THE EXPOSURE HISTORY OF THE APOLLO 16 SITE. AN ASSESSMENT BASED ON METHANE AND CARBIDE MEASUREMENTS

C. T. PILLINGER, C. EGLINTON, A. P. GOWAR, A. J. T. JULL AND J. R. MAXWELL

234

A Preprint of a Manuscript from

THE PROCEEDINGS OF THE SOVIET-AMERICAN CONFERENCE ON THE COSMOCHEMISTRY OF THE MOON AND PLANETS

HELD IN MOSCOW, USSR, ON JUNE 4–8, 1974

Distributed by

THE LUNAR SCIENCE INSTITUTE
HOUSTON, TEXAS 77058

TO MAKE THE INFORMATION CONTAINED HEREIN AS WIDELY AND AS RAPIDLY AVAILABLE TO THE SCIENTIFIC COMMUNITY AS POSSIBLE. NASA EXPECTS TO PUBLISH THE ENGLISH-LANGUAGE VERSION OF THE PROCEEDINGS IN LATE 1975. THE FINAL TEXT MAY INCLUDE MINOR EDITORIAL CHANGES IN FORMAT, etc.

JOHN H. POMEROY, NASA HEADQUARTERS
TECHNICAL EDITOR

SEP 19 1974

(original)

The exposure history of the Apollo 16 site. An assessment based on methane and carbide measurements.

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 BS8 1TS, U.K.

ABSTRACT

Nineteen soils from eight stations at the Apollo 16 landing site have been analysed for methane and carbide. These results, in conjunction with published data from photogeology, bulk chemistry, rare gases, primordial and 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

INTRODUCTION

Analysis of the gases released from lunar fines and soil breccias by DCl dissolution has revealed that trapped hydrocarbons (particularly CH_4) and metal carbide (indicated by the evolution of deuterocarbons, predominantly CD_4) are ubiquitous components of these samples (Abell et al., 1971, Cadogan et al., 1972). The location of methane and carbide at particle surfaces (Cadogan et al., 1972), a number of correlation studies (Abell et al., 1971, Cadogan et al., 1971, Cadogan et al,1972) and the simulation of lunar conditions (Pillinger et al., 1972) suggest that the distribution of both types of carbon is controlled by extra-lunar processes. More specific location studies (Cadogan et al., 1973a and b) have identified the particle types containing the highest concentrations of methane and carbide as very fine grains (0.5 - 10μm 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 comminuting, aggregating and reworking the soil. Recently, it has been shown (Pillinger et al., 1973, 1974) that the formation of the carbide giving rise to CD_4 is also dependent on the availability of Fe^{II} in silicate for reduction to Fe^0. Thus, the major carbide species is presumably some form of iron carbide as previously anticipated (Chang et al., 1970, Abell et al., 1971). The reduction process is also thought to be exposure induced and to involve a reducing agent such as implanted solar wind hydrogen (Carter and McKay, 1972, Grant et al., 1973; Housley et al., 1973; Pillinger et al, 1973, 1974).

All the evidence now available suggest that methane and iron carbide 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 (Wszolek et al., 1973). In the case of the double core, methane and carbide 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 (Cadogan et al., 1972). For the Apollo 14 samples both natural lunar and accidental (astronaut-induced) mixing of soils have been inferred from the amounts of CH_4 and CD_4 released by acid dissolution (Cadogan et al., 1972; Mays, 1973).

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

EXPERIMENTAL

All acid dissolution studies to measure CH_4 and CD_4 were performed using DCl (38% in D_2O) on bulk soil samples (10 - 20 mg) in the usual way (Cadogan et al., 1972; Cadogan et al., 1973). To check that systematic errors were unaltered, a sample of Apollo 11 fines 10086 was analysed and the CH_4 and CD_4 concentrations released shown to be within $\pm$ 10% of those from samples previously measured.

All the samples analysed are soils (Table 1). The majority (those having 1 as the final interger of their catalogue number) have been sieved at the curatorial facility to remove particles greater than 1 mm in diameter. Samples having a catalogue mumber 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 Fig. 1.

