

N72-28831

ATTACHMENT TO MANUSCRIPT

Grossman, Mukherjee and Ryan,

Microphysical, Microchemical and Adhesive Properties of
Lunar Material III: Gas Interaction with Lunar Material

1. List of samples mentioned in paper:

Apollo 11: 10087,5
Apollo 12: 12001,118
 12033,46
Apollo 14: 14259,80
 14259,93
 14259,113
Apollo 15: 15401,48

**CASE FILE
COPY**

2. Key indexing words not in title:

Adsorption
BET
Isotherms
Hysteresis
Cosmic Ray Tracks
Cosmic Ray Damage
A
A₂
He
H₂
Kr
O₂
H₂O
Surface Area
Vacuum Samples
Solar Wind
Stored Energy
Non-equilibrium Processes
Energy Release

MICROPHYSICAL, MICROCHEMICAL AND ADHESIVE PROPERTIES OF
LUNAR MATERIAL III: GAS INTERACTION WITH LUNAR MATERIAL

J. J. Grossman, N. R. Mukherjee, and J. A. Ryan
Space Sciences Department
McDonnell Douglas Astronautics Company - West
Huntington Beach, California 92647

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, Ar, 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 adsorbate-produced opening of microcracks and micropores which

allowed escape of trapped gases derived from solar particulate radiation interaction with the material. These results indicate that the gas adsorption technique can be of value in the study of lunar regolith chronology.

MICROPHYSICAL, MICROCHEMICAL AND ADHESIVE PROPERTIES OF
LUNAR MATERIAL III: GAS INTERACTION WITH LUNAR MATERIAL

J. J. Grossman, N. R. Mukherjee, and J. A. Ryan
McDonnell Douglas Astronautics Company - West
Huntington Beach, California 92647

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 O_2 and H_2O 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 ($\sim 10^8$ to $\sim 10^{10}$ 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 $25 \pm 2^\circ\text{C}$ and relative humidity of $60 \pm 5\%$. 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 N_2 and CO at -196°C gave virtually identical results of $1.15 \text{ m}^2 \text{ gm}^{-1}$ for the Apollo 11 sample and less than $0.05 \text{ m}^2 \text{ gm}^{-1}$ for the Apollo 12 sample. Adsorption/desorption of A , N_2 , O_2 and CO on the Apollo 11 sample showed the material surfaces to be quite nonpolar, but repeated and prolonged H_2O adsorption/desorption decreased capacity of water adsorption with increasingly higher H_2O retention; although the capacity of N_2 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 ($74\text{-}147\mu\text{m}$, and $147\text{-}256\mu\text{m}$) of Apollo 11 fines (Sample No. 10084) by using Kr at liquid nitrogen temperature (LN_2), 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 LN₂ (-196°C) using krypton as the measuring gas in a LN₂ trapped oil diffusion pumped system (volumetric). Adsorption/desorption studies were performed by the same volumetric system at LN₂ (-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 N₂-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 N₂-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 N₂ 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 ~ 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 $\sim 2 \times 10^{-6}$ 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 $80 \pm 2^\circ\text{C}$ and $\sim 5 \times 10^{-8}$ 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 $21.3 \pm 0.1^\circ\text{C}$ and $25 \pm 0.3^\circ\text{C}$ and pressure $\sim 3 \times 10^{-6}$ to 760 Torr for N₂, O₂, A and $\sim 3 \times 10^{-6}$ 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 $\sim 5 \times 10^{-8}$ 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 $\sim 3 \times 10^{-6}$ 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 $\sim 3 \times 10^{-6}$ Torr and $21.3^\circ C$.

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, micro-balance temperature, zero shift effects at different temperatures and pressures.

RESULTS AND DISCUSSION

Surface Areas

At LN₂ temperature our Kr measured surface areas were 0.61 m² gm⁻¹ for the Apollo 14 sample and 0.40 m² 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 N₂ adsorption may be as high as 1000. All values of C shown in Table I are less than 140 except for O₂ on Sample 14259,93. This is the sample for which we observed hysteresis with O₂ at LN₂ temperature.

Calculations of the C value in the BET equation was not possible for the N₂ 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 (N₂ 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 m² gm⁻¹. This surface area value is in reasonable agreement with the measured value (<0.05 m² 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 N₂ 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.)

