

# EFFECTS OF VAPOR-PHASE DEPOSITION PROCESSES ON THE OPTICAL, CHEMICAL, AND MAGNETIC PROPERTIES OF THE LUNAR REGOLITH

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**Abstract.** The processes of solar wind sputtering and meteoritic impact vaporization have created materials in the lunar regolith which were deposited from a vapor phase. Although the quantity of such exotic condensed substances should theoretically be comparable with that of materials which have been melted by impacts, their existence in the fines has not been generally recognized. We have investigated the physical and chemical properties of materials deposited from vapors generated by hydrogen-ion sputtering and thermal evaporation of lunar and artificial ferrosilicates. Both processes are highly reducing. The deposits are enriched in Fe, have large, nonselective, optical absorptivities, and contain abundant sub-microscopic, superparamagnetic grains of metallic Fe which exhibit the characteristic  $g=2.1$  ESR resonance. The sputter-deposited films are enriched in heavy elements. Thus the hypothesis that the lunar fines contain several percent of materials deposited from the vapor phase accounts in a natural manner for many of the unusual optical, physical and chemical properties of lunar soils. The vapor-deposits are probably concentrated in the agglutinate particles of the regolith.

## 1. Introduction

Lunar regolith samples have a number of interesting physical and chemical properties compared to lunar crystalline rocks of similar composition. In order to account for these properties, some of which were anticipated from earth-based observations but most of which were totally unexpected, several rather ad hoc, unrelated hypotheses have been advanced. These properties and hypotheses are discussed in the next section.

An important constituent of the lunar fines is glass. It is almost universally assumed that this glass has been formed by simple melting. However, recent estimates of the rates of melting and vaporization by micrometeorite impact and by sputtering by the solar wind lead to the conclusion that approximately one half of the amorphous material in the fines has been formed by deposition from a vapor phase, rather than by vitrification (Hapke, 1973). We have investigated a number of the physical and chemical properties of materials deposited from vapor phases. It is the purpose of this paper to summarize these properties and to point out that they are precisely those required to account for many of the unusual characteristics of the lunar fines. We emphasize that this paper is a preliminary report, and that several papers are in preparation which describe in detail the results of our experiments.

## 2. Selected Characteristics of Lunar and Laboratory Materials

### 2.1. OPTICAL PROPERTIES

The albedos of lunar fines are considerably lower than those of pulverized lunar crystalline rocks of similar composition. The spectra of the rocks have a number of

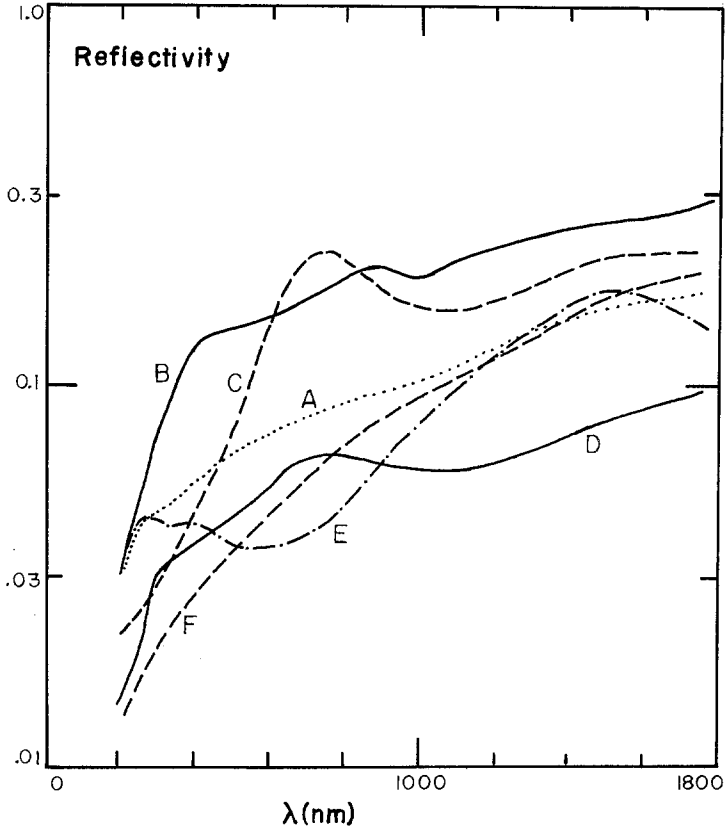


Fig. 1. Bi-directional reflectance spectra (relative to  $\text{BaSO}_4$ ) of lunar and artificial samples of Apollo 11 composition pulverized to 400f. A. Fines 10084. B. Rock 10022. C. Rock 10022 melted in vacuum. D. Artificial glass melted in air. E. Artificial glass melted in vacuum and reheated in vacuum to 800 °C for 1 hour. F. Film 3  $\mu\text{m}$  thick evaporated from artificial glass using electron-bombardment furnace in vacuum at 1900 °C, scraped from substrate and ground to 400f.

absorption bands, such as the 1000 nm band of  $\text{Fe}^{+2}$ , which are much subdued or missing in the spectra of the fines (Hapke *et al.*, 1970; O'Leary and Briggs, 1970; Conel and Nash, 1970) (see A and B in Figure 1). Therefore, whatever processes were involved in converting the rocks into regolith must also be able to create a substance of low reflectivity with no (or at most *extremely* subdued) absorption bands, and with an absorbance which decreases as the wavelength increases. The effects of these processes have apparently been concentrated in the poorly-understood agglutinate particles, which are darker and contain more metallic Fe than the bulk soil (Agrell *et al.*, 1970; Adams and McCord, 1973).

