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INVESTIGATION OF SPUTTERING EFFECTS ON THE MOON'S SURFACE

Thirteenth Quarterly Status Report

Contract NASw-751

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ABSTRACT

Experiments to build up thick crusts of powder bombarded by ions throughout its bulk are reported. Cementation of copper powder under dc mercury ion bombardment in a low-pressure plasma was demonstrated. But rf bombardment was accompanied by difficulties due to spontaneous formation in the ion sheath of long conducting chains of powder particles that shorted the sample to rf ground. DC bombardment of insulating powders could not be accomplished in the plasma, but negligible rf alignment and lifting effects were observed for insulating powders which are not rendered conducting by ion bombardment. Slow cementation of Al_2O_3 powder occurs under mercury-ion bombardment and became more rapid if a small flux of atoms sputtered from Al_2O_3 was returned to the surface. A realistic returning flux for lunar surface simulation is not known in the absence of suitable data on the velocities of sputtered atoms.

An experiment designed to detect small fluxes of H_2O emitted from silicates (or other oxides) bombarded by ions from a hydrogen discharge plasma revealed significant mass transport of carbon within the discharge region due to chemical attack of carbon (from contaminants) on the vacuum tube walls. H_2O formation under these conditions was small

for a basaltic powder and consistent with zero. Some injection of carbon into a surface layer in previous experiments with silicates is suggested as a possible contributor to the optical darkening there observed. The analogous process occurring at the lunar surface is examined quantitatively in the light of a recent suggestion that photospheric abundances of the elements may probably be expected in the solar-wind flux. It is concluded that significant carbon concentrations may accumulate in a 10^{-5} cm layer of silicate particles exposed on the lunar surface for total times of the order of 10^4 yr.

I. INTRODUCTION

The work of this quarter has concentrated on cementation and chemical effects of the solar wind. "Cementation" refers to a bulk property of powder samples subject to solar-wind bombardment. Partial erosion of the powder particles furnishes material to crucial contact areas between the particles so that bonds between the particles tend to become stronger. The crusting reported here reveals a dependence of cementation on the amount of transported material that shows that the cementing action in our experiments is not just due to changes in the strength of the forces at interparticle contact points (e.g., due to a damaged surface) but is due to sputtered material.

The chemical effect to be studied was the possible production of water from silicates (oxides) by hydrogen bombardment. The study turned to the subject of hydrides of carbon instead of oxygen because of carbon contamination. It spurred the realization that the solar wind is contaminated also and added a complicating dimension to the subject of solar-wind effects at the lunar surface, namely, the effects of ions in the solar wind more massive, but much less abundant, than hydrogen and helium.

A paper titled "Modification of Optical Properties of Lunar Surface Powder by Solar-Wind Bombardment" was submitted to the Journal of Geophysical Research and has been returned for minor revisions. Since it is a streamlined and only slightly revised form of the optical studies reported in the Eighth and Twelfth Quarterly Reports, we will not reproduce it here. We plan, however, to incorporate it into a future quarterly report when reprints become available.

II. CRUST BUILDUP ON A POWDERED SURFACE BY ION BOMBARDMENT

As we have previously remarked,(1) the properties of a thick crust of powder bombarded by ions throughout its bulk would be of great interest. The optical properties might be substantially different from those of a surface-bombarded-only sample and its structural properties could be measured. An electromagnetic shaker device, used in flash evaporation sources, was obtained from Balzers (Liechtenstein) capable of delivering a small uniform stream of powder in a vacuum environment. A modified version of this device, with the driving mechanism outside the vacuum chamber, was constructed. Several experiments were conducted to survey the results that might be expected.

For the first experiments, 200-230 grit copper powder was deposited in a slow stream onto a copper plate being bombarded by 8 mA of 1000 V mercury ions. After 2 hr of deposition and bombardment a cylindrical column was built up. It was ~ 2 cm high and ~ 1 cm in diameter. Fig. 1 shows this column. During deposition, copper particles were observed to migrate to the perimeter of the top. Collisions of incoming particles initiated the migration. The perimeter therefore represents the edge of the area hit by incoming particles. Upon reaching the perimeter, they stopped and were then cemented to form a crust by the bombarding mercury ions. Some charging and alignment of particles took place in the ion sheath as indicated by the "hairy" appearance of the side surfaces. The material in the center of the column was not bombarded for a long enough time to be cemented together before being covered up. The perimeter is bombarded by higher current densities than the column center.

