

# DARKENING OF SILICATE ROCK POWDERS BY SOLAR WIND SPUTTERING\*

BRUCE HAPKE

*Department of Earth and Planetary Sciences, University of Pittsburgh,  
Pittsburgh, Pa., U.S.A.*

(Received 27 November, 1972)

**Abstract.** Hydrogen ion irradiation of powdered igneous rocks, including Apollo rocks, has been observed in the laboratory to darken the powders and to make their optical properties similar to the Moon's. An extensive series of investigations shows that this darkening is not spurious. These results are consistent with those of other investigators, including Nash (1967). Darkening of lunar igneous rock powders by the formation of solar wind-sputtered glass films is a real process which occurs on the Moon. The time scale for darkening of undisturbed lunar soil is of the order of 50000–100000 yr. Comparison of the rates of the formation of glasses on the lunar surface by solar wind sputter-deposition, meteorite impact melting and impact vaporization-deposition indicates that these processes are of comparable importance under the present flux of meteorites. Thus the formation of glass by sputter-deposition must be regarded as a major process on the lunar surface.

## 1. Introduction

There is abundant observational evidence indicating the importance of one or more processes which darken lunar surface material. This fact was first emphasized by Gold (1955) and more recently has been extensively reviewed by Hapke (1970, 1971). The availability of Apollo lunar materials has confirmed these observations (Hapke *et al.*, 1970). Although the lunar fines are believed to be essentially lunar rocks pulverized and modified by meteorite impacts, the albedos of powdered crystalline Apollo rocks are approximately twice the albedos of the associated fines.

Three processes have been advanced to account for the darkening: solar wind sputtering (Hapke, 1964; Rosenberg and Wehner, 1964), impact vitrification (Conel and Nash, 1970), and impact vaporization-deposition (Hapke *et al.*, 1971). Vitrification darkens a lunar silicate rock powder for the following reason: the elements which are mainly responsible for the absorption of light in lunar materials are the transition elements Fe and Ti. In the crystalline rocks these elements are commonly present in the opaque minerals ilmenite and metallic iron. In rocks containing minerals which are opaque, only Fe and Ti near the surfaces of the opaque grains contribute importantly to light absorption, but vitrifying the rocks spreads these elements more or less evenly throughout the volume of material so that all Fe and Ti can take part in light absorption. The processes of sputtering and impact-vaporization also result in the formation of re-deposited, amorphous films of silicate material containing dis-

\* Paper dedicated to Professor Harold C. Urey on the occasion of his 80th birthday on 29 April 1973.

tributed Fe and Ti, but in addition, mechanisms are apparently created during the evaporation and deposition processes which are even more efficient absorbers of light than those present in glass made by merely melting rocks.

Darkening of lunar surface materials by solar wind bombardment was first proposed by Wehner (1961) and Hapke and Van Horn (1963) and was subsequently investigated by these authors and their coworkers (Hapke, 1965, 1966, 1968; Rosenberg and Wehner, 1964; KenKnight *et al.*, 1967). It is now well established that ion irradiation of ferro-silicate rock powders will cause these materials to closely match the lunar surface in optical properties (Hapke, 1968; see Hapke 1971 for a thorough review), and thus these results need not be repeated here. However Nash (1967) and Dybwad (1971) also bombarded silicate materials with hydrogen ions but were not able to confirm the darkening phenomena; they suggested that the observed darkening was due to spurious causes, such as cracked pump oil or sputtering of iron from accelerator grids. In this paper I report the results of an extensive series of laboratory studies in which these and several other possible hypotheses for spurious darkening mechanisms were tested and rejected. I believe that I have demonstrated beyond reasonable doubt that solar wind darkening is, indeed, a real phenomenon. I will also show that this process is competitive with vitrification darkening under present conditions and, moreover, that it may have been the dominant process over most of the lifetime of the lunar surface.

## 2. Apparatus

Because of the importance of the experimental conditions to the conclusions of this paper the apparatus used will be described in detail. Two types of vacuum systems were used, a diffusion-pumped system located in the Center for Radiophysics and Space Research at Cornell University, Ithaca, New York, and a sputter-ion pumped system located in the Space Research Coordination Center, University of Pittsburgh, Pittsburgh, Pennsylvania.

### A. THE DIFFUSION-PUMPED SYSTEM (D-SYSTEM)

The vacuum system was manufactured by the NRC Corporation, and consists of a stainless steel base plate and bell jar, an NRC 15001/s diffusion pump, and a mechanical forepump which is used both to back the diffusion pump and to rough pump the bell jar. To reduce backsteaming the diffusion pump has a water cooled cap, above which is a liquid nitrogen cold trap. The fluid used is DC-705, which is well-known for its low vapor pressure. Viton rubber O-rings, which require no vacuum grease, are used. The system is bakable to 300°C, the Viton O-rings being water cooled during bake out. Base pressure is about  $1 \times 10^{-9}$  torr.