One process which is widely accepted as being the primary agent responsible for the alteration of optical properties is impact vitrification. In support of this hypothesis Conel and Nash (1970, 1973) and Adams and McCord (1971) have published spectra of vitrified rocks which are dark and have subdued bands. However, we have been unable

to duplicate these spectra when the melting takes place in a vacuum or under mildly reducing conditions (see *C* in Figure 1). Although these authors do not describe their vitrification conditions in detail, they state that a Pt crucible was used and that dry  $N_2$  was allowed to flow over the sample. Since most commercial  $N_2$  gas contains on the order of  $10^{-4}$  or more of  $O_2$  and  $H_2O$  impurities, it is likely that the chemical environment during melting was oxidizing. When we vitrify in air (see *D* in Figure 1) we indeed obtain a glass with optical properties similar to those of the above authors. However, it is difficult to imagine how oxidizing conditions could occur on the lunar surface during impact, especially in view of the strongly reduced nature of the fines. Further, the spectra of the oxidized glass still exhibits pronounced absorption bands around 600 and 1000 nm.

A dark material can be produced from a glass made in vacuum if the glass is reheated (see *E* in Figure 1). Annealing a glass in vacuum at  $800^\circ\text{C}$  for one hour causes

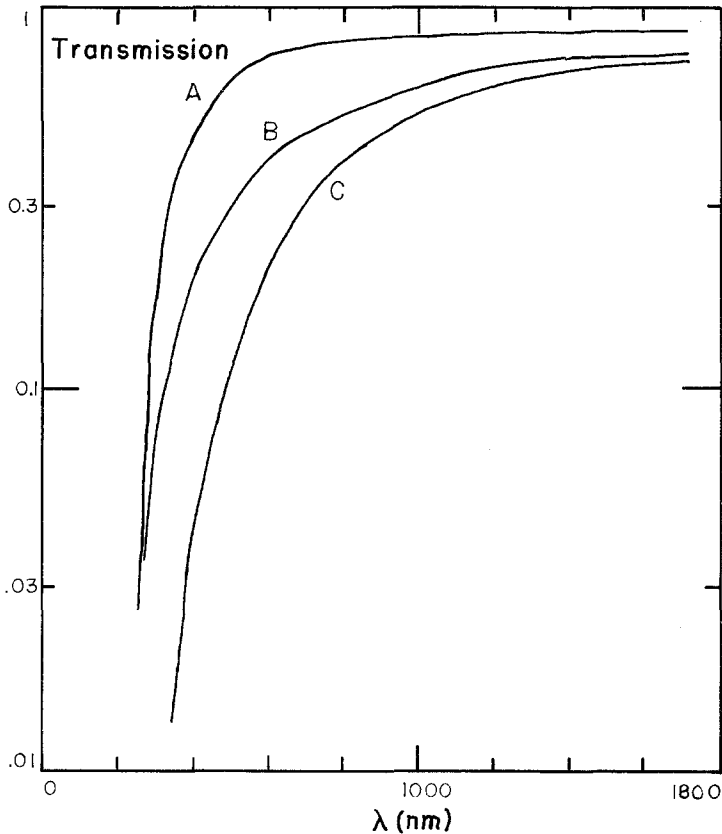


Fig. 2. Transmission spectra of vapor-deposited films on  $SiO_2$  substrate. *A*. Apollo 11 rock 10017 sputtered by 2 keV H ions (deposition rate  $\sim 20 \text{ \AA h}^{-1}$ ). *B*. Rock 10017 evaporated by dipping tungsten filament in rock powder and flashing in vacuum at about  $3000^\circ\text{C}$ . Film thicknesses are unknown but are estimated to be about  $0.5 \mu\text{m}$ . *C*. Film made by evaporating artificial glass of Apollo 11 composition in vacuum using electron-bombardment furnace at  $1900^\circ\text{C}$ ; film thickness  $0.7 \mu\text{m}$ .

the precipitation of microscopic crystals of a dark, opaque phase, which we tentatively identify as ilmenite or a similar Fe-Ti mineral. Thus, partial devitrification of glass by reheating may be a factor in the lunar darkening process (Hapke *et al.*, 1973; Cassidy and Hapke, 1975). However, it is probably not the primary darkening process because the spectrum of the reheated glass still contains a pronounced band at 600 nm which is not present in the fines.

