

# The Exposure History of the Apollo 16 Site: An Assessment Based on Methane and Hydrolysable Carbon

C. T. Pillinger, G. Eglinton, A. P. Gowar, A. J. T. Jull,  
and J. R Maxwell

*Organic Geochemistry Unit, School of Chemistry  
University of Bristol  
Bristol, United Kingdom*

Nineteen soils from eight stations at the Apollo 16 landing site have been analyzed for methane and hydrolysable carbon. These results, in conjunction with published data from photogeology, bulk chemistry, rare gases, primordial and cosmogenic radionuclides, and agglutinate abundances have been interpreted in terms of differing contributions from three components—North and South Ray Crater ejecta and Cayley Plains material.

Analysis of the gases released from lunar fines and soil breccias by DCI dissolution has revealed that trapped hydrocarbons (particularly CH<sub>4</sub>) and hydrolysable carbon (indicated by the evolution of deuterocarbons, predominantly CD<sub>4</sub>) are ubiquitous components of these samples (refs. 1 and 2). The location of methane and hydrolysable carbon at particle surfaces (ref. 2), a number of correlation studies (refs. 1, 2, and 3), and the simulation of lunar conditions (ref. 4) suggest that the distribution of both types of carbon is controlled by extralunar processes. More specific location studies (refs. 5 and 6) have identified the particle types containing the highest concentrations of methane and hydrolysable carbon as very fine grains (0.5 to 10 μm in diameter) and glassy agglutinates and microbreccias, both the latter being themselves aggregates of finer grains. These observations are consistent with the finest grains' being the major reaction site for the initial synthesis of lunar carbon compounds from solar-wind-implanted species. The energy for further reaction to take place is presumably provided by micrometeorite impact, which is also responsible for commi-

nuting, aggregating, and reworking the soil. Recently, it has been shown (refs. 7 and 8) that the formation of the hydrolysable carbon giving rise to CD<sub>4</sub> is also dependent on the availability of Fe<sup>II</sup> in silicate for reduction to Fe<sup>0</sup>. The major hydrolysable carbon species is in fact carbon in solid solution in iron (ref. 9) and not iron carbide as previously anticipated (refs. 1 and 10). The reduction process is also thought to be exposure-induced and to involve a reducing agent such as implanted solar wind hydrogen (refs. 7, 8, 11, 12, and 13).

All the evidence now available suggests that methane and hydrolysable carbon are formed as a result of exposure of lunar samples at the very surface of the regolith. As a corollary, the abundance of these carbon species should be important indicators of exposure and reworking, provided the effects of bulk chemistry are taken into consideration. Indeed, carbon chemistry has already contributed to the understanding of the history of the lunar regolith as a result of the analysis of the Apollo 12 double core, the Apollo 14 surface samples, and the Apollo 15 and 16 drill stems (ref. 14). In the case of the

double core, methane and hydrolysable carbon measurements have indicated that although layer-by-layer deposition may be the predominant mechanism of regolith formation, small-scale mixing across stratigraphic boundaries can be important (ref. 2). For the Apollo 14 samples, both natural lunar and accidental (astronaut-induced) mixings of soils have been inferred from the amounts of  $\text{CH}_4$  and  $\text{CD}_4$  released by acid dissolution (refs. 2 and 15).

The purpose of the present paper is to demonstrate that carbon chemistry, in conjunction with other exposure measurements and geochemical data, may assist in recognizing the major events at the Apollo 16 site.

## Experimental Studies

All acid dissolution studies to measure  $\text{CH}_4$  and  $\text{CD}_4$  were performed by use of DCl

(38 percent in  $\text{D}_2\text{O}$ ) on bulk soils samples (10–20 mg) in the usual way (refs. 2 and 6). To check that systematic errors were unaltered, a sample of Apollo 11 fines 10086 was analyzed and the  $\text{CH}_4$  and  $\text{CD}_4$  concentrations released shown to be within  $\pm 10$  percent of those from samples previously measured.

All the samples analyzed are soils (table 1). The majority (those having 1 as the final integer of their catalog number) have been sieved at the curatorial facility to remove particles greater than 1 mm in diameter. Samples having a catalog number which ends in 0 are unsieved. For the purposes of comparison in this discussion, sieved and unsieved samples are assumed to be identical. A map showing the essential features of the Apollo 16 landing site, together with the location of the various sampling stations, is shown as figure 1.

Table 1.— $\text{CD}_4$  and  $\text{CH}_4$  Released by DCl Dissolution of Apollo 16 Bulk Soils