RESULTS

The amounts of CH_4 and CD_4 released by DCl dissolution are given in Table 1. We have previously reported (Pillinger et al., 1973, 1974) that the concentrations of carbide, as indicated by CD_4, in Apollo 16 lunar fines are decreased compared to samples from other missions having similar exposure (estimated from the abundance of solar wind implanted ^{36}Ar). Thus, we suggested that synthesis of carbide was dependent not only on exposure of the samples but also on the availability of Fe^{II} for reduction to Fe^{o}. At present, no definite relationship between CH_4 and Fe^{II} has been observed, although the quantities of CH_4 released from Apollo 16 samples also appear to be reduced compared to previous missions (Pillinger et al., 1974). Such differences may be due to increased diffusion losses from minerals low in Fe^{II} rather than the lessened extent of a hypothetical synthetic process for CH_4 involving either Fe^{II} or Fe^{o} (Royal Society Luna Sample Investigation Team, 1974).

In addition to the differences observed between the CH_4 and carbide 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 CD_4 and CH_4 than samples from north of the LM (63321, 63340, 63500, 67701, 67941, 67960). Soils from approximately the same latitude as the LM (60501, 61141, 61161, 61501) release intermediate quantities. Although bulk chemistry varies across the site [for example, iron as FeO increases from 4.0 in the north to 6.1% in the south (see inter alia Bansal et al., 1973; Brunfelt et al., 1973; Compston et al., 1973; Laul and Schmitt, 1973)], the differences involved are insufficent to account for the large variations observed in CH_4 and carbide. The small increase in the amount of Fe^{II}

available for reduction to Fe^o south of the LM could play only a minor role in accounting for the increased quantities of carbide found in samples from this region. The major differences in CH_4 and carbide 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. (1973) 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 (Butler et al., 1973) and a smaller proportion of agglutinates (McKay and Heiken, 1973) compared to 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 (AFGIT, 1973). The exposure ages for rocks thought to be North and South Ray crater ejecta have been estimated from track and rare gas measurements as 46-50 x 10^6 years and 2 x 10^6 years respectively (Behrmann et al., 1973; Turner et al., 1973). The ^{21}Ne exposure ages for soils suggest a 50-60 x 10^6 yr age (Kirsten et al., 1973; Walton et al., 1973) for North Ray wich is in good agreement with the rock age and photogeologic sequencing. The high ages (> 200 x 10^6 yrs) measured for almost all soils south of the LM (Kirsten et al., 1973; Walton et al., 1973) suggest that these materials were not formed from south Ray crater ejecta. McKay and Heiken (1973) 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 recognised. The CH_4 and carbide data for the majority of samples analysed 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 (McKay and Heiken, 1973)). Therefore, the amounts of CH_4 and carbide 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 (AFGIT, 1973); during a 46-60 x 10^6 year exposure 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 μg/g (67960) and carbide only 3.4 μg/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 (AFGIT, 1973); 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 CH_4 (2.4 μg/g) and CD_4 (9.5 μg/g) released from the surface skim (69921) collected at Station 9 suggests a well-exposed mature regolith consistent with the high ^{21}Ne exposure age of 240 x 10^6yr (Walton et al., 1973)

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 carbide than does 69921 (Table 1). Sample 69941, which was scooped from immediately below 69921 is intermediate both in absolute amounts of CH_4 and carbide and in CD_4/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 (Laul and Schmitt, 1973) and primordial radionuclide content (Rancitelli et al., 1973). 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 analysed. 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 CH_4 and 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 (Laul and Schmitt, 1973) 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 contaning North Ray ejecta and Cayley Plains material

From photogeology (AFGIT, 1973) Station 13 lies on the North Ray Crater ejecta blanket. However, methane and carbide 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 (represeneed 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 clculations suggest that the quantities of CH_4 and CD_4 which might be released from 63500 would be 1.6 μg/g and 5.3 μg/g, respectively. These values are in good agreement with the actual experimental data (CH_4, 1.1 μg/g; CD_4, 5.7 μg/g) obtained for 63500. The CH_4 and carbide in sample 63321, which was from the permanently shaded area under the boulder at Station13, 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 CH_4 or carbide) and mature Cayley Plains fines. Again the calculated values for CH_4 and CD_4 (0.8 μg/g and 3.2 μg/g respectively) are in good agreement with the measured values (1.1 μg/g and 3.1 μg/g respectively). Sample 63340 has also been shielded since the North Ray event. However, the slightly greater quantities of CH_4 and 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; ie. this sample was collected from a slightly greater depth (below 63321) and may have sampled more material from an underlying layer.

