

Survey of lunar carbon compounds. I. The presence of indigenous gases and hydrolysable carbon compounds in Apollo 11 and Apollo 12 samples

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Abstract—Indigenous gases and chemical reaction products released by acid etch of Apollo 11 and Apollo 12 lunar samples have been examined by gas chromatography, mass spectrometry, and combined gas chromatography-mass spectrometry. Methane, ethane, ethylene, acetylene, and carbon monoxide are among the species identified and quantified. Hydrocarbons have been resolved into indigenous species and chemical reaction products by the use of deuterium-labelled reagents. The samples examined included size-differentiated fines, interior fragments of an igneous rock chip, and Apollo 12 fines from different locations. Possible sources of the indigenous hydrocarbons include solar wind implantation and a small primordial contribution. The hydrocarbons formed during acid etch probably arise from carbide or carbide-like materials contributed by meteoritic impact and solar wind implantation.

INTRODUCTION

ANALYSIS OF APOLLO 11 fines by a number of workers using a considerable variety of techniques has indicated that the quantities of organic compounds isolatable by solvent extraction were extremely low (ABELL *et al.*, 1970a; BURLINGAME *et al.*, 1970; HARE *et al.*, 1970; KVENVOLDEN *et al.*, 1970; HODGSON *et al.*, 1970; MEINSCHEN *et al.*, 1970; SR. M. E. MURPHY *et al.*, 1970; R. C. MURPHY *et al.*, 1970; ORÓ *et al.*, 1970; RHO *et al.*, 1970). Preliminary mass spectrometric organic analysis of various Apollo 12 samples (LSPET, 1970) indicated that these might be expected to contain concentrations of solvent-extractable material even lower than those of Apollo 11 fines.

Other analytical methods applied at Bristol to the Apollo 11 fines included programmed heating, vacuum crushing and acid etching (ABELL *et al.*, 1970a). We have concentrated on the last two methods for the examination of indigenous gases and hydrolysable carbon compounds with particular reference to their possible origins. Preliminary investigations of the Apollo 11 fines showed that some of the carbon could be released as gaseous hydrocarbons on treatment with aqueous mineral acids. Mass spectrometric analysis of the gases released from hydrofluoric acid etch of the fines indicated the presence of CH₄ at parts per million concentrations (ABELL *et al.*, 1970a; BURLINGAME *et al.*, 1970). Analysis by gas chromatography (gc) (CHANG *et al.*, 1970) and gas chromatography-mass spectrometry (gc-ms) (ORÓ *et al.*, 1970) of the

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products of hydrochloric acid etch showed that CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , and a number of unidentified C_3 and C_4 hydrocarbons were present. A less efficient etching reagent, phosphoric acid, released similar products but at reduced concentrations (CHANG *et al.*, 1970). The same reagent afforded hydrocarbons from breccias at similar concentrations to those observed for the fines, whereas the concentrations released from two crystalline rocks were lower by an order of magnitude (CHANG *et al.*, 1970). Release of carbon monoxide by hydrofluoric acid (BURLINGAME *et al.*, 1970) and carbon dioxide by sulphuric acid (ORÓ *et al.*, 1970) was also reported for two samples of the fines.

At the time of the Apollo 11 Conference it was uncertain whether the hydrocarbons released were formed by acid hydrolysis of carbides or were present as such. However, the presence of cohenite, $(\text{Fe}, \text{Ni})_3\text{C}$, has been reported in the Apollo 11 fines (FRONDEL *et al.*, 1970) and unidentified carbide has been reported in breccia 10,046 (ADLER *et al.*, 1970). Hydrolysis of cohenite of meteoritic origin with aqueous mineral acid affords a mixture of hydrocarbon gases, including CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 (CHANG *et al.*, 1970; ABELL *et al.*, 1970b).

Detailed studies of the gaseous carbon compounds released from lunar samples are necessary to reveal the origin, location, and distribution of the carbon in question. The initial requirement of these studies is the distinction between indigenous entities and those formed as the result of the chemical treatment. We have devised an isotopic labelling method which distinguishes between indigenous hydrocarbon gases and those formed from other carbon compounds by hydrolysis during the etching procedures; The method has been previously outlined (ABELL *et al.*, 1970b); full experimental details are reported herein, together with a gas chromatographic procedure for the routine analysis of hydrocarbons, deuterocarbons, and carbon oxides. Application of these methods to a variety of samples provides a measure of the carbon present as indigenous hydrocarbons and hydrolysable species. The use of selective etching reagents should allow definition of the physical location and hence, the origin of these compounds. Since lunar carbon compounds are abiologically derived, their study in this way may afford an insight into (1) the nature of carbon compounds contributed to the primitive Earth and (2) the origin of carbon compounds and the fate of carbon in the solar system, studies until now based mainly on terrestrial experience.

EXPERIMENTAL TECHNIQUES

General

All Apollo 12 samples are referred to by sample number. Unless otherwise stated, Apollo 11 fines refers to aliquots of the 10,086 Bulk Fines D sample. Sample handling and storage was carried out in a clean area using the methods previously described (ABELL *et al.*, 1970a). Prior to etching or vacuum crushing, samples and reagents were outgassed in a vacuum system incorporating a liquid nitrogen trap, a mercury diffusion pump, and a rotary pump. The earliest experiments were carried out with a McLeod gauge in the system; this has now been replaced by a Penning gauge. In one experiment (see Results) a tungsten filament ion gauge was used.

Vacuum Crushing

Apollo 11 lunar fines (0.670 g) were pulverised by continuous shaking (16 hr) in an evacuated all-glass ball mill (50 ml. capacity and wall thickness 0.25 in.), containing two balls of diameter

0.5 in. and fitted with a break seal for gas analysis. This vessel was used in place of the metal capsule previously described (ABELL *et al.*, 1970a). Adsorbed terrestrial gases were removed as far as possible from the vessel and sample by baking at 150°C for one hour under vacuum (10^{-5} torr). The gases released during the crushing procedure were examined using the mass-spectrometer gas analysis system. Blank experiments were conducted by vibrating the empty ball mill.

Aliquots of Apollo 11 lunar fines (*ca.* 0.5 g) were also pulverised in the presence of deuterium oxide (isotopic purity 99.8%, 1 ml) in order to exchange as far as possible protonated species (particularly H_2O) with deuterated analogues. The D_2O (0.015g) was degassed using a freeze/pump/thaw cycle and sealed into a small glass ampoule which was crushed together with the sample. The interior chip of an olivine basaltic rock (12022,79; 1.54g) was broken into small fragments on pre-extracted aluminium foil with a stainless steel hammer and chisel. The fragments were then pulverised to powder in the evacuated ball mill and the gases released analysed. The fine powder was then used for acid etching experiments. Uncrushed fragments of rock remaining in the ball mill after 16 hr were re-crushed in vacuo.

Acid Etching

Acid etching experiments were performed using hydrofluoric acid, (40%; Hopkin and Williams "AnalaR" grade), deuterium chloride (38% in D_2O ; Ciba, isotopic purity 99.5 atom percent D) and deuterium fluoride (20% in D_2O ; Merck, Sharp and Dohme; isotopic purity >99.5%). The essential technical details for this experiment have already been reported (ABELL *et al.*, 1970a). Here we specify minor additions or modifications made to the established procedure. Immediately prior to mixing a sample and the acid, the actual acid to be used for the etch was examined for dissolved gaseous contaminants. This was achieved by means of the extra side arm and break seal incorporated into the reaction vessel (Fig. 1). To keep partially deuterated reaction products to a minimum when using deuterated acids, it was necessary to exchange as far as possible protonated species (particularly adsorbed H_2O) with deuterium. This was accomplished by treating aliquots of fines with an excess of D_2O during the degassing procedure (ABELL *et al.*, 1970b). The reaction time for acid etch was increased to 16 hr. In one experiment, using deuterium chloride as etching reagent, the reaction vessel was heated for 90 hr at 120°C. Meteoritic cohenite (4.4 mg; courtesy of Dr. R. Brett, Manned Spacecraft Center, Houston, Texas) was etched using the same procedure. Blank experiments were carried out with no sample in the reaction vessel. The gases released were examined by mass spectrometry, gc or gc-ms.

