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Volatile-Rich Lunar Soil: Evidence of Possible Cometary Impact

Abstract. *A subsurface Apollo 16 soil, 61221, is much richer in volatile compounds than soils from any other locations or sites as shown by thermal analysis–gas release measurements. A weight loss of 0.03 percent during the interval 175° to 350°C was associated with the release of water, carbon dioxide, methane, hydrogen cyanide, hydrogen, and minor amounts of hydrocarbons and other species. These volatile components may have been brought to this site by a comet, which may have formed North Ray crater.*

One of the fundamental characteristics of the moon is its low abundance of the volatile elements hydrogen, carbon, nitrogen, and oxygen and their associated low molecular weight compounds and mineral phases (*1*). Anders (*2*) noted that the low abundances of other volatiles, such as lead, bismuth, and thallium, are probably associated with the accretional history of the moon. The only exceptions to the consistent depletion of volatile elements and compounds in samples from all lunar sites are the enrichments in the soils and selected breccias of elements derived from the solar wind (such as hydrogen, helium, carbon, and nitrogen) (*1, 3*). We now report the first occurrence of a volatile-rich subsurface sample derived from North Ray crater (sample 61221). The volatiles in this sample are believed not to be of solar wind origin, but may have arisen from the cometary impact that created North Ray crater.

Apollo 16 soil sample 61221 contains an unusually large amount of low-temperature volatile components. The sample, collected at station 1 near Plum crater by astronaut Duke, was taken at a depth of about 30 to 35 cm beneath the surface (*4, 5*). It is unusually white in color, much coarser in grain size (median size ranging from 250 to 300 µm compared to 76 to 122 µm for other Apollo 16 soils, exclusive of those from North Ray crater), and distinctly different petrographically from the normal medium-gray surface soil which covered the white soil (*6*). The sample contains an exceptionally small amount of glass agglutinates (8 percent), in contrast to the darker-colored soil 61241 (greater than 50 percent agglutinates) which covers the subsurface sample [table 3 in (*6*)]. McKay and coworkers (*7*) have shown that the percentage of glass agglutinates in a lunar soil provides a relative index of maturity or residence time on the lunar surface; we conclude that the darker upper soil 61241 is a more mature soil than 61221 (*6*). The grain sizes and abundance of agglutinates in 61221 are similar to those of Apollo 16 soils collected at North Ray crater and station 13 (on the ejecta blanket of North Ray crater) (*5, 6*). Further evidence of the similarity of soil 61221 to North Ray crater material is found in the major and minor element chemistry of samples from these two sites. Table 1 gives the composition of these samples as reported previously (*6*). Soils from the North Ray crater site and sample 61221 have low nickel contents (109 to 176 parts per million). The low nickel content, low abundance of agglutinates, large grain size, and major and minor element chemistry of sample 61221 point to a very immature lunar soil, which is probably associated with the North Ray crater event. In contrast, a comparison of the composition of the surface soil (61241) with those of subsurface sample 61221 and of samples collected from stations which are believed to lie on ray material from South Ray crater indicates that the upper material (61241) is probably derived from South Ray crater (Table 1). The relatively nickel-rich soils (316 to 363 ppm of nickel) from the ejecta blanket and rays of South Ray crater (including sample 61241) indicate that it could be the result of the impact of an iron-rich meteorite. Clearly, the mode of origin of North Ray crater was different from that of South Ray crater.

The total carbon analysis of sample 61221 gave 100 ± 10 ppm of carbon, whereas the darker mature soil 61241 overlying it contained 110 ± 10 ppm of carbon (*6*). Moore *et al.* (*3*) have postulated that the majority of the carbon found in lunar soils is derived from the solar wind. In this case, the high carbon content of soil 61221 is inconsistent with its immaturity or apparent lack of exposure to the solar wind. The anorthosite-rich rocks at the Apollo 16 site are extremely low in their carbon contents. Most of the rocks contain less than 6 ppm of total carbon (*6*). Sample 61221, although composed of mostly anorthositic components, typically with less than 6 ppm of carbon, is unusually rich in carbon. Thus, some special origin or genesis is required for this sample to explain its high carbon abundance.