^{36}Ar concentrations for the Station 13 soils measured by Kirsten et al., (1973) and Eberhardt et al., (1973), are also consistent with an approximately 2:1 mixture of North Ray crater ejecta and Cayley Plains material.

Comparison of the CH_4 and carbide 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" (Silver 1972, 1973; Reed et al., 1972) This is in agreement with the observation that shaded soils do not show the presence of excess lead in comparison with reference samples (Silver, 1973) and with other CH_4 and carbide measurements of 63320 and 63340 (Wszolek et al., 1973).

Soils derived from South Ray Crater ejecta and Cayley Plains material

The presence of rocks of low exposure age (ca 2 x 10^6 yrs) (Morrison, D. et al., 1973) confirms the interpretation of photogeologic sequencing that Station 8 at the Apollo 16 site lies on a ray of ejecta from South Ray crater (AFGIT, 1973). However a boulder fillet soil (68121) from this station releases quantities of CH_4 and CD_4 (4.1μg/g and 12.2μg/g respectively) indicative of mature fines. The fillet also has a similar major element chemistry (Compston et al., 1973; Laul and Schmitt, 1973) and primordial radionuclide content (Rancitelli et al., 1973) 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 (CH_4, 1.8μg/g; CD_4, 5.7μg/g) than 68121.

The differences in CH_4 and carbide concentrations between 68121 and 68501 are explicable in terms of one of two mchanisms proposed by Hörz et al., (1972) 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 whilst the potassium contents of 68121 and the adjacent boulder (68115) are similar, the thorium and uranium contents are very different; thus Rancitelli et al., (1973) have concluded that the fillet could not have resulted from boulder erosion. The alternative mechanism for fillet formation, ie. lateral displacement of the regolith at the time of boulder deposition (Hörz et al., 1972), 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 travelling 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 CH_4 and CD_4 released from a well gardened North Ray crater soil (exposure age 46 - 60 x 10^6 yrs) are 1.7μg/g and 3.4μg/g respectively; therefore, during a 2 x 10^6 exposure age fresh south Ray crater soil which was well gardened and exposed to the solar wind, would accumulate very little CH_4 and carbide. Assuming the same rate of production as for North Ray material then a 2 x 10^6 yr soil would release not more than 0.07μg/g CH_4 and 0.25μg/g. Therefore, the observed CH_4 and carbide 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 approx. ratio 1:1 (compare calculated CH_4 = 1.3μg/g and CD_4 = 4.9μg/g, with actual experimental results CH_4 = 1.7μg/g and CD_4 = 5.7μg/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 (DesMarais et al., 1973) and major element chemistry. The bulk chemistry (Bansal et al., 1973) of 68501 shows differences from 68121 (Compston et al., 1973) and 69921 (Laul and Schmitt, 1973); for example, the FeO and MgO are diminished while CaO and Al_2O_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 ar Station 10, although photogeology suggests that the LM landed in an area of low albedo (AFGIT, 1973). A rock, 60315, of exposure age 2 x 10^6 yrs (Morrison D., et al., 1973) has been identified at this location. Methane and carbide measurements from sample 60501, supported by bulk chemistry (Compston et al., 1973) primordial (Rancitelli et al., 1973a) and cosmogenic radionuclides (Rancitelli et al., 1973b) suggest that the composition of the soil at Station 10 approximates to 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 (Cadogan et al., 1973) 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 (AFGIT, 1973). 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 (Morrison G. H. et al., 1973) would support this. However, CH_4 rare gas measurements (Kirsten et al., 1973) and agglutinate data (McKay and Heiken, 1973) indicate that 64501 is a mature soil. Another sample (64421) analysed from the bottom of a trench at Station 4, is mature as indicated by carbon chemistry, rare gases (Kirsten et al., 1973) and agglutinate content (McKay and Heiken, 1973). This sample also has concentrations of FeO and MgO (Compston et al., 1973) 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 (AFGIT, 1973). 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 (Wänke et al, 1973) for 61141, 61161, 61501, all of which have lower FeO contents than 68501 (Compston et al., 1973). North Ray crater soil (67701), as well as being immature, has a low FeO content (Compston et al., 1973). 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 μg/g and CD_4, 7.5 μg/g with the measured quantities of 3.2 μg/g and 7.2 - 7.4 μg/g, respectively). All three soil samples from Station 1 have uranium and ^{26}Al contents (Rancitelli et al., 1973a and b; Wrigley et al., 1973) which suggest similarities to soil 67701 rather than 68501.

