Reports

Water Vapor from a Lunar Breccia: Implications for Evolving Planetary Atmospheres

Abstract. *The exposure of a typical complex lunar breccia to hydrogen after a thorough outgassing produces a fully reduced surface state. Subsequent outgassing over a wide temperature range results in the production of water vapor formed from the chemisorbed hydrogen and oxygen from the lunar sample; the proposed mechanism has been confirmed in terms of the chemisorption of deuterium and the release of heavy water. Since the conditions of the experiments are consistent with those on the lunar surface, it is postulated that water vapor will be produced on the moon through the interaction of the solar wind with lunar soil. It is also proposed that such a process could play an important role in the early history of many planets where an oxygen-rich soil is exposed to a reducing atmosphere.*

In a recent report in the *Proceedings of the Third Lunar Science Conference* (*1*) Freeman *et al.* described a series of events that occurred on the lunar surface on 7 March 1971, namely, the instrumented observation of a sequence of apparent water vapor pulses. After due consideration of a number of aspects of these phenomena, these investigators concluded that the water vapor was not the result of contamination but was lunar in origin. Although this conclusion may or may not be correct, it is of interest to consider possible means of producing water vapor, not only on the moon, but on any planet lacking an atmosphere or lacking this particular constituent in its atmosphere.

For some time now, we have felt that a heterogeneous process could play such a role and that water vapor could be created from the combination of hydrogen (molecular or atomic) from a reducing atmosphere with oxygen in the planetary soil. Having available a number of lunar samples, we therefore designed a sequence of experiments to determine whether water vapor could be formed if these materials were exposed to a reducing atmosphere.

The complete sequence of experiments described here was performed on 1.2303 g of rock fragments 15565,3 [a typical complex breccia (*2*)], although similar and complementary studies were carried out on a variety of other samples (*3–5*). The experiments were conducted in an ultrahigh-vacuum, volumetric gas-adsorption system capable of attaining a background pressure of 10^{-10} torr and equipped with a quadrupole residual gas analyzer (RGA) (Electronic Associates, Inc., model 1110 A) (*6*). Details of this system will be published elsewhere (*7*). In essence, three separate experiments were carried out:

1) A preliminary lengthy outgassing of each sample plus system (25° to 150°C) accompanied by a study of the gases evolved from the samples as a funtion of temperature (150° to 400°C). This was followed by two rapid outgassings of each sample plus system to ensure that gas removal over this temperature range was essentially complete.

2) Equilibration of the sample at 150°C with a hydrogen atmosphere followed by a fourth outgassing (25° to 400°C).

3) Equilibration of the sample at 150°C with a deuterium atmosphere followed by a fifth outgassing (25° to 400°C).

We carried out the first outgassing by maintaining the sample plus system at 150°C for 20 hours, after which the sample temperature was raised in 20° to 30° steps at 1-hour intervals to 400°C, where it was maintained for some 10 hours. The total outgassing time was approximately 40 hours. After the first 20-hour period an equilibrium background gas pressure of 10^{-8} torr was attained. The subsequent sample outgassing (150° to 400°C) was carried out under steady-state pressure conditions in the 10^{-8} torr range, gas removal being accomplished with the use of two 8-liter/sec Vac-ion pumps. The spectra recorded on the RGA (150°C and above) indicated the release (in decreasing order of magnitude) of: water vapor; hydrogen; nitrogen or carbon monoxide, or both; carbon dioxide; methane; and other gases over the entire temperature range. Since similar spectra have been published elsewhere (*8*), and since we are not concerned here with the precise relative amounts of these gases, we wish only to state that, on the basis of our prolonged outgassing at 150°C, and in spite of exposure of the sample to a terrestrial atmosphere (*9*), we believe that much of the water vapor released at 150°C and above is nonterrestrial in origin. The sample plus system were then subjected to a second outgassing at 350°C for 5 hours and allowed to cool slowly overnight. The resultant background equilibrium pressure was 1.2×10^{-9} torr. The sample was then heated up to 400°C over a period of 3½ hours. On the scale of the data shown in Fig. 1, virtually no water vapor could be detected except close to 400°C where traces were found. We concluded from this preliminary treatment that all contaminant water vapor which could be released at or near 150°C had been removed.

The sample was then exposed to molecular hydrogen at 150°C, and an adsorption isotherm was obtained up to effective monomolecular coverage (approximately 0.1 m^2/g, as measured by xenon adsorption). The initial pulse of hydrogen showed a pressure maximum with time, indicating the displacement of trace surface gas. Hydrogen subsequently admitted showed no such effect. Although atomic hydrogen can chemisorb over a wide temperature range (*4, 5*), molecular hydrogen physisorbs at −196°C (*3*), with no further adsorption taking place until a temperature of over 100°C when the gas chemisorbs on typical lunar samples. The relatively slow kinetics of the process at approximately 150°C indicate that we are dealing with an activated dissociative chemisorption. The RGA detected virtually no molecular hydrogen but large amounts of water vapor at 100° to 150°C in the gas phase after the adsorption of molecular hydrogen was complete. After the temperature had been rapidly raised to 400°C, a water vapor peak was again obtained in the 250° to 300°C region (see Fig. 1). The peak was about half of that obtained on the initial desorption described above. In evaluating the data in Fig. 1, one should bear in mind the steady-state nature of the results. Thus the relative magnitudes of the ordinates reflect the different rates at which water was removed at the various temperatures. The fact that the data approximate a single peak suggests that the water source is essentially the same over the entire temperature range from 100° to 400°C. No significant amount of hydrogen was observed. In the absence of contaminant water vapor, the observed water vapor must have arisen from the combination of adsorbed hydrogen and sample oxygen. A small amount of this sample oxygen could itself have originated from contamination (*4*); however, most of the oxygen used must have been present in the original sample.