Thermal analysis–gas release studies of 61221 provide further evidence of the unusual nature of this sample. The analyses were carried out by using a computer-controlled interfaced thermal analyzer–quadrupole mass spectrometer

Table 1. X-ray fluorescence analysis of Apollo 16 soils (*6*). Sample 61220,2 is the bulk sample from which 61221,11 was taken. Two samples were taken from North Ray crater and four samples from South Ray crater ejecta.

Component	61220,2 Station 1 subsurface white soil	Composition ranges of soil		61241,2 Station 1 surface soil
		North Ray crater	Stations 4, 5, 6 (South Ray crater ejecta)	
SiO_2 (%)	45.35	44.95– 45.28	44.88– 45.38	45.32
TiO_2 (%)	0.49	0.41– 0.42	0.55– 0.67	0.57
Al_2O_3 (%)	28.25	28.93– 29.01	26.22– 27.60	27.15
FeO (%)	4.55	4.09– 4.66	5.03– 6.08	5.33
MnO (%)	0.06	0.06	0.06– 0.08	0.07
MgO (%)	5.02	4.20– 4.75	5.35– 6.39	5.75
CaO (%)	16.21	16.40– 16.54	15.28– 15.81	15.69
Na_2O (%)	0.42	0.42– 0.44	0.38– 0.41	0.55
K_2O (%)	0.09	0.06– 0.07	0.10– 0.13	0.10
P_2O_5 (%)	0.10	0.06– 0.13	0.13– 0.15	0.13
S (%)	0.06	0.03– 0.04	0.07– 0.09	0.07
Sum (%)	100.6	100.4 –100.5	99.9 –100.6	100.7
		Trace elements		
Sr (ppm)	182	180–194	167–173	175
Ni (ppm)	109	111–176	316–362	320
Cr (ppm)	590	520–540	710–830	720
C (ppm)	100			110

system (*8*). Samples were heated at 6°C per minute from room temperature to 1000°C under a vacuum of 10^{-6} torr. The sample's weight loss, along with released gaseous species, abundances, temperature ranges, and sequences of release, were determined simultaneously during the heating cycle. The sensitivity of the analytical balance was ± 0.01 mg; hence, extremely small weight-loss changes could be observed. Between 175° and 350°C, sample 61221 lost 0.03 percent by weight (approximately 300 ppm of volatiles). Figure 1 shows the weight-loss curve and gas release pattern. All lunar samples analyzed previously (approximately 30 from Apollo 11 through Apollo 16) show no measurable weight loss at temperatures below 800°C (*8*). The gas release profile of sample 61221 shows that the volatile components lost between 175° and 350°C include H_2O, H_2, CO_2, HCN, and CH_4. Minor amounts of CO, N_2, and C_2H_6; hydrocarbon fragments of masses 39, 41, and 43; and possibly other volatile species were also present during this weight-loss step. A semiquantitative analysis showed the following relative concentrations of gases released during the weight-loss step (percent by weight): H_2O (40–50), CO_2 (15–20), H_2 (5–10), HCN (5–10), CH_4 (5–10), CO or N_2 or both (2–5), and hydrocarbons (1–5). The volatiles released in the interval 175° to 350°C are distinctly different in their release profiles from terrestrially adsorbed species and gases derived from the solar wind (*8*). The abundance of hydrogen derived from the solar wind (H_2 released between 300° and 700°C) (Fig. 1) is much lower for soil 61221 than the amount of H_2 found in more mature lunar soils (*8*). This is further evidence of the short surface residence time of soil sample 61221. The quantity of CO_2 released in the weight-loss region is considerably greater than for any previously analyzed lunar sample which we have seen. Hayes (*9*) noted that the normal CO/CO_2 ratio for mature lunar soils is approximately 6 to 8, whereas sample 61221 has a ratio of 2 to 3. The lower ratio suggests that 61221 was subjected to a more oxidizing environment than were previously examined lunar samples, except possibly the Apollo 16 rocks which contain the goethite (*6*).