The ion source has been described in Hapke (1965) and consists of an electron bombardment plasma source and an ion accelerator. The device contains a cylindrical anode 10 cm in diam by 10 cm long held at a potential of about 100 V above cathode plates located at both ends of the cylinder. An axial hot tungsten filament is held at cathode potential. Surrounding the ion source are a set of coils which generate a

DC magnetic field of about 25 G. Gas pressure in the device is about  $1 \times 10^{-3}$  torr, and  $H_2$  gas is admitted by means of a variable-leak after first passing through a liquid nitrogen trap to remove condensable gases. The source is held at a potential of 2 kV above ground. The lower cathode plate is perforated and the holes aligned with a matching set of holes in an accelerator grid at ground potential 3 mm below the lower cathode plate. Ions are thus extracted from the plasma in the source. The resulting beam, as measured by a movable, shielded Faraday cup, is about 5 cm in diameter with a current density of about  $0.5 \text{ mA cm}^{-2}$  and has a median energy of about 1.6 kV. Gas pressure near the target is about  $1 \times 10^{-5}$  torr due to leakage of  $H_2$  gas through the grids.

The ion beam is current-neutralized by a tungsten wire held about 20 V above ground and passing through the beam below the grounded accelerator grid. Current neutralization is absolutely necessary when irradiating insulating targets to prevent the potential of the target from rising to ion beam potential and repelling most or all of the ions.

The target powders were held on glass microscope slides placed on a stainless steel table located above all other objects which might be hit by the ion beam, so that no contamination by sputtering from adjacent material would occur. Target temperature was measured by attaching a thermocouple to a 1 cm diam Cu plate placed on powder in the beam, and was found to be  $340^\circ\text{C}$ , close to the radiative equilibrium temperature. This temperature was checked by placing small pieces of Pb ( $T_m = 327^\circ\text{C}$ ) and Zn ( $T_m = 419^\circ\text{C}$ ) on a powder surface in the beam; the Pb melted, but the Zn did not. (Early preliminary measurements reported previously (Hapke, 1965) had indicated a beam current density of  $1 \text{ mA cm}^{-2}$  and target temperature of  $170^\circ\text{C}$ . These values were carefully re-measured and were found to be incorrect.)

The optical properties of the powders were measured using a tungsten filament light source and photomultiplier tube. The normal albedos were measured using a narrow-band interference filter centered at  $5500 \text{ \AA}$  and are relative to an MgO standard.

#### B. THE SPUTTER-ION PUMPED SYSTEM (S-SYSTEM)

The vacuum system was constructed of standard Varian components. The main pump is a 5001/s Vac-Ion pump; roughing is by a cryogenic Vac-Sorb pump. Working volume is provided by a 6-in. tee with flanges. The entire system is constructed of stainless steel, ceramic, and glass components; only Cu gaskets are used. The system, including the roughing valve, is bakable to  $300^\circ\text{C}$ . Base pressure is below  $5 \times 10^{-10}$  torr. No greases, oils, or rubber have ever been used in the system.

The ion source is similar to that used in the D-system except for smaller dimensions, 2.5 cm diam by 5 cm long. The smaller dimensions require a higher magnetic field of 100 G. In addition, an einzel lens, with the center electrode held at 2 kV, is located between the accelerator grids and the neutralizing filament to concentrate the beam. The resulting ion beam is about one cm in diameter, with a current density of  $0.33 \text{ mA cm}^{-2}$  and energy of 2.0 kV. This beam was also current neutralized. Mag-

netic mass analysis indicates that the beam consists primarily of  $H_1^+$  and  $H_3^+$  ions in approximately equal amounts. Appreciable  $H_3^+$  ions are present due to the fast 3-body reaction  $H_1^+ + H_2 + H_2 \rightarrow H_3^+ + H_2$ .

Gas pressure near the target during irradiation was about  $1 \times 10^{-5}$  torr of  $H_2$ . The abundances of other gases was measured using an EMI residual gas analyzer and was found to consist of the following: AMU=16, 17, 18 ( $H_2O$ ), 1%; AMU=28 ( $N_2$ , CO), 0.5%; AMU=20,40 (Ar), 0.5%; AMU=4 (He), 0.04%; AMU=44 ( $CO_2$ ), 0.02%; no AMU=12 (C) or AMU>44, which might indicate the presence of higher hydrocarbons or silicones, were detected, the upper limit being  $5 \times 10^{-10}$  torr during irradiation and  $5 \times 10^{-13}$  torr with the gas leak closed.

As in the D-System, albedos are relative to MgO at 5500 Å.

### 3. Possible Spurious Darkening Mechanisms

After various powdered materials were irradiated for about 20 h, sufficient to deliver a dose of the order of  $30C \text{ cm}^{-2}$  of hydrogen ions, they were observed to darken. Little difference could be noted between the D and S system as far as darkening rates or effects on optical properties were concerned. In this section of the paper I will discuss various hypotheses which attribute the darkening to spurious causes and describe the experiments which argue against them. Unless otherwise stated, the silicate powder samples referred to in this section are an olivine basalt from Jefferson County, Colorado, dry-ground to finer than  $37 \mu\text{m}$  in an alumina mortar and pestle. In addition, other materials including powdered rhyolite, dunite and a chondrite (Plainview) were sometimes irradiated under similar conditions.