The glasses discussed in this paper were made either in a N<sub>2</sub> atmosphere in a closed graphite crucible to insure reducing conditions or in a vacuum furnace at a pressure of  $2 \times 10^{-6}$  torr. For the vacuum furnace, open crucibles of graphite, metallic Fe, BN and Pt foil were used. No sensible differences were apparent between the reflection spectra of the glasses produced under the various conditions. Starting materials were both Apollo 11 and 12 crystalline rocks, and reagent-grade oxides in the same proportions as the major elements in the lunar rocks. A typical artificial glass had the composition: 40% SiO<sub>2</sub>, 12.5% Al<sub>2</sub>O<sub>3</sub>, 10% CaO, 7.5% MgO, 20% FeO, 10% TiO<sub>2</sub>. FeO was added in the form of ferrous oxalate thermally decomposed in vacuum.

Vapor-deposited films were made from these and other materials in a variety of ways. Films of sputtered glass were made using beams of 2 keV H or He ions at a current density of about 0.3 mA cm<sup>-2</sup> (Hapke, 1973). Thermally-evaporated deposits were made in vacuum using an electron-beam furnace at about 2000°C, by coating a tungsten filament with powder and flashing it at about 3000°C, and by using a laser which delivered millisecond pulses of several joules. The general properties of the films produced in the various ways are similar.

Some of the optical properties of the vapor-deposited materials are shown in Figures 1 and 2. These materials have very high absorption coefficients, lack discrete absorption bands, and have absorptivities which decrease as the wavelength increases. It will be demonstrated below that these properties are probably caused by the presence of submicroscopic metallic Fe in the films.

## 2.2. CHEMICAL PROPERTIES

The fines are enriched in metallic Fe relative to the crystalline rocks. The rocks typically have of the order of 0.1% Fe, while the fines contain about 0.5% Fe, much of which is in the superparamagnetic size range (Nagata *et al.*, 1970; Fuller, 1974). Surfaces of many of the grains in the fines are coated with an amorphous layer about 0.1 μm thick (Borg *et al.*, 1971; Maurette and Price, 1975) and are enriched in Fe (Hapke *et al.*, 1970; Gold *et al.*, 1974). However, there is some conflicting evidence concerning the Fe (Grant *et al.*, 1975). Both the fraction of grains coated and the degree of Fe enrichment are correlated with albedo. The fines are deficient in oxygen relative to the crystalline rocks (Ehmann and Morgan, 1970), although the extent to which this is due to the excess Fe or due to a separate phenomenon is not clear.

The fines have an excess of heavy elements when compared to the crystalline rocks (Ganapathy *et al.*, 1970; Laul *et al.*, 1971). Heavy isotopes of certain elements including S, Si, C, K, and O are enriched in the fines (Epstein and Taylor, 1971; Grossman *et al.*, 1975; and Clayton *et al.*, 1975).

A variety of hypotheses have been proposed to account for the increased Fe content of the fines. These hypotheses are discussed in greater detail in the next section in connection with the question of the origin of the superparamagnetic Fe. Laul *et al.* (1971) ascribe the heavy element enrichment to addition of 1% carbonaceous chondrite material to the fines. While this hypothesis accounts for the order of magnitude of the enrichment it does not explain the details. Heavy isotope enrichments are suggested to be due to fractionation during vapor-phase transport (Epstein and Taylor, 1971).

Electron microprobe analyses were made of films deposited by sputtering and thermal evaporation onto Mo foil substrates. Adequate sample thickness was insured by the fact that the Mo peaks on the films were not above background level. Polished samples of the parent glass were also analyzed. Figures 3 and 4 show the ratios of count rates (corrected for background) of the films to the count rates of the parent glass for each element.

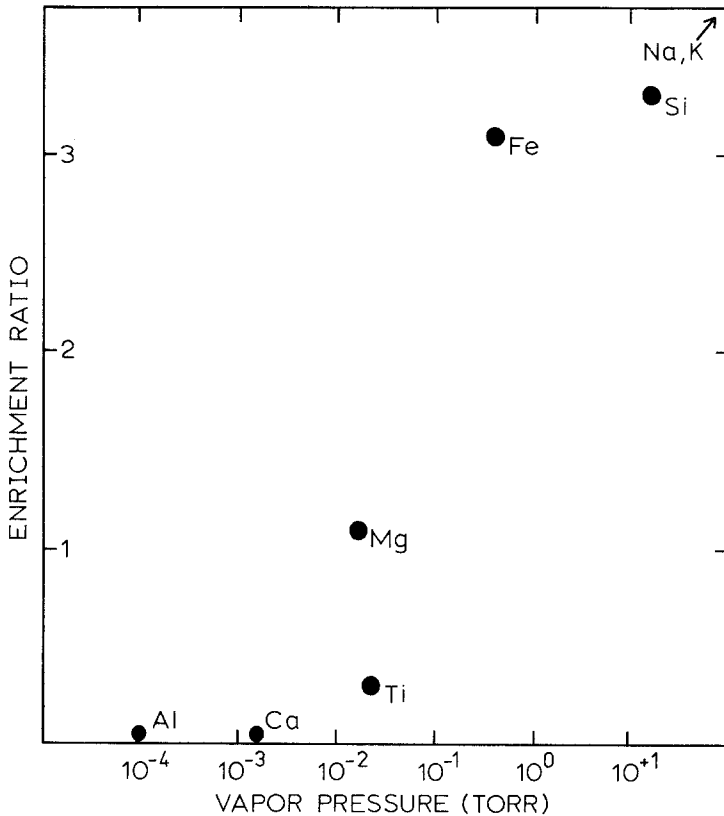


Fig. 3. Enrichment ratio (ratio of electron microprobe count rate corrected for background of film to count rate of parent glass) of evaporated film versus vapor pressure of oxide at 1900°C. Film was evaporated from glass of Apollo 11 composition at 1900°C in vacuum using electron-bombardment furnace.