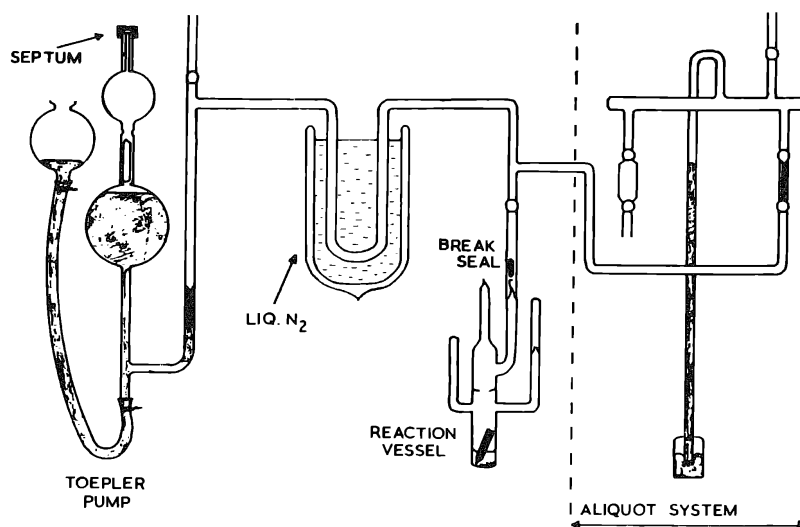


Fig. 1. Reaction and fractionation system for gas analysis.

Alkali etching

Alkali etching experiments were performed using sodium deuterioxide (40% in D_2O ; B.D.H.; isotopic purity, 99%, 1 ml). The vessel used was identical to that used for acid etching, and the D_2O exchange and degas procedures were as outlined above. Unsieved (61.4 mg) and sieved Apollo 11 fines (200–240 mesh, 51.2 mg) were each etched for about 6 days. The gases released were analysed for CH_4 and CD_4 content at regular intervals by gas chromatography. In the second experiment, the total condensed fraction (see below) obtained after 6 days was analysed by gas chromatography for the presence of C_2 hydrocarbons.

Gas fractionation and concentration system

The apparatus shown schematically in Fig. 1 was used for the concentration of the gases released by etching prior to transfer to the gas chromatographic system for analysis. Greaseless stopcocks (Springham Valves, Ltd.) were used as valves throughout this system. Any gas released from the reaction vessel can be transferred to a point beneath the septum using the Toepler pump, withdrawn with a gas-tight syringe (100 or 250 μ l, Scientific Glass Engineering) and analyzed by gc or gc-ms. The reaction vessel was attached to the system and the space above the break seal evacuated to *ca.* 10^{-3} torr with the Toepler pump. A sample of the gas removed was analyzed by gc as a contamination control. To avoid interference from either HF or DF gas and water vapour the reaction vessel was cooled to $-65^\circ C$ (chloroform slush bath) and the remaining volatile material was transferred to the analytical system by fracturing the break seal with a magnetic weight. The gaseous reaction products were fractionated separately into two volatility ranges by the liquid nitrogen trap. Components not condensed at $-195^\circ C$ (H_2 , D_2 , Ne, N_2 , O_2 , Ar, CO, CH_4 , CD_4) were concentrated and removed for analysis. The trap was warmed to ambient and the less volatile fraction (CO_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , H_2S , etc.) treated in the same way. Prior to etching, the acid reagent was examined for the presence of gaseous contaminants using the same system.

To improve the recovery of the small amounts of gases released on NaOD etching, helium (50 μ l) was injected into the system, via the Toepler pump septum, and allowed to equilibrate with the released gasses. Immediately prior to gas concentration, the reaction mixture was briefly warmed ($50^\circ C$) to release gases trapped in the viscous reagent. JOHNSON *et al.* (1970) suggested that trace amounts of a number of species, in particular CO and CH_4 , can be generated from a variety of hydrocarbons in a Toepler pump. Continuous recycling of ethane at 10 cm pressure for 60 minutes with a Toepler pump generated only submicrogram quantities of CH_4 and CO. It is unlikely that gas generated by this process would make a significant contribution to the gases under investigation. There was no evidence for the presence of CO when aliquots of standard gases, including methane and ethane, were processed through the complete analytical sequence.

Gas chromatography

Gas chromatography was performed using a Varian Aerograph 1200 series gas chromatograph fitted with a microkatharometer (Servomex Controls, Ltd.) in series with a flame ionisation detector (FID). The gases released from lunar samples were analysed using a $25' \times \frac{1}{16}"$ o.d. stainless steel column packed with 60–80 mesh Graphon (DICORCIA and BRUNER, 1970) operated with 2–4 ml/min of helium as carrier gas (Fig. 2).

The non-condensed fraction was concentrated with the Toepler pump and analysed at $-78^\circ C$ (solid CO_2 /acetone). Under these conditions an equimolar mixture of CD_4 (Stohler Isotopic Chemicals, Ltd.) and CH_4 gave a 50% valley (10,000 theoretical plates). CD_4 and CD_3H were not separated under these conditions. The CD_4 released from the lunar samples always exceed the CH_4 (in the ratio 2.5–7.6) and the effective separations between CD_4 and CH_4 were poorer (Fig. 3) than that measured for the standard equimolar mixture. The condensed fraction was analysed at $0^\circ C$ to allow separation of C_2D_6 and C_2H_6 . Retention times on Graphon under these conditions did not permit the measurement of C_3 or C_4 hydrocarbons or deuterocarbons. These species, released from two samples of Apollo 11 fines, were analysed at $100^\circ C$ with a $20' \times \frac{1}{16}"$ o.d.

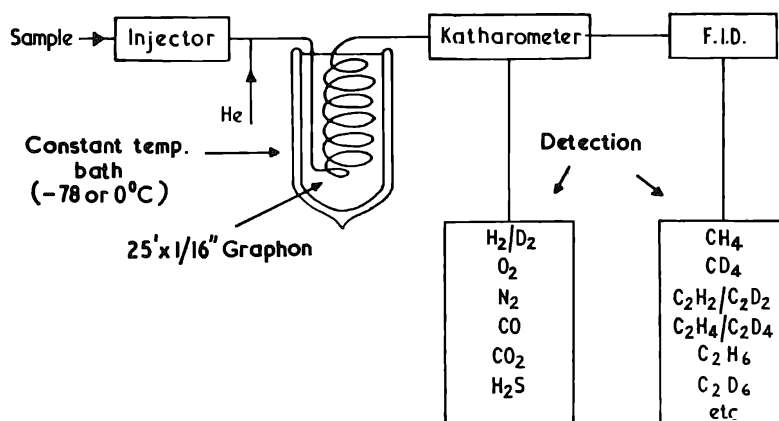


Fig. 2. Gas chromatographic system for analysis of low molecular weight gases.

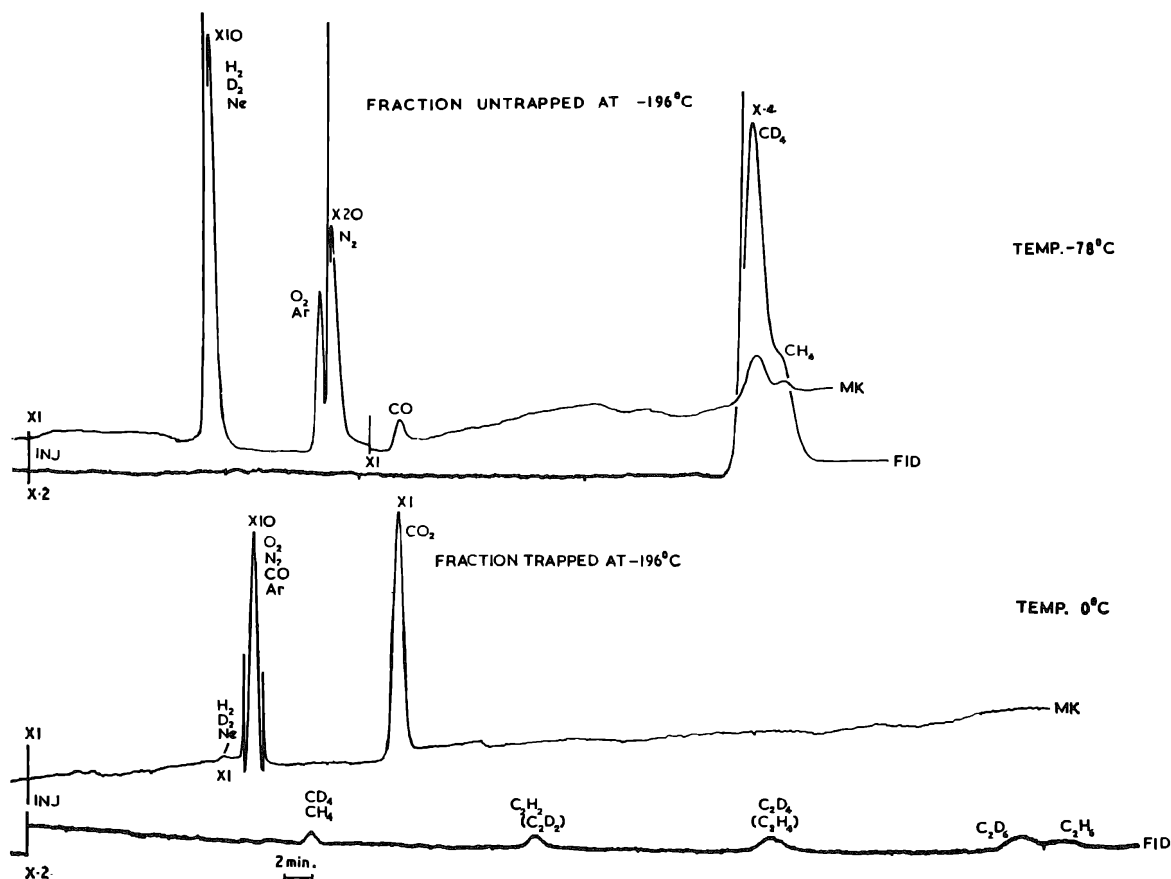


Fig. 3. Gas chromatographic analysis of gases released on DF treatment of lunar fines (12023, 47.4 mg). Column: $25' \times \frac{1}{16}''$ od, 60–80 mesh Graphon, He 2 ml/min, MK = microkatharometer response, FID = Flame ionisation detector response. Attenuation factors are marked where appropriate.

stainless steel column packed with 100–120 mesh Porapak T with 6–8 ml/min of helium as carrier gas.