<u>Apollo Mission and Sample No.</u>	<u>Measuring Gas</u>	<u>Surface Area m² gm⁻¹</u>	<u>P_m/P_s</u>	<u>E₁-E_l</u>	<u>C</u>	<u>Authors</u>
Apollo 11						
10087,5	N ₂	1.1	0.19	450	40	FULLER <u>et al.</u>
10087,5	CO	1.1	0.08	750	130	FULLER <u>et al.</u>
10048						
Sieved fraction						
74-147μm	Kr.	0.26	0.20	-	16	FANALE <u>et al.</u>
147-256μm	Kr.	0.31	0.16	-	29	FANALE <u>et al.</u>
Apollo 12						
12033,46	N ₂	0.05		-	-	FULLER <u>et al.</u>
12001,118*	N ₂	0.08	(10 ⁻⁴ atm)	-	-	GROSSMAN <u>et al.</u>
Apollo 14						
14163,111	N ₂	0.21	-	-	-	CADENHEAD <u>et al.</u>
14321,156	N ₂	0.34	-	-	-	CADENHEAD <u>et al.</u>
14259,93	Kr.	0.61	0.087	720	109	GROSSMAN <u>et al.</u>
14259,93	O ₂	0.37	0.048	916	386	GROSSMAN <u>et al.</u>
Apollo 15						
15401,48	Kr.	0.40	0.108	650	68	GROSSMAN <u>et al.</u>
<u>Crushed Terrestrial</u>						
Gabbro	Kr.	0.19	0.16	-	28	FANALE <u>et al.</u>
Basalt Cinder	Kr.	0.26	0.13	-	44	FANALE <u>et al.</u>
Vacaville Bas.	Kr.	3.98	0.10	-	74	FANALE <u>et al.</u>

*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 N₂-Stored Apollo 14 Sample at Liquid Nitrogen Temperature (-196°C)

The adsorption isotherms for research grade O₂ first and then N₂ were determined at LN₂ 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 N₂-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 N₂, or by FULLER et al. (1971) with O₂ 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 O₂ run the BET surface area of 0.37 m² 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 O₂ data of FULLER et al. (1971).

Four N₂ runs at LN₂ temperature, which followed the O₂ measurements, are shown sequentially in Figure 4. The first N₂ 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 μmole gm⁻¹ between P/P_s = 0.05 to 0.8 is consistent with one monolayer calculated from the O₂ isotherm or 0.6 monolayer from the Kr surface area determination. The first desorption isotherm starts from 400 μmoles gm⁻¹ showing hysteresis down to zero pressure and a net retention of 10.4 μmoles gm⁻¹. The second adsorption rises to a

maximum of five monolayers (O_2 surface area) at $P/P_s = 0.15$ the amount decreasing from there to $P/P_s = 0.66$ and then increasing again to $300 \mu\text{moles gm}^{-1}$ 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 $18 \mu\text{moles gm}^{-1}$ 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 H_2O 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 LN_2 temperature was checked by studying the adsorption behavior at room temperature using the gas sequence: relatively inert gas, N_2 , a reactive gas, H_2O vapor, and then N_2 . 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 $21.3 \pm 0.1^\circ\text{C}$

The adsorption isotherms of N_2 and H_2O vapor are shown in Figures 5 and 6 respectively. The first experiment is N_2 Run 1 of Figure 5, the second and third experiments are H_2O vapor Runs 2 and 3 of Figure 6, and the fourth, fifth and sixth are the N_2 runs performed after the H_2O 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 ($\pm 3 \mu\text{gm/gm}$ for pressures greater than 0.5 Torr, $\pm 4.5 \mu\text{gm/gm}$ 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 $3.6 \mu\text{mole/gm}$ 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 $5.6 \mu\text{moles}$ of H_2O which is equivalent to $3.6 \mu\text{mole}$ of N_2 and the difference between the two parallel adsorption curves of Runs 1 and 4 is about $2 \mu\text{mole}$. The retention of $5.6 \mu\text{moles}$ of water by a sample weight of 0.39574 gm with a surface area $\sim 0.6 \text{ m}^2 \text{ gm}^{-1}$ 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 $3.6 \mu\text{mole}$.

At all pressures lower than 200 Torr Run 4 shows a negative hysteresis similar to that observed at LN_2 (Figure 4). At pressures $\lesssim 50$ 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 H₂O 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 H₂O. This amount was retained by the sample even after continuous pumping at a pressure of $\sim 3 \times 10^{-6}$ 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 H₂O retention point was determined by continuous pumping at a pressure of $\sim 3 \times 10^{-6}$ 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 H₂O adsorption run at 25°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 $\mu\text{moles gm}^{-1}$ have been reported, H_2 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 O_2 and H_2O 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 N_2 is released, the penetration of the damaged layer is less than 100 nm since H_2 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 $300 \mu\text{gm gm}^{-1}$ and the 300°C 24 hour weight loss was $940 \mu\text{gm gm}^{-1}$, 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_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_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_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 ($25 \pm 0.3^\circ\text{C}$) for the UHV-stored Apollo 12 vacuum sample (12001,118) using a gravimetric System II. (There was no permanent retention of 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 N_2]. The Argon isotherm obtained after 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 N_2 temperature (-196°C) using a volumetric system. (The cumulative error for a 16 point adsorption/desorption isotherm is $1.6 \mu\text{mole gm}^{-1}$.)

Figure 4. Nitrogen adsorption and desorption isotherm series at liquid N_2 temperature on the Apollo 14 sample (14259,93) after 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 $1.6 \mu\text{mole gm}^{-1}$.)

Figure 5. Nitrogen adsorption and desorption isotherms for the Apollo 14 sample (14359,113) at constant temperature of $21.3 \pm 0.1^\circ\text{C}$ 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 $\pm 3\mu\text{gm/gm}$ for pressures greater than 0.5 Torr, $\pm 4.5 \mu\text{gm}$ 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 $21.3 \pm 0.1^\circ\text{C}$ 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 $\pm 2.5 \mu\text{gm/gm}$ for pressures greater than 0.5 Torr, $\pm 3 \mu\text{gm/gm}$ for pressures less than 0.5 Torr.)