| Latitude                     | Sample Number | Station | $\text{CD}_4$ ( $\mu\text{g/g}$ as C) | $\text{CH}_4$ ( $\mu\text{g/g}$ as C) | $\text{CD}_4/\text{CH}_4$ |
|------------------------------|---------------|---------|---------------------------------------|---------------------------------------|---------------------------|
| North<br>of<br>LM            | 63321         | 13      | 3.1                                   | 1.1                                   | 2.9                       |
|                              | 63340         | 13      | 4.2                                   | 1.6                                   | 2.6                       |
|                              | 63500         | 13      | 5.7                                   | 1.1                                   | 5.1                       |
|                              | 67701         | 11      | 3.4                                   | 1.6                                   | 2.2                       |
|                              | 67941         | 11      | 2.4                                   | 0.7                                   | 3.3                       |
|                              | 67960         | 11      | 2.2                                   | 1.7                                   | 1.3                       |
| Same<br>Latitude<br>as<br>LM | 60501         | 10      | 5.4                                   | 1.6                                   | 3.4                       |
|                              | 61141         | 1       | 7.2                                   | 3.2                                   | 2.2                       |
|                              | 61161         | 1       | 7.4                                   | 3.2                                   | 2.3                       |
|                              | 61501         | 1       | 4.6                                   | 2.3                                   | 2.0                       |
| South<br>of<br>LM            | 64421         | 4       | 8.8                                   | 3.2                                   | 2.8                       |
|                              | 64501         | 4       | 3.6                                   | 2.2                                   | 1.6                       |
|                              | 66040         | 6       | 10.6                                  | 3.5                                   | 3.0                       |
|                              | 66081         | 6       | 10.8                                  | 4.1                                   | 2.7                       |
|                              | 68121         | 8       | 12.2                                  | 4.1                                   | 2.9                       |
|                              | 68501         | 8       | 5.7                                   | 1.8                                   | 3.1                       |
|                              | 69921         | 9       | 9.5                                   | 2.4                                   | 4.0                       |
|                              | 69941         | 9       | 9.7                                   | 2.7                                   | 3.7                       |
|                              | 69961         | 9       | 15.7                                  | 5.4                                   | 2.9                       |

Note on Errors: Absolute amounts of  $\text{CD}_4$  and  $\text{CH}_4$  are measured  $\pm 10$  percent by gas chromatography.

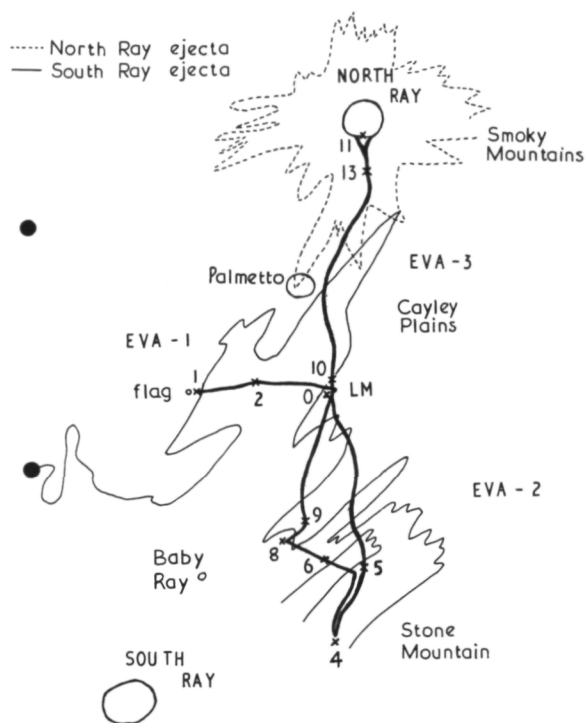


Figure 1.—Map of the Apollo 16 landing site: sampling stations are indicated by number. The extent of the North and South Ray Crater ejecta blankets is outlined, as determined by photogeology (refs. 16 and 17).

## Results

The amounts of  $\text{CH}_4$  and  $\text{CD}_4$  released by  $\text{DCl}$  dissolution are given in table 1. We have previously reported (refs. 7 and 8) that the concentrations of hydrolysable carbon as indicated by  $\text{CD}_4$  in Apollo 16 lunar fines are decreased in comparison with samples from other missions having similar exposure (estimated from the abundance of solar-wind-implanted  $^{36}\text{Ar}$ ). Thus, we suggested that synthesis of hydrolysable carbon was dependent not only on exposure of the samples but also on the availability of  $\text{Fe}^{\text{II}}$  for reduction to  $\text{Fe}^0$ . At present, no definite relationship between  $\text{CH}_4$  and  $\text{Fe}^{\text{II}}$  has been observed, although the quantities of  $\text{CH}_4$  released from Apollo 16 samples also appear to be reduced compared with amounts in previous missions (ref. 8). Such differences may be due to in-

creased diffusion losses from minerals low in  $\text{Fe}^{\text{II}}$  rather than the lessened extent of a hypothetical synthetic process for  $\text{CH}_4$  involving either  $\text{Fe}^{\text{II}}$  or  $\text{Fe}^0$  (ref. 18).

In addition to the differences observed between the  $\text{CH}_4$  and hydrolysable carbon contents of Apollo 16 soils and those of samples from other sites, considerable differences are apparent between samples collected at various stations of the Apollo 16 site. Samples from stations south of the Lunar Module (LM) (64421, 66081, 68121, 69921, 69941, and 69961), with the exception of 68501 and 64501, release more  $\text{CD}_4$  and  $\text{CH}_4$  than samples from north of the LM (63321, 63340, 63500, 67701, 67941, and 67960). Soils from approximately the same latitude as the LM (60501, 61141, 61161, and 61501) release intermediate quantities. Although bulk chemistry varies across the site (for example, iron as  $\text{FeO}$  increases from 4.0 in the north to 6.1 percent in the south (see, among others, refs. 19–22)), the differences involved are insufficient to account for the large variations observed in  $\text{CH}_4$  and hydrolysable carbon. The small increase in the amount of  $\text{Fe}^{\text{II}}$  available for reduction to  $\text{Fe}^0$  south of the LM could play only a minor role in accounting for the increased quantities of hydrolysable carbon found in samples from this region. The major differences in  $\text{CH}_4$  and hydrolysable carbon content must reflect the exposure history of the samples.

