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   - Apollo 14: 14259,80
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   - Stored Energy
   - Non-equilibrium Processes
   - Energy Release
MICROPHYSICAL, MICROCHEMICAL AND ADHESIVE PROPERTIES OF LUNAR MATERIAL III: GAS INTERACTION WITH LUNAR MATERIAL

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ABSTRACT

Knowledge of the reactivity of lunar material surfaces is important for understanding the effects of the lunar or space environment upon this material, particularly its nature, behavior and exposure history in comparison to terrestrial materials. Adsorptive properties are one of the important techniques for such studies. Gas adsorption measurements were made on an Apollo 12 ultrahigh vacuum-stored sample and Apollo 14 and 15 N₂-stored samples. Surface area measurements were made on the latter two. Adsorbate gases used were N₂, A, O₂ and H₂O. Krypton was used for the surface area determinations. Runs were made at room and liquid nitrogen temperature in volumetric and gravimetric systems. It was found that the adsorptive/desorptive behavior was in general significantly different from that of terrestrial materials of similar type and form. Specifically a) the UHV-stored sample exhibited very high initial adsorption indicative of high surface reactivity, and b) the N₂-stored samples at room and liquid nitrogen temperatures showed that more gas was desorbed than introduced during adsorption, indicative of gas release from the samples. We ascribe the high reactivity to be a result of cosmic ray track and solar wind damage. We ascribe the gas release to be a result of absorbate-produced opening of microcracks and micropores which
allowed escape of trapped gases derived from solar particulate radiation
teraction with the material. These results indicate that the gas adsorption
technique can be of value in the study of lunar regolith chronology.
INTRODUCTION

The purpose of this study is to determine the manner in which various gases interact with lunar materials and the interaction differences, if any, between lunar and terrestrial materials. The importance of such studies lies in the fact that the lunar and terrestrial materials have had differing histories, the former being directly exposed to the various space radiations and the latter being exposed to the earth's atmosphere, in both instances for a considerable period of time. Information provided by such studies could provide knowledge toward the understanding of the interaction of lunar surface material with gases of various origin. The work reported here is concerned with surface area measurements of Apollo 14 and 15 samples plus gas adsorption/desorption studies of UHV-stored Apollo 12 and N2-stored Apollo 14 samples.

This study is an outgrowth of our previous studies on Apollo 11 and 12 lunar samples, particularly gas exposure effects on the samples (GROSSMAN et al. 1970a, b, and 1971). Upon exposure to O2, H2O vapor, their mixtures, organic and inorganic acids and bases, disruptions of some of the bonded particle were observed. Exposure to dry N2 did not show any noticeable change, although N2-exposed samples gained weight during storage in N2 for about one year. The lunar soil under vacuum and upon exposure to ambient atmosphere exhibited noticeable electrostatic charging. The bonding between
gas-disrupted particles could well be of the same origin, but other bonding mechanisms cannot be excluded at present. For instance, prior to gas exposure, the bonded particles were purposely subjected to considerable mechanical disturbance, such as lateral motions, roll and impact by other particles. Some of the particles which appeared bonded separated (or changed in orientation) as a result, but others disrupted only upon exposure to gases. A detailed examination of O₂ and H₂O vapor disrupted surfaces by petrographic microscope (X500) and scanning electron microscope (X20,000) revealed that each disrupted area was sufficiently porous to permit interparticle diffusion of a gas, and that the geometrical area was much smaller than the real area due to fractures, voids, craters, and particle agglomerates. The shape of individual small particles and protrusions on larger plate-like crystals suggested some deposition and agglomeration might have occurred, such as from a liquid spray(s).

Samples examined by us and others (CROZAZ et al. 1970 and 1971; FLEISCHER et al. 1970 and 1971; COMSTOCK et al. 1971; ARRHENIUS et al. 1971) showed high cosmic ray track densities (≈10⁸ to ≈10¹⁰ cm⁻²) within 100 nm of the surface. Most particles were also found to be coated with an amorphous or ultramicrocrystalline layer of thickness 20 to 100 nm (GOLD et al. 1970; HAPKE et al. 1970; BORG et al. 1971). If these coatings were composed of purely radiation-damaged material, they would contain high stored energy. HOYT et al. (1970) found calorimetrically that stored energy is large in thermodynamically unstable lunar glassy spherules and grains, but small due to cosmic ray damage in the interior of minerals. However, they calculated that the relatively large amount of stored energy present in the highly damaged particle surfaces could not be detected by calorimetry. This strongly suggests a need for the determination of surface reactivity directly in
experiments which are insensitive to the bulk volume effects of lunar material to improve our understanding of solid phenomena of space-environment exposed materials.