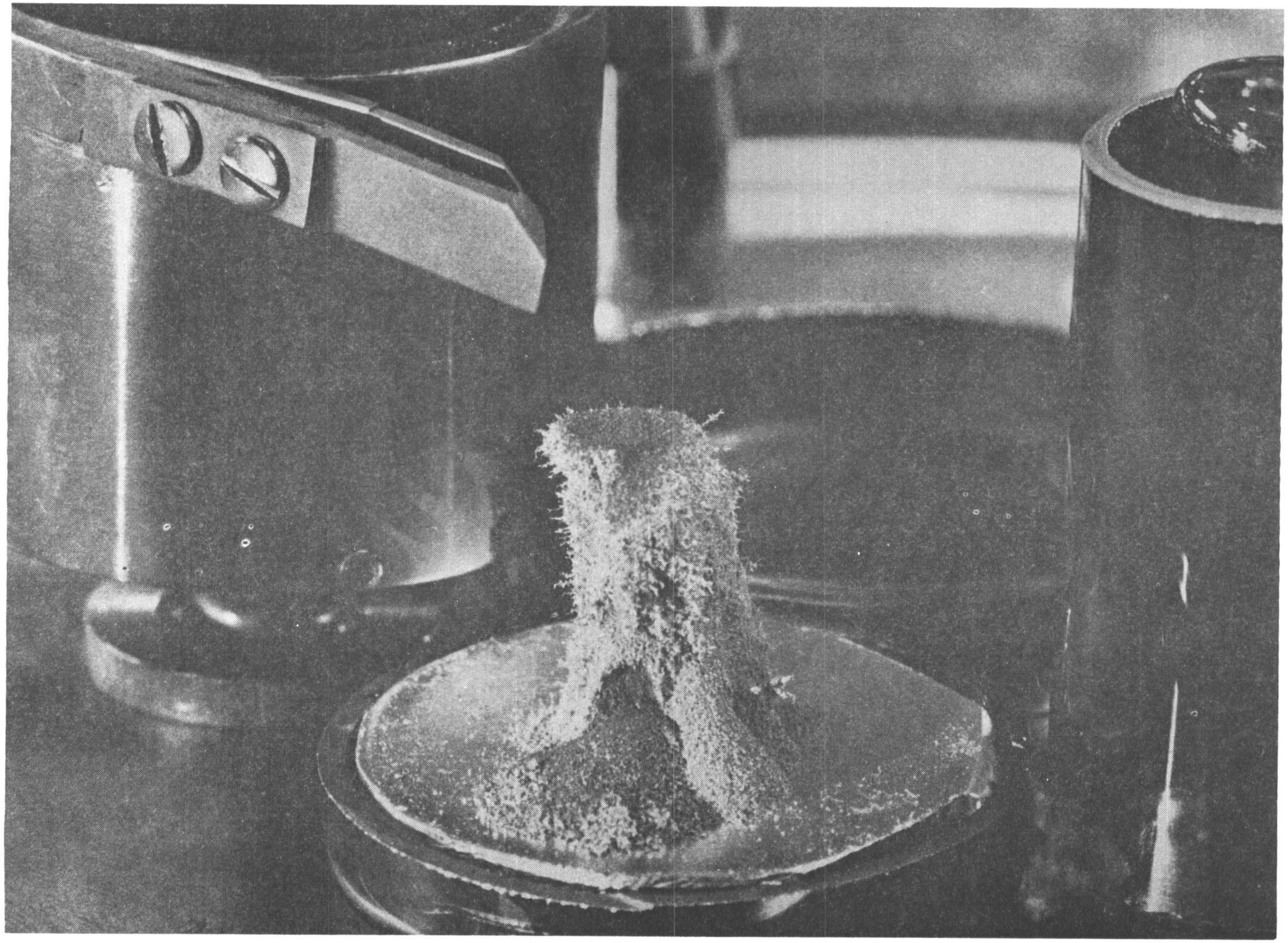

Fig. 1 Cylinder of copper powder built up during 2 hr of deposition from the powder feeder at the left, dc bombardment by 1000 V Hg^+ ions.

The base of the column broke open when the pressure due to the column became too great. The "alluvial fan" formed is the darker material seen at the base. The crust around the base had been weakened by material falling over the near edge of the top. This experiment was repeated with plasma only, no ion bombardment of the sample. The resulting uncemented mound of material is shown in Fig. 2. We conclude that cementation evident in Fig. 1 was due to sputtering.

Another experiment was run with the 200-230 grit copper powder in which ion bombardment was accomplished in rf electric fields rather than in dc fields. Here the powder was slowly deposited on a quartz surface with an rf electrode under it. A peculiar and fascinating thing about this experiment was the formation of long (cm) strings of copper particles in the rf ion sheath. The strings would extend from the surface to the edge of the plasma sheath. The upper portion would then lie in the plasma-sheath interface. Any portion of a chain protruding through the sheath into the plasma would be heated to incandescence. In several instances, small droplets of molten copper were formed on the ends of the chains. The chains formed in ~ 1 sec and were up to several centimeters long depending on the powder deposition rate. The chains grow by addition to the bottom. The bottom can migrate down a slope during formation. A surface bombarded in this way is shown in Fig. 3.

The rf experiment was repeated using the above copper powder plus 200 grit alumina powder in a mixture. The same chain formation takes place. The main string of the chain is entirely copper though some of the short appendages are terminated by an aluminum oxide particle.

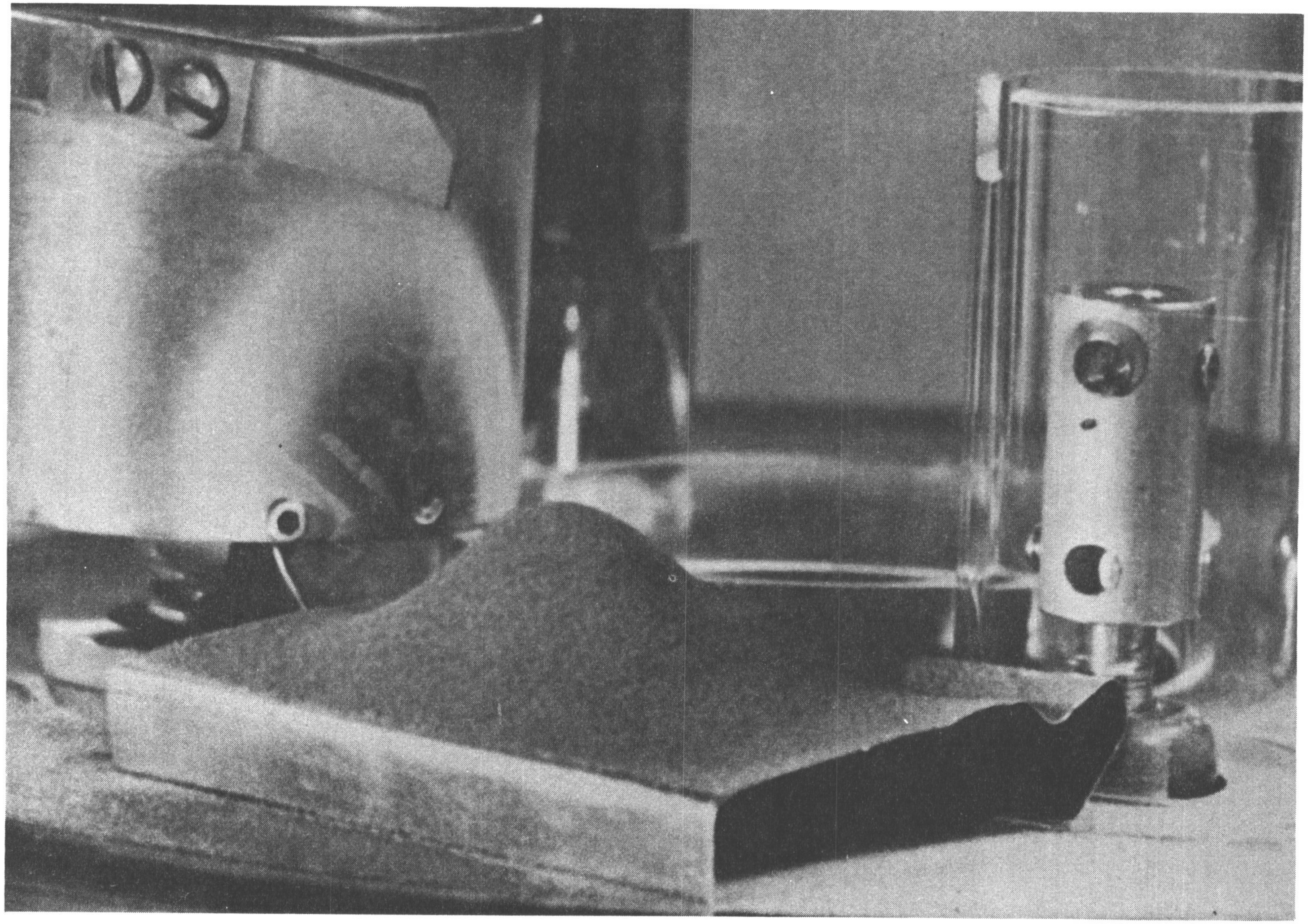

Fig. 2 Mound of copper powder built up during 2 hr of deposition in Hg^+ plasma, no sputtering by high-energy ions.