Calibration was carried out with known quantities of individual gases or mixtures (e.g., CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₈, *n*-C₄H₁₀, CO, CO₂) from the aliquot system (Fig. 1) and passing them through the complete analytical sequence. The gases were quantitated either by digital integration of the gas chromatograph output (Kent Chromalog 2) or by weighing peaks cut from the chart paper. An estimate of the overall error involved in the complete analytical sequence (fractionation and concentration system, syringe transfer, gas chromatographic peak integration) was made by processing aliquots through the complete sequence and by injecting standard aliquots of hydrocarbons directly into the chromatograph. The overall error in the sequence is $\pm 20\%$. Recoveries of the C₁ to C₃ hydrocarbons are greater than 90%.

Mass spectrometry

Mass spectrometry was used to analyse a limited number of samples of Apollo 11 fines (but was subsequently replaced by the gas chromatographic method). Gases released by in vacuo crushing and by DCl etching were analysed in the system described previously (ABELL *et al.*, 1970a). An isopentane/liquid N₂ slush bath (-140°C) was used to prevent DCl vapour from reaching the ion source.

Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry was performed using a Varian MAT CH-7 mass spectrometer coupled to a Varian Aerograph 1200 gas chromatograph, via an all-glass, single-stage, Watson-Biemann helium separator. Analyses were carried out with a $20' \times \frac{1}{16}"$ stainless steel column packed with 100–120 mesh Porapak T, operated with 4 ml/min of helium as carrier gas. The non-condensed and condensed fractions, released by DF etch from Apollo 11 fines (0.200g), were chromatographed isothermally at 20°C and 80°C , respectively. Mass spectra were recorded continuously by repetitive scanning (5 sec/decade) over the range m/e 10–80.

RESULTS

The use of deuterium-labelled reagents allows distinction between indigenous hydrocarbon gases and those formed by chemical reaction during isolation. Thus, for example, methane released as CH₄ represents an indigenous component of the samples. methane released as CD₄ represents a synthetic product. Quantitative data for all carbon compounds are expressed in $\mu\text{g/g}$ as carbon in the samples.

Vacuum crushing

Crushing in vacuo was chosen as a possible non-chemical method for releasing indigenous gases (ABELL *et al.*, 1970a). Mass spectrometric analysis of the gases released by in vacuo crushing (Apollo 11 fines) revealed the presence of the rare gases He, Ne, and Ar. The quantities of these gases were substantially less than those obtained by the thermal extraction methods of other workers (e.g., HINTENBERGER *et al.*, 1970; HEYMANN and YANIV, 1970; EBERHARDT *et al.*, 1970); however, the relative abundances of the Ne and Ar isotopes were similar to those already observed. Methane ($0.9 \mu\text{g/g}$) and ethane ($0.1 \mu\text{g/g}$) were present in the released gases. A blank experiment performed on the empty ball mill showed only trace quantities of terrestrial atmospheric gases (O₂, N₂, ⁴⁰Ar, CO₂). Crushing two other samples in the presence of D₂O also liberated the rare gases; greater than 95% of the methane released could

be accounted for as CH_4 (0.24 $\mu\text{g/g}$, 0.24 $\mu\text{g/g}$), CD_3H (0.16 $\mu\text{g/g}$, 0.06 $\mu\text{g/g}$) and CD_4 (0.36 $\mu\text{g/g}$, 0.43 $\mu\text{g/g}$). Similarly, about 75% of the ethane could be accounted for as C_2H_6 (0.06 $\mu\text{g/g}$, 0.03 $\mu\text{g/g}$), C_2D_6 (0.05 $\mu\text{g/g}$, 0.03 $\mu\text{g/g}$) and $\text{C}_2\text{D}_5\text{H}$ (0.03 $\mu\text{g/g}$, 0.06 $\mu\text{g/g}$). The resolution of the mass spectrometer was not sufficient ($M/\Delta M = 800$) to distinguish between N_2 and CO (m/e 28). The second most abundant ion in the mass spectrum of CO is m/e 12, but the observed abundance of this ion could be accounted for by the methane species present in the same fraction and it is unlikely that there was a major contribution by CO to the ion m/e 28. The only other species identified among the gases were O_2 and CO_2 at concentrations similar to those observed in the blank experiments. The crushing method indicated that indigenous methane and ethane are present as CH_4 and C_2H_6 in the fines. However, the method has certain disadvantages: (1) it is inefficient; less than 10% of the indigenous hydrocarbon gases released by acid etching are released by crushing and thus species present in low abundance are not observed; and (2) it also releases gases formed by the hydrolysis of carbides, presumably arising as a result of localised high temperatures and the presence of adsorbed terrestrial water.

Vacuum crushing has been used to prepare rock samples prior to acid etching. The gases released by crushing rock 12022,79 were analysed by gas chromatography. A small methane peak was detected (0.5 $\mu\text{g/g}$). No peak was detected for CO , and all of the CO_2 seen could be ascribed to terrestrial contamination.

Acid etching

The results of the acid etching experiments are described in the following three sections.

(1) *Mass Spectrometry*. Mass spectrometry was used to examine the hydrocarbons and deuterocarbons released by DCl treatment of two samples of Apollo 11 fines. The mass spectrum of the gases released from one of the samples (Fig. 4b) shows that 18%

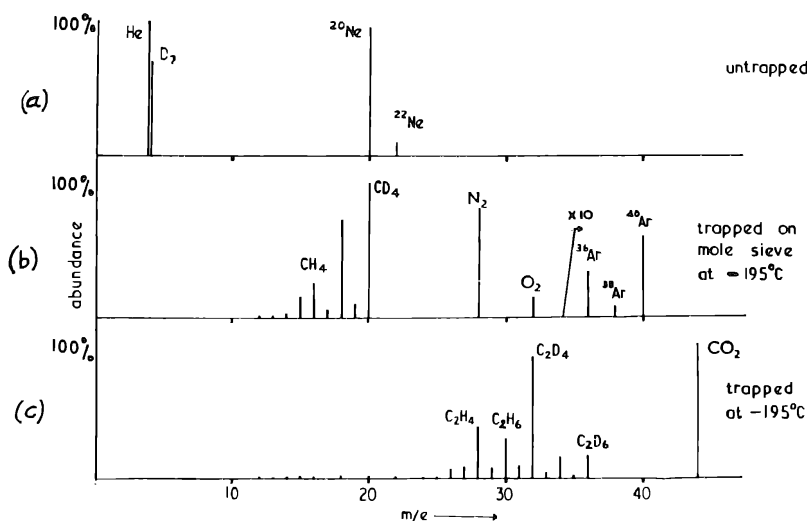


Fig. 4. Mass spectra of gases released by DCl treatment of Apollo 11 lunar fines and admitted to the mass spectrometer via gas inlet system. In (b) abundance of ions above m/e 34 are multiplied by a factor of 10.

of the carbon released as methane is in the form CH_4 , almost all (90%) of the remainder being as CD_4 . Likewise (Fig. 4c) 31% of the carbon released as ethane is in the form C_2H_6 , 90% of the remainder is present as either C_2D_6 or $\text{C}_2\text{D}_5\text{H}$. The quantities of carbon released from the fines vary with the particle size. The CH_4 content of two samples of the unsieved bulk fines (1.3 $\mu\text{g/g}$, 1.3 $\mu\text{g/g}$) falls between the quantities of CH_4 liberated from 30–100 mesh fines (0.7 $\mu\text{g/g}$) and fines smaller than 200 mesh (1.8 $\mu\text{g/g}$). The CD_4 and CD_3H values follow a similar trend; the $\text{CD}_4 + \text{CD}_3\text{H}$ content of the unsieved bulk fines (5.8 $\mu\text{g/g}$, 5.8 $\mu\text{g/g}$) falls between the quantities liberated from 30–100 mesh fines (3.1 $\mu\text{g/g}$) and the fines smaller than 200 mesh (7.6 $\mu\text{g/g}$). It is noteworthy that the $(\text{CD}_4 + \text{CD}_3\text{H})/\text{CH}_4$ ratio is approximately constant (4.2–4.5). Evidently, the quantities of the indigenous methane and the hydrolysis products (CD_4 , CD_3H) vary with the particle size in a similar fashion.