Figure 5. Nitrogen adsorption and desorption isotherms for the Apollo 14 sample (14359,113) at constant temperature of $21.3 \pm 0.1^\circ\text{C}$ 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 $\pm 3\mu\text{gm/gm}$ for pressures greater than 0.5 Torr, $\pm 4.5\mu\text{gm}$ 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 $21.3 \pm 0.1^\circ\text{C}$ using gravimetric System I. (These two water runs were made after nitrogen Run I shown in Figure 4. After these water runs nitrogen Runs 4 to 6, also shown in Figure 5, were made.) Error $\pm 2.5\mu\text{gm/gm}$ for pressures greater than 0.5 Torr, $\pm 3\mu\text{gm/gm}$ for pressures less than 0.5 Torr.

REFERENCES

- ARRHENIUS G., LIANG S., MACDOUGALL D., WILKENNIG L., BHANDARI N., BHAT S., LAL D., RAJAGOPALAN G., TAMHANE A. S. and VENKATAVARADAN V. S. (1971) The exposure history of the Apollo 12 regolith. Proc. Second Lunar Sci. Conf., Vol. 3, 2583-2598. M.I.T. Press.
- BORG J., MAURETTE M., DURRIEU L., and JOURET C. (1971) Ultramicroscopic features in micron-sized lunar dust grains and cosmophysics. Proc. Second Lunar Sci. Conf., Vol. 3, 2027-2040. M.I.T. Press.
- CADENHEAD D. A., WAGNER N. J., JONES B. R., and STETTER J. R. (1972) Some surface characteristics and gas interactions of Apollo 14 fines and rock fragments. In Lunar Science - III (Editor C. Watkins) 110-112, Lunar Science Institute Contr. No. 88.
- COMSTOCK G. M., EVWARAYE A. O., FLEISCHER R. L., and HART H. R. (1971) The particle track record of lunar soil. Proc. Second Lunar Sci. Conf., Vol. 3, 2569-2582. M.I.T. Press.
- CROZAZ G., HAACK U., HAIR M., MAURETTE M., WALKER R., and WOOLUM D. (1970) Nuclear track studies of ancient solar radiations and dynamic lunar processes. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta. Suppl. 1, Vol. 3, 2051-2080. Pergamon Press.
- CROZAZ G., WALKER R., and WOOLUM D. (1971) Nuclear tract studies of dynamic surface processes on the moon and the constancy of solar activity. Proc. Second Lunar Sci. Conf., Vol. 3, 2543-2558. M.I.T. Press.
- EBERHARDT P., GEISS J., GRAFF H., GRÖGLER N., KRÄHENBÜHL U., SCHWALLER H., SCHWARZMULLER J., and STEITLER A. (1970) Trapped solar wind noble gases, Kr^{81}/Kr exposure ages and K/Ar ages in Apollo 11 lunar material. Science, 167, 558-560.

- EPSTEIN S. and TAYLOR JR. H. P. (1970) $^{18}\text{O}/^{16}\text{O}$, $^{30}\text{Si}/^{28}\text{Si}$, D/H, and $^{13}\text{C}/^{12}\text{C}$ studies of lunar rocks and minerals. Science, 167, 533-535.
- FANALE F. P., NASH D. B., and CANNON W. A. (1971) Lunar fines and terrestrial rock powders: relative surface areas and heats of adsorption. J. Geophys. Res., 76, 6459-6461.
- FLEISCHER R. L., HAINES E. L., HART H. R., WOODS R. T., and COMSTOCK G. M. (1970) The particle track record of the sea of tranquility. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 1, Vol. 3, 2103-2120. Pergamon Press.
- FLEISCHER R. L., HART H. R., COMSTOCK G. M., and EVWARAYE A. O. (1971) The particle track record of the ocean of storms. Proc. Second Lunar Sci. Conf., Vol. 3, 2559-2568. M.I.T. Press.
- FRIEDMAN I., O'NEIL J. R., ADAMI L. H., GLEASON J. D., and HARDCASTLE K. (1970) Water, hydrogen, deuterium, carbon, carbon-13, oxygen 18 content of selected lunar material. Science, 167, 538-541.
- FULLER E. L., HOLMES H. F., GAMMAGE R. B., and BECKER K. (1971) Interaction of gases with lunar materials: preliminary results. Proc. Second Lunar Sci. Conf., Vol. 3, 2009-2019. M.I.T. Press.
- FUNKHOUSER J. G., SCHAEFFER O. A., BOGARD D. D., and ZÄHRINGER J. (1970) Gas analysis of the lunar surface. Science, 167, 561-563.
- FUNKHOUSER J., JESSBERGER E., MULLER O., and ZÄHRINGER J. (1971) Active and inert gases in Apollo 12 and Apollo 11 samples released by crushing at room temperature and by heating at low temperatures. Proc. Second Lunar Sci. Conf., Vol. 2, 1381-1396. M.I.T. Press.
- GIBSON JR. E. K. and JOHNSON S. M. (1971) Thermal analysis-inorganic gas release studies of lunar samples. Proc. Second Lunar Sci. Conf., Vol. 2, 1351-1366. M.I.T. Press.