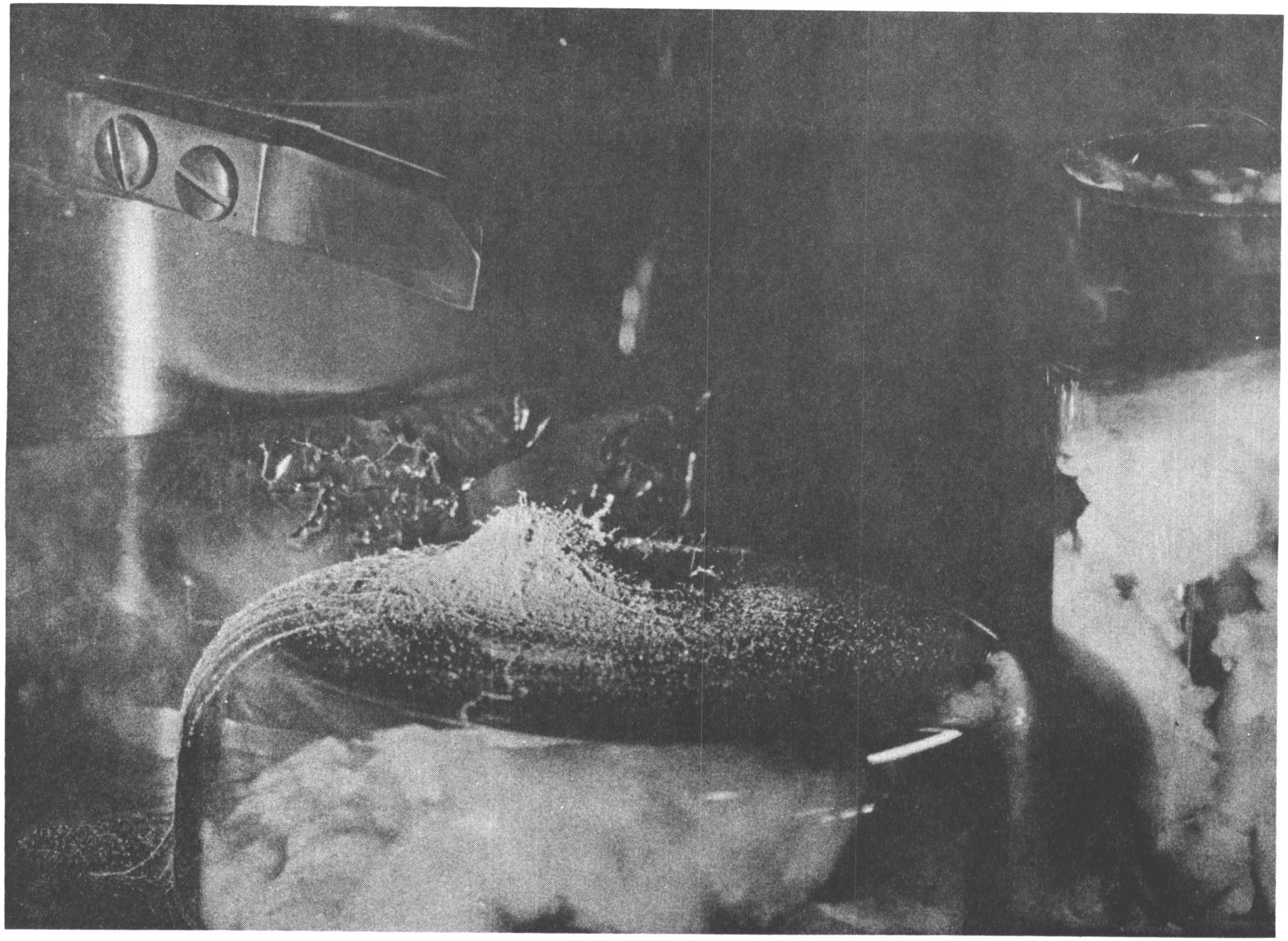

Fig. 3 Copper powder sputtered by ion bombardment in rf (2 Mc/s) fields. Note the chains of copper particles draping over the edge of the quartz dish that were formed in the rf ion sheath.

The chains formed are continuous physically and electrically and remain so on removal from the vacuum. The fusing is probably caused by the conduction of rf currents along the chain. Figure 4 shows some of these continuous chains of copper particles. We conclude that experiments in which particles are rendered conducting or are initially conducting may be attended by this distracting particle alignment in an rf-modulated plasma sheath.

We next describe some experiments with initially insulating powders. Here, unless the powders can be rendered conducting by ion bombardment, the bombardment by ions from a plasma necessarily requires an rf-modulated plasma sheath. We did try to accomplish dc sputtering of an insulating surface by placing it in the center of a conducting plate and biasing the plate to a large (3 kV) negative potential in a plasma sufficiently rarified so that the plasma sheath was somewhat thicker than the diameter of the supporting plate. Thus ions were accelerated toward the insulating powder and could be deflected away from the powder area only if it were able to support a large potential difference from top to bottom. We were correct in hoping that leakage currents would not permit such large potential differences. In one experiment 180 grit alumina (Al_2O_3) was dropped onto a Ni base plate. Fusing and darkening were both present but both of these effects were mainly due to Ni that had found its way indirectly to the alumina surface. Fragments of the crust were clearly magnetic. We therefore covered the plate initially with a thin layer of alumina, assuming that the underside of the plate would suffice to enforce the 3 kV bias. After 8 hr of bombardment, the