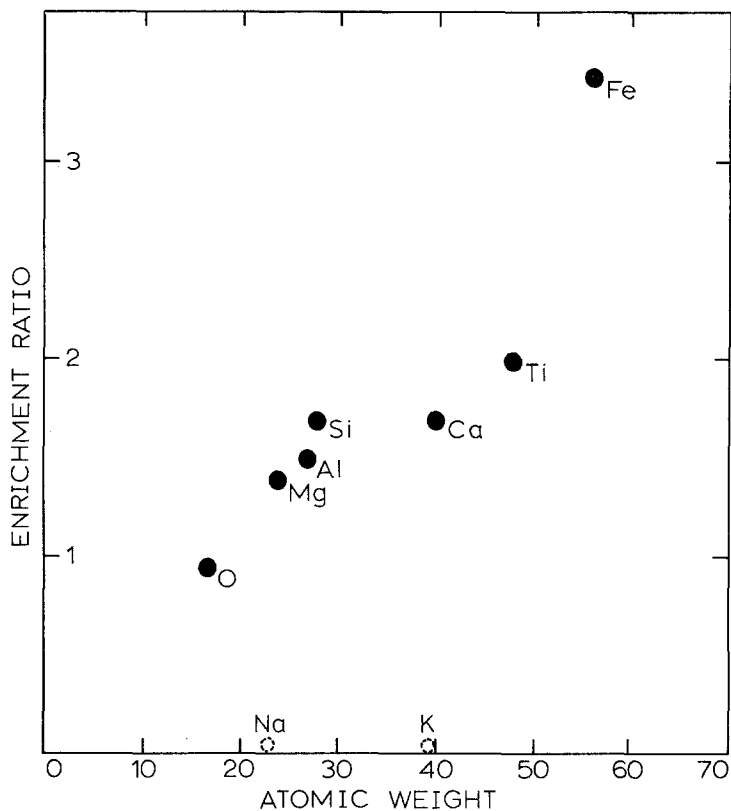


Fig. 4. Enrichment ratio (ratio of electron microprobe count rate corrected for background of film to count rate of parent glass) of sputtered film versus atomic weight. Film was sputtered from glass of Apollo 11 composition by beam of 2 keV H ions at current density of  $0.33 \text{ mA cm}^{-2}$  at background pressure of  $1 \times 10^{-5}$  torr of  $\text{H}_2$ . Na and K were detected but their abundances were not measured quantitatively.

As might be expected, in the thermally-evaporated films the enrichment ratio of an element is a monotonically-increasing function of the vapor pressure of the oxide of the element at the evaporation temperature. Since elemental Fe and oxides of Fe, Si and Ti have higher vapor pressures than oxides of the other major elements, the films are enriched in these elements. Since Fe and Ti are primarily responsible for optical absorption in lunar materials it is not surprising that the films are dark. However, one expects to see pronounced optical bands at 550 and 1000 nm associated with the known major absorption bands of  $\text{Ti}^{+3}$  and  $\text{Fe}^{+2}$ , respectively. Since such bands are not apparent (Figures 1 and 2) we must conclude, somewhat surprisingly, that crystal-field absorption does not play a major role in the optical properties of these films. The magnetic measurements described in the following section show that much of the Fe in the films is in the form of metallic Fe.

A particularly interesting correlation appears when the enrichment ratios for the

sputtered film are plotted versus the atomic weights of the element (Figure 4). With the exception of the alkali elements, the enrichment ratio appears to be linearly proportional to mass. Since Fe and Ti are the heaviest of the major elements the films are enriched in these cations and depleted in O, a light element. If sputter-deposition has been a major process on the lunar surface, the correlation we observe between enrichment ratio and atomic mass must contribute to the over-abundance of heavy elements in the fines. Since the correlation is obeyed by elements with greatly differing chemical properties it is reasonable to expect that it is also obeyed by isotopes of the same element, thus indicating a possible mechanism to account for the enrichment of heavy isotopes in the fines.

At present, we do not have an adequate explanation for the linear relation between enrichment ratio and atomic mass under sputter-deposition. It is extremely unlikely that the fractionation occurs during the sputtering process. Sputtering is essentially a surface phenomenon, and atoms should be removed in proportion to their occurrence on the surface; that is, for a multi-element compound the sputtering yield should be stoichiometric. The fractionation most likely occurs during accommodation onto the receiving surface. It is reasonable that oxygen would have a low enrichment ratio since it is volatile and will have a high probability of escape before finding a site where it is tightly bound. However, the linear relationship involving other elements implies a sticking probability which is inversely dependent on either energy or momentum of the arriving atom. We are currently investigating this phenomenon.