- GOLD T., CAMPBELL M. J. and O'LEARY B. T. (1970) Optical and high-frequency electrical properties of lunar samples. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta. Suppl. 1, Vol. 3, 2149-2154. Pergamon Press.
- GROSSMAN J. J., RYAN J. A., MUKHERJEE N. R., and WEGNER M. W. (1970a) Surface properties of lunar samples. Science, 167, 743-745.
- GROSSMAN J. J., RYAN J. A., MUKHERJEE N. R. and WEGNER M. W. (1970b) Microchemical, microphysical and adhesive properties of lunar material. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta. Suppl. 1, Vol. 3, 2171-2181. Pergamon Press.
- GROSSMAN J. J., RYAN J. A., MUKHERJEE N. R., and WEGNER M. W. (1971) Microchemical, microphysical, and adhesive properties of lunar material II. Proc. Second Lunar Sci. Conf., Vol. 3, 2153-2164. M.I.T. Press.
- HAPKE B. W., COHEN A. J., CASSIDY W. A., and WELLS E. N. (1970) Solar radiation effects on the optical properties of Apollo 11 samples. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta. Suppl. 1, Vol. 3, 2199-2212. Pergamon Press.
- HOYT H., KARDOS J. L., MIYAJIMA M., SEITZ M. G., SUN S. S., WALKER R. M., and WITTELS M. C. (1970) Thermoluminescence, X-ray and stored energy measurements of Apollo 11 samples. Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta. Suppl. 1, Vol. 3, 2269-2287. Pergamon Press.
- KIRSTEN T., STEINBRUNN F., and ZÄHRINGER J. (1971) Location and variation of trapped rare gases in Apollo 12 lunar samples. Proc. Second Lunar Sci. Conf., Vol. 2, 1651-1669. M.I.T. Press.
- MOORE C. B., LEWIS C. F., LARIMER J. W., DELLES F. M., COOLEY R. C., and NICHIPORUK W. (1971) Total carbon and nitrogen abundances in Apollo 12 lunar samples. Proc. Second Lunar Sci. Conf., Vol. 2, 1343-1350. M.I.T. Press.