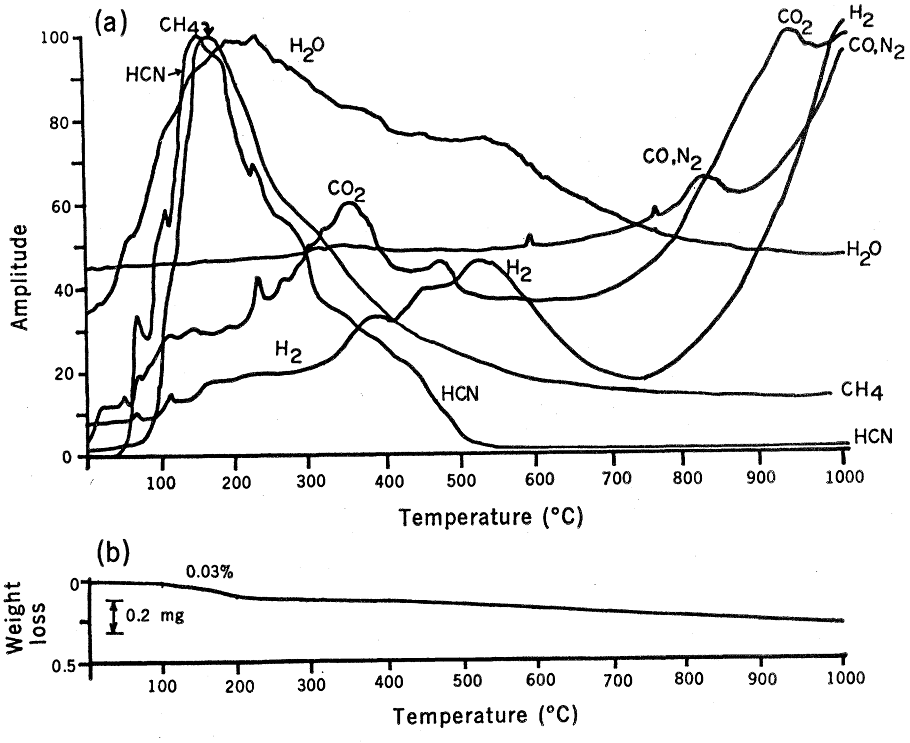

Fig. 1. (a) Gas release pattern and (b) weight-loss curve for Apollo 16 subsurface soil 61221,11. The sample, which weighed 320 mg, was heated at 6°C per minute to 1000°C; the total weight loss was 0.07 percent. The patterns of gas release have been plotted so that each gas is normalized to 100 percent amplitude in its region of greatest abundance.

The low-temperature profiles for release of water and hydrogen from soil 61221 (Fig. 1) are unique for lunar samples. Determinations of the H/D ratio of these gases along with the $^{12}C/^{13}C$ ratio of the CO_2 of the low-temperature volatiles will be important in establishing whether these components are of terrestrial or extraterrestrial origin.

The precise source of the volatile components in 61221 is presently unknown. Contamination of the sample during collection, return, and subsequent processing and handling seems unlikely because of the absence of loosely adsorbed contaminants (H_2O, N_2, and CO_2 released below 150°C) and the fact that the sample was returned to Earth in an Apollo Lunar Sample Return Container (ALSRC). The low-temperature volatiles are not typical of those associated with carbonaceous chondrite type materials (*8*). Sulfur-containing species (SO_2, H_2S, CS_2) are generally released from carbonaceous chondrite material around 400° to 600°C. Sample 61221 did not evolve any sulfur-containing gases until temperatures above 900°C, and these high-temperature sulfur gases are reaction products of sulfur-bearing phases found in the soils with the silicate phases (8).