The quantities of C_1 and C_2 hydrocarbons and deuterocarbons released from Apollo 11 bulk fines (by DCl etch) and measured by mass spectrometry, are smaller than those measured by the gas chromatographic method (using DCl and DF). It is likely that the quantitative data obtained by mass spectrometry are low because the response of the mass spectrometer does not have a linear relationship with the sample pressure. The lunar sample gases and calibrant gases were analysed in the same way but the source pressures were different. The mass spectrometric data for the DCl etch are self-consistent, as are the results similarly obtained in three crushing experiments. We believe that quantitation afforded by mass spectrometry alone is low, but that the trend observed for the DCl etch of size-differentiated fines is real.

Figure 4c shows the presence of much greater quantities of CO_2 than were observed in the crushing experiments. It was impossible to obtain quantitative data for this gas; a major portion of it was condensed in the -140°C trap. However, CO_2 was present in sufficient quantities (compared to N_2 and O_2) to preclude terrestrial atmospheric background *in the system* as its source (see Discussion). The ion m/e 28 (Fig. 4b) is assigned as N_2 by an argument similar to that already presented for the crushing experiments. The rare gases (He, Ne and Ar) are observed in non-terrestrial isotopic abundances (Fig. 4a,b).

Examination of the DCl for hydrocarbon and deuterocarbon contaminants established that these were not present in quantities above the detection limits. The possibility of hydrocarbons arising from deuterocarbons by exchange was investigated by examining the reaction of DCl with cohenite; deuterocarbons, but not hydrocarbons, were observed.

(2) *Gas chromatography. Apollo 11 Samples* (Table 1). The detection limit for an individual hydrocarbon was equivalent to 0.1 $\mu\text{g/g}$ as carbon for a 50 mg sample. Analysis of the gases released by etching Apollo 11 fines with undeuterated acids (HF and HF/HCl) indicates that 25–35 $\mu\text{g/g}$ of carbon in the sample can be released as C_1 – C_2 hydrocarbons. The use of deuterated acids (DCl and DF) indicates that the methane and ethane are mixtures of undeuterated and fully deuterated compounds. Deuterated and undeuterated compounds were not completely resolved. The small contributions of CD_3H and $\text{C}_2\text{D}_5\text{H}$ identified by mass spectrometry and gc–ms (see below) were not separable from their fully deuterated counterparts; CD_3H and $\text{C}_2\text{D}_5\text{H}$

obviously arise from the same source as the fully deuterated analogues. Thus, the quantitative data expressed as CD_4 and C_2D_6 include a small contribution from these species. The ratio of carbon as CD_4 (19–22 $\mu\text{g/g}$) to CH_4 (4.8–5.2 $\mu\text{g/g}$) released on acid etch is reasonably consistent (3.6–4.3). The relative and absolute yields of C_2H_6 and C_2D_6 are more variable (0.16–0.9 and 1.2–3.6 $\mu\text{g/g}$, respectively). Analysis on Porapak T of the gases released by HF etch indicated the presence of species with retention times corresponding to propane and propene (cf. CHANG *et al.*, 1970; HENDERSON *et al.*, 1971). In the gases released from one sample, species with retention times of methylacetylene and allene were observed. Deuterated and undeuterated species are not resolved on Porapak and we are unable to decide at present whether the C_3 hydrocarbons occur as such, or represent hydrolysis products.

Only deuterocarbons were released (Table 1) by the action of DF on cohenite; acetylene was absent. The yield of carbon as gaseous deuterocarbons was low (*ca.* 1.0%, assuming Fe_3C); this could result, in part, from the relatively large size of the cohenite fragments (*ca.* 40–60 mesh). The ratio of $\text{CD}_4/\text{C}_2\text{D}_6$ from cohenite was similar to that observed for lunar fines (*ca.* 10:1).

Gas chromatography indicated that CO was released from the fines in amounts ranging from 1.2 to 3.0 $\mu\text{g/g}$. One value (8.6 $\mu\text{g/g}$) was obtained when an ion gauge was incorporated in the vacuum system: CO is known to be synthesised on hot filaments in vacuum systems and this high value probably reflects a contribution from this source. In one experiment in which the sample was etched with DCl for 90 hours at 120°C, CO (*ca.* 65 $\mu\text{g/g}$ as carbon) was detected. The detection limit for CO was 0.5 $\mu\text{g/g}$ for a 50-mg sample.

CO_2 was found in the hydrolysis products at concentrations ranging from 4 to 76 $\mu\text{g/g}$. Initially, blank experiments were free from CO_2 but significant quantities appeared in later blanks.

(3) *Gas chromatography. Apollo 12 Samples.* (Table 2) Gas chromatographic analyses of gases released by DF etch of fines having high contents of total carbon (12001, 12023, 12042; *ca.* 130 $\mu\text{g/g}$; MOORE *et al.*, 1971) showed the presence of deuterated and undeuterated C_1 and C_2 hydrocarbons. The quantities of CD_4 and CH_4 released from these samples (8–15 $\mu\text{g/g}$ and 2.1–2.2 $\mu\text{g/g}$) were somewhat smaller than those obtained from Apollo 11 fines and there appeared to be more variability in the CD_4/CH_4 ratios (3.8–7.2). The quantities of C_2 hydrocarbons released from these samples were similar to, or lower than, those obtained from Apollo 11 fines but with slightly smaller $\text{C}_2\text{D}_6/\text{C}_2\text{H}_6$ ratios. The CO released by DF at ambient was consistently less than 2 $\mu\text{g/g}$. Two samples (12023 and 12037) treated with DCl at 120°C (90 hr) released CO in quantities < 1 $\mu\text{g/g}$.

DF etching of fines of lower carbon content (12037, total carbon 82 $\mu\text{g/g}$; MOORE *et al.*, 1971) released correspondingly smaller amounts of methane (1.2 $\mu\text{g/g}$ CH_4 ; 3.0 $\mu\text{g/g}$ CD_4); the quantities of C_2 hydrocarbons released barely exceeded the detection limit. Two samples of fines with very low total carbon content (12032, 12033; 25–60 $\mu\text{g/g}$; MOORE *et al.*, 1970) were also analysed and only very small quantities of methane were detected. Traces of C_2 hydrocarbons were observed. DF etching of an interior chip of an olivine basaltic rock (12022,79; total carbon 50 $\mu\text{g/g}$; MOORE *et al.*,

1970), previously crushed in vacuo, was carried out. In the two analyses, methane (0.78, 1.1 $\mu\text{g/g}$) and ethane (0.10, 0.14 $\mu\text{g/g}$) were undeuterated, indicating the absence of hydrolysable carbide. Acetylene and ethylene (*ca.* 0.1 $\mu\text{g/g}$) were observed but in neither case could the extent of deuteration be determined (see above). A trace of CO (*ca.* 0.1 $\mu\text{g/g}$) was detected in one analysis.

GC-MS

The application of gc-ms was limited because of the poor sensitivity arising from sample losses in the separator. However, we have used the method to analyse the gases released by DF etch of two samples of Apollo 11 fines. This experiment was designed to confirm the validity of the isotopic labelling/gc procedure and to determine the isotopic composition of species not separated by the gas chromatographic method. Continuous scanning of the column effluent confirmed the presence of CD_4 and CH_4 , together with trace quantities of CD_3H . Similarly, only trace quantities of $\text{C}_2\text{D}_5\text{H}$ accompanied C_2D_6 and C_2H_6 . The mass spectrum indicated that ethylene comprised almost entirely C_2D_4 . The isotopic composition of acetylene could not be determined because of the small quantities released. The chromatographic conditions allowed partial resolution of CO and N_2 . There was no distinct peak corresponding to CO in the chromatogram. However, continuous scanning revealed the presence of an ion of m/e 12 in the tail of the nitrogen peak. If it is assumed that m/e 12 arose from CO, then, up to 3 $\mu\text{g/g}$ of lunar carbon could have been released as CO from the lunar fines.