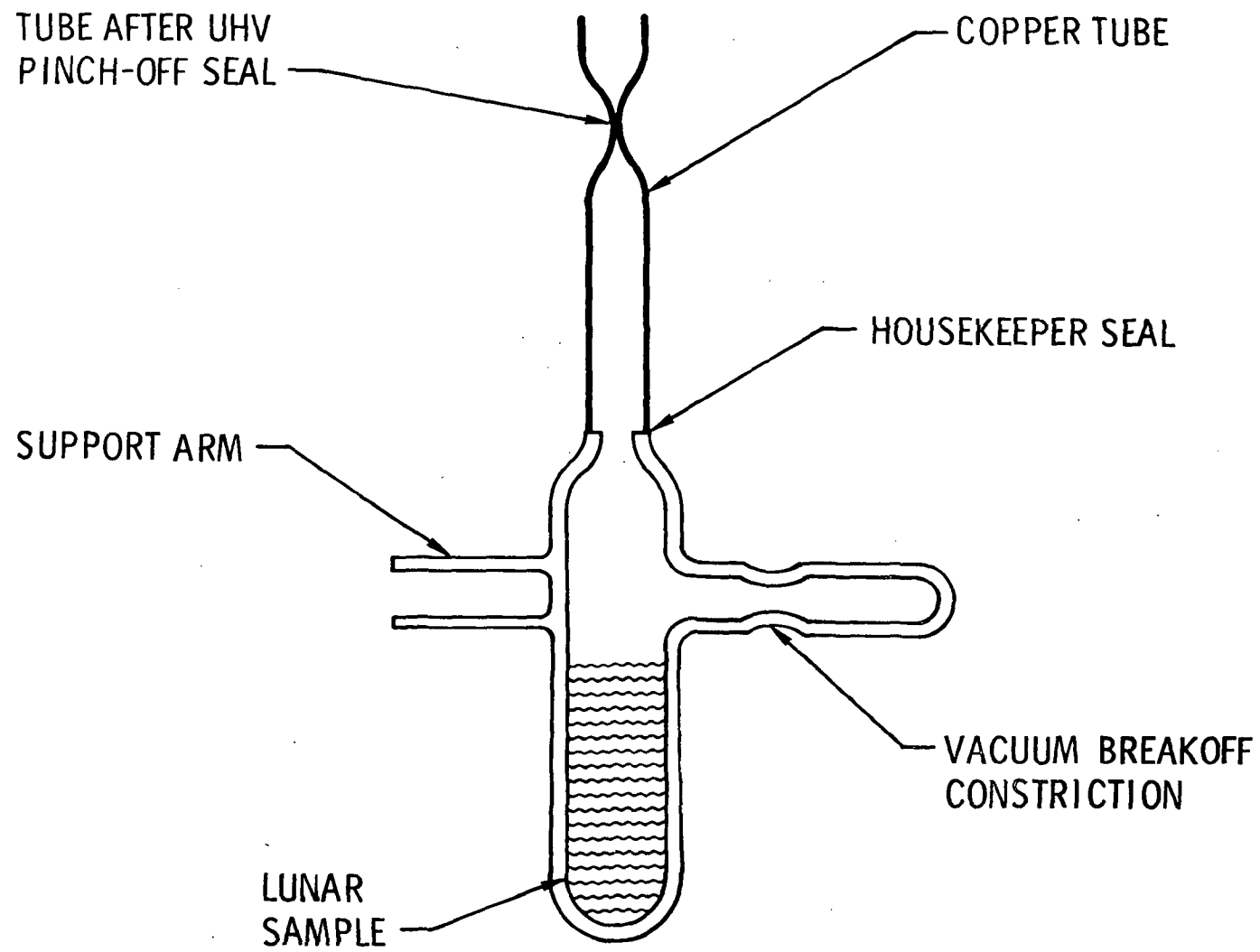


Figure 1

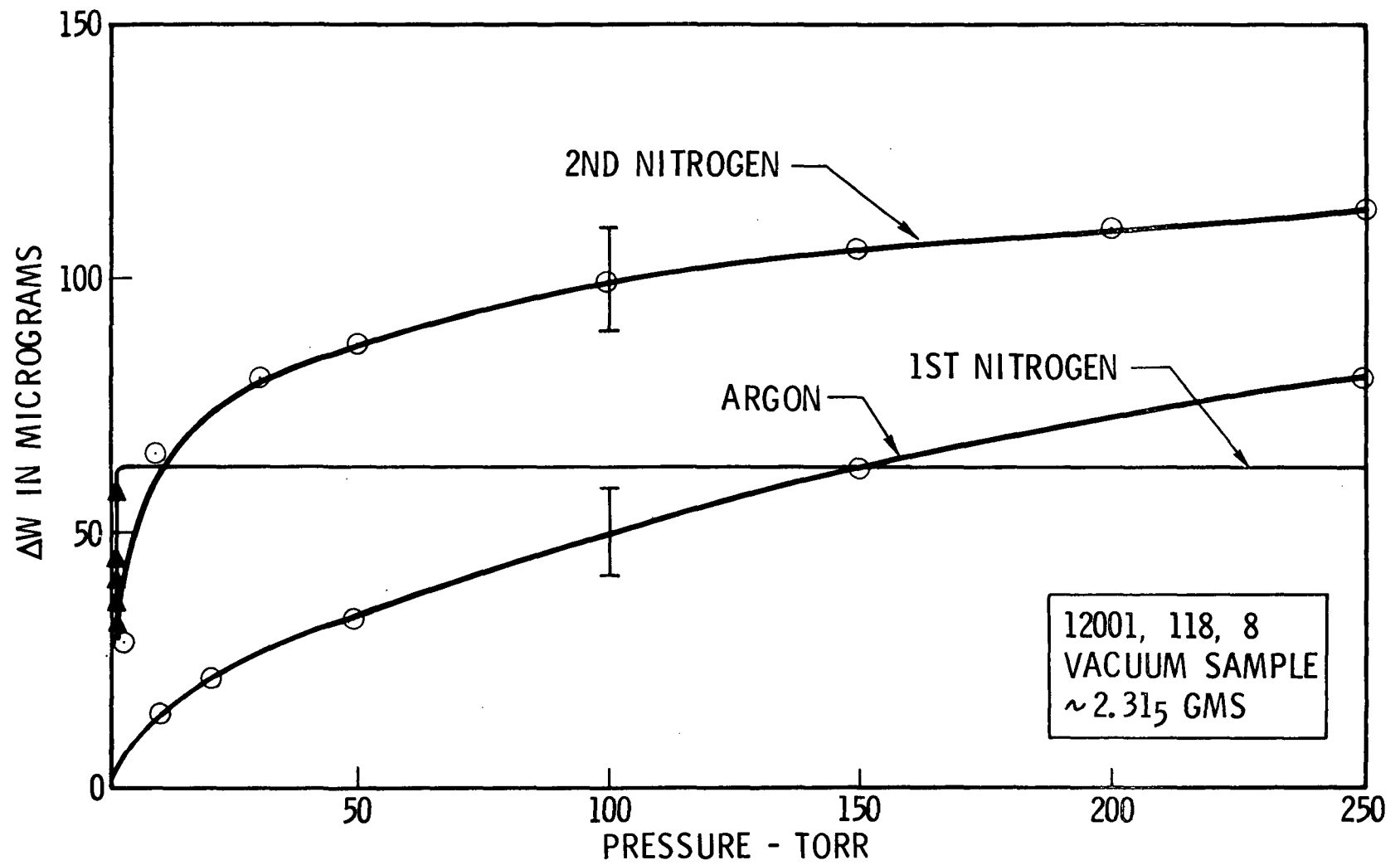