## Discussion

Gross differences between samples from opposite ends of the Apollo 16 landing site have previously been reported for a number of other parameters. Kirsten et al. (ref. 23) have suggested that the concentrations of trapped solar rare gases in soils increase from north to south. Similarly, samples collected at the rim of North Ray Crater have larger graphic mean grain sizes (ref. 24) and a smaller proportion of agglutinates (ref. 25) compared with those from south of the LM.

Photogeologic sequencing suggests that North Ray Crater was formed at an earlier stage of the Moon's history than South Ray

Crater (ref. 16). The exposure ages for rocks thought to be North and South Ray Crater ejecta have been estimated from track and rare gas measurements as  $46\text{--}50 \times 10^6$  years and  $2 \times 10^6$  years, respectively (refs. 26 and 27). The  $^{21}\text{Ne}$  exposure ages for soils suggest an age of  $50\text{--}60 \times 10^6$  years (refs. 23 and 28) for North Ray, which is in good agreement with the rock age and photogeologic sequencing. The high ages ( $> 200 \times 10^6$  years) measured for almost all soils of the LM (refs. 23 and 28) suggest that these materials were not formed from South Ray Crater ejecta. McKay and Heiken (ref. 25) have suggested that the apparent discrepancy may be explained if soils south of the LM are pre-existing regolith onto which blocks and fragments from South Ray Crater have been scattered. This argument is strongly supported by carbon chemistry data, and a station-by-station examination of the soils returned by the Apollo 16 mission leads us to conclude that no soil solely from South Ray Crater has been sampled. However, both North Ray Crater soil and a mature soil (referred to as Cayley Plains soil) can be recognized. The  $\text{CH}_4$  and hydrolysable carbon data for the majority of samples analyzed may be explained in terms of mixtures of Cayley Plains material with either North or South Ray ejecta (table 2). Wherever possible, we have attempted to verify the assignments made by reference to other appropriate data such as bulk chemistry, primordial and cosmogenic radionuclides, rare gases, and the proportion of glassy agglutinates (table 2).

### NORTH RAY CRATER SOIL

Soils from Station 11 at the very edge of North Ray Crater must have derived from the ejecta of this crater. They are very immature and consist mainly of freshly ejected material (i.e., low content of glassy agglutinates (ref. 25)). Therefore, the amounts of  $\text{CH}_4$  and hydrolysable carbon now observed in samples 67701, 67941, and 67960 are presumably due to the exposure of these soils since

the North Ray Crater event. The regolith at Station 11 appeared to be very thin (ref. 16); during an exposure of  $46\text{--}60 \times 10^6$  years, it should have been very well gardened and thus spent a considerable time exposed to the solar wind. However, methane has only reached a maximum of  $1.7\mu\text{g/g}$  (67960) and hydrolysable carbon only  $3.4\mu\text{g/g}$  (67701), showing that the accumulation of both species is slow. For the purpose of later discussion, sample 67701 is considered typical of North Ray Crater soil.

### CAYLEY PLAINS SOIL

Photogeology shows that Station 9 is in an area of low albedo (ref. 16). This location should be characteristic of Cayley Plains material unaffected by the recent addition of immature ejecta from either North or South Ray Craters.

The  $\text{CH}_4$  ( $2.4\mu\text{g/g}$ ) and  $\text{CD}_4$  ( $9.5\mu\text{g/g}$ ) released from the surface skim (69921) collected at Station 9 suggests a well-exposed mature regolith consistent with the high  $^{21}\text{Ne}$  exposure age of  $240 \times 10^6$  years (ref. 28).

For the purposes of later discussion sample 69921 is considered typical of Cayley Plains soil.

Two other soil samples were collected from Station 9. A sample (69961) from beneath a boulder has even higher quantities of both methane and hydrolysable carbon than does 69921 (table 1). Sample 69941, which was scooped from immediately below 69921, is intermediate both in absolute amounts of  $\text{CH}_4$  and hydrolysable carbon and in  $\text{CD}_4/\text{CH}_4$  ratio. Possibly during collection of 69941, the scoop may have passed through the highly exposed layer represented by 69921, to collect a small amount of the even more highly exposed layer represented by 69961. On this basis, the latter layer would need to extend horizontally beneath Station 9 for at least a meter.

All three soils (69921, 69941, and 69961) have the same major element chemistry (ref. 22) and primordial radionuclide content