CONCLUSIONS

Several different individual measurements such as rare gas data (Walton et al.,1973; Kirsten et al., 1973) agglutinate abundances (McKay and Heiken, 1973) and particle size distibution (Butler et al., 1973) 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)(Cadogan et al., 1973). 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 infomation 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 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 analysed can be traced to a comparatively minor number of major events. Only a small number of discrete components have been recognised, the remaining soils being attributed to mixtures of these components. Wherever possible we have attempted to establish the proportions of soils recognised as mixtures.

adventitiously
At Station 9 mixing may have occurred 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 (ALGIT, 1973). 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^{II} (North Ray (67701) ca. 4.2% as FeO and South Ray soil estimated as ca. 5.2% FeO from sample 68501) compared to the mature Cayley Plains (5.7 - 6.0% 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.

Acknowledgements

We thank the Science Research Council for the Research Grants (SGS - 128 and SGS - 232) and the British Steel Corporation for a Fellowship (CTP).

REFERENCES

Abell P. I., Cadogan P. H., Eglinton G., Maxwell J. R., and Pillinger C.T., (1971) 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 Sci. Conf., Geochim Cosmochim Acta, Suppl.2. Vol 2, 1843 - 1863. M.I.T Press

AFGIT (Apollo Field Geology Investigation Team) (1973) Apollo 16 exploration of Descartes: A geologic summary. Science, 179, 62 - 69.

ALGIT (Apollo Lunar Geology Investigation Team) (1973) Documentation and environment of the Apollo 16 samples: A preliminary report, Astrogeology 51

Bansal B.M., Gast P. W., Hubbard N. J., Nyquist L. E., Rhodes J. M., Shih C.Y., and Weismann H. (1973) Lunar rock types. Lunar Science - IV, 48 - 50

Behrmann C., Crozaz G., Drozd R., Hohenberg C., Ralston C., Walker R. and Yuhas D. (1973) Cosmic-ray exposure history of North Ray and South Ray material. Proc. Fourth Lunar Sci. Conf., Geochim Cosmochim Acta., Suppl.4, Vol 2, 1957 - 1974

Brunfelt A.O., Heier K.S., Nilsson B., Steinnes E and Sundvoll B. (1973) Elemental composition of Apollo 15 and 16 rocks fines and materials. Lunar Science - IV, 100 - 102

Butler J.C., Greene G.M., and King E.A. (1973) Grain size frequency distribution of Apollo 16 fines samples and modal analyses of grain size fractions from Apollo 15 and Apollo 16 fines. Lunar Science - IV, 106 - 108

Cadogan P. H., Eglinton G., Maxwell J. R., and Pillinger C.T. (1971) Carbon Chemistry of the Lunar Surface. Nature, 231 29 - 31

Cadogan P.H., Eglinton C., Firth J.N.M., Maxwell J. R., Mays B.J. and Pillinger C.T. (1972) Survey of Lunar carbon compounds: II. The carbon chemistry of Apollo 11, 12, 14 and 15 samples. Proc. Third Lunar Sci. Conf., Geochim. Cosmochim Acta, Suppl.3, Vol 2, 2069 - 2090. M.I.T. Press

Cadogan P.H., Eglinton, G., Maxwell J.R., and Pillinger C.T. (1973a) Distribution of methane and carbide in Apollo 11 fines. Nature Phys. Sci, 241, 81 - 82

Cadogan P.H., Eglinton G., Gowar A.P., Jull A.J.T., Maxwell J.R., and Pillinger C.T. (1973b) Location of methane and carbide in Apollo 11 and 16 lunar fines. Proc.Fouth Lunar Sci. Conf., Geochim Cosmochim Acta., Suppl.4, Vol 2. 1493 - 1508, Pergamon.