Figure 2

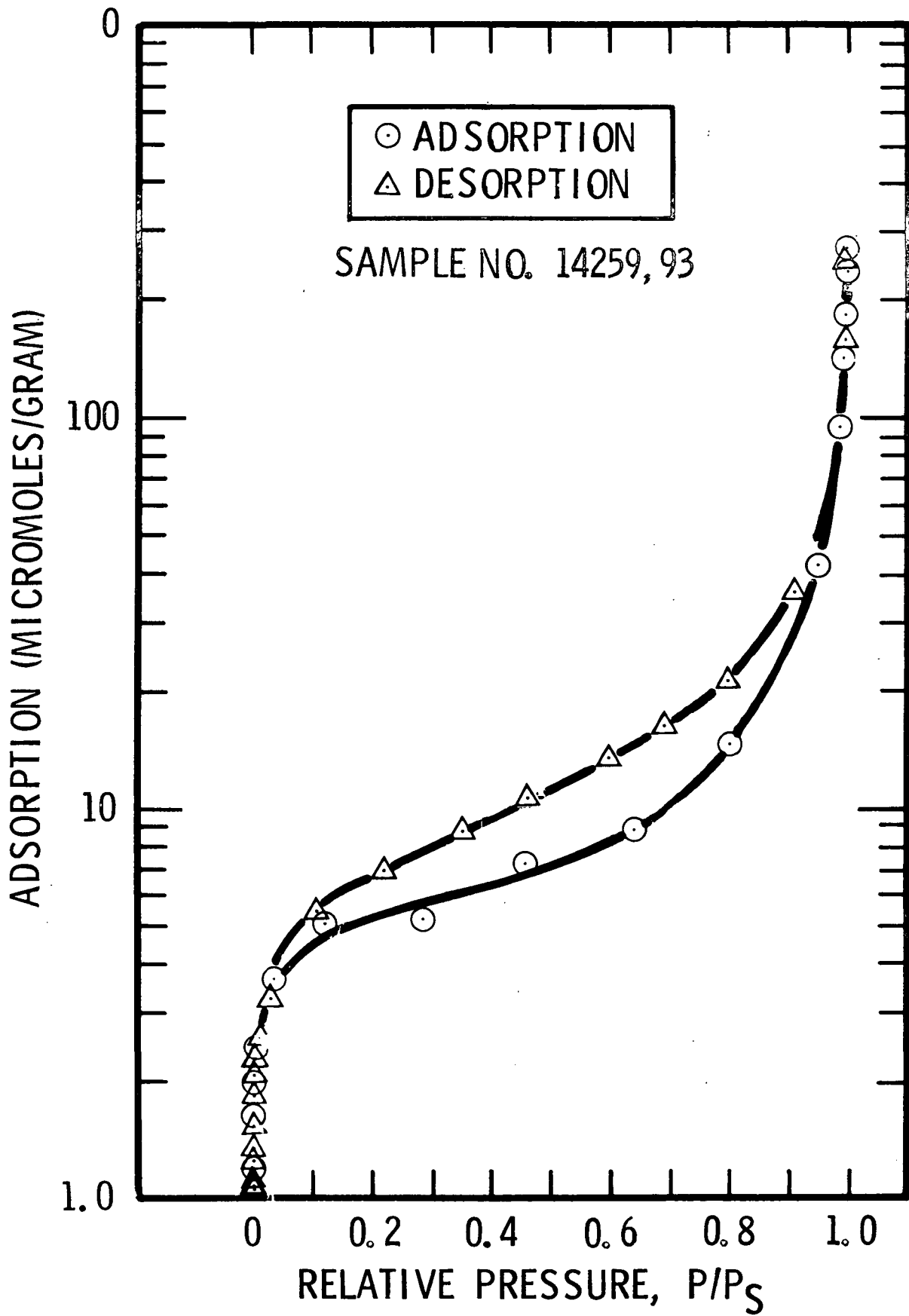


Figure 3