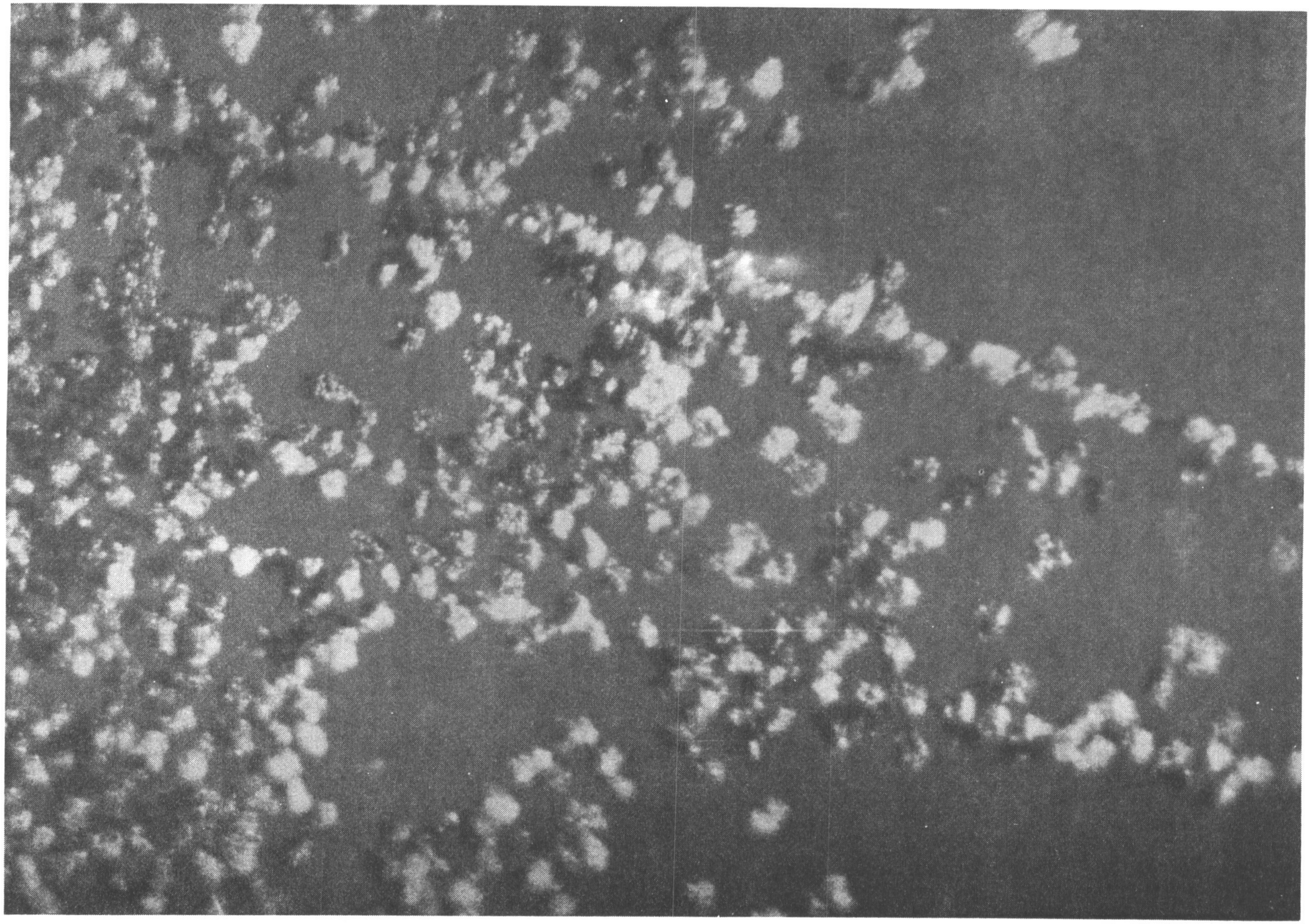

Fig. 4 Detail of chains of copper particles formed in the rf ion sheath when a mixture of alumina and copper powders was being sputtered.

powder surface was darkened and slightly fused. The crust was not obviously magnetic but the appearance of the base plate revealed some sputtering of the plate had occurred due to ions penetrating small holes in the alumina layer. We assume that Ni furnished the conductivity of the alumina layer and have abandoned hope that dc bombardment of dielectric powder layers can be accomplished free from objection.

From previous experiments with mercury-ion bombardment of alumina,(2) we know that darkening plus a weak, fragile crusting results after very extensive bombardment (>100 C/cm^2) using an rf-modulated plasma sheath. No marked filament formation was seen.

Surely some fraction of the sputtered atoms leaving an elemental area of the moon's surface returns elsewhere to the surface. Since half the moon is being sputtered at any given time (ignoring questions of deflection of the solar-wind ions), this is equivalent to an incident flux of sputtered atoms on that elemental area. We do not know what fraction of the emitted flux this should be nor whether each element returns in the emitted proportion because we do not know the velocity distributions of atoms sputtered from compounds by hydrogen and helium atoms of kiloelectron volt energies. Nevertheless, we conducted an experiment to qualitatively assess the importance of a returning flux.

A nickel plate was uniformly covered with 180 grit alumina before bombardment, and two alumina cylinders were suspended above the sample by wire cores. The covered plate and alumina cylinders were then rf-bombarded by Hg ions for about 10 hr. During this time, some additional alumina powder was deposited onto one area of the plate so as to accumulate a few layers of bombarded alumina. On removal from the vacuum chamber, the surface was found to be darkened and fused. Some sectors of the crust were cracked and were self-supporting. This is by far the greatest amount of surface cementation we have observed with aluminum oxide. We conclude that a "returning flux" of sputtered atoms will greatly speed cementation of a sputtered powder surface.

III. EXPERIMENTS ON WATER VAPOR FORMATION DUE TO HYDROGEN ION BOMBARDMENT OF OXIDES

Recent work by Blauth and Meyer(3) showed that atomic hydrogen can attack at least a monolayer of oxygen on glass and form water molecules. Since sputtering can reveal fresh surfaces for further attack, we were stimulated to investigate whether hydrogen sputtering of oxides is accompanied by water molecule formation. The experiments reported here were inconclusive with respect to the central question of water molecule formation, but revealed a contamination problem in the apparatus that has been previously used for bombardment of samples that were studied as to optical properties. In addition, the measurements illustrate certain practical difficulties in the intended research.

First of all, we adopted the philosophy that it is not necessary to directly detect H_2O molecules emitted from the sample. On the moon, some (unknown) fraction of the sputtered and thermally desorbed efflux from a given area returns to other areas on the moon. Because of this mixing process on the moon, it seems reasonable as a first approximation to conduct an experiment in which the sputtered and thermally desorbed fluxes from a sample are alike allowed to fall on a cold trap surface. If the residence time for H_2O molecules that either arrive at or are formed on the cold surface is long enough, then appreciable masses of H_2O can be accumulated. Direct detection would call for extremely sensitive techniques that could hardly be justified before the existence of any mechanism for H_2O formation, direct or indirect, were demonstrated.

