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LUNAR SAMPLE ANALYSIS

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by

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Principal Investigator

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LUNAR SAMPLE ANALYSIS
ANNUAL REPORT No. 6

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ESCA, Atomic Absorption, Lead, Cadmium, Zinc, Sodium, Sulfur, Surface Composition, Volcanic Volatiles

We report results of our continuing studies of the evolution of the lunar regolith, the transport of volatile trace metals, and the surface composition of lunar samples. Experimental techniques utilized include x-ray photoemission spectroscopy, flameless atomic absorption, ferromagnetic resonance, scanning electron microscopy and Mössbauer spectroscopy. We also report initial results of an effort to model lunar volcanos.
MODELING LUNAR VOLCANIC ERUPTIONS. R. M. Housley, Rockwell International Science Center, Thousand Oaks, California 91360.

From the time the first returned lunar samples were examined, it has been known that early in its history the moon underwent a period of volcanism, during which a large quantity of volatile poor basaltic magma was erupted. The nature of the volcanism and the influence of outgassing and volatile transport in the lunar vacuum have been extensively debated ever since.

Although photogeologists interpreted features on several areas of the moon as pyroclastic deposits, it was not until after the Apollo 17 mission that pyroclastic materials were convincingly identified in the returned lunar samples. The case for so identifying the Apollo 17 orange and black glasses and the Apollo 15 green glass has since been systematically argued by Heiken et al. (1) on the basis of chemical, petrographic and photogeologic evidence.

A plausible explanation for the puzzling fact that these glasses do not resemble terrestrial pyroclastic materials has been offered by O'Keefe (2). He pointed out that the frothy nature of terrestrial pyroclastics may depend on the fact that the surface tension of the melt increases as water is vaporized from it.

A plausible though modest source of volatiles that is compatible with the geochemical constraints imposed by the reduced nature of the lunar basalts has recently been suggested by Sato (3). He showed that all available data can be interpreted by assuming that about 100 ppm of finely divided graphite was present in the magma at depth. Above about 3 km, this graphite would react with the melt to form bubbles containing CO and CO$_2$ and leave finely divided grains of Fe metal in the melt. This avoids any problem associated with the nucleation of bubbles in a volatile poor magma and could help explain the different physical characteristics of lunar and terrestrial pyroclastics.

Thus, the stage is set for serious efforts to model lunar volcanic eruptions. We proceed in three steps, considering first, the transport of magma to the lunar surface; then the nature of the transient lunar atmosphere produced by the gas released; and finally, the processes that could occur in the vicinity of the point of eruption.

As a starting point for modeling magma transport, we assume that the volcanic plumbing is similar for lunar volcanoes and for terrestrial oceanic volcanoes. From a visual inspection of recent Hawaiian craters, by allowing for near surface flaring, we obtain an order of magnitude estimate of about 10 m for the typical diameter of terrestrial magma conduits.

It is important to note that in a conduit of this size any reasonable estimates of flow velocity and magma viscosity yield very high Reynolds numbers, implying that the flow must be highly turbulent. In this case, the average flow velocity depends strongly on the roughness of the conduit, but only weakly on the viscosity (4). Thus, we reach the surprising conclusion that the much lower viscosities of lunar magmas in comparison to their terrestrial counterparts will not lead to substantially increased eruption velocities.

In both lunar and terrestrial volcanos, the ultimate driving force responsible for magma migration is the difference in average density between the fluid and the rock through which it moves. Although the near surface
behavior of terrestrial magmas is complicated by the large volatile component present, we may roughly check whether our estimated conduit diameter is realistic by comparing calculated eruption characteristics with the recorded behavior of Hawaiian volcanos (5). Assuming the maximum reasonable density contrast of 10%, a viscosity of 145 poise (1), and an average surface roughness of 0.5 m in a 10 m diameter conduit, we can use the hydraulic engineering data graphically presented in (4) to calculate an average flow velocity of 16.5 m/sec, an eruption rate of $4.7 \times 10^6$ m$^3$/hr, and a Reynolds number of $3.4 \times 10^4$.

The eruption rate of $4.7 \times 10^6$ m$^3$/hr is about a factor of 5 high for typical recent Hawaiian eruptions (5), probably because the assumed effective pressure head is too large.

With the same conduit diameter and density contrast and a viscosity of 10 poise (1), the calculated lunar eruption rate is $1.9 \times 10^5$ m$^3$/hr, with a Reynolds number of $2 \times 10^3$ and a flow velocity of 6.8 m/sec.