#### *Hypothesis 1*

The darkening may be due to a condensible substance, such as pump oil or vapor from O-rings, which collects on the powder and is subsequently pyrolyzed by the ion beam or by heat.

Experimental results:

(a) Irradiation in the S-System, which is completely free of all oils, greases and rubber materials, still caused a darkening of silicate materials.

(b) Pure reagent-grade  $SiO_2$  and  $Al_2O_3$  powders showed absolutely *no* decrease in albedo when irradiated by hydrogen ions in both the S and D systems.

(c) Darkening depends strongly on the composition of the target materials, being especially pronounced for iron-bearing minerals. The albedos of a number of materials before and after irradiation are given in Table I. Pure reagent grade powders of MgO,  $Al_2O_3$  and  $SiO_2$  and 1:1 mixtures of these powders were simultaneously irradiated in the D-System. The albedos of the mixtures are seen to have decreased much more than the pure powders. While it might be argued (Nash, 1967) that different materials may contamination-darken at different rates because of specific catalytic properties, it is very difficult to see how catalysis could cause the pronounced darkening of a simple physical mixture of substances which do not darken separately. Also, pure  $SiO_2$  did

TABLE I  
Albedo change of selected materials due to  
hydrogen ion irradiation (dose  $\sim 30\text{C cm}^{-2}$ )

Material	Normal albedos	
	Unirradiated	Irradiated
SiO <sub>2</sub>	0.58	0.58
Al <sub>2</sub> O <sub>3</sub>	0.77	0.78
MgO	0.96	0.87
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	0.66	0.44
Al <sub>2</sub> O <sub>3</sub> + MgO	0.84	0.79
MgO + SiO <sub>2</sub>	0.72	0.41
Quartz < 7 $\mu$	0.64	0.35
Enstatite < 7 $\mu$		0.18
Bronzite < 7 $\mu$	0.52	0.12
Hypersthene < 7 $\mu$		0.08
Olivine Basalt < 37 $\mu$	0.31	0.17
Olivine Basalt < 7 $\mu$	0.46	0.11
Plainview Chondrite < 7 $\mu$	0.16	0.04
Lunar Rock 10022 < 37 $\mu$	0.18	0.12
Lunar Fines 10084	0.09	0.09

not darken at all, but the albedo of a sample of natural quartz decreased somewhat, presumably because of impurities in the latter.

(d) The darkening is confined completely to the portion of the powders struck by the beam. Glass or metal objects in the beam but not covered with powder did not darken, nor did portions of the powder outside the beam.

(e) The darkening depends strongly on the state of the target material. Loose olivine basalt powder darkened readily. The surface of solid olivine basalt exposed to the ion beam did not darken. Powder compacted into a solid pellet darkened only slightly when irradiated (Figure 1).

(f). Pulverized Apollo 11 lunar rock 10022 darkened, but Apollo 11 fines 10084 showed negligible decrease in albedo (Table I).

### *Hypothesis 2*

The darkening may be due to iron or other material sputtered from the accelerator grids or other structures.

Experimental results:

(a) Darkening did not occur with the ion beam on at full strength but with the neutralizer filament turned off (S and D Systems).

(b) With the einzel lens in the S-System at ground potential but with the neutralizer filament on, the ion beam was spread out and the current density at the target reduced by a factor of approximately 6. However, the same ion current density was passing through the grid. In addition, the spread-out ion beam could now strike more of the surrounding structures and increase the probability of sputter-contamination. In spite of the foregoing, the rate of darkening decreased by approximately a factor of 6 also.