### 2.3. MAGNETIC AND ESR PROPERTIES

A number of hypotheses have been advanced to account for the excess metallic Fe and particularly the superparamagnetic Fe in the fines. These suggestions include annealing in thermal blankets (Pearce *et al.*, 1972), reduction by melting of fines saturated with solar wind-implanted H (Housley *et al.*, 1973) and precipitation of metallic Fe by shock (Cisowski *et al.*, 1973).

In support of their model, Pearce *et al.* (1972) annealed glasses of lunar composition for several days in a reducing atmosphere and showed that some of the FeO in the glasses was reduced to metallic Fe. This model may be debated on several grounds. The first is that the existence of thermal blankets on the Moon is still unproved. Second, the ubiquity of the excess Fe would require that all fines without exception are partially derived from thermal blankets. Third, a reducing atmosphere is required for appreciable production of Fe. We heated a glass of lunar composition for 3 days at 900°C in a BN crucible in a vacuum of  $1 \times 10^{-6}$  torr. The magnetization curve of the glass, measured before and after heating, showed only a slight change (Table I) indicating that no appreciable reduction of Fe occurred.

Housley's mechanism is ingenious, but it has not been demonstrated experimentally. Objections to its feasibility are that the solar wind implanted H is confined exclusively to within a few hundred angstroms of the surfaces of the grains, and that the H molecule is physically small and diffuses easily through silicate lattices at elevated temperatures. Thus it is likely that upon melting of the grain much of the implanted

TABLE I  
Magnetization curve parameters

Material	$I_s$ (emu gm <sup>-1</sup> )	$\chi_H$ (cgs gm <sup>-1</sup> )	Equivalent FeO	
			Assuming no SPM Fe	SMD Fe
Artificial glass of Apollo 11 composition	0.017	$2.1 \times 10^{-5}$	12%	0.008%
Glass after prolonged heating	0.028	$2.3 \times 10^{-5}$	14%	0.013%
Evaporated glass	0.10	$36.1 \times 10^{-5}$	214%	0.5%
Evaporated glass after flash-heating	23.2	$16.2 \times 10^{-5}$	96%	10.8%

H would immediately escape by diffusion without causing appreciable reduction reactions.

The shock-precipitation of metallic Fe has been demonstrated experimentally at threshold shock pressures of approximately 250 kb (Cisowski *et al.*, 1973). This pressure is in the range of incipient vaporization (Gault *et al.*, 1972) so that the shock reduction may be another manifestation of the impact vaporization reduction process discussed here.

The fines have a broad ESR resonance at a fine-structure splitting factor of  $g = 2.1$ . This so-called 'characteristic resonance' was early recognized as a ferromagnetic resonance involving Fe (Weeks *et al.*, 1970; Manett *et al.*, 1970) but the chemical nature of the Fe phase in the fines which is responsible for the resonance is controversial. Tsay *et al.* (1971) have emphasized that it is probably due to the metallic Fe in the fines. However, Griscom and Marquardt (1972) point out that the  $g$  value at which the resonance occurs is strongly shape-dependent for Fe, so that the Fe particles would have to be spherical to within a few percent, which they regard as unreasonably restrictive. Griscom and Marquardt (1972) and Kolopus *et al.* (1971) have suggested that the resonance is due to a 'magnetite-like' phase involving Fe<sup>+3</sup>. Because of the lower magnetization of magnetite the resonance is only weakly dependent on shape. However, the latter hypothesis requires that several percent of the Fe be present as Fe<sup>+3</sup> in the magnetite, and in view of the reduced nature of the fines it is difficult to understand where this magnetite-like substance could come from.

Magnetization curves of thermally-evaporated films and parent glasses of Apollo 11 composition were measured at room temperature using a vibration magnetometer to fields of 16000 Oe. Curves of the sputter-deposited films could not be measured because of the small size of the samples. However, the remanent magnetization induced in the samples by exposure to fields of 6000 Oe were measured using an SCT cryogenic magnetometer utilizing a weak link sensor. The results of the measurements are given in Table I and II.



TABLE II  
Remanent magnetizations

Material	$I_r(\text{emu gm}^{-1})$
Artificial glass of Apollo 11 composition	$1 \times 10^{-4}$
Evaporated glass	$3 \times 10^{-3}$
Sputter-deposited glass	$3 \times 10^{-2}$

The high-field susceptibility  $\chi_H$  is dependent on the amount of paramagnetic material (i.e.,  $\text{Fe}^{+2}$ ) and superparamagnetic (SPM) Fe (i.e., metallic Fe of grain size smaller than about 80 Å), through the relation

$$\chi_H = (n\mu^2 + CN_0p^2\mu_B^2/M)/3kT, \quad (1)$$

where:

$n$  = number of SPM Fe particles per gram of sample,

$\mu$  = magnetization per particle =  $\pi d^3 \rho \sigma / 6$ ,

$d$  = particle diameter,

$\rho$  = particle density,

$\sigma$  = magnetization per gram,

$C$  = weight fraction of paramagnetic Fe in the sample,

$p$  = effective electron spin value in  $\text{Fe}^{+2}$ ,

$\mu_B$  = Bohr magneton,

$M$  = molecular weight of Fe,

$k$  = Boltzmann's constant,

$T$  = absolute temperature.