From the Fe metal content of lunar basalts, we can calculate the amount of CO they must have evolved (3). Using 0.15 wt% Fe metal as determined by Morris and Gose (6) for 74001 glass, this is 0.075 wt%. Thus, our hypothetical eruption brings CO to the lunar surface at the rate of about $1.2 \times 10^5$ gm/sec.

As a first approximation, we assume that at modest distances from the source this gas expands hemispherically. A limiting velocity of about 1.5 km/sec will be reached when all the thermal energy is converted into kinetic energy of flow. The density $\rho$ and velocity $v$ at any radius $r$ and mass flow rate $m$ are related by

$$2\pi^2 \rho v = m.$$ 

At distances where $v$ is close to its limiting value with the above mass flow rate

$$\rho = \frac{1.3 \times 10^{-4}}{R^2} \frac{\text{gm}}{\text{cm}^2},$$

where $R$ is the radius in m. The °C pressure corresponding to this $\rho$ is

$$P = \frac{1.04 \times 10^{-1}}{R^2} \text{ atoms, or } P = \frac{7.9 \times 10^4}{R^2} \text{ torr}.$$ 

Thus, we see that the pressure only falls off to $10^{-8}$ torr at about 100 km from the eruption site. Yet this formula suggests that pressure may remain quite modest near the eruption site, although a more complete calculation is needed to describe this region.

Fountaining during terrestrial volcanic eruptions appears to be caused by the evolution of gas from the magma in the conduit as it moves toward the surface. The observed fountaining, in fact, requires the evolution of only a fraction of the total gas present.

Our estimated molar abundance of CO in lunar magmas is about a factor of 10 lower than the volatile content of terrestrial magmas. However, it may more completely evolve in the conduit and on an equal molar basis will occupy 6 times the volume because of the lower pressure in the lunar conduit. Taking
into account these facts, we have estimated that lunar magmas could reasonably 
fountain to a height of about 1 km.

At the point of eruption the gas would occupy considerably more than half 
the volume and would still be under sufficient pressure to expand violently 
separating much of the material into small droplets with velocities of the 
order of tens of m/sec.

This modeling effort clearly can be refined and extended in many ways. 
For example, the ability of the expanding gas cloud to transport solid particles 
and perhaps to generate lunar dust storms can be investigated.

At the present stage, it suggests several important experiments. The 
kinetics of graphite reaction with Fe silicate melts should be investigated. 
The partitioning of trace volatiles between gas and liquid should be studied. 
And the behavior of a dry vesicle ladden melt on sudden decompression should 
be checked.

It also strongly suggests the following conclusions: 1) The difference 
in viscosity between lunar and terrestrial magmas is of minor importance in 
comparing their eruption characteristics. 2) Magma may fountain to heights 
of the order of 1 km during lunar eruptions. 3) Violent expansion of CO 
bubbles at the instant of surface arrival can lead to the formation of 
abundant ~ 100 um glass balls and their distribution over a radius of hundreds 
of meters. 4) A major fraction of the more volatile elements in the magma 
may be in the bubbles and, hence, escape into the transient atmosphere.
5) The expansion of the transient atmosphere will distribute volatile elements 
especially over the entire moon.

p. 1703-1718.
Editor, McGraw-Hill, Section 3, p. 48-62.

We report further developments in our study of vapor transport processes using a flameless atomic absorption technique (1,2) to analyze the volatile trace metals Pb and Cd in orange and black glass core samples 74002/74001 and nearby surface samples 74220 and 74241.

Many workers have shown that volatile elements are enriched in the orange and black glasses and that, in general, the concentrations of these volatile elements are surface correlated (3,4). Previous workers have provided strong arguments supporting a volcanic origin for these glasses and have proposed lava fountain mechanisms (5,6).

Our Pb results on dry sieved core tube sample 74001-105 from the depth of 39-39.5 cm also shows that the concentration of Pb increases as the grain size decreases (Fig. 1). A scanning electron microscope study (Fig. 2) of this black glass shows that most of the small grain size material is made up of broken pieces. This provides strong evidence that the volatile trace metals were deposited after the glass was broken. The glass balls could have been broken either upon landing on the lunar surface during the initial deposition from the volcanic eruption or by shock during the recent Shorty Crater event.

Reed and his coworkers (7) and Heiken and McKay (5) both proposed separate lava fountaining mechanisms to account for the formation of the orange and black glasses.