After the sample had been held at a temperature of 400°C overnight and then cooled to 150°C (residual pressure, 3.5×10^{-9} torr), it was then exposed to deuterium at a pressure of 10^{-1} torr for 48 hours. The residual gas, as expected, contained little or no deuterium but significant amounts of water vapor (DO or H_2O, DHO, and D_2O). After the system had been pumped out and the sample heated to 400°C, the amounts of gases noted in Fig. 1 were observed. We can only conclude that the deuterated water observed originated from chemisorbed deuterium and sample oxygen.

On the basis of the above evidence, we believe that a thoroughly outgassed lunar sample chemisorbed hydrogen and desorbed water vapor, with the sample itself contributing the oxygen. The sample, a typical complex breccia, consists of a mixture of compacted silicate soil particles (*2*). This work coupled with similar partial studies on other samples led us to conclude that most complex silicate materials would behave in a similar way. The conditions used here approximate a lunar situation. Thus, we believe that the sample surface has a degree of cleanliness comparable to that obtainable under lunar conditions. Reduction by hydrogen molecules at high pressures, short times, and 150°C produces results equivalent to those achieved by hydrogen atoms at low pressures, long times, and lower temperatures (*4, 5*). Finally, we have demonstrated that the resultant water is desorbed in the 100° to 150°C range (well within the range of lunar temperatures). At this time, however, with the limited range of samples examined, it would be difficult to quantitatively predict the precise amounts of water vapor that would be obtained from a "typical" soil sample. Certainly, there is little doubt that under lunar conditions some water vapor will be produced in this way. If Bibring *et al.* (*10*) are correct in suggesting that the surfaces of lunar samples exposed to solar radiation possess ultrathin amorphous coatings (500 to 1000 Å thick), it would seem reasonable that the oxygen supply would not be limited to the immediate outer layer of the soil particles but that much of the oxygen in the amorphous region would be utilized. We envisage that hydrogen atoms would penetrate the defect structure, combining chemically with the oxygen to form hydroxyl groups (*11*) and ultimately water vapor. Moreover, meteorite bombardment would constantly create new surfaces and new sources of oxygen.

Irrespective of the precise rate of formation of water in the manner described here, measurements of the composition of the lunar atmosphere (*12*) suggest that the partial pressure of water vapor must be extremely low, and that loss of water vapor through ionization and thermal effects are the controlling factors. The observations of Freeman *et al.* (*1*) cannot be explained solely on the basis of our findings.

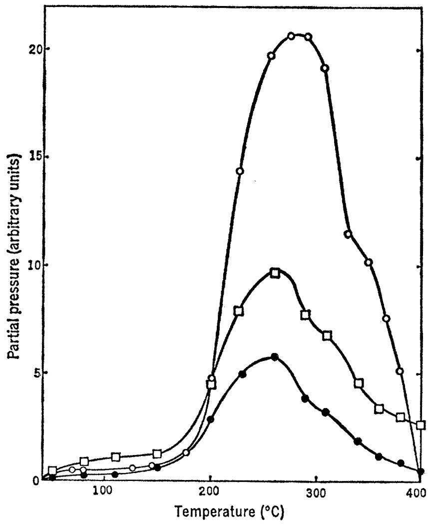

Fig. 1. Partial pressure of H_2O (experiment 2) and of HDO and D_2O (experiment 3) as a function of temperature (40° to 400°C) after the sample had been exposed to hydrogen gas (experiment 2) or deuterium gas (experiment 3): ○, H_2O; □, HDO; and ●, D_2O. The absolute pressure rose from approximately 10^{-8} torr at 100°C to 8×10^{-8} torr at 300°C. An approximate calibration of the arbitrary scale of the ordinate may be made, based on an estimated effective pumping capacity of 10 liter/sec and a ultrahigh-vacuum system volume of 2.5 liters. Before the sample was exposed to hydrogen or deuterium, the concentrations of all three oxides were zero over the entire temperature range, except for H_2O where traces were seen at (and above) 400°C. The H_2O curve has been corrected for these amounts so that it shows only the difference before and after exposure to hydrogen.