H_2S was identified but it is unlikely to be indigenous to the fines. The most likely origin is from isotopic exchange of D_2S synthesized by the reaction of DF on sulphide minerals. Isotopic exchange of D_2S occurs on the column used. Only H_2S was observed in the ion source of the mass spectrometer when D_2S was injected into the gc-ms system. Deuterium, presumably arising from the reaction of the acid on metals such as iron and nickel, accounted for the major part of the gas mixture.

Alkali etch

The gases evolved by etching one sample of Apollo 11 fines with sodium deuterioxide at ambient temperature were analysed by gas chromatography at regular intervals. In comparison with the acid etch, where gas evolution is vigorous, there was no visible evolution of gas during NaOD etch at ambient. The samples appeared to be unaltered. In one experiment in which unsieved fines were used, a large proportion (70% = 3.7 $\mu\text{g/g}$) of the CH_4 present (as determined by DF etching) was released after 120 hours. The CD_4 (3.4 $\mu\text{g/g}$) evolved amounted to <20% of that from etching with DF. Very little CH_4 and CD_4 were evolved after 120 hours. In a second experiment, etching of a 200–240 mesh aliquot also produced a high proportion (*ca.* 60%) of the CH_4 released by acid etch, whereas the quantity of CD_4 released was comparatively small (Fig. 5). At present little is known about the rate of hydrolysis of carbides under alkaline conditions. The rate of evolution of CH_4 was approximately constant throughout the reaction. The total quantity (1.1 $\mu\text{g/g}$) of C_2H_6 released after 139 hr. was comparable to, or greater than, that released by acid etch of unsieved fines. The

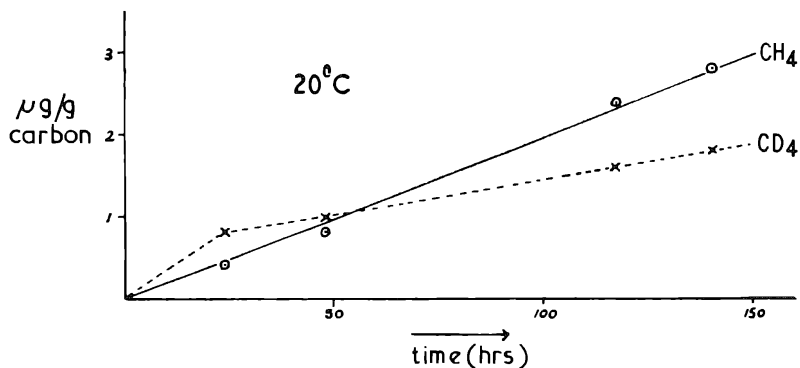


Fig. 5. Quantities of CD₄ and CH₄ released by NaOD etch of Apollo 11 fines. Total quantities of gas are plotted against duration of etch.

Table 1. C₁ and C₂ hydrocarbons and deuterocarbons released by acid etch of Apollo 11 fines (10,086 bulk fines D; ca 140 μg/g total C).

Sample wt. (mg.)	Reagent	Carbon (μg/g) released as						Ratio CD ₄ /CH ₄	Carbon accounted for (to 1 μg)
		CH ₄	CD ₄	C ₂ H ₆	C ₂ D ₆	C ₂ H ₄ and/ C ₂ D ₄	C ₂ H ₂ and/ C ₂ D ₂		
50.9	HF (40%)	20		1.6		3.4	0.3	—	25
49.4	HF (40%)	32		1.4		1.0	0.2	—	35
101.0	HF/HCl (20%)	24		0.6		0.1	tr.	—	25
39.5	DF (20%)	5.2	19	0.9	3.6	2.2	1.3	3.6	32
60.6	DF (20%)	4.8	18	0.4	2.2	3.2	0.7	3.8	29
47.0	DCl (40%)	5.1	22	0.16	1.2	1.2	0.3	4.3	30
Cohenite (4.4 mg)	DF (20%)	*	500	*	58	16	*	—	574

tr. = trace.
* not detected.

C₂D₆ (0.26 μg/g), however, was considerably less abundant than that from acid etch of unsieved fines (ca. 2 μg/g).

DISCUSSION

Table 1 lists the quantities of C₁ and C₂ hydrocarbons and deuterocarbons (measured by gas chromatography) released by acid etch of Apollo 11 fines. Several acidic reagents (HF, HF/HCl, DCl, and DF) have been used and the quantities of gases released are reasonably consistent although the samples were not size-differentiated, crushed or aliquotted. A significant fraction (25–35 μg/g) of the total carbon can be released as C₁ and C₂ hydrocarbon species. HENDERSON *et al.* (1971) and CHANG *et al.* (1970) have reported values of 16 μg/g for the C₁ and C₂ hydrocarbon species released from 10,086 fines by HF and HCl etch, respectively.

The isotopic labelling method (ABELL *et al.*, 1970b and the present paper), used for crushing experiments and acid-etching experiments, demonstrates that both indigenous hydrocarbons and hydrolysable carbon compounds are present in lunar fines. It is likely, as suggested by CHANG *et al.* (1970), that the hydrolysable material is carbide, including cohenite [(Fe, Ni)₃C], as shown by the evolution of CD₄, C₂D₆, and almost completely deuterated hydrocarbons (eg., CD₃H). The quantities of CH₄, CD₄, C₂H₆, and C₂D₆ indicate that the indigenous hydrocarbons (CH₄ + C₂H₆)

contribute *ca.* 5 $\mu\text{g/g}$ and carbides ($\text{CD}_4 + \text{C}_2\text{D}_6$) contribute *ca.* 22 $\mu\text{g/g}$ to the carbon in the Apollo 11 fines.

Table 2 shows the quantities of C_1 and C_2 hydrocarbons and deuterocarbons released from a variety of Apollo 12 fines. The concentrations of indigenous hydrocarbons and carbides are less than those measured for the Apollo 11 fines. The CD_4/CH_4 ratios (Tables 1, 2) show that carbide and methane are also present in different proportions. One sample of the fines (12023) has been examined independently by CHANG *et al.* (1971) using 6 *N* DCl: their values for CH_4 (1.6 $\mu\text{g/g}$) and carbide (6.7 $\mu\text{g/g}$) are similar to those shown in Table 2, although no C_2H_6 was reported by these authors. HENDERSON *et al.* (1971) have independently examined the hydrocarbon products of HF etch of all of the Apollo 12 fines listed in Table 2, with the exception of 12037 fines: their results for total C_1 and C_2 hydrocarbons are similar to those that can be derived from the values for hydrocarbons and deuterocarbons listed in Table 2.

The concentrations of carbon accounted for both as indigenous hydrocarbons and carbide probably represent minimum values. At present, the gas chromatographic method does not allow distinction between the indigenous and synthetic components of species other than methane and ethane. Thus, the isotopic composition of the ethylene, acetylene and higher hydrocarbons released, when determined, will provide more accurate values for the indigenous and synthetic components.

In addition, it is unlikely that all of the carbon present as hydrolysable carbides is evolved as hydrocarbons on acid treatment. A small sample of cohenite of meteoritic origin liberated only 1–2% of the carbon as C_1 and C_2 hydrocarbons or deuterocarbons when treated with HCl (CHANG *et al.*, 1970) or DF, respectively (see above). However, the lunar carbide is likely to be much more finely divided than the fragments

Table 2. C_1 and C_2 species from DF etch of Apollo 12 samples.

Sample	wt. (mg)	Carbon ($\mu\text{g/g}$) released as							Ratio CD_4/CH_4	Carbon accounted for (to 1 μg)	Total Carbon†
		CH_4	CD_4	C_2H_6	C_2D_6	C_2D_2 and/ or C_2H_2	C_2D_4 and/ or C_2H_4	CO			
12001 fines	55.4	2.2	12	0.38	0.76	*	1.0	†	5.0	16	130
12023 fines	47.4	2.1	8.0	0.08	0.16	0.08	0.12	1.8	3.8	12	135 166
12037 fines	53.5	1.2	3.0	†	0.06	0.10	0.12	1.3	2.5	6	82
12042 fines	49.9	2.1	15	†	*	0.36	1.1	†	7.2	19	130 140
12032 fines	101.9	0.28	1.7	†	†	0.24	0.40	0.3	6.1	3	60 25
12033 fines	105.0	0.11	0.84	†	tr	†	tr	†	7.6	1	50 23
12022 interior chip	218.0	1.1	†	0.10	†	0.12	0.07	<1	0.0	1	50
12022 interior chip	140.0	0.78	†	0.14	†	0.15	0.10	0.1	0.0	1	50

* not measured.
† not detected.
tr trace.
‡ Measured by combustion (MOORE *et al.*, 1970).

of cohenite. The yield of deuterocarbons from lunar carbide is likely to be higher but not quantitative.