Carter J.L. and McKay D.S. (1972) 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 Sci.Conf., Geochim. Cosmochim Acta, Suppl 3., Vol 1., 953 - 970 M.I.T. Press

Chang S., Smith J.W., Kaplan I., Lawless J., Kvenvolden K.A. and Ponnamperuma C. (1970) Carbon compounds in lunar fines from Mare Tranquillitatis IV. Evidence for oxides and carbides. Proc. Apollo 11 Lunar Sci.Conf., Geochim.Cosmochim. Acta, Suppl 1. Vol 2, 1857 - 1869 Pergamon

Compston W., Vernon M.J., Chappell B.W. and Freeman R (1973) Rb - Sr Model ages and chemical composition of nine Apollo 16 soils. Lunar Science IV, 158 - 158b

DesMarais D.J., Hayes J.M. and Meinschein W. G. (1973) The distribution in lunar soil of carbon released by pyrolysis. Proc. Fourth Lunar Sci. Conf. Geochim Cosmochim Acta, Suppl.4, Vol 2, 1453 - 1458, Pergamon

Eberhardt P., Eügster O., Geiss J., Gröglar N and Morgeli M (1973) Noble gases in Apollo 16 lunar fines. Lunar Science IV, 209 - 211

Grant R.W., Housley R.M. and Paton N.E. (1973) Origin and characteristics of excess Fe metal in lunar glass welded aggregates. Proc. Fourth Lunar Sci. Conf., Geochim Cosmochim Acta, Suppl.4, Vol 3, 2737 - 2749, Pergamon.

Hörz, F., Carries, W.D., Young, J.W., Duke, C.M., Nagle, J.S. and Fryxell, R. (1972) Apollo 16 Special Samples. Supplementary report of the Apollo 16 Lunar Sample Information Catalog.

Housley R.M., Grant R.W., and Abdel-Gawad M. (1972) Study of excess Fe metal in lunar fines by magnetic separation, Mossbauer spectroscopy and microscopic examination. Proc. Third Lunar Sci. Conf., Geochim Cosmochim Acta, Suppl. 3, Vol 1, 1065 - 1076 M.I.T. Press

Kirsten T., Horn P., and Kiko J. (1973) Ar^{40} - Ar^{39} dating of Apollo 16 and Apollo 15 rocks and rare gas analysis of Apollo 16 soils. Lunar Science - IV, 438 - 440

Laul J.C., and Schmitt R.A. (1973) Chemical composition of Apollo 15, 16 and 17 samples. Proc. Fourth Lunar Sci. Conf., Geochim Cosmochim Acta., Suppl. 4., Vol 2, 1349 - 1367. Pergamon

Mays B. J., Survey of Apollo 14, 15 and 16 carbon chemistry. M.Sc., Thesis, University of Bristol, England

McKay D.S., and Heiken G.H. (1973) The South Ray Crater Age paradox. Proc. Fourth Lunar Sci.Conf., Geochim Cosmochim Acta, Suppl.4, Vol 1, 41 - 47 Pergamon

Morrison D.A., McKay D.S. and Moore H.J. (1973) Microcraters on Apollo 15 and 16 rocks. Lunar Science IV, 540 - 542

Morrison G.H., Nadkarni R.A., Jaworski J., Botto R.B., Roth J.R., and Tunekian K.K. (1973) Elemental abundances of Apollo 16 samples. Lunar Science IV, 543 - 545

Pillinger C.T., Cadogan, P.H., Eglinton, G. Maxwell J.R., Mays B.J., Grant W.A. and Nobes M. J. (1972) Simulation Study of lunar carbon chemistry, Nature, 235 108 - 109

Pillinger C.T., Batts B.D., Eglinton G., Gowar A.P., Jull A.J.T. and Maxwell J.R. (1973) Formation of lunar carbide from lunar iron silicates. Nature Phys. Sci., 245, 3 - 5.

Pillinger C.T., Davis, P.R., Eglinton G., Gowar A.P., Jull A.J.T., Maxwell J.R., Housley R.M. and Cirlin E.H. (1974) Proc.Fifth Lunar Sci.Conf., Geochim.Cosmochim Acta (in press)

Rancitelli L.A., Perkins R.W., Felix W.D., and Wogman N.A. (1973a) Primordial radionuclides in soils and rocks from the Apollo 16 site. Lunar Science IV, 615 - 617.