If the high-field line is extended to zero field the extrapolated  $I$ -intercept  $I_s$  is the saturation magnetization due to the total amount of single and multidomain (SMD) metallic Fe in the sample. The amount of large-grained Fe can be calculated from measurements on calibrated samples.

The preceding analysis assumes that no magnetite is present, which is a reasonable assumption in view of the care which was taken to insure that the samples were not oxidized during preparation.

The amount of FeO necessary to account for the  $\chi_H$  of the parent glass is 12.3% by weight. This is in reasonable agreement with the 15% FeO originally added to the glass. Therefore it is likely that the  $\chi_H$  is due entirely to  $\text{Fe}^{+2}$  and that the quantity of SPM Fe is negligible in this sample. The amount of SMD Fe deduced from the  $I_s$  is 0.008%. Extended annealing of this glass in vacuum changed these quantities to 14% FeO and 0.013% SMD Fe, implying that a reducing atmosphere is necessary before appreciable reduction of Fe will occur.

For the thermally evaporated film the amount of FeO which would have to be

present to cause the observed  $\chi_H$  is 214%, which is physically impossible. Obviously most of the  $\chi_H$  must be due to SPM Fe. In order to calculate the amount of SPM Fe, the amount of FeO and diameter of the SPM Fe grains must be known. These quantities can be determined by measuring the magnetization at low temperatures; this work is presently being carried out, and preliminary estimates indicate that of the order of 10% by weight of the sample is SPM Fe. About 0.05% of the film is SMD Fe. That the ferromagnetic phase is primarily metallic Fe was confirmed by measuring the Curie temperature of the film. When examined under a petrographic microscope the film was completely clear and amorphous, showing that, indeed, the Fe is contained solely in submicroscopic grains.

The film was next annealed for one minute at 800°C in vacuum. The  $\chi_H$  was decreased by this treatment by a factor of 2, but the SMD Fe increased to 10.8%. Evidently annealing for even this extremely short period of time caused many of the SPM Fe grains to rapidly coalesce into larger particles, probably by solid state diffu-

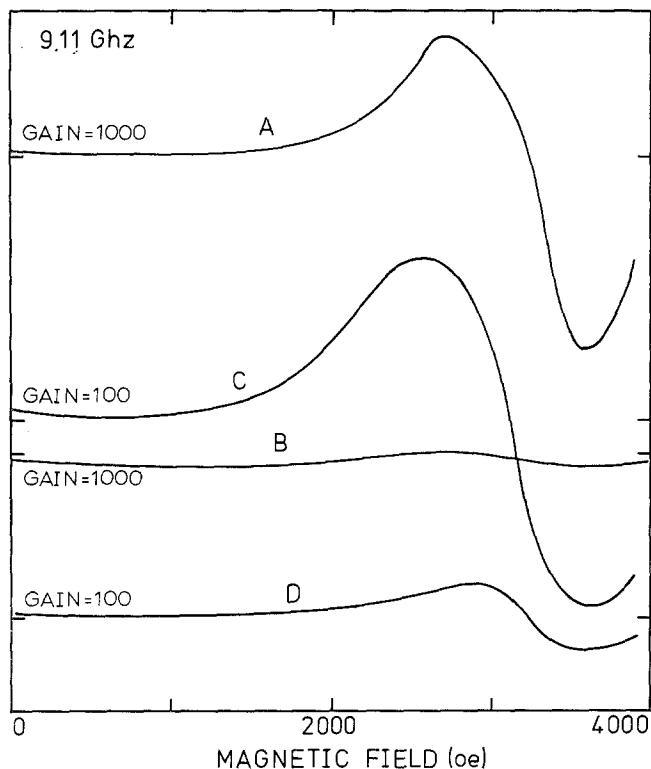


Fig. 5. ESR spectra of lunar and artificial materials of Apollo 11 composition. *A.* Fines 10084. *B.* Film evaporated from artificial glass of Apollo 11 composition in electron-bombardment furnace at 1900°C in vacuum. *C.* Film of curve *B* heated for 1 minute at 800°C in vacuum. *D.* Film of curve *B* heated for 1 hour in air at 650°C; the lunar fines show a similar effect (Griscom and Marquardt, 1972).

sion. It may be inferred that the unheated film contains more than 10% SPM Fe. We believe that the mechanism of grain growth by coalescence during rapid heating accounts adequately for the apparent correlation between metamorphic grade of lunar breccias and size distribution of Fe particles in the breccias (Fuller, 1974).

Although comparable magnetization measurements could not be made on the sputter-deposited samples, the large induced remanent magnetizations (Table II) imply that materials made by this process contain as much metallic Fe as the thermally-evaporated films. The sputtered films are also clear and amorphous.