The choice of a cold trap temperature is straightforward. According to Beard(4) the flux of molecules of mass m evaporating from a surface of the same substance at temperature T is

$$\dot{N} = A\ 10^{-B/T}\ (3\ mkT/4)^{-\frac{1}{2}}\ .$$

For water A = 3.85×10^{13} dyne/cm^2 and B $\simeq$ 2675°K. Dry ice temperature, -78.5°C, is not cold enough because the evaporating flux is 9.0×10^{17} H_2O/cm^2 sec. The vapor pressure is 0.53 mTorr. But at liquid nitrogen temperature, 80°K, the evaporating flux is only 2.8×10^{-2} H_2O/cm^2 sec; the vapor pressure is 1.0×10^{-23} Torr. An intermediate temperature would be adequate and the conditions described below seem to suggest using an intermediate temperature, but liquid nitrogen cooling was employed because of its convenience. The fluxes to be discussed below are greater than 10^9 cm^{-2} sec^{-1}. Hence, for the purposes of this discussion, gases can be considered to be trapped whose vapor pressures are <u>less</u> than 5×10^{-13} Torr at 80°K. This does <u>not</u> include H_2, He, N_2, O_2, and Ne, obviously, because their boiling points are all below 80°K. CO, Ar, and CH_4 should also not be trapped and even CO_2, whose vapor pressure at 80°K is about 10^{-7} Torr, should not be very effectively held on the surface, its efflux being 1.1×10^{14} CO_2/cm^2 sec. A number of light hydrocarbons also have high vapor pressure at 80°K: C_2H_4, C_2H_2, C_2H_6O, C_4H_{10}, for example.

The cold trap that was installed in the vacuum system previously used for ion bombardments in a hydrogen plasma was of the re-entrant type. A cylinder of 4.5 cm diameter is capped by a hemisphere which is

9.5 cm from the sample being sputtered. It is sealed within the main tube of 5.8 cm inside diameter. Thus the area of the hemisphere subject to direct bombardment by sputtered or desorbed atoms from the sample is about 30 cm^2 and the solid angle subtended is $2\pi \times 0.176$. About 35% of the emitted atoms should fall on the cold trap, assuming a cosine distribution for the emission.

Analysis of the atoms desorbed from the cold trap upon warming in a volume of 2.50ℓ when the pump was valved off was accomplished by a Consolidated Electrodynamics Corporation Type 21-611 residual gas analyzer. Calibration of the pressures was approximate, a Bayard-Alpert gauge on the same sidearm as the gas analyzer being the reference. The lowest pressure detectable for a given gas was 2×10^{-9} Torr. Total pressures greater than 1 mTorr were measured by a thermocouple gauge with correction being applied for gas composition.

The procedure in the experiments to be discussed was as follows. Partially valve off system (pumping speed ~1/3 ℓ/sec) and admit 20μ H_2 through Pd leak. Except in control experiment without plasma, strike discharge with several hundred watts of 40 Mc/s power. After about 1 hr, cool trap with liquid nitrogen for 15 min to detect H_2O. Shut off discharge and H_2 gas supply, open valve to pump. Start gas analyzer (which could not be on when discharge rf was on) and wait 15 min for it to stabilize. Drive coolant from trap, closing the valves to the pump just before warming starts. Follow H_2O pressure rise with occasional checks on other masses. Desorption was essentially complete in 15 min, when a complete spectrum was scanned.

The main result of these experiments is that large masses of H_2 were trapped whenever a hydrogen plasma was maintained in the volume between sample and cold trap. In fact, the amount of H_2 trapped was so great that lengthy exposures to accumulate large masses of H_2O were impossible. The sorbed H_2 that resulted from exposing the cold trap to the plasma for 15 min raised the total pressure in 2.5ℓ to 10-14 mTorr upon desorption. At such high pressure the mass spectrometer response is no longer linear. Appreciable amounts of CH_4 and heavier hydrocarbons were also trapped. Since these gases should not have been trapped at 80°K in contact with an inert surface or even a surface partially covered with sorbed gases like H_2, CH_4, etc., the presence of an active substance on the cold trap was indicated. If, after desorbing the trapped gases in the closed 2.5ℓ volume, the trap was again cooled by liquid nitrogen, only the partial pressures of H_2O and CO_2 decreased. Therefore the trapping mechanism was not reversible but arose from a substance dynamically supplied to the cold trap surface while a plasma was being maintained. The probable active substance is carbon or an hydrogeneous compound of high carbon content.

The results from four experiments are given in Tables Ia and Ib. The pressures given are increases in 15 min in excess of the (usually negligible) pressure increases in 15 min with the trap warm, except as noted. A small ($\sim 3 \times 10^{-7}$ Torr-ℓ/sec) leak at one of the feedthroughs in the gas analyzer persistently opened whenever the system was baked. For these four experiments the leak was constant at 9×10^{15} N_2/900 sec

Table Ia. Approximate partial pressures (Torr) of gases desorbed from about 60 cm^2 of cold trap surface into a 2.5ℓ volume following 900 sec exposures of cold trap (liquid nitrogen) to hydrogen discharge or hydrogen gas only.

A) Discharge in 20 mTorr H_2
B) Exposure to 20 mTorr H_2 only
C) Discharge plus sputtering of tholeiitic basalt powder sample
D) As in (C) except discharge for 2 hr and sputtering for 1 hr previous to cooling the trap for 15 min. Powder sample heated by strong light for 3 min previous to cooling the trap so that H_2O on sample should not be transferred to cold trap.

Gas	H_2	CH_4	H_2O	CO	C_2H_6	O_2*	CO_2
Run A	1.4×10^{-2}	$\sim 1.6\times10^{-4}$	$> 1.6\times10^{-6}$	--	--	$< 2\times10^{-7}$	4×10^{-6}
B	5.3×10^{-5}	0.12×10^{-4}	0.6×10^{-6}	$< 2\times10^{-5}$	$< 2\times10^{-7}$	3×10^{-8}	0.95×10^{-6}
C	1.3×10^{-2}	1.3×10^{-4}	$> 24\times10^{-6}$	--	--	--	3×10^{-6}
D	1.0×10^{-2}	0.64×10^{-4}	$> 0.4\times10^{-6}$	--	--	$< 5\times10^{-8}$	0.41×10^{-6}

Table Ib. Numbers of molecules of gases desorbed in above experiments.