Rancitelli L.A., Perkins R.W., Felix W.D. and Wogman N.A. (1973b) Lunar surface and solar process analyses from cosmogenic radionuclide measurements at the Apollo 16 site. Lunar Science IV, 609 - 611.

Reed G.W., Jovanovic S. and Fuchs L. (1972) Trace element relations between Apollo 14 and 15 and other lunar samples, and the implications of a moon-wide CI - KREEP coherence and Pt metal noncoherence. Proc.Third Lunar Sci.Conf., Geochim.Cosmochim.Acta, Suppl.2, Vol.2, 1989-2001. Pergamon.

Royal Society Luna Sample Investigation Team (1974) The analysis of various size, visually selected and density and magnetically separated fractions of Luna 16 - 20 samples.

Silver L.T. (1972) Lead volatilization and volatile transfer processes on the moon Lunar Science - III, 701-703.

Silver L.T. (1973) Uranium-thorium-lead isotopic characterisation in some regolith materials from the Descartes region. Lunar Science - IV 672-674.

Turner G., Cadogan P.H. and Yonge C.J. (1973) Argon selenochronology. Proc. Fourth Lunar Sci.Conf. Geochim.Cosmochim.Acta, Suppl.4, Vol.2, 1889 - 1914. Pergamon.

Walton J.R., Lakatos S. and Heymann D. (1973) Distribution of inert gases in fines from the Cayley - Descartes region. Proc.Fourth Lunar Sci. Conf. Geochim.Cosmochim.Acta, Suppl.4, Vol.2, 2079-2095. Pergamon.

Wänke H., Baddenhausen H., Dreibus G., Quijano-Rico H., Palme H., Spettel B., and Teschke F. (1973) Multielement analysis of Apollo 16 samples and about the composition of the whole moon. Lunar Science- IV, 761-763.

Wszolek P.C., Jackson R.F. and Burlingame A.L. (1973) Carbon chemistry of Apollo 15 and 16 samples and solar wind simulation studies, Lunar Science - IV, 801-803.

Wszolek P.C. and Burlingame A.L. (1973) Carbon chemistry of the Apollo 15 and 16 deep drill cores, Proc.Fourth Lunar Sci.Conf., Geochim.Cosmochim. Acta, Suppl.4, Vol.2, 1681-1692, Pergamon.

Table 1 CD_4 and CH_4 released by DCl dissolution of Apollo 16 bulk soils

Latitude	Sample No.	Station	CD_4 (μg/g as C)	CH_4 (μg/g as C)	CD_4/CH_4
North of 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 Latitude as 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 of 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

Errors

Absolute amounts of CD_4 and CH_4 are measured $\pm$ 10% by gas chromatography

Table 2 Proposed origins of soils at the Apollo 16 landing site

Sample No.	Station	Proposed Origin based on Carbon Chemistry‡			Other data used for corroboration*					
		North Ray Crater	South Ray Crater	Cayley Plains	Bulk Chemistry[(a)]	Primordial Radionuclides[(b)]	Cosmogenic Radionuclides[(c)]	Rare Gases[(d)]	Propotion of glassy agglut-inates[(e)]	Photo geology[(f)]
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		§		+			+	+	n.a.
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	+	+				+

Footnotes for Table 2

‡		Composition of mixtures given in brackets; blank spaces indicate no contribution
*	+	denotes agreement; blank spaces indicate data not available
	−	denotes contradiction
§		see text