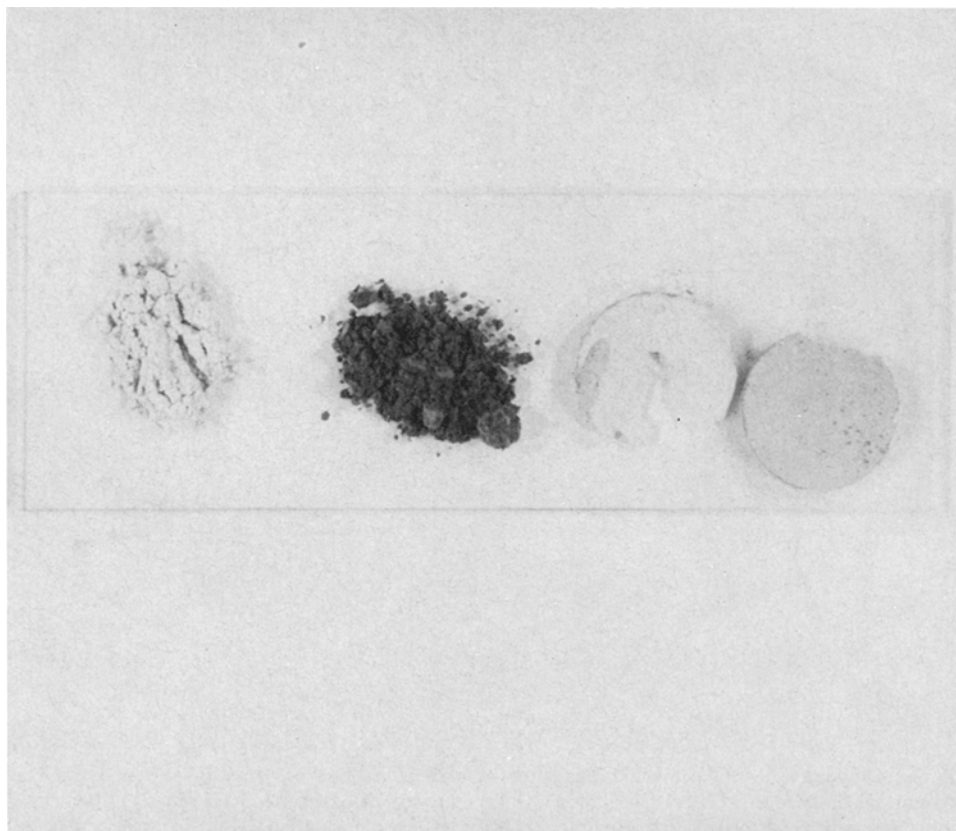


Fig. 1. Effect of compaction on darkening of andesite powder  $< 20\mu$ . From left to right: (1) Unirradiated loose powder. (2) Irradiated loose powder ( $\sim 30C\text{ cm}^{-2}$ ). (3) Slice from inside of pellet of compacted powder showing surface shielded from ion beam. (4) Irradiated surface of pellet of compacted powder. Samples (2) and (4) were irradiated simultaneously side-by-side.

(c) Silicate powders were deliberately contaminated with metallic iron in two ways, by mixing in about 10% of fine iron particles and by placing an iron screen over the powder. After irradiation in the D-System, the spectra of the powders were relatively flat, characteristic of metals; however, the spectra of uncontaminated powders are reddish, similar to that of the Moon.

- (d) Same as 1b.
- (e) Same as 1c.
- (f) Same as 1d.
- (g) Same as 1e.
- (h) Same as 1f.

### *Hypothesis 3*

The darkening may be due to the  $\text{CO}_2$  or other gases present in trace amounts in the vacuum system.

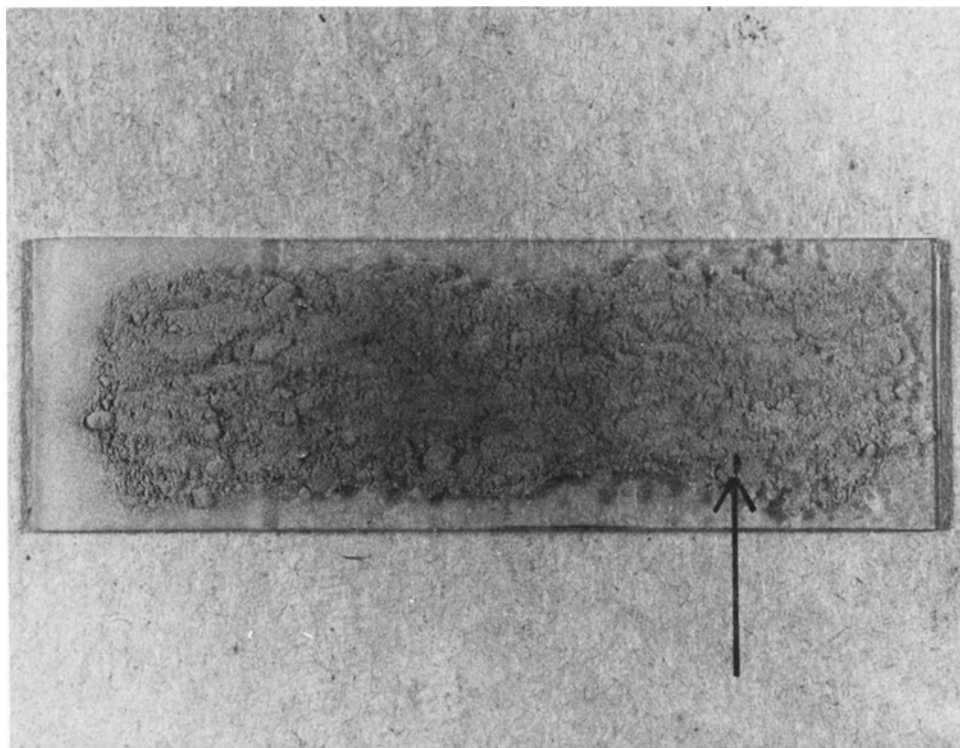


Fig. 2. Olivine basalt powder  $< 37\mu$  irradiated by magnetically-deflected hydrogen ion beam. The two darkened strips are due to irradiation by the mass-separated  $H_1^+$  and  $H_3^+$  ions ( $\sim 10C\text{ cm}^{-2}$  each). The powder at the position where the undeflected beam normally strikes the target, indicated by the arrow, shows no sign of darkening.

Experimental results:

(a) Instead of using  $H_2$  gas,  $CO_2$  was admitted to the ion source through the variable leak of the D-System. The albedos of powders irradiated by the dissociation products of  $CO_2$  decreased slightly, but by a much smaller amount than when  $H_2$  was used.