If the soil 61221 is associated with North Ray crater, as suggested by morphological and chemical characteristics, we suggest that the volatile material may have been brought to this site by the object that formed North Ray crater. Whipple (10) and Wurm (11) noted that the neutral molecules CN, C_2, C_3, NH, CH, OH, and NH_2, along with the ionized molecules CO^+, N_2^+, CH^+, CO_2^+, and OH^+, are characteristic components of comets. The possible parent compounds (H_2O, CO_2, HCN, H_2, CO, CH_4, N_2) of all these cometary species have been identified in lunar soil 61221. The large abundance of HCN in soil 61221, as compared to other lunar soils, is particularly strong evidence for this hypothesis. Hydrogen cyanide and hydrocarbon fragments have been previously identified in lunar soils and as exhaust products of the lunar module (LM) (12), but their abundance and temperature release profiles are distinctly different from the pattern observed for sample 61221. The subsurface location of sample 61221 further reduces the possibility of LM exhaust contamination. Kopal (13) points out that the total amount of gas which can be acquired by the moon in a catastrophic encounter with a comet is far from negligible. Although the exact composition of the gases associated with a cold cometary nucleus is not known at the present time, those gases identified in the spectra of cometary tails provide us with evidence of possible constituents that might be derived from a comet during impact.

If North Ray crater was formed by a cometary impact, it is possible that portions of the volatiles in the comet were retained in ray material thrown out as a result of the impact. Had the impact occurred during the cold lunar night the retention of volatiles would have been even more efficient. If the Apollo 15 heat flow measurements can be extrapolated to the Apollo 16 site (14), that part of the crater ray at a depth of 30 to 35 cm would have had a mean temperature of approximately 0°C after it cooled. Further burial would result from the base surge deposits emanating from younger craters, such as South Ray crater and secondary craters in the area immediately surrounding Plum crater. The probability of the retention of gases and volatiles from the comet after impact is quite low, but rapid burial might allow a small portion of them to be preserved. The presence of HCN, the low-temperature release of CH_4, and the unique weight-loss profile of sample 61221 suggest that it may have formed in the manner outlined. Studies of the abundances of such volatile elements as bismuth, lead, and thallium in sample 61221 may further test the proposed unique origin of this volatile-rich lunar soil.

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Breccias from the Lunar Highlands: Preliminary Petrographic Report on Apollo 16 Samples 60017 and 63335

Abstract. *Lunar samples 60017,4 and 63335,14 are composed of microbreccias and devitrified glass. These components are predominantly anorthositic, with the exception of a cryptocrystalline clast found in the microbreccia portion of 63335,14 which contains 2.7 percent potassium oxide and 66.7 percent silicon dioxide. The samples have been subjected to extreme shock and thermal metamorphism. The parent materials of the microbreccias include both a coarse-grained anorthosite and a fine-grained subophitic anorthositic gabbro.*

Breccia 63335 was collected from Shadow Rock, a 5-m boulder at station 13 on the Cayley Plains of the lunar highlands. The collection site of 60017 is known with less certainty, although it too was probably collected from Shadow Rock (1). Thin sections 60017,4 and 63335,14 (shown in Fig. 1, a and b) were studied by using the petrographic microscope and the electron microprobe. Although no complete mineral analyses are presented in this paper, they are available from the authors on request.

60017. Sample 60017,4 consists of two distinct lithologies. One corner of the section (Fig. 1a) consists of a light gray devitrified anorthositic glass, while the rest of the section consists of a darker gray microbreccia. It is impossible to determine from this particular thin section whether either of these lithologies is incorporated within the other.

The devitrified anorthositic glass contains variolitic plagioclase with 93 to 95 mole percent anorthite (An_{93-95}), which decreases in grain size from the outer edge of the section inward toward the contact with the microbreccia. In addition, the glass contains interstitial olivine with 68 mole percent forsterite (Fo_{68}), ilmenite, and metallic iron.

The microbreccia is composed primarily of well-rounded anorthositic gabbro clasts, mosaically recrystallized