Application of the isotopic labelling procedure allows distinction between indigenous hydrocarbons and carbides. A closer examination of these two species can now be made.

Indigenous hydrocarbons in lunar fines

The quantities of carbon accounted for as CH_4 and C_2H_6 from acid etch (Table 2) approximately parallel the abundances of total carbon for the Apollo 12 fines as measured by MOORE *et al.* (1971). Three samples of the fines (12001, 12023, and 12042) are dark in colour and have high values for total carbon. These samples also contain correspondingly high values for CH_4 and C_2H_6 . Three samples (12032, 12033, and 12037) of light-colored fines have been examined, CH_4 being the only indigenous species identified (Table 2). The 12032 and 12033 fines have low total carbon abundance and low CH_4 content, whereas 12037 has an intermediate total carbon abundance and an intermediate CH_4 content.

Apollo 11 bulk fines have the highest total carbon abundance (MOORE *et al.*, 1970), are very dark in colour, and have the highest indigenous hydrocarbon content. The relationship between CH_4 and total carbon abundance is also valid for size-differentiated fines. MOORE *et al.* (1970) observed that the fines were enriched in carbon compared to the igneous rocks and that, for the fines, the total carbon abundance increased with decreasing particle size. Our preliminary mass spectrometric data obtained by DCI etch of size-differentiated Apollo 11 fines show that CH_4 is also concentrated in the finest fines. These observations suggest that a surface-correlated phenomenon is the source of some of the carbon present in the lunar fines and that the indigenous hydrocarbons are derived from this implanted carbon.

Table 3 lists the quantities of CH_4 released by DF etch of Apollo 11 fines and various samples of Apollo 12 fines; also listed are a number of other available parameters for the same samples (^{36}Ar abundance, cosmic ray track density, cosmic ray exposure age and fraction of grains with an amorphous surface coating). The data in Table 3 indicate possible correlations between (1) the CH_4 content and the ^{36}Ar content. It is generally agreed that the high abundances of the rare gases in the fines could indicate a major contribution from solar wind implantation, although little is known about the respective diffusion losses of ^{36}Ar and CH_4 ; (2) the CH_4 content of the fines and the fraction of mineral grains in the 400 mesh residue which show an amorphous coating. Unfortunately, this comparison is restricted to two samples. However, the fines with the high CH_4 content have the higher fraction of these grains. Conversely, the fines with a low CH_4 content have a much lower fraction of the grains. The amorphous coating of a grain is highly disordered in comparison with the crystalline interior; it extends to a depth of 200–800 Å, and has been tentatively attributed to solar wind implantation (BORG *et al.*, 1971; DRAN *et al.*, 1970). A high latent track density ($>10^{10}$ tracks/cm²), attributable to solar suprathermal ions, is also found in these grains. It has also been suggested that the grains with an amorphous coating represent cosmic dust irradiated in space and accreted by the

Table 3. Correlation of the quantities of CH₄ and CD₄ released by DF etch from lunar fines with various measurements relating to surface exposure.

Sample No.	CH ₄ (μg/g)	CD ₄ (μg/g)	³⁶ Ar (10 ⁻⁸ cc/g) (PEPIN, 1971)	Fraction of grains with amorphous coating in 400 mesh residue (BORG <i>et al.</i> , 1971)	Fraction of particles with track density ≥10 ⁸ /cm ² (BHANDARI <i>et al.</i> , 1971)	Average track density (10 ⁶) of particles with < 10 ⁸ /cm ² (BHANDARI <i>et al.</i> , 1971)	Cosmic ray exposure age (10 ⁶ yr.) (BHANDARI <i>et al.</i> , 1971)
Apollo 11 bulk fines	ca. 5‡	ca. 22‡	38,000†	67%	> 0.9§	*	> 100§
12042	2.1	15	28,000	n.d.	0.92	54.9	160
12001	2.2	12	n.d.	n.d.	0.68	48.2	80
12037	1.2	3	n.d.	n.d.	0.52	16	20
12032	0.28	1.7	4,200	15%	0.17	13	10
12033	0.11	0.8	2,800	n.d.	0.03	5.6	100**

* lowest track density observed (10084) = 1 × 10⁷ (LAL *et al.*, 1970).
† 10084, HINTENBERGER *et al.* (1970); PEPIN *et al.* (1970).
n.d. not determined.
‡ 10,086 D.
§ 10,084; 10,085 LAL *et al.* (1970).
|| 10,084.
** total in situ exposure age.

moon (BARBER *et al.*, 1970); (3) The CH₄ content and the cosmic ray track density (and, hence, possibly “cosmic ray exposure age”). BHANDARI *et al.* (1971) have examined a large number of individual grains of pyroxene and feldspar selected from several samples of Apollo 12 fines. The fossil cosmic ray tracks occur within 10 μ of the surface of a grain. Table 3 lists the fraction of particles having a track density ≥ 10⁸ tracks/cm², the average track density for the remaining particles, and the corresponding exposure age. A high CH₄ abundance is observed in samples of fines (e.g., 12042) having a high frequency of particles with track density ≥ 10⁸ tracks/cm², a high average track density for the remaining particles and a correspondingly long exposure age. A low CH₄ abundance is observed (e.g., 12032) when the other parameters are also low. Similar figures are not available for Apollo 11 fines. However, LAL *et al.* (1970) have reported the following observations for 10084 and 10085 fines: (a) 90% of the particles have track densities > 10⁸ tracks/cm²; (b) the minimum track density is 1 × 10⁷ tracks/cm²; and (c) the cosmic ray exposure age is several hundred million years. The CH₄ abundance (5 μg/g) for 10,086 bulk fines is the highest so far observed for any sample of fines.

Cosmic ray exposure ages and solar wind exposure ages need not be directly related. BHANDARI *et al.* (1971) have suggested that grains having a track density of at least 5 × 10⁸ tracks/cm² have been exposed “unshielded” on the lunar surface. Grains having such track densities could also represent particles abraded from rock surfaces which had an “unshielded” exposure. In contrast, it is thought that grains with track densities in the range 10⁶–10⁷ have been located within the regolith at depths between 0.05 and 10 cm. Unshielded exposure to cosmic rays indicates a greater likelihood of exposure to the solar wind, i.e., grains with track density ≥ 10⁸ are more likely to have been exposed to solar wind. The correlations outlined under (1), (2), and (3) are explicable in terms of an extralunar origin for the CH₄, possibly as a result of solar

wind activity. If indeed solar wind implantation is the major source of the CH_4 observed in the Apollo 11 and 12 fines, it should be located well within the outer 1000 Å of an individual grain.

A method of shallow etching of lunar fines should provide information about the location of the hydrocarbon gases in relation to the surfaces of the grains. NaOH has been used to reveal the tracks left by cosmogenic heavy nuclei which impinged on silicate grains in meteorites (LAL *et al.*, 1968). The rate of etch of silicate minerals will depend both on the mineralogy and on the track densities present. Etching of these minerals is slow at elevated temperature (*ca.* 160°C); the rate of etch of lunar fines at ambient must be even slower. In comparison with acid treatment, where gas evolution is vigorous and the residue is an off-white flocculent material, alkali treatment affords no visible gas evolution and the samples appear unaltered. The use of NaOD as etching reagent allows indigenous hydrocarbons and hydrolysis products to be distinguished without appreciably altering the slow rate of etch. NaOD treatment of both Apollo 11 fines and a size-differentiated sample of these fines (200–240 mesh) showed that >60% of the CH_4 released by acid etch can be released by this reagent (Fig. 5). The quantity of CD_4 concurrently released is small. Although we are unable at present to measure accurately the depth of etch, these preliminary data indicate that a significant proportion of the CH_4 may be located at the surface of the fines. An NaOD etch of mineral concentrates having a narrow size-distribution and a known rate of etch should confirm the surface location of the CH_4 .

We have previously outlined a number of synthetic processes which could lead to the formation of hydrocarbons from lunar, meteoritic, or solar carbon as a result of solar wind bombardment of the lunar surface (ABELL *et al.*, 1970a, 1970b). There are several distant laboratory analogies for such reactions. Irradiation of diamond crystals with protons or deuterons (0.7–1.5 MeV) affords products with carbon-hydrogen or carbon-deuterium bonds, respectively (ZELLER and DRESCHOFF, 1968). Protons produced by microwave discharge react with soot (HARRIS and TICKENER, 1947) or graphite (SHAHIN, 1962) to produce C_1 and C_2 hydrocarbons. Similarly protons or tritium atoms produced from a hot tungsten filament afforded C_1 – C_4 hydrocarbons after reaction with lampblack, graphite or diamond dust (GILL *et al.*, 1967). The conditions prevailing in these reactions are somewhat different from those which might be expected during a solar wind synthesis; however, it is noteworthy that methane and other low molecular weight saturated and unsaturated hydrocarbons were always observed among the products obtained from the interaction of hydrogen atoms and various forms of carbon.