(b) In the S-System the ion beam was mass-separated by means of a permanent magnet between the einzel lens and the neutralizer filament. The target powder was darkened only at positions of relatively large deflections corresponding to  $H_1^+$  and  $H_3^+$  ions, but no darkening at all was observed at positions of smaller deflections where ions of large mass would be expected (Figure 2).

(c) Same as 1b.

(d) Same as 1d.

*Hypothesis 4*

The darkening may be due to atoms or ions of tungsten or tungsten hydride evaporated from the filament in the ion source.

Experimental results:

(a) In the D-System the bottom cathode of the ion source and the accelerator grid were removed and the cathode potential of the source held at ground. Dunite and MgO powder samples were placed directly below the source so that plasma at a potential of about +90 V and evaporation products from the filament could impinge directly. The dunite darkened considerably but the albedo of the MgO decreased by a barely observable amount. This experiment indicates that tungsten contamination is at most a very minor contributor to darkening.

- (b) Same as 1b.
- (c) Same as 1c.
- (d) Same as 1e.
- (e) Same as 1f.
- (f) Same as 2a.
- (g) Same as 2b.
- (h) Same as 3b.

### *Hypothesis 5*

The darkening may be caused by the neutralizing filament, either by evaporated tungsten or tungsten hydride or by electron bombardment.

Experimental results:

- (a) With the ion source off, but with the neutralizer filament on, and hydrogen gas being admitted to the source no darkening occurred.
- (b) The tungsten wire through the ion beam was replaced by a circular neutralizing

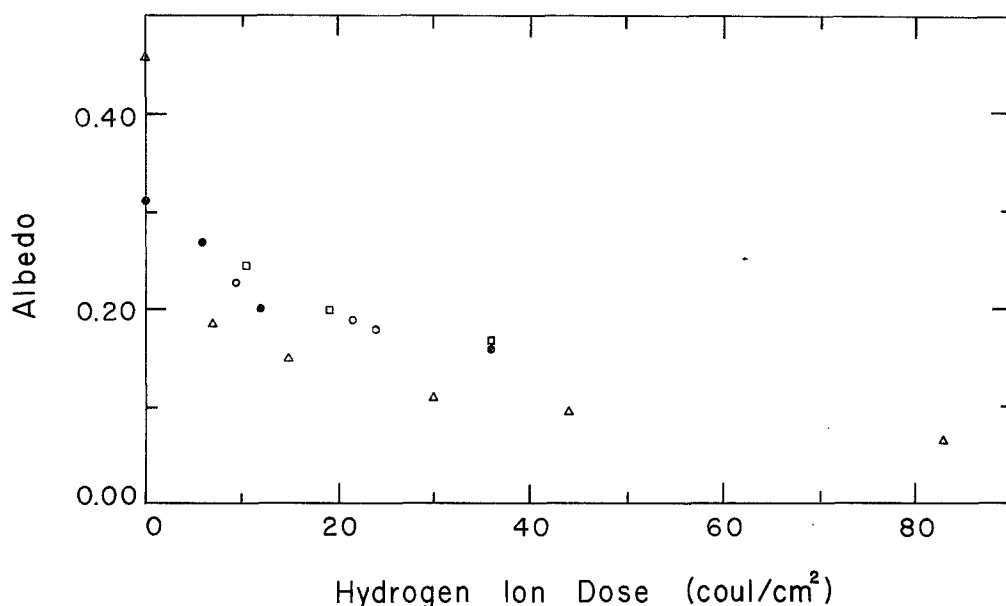


Fig. 3. Albedo of olivine basalt powder versus total dose of H-ions for varying ion beam current densities and particle sizes. Filled circles: 0.33 mA cm<sup>-2</sup>, < 37 μm; open circles: 0.17 mA cm<sup>-2</sup>, < 37 μm; squares: 0.09 mA cm<sup>-2</sup>, < 37 μm; triangles: 0.50 mA cm<sup>-2</sup>, < 7 μm.



filament surrounding the beam but shielded by metal electrodes from the target. Darkening still occurred.

(c) Silicate powders were irradiated in the S-System at one-half and one-fourth the current and power densities so that the temperature at the target was not far above room temperature. However the neutralizer filament was on at its full value. The powder darkened at much slower rates, requiring the same total radiation dose to produce the same decrease in albedo (Figure 3).

(d) Silicate powder samples were irradiated with a beam of 3 kV electrons at sufficient current to heat the powder to 300°C for 23 h. No significant darkening occurred.

(e) Same as 1b.

(f) Same as 1c.

(g) Same as 1d.

(h) Same as 1e.

(i) Same as 1f.

(j) Same as 2b.

(k) Same as 3b.

### *Hypothesis 6*

The darkening may be due primarily to simply heating the samples to 340°C rather than to ion bombardment.

Experimental results:

(a) Same as 5c.

(b) Same as 5d.