Gas	H_2	CH_4	H_2O	CO	C_2H_6	O_2*	CO_2
Run A	1.25×10^{18}	1.4×10^{16}	$> 1.4\times10^{14}$	--	--	$< 1.8\times10^{13}$	3.5×10^{14}
B	4.7×10^{15}	1.1×10^{15}	0.53×10^{14}	$< 1.8\times10^{15}$	$< 1.8\times10^{13}$	2.7×10^{12}	0.8×10^{14}
C	1.15×10^{18}	1.2×10^{16}	$> 21\times10^{14}$	--	--	--	2.7×10^{14}
D	0.9×10^{18}	0.57×10^{16}	$> 0.35\times10^{14}$	--	--	$< 4.5\times10^{12}$	0.36×10^{14}

*O_2 was not necessarily desorbed from the trap as it may be wholly due to an air leak giving 9×10^{15} N_2/900 sec. The low O_2 pressure implies a quantitative conversion of O_2 into oxides in the system.

so that CO was obscured, in general. One estimate of CO is offered from a consideration of the intensities of C^+ resulting from CH_4 and CO. The expected number of O_2 after 2700 sec (the 45 min from system closing to final mass spectrum) from this leak is 7.3×10^{15}. The observed number of O_2 molecules in the 2.5ℓ volume is 2700X smaller than the expected number if no discharge was run and is probably not larger following a discharge so O_2 is quantitatively converted to oxides in the system. The hot filament in the gas analyzer is the probable agent for conversion. CO is the probable end product, with carbon being supplied to the hot filament by CH_4, but this point was not investigated in detail. It was not realized at the time of these experiments that the 2.7×10^{14} H_2O molecules entering the system in 45 min with air of 40% relative humidity would be comparable to the observed number of H_2O molecules following the sputtering run. Clearly air leaks must be kept far smaller in future experiments.

The ion current to the basalt powder sample when being sputtered was about 3.8 mA or 2.4×10^{16} H_2^+ sec. In 900 sec the surface was bombarded by 4.3×10^{19} H ions of about 250 eV energy, considering that H_2^+ ions of 500 eV energy are equivalent to two protons of 250 eV energy as far as sputtering and chemical effects are concerned. We estimate a sputtering yield of 0.9×10^{-3} atom/H^+ at this energy, where "atom" means an atom of any identity in the basalt composition. Thus we estimate that 4×10^{16} atoms of all identities should be sputtered off the powder particles. Of these, about 2.5×10^{16} O atoms are expected and perhaps only 1 x 10^{16} O atoms will actually escape the rough powder surface. At least 35% of the emitted atoms should fall on the cold trap directly and a large segment of the remaining 65% might reach it indirectly, particularly if the O atoms were emitted from the sample mostly as H_2O molecules. Therefore we expected at least 5 x 10^{15} H_2O molecules on the cold trap surface if all the O atoms are emitted in the form of H_2O molecules. On 30 cm^2 of surface, this number of molecules constitutes only a fraction of a monolayer. Upon desorption, many of these molecules might transfer to other wall areas and be bound. They would therefore not be registered in the gas analyzer. It was hoped to evaluate the importance of these wall effects by using runs of different length and by comparing likely lunar materials (like basalt) with materials like CuO, which is apt to form H_2O molecules with high efficiency. At this writing, 900 sec runs are already too long because of the H_2 trapping phenomenon and shorter runs are not apt to be meaningful in view of the small H_2O masses that are involved.

In Table Ib the numbers of observed H_2O molecules are of the order of 10^{14}. The larger number of H_2O molecules in run C where the sample was sputtered must be due to H_2O desorbed from the powder sample when heated by the ion bombardment (probably to nearly 300°C). When a strong light was focused on the sample after run C, the partial pressure of H_2O tripled within 1 min in the (pumped) system. Therefore in a control run D, measures were taken to desorb H_2O from the sample immediately before the trap was cooled for H_2O detection. Not only was the trapped

H_2O the lowest in all the runs, but the trapped H_2, CH_4, and CO_2 were also smaller than in runs A and C, in which a plasma had also been present. In fact, the H_2O was 8X less than might have been expected to enter the system through the leak in the gas analyzer. The H_2O in run D was comparable to that in the "gas only" run B. This implies: (1) that the observed amount of H_2O is consistent with zero formation due to sputtering, (2) that the observed amount of H_2O is consistent with zero formation of H_2O due to the presence of a plasma (which creates H atoms), and (3) that the observed amount of H_2O requires either that (a) H_2O entering the leak is converted to some other form as is O_2 entering the leak or (b) a significant fraction of the H_2O added in these small amounts in the system are immediately bound on the walls. In view of the possible losses of H_2O and the fact that (2) is not consistent with the observation of Blauth and Meyer,(3) conclusion (1) is certainly not established. But the yield Y_w of oxygen atoms in the final form of H_2O molecules in comparison to oxygen atoms in all its final products may well be less than 10^{-2}. This follows from a predicted number of 5×10^{15} trapped H_2O molecules if $Y_w = 1$ and an observed number possibly not greater than 5×10^{13}.

IV. THE VOLATILIZATION OF CARBON AT HYDROGEN DISCHARGE WALLS

Let us now consider the above suggestion that carbon furnishes the trapping matrix in which H_2 and other gases are sorbed at 80°K. The active area for trapping was between 32 and 60 cm^2. The density of sorbed H_2 was $(2\text{-}4) \times 10^{16}$ cm^{-2} so that several monolayers were trapped. In that case a trapping matrix is certainly necessary. And if that matrix changes structure upon warming to room temperature so that the gas escapes, it is not surprising that no more than a fraction of a monolayer of H_2 can be sorbed on the new structure following cooling to 80°K again. It seems improbable that the active atoms could be less numerous than 1×10^{16} cm^{-2}; many more might be required. The minimum influx of active atoms was 10^{13} cm^{-2} sec^{-1}. It is not hard to show that this flux of atoms must have arisen as a result of events at the other walls containing the plasma because events in the volume of the plasma are not sufficiently rapid at these low pressures. To be generous in all estimates, suppose an impurity gas present in the main plasma volume (6 cm diameter x 5 cm long) at a pressure of 2×10^{-7} Torr or 7×10^{9} atom/cm^3 in 140 cm^3, 1×10^{12} atoms. An electron flux $nv \simeq 10^{10}$ $cm^{-2} \times 10^{8}$ cm/sec shall all be assumed to be energetic enough to cause some form of activation of the impurity gas with a cross section of 10^{-17} cm^2. Then the 10^{12} atoms are activated at a rate of 10 sec^{-1} and fly to about 150 cm^2 of wall. The flux from the volume of the plasma is thus certainly less than 10^{11} cm^{-2} sec^{-1}. But at least 10^{15} H_2^+ ions cm^{-2} sec^{-1} drift thermally to the plasma sheath at every boundary of the plasma and are then accelerated to the wall to final energies of 20-40 eV (the floating potential). Doubtless comparable or larger fluxes of H atoms are incident on all the walls. Then only a low efficiency like 10^{-2} active atom/H atom or H_2^+ ion is required to account for an influx of active atoms of 10^{13} cm^{-2} sec^{-1} at the cold trap.

