0	125, 650, 850	B
Kaolinite	$Al_4Si_4O_{10}(OH)_8$	14.0	600	1983
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	5.0	630–850	6800
	Alkali-$Al_2O_3\text{-}SiO_2\text{-}H_2O$			
Paragonite	$NaAl_2(AlSi_3)O_{10}(OH)_2$	4.7	700–900	C
Muscovite	$KAl_2(Al_1Si_3)O_{10}(OH)_2$	4.5	700–900	5100
Biotite	$K(Mg, Fe)_3(Al, Si_3)O_{10}(OH)_2$	2.2 to 4.3	1100	D
Analcite	$NaAlSi_2O_6 \cdot H_2O$	8.2	300–400	B
Thomsonite	$Na_3CaAl_3Si_3O_{12}CO_3, OH_2$	3.9	400	C
Natrolite	$Na_2Al_2Si_3O_{10} \cdot 2H_2O$	9.5	420	B
Many other zeolites		8–28 (most around 15)		BC
	$CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$			
Amphiboles	$Ca_2(Mg\,Fe)_5(Al, Si)O_{22}(OH)_2$	2.2	1000–1100	D
Zoisite	$Ca_2Al_3Si_3O_{12}(OH)_2$	2.0	1000	D
Prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2$	4.4	825	CD
Laumontite	$Ca_7Al_{14}Si_{26}O_{80}\,25H_2O$	14.5	270, 450	B
Many zeolites		Around 15	Up to 400	BC
	Others			
Gypsum	$CaSO_4 \cdot 2H_2O$	20.9	200	A
Alums	e.g., $KAl(SO_4)_2 \cdot 12H_2O$	45.6	550, 850	A
Opal	$SiO_2 \cdot n(H_2O)$	1 to 28	100–400	A
Geothite	$Fe(OH)_3$		300	932

*A < 1500 cal/g H_2O
B = 1500–3000 cal/g H_2O
C = 3000–7500 cal/g H_2O
D > 7500 cal/g H_2O

De-adsorption in the latter material occurred at around 150°C.

d. Pore Water. Liquid or solid water may occur in pore spaces in near-surface lunar rocks in which water permeability is very low.

e. Surface Condensates. Some water which reaches the lunar surface will be concentrated in cold traps in shadowed parts of the lunar surface. Surface ice will probably be most prevalent at high latitudes. This problem has been discussed by Vestine (Ref. 4) and Watson (Ref. 2).

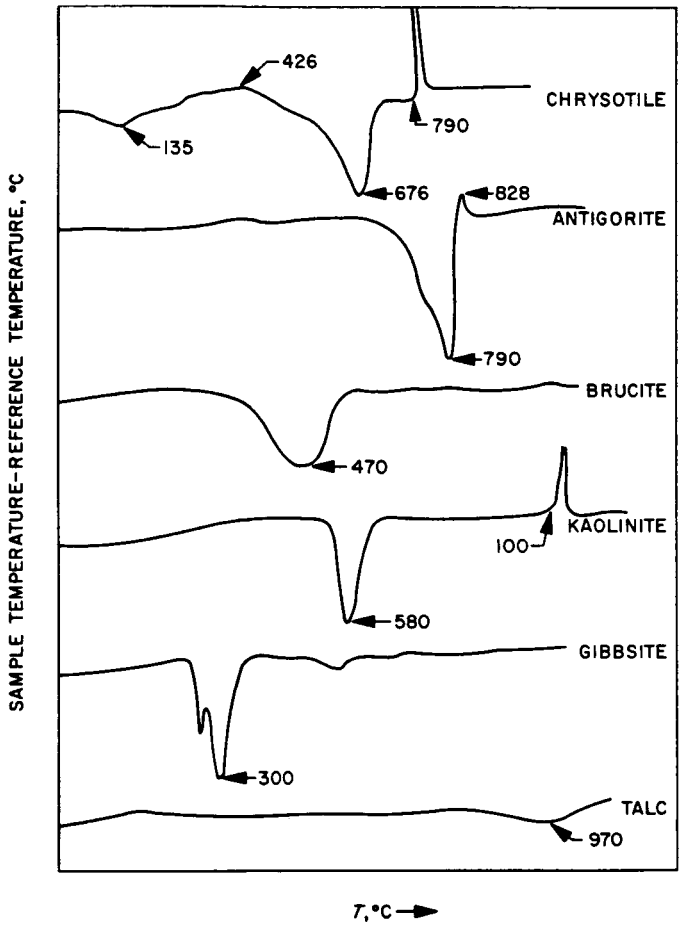

Fig. 1. Differential thermal analysis curves for selected hydrous minerals (reference: α Al_2O_3)

III. METHODS OF EXPLORATION FOR LUNAR WATER

A number of methods could possibly be used from unmanned and manned spacecraft for delineating the water content of surface or near-surface lunar rocks.

