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LUNAR SAMPLE ANALYSIS

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**Key Words:** Lunar regolith, solar wind, hypervelocity impact, sputtering, maturation, fine-grained Fe metal, graphite, C-H-O-S fluid, alteration, platinum, palladium, Stillwater Complex.

**Abstract:**

We present new results and a new analysis of the evolution of the lunar regolith under solar wind and micrometeorite bombardment. We also present an initial description of a massive graphite, platinum, palladium association from the Stillwater Complex, Montana.
LUNAR REGOLITH EVOLUTION, R. M. Housley, Rockwell International Science Center, Thousand Oaks, California 91360.

Since the first lunar regolith samples were returned by the Apollo and Luna missions, a large amount of effort has been devoted to characterizing them and to identifying the processes that have been important during their formation and evolution. This is an attempt to synthesize what has been learned and to outline a consistent working model that can account for the key observations in a plausible way.

Upon microscopic examination, it is immediately apparent that hypervelocity impacts have played the dominant role in altering lunar regolith materials. At a typical collision velocity of 20 km/sec, the kinetic energy of impact is more than enough to vaporize the meteorite and to melt several times its mass of the target. It is important to determine how this energy is actually partitioned.

This can be approached by making use of the residues from partial vaporization that are now recognized in the regolith (1-5). The high alumina, silica poor HASP glasses (2-4) found in highlands regolith are the most widely accepted. Using the data summarized in (2), we can infer that they constitute about 0.4 percent of mature highlands fines. It can be convincingly argued (3) that many additional glasses, including the highland gabbroic anorthosites, have lost lesser amounts of silica. Using the modal data in (3) and (4), we can estimate these to have an abundance of about 1.5 percent. Using the analysis of (2) and (4), we find that HASP and gabbroic anorthosite glasses have respectively lost at least about 20 and 6 percent of their initial mass by silica vaporization. Combining these results, we see that about 0.17 percent silica vaporization can be well documented from mature highlands regolith. There is no obvious reason why results from other sites should be drastically different.

It is now important to enquire into the initial temperature of these droplets, which will be close to the temperature where most of the vapor was evolved. Since the evaporation rate depends exponentially on 1/T while radiative cooling depends on T^4 we can expect that at high enough temperatures evaporative cooling will dominate. De Maria et al. (7) have shown that silica evaporates primarily as SiO plus O from melts of lunar composition and have presented vapor pressure versus 1/T data. Using this, we find that evaporation is the dominant cooling mechanism above about 2500°K. We can derive the following simple formula to relate change in mass M and change in temperature T in the high temperature regime.

\[ \left( \frac{M_f}{M_i} \right)^{4/9} = \frac{L - 4RT_f}{L - 4RT_i} \]

The subscripts i and f refer to initial and final, L is the low temperature latent heat of evaporation of SiO₂ plus the heat of dissociation to SiO + O and is taken to be 185 kcal/mole, R is the gas constant. Using this we find that the gabbroic anorthosite glasses had initial temperatures around 3000°K, typical HASP glasses had initial temperatures around 4400°K, and the most silica depleted HASP glass (2) had an initial temperature of 5300°K. These latter temperatures are high enough that largely unfractonated evaporation may have occurred. Therefore, the total mass of material vaporized and the true initial temperatures may exceed these estimates.

The above estimates of vaporized fraction and initial temperature are on the low side, but within the ballpark, of those required to account for
observed isotopic fractionations in the regolith (8) by partial loss of impact vapor from the moon (6). There is evidence that alkali metals (5) and probably sulfur have been vaporized from a much larger fraction of lunar glass particles. Hence they would preferentially be sited on grain surfaces, available for sputtering. Oxygen would be depleted in material redeposited following partial vapor loss essentially independent of composition.

Solar wind sputtering must occur, but its global effects cannot be quantitatively predicted since no information is available on the velocity distributions or partial sputtering yields of species sputtered from lunar material by H and He. Probably sputtering makes a substantial contribution to the isotopic effects in K and S (8). Sputtering should probably also lead to an essentially composition independent preferential loss of oxygen.