The ESR spectra of several materials at a frequency of 9.1 Ghz are shown in Figure 5. Glass of Apollo 11 composition has only the very broad, weak absorption characteristic of ferromagnetic material whose grain size is larger than the skin depth of RF radiation. The thermally evaporated film has the characteristic  $g = 2.1$  resonance, but the amplitude is very small. However, on flash-annealing to promote coalescence of the Fe grains the strength of the resonance grows by a factor of 100. To our knowledge this is the first demonstration of a laboratory material in which submicroscopic Fe is unambiguously shown to have the characteristic ferromagnetic resonance. Thus this work confirms the discussion of Tsay *et al.* (1971). It should be noted that only extremely short heating times are required to produce a strong resonance in the film. Such heating could occur either in an adjacent micrometeorite impact or possibly by deposition on hot grains during a single event. In any case, a thermal blanket is not required. In fact, extended heating probably would destroy the ESR resonance because the Fe grains would grow to a size larger than the RF skin depth.

### 3. Discussion

The reason that both the sputter-deposited and thermally-evaporated silicate materials are rich in metallic Fe becomes clear on examining the physicochemical reactions which occur during the processes. During sputtering the oxides are decomposed to elements and transferred to the substrate as individual neutral atoms. The newly arrived atoms are not strongly bound to the growing film immediately, and, depending on their chemical and volatilization properties, have a finite probability of re-evaporating. Since O is much more volatile than the metals, it has a higher escape probability and the film becomes deficient in O. Evidently this O-deficiency manifests itself by keeping some of the most easily reduced cations, in this case Fe, in the metallic form.

In the case of thermal evaporation-deposition, the mechanism is different but the final results are similar. In the vapor state the common rock-forming oxides are dissociated to varying degrees (deMaria, 1970). The most common vapor species over evaporating lunar rocks are (deMaria *et al.*, 1971) Fe, SiO, TiO<sub>2</sub>, TiO, Ca, K, Al, Mg, Na, O<sub>2</sub> and O. Again, the more volatile O is less strongly accommodated on the deposition surface than the reduced oxides and an O-deficient, metallic-Fe-rich material results.

The effect of the submicroscopic metallic Fe on the albedo of the fines can be estimated as follows. We confine ourselves to visible light,  $\lambda \sim 550$  nm. The reflectivity

$R$  of an optically-thick layer of powder can be estimated from the two-stream or Kubelka-Munk equation (Kortum, 1969)

$$R = \frac{1 - \sqrt{1 - w}}{1 + \sqrt{1 - w}}, \quad (2)$$

where  $w$  is the effective single-scattering albedo of a particle of the powder. For a mixture of a different types of particles  $w$  is the averaged albedo weighted by cross-sectional area

$$w = w_m = \left( \sum_i n_i \sigma_i Q_{si} \right) / \left( \sum_i n_i \sigma_i Q_{ei} \right), \quad (3)$$

where:

$n$  = number of particles per unit volume,

$\sigma$  = geometrical cross-section,

$Q_s$  = scattering efficiency,

$Q_e$  = extinction efficiency,

subscript  $i$  denotes particle of type  $i$ .

Powders of crushed lunar crystalline rock typically have  $R = R_R \sim 0.2-0.3$  (Hapke *et al.*, 1970; Antipova-Karataeva *et al.*, 1972) and, therefore, typically  $w = w_R = Q_{sR}/Q_{eR} \sim 0.6$ . We now ask by how much the average single scattering albedo will be reduced when 0.5% submicroscopic metallic Fe is added to the powdered crystalline rocks. From (3) it follows that

$$w_m = (n_R \sigma_R Q_{sR} + n_{Fe} \sigma_{Fe} Q_{sFe}) / (n_R \sigma_R Q_{eR} + n_{Fe} \sigma_{Fe} Q_{eFe}). \quad (4)$$

Now the mean particle size of the fines is of the order of  $50 \mu\text{m}$  (Duke *et al.*, 1970; Hapke *et al.*, 1970; Gold *et al.*, 1971). For particles of radius  $r$ , large compared with the wavelength  $\lambda$  of light,  $Q_e \approx 2$  (Kerker, 1969). However, for Fe particles with  $2\pi r/\lambda \ll 1$ ,  $Q_s = (8/3) |(m^2 - 1)/(m^2 + 2)| (2\pi r/\lambda)^4$ , and  $Q_e = -4Im [(m^2 - 1)/(m^2 + 2)] (2\pi r/\lambda) \approx 6\pi r/\lambda$ , where  $m$  is the complex refractive index. Thus the second term in the numerator of (4) can be ignored. Also, if we take the particles as roughly spherical,

$$n_i \sigma_i \approx 3M_i/4\rho_i r_i, \quad (5)$$

where:

$M$  = bulk density in fines,

$\rho$  = solid density,

$r$  = radius of particle.