The total Cd (Fig. 3), total Pb and PbCl₂ (Fig. 4) concentration in core tube samples 74002/74001 decrease as core tube depth increases. Our study also shows that a considerable amount of Pb in the surface sample 74220 and in the samples near the surface 74001-1069 is in the form of PbCl₂.

The presence of orange glass down to a depth of about 25 cm in the upper core section 74002 and black glasses for the rest of 74002 and all of 74001 was noticed by Schmitt (8).

If these orange and black glasses were formed during different lava fountains as suggested by Reed et al. (7) and Heiken et al. (5), then discontinuity of the concentration of volatile elements at about 25 cm depth would be expected. Our data shows a continuity in concentration of volatile metals throughout the core.

Our data suggest that either the volatile trace metals were completely redistributed by the Shorty Crater impact or that the original strata, if formed by a lava fountain, and assuming a single fountain mechanism, was totally preserved. Since it seems very unlikely that the original strata are well preserved at the rim of Shorty Crater where the samples were collected, our results seem to suggest that volatile trace metals were redistributed and that PbCl₂, being volatile, was transported to the upper surface as vapor from below while the lower strata slowly cooled.

The Pb concentrations in samples 74220 (2.29 ppm), 74241 (2.21 ppm) and the near surface sample 74001-1069 (2.40 ppm) are about the same, indicating a single exposure to Pb.

Fig. 1 Total Pb concentration in sample 74001-105 from the depth of 39-39.5 cm as a function of grain size.

Fig. 2 Scanning electron micrograph of core tube sample 74001.
Fig. 3 Total Cd concentration in core tube samples 74002/74001 as a function of core tube depth.

Fig. 4 Total Pb and PbCl₂ concentration in core tube samples 74002/74001 and surface orange glass sample 74220.
AN XPS STUDY OF APOLLO 17 ORANGE AND BLACK GLASSES. R. W. Grant and R. M. Housley, Rockwell International Science Center, Thousand Oaks, California 91360.

We report results of a detailed study of the surface chemistry of grain size fractions dry sieved from Apollo 17 black glass sample 74001.105. This sample from a depth of 39.0-39.5 cm in the double drive tube is free from agglutinitic contamination. In its finer fractions broken surfaces strongly predominate over original spherical surfaces.

We have studied a 75-1000 \mu m sample cemented to a recessed sample holder with colloidal graphite and two < 20 \mu m samples, one prepared according to our normal procedure by sedimentation from ethanol, and one packed dry into a recessed sample holder. These latter two samples gave indistinguishable results indicating that our data are not influenced by the method of sample preparation.

Both size fractions showed high surface concentrations of Zn, Na, and S. No other minor or trace elements were present in comparable amounts.

Although the 75-1000 \mu m fraction presents more than 50\% unbroken surfaces, it only showed concentrations about a factor of two higher than those in the < 20 \mu m fraction, which presents at most a few \% unbroken surfaces. Therefore, considerable redistribution of volatiles must have taken place after the grains were broken. This could have been either in the fountaining process itself or as the result of a subsequent impact.

In Figs. 1 and 2 we present raw peak intensity versus sputtering time profiles for Zn and Na in the two size fractions. The sputtering rate for a flat SiO$_2$ surface under the conditions used is 0.7 Å per minute. It appears that although the surface enrichments are thin in both cases that they are somewhat thicker on the unbroken surfaces.

When we initially ran the samples after pump down at room temperature, about half the S was in an oxidized form. Counting both the oxidized and sulfide forms, there still was about a factor of two too little S present to correspond with the observed Zn. Before sputtering, we heated the samples to 300°C for an hour. This removed the majority of the oxidized S in agreement with mass spectroscopic results previously reported by Simonait et al. (1).

We feel the data suggest that the Zn was originally transported and deposited as ZnS and that much of the S has been oxidized and lost since the samples were returned.

Fig. 1 Raw intensity profiles of Zn and Na on 75-1000 μm black glass 74001 as a function of sputter time. Initial rise is due to removal of carbon contamination.
Fig. 2: Raw intensity profiles of Zn and Na on <20 μm black glass 74001 as a function of sputter time. Initial rise is due to removal of carbon contamination.

The excess iron metal in lunar fines samples has been shown to be related to their surface exposure ages (1). Recent techniques permit the iron to be quantitatively determined (2), and these methods are currently in use to measure the relative surface exposure ages of core samples (3-5).