Considerable evidence shows that the rate of production of fine-grained Fe metal in lunar agglutinates is proportional to the FeO content at the site. There is no explanation for this if either partial vapor loss or sputtering is the primary reduction mechanism. However, it follows simply from thermodynamics if reduction by solar wind hydrogen is assumed to be dominant,

\[
\frac{[H_2O]}{[H_2]} = K \frac{[FeO]}{[Fe]}
\]

with K around one. Some subtle points connected with this will be discussed.


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In this report we briefly describe some of the most interesting characteristics of unusual banded graphite-sulfide-oxide-silicate formations occurring in pipe-like structures in the Stillwater complex of Montana. We interpret these as forming through the interaction of a C-H-O-S fluid phase with the host rock. If this is so, an improved understanding of the sequence of reactions which took place and the corresponding evolution in composition of the fluid, will contribute to our understanding of the general behavior of volatiles during planetary crustal evolution.

This is true regardless of whether or not the volatiles involved were indigenous to the intrusion or were a later injection either from the mantle or from the surrounding crustal rocks. In any case, the pegmatoid nature of the pyroxene in the pipes suggests that a fluid phase was present even while the rock was too hot for hydrated minerals to be stable.

The samples we describe are from the Janet-50 claims of the Manville Corporation. Drilling in this area and our SEM and mineralogic studies have outlined a significant concentration of sulfides; have detected arsenides, bismuth minerals, silver, palladium, and platinum minerals and major graphite in associations of great complexity and exhibiting multiple generations. This mineralization follows a stockwork of irregular pipe-like cross cutting coarse pyroxenite pegmatoids intruding (?) and spreading along the contract zone between the Ultramafic and the Banded Upper Zones of Page and Nokleberg (1). These zones correspond to the Upper Bronzitite (UBZ) and Norite 1 (NZI) zones of Todd et al (2). Considerable disseminated graphite has been also found by Dr. E. L. Mann, of the Manville Corporation and one of us (AV) in the so-called Coors Swamp Anomaly halfway between East Boulder River and about 300 meters east of Lost Mountain, apparently in the Gabbro 1 and Norite 1 zones of the lower Banded Zone of Todd et al (3). Some graphite has been seen by one of us (AV) in the poC cumulate of the J-M reef in the Troctolite Anorthosite zone (TAZ 1) at the entrance of the Frog Pond Adit, about 300 meters south of Brownlee Creek. Graphite has been also reported from the so-called West Fork Adit on the north side of the Stillwater River between the Bluebird Thrust and the Iron Creek fault in the Troctolite Anorthosite zone (sheet 2, Page and Nokleberg, (1)).

In the material we have examined, graphite appears to have formed in several generations, and a variety of forms. There also seem to be several generations of sulfides and silicates, and at least three generations of carbonates, including dolomite, ferroan calcite, and nearly pure calcite. Well-crystallized graphite commonly replaces bronzite as is illustrated in Fig. 1A and C. Ring-like alternations of graphite with sulfides, arsenites, and silicates forming botryoidal, pod-like, vein-like, and pipe-like bodies as illustrated in Fig. 1B, are very common. Graphite also occurs disseminated in serpentine as in Fig. 1D, as well as in fine-grained veinlets cross cutting silicates and sulfide blebs. Very fine-grained platinum, palladium, tellurium, bismuth, arsenic, nickel, cobalt, copper and iron minerals, occur throughout the graphite, sulfide-rich rocks.

Fig. 1. Oblique reflected light micrographs of typical Stillwater graphite associations. Graphite, dark gray, silicates, medium gray, sulfides, bright. A. Graphite replacing bronzite. B. Dense graphite and silicates, mostly serpentine, with triangular cavity. C. Bronzite with graphite surrounded by complex fine-grained mixture. D. Graphite globules in serpentine.