Table 2.—Proposed Origins of Soils at the Apollo 16 Landing Site

| Sample Number | Station | Proposed Origin Based on Carbon Chemistry <sup>(1)</sup> |                  |               | Other Data Used for Corroboration <sup>(2)</sup> |   |   |                           |  |                               |
|---------------|---------|--|------------------|---------------|--|---|---|---------------------------|--|-------------------------------|
|               |         | North Ray Crater   | South Ray Crater | Cayley Plains | Bulk <sup>(3)</sup> Chemistry                    | Primordial <sup>(4)</sup> Radionuclides | Cosmogenic <sup>(5)</sup> Radionuclides | Rare <sup>(6)</sup> Gases | Proportion <sup>(7)</sup> of Glassy Agglutinates | Photo- <sup>(8)</sup> geology |
| 60501         | 10      |  | X (1)            | X (1)         | +  | +                                       |   |                           | +  | -                             |
| 61141         | 1       | X (1)  |                  | X (2)         | +  | +                                       | +                                       |                           |  | -                             |
| 61161         | 1       | X (1)  |                  | X (2)         | +  | +                                       | +                                       |                           |  | -                             |
| 61501         | 1       | X  |                  | X             | +  | +                                       | +                                       |                           |  | -                             |
| 63321         | 13      | X (2)  |                  | X (1)         | +  |   |   | +                         |  | +                             |
| 63340         | 13      | X (2)  |                  | X (1)         | +  |   |   | +                         |  | +                             |
| 63500         | 13      | X (2)  |                  | X (1)         | +  |   |   | +                         |  | +                             |
| 64421         | 4       |  | (see text)       |               | +  |   |   | +                         | +  | (not applicable)              |
| 64501         | 4       |  | X                |               | +  |   |   | -                         | -  | +                             |
| 66040         | 6       |  |                  | X             | +  |   |   |                           | +  | -                             |
| 66081         | 6       |  |                  | X             | +  |   |   |                           | +  | -                             |
| 67701         | 11      | X  |                  |               | +  | +                                       | +                                       | +                         | +  | +                             |
| 67941         | 11      | X  |                  |               |  |   |   |                           | +  | +                             |
| 67960         | 11      | X  |                  |               |  |   |   |                           |  | +                             |
| 68121         | 8       |  |                  | X             | +  | +                                       |   |                           |  | -                             |
| 68501         | 8       |  | X (1)            | X (1)         | +  | +                                       | +                                       |                           |  | +                             |
| 69921         | 9       |  |                  | X             | +  | +                                       |   | +                         |  | +                             |
| 69941         | 9       |  |                  | X             | +  | +                                       |   |                           | +  | +                             |
| 69961         | 9       |  |                  | X             | +  | +                                       |   |                           |  | +                             |

NOTES: (1) Composition of mixtures is given in parentheses; blank spaces indicate no contribution.  
 (2) Symbols: + Denotes agreement; blank spaces indicate data not available.  
 - Denotes contradiction.  
 (3) See references 19, 21, 22, and 29.  
 (4) See references 30 and 31.

(5) See references 32 and 31.  
 (6) See references 33, 23, and 28.  
 (7) See reference 25.  
 (8) See references 16 and 17.

(ref. 30). Thus, the mature layers probably derived from the same source material.

Photogeology indicates that Station 6 lies on a ray from South Ray Crater. Two samples from Station 6 have been analyzed. The first, 66081, had been collected from a patch of white, indurated material lying on top of the regolith; and the second, 66040, was typical local regolith. The amounts of  $\text{CH}_4$  and  $\text{CD}_4$  released by the two samples (table 1) suggest that they are essentially similar to each other and highly mature, like 69921. It appears, therefore, that neither sample represents South Ray Crater ejecta as suggested by photogeology and that the white patch could have arisen from a small local impact. Bulk chemistry (ref. 22) indicates that both samples have slightly more total iron than presumed Cayley Plains fines (69921), but nevertheless they probably represent part of the same formation.

#### SOILS CONTAINING NORTH RAY EJECTA AND CAYLEY PLAINS MATERIAL

From photogeology (ref. 16), Station 13 lies on the North Ray Crater ejecta blanket. However, methane and hydrolysable carbon data, supported by bulk chemistry and rare gas analyses, indicate that soils collected from this site are intermediate between North Ray crater ejecta and Cayley Plains soils, and thus soil mixing may have occurred. We have interpreted the bulk chemical data to indicate that samples 63321, 63340, and 63500 may be a 2 to 1 mixture of North Ray Crater fines (represented by 67701) and Cayley Plains material (represented by 69921). Assuming that the turnover rate for 63500 (the exposed regolith at Station 13) was similar to the turnover rate at Station 11, then calculations suggest that the quantities of  $\text{CH}_4$  and  $\text{CD}_4$  which might be released from 63500 would be  $1.6\mu\text{g/g}$  and  $5.3\mu\text{g/g}$ , respectively. These values are in good agreement with the actual experimental data ( $\text{CH}_4$ ,  $1.1\mu\text{g/g}$ ;  $\text{CD}_4$ ,  $5.7\mu\text{g/g}$ ) obtained for 63500. The  $\text{CH}_4$  and hydrolysable carbon in sample 63321, which

was from the permanently shaded area under the boulder at Station 13, would presumably not have received any further contribution from exposure if the shielding boulder was emplaced by the North Ray cratering event. Thus, it may be explained as a 2:1 mixture of North Ray soil (containing no  $\text{CH}_4$  or hydrolysable carbon) and mature Cayley Plains fines. Again, the calculated values for  $\text{CH}_4$  and  $\text{CD}_4$  ( $0.8\mu\text{g/g}$  and  $3.2\mu\text{g/g}$  respectively) are in good agreement with the measured values ( $1.1\mu\text{g/g}$  and  $3.1\mu\text{g/g}$ , respectively). Sample 63340 has also been shielded since the North Ray event. However, the slightly greater quantities of  $\text{CH}_4$  and  $\text{CD}_4$  released from this sample may be explained if this sample contains a slightly increased proportion of mature Cayley Plains material. The slightly greater amount of mature soil required would be consistent with the known sampling conditions for 63340; i.e., this sample was collected from a slightly greater depth (below 63321) and may have sampled more material from an underlying layer.