We previously reported(5) that hydrogen ions (mostly H_2^+) of several hundred electron volt energy erode graphite at a rate of 0.5 to 1.0 atom/ion. We report here the recent identification of the principal impurity ions from an oil-pumped unoplasmatron running with deuterium gas: CD_4^+ and CD_5^+. The latter ion, like D_3^+, arises from excited molecule-molecule or ion-molecule reactions in the gas phase of the form

$$X^* + D_2 \rightarrow XD^+ + D + e$$

$$X^+ + D_2 \rightarrow XD^+ + D$$

Other ions present were C^+ and masses 16, 18, 28, 32, possibly 14. These could be CD_2^+, CD_3^+, $C_2D_2^+$, $C_2D_4^+$, and CD^+ but could also be O^+, OD^+ (or H_2O^+), N_2^+, O_2^+, N^+ though no air leak was detectable at the 10^{-7} Torr-ℓ/sec level. The extreme weakness of mass 14 (N^+?) in comparison to mass 16 (O^+?) when mass 28 was considerably stronger than mass 32 (as expected for N_2^+ and O_2^+) makes the air leak explanation unattractive. The striking thing about these identifications is the absence of masses 15, 17, 19, and 21. Since the carbon was derived from hydrogeneous pump oils, not deuterated oil, one might expect ions like CDH^+, CH_3D^+, CD_3H^+, and CD_4H^+ unless the oil is very completely broken down into carbon before being attacked by the deuterium discharge.

The indicated process is decomposition on hot tungsten and tantalum surfaces in the unoplasmatron cathode followed by emission in pure carbon form to surfaces bounding the deuterium plasma where the carbon is then deuterated and volatilized again. As in the rf discharge, not more than 20-40 eV is available at the plasma boundary to accelerate deuterium ions, if indeed ions are importantly involved in the volatilization of the carbon.

It has long been clear that electrical discharges tend to deposit pump oils on the plasma boundaries in carbonaceous form. The above observations suggest that in the case of low pressure hydrogen discharges, the carbon on the walls has a considerable "volatility" as a consequence of the possibility of chemical attack. Thus the above sorption of H_2 at 80°K can be understood as the consequence of mass transfer of carbon from warm walls to a cold one. Of course, the competing processes of volatilization and carbonizing are operative on the walls without regard for the wall temperature but the residence time for the volatile phase is greater on the cold surface so a mass transfer ensues.

What, then, will tend to happen at a wall whose electrical potential is arranged so that the rate of volatilization is increased? Namely, does one expect that our sputtered sample is cleaned of carbon films due to bombardment by energetic hydrogen ions? The answer is a qualified yes: the samples should become <u>relatively</u> clean of surface carbon films in comparison to other surfaces exposed to the same plasma. But once a certain mass of carbon is present on all the surfaces facing the plasma, the coverage on different areas will depend on the ratios of the volatilities at those areas, and the ratio cannot be zero or infinite. But as long as the carbon layers on the weakly bombarded areas do not cause appreciable optical opacity, it should be clear that optical darkening of our strongly bombarded samples cannot be due to optically opaque surface carbon films deposited on our samples.

On the other hand, the above remarks do not imply that our darkening of numerous silicates reported in Quarterly Reports 5-12 and a publication(6) did not partially involve carbon. It is now clear that we bombarded those samples not only with energetic hydrogen ions but also with a small, but uncontrolled flux of carbon-carrying ions. Therefore carbon was injected into the bulk of these samples and that carbon could not become volatile until sputtering of the surface exposed it again. We are not prepared to state at this time how important a role carbon injection might have played in our results. Experiments with known fluxes of hydrogen and carbon ions are forthcoming. The point of the next section is that carbon injection is probably also important at the lunar surface. Therefore our previous work may turn out to have been fairly realistic in spite of the carbon injection, though certainly additional experiments are imperative to clarify the role of carbon in optical properties of silicates.

V. CARBON AND OTHER HEAVY ELEMENTS IN THE SOLAR WIND

Simple hydrodynamic and evaporative models of the solar wind predict a significant decrease for the abundance of heavy elements in the solar wind if the coronal abundances are taken to be the photospheric abundances. The close relationship of these differently formulated models was recently emphasized by Lemaire.(7) But recent measurements of coronal abundances(8) indicated enhancements of heavy elements in the corona. Therefore Brandt(9) coupled this observation with his realization that the entire corona has to be replenished in a time equal to some weeks and suggested that the abundances in the solar wind by flux should equal the photospheric abundances. Checking this suggestion is by no means experimentally easy since the charge-to-mass ratio for the important elements C, N, O, and Ne will equal that for He^{+2}. And Brandt(9) warns that helium might not be significantly enhanced in abundance in the corona because its abundance influences the temperature required for the support of the corona. Cosmogonical considerations and astrophysical observations on hot stars have led to suggestions for He/H ratios in the sun from 0.1 to 0.2. Biswas et al.(10) determined a solar photospheric ratio of He/H of 0.095 ± 0.035 from a combination of spectroscopic and solar-cosmic-ray observations. From an analysis of Mariner 2 data that selected low solar-wind velocity conditions, Neugebauer and Snyder(11) found a He/H ratio of 0.046 ± 0.038. They warned that this low value could conceivably be biased by the choice of low solar-wind velocities and that possibly greater amounts of helium were carried in high-velocity plasma streams. The latter are difficult to interpret unambiguously in their electrostatic analyzer, which responds to mv^2/ze for a particle, namely, kinetic energy per elementary charge.

Certainly photospheric abundances by flux in the solar wind are an upper limit and circumstances not now understood may well reduce fluxes of heavy elements after all. Nevertheless, the observation of excess abundances in the corona encourages the consideration of heavy element fluxes at photospheric abundances.

In Table II are given photospheric abundances as given by Aller.(12) Most of these values are uncertain by about 0.1 in the logarithm; helium and sulfur are uncertain by at least 0.3 in the logarithm. Urey(13) has argued for a lower abundance of Si in the sun on the basis of comparison to meteorite abundances and to avoid having to account for an extremely low Fe/Si ratio in the sun in comparison to planetary and meteoritic bodies.

As a first check on the implications of photospheric abundances by flux in the solar wind, let us estimate the sputtering rates due to heavy elements in comparison to hydrogen and helium. We shall assume undeviated flow of the solar wind to the lunar surface for He^{+2}, C^{+6}, etc. We assume, as usual, that all ions have the same mean velocity at 1 A.U. because of the interplanetary magnetic field. Thus He^{+2} has a value of mv/ze that is twice as great as H^+. The difficulty of calculating the deviated flow problem for the moon has been stated by Michel(14) and Ness.(15) It seems probable that some H^+ is deviated

Table II. Photospheric abundances as given by Aller(12) and sputtering rates for a hypothetical element having M_2 = 30 atomic units subject to bombardment by an undeviated solar wind having photospheric abundance by flux and ions of a single mean speed.