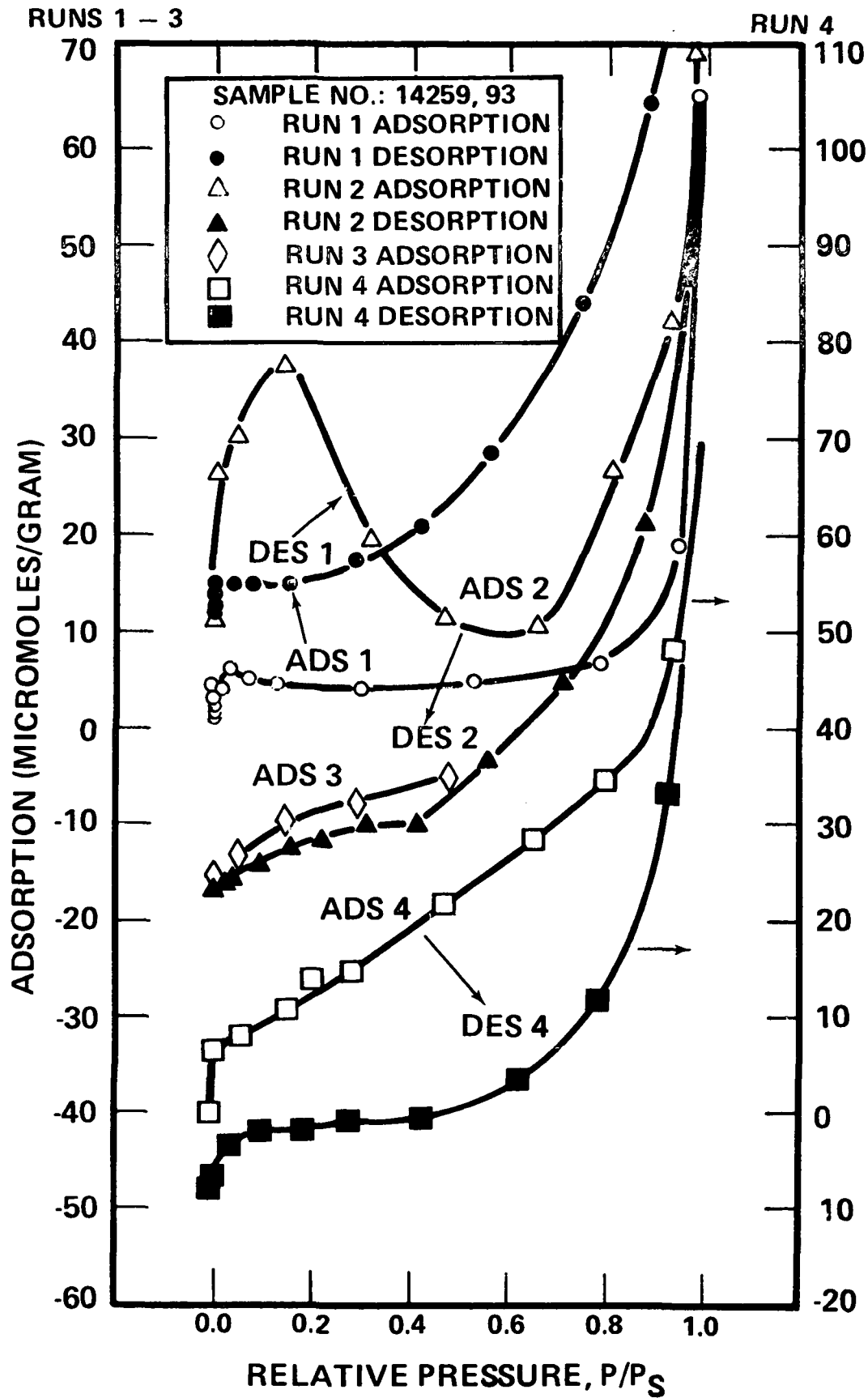


Figure 4

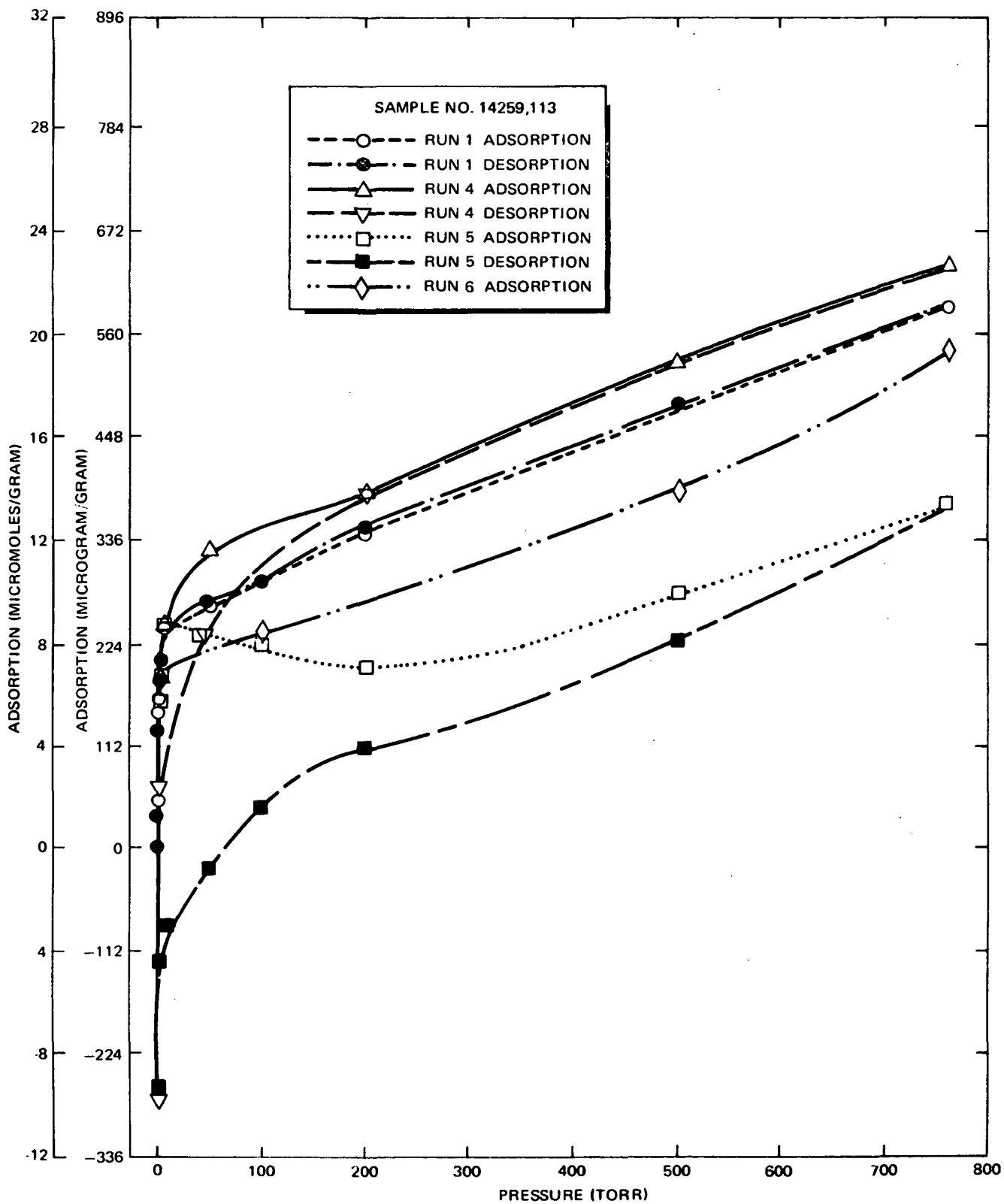