A. Spectral Analysis of the Lunar Thermal Emission From an Orbiting Vehicle

Hydroxyl (2.6 to 3μ) or molecular water (6.1μ) emission (or adsorption) minima may be detectable, and variations in the strength of these bands would be indicative of water abundance in the surface materials if variations in surface geometry on the spectra are understood (Ref. 5). Furthermore, spectral emittance at higher wavelengths (9 to 25 μ) is in many cases diagnostic of hydrous silicates. Figure 2 shows adsorption spectra of four magnesium silicates in which adsorption bands from 8–11 μ differ in the hydrous and anhydrous ones.

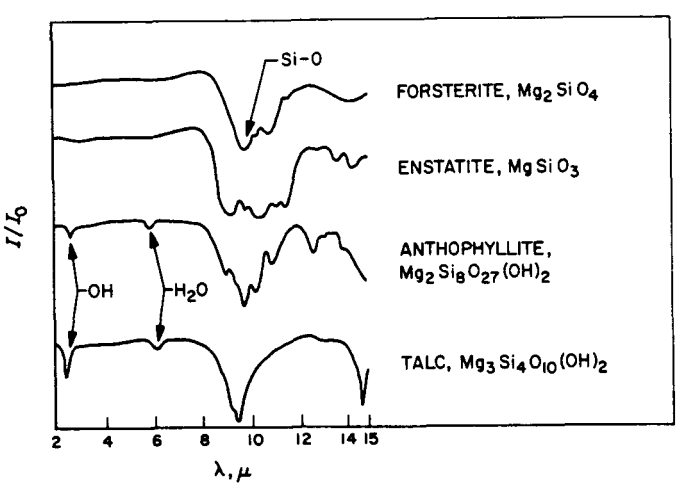

Fig. 2. Spectra of some silicates in the system $MgO\text{-}SiO_2\text{-}H_2O$

B. Ground-Based Geophysical Surveys

Combined magnetic, gravity, and possibly, seismic surveys in certain rock types can delineate variations in the degree of hydration in these rocks. Figure 3 shows a magnetic traverse across a serpentinite near San Luis Obispo, California. Chemical composition and mineralogical changes across the body indicate that hydration in this rock mass has proceeded generally according to the reaction

$$\underset{\text{olivine}}{Mg_{24}Fe_6Si_{15}O_{60}} + 16H_2O + SiO_2 + O_2 \rightarrow$$
$$\underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{antigorite}}{4[Mg_6Si_4O_{10}(OH)_8]}$$

Textural evidence, however, indicates that the reaction took place with volume-for-volume replacement of the left-hand assemblage by the right-hand one rather than maintaining a closed chemical system. Figure 3 shows that the degree of oxidation of the iron and the magnetic susceptibility vary sympathetically across the body with water content; density varies antipathetically with water content. Consequently, the above reaction has gone furthest along the borders and least far in the center. The magnetic profile may be interpreted as superimposed anomalies across three adjacent dike-shaped bodies. The exterior bodies have greater magnetic field intensities than the inner one, and this difference may be correlated with their higher water content.