## **4. Results of Other Investigators**

Positive observations of darkening of terrestrial silicate rock powders under proton bombardment have also been reported by Wehner and his coworkers (Rosenberg and Wehner, 1964; KenKnight *et al.*, 1967) and by Dollfus and Geake (1967). Yin *et al.* (1972) have reported reduction of iron oxides under Ar ion bombardment. Pulverized lunar crystalline rock powders have been observed to darken by simulated solar wind irradiations by Hapke *et al.* (1971) and by Conel and Nash (1970). However, lack of darkening has been reported by Nash (1967) and Dybwad (1971), and it is pertinent to inquire into possible reasons for these discrepancies.

Dybwad used a beam of 5 keV protons at  $10 \mu\text{A cm}^{-2}$  and carried out irradiations to a maximum apparent dose of about  $3\text{C cm}^{-2}$ . However his samples were flat single crystals. This geometry is not suitable for collecting the thin films of sputtered material on which the darkening evidently depends. Also Dybwad did not provide for neutralization of his ion beam. Thus the current density and energy of the ion beam actually hitting the surface of his insulating crystals are highly uncertain and may have been considerably less than reported.

Nash used a  $20 \mu\text{A cm}^{-2}$  beam of 5 keV ions and carried out a number of irradiations while studying proton-induced fluorescence of silicates. Although he carried out his irradiations to a maximum dose of  $23\text{C cm}^{-2}$  most of his work was done without

beam neutralization and using samples in which the powder was tightly packed into a cup. Unfortunately, with this geometry most of the incident ions cannot penetrate into the interstices between grains and the rate of build-up of absorbing sputtered films is greatly reduced. A few experiments were carried out by Nash on uncompacted powders using a neutralized beam to deliver a total dose of about  $3\text{C cm}^{-2}$ . This dose is barely sufficient to cause observable darkening ( $\sim 10\%$  decrease in albedo) in my systems. Under these conditions Nash also reports a similar decrease in albedo for both terrestrial and lunar igneous rock powders.

In my studies there was no significant dependence of darkening on dose rate over a range of current density from  $0.08$  to  $0.5\text{ mA cm}^{-2}$ . By contrast, Nash observed a positive dose rate dependence. However, the three samples for which he obtained an anomalously large degree of darkening were bombarded by  $16\text{ keV}$  ions, whereas  $2\text{ keV}$  ions were used for most of his irradiations. Since sputtering yields are strongly energy-dependent (Wehner, 1967), several times as much sputter-deposited glass would have been made by  $16\text{ keV}$  ions as by the same dose of  $2\text{ keV}$  ions, and an increased darkening rate is to be expected.

Thus, there appears to be no significant discrepancy between the results of the various workers in this field. I believe that the set of experiments described above are sufficiently comprehensive that the observed laboratory darkening cannot be rejected as spurious, and that the reality of darkening of lunar silicate rock powder by solar wind sputtering can be regarded as established.

## 5. Darkening Mechanisms

Two kinds of mechanisms have been proposed to account for the sputter-darkening. The first is the reduction of metal oxides on the surfaces of the grains to free metal by physical-chemical processes (Wehner, 1961). Although this effect has been observed by Yin *et al.* (1972) (see also Hapke, 1965) in iron oxides, it is probably unimportant for the Moon because the upper surfaces of most igneous rocks and minerals remain clean and apparently unaffected under proton bombardment. The only exceptions to the latter statement are rocks rich in hematite, which is rapidly reduced to magnetite or free iron by irradiation; however, the lunar igneous rocks contain virtually no ferric iron.

The second mechanism is the formation of absorbing, amorphous, thin films on grains by growth of material sputtered by solar wind ions from adjacent grains. The material which is responsible for the low lunar albedo must have a high absorption coefficient, be more absorbing in the blue than in the red, but without discrete bands in the near-UV, visible or near-IR. Films sputtered in the laboratory from Apollo 11 rocks onto fused  $\text{SiO}_2$  substrates have exactly these properties (Figure 4). As was discussed in the introduction of this paper, such films made from igneous rocks will be somewhat absorbing because of the redistribution of the Fe and Ti from opaque minerals. However, the following arguments indicate that this mechanism is only of secondary importance. (1) The absorption coefficients of the sputtered rock films

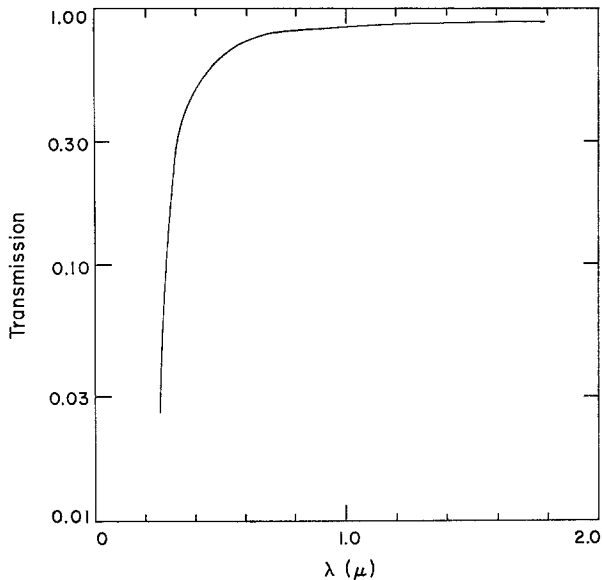


Fig. 4. Transmission spectrum of glass film deposited on fused  $\text{SiO}_2$  substrate by H-ion sputtering from lunar rock 10017. Exact thickness of film is not known, but is estimated to be  $\sim 1 \mu\text{m}$ .

are an order of magnitude larger than those of glass made by melting. (2) Glass powders made by melting rocks darken further upon irradiation. (3) Irradiation of certain pure minerals, such as bronzite, with no opaque minerals present still results in appreciable decrease in albedo (Table I).