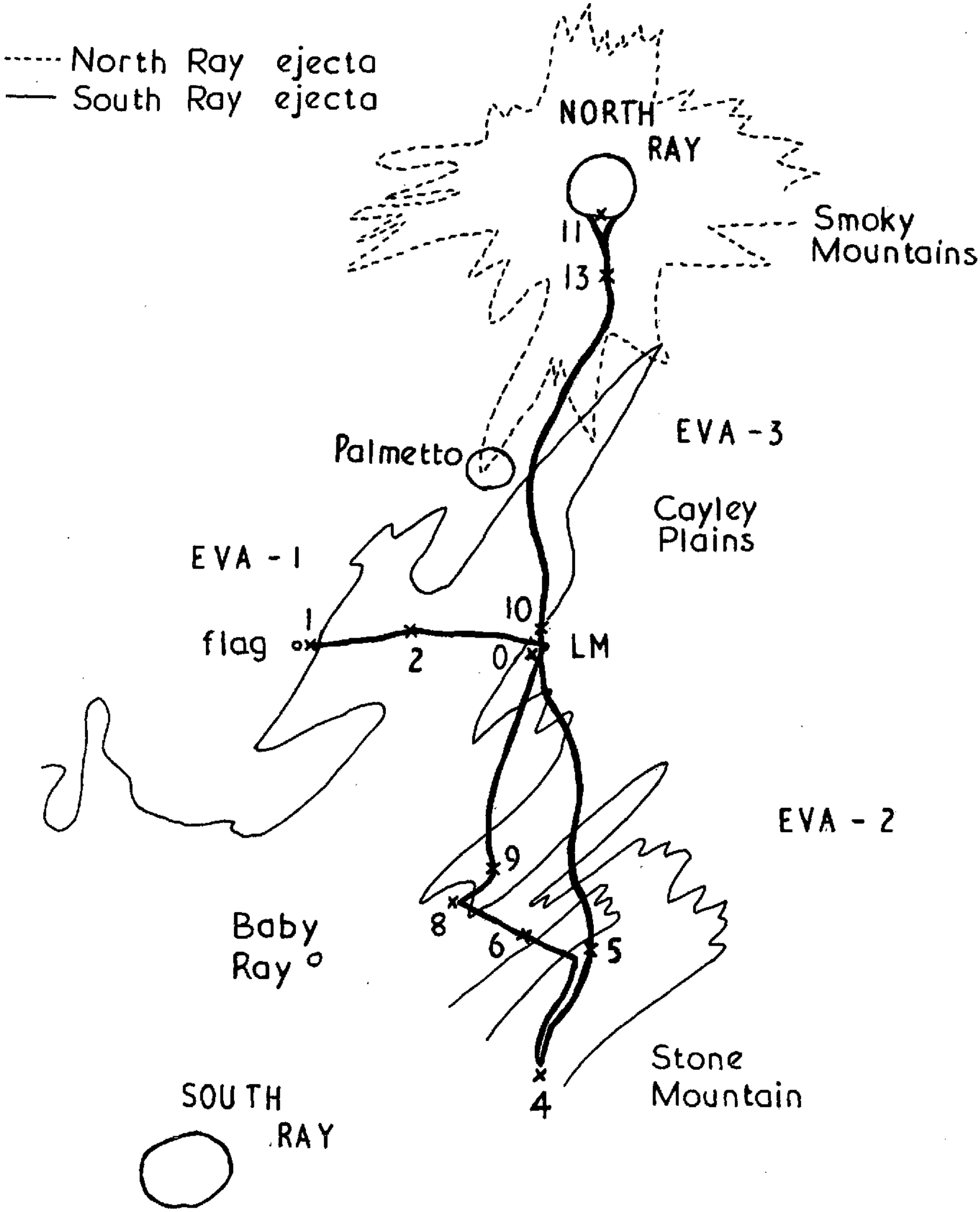
Data from:

(a)	Bansal et al., 1973; Compston et al, 1973; Laul and Schmitt, 1973; Wänke et al., 1973
(b)	Rancitelli et al., 1973a; Wrigley et al., 1973
(c)	Rancitelli et al., 1973b; Wrigley et al., 1973
(d)	Eberhardt et al., 1973; Kirsten et al., 1973; Walton et al., 1973
(e)	McKay and Heiken, 1973
(f)	AFGIT, 1973; ALGIT, 1973
n.a.	not applicable

Figure Legend

Map of the Apollo 16 Landing Site: Sampling stations are indicated by number. The extent of the North and South Ray Crater ejecta blankets as determined by photogeology (AFGIT, 1973; ALGIT, 1973) are outlined.

FIGURE 1



North Ray ejecta
South Ray ejecta
NORTH RAY
Smoky Mountains
11
13
EVA - 3
Palmetto
Cayley Plains
EVA - 1
1
flag
2
10
0
LM
EVA - 2
9
8
6
5
Baby Ray
Stone Mountain
4
SOUTH RAY