Concentrations of  $^{36}\text{Ar}$  for the Station 13 soils measured by Kirsten et al. (ref. 23) and Eberhardt et al. (ref. 33), are also consistent with an approximately 2:1 mixture of North Ray Crater ejecta and Cayley Plains material.

Comparison of the  $\text{CH}_4$  and hydrolysable carbon concentrations of 63500, the local exposed regolith, and the shaded soil 63321 shows no evidence of migration of lunar volatiles to the latter sample as a "cold trap" (refs. 34, 35, and 36). This is in agreement with the observation that shaded soils do not show the presence of excess lead in comparison with reference samples (ref. 35) and with other  $\text{CH}_4$  and hydrolysable carbon measurements of 63320 and 63340 (ref. 37).

#### SOILS DERIVED FROM SOUTH RAY CRATER EJECTA AND CAYLEY PLAINS MATERIAL

The presence of rocks of low exposure age (about  $2 \times 10^6$  yrs) (ref. 38) confirms

the interpretation of photogeologic sequencing that Station 8 at the Apollo 16 site lies on a ray of ejecta from South Ray Crater (ref. 16). However, a boulder fillet soil (68121) from this station releases quantities of  $\text{CH}_4$  and  $\text{CD}_4$  ( $4.1\mu\text{g/g}$  and  $12.2\mu\text{g/g}$ , respectively) indicative of mature fines. The fillet also has a similar major element chemistry (refs. 21 and 22) and primordial radionuclide content (ref. 30) to 69921. Therefore, like other mature soils south of the LM, 68121 may represent Cayley Plains soil. Another soil (68501) collected at Station 8 is far less mature ( $\text{CH}_4$ ,  $1.8\mu\text{g/g}$ ;  $\text{CD}_4$ ,  $5.7\mu\text{g/g}$ ) than 68121.

The differences in  $\text{CH}_4$  and hydrolysable carbon concentrations between 68121 and 68501 are explicable in terms of one of two mechanisms proposed by Hörz et al. (ref. 39) for the formation of boulder fillets. Formation by micrometeorite erosion of the adjacent boulder requires that the fillet and parent boulder should differ only with respect to exposure history; major and minor element chemistry should be basically similar. Primordial radionuclide measurements show that while the potassium contents of 68121 and the adjacent boulder (68115) are similar, the thorium and uranium contents are very different; thus Rancitelli et al., (ref. 30) have concluded that the fillet could not have resulted from boulder erosion. The alternative mechanism for fillet formation, i.e., lateral displacement of the regolith at the time of boulder deposition (ref. 39), is more consistent with the carbon chemistry data. Thus fillet 68121, located at the north west face of boulder 68115, which is presumably South Ray ejecta, appears to be mature regolith shielded by the boulder from burial by fine material traveling on a ballistic trajectory from South Ray Crater.

The lower maturity of the soil represented by 68501 may be explicable in terms of an addition of fresh South Ray soil ejecta to an area of mature unshielded soil.

The maximum quantities of  $\text{CH}_4$  and  $\text{CD}_4$  released from a well-gardened North Ray Crater soil (exposure age, 46 to  $60 \times 10^6$  years) are  $1.7\mu\text{g/g}$  and  $3.4\mu\text{g/g}$ , respectively;

therefore, during an exposure age of  $2 \times 10^6$  years, fresh South Ray crater soil which was well gardened and exposed to the solar wind, would accumulate very little  $\text{CH}_4$  and hydrolysable carbon. Assuming the same rate of production as for North Ray material, then a soil of  $2 \times 10^6$  years would release not more than  $0.07\mu\text{g/g}$   $\text{CH}_4$  and  $0.25\mu\text{g/g}$  hydrolysable carbon. Therefore, the observed  $\text{CH}_4$  and hydrolysable carbon content of 68501 could be explained if the sample was a mixture of immature South Ray Crater soil and mature Cayley Plains fines in the approximate ratio 1:1 (compare calculated  $\text{CH}_4 = 1.3\mu\text{g/g}$  and  $\text{CD}_4 = 4.9\mu\text{g/g}$ , with actual experimental results  $\text{CH}_4 = 1.7\mu\text{g/g}$  and  $\text{CD}_4 = 5.7\mu\text{g/g}$ ).

The hypothesis that 68501 is an admixture of South Ray Crater fines and Cayley Plains soil is supported by the abundance of carbon species released by pyrolysis (ref. 40) and major element chemistry. The bulk chemistry (ref. 19) of 68501 shows differences from 68121 (ref. 21) and 69921 (ref. 22); for example, the FeO and MgO are diminished while CaO and  $\text{Al}_2\text{O}_3$  are increased. This may suggest that South Ray Crater ejecta is more typical of highland material than is Cayley Plains soil.