Indigenous gases in lunar basalt 12022

Gas chromatographic analysis was carried out on the gases released by in vacuo crushing of two interior chips of the crystalline rock 12022; CH_4 was the only gas observed and was present in concentrations just in excess of the detection limit of the analytical method. Acid etch (DF) of the crushed sample released (Table 2) methane as CH_4 and ethane as C_2H_6 . No CD_4 or C_2D_6 was observed. It is unlikely that the CH_4 and C_2H_6 could be contaminants arising from adhering fines; fully deuterated species would also be released from this source of contamination, if present. No data

are at present available for the isotopic composition of the acetylene and ethylene released; however, it appears that the CH_4 and C_2H_6 are of primordial origin. If this is the case, there may be a small primordial component in the fines, although the extent of losses of this component during formation of the fines is unknown. BLOCH *et al.* (1971) have examined the gases released from a number of crystalline rocks (12021, 12063, 12075, 10057) using an inefficient in vacuo crushing procedure. The only carbon-containing species observed was CH_4 at concentrations ranging from 0.01 to 1.0 ng/g. BLOCH *et al.* suggest that the CH_4 is representative of the magmatic gas phase (primordial). Application of the same crushing procedure to a number of breccias released 10^2 – 10^3 times the concentration of trapped gas as did the crystalline rocks. CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 were among the species observed. Although the crushing procedure used is mild, it is not impossible that hydrolysis reactions take place. Synthetic products would be recognised by D_2O exchange prior to crushing. Glow discharges in gas emissions have been proposed as explanations for transient lunar phenomena. If magmatic hydrocarbon gases are indeed observed in a range of igneous rocks, their presence may explain the carbon-containing species in the spectrum observed (KOZYREV, 1959) during such an event.

Carbides in lunar fines

Mineralogical observations have indicated the presence of cohenite in the Apollo 11 fines (FRONDEL *et al.*, 1970; ANDERSON *et al.*, 1970). Acid hydrolysis (DF) of cohenite liberates the same C_1 and C_2 deuterocarbons (with the exception of acetylene) and in similar relative proportions, as do the Apollo 11 fines. Cohenite must be partly responsible for the hydrocarbon species liberated from the fines; the same conclusion was reached by CHANG *et al.* (1970), using undeuterated acid. However, hydrolysis of cohenite yields only 1–2% of hydrocarbons. Assuming similar yields from lunar carbides, the quantities of deuterocarbons released from the lunar fines by deuterated acids would require carbon contents greatly in excess of those observed. A significant proportion of the carbide in the fines is thus likely to be extremely finely divided. At present there is no mineralogical evidence for the presence of carbide in Apollo 12 fines. DF etch (Table 2) shows that carbides are present in all samples of Apollo 12 fines studied. Their presence should be sought by mineralogical examination. No CD_4 or C_2D_6 was observed among the products of DF etch of the olivine basaltic rock 12022. The isotopic composition of the acetylene and ethylene released is unknown and their source (indigenous gases or carbide hydrolysis products) remains uncertain. More data from a variety of crystalline rocks are clearly necessary; however, the absence of CD_4 and C_2D_6 from the gases released from rock 12022 is in agreement with an extralunar origin for the carbide in the fines giving rise to these species. An extralunar origin could indicate contributions from meteoritic impact, solar wind implantation, or both.

A number of pieces of evidence must be considered in relation to these origins. (1) Meteoritic cohenite is found almost exclusively in coarse octahedrites containing 6–8% by wt. nickel (BRETT, 1967). All lunar petrographers have observed the presence of metallic iron without nickel in the Apollo 11 crystalline rocks, but in the fines and

breccias some of the iron is associated with nickel (JEDWAB and HERBOSCH, 1970). FRONDEL *et al.* (1970) have reported that the nickel content of the iron–nickel grains and inclusions ranges from 3 to 14.6%, most particles being in the range 6–7%. GOLDSTEIN and YAKOWITZ (1971) have measured the nickel and cobalt contents of a number of iron particles and inclusions in Apollo 12 fines. Approximately 15% of the metal inclusions had nickel and cobalt contents in the known range for meteoritic composition; four of the six individual metal grains studied were of meteoritic origin. We infer that there are in the lunar fines, iron–nickel grains and inclusions of meteoritic origin, with iron–nickel ratios in the range necessary for cohenite to be present. Thus, both Apollo 11 and 12 fines contain meteoritic iron grains and inclusions with nickel contents compatible with those observed in meteorites containing cohenite. (2) The two values for the $\delta^{13}\text{C}$ value (+5, +14 per mil) for the total hydrocarbons released by HCl etch of 12023 fines (CHANG *et al.*, 1971) are outside the range of the $\delta^{13}\text{C}$ values (–4 to –8 per mil) reported for meteoritic carbide. The hydrocarbons released from this sample also contain an indigenous component (*ca.* 25%, Table 2) and the conversion of carbide to hydrocarbons may not be quantitative. Despite these considerations, the disparity in $\delta^{13}\text{C}$ values indicates that the carbide in lunar samples is different from carbide of known meteoritic origin. (3) The carbon accounted for as CD_4 and C_2D_6 from acid etch of Apollo 11 and Apollo 12 fines (Tables 1 and 2) approximately parallels the total carbon abundances of the samples (MOORE *et al.*, 1970; MOORE *et al.*, 1971). Similar observation can be made for the indigenous hydrocarbons (see above). The parallelism observed in each case can only be approximate because of the variations in the measured CD_4/CH_4 ratios. In addition, this relationship between CD_4 and total carbon content appears to be valid for the size-differentiated fines: a surface area-correlated phenomenon could be responsible for a fraction of the carbide in the fines. (4) The quantities of CD_4 , like those of CH_4 , released by DF etch of Apollo 11 and Apollo 12 fines, appear to correlate with the ^{36}Ar abundances, cosmic ray exposure ages and extent of amorphous surface coating, measured for the same samples (Table 3). The trend appears to be valid although as already indicated, the CD_4/CH_4 ratios vary between samples. These observations suggest that the carbide, like the CH_4 , may have a component resulting from exposure on the lunar surface.

In summary, (1) suggests that the presence in lunar fines of iron/nickel particles of meteoritic origin is compatible with a contribution of meteoritic carbide. The microscopic carbide grains observed in Apollo 11 samples (FRONDEL *et al.*, 1970; ANDERSON *et al.*, 1970; ADLER *et al.*, 1970) probably arise from this source. Isotope ratio measurements, (2) above, suggest that overall, lunar carbide in Apollo 12 fines is different from meteoritic carbide. However, the “hydrogen stripping” process proposed by BERGER (1970) and KAPLAN and SMITH (1970) can be invoked to explain the ^{13}C enrichment (CHANG *et al.*, 1971). Considerations (3) and (4) suggest that the lunar carbide may have a contribution arising from solar wind implantation. Thus, the data at present available point towards a solar wind contribution and a meteoritic contribution to lunar carbide. Carbon atoms implanted by the solar wind into metal grains and inclusions could generate sub-microscopic moieties having the stoichiometry of carbides (*cf.* CHANG *et al.*, 1971). The necessary metal particles are available from

both meteorites and lunar igneous rocks (GOLDSTEIN and YAKOWITZ, 1971; REID *et al.*, 1970). The major portion (80%) of the metal inclusions in the Apollo 12 fines originates in the igneous rocks (GOLDSTEIN and YAKOWITZ, 1971). Rock 12022 does not contain hydrolysable carbide. If this result proves to be typical of other rocks, then definitive evidence for carbide or carbidelike materials arising from solar wind implantation could be provided by DF or DCl etch of abraded material containing metal inclusions, selected from the fines.

Other gases

The quantities of CO observed among the gases released by DF etch of both Apollo 11 and Apollo 12 fines are of the order of 1–3 $\mu\text{g/g}$. However, the reaction of one sample of Apollo 11 fines with DCl at elevated temperature (120°C for 90 hr) afforded CO at a concentration of 65 $\mu\text{g/g}$. Similar experiments on Apollo 12 fines (12023 and 12037) released CO in quantities < 1 $\mu\text{g/g}$. We are unable at present to explain this one anomalously high result. At present insufficient data are available for comparisons to be drawn between CO content and other parameters such as total carbon content, particle size, exposure age, etc. ORÓ *et al.* (1971) have suggested that the CO₂ released from Apollo 11 fines by heating at temperatures up to 700°C may be ascribed to terrestrial contamination. The CO₂ observed in our mass spectrometric analyses could not be completely accounted for by residual air in the analytical system. However, it could have arisen through adsorption on to the surfaces of the fines during the handling procedures at Houston and Bristol. We hope to resolve soon the ambiguities in the CO₂ measurements made from gas chromatographic analysis of the products of acid etch. At present we are unable to decide whether the CO₂ is present in the lunar fines as such, is released from carbonates by reaction with acid or is adsorbed contamination.