An important technique for the studies of surface reactivity is the measurement of adsorption/desorption behavior for selected gases. It is highly desirable to use ultrahigh vacuum lunar samples for this because some of the surface reactivity is likely to be destroyed by prior gas exposure.

FULLER et al. (1971) determined surface areas of Apollo 11 fines (Sample No. 10087,5) and Apollo 12 lunar fines (Sample No. 12033,46), and studied the adsorption/desorption on the former sample. Their samples had previously been exposed to laboratory atmosphere for a week or so at 25 ± 2°C and relative humidity of 60 ± 5%. Prior to their studies they degassed the samples at 300°C and 10⁻⁵ torr for 24 hours. The specific surface area measured by using N₂ and CO at -196°C gave virtually identical results of 1.15 m² gm⁻¹ for the Apollo 11 sample and less than 0.05 m² gm⁻¹ for the Apollo 12 sample. Adsorption/desorption of A, N₂, O₂ and CO on the Apollo 11 sample showed the material surfaces to be quite nonpolar, but repeated and prolonged H₂O adsorption/desorption decreased capacity of water adsorption with increasingly higher H₂O retention; although the capacity of N₂ adsorption remained unaltered. Such behavior they interpreted to be due to a unique micropore structure in the amorphous, radiation damaged surfaces of the lunar particles. FANALE et al. (1971) determined the surface areas of two fractions of sieved size ranges (74-147 μm, and 147-256μm) of Apollo 11 fines (Sample No. 10084) by using Kr at liquid nitrogen temperature (LN₂), and found them to have effective surface areas similar to ground terrestrial mafic rock powders of about the same size distribution. They suggest on the basis of their finding of the BET parameter C that apparently low heats of adsorption for Kr on lunar fines are consistent with the presence of glassy or glass-coated particles.
EXPERIMENTAL TECHNIQUES

Experimental techniques utilized were dependent on the parameters to be measured as well as lunar sample type. Surface area measurements were made at LN$_2$ (-196°C) using krypton as the measuring gas in a LN$_2$ trapped oil diffusion pumped system (volumetric). Adsorption/desorption studies were performed by the same volumetric system at LN$_2$ (-196°C) and by two gravimetric systems using a Cahn RG balance in System I, and a Cahn RH balance in System II, at room temperature (25 ± 0.3°C) or at a thermostated water bath temperature of 21.3 ± 0.1°C.

Sample Type Received and Handling

We received two types of samples: a vacuum sample from the Apollo 12 mission and N$_2$-stored samples from the Apollo 14 and 15 missions. Since it was received by us the Apollo 12 sample was stored under ultrahigh vacuum (UHV) condition (<10$^{-8}$ Torr) at room temperature for about one year. This sample, however, was exposed to a pressure of about 10$^{-2}$ Torr during transit from the moon to the earth. Since the sample was kept under the UHV condition for about one year, most of the non-chemisorbed contaminant gases from 10$^{-2}$ Torr exposure were probably removed from the sample.

The techniques for handling and transfer of an UHV sample are given by GROSSMAN et al. (1971). The UHV-stored Apollo 12 sample (12001,118) was handled in a similar manner, the sample never having been exposed to any gas at or subsequent to receipt from the LRL prior to gas reaction and adsorption studies of some portions of the sample. Adsorption studies of this sample were done in System II. The N$_2$-stored sample portions of Apollo 14 (14259,80 and 14259,113) used for adsorption studies in System I were handled and loaded in a dry N$_2$ glove box atmosphere. The Apollo 14 sample 14259,93 and Apollo
15 sample 15401.48 used for adsorption studies in the volumetric system were exposed to air for about 20 minutes during insertion into the system.

**Apparatus**

The volumetric apparatus is of standard design and further details are not given.

Gravimetric System I consists of two main parts: (a) the gas adsorption subsystem made of stainless steel and (b) the reference subsystem for measuring pressure in the adsorption chamber containing a Cahn RG microbalance. Ultra-high vacuum (pressure \( \sim 10^{-8} \) Torr) is achieved by a system of two LN\(_2\) trapped diffusion pumps and two ion pumps (capacity 500 liter sec\(^{-1}\) and 50 liter sec\(^{-1}\) pumping speed). The pressure measurement up to \( 10^{-5} \) Torr are made with Bayard-Alpert ion gages directly connected to (a). Measurements from \( 10^{-4} \) to 760 Torr are made using the reference system and capacitance manometers. The microbalance chamber is vibration isolated from the floor, and decoupled as well as possible from the rest of the system by use of stainless steel flexible tubing. Provisions are incorporated to check the microbalance zero repeatedly throughout the runs utilizing a manipulation system which allows removal and replacement of the sample and tare while at vacuum.