The South Ray Crater soil observed at Station 8 may extend as far as Station 10, although photogeology suggests that the LM landed in an area of low albedo (ref. 16). A rock, 60315, with an exposure age of  $2 \times 10^6$  years (ref. 38), has been identified at this location. Methane and hydrolysable carbon measurements from sample 60501, supported by bulk chemistry (ref. 21) and primordial (ref. 30) and cosmogenic radionuclides (ref. 32) suggest that the composition of the soil at Station 10 approximates that of unshielded Station 8 material, as represented by 68501. Therefore, 60501 may be an approximately 1:1 mixture of South Ray Crater soil and Cayley Plains material. The content of highly reworked glassy agglutinates and mineral grains and metamorphic microbreccias in 60501 (ref. 6) confirms the presence of both recent and mature particles at Station 10.

Station 4 on Stone Mountain appears to be similar to Stations 8 and 10. The site has many angular blocks covering the sampling area, and may be part of the South Ray Crater ejecta blanket (ref. 16). The low quantities of  $CD_4$  from surface fines 64501 suggest the presence of immature South Ray Crater soil, and the low FeO and MgO contents (ref. 41) would support this. However,  $CH_4$  rare gas measurements (ref. 23) and agglutinate data (ref. 25) indicate that 64501 is a mature soil. Another sample (64421) analyzed from the bottom of a trench at Station 4, is mature as indicated by carbon chemistry, rare gases (ref. 23), and agglutinate content (ref. 25). This sample also has concentrations of FeO and MgO (ref. 21) much lower than does Cayley Plains soil. Clearly, Station 4 is an interesting site and requires further study by all techniques.

## STATION 1

Photogeology suggests that Station 1 is situated on a ray from South Ray Crater (ref. 16). However, this site is in a region where ejecta from both South and North Ray Craters might be found. Carbon chemistry data, considered together with bulk chemistry and primordial and cosmogenic radionuclide measurements, indicate that the ray at Station 1 is from North Ray Crater.

The  $CH_4$  and  $CD_4$  released from samples 61141, 61161, and 61501 are consistent with samples of intermediate maturity or a mixture of mature and immature fines. Assuming the mature material is Cayley Plains soil, then the immature material could be either South or North Ray Crater soil. South Ray Crater soil is presumed to be extremely immature (see above) and only a very small proportion need be added to Cayley Plains fines (i.e., less than the amount added to Cayley Plains fines to generate 68501 at Station 8) to obtain the quantities of  $CH_4$  and  $CD_4$  released from Station 1 soils. Such a small amount would not be consistent with the bulk chemistry data (ref. 29) for 61141, 61161, and 61501, all of which have lower

FeO contents than 68501 (ref. 21). North Ray Crater soil (67701), as well as being immature, has a low FeO content (ref. 21). Thus, 61141 and 61161 could represent an approximately 2:1 mixture of mature Cayley Plains material and immature North Ray soil (compare calculated  $CH_4$ ,  $2.2\mu\text{g/g}$ ; and  $CD_4$ ,  $7.5\mu\text{g/g}$  with the measured quantities of  $3.2\mu\text{g/g}$  and 7.2 to  $7.4\mu\text{g/g}$ , respectively). All three soil samples from Station 1 have uranium and  $^{26}\text{Al}$  contents (refs. 30, 31, and 32) which suggest similarities to soil 67701 rather than 68501.

## Conclusions

Several different individual measurements such as rare gas data (refs. 23 and 28), agglutinate abundances (ref. 25), and particle size distribution (ref. 24) have been used previously to discuss the exposure history of the Apollo 16 site. The  $CH_4$  and  $CD_4$  data obtained from the DCl dissolution of lunar soils could also be good indicators of relative surface exposure (at present, insufficient data are available to allow absolute determination) (ref. 2). However, it is more satisfactory to interrelate several parameters. The understanding of regolith dynamics will depend on disentangling the various source materials contributed to the regolith, at a particular site, by taking into consideration all the available information concerning the chemical and physical properties of the soil. In this paper we have used carbon chemistry in conjunction with bulk chemistry, rare gases, primordial and cosmogenic radionuclides, the proportion of glassy agglutinates, and photogeologic sequencing. Other data which would be desirable include mineralogy and petrology, particle size distribution, and total carbon and nitrogen.

At the Apollo 16 site almost all the soils analyzed can be traced to a comparatively minor number of major events. Only a small number of discrete components have been recognized, the remaining soils being attributed to mixtures of these components. Wherever possible, we have attempted to es-



establish the proportions of soils recognized as mixtures.

At Station 9, mixing may have occurred adventitiously during collection of the samples. However, at Stations 1, 8, 10, and 11, a thin surface layer of more recent ejecta would have been apparent to the astronauts (ref. 17). In these cases, immature South or North Ray Crater material may have been stirred into the surface of well-exposed Cayley Plains soil. Only the careful examination of core material from the various stations of the Apollo 16 site will be able to detect whether distinct layers have been deposited or whether mixing to a depth of a few centimeters has occurred.

The two immature materials indicated by the carbon chemistry measurements both appear to be low in Fe<sup>II</sup> (North Ray (67701) about 4.2 percent as FeO, and South Ray soil estimated as about 5.2 percent FeO from sample 68501) compared with the mature Cayley Plains (5.7 to 6.0 percent FeO). In each case, the immature samples appear to have come from impacts into more truly highland anorthosite type materials. South Ray ejecta may represent Descartes formation, and the North Ray impact may have penetrated the Cayley basin to reveal material from the Smoky Mountains.

## Acknowledgment

The authors express their thanks to the Science Research Council for the Research Grants (SGS-128 and SGS-232), and to the British Steel Corporation for a Fellowship (CTP).