Fig. 2. Backscattered electron SEM images of peculiar graphite nodule. A. Whole nodule surrounded by continuous sulfide, magnetite rim. B. Central region showing sulfide "stars" in graphite. C. Higher magnification.
CONCERNING THE SIZE DISTRIBUTION OF ULTRAFINE IRON IN LUNAR SOIL.
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It has been recognised since soon after the return of the Apollo 11 lunar
samples that the magnetic characteristics of the soil fines are determined to
a great extent by ultrafine iron particles. These particles are mostly less
than about 30nm in diameter and are disseminated throughout agglutinatic
glass, often following schlieren patterns. The importance of the reduced
iron is demonstrated by the fact that the ratio of its ferromagnetic resonance
response I, to the total iron in the soil FeO is the most widely used index of
soil maturity(1). Despite considerable attention however, many questions
pertinent to the formation mechanism and subsequent history of the iron
droplets remain unanswered. Chemically it is known that the iron has a low Ni
content but contains appreciable quantities of carbon - designated hydro-
lysable carbon and thought to be in solid solution - which is released as
deuterocarbons, mainly CD₄, on reaction with DCI(2). In terms of physical
properties, there is evidence that α-iron is present and Curie point measure-
ments confirm that in essence the particles are high purity iron metal (3).
The shape of the ferromagnetic resonance response curves (see 4) are also
wholly consistent with this; they indicate iron metal with low levels of
impurity.

It happens that the size distribution of the iron droplets is a crucial
factor in discussing various physical and chemical characteristics (see 5, 6).
On the basis of detailed magnetic investigations, Stephenson (7, 8) suggested
that the distribution might be inverse square, or approximately so. Magnetic
measurements on Apollo 15 fines (9) and an Apollo 14 breccia (10) indicated a
similar functional dependence. For 10084 soil fines, Housley et al. (11)
obtained data on the size distribution of iron spheres over the diameter
range 7 to 24nm by direct counting from transmission electron micrographs.

In an alternative approach, Pearce et al. (12) precipitated metallic
iron droplets by subsolidus reduction of synthetic lunar composition glasses.
They found that at temperatures below 950°C, appreciable quantities of single
domain (diameters 15 to 30 nm) and smaller iron droplets were produced. By
contrast, above 950°C almost all the iron was larger than 30nm. Size deter-
minations of these larger grains showed a distribution peaked at around 43nm.

Fallick et al. (13, 9) measured magnetic susceptibility χ and stable
isothermal remanent magnetisation IRM on the 75-106μm soil size fraction of
thirteen Apollo 16 soils and demonstrated statistically significant linear
correlation of χ and IRM for each soil, although the gradient and intercept of
the regression line varied amongst soils. They proved, in addition, that
this is not consistent with a pure inverse square distribution of iron
droplet sizes on the conventional (7, 8) magnetic theory, and outlined a
possible resolution of the dilemma by permitting small deviations from inverse
square functionality.

There is a substantial and established literature on the statistics of
small particles (e.g. 14). Granqvist and Buhrmann (15, 16) have investigated
the size distribution of ultrafine metal particles both experimentally and
Theoretically, for a variety of mechanisms of formation of small droplets, they showed that the logarithm of the particle diameters had a Gaussian distribution. This empirical result was buttressed by a theoretical analysis of the statistics of growth, which accounted satisfactorily for the observations. Large particles with well-defined crystal habit, however, did not exhibit lognormal behaviour, presumably because factors other than liquid-like coalescence become important in particle growth. We have now applied these ideas to the iron droplets in lunar soil fines. Figure 1 shows a log-probability plot for the droplet size determinations of soil 10084 (11). It is apparent that the data fit reasonably a line, with an overabundance of small particles (diameter < 8 nm). A straight line on a log-probability plot is usually taken as prima facie evidence of a lognormal distribution (e.g. 17). Granqvist and Buhrman (15) frequently observed an excess amount of small particles, and in a variety of materials, so the deviation from linearity in Figure 1 for small particles is not exceptional, rather it is a common feature of ultrafine distributions. By contrast, the data of Pearce et al. (12) on soil analogues do not show a linear relationship on a log-probability plot: this is likely a consequence of growth beyond the size threshold where coalescence is predominant. The distribution parameters $\sigma$ (geometric standard deviation) and $\mu$ (mean diameter) evaluated from Figure 1 were 1.40 and 8.9 respectively. For coalescing islands in discontinuous films, Granqvist and Buhrman found $1.36 < \sigma < 1.60$ consistently. We conclude, therefore, that the very fine iron droplets in lunar soil 10084 have a directly measured size distribution which is consistent with a truncated lognormal distribution but it is not yet possible to decide from magnetic measurements between this and the approximate inverse square volume distribution referred to earlier.

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FIGURE: Log-probability plot of mean particle diameter $X$ versus number percentage of particles smaller than $X$ for the very fine iron droplets measured from transmission electron micrographs of soil 10084 (11).

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