The hang wire on each arm of the balance for holding either sample pan or counterweight pan is about 40 cm long. It consists of two sections of about 12 cm and 28 cm lengths. The shorter section nearer to the balance arm is made of 0.05 cm diameter aluminum wire and the longer section is made of 0.02 cm diameter titanium wire. Each hang wire is housed in a 3 cm diameter stainless steel nipple. To minimize thermomolecular effects each of the thin titanium wires is hung through \( \sim 3 \) mm diameter holes at the centers of two baffles in the nipple. The baffles are made from thin nickel sheet and
separated by about 20 cm. The pans for the sample and counterweight are identical. Each is made of thin sheet aluminum and has two levels or stages so that the adsorbent can be spread out in thin layers in order to minimize the gas diffusion rate through the sample layer. Provisions are incorporated to control separately the temperature of the chamber housing the microbalance and the nipples containing the hang wires with samples and counterweight.

Gravimetric System II also consists of two main parts similar to gravimetric System I, except that it contains a Cahn RH microbalance housed in a metal bell jar, and that pressure of the adsorbate gas is measured by gages directly connected to the bell jar.

**Procedure**

Standard procedure was followed for the volumetric technique used to measure the surface areas of the Apollo 14 and 15 samples using Kr as the probing gas, and to determine adsorption isotherms of pure O₂ and N₂ (impurity <5 ppm) at LN₂ temperature. Each sample was baked initially and before each run at 110°C and ~2 x 10⁻⁶ Torr for about two hours (the temperature 110°C being chosen so as not to exceed the maximum sample exposure temperature at the lunar surface).

The procedure for adsorption studies in System I was as follows. The system was baked at 80 ± 2°C and ~5 x 10⁻⁸ Torr for two weeks. For each adsorbate gas the system was calibrated using 3 mm size spherical pyrex glass beads on the sample pan and standard weight pieces on the counterweight pan. The weight of the glass beads was about the same as the sample weight desired. The calibrations were made for the temperature and pressure ranges to be used for adsorption studies (i.e., temperature 21.3 ± 0.1°C and 25 ± 0.3°C and pressure ~3 x 10⁻⁶ to 760 Torr for N₂, O₂, A and ~3 x 10⁻⁶ to 18.5 Torr for H₂O vapor). The N₂-stored samples as received from LRL were opened in a dry
$N_2$ glove box, and a portion (0.395735 gm) distributed evenly on each stage of the two-stage sample pan which was accurately weighed with a Cahn G-2 balance in the glove box. Appropriate standard weight pieces were put on the two-stage counterweight pan while the chamber and the nipples are in dry $N_2$ atmosphere and the nipple was closed UHV-vacuum tight. The sample pan from the glove box was then transferred in dry $N_2$ atmosphere to System I. The sample housing nipple was closed UHV vacuum-tight, and pumped down to a pressure of $\approx 5 \times 10^{-8}$ Torr, and the sample was baked at a temperature of $120 \pm 1^\circ$C (equivalent to lunar noon temperature) for 100 hours. Then the sample was cooled to room temperature, the stainless nipple was put in a thermostatic water bath, and then the adsorption runs were started.

The first adsorption/desorption run was made with pure $N_2$ (impurity <5 ppm), followed by two runs with pure $H_2O$ vapor, and then followed by three $N_2$ runs. The sample was baked at $120 \pm 1^\circ$C and $\approx 3 \times 10^{-6}$ Torr for 100 hours after the first $N_2$ run, for 150 hours after the two $H_2O$ runs. Between the two $H_2O$ runs and the last three $N_2$ runs the sample was not baked, but was evacuated for about 80 hours at $\approx 3 \times 10^{-6}$ Torr and 21.3°C.