## References

1. ABELL, P. I., P. H. CADOGAN, G. EGLINTON, J. R. MAXWELL, AND C. T. PILLINGER, Survey of Lunar Carbon Compounds: I. The Presence of Indigenous Gases and Hydrolysable Carbon Compounds in Apollo 11 and Apollo 12 Samples. *Proc. Second Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 2, Vol. 2, 1971, pp. 1843-1863.
2. CADOGAN, P. H., G. EGLINTON, J. N. M. FIRTH, J. R. MAXWELL, B. J. MAYS, AND C. T. PILLINGER, Survey of Lunar Carbon Compounds: II. The Carbon Chemistry of Apollo 11, 12, 14 and 15 Samples. *Proc. Third Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 3, Vol. 2, 1972, pp. 2069-2090.
3. CADOGAN, P. H., G. EGLINTON, J. R. MAXWELL, AND C. T. PILLINGER, Carbon Chemistry of the Lunar Surface. *Nature*, Vol. 231, 1971, pp. 29-31.
4. PILLINGER, C. T., P. H. CADOGAN, G. EGLINTON, J. R. MAXWELL, B. J. MAYS, W. A. GRANT, AND M. J. NOBES, Simulation Study of Lunar Carbon Chemistry. *Nature*, Vol. 235, 1972, pp. 108-109.
5. CADOGAN, P. H., G. EGLINTON, J. R. MAXWELL, AND C. T. PILLINGER, Distribution of Methane and Carbide in Apollo 11 Fines. *Nature Phys. Sci.*, Vol. 241, 1973, pp. 81-82.
6. CADOGAN, P. H., G. EGLINTON, A. P. GOWAR, A. J. T. JULL, J. R. MAXWELL, AND C. T. PILLINGER, Location of Methane and Carbide in Apollo 11 and 16 Lunar Fines. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1493-1508.
7. PILLINGER, C. T., B. D. BATTS, G. EGLINTON, A. P. GOWAR, A. J. T. JULL, AND J. R. MAXWELL, Formation of Lunar Carbide From Lunar Iron Silicates. *Nature Phys. Sci.*, Vol. 245, 1973, pp. 3-5.
8. PILLINGER, C. T., P. R. DAVIS, G. EGLINTON, A. P. GOWAR, A. J. T. JULL, J. R. MAXWELL, R. M. HOUSLEY, AND E. H. CIRLIN, *Proc. Fifth Lunar Science Conference, Geochimica et Cosmochimica Acta*, in press, 1974.
9. JULL, A. J. T., P. R. DAVIS, G. EGLINTON, L. R. GARDNER, J. R. MAXWELL, C. T. PILLINGER, G. M. BIGGAR, D. HUMPHRIES, AND B. D. BATTS, Simulation of Lunar Processes: II—Redistribution of Carbon in the Lunar Regolith During Meteorite Impact. *Lunar Science*, Vol. VI, pp. 457-459.
10. CHANG, S., J. W. SMITH, I. KAPLAN, J. LAWLESS, K. A. KVENVOLDEN, AND C. PONNAMPERUMA, Carbon Compounds in Lunar Fines From Mare Tranquillitatis: IV. Evidence for Oxides and Carbides. *Proc. Apollo 11 Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 1, Vol. 2, 1970, pp. 1857-1869.
11. CARTER, J. L., AND D. S. MCKAY, Metallic Mounds Produced by Reduction of Material of Simulated Lunar Composition and Implications on the Origins of Metallic Mounds on Lunar Glasses. *Proc. Third Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 3, Vol. 1, 1972, pp. 953-970.
12. GRANT, R. W., R. M. HOUSLEY, AND N. E. PATON, Origin and Characteristics of Excess Fe Metal