What is much more important is that, on any planet having a sufficient gravitational pull, possessing oxygen-containing primary minerals, and being bathed in a reducing atmosphere (a situation that should exist in the early development of most planets), the proposed mechanism could be a significant factor in the development of a planetary atmosphere. The situation could be self-regulating in that, as the atmosphere builds up, the source of the hydrogen would be restricted. Nor would such a mechanism be limited to the formation of water vapor. Pillinger *et al.* (*13*) have proposed that hydrocarbons may be generated through solar wind reduction of surface carbon, and we did, in fact, detect trace amounts of methane on outgassing after exposure of the sample to hydrogen. At this stage, however, we cannot be certain that the observed trace methane was synthesized since any CD_4 formed on exposure to deuterium would be lost in the large peak due to D_2O. What is clear is that cosmologists should give serious consideration to surface reactions when theorizing on the origins of planetary atmospheres.

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References and Notes

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Fine Particles Produced from Automotive Emissions-Control Catalysts

Abstract. *High concentrations of metal-containing condensation nuclei have been thermally induced from stabilized catalysts containing chromium, copper, and nickel under conditions closely resembling those found in automobile exhaust. Commercial and developmental catalyst formulations have been found to emit fine particles under a broad range of controlled conditions at temperatures ranging from 185° to 800°C, in filtered air, in a mixture of 3 percent carbon monoxide in molecular nitrogen, and in the product stream of a pulsed flame combustor.*

The intention of the automobile manufacturers to install oxidative catalytic emissions-control systems on passenger vehicles beginning with the 1975 model year, in response to federal emission standards, raises key questions regarding the use of catalysts for these purposes. Certain catalyst compositions typical of those now being developed for the control of automotive exhaust pollutants in 1976 (particularly nitrogen oxides, NO_x) are reported to contain, in addition to Pt, Cr, Ni, and other elements of known toxicity. In studies published by the industry the claim has been made that there is no hazard from nickel carbonyl [$Ni(CO)_4$] derived from exhaust CO in contact with a Ni-containing catalyst (Monel Metal) (*1*). However, in view of the fact that particulate Ni is not detected by colorimetric tests for the carbonyl group, the possibility of the thermal decomposition of $Ni(CO)_4$ (if formed) to free Ni in passage through the exhaust system cannot be discounted. This would result in the emission of fine particles of Ni in the respirable size ranges (that is, less than 1 μm in diameter).

The effect of certain gaseous constituents (namely, the halogens), even in trace concentrations, on the rates of emission of particles from heated Pt wire has been reported by Vonnegut (*2*). Chaston attributed the apparent volatility of Pt in air or O_2 at temperatures above 500°C to the formation of PtO_2 vapor (*3*). Since oxidative-type Pt catalytic converters operate in the temperature range from 500° to 1000°C (mid-bed temperature), it is not unreasonable to expect some loss of Pt as PtO_2 vapor. The PtO_2 vapor emerging from the converter would undergo decomposition and subsequent condensation into a finely dispersed Pt aerosol as the exhaust cools.

Table 1. Onset of thermal CN evolution from catalytic materials.

Material	Atmosphere	Temperature (°C)
Monel 400, sintered	3% CO in N_2	185
Monel 400, sintered	Air	630
Girdler G-22	3% CO in N_2	240
Girdler G-22	Air	615
CuCr on Kaiser KA-201	3% CO in N_2	240
CuCr on Kaiser KA-201	Air	610
Kaiser KA-201 without catalyst	3% CO in N_2	> 810
Kaiser KA-201 without catalyst	Air	> 810

An extremely sensitive instrument for detecting fine particles in the mid- to lower-respirable size ranges, without regard for chemical composition, is the condensation nuclei counter (CNC). This instrument detects submicroscopic airborne particles in the approximate range from 0.001 to 0.1 μm in diameter and is sensitive to concentrations as low as 10^{-14} g/cm^3. In this study a thermoparticulate analysis (TPA) system was used similar to one described by Murphy *et al.* (*4*). The carrier gas (room air or 3 percent CO in N_2) passed through an absolute filter producing an aerosol with less that 1000 condensation nuclei (CN) per cubic centimeter, the approximate threshold of the instrument. The filtered carrier gas then passed over the sample which was contained in a heated Vycor tube placed centrally with respect to the horizontal electric furnace. The sample temperature was regulated to ± 10°C and recorded. The resulting aerosol was cooled before entry into the CNC. Temperature and CNC output were recorded on the same chart.

A pulsed flame combustor (PFC), described by Meguerian (*5*), was used to produce a gas stream quite similar in composition to the exhaust gas from an internal-combustion engine. The aerosol sample resulting from contact of the PFC exhaust with the catalyst was diluted by a factor of 8 with filtered air to prevent condensation of H_2O vapor in the cooling system.

On the basis of currently available information pertaining to NO_x reduction catalysts for use in two-stage catalytic emissions-control systems (*6*), two representative compositions were selected for study: copper chromite (the composition of this material is variable; in this report copper chromite will be represented by the formula CuCr) and Monel Metal (70 percent Ni, 30 percent Cu). The four samples chosen include the following: (i) sintered Monel 400; (ii) Girdler G-22, Ba-promoted CuCr; (iii) CuCr supported on Kaiser KA-201 gamma alumina beads; and (iv) KA-201 beads (specific surface, 340 m^2/g) as received without catalyst impregnate. The