Element	log N	$F = 10^{-4}$ N	$Y(M_1), M_2 = 30$	FY
H	12.00	1×10^8	0.01	1.0×10^6
He	11.21	1.62×10^7	0.1	1.6×10^6
C	8.60	3.98×10^4	0.59	2.4×10^4
N	8.05	1.12×10^4	0.73	0.82×10^4
O	8.95	8.9×10^4	0.87	7.7×10^4
Ne	8.70	5.02×10^4	1.09	5.5×10^4
Mg	7.40	2.51×10^3	1.45	3.6×10^3
Al	6.22	1.66×10^2	1.62	2.7×10^2
Si	7.50	3.16×10^3	1.69	5.3×10^3
Si	7.24[a]	1.74×10^3	1.69	2.9×10^3
S	7.35	2.24×10^3	1.93	4.3×10^3
Ar	6.88	7.6×10^2	2.11	1.6×10^3
Ca	6.19	1.55×10^2	2.36	3.6×10^2
Fe	6.57	3.72×10^2	3.06	1.1×10^3

[a] Revised photospheric abundance for Si proposed by Urey.(13)

most of the time, especially in view of the possible detection of a lunar magnetohydrodynamic wake by Explorer 18.(15) But the fraction of He^{+2} and heavier ions that is deviated is doubtless significantly smaller than for H^+ because of differences in cyclotron radius. As helium contributes most of the sputtering, a comparison of sputtering by helium ions and by heavier ions should be free from objections about deviated ions.

In sputtering yield determinations for light ions normally incident on numerous metals at 3-10 keV,(16) we have found that the dependence on ion mass and energy approximately confirms a sputtering theory due to Rol.(17-19) In that theory the sputtering yield

$$Y = K \frac{E}{\lambda} \frac{M_1 M_2}{(M_1 + M_2)^2}$$

where E is the ion energy

M_1, M_2 are the ion and target atom masses, respectively

K is a constant depending only on target parameters

λ is a mean free path for energetic elastic collisions.

In the energy range of interest here, λ depends upon ion parameters principally through a factor $M_1 v^2/z_1$, which is constant according to the above assumptions for He^{+2} and heavier ions of the solar wind. The ion energy E is proportional to M_1. As a first approximation we may assign an average target atom mass of, say, $M_2 = 30$. The sputtering yields for the various ions should vary as $M_1^2/(M_1 + M_2)^2$. The sputtering yields given in Table II for H and He are appropriate for sputtering from Si or Fe while the remaining sputtering yields are calculated as outlined. The calculated yields for Ne and Ar are in good agreement with values measured for Fe by Almen and Bruce.(20)

In units of flux in which we have 1×10^8 H/cm^2 sec in the solar wind, which is a representative value, the solar wind should contain the fluxes stated in Table II according to Aller's abundances and Brandt's hypothesis. Note especially the C, N, O, Ne fluxes in the 10^4 cm^{-2} sec^{-1} range. The sputtering due to each solar wind ion is the product of the flux and the sputtering yield. The sputtering due to all ions heavier than helium is 0.18×10^6 atom/cm^2 sec, which is an order of magnitude less than that due to helium. Even if the helium abundance in Table II should be 9% instead of 16%, the heavy ions increase the sputtering by only 20% over that due to helium. Because some of the hydrogen may be deviated or slowed before striking the moon, the contribution of hydrogen to physical sputtering should be viewed as an upper limit in these flux units. Note that most of the heavy ion sputtering would be caused by O and Ne ions of about 20 keV energy (450 km/sec wind). We conclude that the upper limit flux of heavy ions in the solar wind will not significantly increase erosion rates over those due to the far more abundant hydrogen and helium ions.

Perhaps skepticism will greet the proposal of fluxes of 20 keV O and Ne in the photospheric ratios since they are emitted from a 200 eV plasma. But perhaps carbon fluxes of the photospheric magnitude are more reasonable. In particular, a carbon flux amounting to a sizable fraction of 0.04% of the hydrogen flux in the solar wind implies interesting new possibilities to understand the optical properties of the moon.

The range of 10 keV carbon ions in quartz is of the order of 10^{-5} cm. This follows from the fact that a principal stopping mechanism for such slow ions is elastic scattering through large angles for which the mean free path is about 5×10^{-6} cm, using a screened coulomb field for the interaction (see, e.g., ref. 20).

Let us consider how many carbon ions will accumulate in a surface layer in quartz subject to solar-wind sputtering. It should be clear from the previous section that carbon in the outermost monolayer or so will be rapidly converted to a volatile form of carbon whose fate should be escape from the lunar atmosphere in a period whose length is less than a few years,(14,21,22) even considering that a fraction of the carbon-carrying molecules will be dissociated and react again with the surface before being scattered out of the lunar atmosphere or carried from it by the magnetic field in the solar wind. Therefore carbon will not accumulate as an exterior layer. There is no reason to expect carbon to diffuse significant distances in silicate lattices at lunar temperatures. Therefore carbon, once implanted at 1000 Å depths in a lunar surface particle, will not be lost without eroding away the silicate surface to where the carbon atom is located. At a removal rate of 2×10^6 atom/cm^2 sec (Table II), 10^{-5} cm of SiO_2

is removed in about 1.3×10^4 yr. In exposure times much less than 10^4 yr, carbon concentrations will build up in an outer 10^{-5} cm layer. After exposure times much longer than 10^4 yr, carbon concentrations of the order of $4y \times 10^4/2 \times 10^6 = 2y$ atomic % will be achieved, where y is the fraction of the photospheric abundance for carbon that is actually present on the average in the solar wind. Certainly such large concentrations of carbon would have important optical effects on silicates, even if $y = 0.1$. Whether lunar surface particles actually will accumulate solar-wind effects for durations of the order of 10^4 yr depends upon the erosion conditions at the lunar surface.

Smaller concentrations of the heavier elements listed in Table II should also be embedded in the same 10^{-5} cm outer layer of lunar surface particles. Most of the elements will not have important optical effects as they are approximately in the proportion to be expected in lunar surface materials or else may reasonably be expected to cause little optical effect if incorporated into silicates. Sulfur is probably analogous to carbon in most respects, but should be less abundant by at least a factor of 20. The noble gases Ne and Ar will probably be partially lost by diffusion.

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