Figure 5

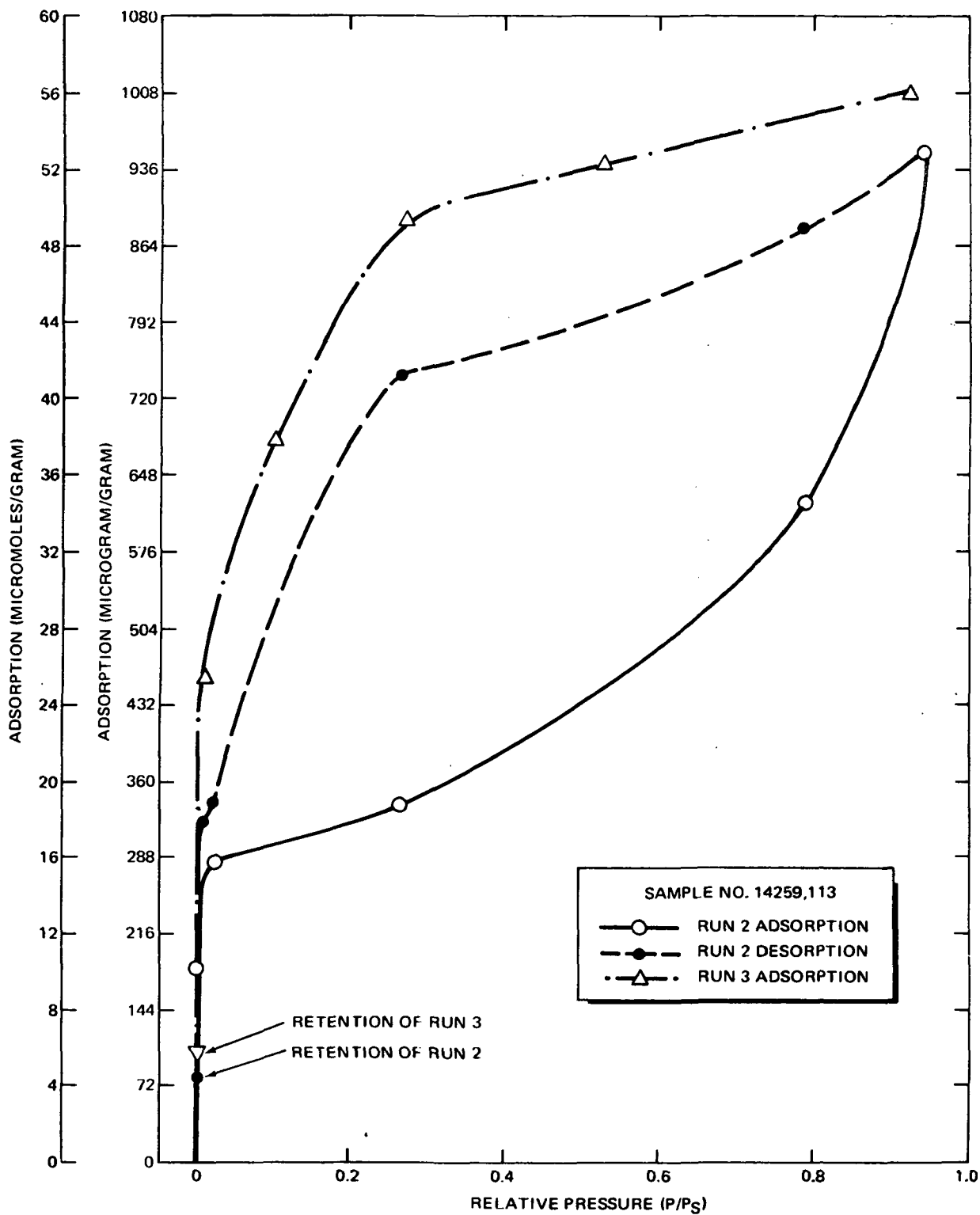


Figure 6