Hapke (1965) has suggested that the high absorbance is associated in some way with partial loss of oxygen in the sputtered film. In the sputtering process, atoms leave the surface as single, uncharged atoms rather than as ions or molecules (Wehner *et al.*, 1963). The metal atoms probably have a probability of the order of unity for sticking to an adjacent cold surface, while the oxygen, being more volatile, would have a slightly lower sticking coefficient. Oxygen ion deficiencies could cause strong absorption in silicates in a number of ways: (1) Color centers are known to be associated with oxygen vacancies in many oxides. However, such centers generally have rather low oscillator strengths, and also it is difficult to explain the dependence of darkening on Fe content by this mechanism. (2) Partial deficiency of oxygen in the film may increase the probability that Fe and other metal ions may be sufficiently close together that strong absorption processes of the charge-transfer type may occur. Phillipp (1971) has recently shown that the yellow color of  $\text{SiO}$  is due to the tail of strong Si-Si bands in the vacuum ultraviolet. (3) The oxygen deficiency may manifest itself by reducing an equivalent number of ferrous ions to metallic iron, while preserving stoichiometry in the remainder of the metal oxides. Such reduced atoms may be able to diffuse fairly easily through the glass and collect into numerous submicroscopic iron particles. An elementary Mie theory calculation indicates that if the sputtered glass contains a

few percent of submicroscopic iron particles the high absorbance and red spectrum could be accounted for.

In an attempt to test the last hypothesis a film of material weighing about 100  $\mu\text{g}$  was sputtered from Apollo 11 rock 10017 onto fused  $\text{SiO}_2$ . Optical and X-ray inspection indicated that the film was amorphous. The magnetic moment of the film was measured using a superconducting magnetometer and was undetectable ( $< 1 \times 10^{-7}$  emu); however, after exposure to a magnetic field of 6000 G the film was found to have an induced remnant moment of  $1 \times 10^{-6}$  emu, which is consistent with a lower limit of submicroscopic iron particles of about 1%. This experiment is only preliminary and must be verified, since other darkening mechanisms may also be involved.

## 6. Applications to the Lunar Surface

Hapke *et al.* (1970) and Conel and Nash (1970) have observed that the albedo of the lunar fines is considerably lower than that of lunar igneous rock powders, as predicted by ground-based observations (Gold, 1955). Hapke *et al.* (1970) showed that hydrogen-ion irradiation will darken powdered lunar crystalline rock 10022 but has a negligible effect on lunar fines 10084 (Table I); this observation is suggestive of saturation from a darkening process which has effects similar to those produced by sputtering. Hapke *et al.* (1971) have emphasized the difficulties involved in accounting for the lunar spectral properties by adding only melted rock to the crystalline rock and have suggested that the amorphous matrix material in the agglutinate particles of lunar fines consists at least partly of glass deposited from a vapor phase. Borg *et al.* (1971) discovered coatings of amorphous material 500 to 1000  $\text{\AA}$  thick on the surfaces of many grains of lunar fines. They showed that there exists a correlation between coatings and albedo. However, Hapke (1972) argued that these layers were probably too thin to account for the decrease in albedo.

Several groups of workers have given independent evidence that the lunar fines are deficient in oxygen relative to the igneous rocks, as predicted by the solar wind darkening hypothesis. Ehman (1970) measured directly the oxygen content of lunar materials; Hapke *et al.* (1971) carried out thermogravimetric analyses; and Epstein *et al.* (1972) measured O/Si ratios. Thus the available evidence from Apollo samples appears to be consistent with the hypothesis of this paper.

Although the details of the sputter-darkening rates in silicate powders depend on composition and particle size, most materials darkened at the following doses and equivalent times, based on a diurnally averaged solar wind flux of  $1 \times 10^8$  protons  $\text{cm}^{-2} \text{s}^{-1}$  (Figure 3). Perceptible decrease in albedo:  $\sim 5\text{C cm}^{-2}$  or 10000 y; major decrease in albedo:  $\sim 30\text{C cm}^{-2}$  or 60000 y; saturation:  $\sim 150\text{C cm}^{-2}$  or 300000 y. (The doses and times for darkening reported previously (Hapke, 1966) are incorrect by a factor of 2 because of the error in the laboratory ion beam current density.) Undisturbed igneous rock powder on the lunar surface would thus darken in 50000 to 100000 yr. However, during the same time meteoritic gardening will continually mix in fresh material from below the surface. The actual time necessary to decrease

the albedo of an area on the Moon will be considerably longer and will depend both on the turnover rate and the thickness of the fresh material.