The procedure for adsorption/desorption studies of the UHV-stored Apollo 12 sample (No. 12001,118) using pure gases, $N_2$ and followed by $A$ is as follows. The UHV-stored sample was transferred under ultrahigh vacuum conditions into a specially designed glass cell through a copper tube which was then pinch-off sealed (Figure 1). After transferring the cell to gravimetric System II and evacuating to $10^{-7}$ Torr, the sample cell was opened by a differential thermal expansion device at the breakoff constriction and adsorbate gas introduced. This UHV-stored sample was not baked. Adsorption/desorption runs were made at room temperature ($25 \pm 0.3^\circ$C).
For each adsorbate gas each adsorption system was calibrated for the temperature and pressure ranges to be used for adsorption studies. The adsorption data were corrected for buoyancy, thermomolecular effects, microbalance temperature, zero shift effects at different temperatures and pressures.
RESULTS AND DISCUSSION

Surface Areas

At LN$_2$ temperature our Kr measured surface areas were 0.61 m$^2$ gm$^{-1}$ for the Apollo 14 sample and 0.40 m$^2$ gm$^{-1}$ for Apollo 15. The results are in the same order of magnitude range for samples returned by other Apollo missions, plus terrestrial fines of about the same grain size distribution (Table I). In the table we have shown surface area, $P_m/P_s$, $E_1-E_2$ and C obtained by us and others for lunar and terrestrial samples. These symbols are defined in the table. The C value of the BET equation is related to the surface energy of the adsorbent, the lower the C value the smaller the surface energy. For active inorganic oxides the C values for N$_2$ adsorption may be as high as 1000. All values of C shown in Table I are less than 140 except for O$_2$ on Sample 14259,93. This is the sample for which we observed hysteresis with O$_2$ at LN$_2$ temperature.

Calculations of the C value in the BET equation was not possible for the N$_2$ run at room temperature because the saturation pressure, $P_s$, could not be defined. However, the maximum heat of adsorption for UHV-stored Apollo 12 sample's Langmuir Type I isotherm (N$_2$ first run, Figure 2) was approximately 9 kcal, a value which is still considered physical adsorption (HOBSON 1967). The surface area inferred from monolayer adsorption that occurred at unusually low pressure of 10$^{-4}$ atm is 0.08 m$^2$ gm$^{-1}$. This surface area value is in reasonable agreement with the measured value (<0.05 m$^2$ gm$^{-1}$) of FULLER et al. (1971) for Apollo 12 sample 12033,46.

Adsorption/Desorption

The first set of experiments was performed on the UHV-stored Apollo 12 sample using pure N$_2$ and A gases at room temperature, the second set on the
Table I  Surface Areas and the BET Parameters

of Lunar and Terrestrial Materials

(P$_m$ is the pressure at which the monolayer formation is complete, P$_s$ is the saturation pressure, E$_1$ is the energy of adsorption which is assumed to be always greater than the liquefaction energy E$_L$, and C is the BET constant which is a measure of the adsorption energy.)

<table>
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<tr>
<th>Apollo Mission and Sample No.</th>
<th>Measuring Gas</th>
<th>Surface Area m$^2$ gm$^{-1}$</th>
<th>P$_m$/P$_s$</th>
<th>E$_1$-E$_L$</th>
<th>C</th>
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<td></td>
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<td>N$_2$</td>
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*Note: Room Temperature Measurement of UHV-stored sample.
N₂-stored Apollo 14 sample using pure O₂ and N₂ at LN₂ temperature, and the third set on the N₂-stored Apollo 14 sample using N₂ and H₂O vapor, the N₂ run being at a thermostatic water bath temperature of 21.3 ± 0.1°C.

Adsorption/Desorption of UHV-Stored Apollo 12 Sample at Room Temperature

Figure 2 shows the research grade N₂ and A adsorbate gas runs at room temperature for the UHV-stored Apollo 12 sample (weight used 2.315 gm). The N₂ run was done first and this run showed high adsorption initially resulting in the entire weight gain at pressures less than 0.5 torr. The sample weight increased by about 60μgm, corresponding to approximately 1 μmole gm⁻¹, which is reasonably close to the 0.6 μmole gm⁻¹ amount required for monolayer formation (Table 1; also FULLER et al., 1971). The sample weight then remained essentially constant up to 760 Torr. On desorption there was no net N₂ retention within the experimental error (see Figure 2 for the absolute error bar). These results were reproducible in two subsequent runs (not shown) indicating that this lunar sample retained high reactivity, although there appears to be no permanent retention of N₂ within the experimental error. For clarity, the data points with no permanent retention are also shown.