- in Lunar Glass Welded Aggregates. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 3, 1973, pp. 2737-2749.
13. HOUSLEY, R. M., R. W. GRANT, AND M. ABDEL-GAWAD, Study of Excess Fe Metal in Lunar Fines by Magnetic Separation, Mossbauer Spectroscopy and Microscopic Examination. *Proc. Third Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 3, Vol. 1, 1972, pp. 1065-1076.
  14. WSOLEK, P. C., AND A. L. BURLINGAME, Carbon Chemistry of the Apollo 15 and 16 Deep Drill Cores. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1681-1692.
  15. MAYS, B. J., Survey of Apollo 14, 15 and 16 Carbon Chemistry. M.Sc. Thesis, University of Bristol, England, 1973.
  16. AFGIT (Apollo Field Geology Investigation Team), Apollo 16 Exploration of Descartes: A Geologic Summary. *Science*, Vol. 179, 1973, pp. 62-69.
  17. ALGIT (Apollo Lunar Geology Investigation Team), Documentation and Environment of the Apollo 16 Samples: A Preliminary Report. *Astrogeology*, Vol. 51, 1973.
  18. Royal Society Luna Sample Investigation Team, *The Analysis of Various Size, Visually Selected and Density and Magnetically Separated Fractions of Luna 16-20 Samples*, 1974.
  19. BANSAL, B. M., P. W. GAST, N. J. HUBBARD, L. E. NYQUIST, J. M. RHODES, C. Y. SHIH, AND H. WEISMANN, Lunar Rock Types. *Lunar Science*, Vol. IV, 1973, pp. 48-50.
  20. BRUNFELT, A. O., K. S. HEIER, B. NILSSON, E. STEINNES, AND B. SUNDVOLL, Elemental Composition of Apollo 15 and 16 Rocks Fines and Materials. *Lunar Science*, Vol. IV, 1973, pp. 100-102.
  21. COMPSTON, W., M. J. VERNON, B. W. CHAPPELL, AND R. FREEMAN, Rb-Sr Model Ages and Chemical Composition of Nine Apollo 16 Soils. *Lunar Science*, Vol. IV, 1973, pp. 158-158b.
  22. LAUL, J. C., AND R. A. SCHMITT, Chemical Composition of Apollo 15, 16 and 17 Samples. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1349-1367.
  23. KIRSTEN, T., P. HORN, AND J. KIKO,  $Ar^{40}$ - $Ar^{39}$  Dating of Apollo 16 and Apollo 15 Rocks and Rare Gas Analysis of Apollo 16 Soils. *Lunar Science*, Vol. IV, 1973, pp. 438-440.
  24. BUTLER, J. C., G. M. GREENE, AND E. A. KING, Grain Size Frequency Distribution of Apollo 16 Fines Samples and Model Analyses of Grain Size Fractions From Apollo 15 and Apollo 16 Fines. *Lunar Science*, Vol. IV, 1973, pp. 106-108.
  25. MCKAY, D. S., AND G. H. HEIKEN, The South Ray Crater Age Paradox. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 1, 1973, pp. 41-47.
  26. BEHRMANN, C., G. CROZAZ, R. DROZD, C. HOHENBERG, C. RALSTON, R. WALKER, AND D. YUHAS, Cosmic-Ray Exposure History of North Ray and South Ray Material. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1957-1974.
  27. TURNER, G., P. H. CADOGAN, AND C. J. YONGE, Argon Selenochronology. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1889-1914.
  28. WALTON, J. R., S. LAKATOS, AND D. HEYMANN, Distribution of Inert Gases in Fines From the Cayley-Descartes Region. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 2079-2095.
  29. WÄNKE, H., H. BADENHAUSER, G. DREIBUS, H. QUIJANO-RICO, H. PALME, B. SPETTEL, AND F. TESCHKE, Multielement Analysis of Apollo 16 Samples and About the Composition of the Whole Moon. *Lunar Science*, Vol. IV, 1973, pp. 761-763.
  30. RANCITELLI, L. A., R. W. PERKINS, W. D. FELIX, AND N. A. WOGMAN, Primordial Radionuclides in Soils and Rocks From the Apollo 16 Site. *Lunar Science*, Vol. IV, 1973, pp. 615-617.
  31. WRIGLEY, R. C., Radionuclides at Descartes. *Lunar Science*, Vol. IV, 1973, pp. 799-800.
  32. RANCITELLI, L. A., R. W. PERKINS, W. D. FELIX, AND N. A. WOGMAN, Lunar Surface and Solar Process Analyses From Cosmogenic Radionuclide Measurements at the Apollo 16 Site. *Lunar Science*, Vol. IV, 1973, pp. 609-611.
  33. EBERHARDT, P., O. EUGSTER, J. GEISS, N. GRÖGLAR, AND M. MORGELI, Noble Gases in Apollo 16 Lunar Fines. *Lunar Science*, Vol. IV, 1973, pp. 209-211.
  34. SILVER, L. T., Lead Volatilization and Volatile Transfer Processes on the Moon. *Lunar Science*, Vol. III, 1972, pp. 701-703.
  35. SILVER, L. T., Uranium-Thorium-Lead Isotopic Characterization in Some Regolith Materials From the Descartes Region. *Lunar Science*, Vol. IV, 1973, pp. 672-674.
  36. REED, G. W., S. JOVANOVIC, AND L. FUCHS, Trace Element Relations Between Apollo 14 and 15 and Other Lunar Samples, and the Implications of a Moon-Wide Cl-KREEP Coherence and Pt Metal Noncoherence. *Proc. Third Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 2, Vol. 2, 1972, pp. 1989-2001.
  37. WSOLEK, P. C., R. F. JACKSON, AND A. L. BURLINGAME, Carbon Chemistry of Apollo 15

- and 16 Samples and Solar Wind Simulation Studies. *Lunar Science*, Vol. IV, 1973, pp. 801-803.
38. MORRISON, D. A., D. S. MCKAY, AND H. J. MOORE, Microcraters on Apollo 15 and 16 Rocks. *Lunar Science*, Vol. IV, 1973, pp. 540-542.
39. HÖRZ, F., W. D. CARRIES, J. W. YOUNG, C. M. DUKE, J. S. NAGLE, AND R. FRYXELL, Apollo 16 Special Samples. *Supplementary Report of the Apollo 16 Lunar Sample Information Catalog*, 1972.
40. DESMARAIS, D. J., J. M. HAYES, AND W. G. MEINSCHEIN, The Distribution in Lunar Soil of Carbon Released by Pyrolysis. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1453-1458.
41. MORRISON, G. H., R. A. NADKARNI, J. JAWORSKI, R. B. BOTTO, J. R. ROTH, AND K. K. TUNEKAN, Elemental Abundances of Apollo 16 Samples. *Lunar Science*, Vol. IV, 1973, pp. 543-545.