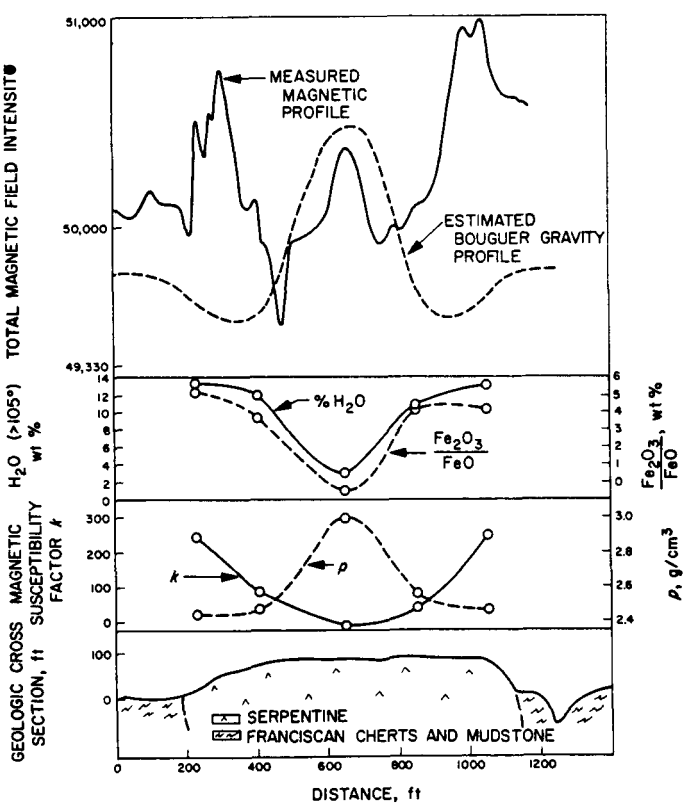

Fig. 3. Correlation of magnetic and gravity anomalies with content across a serpentine near San Luis Obispo, California

A gravity profile across this serpentinite has not yet been measured, but the variation in density is shown in Fig. 3d. Bouguer gravity anomalies of 1 to 7 milligal are calculated for the density variations in this body for various assumed configurations and depths of the body. If topographic corrections are very small, gravity anomalies might be useful in delineating zones of maximum hydration in ultrabasic rocks on the Moon.

Seismic velocities may also provide information on areas of maximum hydration in ultrabasic rocks. Compressional wave velocity in dunite (an anhydrous equivalent of serpentinite) is 8.6 km/sec, whereas compressional velocity of pure serpentine is 5.6 km/sec.

C. *Neutron Albedo*

The high thermal neutron cross-section of hydrogen may be a key to mapping zones of hydrous lunar rocks. Lingenfelter *et al.* (Ref. 6) have shown that ratios of thermal to fast neutrons leaking out of the lunar surface could provide information on the hydrogen content of lunar surface rocks. The utility of this method is not clear, however, since potentially high-spallation hydrogen content of surface rocks may provide an excessive background for measurement of amounts of hydrogen as water.

D. *Possible Qualitative Indicators of Hydrous Rocks*

1. Structures

Certain geologic structures may indicate paths of preferred movement of water in the peripheral part of the zone of lunar hydration. In the zone in which lunar rocks have sufficient strength to fracture, water would preferentially move out of these open spaces, since the chemical potential would be governed by hydrostatic rather than lithostatic pressure gradients. Rocks on the walls of these fissures may be highly hydrated. In particular, faults, fractures, fracture intersections, and other numerous linear features on the lunar surface might be zones of intense hydration. Furthermore, craters with observed activity (e.g., Alphonsus) should be examined.

2. Chemical Indicators

Anomalies in surface concentration of K^{40} and the uranium isotopes which could be mapped by an orbiting gamma-ray spectrometer may be indicative of zones of hydration. Both K and U are geochemically lithophyllic and may be dissolved in water moving toward the lunar surface. Precipitation of these materials during surface evaporation of water or incorporation in phases formed by hydration would concentrate these elements at places where the most water has reached the lunar surface.

In a similar manner, surface deposits of soluble salts may be indicative of places where water has preferentially reached the surface and at which hydration may have been widespread.

In the reaction involving hydration of ultrabasic rocks discussed in Section IIIB, it was mentioned that petrographic evidence indicates that the hydration proceeded volume-for-volume in an apparently open chemical system. This mode of hydration appears to be widespread on Earth, and the volume of the resulting lower-density hydrate assemblage is the same as that of the original anhydrous material. Consequently, some components must leave the system during the reaction. In the case of ultrabasic hydration, MgO must be given off. Consequently, concentrations of surficial magnesian salts may be indicative of hydration of ultrabasic rocks below. These minerals could possibly be detected by their thermal emission spectra.

E. *Other*

Lunar surface and subsurface materials would be analyzed for water during the course of general scientific exploration of the Moon. Ostensibly, lunar rocks will be investigated by unmanned and manned expeditions using conventional petrologic instrumentation such as x-ray diffraction, infrared adsorption, differential thermal analysis, and various methods of direct chemical analysis. Numerous simple methods of quantitative water analysis exist and could be used in conjunction with the foregoing experiments.

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