In order to ascertain the change in the surface reactivity, the sample was exposed to air for a short period (~5 Torr seconds) at a pressure less than 2 Torr and then evacuated to a pressure less than 10⁻⁷ Torr. The subsequent N₂ run showed a change in the desorption isotherm and the knee moved to about 25 Torr (second N₂, Figure 2) with larger total weight gain. Argon also exhibited a similar (Type I) adsorption isotherm. These results strongly suggest that the surface characteristics of this UHV-stored samples changed even upon a very brief exposure to air. Unfortunately, there was no more UHV-stored sample remaining to conduct another series of runs. However, in our previous studies (GROSSMAN et al., 1970a, b; 1971), Apollo 11 and 12
samples were found to exhibit high reactivity when exposed to oxygen, water vapor and their mixtures.

Adsorption/Desorption of \( N_2 \)-Stored Apollo 14 Sample at Liquid Nitrogen Temperature (-196°C)

The adsorption isotherms for research grade \( O_2 \) first and then \( N_2 \) were determined at LN\(_2\) temperature, by using the volumetric system, for Apollo 14 sample 14259,93 (see Figures 3 and 4). A definite hysteresis (see the error range in the figure title), not found by prior investigators on an Apollo 11 sample (FULLER et al., 1971), was observed. Although the sample was baked at 110°C for about two hours, this hysteresis was unexpected, because of the following: (a) this \( N_2 \)-stored sample was exposed to air for about 20 minutes during weighing and insertion into the volumetric system, and (b) no hysteresis was observed for the UHV-stored Apollo 12 sample with \( N_2 \), or by FULLER et al. (1971) with \( O_2 \) on Apollo 11 sample. In the studies by FULLER et al. the Apollo 11 sample was exposed to air for a week, but baked at 300°C and \( 10^{-5} \) Torr for 24 hours prior to their adsorption runs. For our \( O_2 \) run the BET surface area of 0.37 m\(^2\) gm\(^{-1}\) found at \( P/P_s = 0.37 \) is comparable to our Kr measured surface area (see Table I). The sigmoidal behavior of our data should be compared with the previously observed slight undulation in the \( O_2 \) data of FULLER et al. (1971).

Four \( N_2 \) runs at LN\(_2\) temperature, which followed the \( O_2 \) measurements, are shown sequentially in Figure 4. The first \( N_2 \) run shows a slight decrease in adsorption with increasing pressure above \( P/P_s = 0.05 \), no additional effects up to 0.8 and then multilayer condensation. The 4 \( \mu \)mole gm\(^{-1}\) between \( P/P_s = 0.05 \) to 0.8 is consistent with one monolayer calculated from the \( O_2 \) isotherm or 0.6 monolayer from the Kr surface area determination. The first desorption isotherm starts from 400 \( \mu \)moles gm\(^{-1}\) showing hysteresis down to zero pressure and a net retention of 10.4 \( \mu \)moles gm\(^{-1}\). The second adsorption rises to a
maximum of five monolayers (O2 surface area) at P/P_s = 0.15 the amount decreasing from there to P/P_s = 0.66 and then increasing again to 300 μmoles gm⁻¹ at P/P_s = 1.0. This second desorption shows negative hysteresis (i.e., the desorption curve lies below the adsorption curve at every pressure P and at P = 0), and 18 μmoles gm⁻¹ more gas was lost than put into the system. The third adsorption isotherm appears to be more normal, though the desorption end point was not determined. Starting then with a new zero, the fourth adsorption isotherm (right hand ordinate) has the more classical sigmoidal shape. However, the desorption again shows negative hysteresis over the entire pressure range. This behavior should be compared with results of FULLER et al. (1971) for H2O vapor on Apollo 11 sample 10087,5. They observed a dip and two plateaus in their adsorption curve for Sorption Cycle #1; however, repeated cycling (adsorption/desorption) led to more conventional isotherms with a more and more pronounced sigmoidal shape. The adsorption decrease is indicative of gas release from the adsorbent. This surprising behavior at LN2 temperature was checked by studying the adsorption behavior at room temperature using the gas sequence: relatively inert gas, N2, a reactive gas, H2O vapor, and then N2. To avoid temperature fluctuation, we immersed the sample and counterweight housing nipples in a thermostatically controlled water bath. The results of these runs are described below.