The line shapes and widths of the FMR absorption vary among lunar fines samples for reasons which are not understood. Linewidths and shapes as well as specific intensities also differ in different size fractions from the same sample. Puzzling temperature and frequency dependences of the linewidths and intensities have also been reported in the past. We are studying the temperature and frequency dependence of the FMR absorption in size fractions of fines samples in the hope that we can understand the mechanisms that control shape and intensity and can in turn use this information to expand our understanding of the evolution of the samples.

The temperature dependencies of the peak-to-peak linewidths of size separates of sample 12C01 are shown in Fig. 1. At room temperature, the linewidths are equivalent, but as the temperature is lowered, the linewidths of the smaller grains increase much more rapidly than that of the larger grains. The derivative and computed absorption curves shown in Fig. 2 show that for the 1-2\(\mu\text{m}\) separate, this linewidth increase is not merely due to the change in the anisotropy field. While this increase in the linewidth may be due to an increasing contribution from a broader resonance component, the maxima of the linewidth at 20-30K for the 2-5\(\mu\text{m}\) and 20-30\(\mu\text{m}\) size separates parallel valence-exchange or impurity broadening of FMR spectra (6). This broadening was shown to occur due to surface oxidation of Ni-Fe films (7).

Double integral values of the 1-2\(\mu\text{m}\) size fraction increase by 39% between 270K and 10K, while those of the 2-5\(\mu\text{m}\) size range increase 28%, and those of the 20-30\(\mu\text{m}\) size fraction increases by 21%. These results indicate that the smaller grains contain a greater proportion of spheroidal iron which is superparamagnetic at high temperatures. We observed only a monotonic increase in the double integral values, and no decrease below 200K as reported by Griscom et al. (8).

Since all iron particles are saturated above about 21K0e, and spherical particles are saturated above about 7K0e, quantitative 35 GHz determinations were carried out to estimate the content of multi-domain Fe\(^{6}\) particles relative to the 9.5 GHz determinations. The results of these measurements are shown in Table I.
TABLE 1

QUANTITATIVE MöSSBAUER MEASUREMENTS AT
9.5 AND 34 GHz FOR 12001 SAMPLES (294K)

<table>
<thead>
<tr>
<th>Size Range (µm)</th>
<th>Weight (mg)</th>
<th>% Fe° at 9.535GHz</th>
<th>% Fe° at 33.982GHz</th>
<th>Relative Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5-2</td>
<td>0.079</td>
<td>1.3</td>
<td>1.72</td>
<td>1.28</td>
</tr>
<tr>
<td>10-2</td>
<td>0.099</td>
<td>0.55</td>
<td>0.751</td>
<td>1.35</td>
</tr>
<tr>
<td>35-45</td>
<td>0.124</td>
<td>0.35</td>
<td>0.525</td>
<td>1.50</td>
</tr>
</tbody>
</table>

All samples showed an apparent increase in the amount of Fe° when measured at 35GHz. The finer size fractions exhibited a smaller increase indicating that they contain smaller spheroidal iron particles.

During these measurements it became apparent that as the amount of sample used was increased, the percentage of Fe° appeared to decrease. This was attributed to loading of the microwave cavity, as shown in Table II.

TABLE II

<table>
<thead>
<tr>
<th>Sample wt (45 µm)</th>
<th>wt (mg)</th>
<th>35GHz</th>
<th>9.5GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ΔHpp</td>
<td>%Fe°</td>
</tr>
<tr>
<td>65,701,13</td>
<td>0.063</td>
<td>672</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>0.552</td>
<td>748</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>67,701,26</td>
<td>0.118</td>
<td>687</td>
<td>0.195</td>
</tr>
<tr>
<td></td>
<td>0.951</td>
<td>725</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td>2.20</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>66,031</td>
<td>0.093</td>
<td>694</td>
<td>0.373</td>
</tr>
<tr>
<td></td>
<td>2.25</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

This anomalous decrease in the Kα band spectra results from loading the microwave cavity so that the intensity is no longer linear. Several results report large variations of the linewidth of the 35GHz resonance while that of the 95GHz resonance is constant. Using samples smaller than about 150µg at 35GHz, (depending on the amount of Fe°), the linewidths are constant to within ±15 Oe and the percentage of Fe° is greater than that measured at 9.5GHz.

REFERENCES


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**Fig. 1**
Peel-to-peak linewidth of the derivative spectra of sample 12001 as a function of temperature.

**Fig. 2**
Derivative spectra and computed absorption between 0 and 7.68 kOe for size separated 12001 samples at high and low temperatures.