Then

$$w_m \approx \frac{Q_{sR}/Q_{eR}}{1 + n_{Fe} \sigma_{Fe} Q_{eFe}/n_R \sigma_R Q_{eR}} \approx \frac{w_R}{1 + (M_{Fe}/M_R) (Q_R/Q_{Fe}) (3\pi r_R/\lambda)}. \quad (6)$$

Taking  $M_{Fe}/M_R = 0.005$ ,  $Q_R/Q_{Fe} = 0.4$ ,  $r_R = 25 \mu\text{m}$ ,  $\lambda = 0.5 \mu\text{m}$ , we find that the effect of the submicroscopic Fe is to reduce  $w$  from 0.60 to 0.31 and  $R$  from 0.23 to 0.09. The

reflectivity of the mixture increases monotonically with  $\lambda$ . Since metallic Fe has no discrete absorption bands, the masking of the bands in the crystalline rock spectra can be explained. It must be emphasized that it is not necessary that the Fe coat the grains; a thorough mixing is sufficient to control the optical properties. A similar analysis applies if the Fe is incorporated into larger, transparent particles.

The vapor-deposited films are of the order of 10% by weight of metallic Fe. If we assume that the 0.5% metallic Fe in the fines is primarily in vapor-deposited material, then this exotic component makes up about 5% of the fines.

Gault *et al.* (1972) estimate that the present rate at which material is being melted by impacts on the lunar surface is  $6.1 \times 10^{-9}$  gm cm<sup>-2</sup> yr<sup>-1</sup> and an additional  $2.7 \times 10^{-9}$  gm cm<sup>-2</sup> yr<sup>-1</sup> is vaporized. The ratio of amount vaporized to melted depends on the velocity of the projectile and increases as the velocity increases. Since most of the impacts are by particles of mass between  $10^{-8}$  and  $10^{-4}$  gm, it is primarily the upper layers of the regolith which are being affected.

The exact fate of the vaporized material is difficult to specify. However, the upward-directed molecules in the expanding cloud of vapor will enter ballistic trajectories. The effective temperature of the molecules will probably be 2500–3000 K, so that while their mean thermal velocities ( $\sqrt{3kT/m}$ ) will be less than the velocity of escape from the Moon, high speed tails in their curves of speed distribution will exist. Any resulting preferential loss to the Moon will favor oxygen, while Fe and Ti will be preferentially retained. The heavier molecules will rain down more-or-less uniformly over the lunar surface. They could account for the brownish patina described by Schmitt (1973) as covering rocks and boulders on the lunar surface. They may also account for the iron-rich outer surfaces of the fines reported by Hapke *et al.* (1970) and Gold *et al.* (1974) and may contribute to the coatings observed using high-voltage electron microscopy by Borg *et al.* (1971). The downward-directed particles of the vapor cloud will condense on the grains of regolith immediately around and below the impact point, where they will mix with the rest of the glass, breccia and debris generated by the event. We suggest that this process is involved in the origin of many of the agglutinate particles in the fines; if so, then of the order of 20% of the glass in the agglutinates has been deposited from a vapor. Agrell *et al.* (1970) have noted in the amorphous matrix material of the agglutinates, submicroscopic inclusions of metallic Fe which are probably not of meteoritic composition because of the low Ni content.

Since the center of the mass of the vapor cloud is moving downward with respect to the surface, more than half of the vapor will plate out very close to the impact point. Thus the composition of the condensate will reflect average local composition and local control of the optical properties will be retained, although with a lowered reflectivity.

Various workers (KenKnight *et al.*, 1967; Hapke, 1973; McDonnell *et al.*, 1972; Maurette and Price, 1975) have estimated that the lunar surface is being sputtered at a rate between  $1.2 \times 10^{-9}$  and  $15 \times 10^{-9}$  gm cm<sup>-2</sup> yr<sup>-1</sup> by the present solar wind. However, because of the highly porous and re-entrant nature of the uppermost layers of the regolith (Hapke and Van Horn, 1963; Hapke, 1970) an appreciable fraction of

the sputtered atoms will impinge on adjacent surfaces of soil particles and will be accommodated there. Hapke (1973) estimates that glass is presently being formed by solar wind sputter-deposition at a rate of  $2.8 \times 10^{-9} \text{ gm cm}^{-2} \text{ yr}^{-1}$ . The atoms which do not hit adjacent particles have energies of the order of eV and thus the lighter species have velocities greater than the lunar escape velocity. However, a portion of the heavier atoms will not escape and will eventually be accommodated on the surface. Atoms which impinge on adjacent surfaces and which are not accommodated have a velocity distribution upon leaving which is unknown, so that it is difficult to predict the type and degree of fractionation which will occur by this effect. However, as long as the soil remains undisturbed, coatings will build up on the undersides of grains and will weld together grains with an amorphous, iron-rich material. Thus this process may also be important in the formation of the agglutinates. It should be noted that the sputter deposits are local also.

If the fluxes of micrometeorites and solar wind have remained constant the total amount of vapor-deposited glass formed by sputtering and thermal evaporation in the last 3 Gyr is  $16.5 \text{ gm cm}^{-2}$ , which is to be compared with the  $18.3 \text{ gm cm}^{-2}$  of glass formed by impact vitrification. Both of these quantities are highly uncertain and are to be regarded as order of magnitude estimates only. However, it is clear that vapor phase transport and deposition have been significant processes on the lunar surface. These processes can account quantitatively for the optical and magnetic peculiarities of the fines and probably contribute significantly to the chemical properties of the regolith as well.

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