Adsorption/Desorption of Apollo 14 Sample at a Constant Temperature of 21.3 ± 0.1°C

The adsorption isotherms of N2 and H2O vapor are shown in Figures 5 and 6 respectively. The first experiment is N2 Run 1 of Figure 5, the second and third experiments are H2O vapor Runs 2 and 3 of Figure 6, and the fourth, fifth and sixth are the N2 runs performed after the H2O runs.
The first \(N_2\) run shows a completely reversible isotherm, without any retention of \(N_2\) by the sample, i.e., the adsorption and desorption are identical within experimental error (\(+3 \mu g m/gm\) for pressures greater than 0.5 Torr, \(+4.5 \mu g m/gm\) for pressures less than 0.5 Torr) given in the figure caption [Note: For the purpose of clarity the adsorption and desorption curves are slightly separated in the drawing]. It should be pointed out that the starting point of adsorption Run 1 is taken to be at zero whereas the starting point of Runs 4 to 6 are at 3.6 \(\mu m o l e/gm\) which is equivalent to the \(H_2O\) retention after Run 3. Although the isotherm shows high adsorption up to a pressure of about 0.5 Torr, the general shape is characteristic of most terrestrial material. This is in contrast to Runs 4 and 5 which were conducted after the two \(H_2O\) vapor runs (see Figure 6). Run 4 shows adsorption apparently higher than Run 1 at all pressures and the adsorption curves of both are almost parallel. This higher adsorption can be explained on the basis of the \(H_2O\) retention shown in Figure 6. The retention after Run 3 is about 5.6 \(\mu m o l e\) of \(H_2O\) which is equivalent to 3.6 \(\mu m o l e\) of \(N_2\) and the difference between the two parallel adsorption curves of Runs 1 and 4 is about 2 \(\mu m o l e\). The retention of 5.6 \(\mu m o l e\) of water by a sample weight of 0.39574 gm with a surface area \(\approx 0.6 \text{ m}^2 \text{ gm}^{-1}\) is just about enough to form a monomolecular adsorption layer of \(H_2O\). The adsorption of \(N_2\) on a monomolecular layer of \(H_2O\) is expected to be less than on "pristine" lunar material surfaces. Therefore, the difference between the two adsorption curves is less than 3.6 \(\mu m o l e\).

At all pressures lower than 200 Torr Run 4 shows a negative hysteresis similar to that observed at \(LN_2\) (Figure 4). At pressures \(<50\) Torr the desorbed amount is greater than the amount of \(H_2O\) retention and \(N_2\) adsorption. This indicates that the sample was losing gas which might have been trapped in the lunar soil grains. Similar behavior is more dramatically evident in the
adsorption/desorption curves of Run 5. In Run 5, the adsorption curve also experiences a dip at pressures between 10 and 425 Torr. At pressures greater than 425 Torr the adsorption curve rises but with a smaller slope than those of Runs 1 and 4. The desorption is larger than the adsorption at all pressures less than 760 Torr at which desorption was started. In Run 6 we have conducted only adsorption experiment. At a particular pressure the adsorbed amount is smaller than that of Runs 1 and 4 but greater than that of Run 5, except for the adsorption at pressures between 5 and 70 torr of Run 5. The adsorption curve of Run 5 is again almost parallel to those of Runs 1 and 4. This may be an indication that after the release of some trapped gas the adsorption behavior is becoming typical.

The \( \text{H}_2\text{O} \) adsorption isotherms shown in Figure 6 are also interesting. The adsorption curve of Run 2 increases sharply at relative pressures \((P/P_s)\) greater than about 0.8 as also was observed by FULLER et al. (1971). A large hysteresis was observed with retention of 4.2 \( \mu \text{mole gm}^{-1} \) of \( \text{H}_2\text{O} \). This amount was retained by the sample even after continuous pumping at a pressure of \( \approx 3 \times 10^{-6} \) torr and temperature of 21.3\( \pm 0.1 \)\( ^\circ \text{C} \) for 80 hours. The adsorption curve of Run 3 is somewhat parallel to the desorption curve of Run 2; however, they are separated by more than 4.2 \( \mu \text{mole gm}^{-1} \) indicating that some adsorption occurred with increase of pressure. The desorption part of Run 3 was not done. However, the \( \text{H}_2\text{O} \) retention point was determined by continuous pumping at a pressure of \( \approx 3 \times 10^{-6} \) Torr and temperature of 120 \( \pm 1 \)\( ^\circ \text{C} \) for more than 150 hours.

The adsorption decrease is indicative of gas release from the adsorbent. As mentioned previously, FULLER et al. (1971) also observed such a decrease for their \( \text{H}_2\text{O} \) adsorption run at 25\( ^\circ \text{C} \). We ascribe this behavior to be due to a group of processes which could be irreversible and cyclical opening and
closing of micropores in lunar material grains. As a result, some of the gases, which could have been solar, lunar, terrestrial or otherwise trapped, might have been released. All low temperature runs were indicative of a non-terrestrial type behavior of the Apollo 14 sample, probably as a result of radiation damage.