It remains to discuss the relative importance of formation of glass in lunar fines by the three processes of impact melting, impact vaporization and recondensation, and solar wind sputtering and recondensation. Wehner *et al.* (1963) calculated that a smooth surface of silicate material exposed on the lunar surface will be sputtered away by the solar wind at the rate of approximately  $0.3 \text{ \AA yr}^{-1}$ . Wehner (1967) and his colleagues later revised this value to take account of improved knowledge of the solar wind and sputtering yields. They estimate a lunar surface erosion rate from solar wind sputtering of  $0.42 \times 10^{-9} \text{ cm yr}^{-1}$ . They also estimate, based on limited experiments, that approximately twice this amount will be retained on the surface as sputter-deposited material. At my request, KenKnight (1972) recently reviewed these calculations and saw no reason to revise them. He believes them to be correct to within a factor of 2. Thus the rate of formation of sputter-deposited glass on the lunar surface is approximately  $0.84 \times 10^{-9} \text{ cm yr}^{-1}$ , which is equivalent to  $2.8 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$ . The manner in which this quantity has varied in the past is not known.

Based on estimates of the present flux of meteorites, Gault *et al.* (1972) calculate that the rate at which material is being melted by meteorite impact on the lunar surface is about  $6.1 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$ , and the rate at which material is vaporized by the same phenomena is  $2.7 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$ . Gault, (1970) and Gault *et al.* (1972) also present arguments which indicate that over most of the lifetime of the Moon the flux of meteorites may have been an order of magnitude lower than the present flux, although this conclusion is rather uncertain.

Thus it appears that the formation of glasses by sputter-deposition is fully comparable with impact melting and vaporization at the present time and may have been the dominant process over most of lunar surface history. Sputter-deposition and its concomitant effects on lunar optical properties and the chemistry of the fines must be regarded as a major process on the lunar surface.

### Acknowledgements

I thank E. Wells, G. Smith, E. Skopinski and K. Shah for help in making the irradiations, M. Fuller and V. Schmidt for help in making the magnetic measurements, and C. KenKnight for discussions of sputtering rates on the lunar surface.

### References

- Borg, J., Maurette, M., Durrieu, J., and Jouret, C.: 1971, *Proceedings of the Second Lunar Science Conference*, MIT Press, Cambridge, p. 2027.
- Conel, J. and Nash, D.: 1970, *Proceedings of the Apollo 11 Lunar Science Conference* Pergamon Press, New York, p. 2013.
- Dollfus, A. and Geake, J.: 1965, *Compt. Rend.* **260**, 4921.
- Dybwad, J.: 1971, *J. Geophys. Res.* **76**, 4023.
- Ehman, W. and Morgan, J.: 1971, *Proceedings of the Second Lunar Science Conference*, MIT Press, Cambridge, p. 1237.

- Epstein, S. and Taylor, H.: 1972, *Proceedings of the Third Lunar Science Conference*, in press.
- Gault, D.: 1970, *Radio Sci.* **5**, 273.
- Gault, D., Horz, F., and Hartung, J.: 1972, *Proceedings of the Third Lunar Science Conference*, in press.
- Gold, T.: 1955, *Monthly Notices Roy. Astron. Soc.* **115**, 585.
- Hapke, B.: 1964, *Trans. Am. Geophys. Union* **45**, No. 2, 347.
- Hapke, B.: 1965, *Ann. N. Y. Acad. Sci.* **123**, 711.
- Hapke, B.: 1966, in W. Hess, D. Menzel and J. O'Keefe, (eds.), *The Nature of the Lunar Surface*, Johns Hopkins Press, Baltimore, p. 141.
- Hapke, B.: 1968, *Science*, **159**, 76.
- Hapke, B.: 1970, *Radio Sci.* **5**, 293.
- Hapke, B.: 1971, in Z. Kopal (ed.), *Physics and Astronomy of the Moon*, 2nd ed., Academic Press, New York, p. 155.
- Hapke, B.: 1972 *Science* **177**, 535.
- Hapke, B. and Van Horn, H.: 1963, *J. Geophys. Res.* **68**, 4545.
- Hapke, B., Cohen, A., Cassidy, W., and Wells, E.: 1970, *Proceedings of the Apollo 11 Lunar Science Conference*, MIT Press, Cambridge, p. 2199.
- Hapke, B., Cassidy, W., and Wells, E.: 1971, paper presented at the Second Lunar Science Conference Houston.
- KenKnight, C.: 1972, private communication.
- KenKnight, C., Rosenberg, D., and Wehner, G.: 1967, *J. Geophys. Res.* **72**, 3105.
- Nash, D.: 1967, *J. Geophys. Res.* **72**, 3089.
- Philipp, H.: 1971, *J. Phys. Chem. Solids* **32**, 1935.
- Rosenberg, D. and Wehner, G.: 1964, *J. Geophys. Res.* **69**, 3307.
- Wehner, G.: 1961, *Am. Rocket Soc. J.* **31**, 438.
- Wehner, G.: 1967, 'Investigation of Sputtering Effects on the Moon's Surface', Final Report to NASA
- Wehner, G., KenKnight, C., and Rosenberg, D.: 1963, *Planetary Space Sci.* **11**, 1257.