FUNKHOUSER et al. (1970), EPSTEIN et al. (1970), EBERHARDT et al. (1970), FRIEDMAN et al. (1970), KIRSTEN et al. (1971), MOORE et al. (1971), FUNKHOUSER et al. (1971), GIBSON et al. (1971), and others have reported the composition, distribution and thermal release of solar wind trapped gases in lunar soil. Up to 90 μmoles gm⁻¹ have been reported, H₂ and He, making up the largest fraction. Well over 90% lies between 100 and 200 nm from the surface (EBERHARDT et al., 1970). An appreciable amount can be driven off by heating at 300°C but not at 100°C.

An hypothesis for the observed lunar material adsorption behavior, based essentially on the irreversible behavior of cosmic ray damaged surfaces, is as follows. As adsorption reaches saturation pressures, the liquid penetrates the radiation damaged pores releasing both stored energy and some solar wind implanted gases, an unusual example of the well known Rebinder effect. With each adsorption more of the surface damaged stored energy is released, and then the lunar sample starts behaving more like terrestrial silicates.

In our experiments the O₂ and H₂O vapor runs might have sensitized the sample as suggested by the change in the adsorption isotherm of UHV-stored sample after a short air exposure so that even liquid nitrogen could penetrate the sample and be retained (first run, Figure 4). After annealing at 100°C the second adsorption releases the trapped gas. If only pore trapped N₂ is released, the penetration of the damaged layer is less than 100 nm since H₂ and He lie deeper in the sample (EBERHARDT et al., 1970). Continued
adsorption deepens the damage layer penetration and the negative hysteresis on the second desorption would then be merely a release of the solar wind $H_2$ and He at that depth. Further annealing and adsorption deepens the penetration further with continued release of trapped gas. Ultimately the sample should become thermodynamically stable and further adsorption/desorption behavior should be like terrestrial materials.

The water adsorption work reported by FULLER et al. (1971) led them to postulate 5 nm pores which we believe to be cosmic ray damage produced. The longer they cycled the Apollo 11 sample the more the adsorption isotherm approached terrestrial silicates. They reported the 100°C bakeout weight loss was 300 $\mu$gm gm$^{-1}$ and the 300°C 24 hour weight loss was 940 $\mu$gm gm$^{-1}$, the latter probably being all the solar and trapped gases. Their air preconditioned sample already reacted with $O_2$ (and $H_2O$); thus the sample changed from its pristine condition. Such a change was observed by us, as discussed previously, for the UHV-stored Apollo 12 sample.
CONCLUSIONS

1. An UHV-stored lunar sample was observed to have unique room temperature gas adsorption properties for N\textsubscript{2} with a Langmuir monolayer uptake at 10^{-4} atm. This behavior may be typical of pristine lunar material.

2. Short exposure to air modifies the behavior but the material appears to be relatively stable in dry nitrogen.

3. Reactive gas may sensitize the surface so that further reaction with liquid N\textsubscript{2} continues release of stored energy, and solar wind trapped gases.

It is evident that further studies are required for the following reasons. First, none of the studies to date are really representative of "pristine" lunar material. Second, differing adsorption behavior has been found by different investigators of lunar samples (FULLER et al., 1971; CADENHEAD et al., 1972; present authors). The exact reasons for these differences need be determined. Finally, the observed non-terrestrial type behavior of lunar materials needs further confirmation both at LN\textsubscript{2} and room temperature and specific reasons for such behavior determined.

The findings indicate that the degree of adsorption is highly dependent on the surface nature, and that sequential use of an inert gas, reactive gas and followed by the inert gas may prove to be a valuable technique for probing the nature of the adsorbent surface, and the effects caused by the reactive gas. Additionally, means should be provided to measure the gas composition in order to definitively determine whether or not gases are indeed released from the samples and if so, the types.
Acknowledgment—The authors thank A. D. Pinkul especially for his work on the Apollo 12 High Vacuum Samples, C. L. Wilkensen for Apollo 12 microbalance measurements, L. Atkins for the volumetric analyses and W. M. Hansen for his help on all phases of the program. This work was supported by NASA Contract NAS 9-11680.
LIST OF FIGURES AND CAPTIONS

Figure 1. Apollo 12 vacuum sample tube. (The sample was transferred through the copper tube that was pinch-off sealed. It was suspended with the vacuum breakoff constriction side arm vertical, held by a support arm until opened at high vacuum and then lowered onto the microbalance.)

Figure 2. Nitrogen and argon adsorption isotherms at room temperature (25 ± 0.3°C) for the UHV-stored Apollo 12 vacuum sample (12001,118) using a gravimetric System II. (There was no permanent retention of \( \text{N}_2 \) within the experimental error, and results were reproducible in two subsequent runs [not shown]. The reproducible Langmuir knee for the first nitrogen adsorption measurements occurs at \( P = 10^{-4} \) atmospheres. The isotherm is modified after air exposure [2nd \( \text{N}_2 \)]. The Argon isotherm obtained after \( \text{N}_2 \) runs is the last of the series.)

Figure 3. Oxygen adsorption and desorption isotherms for the Apollo 14 sample (14359,93) at liquid \( \text{N}_2 \) temperature (-196°C) using a volumetric system. (The cumulative error for a 16 point adsorption/desorption isotherm is 1.6 \( \mu \)mole gm\(^{-1} \).)

Figure 4. Nitrogen adsorption and desorption isotherm series at liquid \( \text{N}_2 \) temperature on the Apollo 14 sample (14259,93) after \( \text{O}_2 \) runs using the volumetric system referred in Figure 3. (The left-hand ordinate is for the upper curves and the right-hand ordinate is for the fourth adsorption/desorption curves [lower two]. The shape and the order indicate the usual gas evolution properties of lunar samples. The cumulative error for a 16 point adsorption/desorption isotherm is 1.6 \( \mu \)mole gm\(^{-1} \).)
Figure 5. Nitrogen adsorption and desorption isotherms for the Apollo 14 sample (14359,113) at constant temperature of 21.3 ± 0.1°C using gravimetric System I. (Sequence of Run: Run 1 is the first run. Runs 4 to 6 are the consecutive runs after two water vapor runs in Figure 6. Error ± 3μgm/gm for pressures greater than 0.5 Torr, ± 4.5 μgm for pressure less than 0.5 Torr.)

Figure 6. Water vapor adsorption and desorption isotherms for the same Apollo 14 sample of Figure 5 at constant temperature of 21.3 ± 0.1°C using gravimetric System I. (These two water runs were made after nitrogen Run I shown in Figure 5. After these water runs nitrogen Runs 4 to 6, also shown in Figure 5, were made. Error ± 2.5 μgm/gm for pressures greater than 0.5 Torr, ± 3 μgm/gm for pressures less than 0.5 Torr.)
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Figure 6. Water vapor adsorption and desorption isotherms for the same Apollo 14 sample of Figure 5 at constant temperature of 21.3 ± 0.1°C using gravimetric System I. (These two water runs were made after nitrogen Run 1 shown in Figure 4. After these water runs nitrogen Runs 4 to 6, also shown in Figure 5, were made.) Error ± 2.5 μgm/gm for pressures greater than 0.5 Torr, ± 3 μgm/gm for pressures less than 0.5 Torr.
REFERENCES


Figure 2

ΔW IN MICROGRAMS

PRESSURE - TORR

2ND NITROGEN

ARGON

1ST NITROGEN

12001, 118, 8
VACUUM SAMPLE
~2.315 GMS
Figure 3

<table>
<thead>
<tr>
<th>ADSORPTION</th>
<th>DESORPTION</th>
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SAMPLE NO. 14259, 93

RELATIVE PRESSURE, P/P₀

ADSORPTION (MICROMOLES/GRAM)
RUNS 1 - 3

SAMPLE NO.: 14259, 93

RUN 1 ADSORPTION
RUN 1 DESORPTION
RUN 2 ADSORPTION
RUN 2 DESORPTION
RUN 3 ADSORPTION
RUN 4 ADSORPTION
RUN 4 DESORPTION

RELATIVE PRESSURE, $P/P_s$

ADSORPTION (MICROMOLES/GRAM)

Figure 4
Figure 5

SAMPLE NO. 14259,113

RUN 1 ADSORPTION
RUN 1 DESORPTION
RUN 4 ADSORPTION
RUN 4 DESORPTION
RUN 5 ADSORPTION
RUN 5 DESORPTION
RUN 6 ADSORPTION

PRESSURE (TORR)

ADSORPTION (MICROMOLE/GRAM)

Figure 5
Figure 6