CONCLUSIONS

All of the Apollo 11 and Apollo 12 samples of fines examined contain indigenous methane and carbide; indigenous ethane has also been detected in several samples. Comparison of the methane content with a number of other parameters indicates that solar wind activity may play a major role in the synthesis of the methane. Synthesis from the solar wind necessarily requires that the methane be located at the surface of the fines and shallow etching at ambient temperature with alkali appears to confirm this surface location. Analysis of interior chips of an olivine basaltic rock (12022) suggests that small quantities of primordial methane are present, which could also contribute to some extent to the methane in the fines. No acid-hydrolysable carbide was detected in the interior of the rock. This observation requires extension to other lunar rocks, but this preliminary result indicates an extralunar origin for the carbide in the fines. The data available at present are in agreement with a dual extralunar origin for the carbide, that is, an origin from both meteoritic impact and solar wind implantation of carbon.

It appears that the chemistry of the carbon on the Moon may be very dependent on the processes operating on the lunar surface (ABELL *et al.*, 1970a, 1970b). More

detailed studies will allow an understanding of the nature of these processes. As we have indicated, it is necessary to integrate the findings obtained from a study of the carbon compounds with the analyses of other elements and with physical measurements such as cosmic ray track density, rate of erosion, etc. The importance of such a study is that the processes involved should be applicable to appropriate planets and other solid bodies in this and other solar systems. Information about these processes cannot be gained from analysis of terrestrial rocks, although laboratory experiments designed to simulate their operation will complement the results from detailed analysis of lunar samples.

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REFERENCES

- ABELL P. I., DRAFFAN G. H., EGLINTON G., HAYES J. M., MAXWELL J. R., and PILLINGER C. T. (1970a) Organic analysis of the returned Apollo 11 lunar sample. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2, pp. 1757-1773. Pergamon.
- ABELL P. I., EGLINTON G., MAXWELL J. R., PILLINGER C. T., and HAYES J. M. (1970b) Indigenous lunar methane and ethane. *Nature* **226**, 251-252.
- ADLER I., WALTER L. S., LOWMAN P. D., GLASS B. P., FRENCH B. M., PHILPOTTS J. A., HEINRICH K. J. F., and GOLDSTEIN J. I. (1970) Electron microprobe analysis of Apollo 11 lunar samples. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 1, pp. 87-92. Pergamon.
- ANDERSON A. T., JR., CREW A. V., GOLDSMITH J. R., MOORE P. B., NEWTON J. C., OLSEN E. J., SMITH J. V., and WYLLIE P. J. (1970) Petrologic history of moon suggested by petrography, mineralogy, and crystallography. *Science* **167**, 587-589.
- BARBER D. J., HUTCHEON I., and PRICE P. B. (1971) Extralunar Dust in Apollo Cores? *Science* **171**, 372-374.
- BERGER R. (1970) Reaction of carbon and sulphur isotopes in Apollo 11 samples with solar hydrogen atoms. *Nature* **226**, 738-739.
- BHANDARI N., BHAT S., LAL D., RAJAGOPALAN G., TAMHANE A. S., and VENKATAVARADAN V. S. (1971) Fossil track studies in lunar materials, II. The near surface and postdepositional exposure history of regolith components at the Apollo 12 site including the double core 25,28. Second Lunar Science Conference (unpublished proceedings).
- BLOCH M., FECHTIG H., FUNKHOUSER J., GENTNER W., JESSBERGER E., KIRSTEN T., MÜLLER O., NEWKUN G., SCHNEIDER E., STEINBRUNN F., and ZÄHRINGER J. (1971) Meteorite impact craters, crater simulations, and the meteorite flux in the early solar system. Second Lunar Science Conference (unpublished proceedings).
- BORG J., DRAN J. C., DURRIEU L., JOURET C., and MAURETTE M. (1970) High voltage electron microscope studies of fossil nuclear particle tracks in extra-terrestrial matter. *Earth Planet. Sci. Lett.* **8**, 379-386.
- BORG J., DURRIEU L., JOURET C., and MAURETTE M. (1970) The ultramicroscopic irradiation record of micron-sized lunar dust grains. Second Lunar Science Conference (unpublished proceedings).

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- BRETT R. (1967) Cohenite: Its occurrence and proposed origin. *Geochim. Cosmochim. Acta* **31**, 143–159.
- BURLINGAME A. L., CALVIN M., HAN J., HENDERSON W., REED W., and SIMONEIT B. R. (1970) Study of carbon compounds in Apollo 11 lunar samples. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 2, pp. 1779–1791. Pergamon.
- 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, pp. 1857–1869. Pergamon.
- CHANG S., KVENVOLDEN K. A., LAWLESS J., PONNAMPERUMA C., and KAPLAN I. R. (1971) Carbon in an Apollo 12 sample: Concentration, isotopic composition, pyrolysis products and evidence for indigenous carbides and methane. Second Lunar Science Conference (unpublished proceedings).
- DI CORCIA A. and BRUNER F. (1970) The use of high efficiency packed columns for gas-solid chromatography, II. The semi-preparative separation of isotopic mixtures. *J. Chromatog.* **49**, 139–145.
- DRAN J. C., DURRIEU L., JOURET C., and MAURETTE M. (1970) Habit and texture studies of lunar and meteoritic materials with a 1 MeV electron microscope. *Earth Planet. Sci. Lett.* **9**, 391–400.
- EBERHARDT P., GEISS J., GRAF H., GRÖGLER N., KRÄHENBÜHL, U., SCHWALLER H., SCHWARZ-MÜLLER J., and STETTLER A. (1970) Trapped solar wind noble gases, exposure age and K/Ar-age in Apollo 11 lunar fine material. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 2, pp. 1037–1070. Pergamon.
- FRONDEL C., KLEIN C., JR., ITO J., and DRAKE J. E. (1970) Mineralogical and chemical studies of Apollo 11 lunar fines and selected rocks. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 1, pp. 445–474. Pergamon.
- GILL P. S., TOOMEY R. E., and MOSER H. C. (1967) Reactions of hydrogen and tritium atoms with carbon at 77°K. *Carbon* **5**, 43–66.
- GOLDSTEIN J. I. and YAKOWITZ H. (1971) Metallic inclusions and metal particles in the Apollo 12 lunar samples. Second Lunar Science Conference (unpublished proceedings).
- HARE P. E., HARADA K., and FOX S. W. (1970) Analyses for amino acids in lunar fines. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 2, pp. 1799–1803. Pergamon.
- HARRIS G. M. and TICKNER A. W. (1947) Reaction of hydrogen atoms with solid carbon. *Nature* **160**, 871.
- HENDERSON W., KRAY W. C., NEWMAN W. A., REED W. E., BURLINGAME A. L., SIMONEIT B. R., and CALVIN M. (1971) Study of carbon compounds in Apollo 11 and Apollo 12 returned lunar samples. Second Lunar Science Conference (unpublished proceedings).
- HEYMANN D. and YANIV A. (1970) Inert gases in the fines from the Sea of Tranquillity. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 2, pp. 1247–1259. Pergamon.
- HINTENBERGER H., WEBER H. W., VOSHAGE H., WÄNKE H., BEGEMANN F., and WLOTZKA F. (1970) Concentrations and isotopic abundances of the rare gases, hydrogen and nitrogen in Apollo 11 lunar matter. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 2, pp. 1269–1282. Pergamon.
- HODGSON G. W., BUNNENBERG E., HALPERN B., PETERSON E., KVENVOLDEN K. A., and PONNAMPERUMA C. (1970) Carbon compounds in lunar fines from Mare Tranquillitatis, II. Search for porphyrins. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 2, pp. 1829–1844. Pergamon.
- JEDWAB J. and HERBOSCH A. (1970) Tentative estimation of the contribution of Type 1 carbonaceous meteorites to the lunar soil. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 2, pp. 551–559. Pergamon.
- JOHNSON J. H., KNIPE R. H., and GORDAN A. S. (1970) Chemical Reactions in a Toepler Pump. *Can. J. Chem.* **48**, 3604–3605.
- KAPLAN I. R. and SMITH J. W. (1970) Concentration and isotopic composition of carbon and sulphur in Apollo 11 lunar samples. *Science* **167**, 541–543.

- KOZYREV N. A. (1959) Volcanic activity on the Moon. *Pokrohy Mat. Fys. Astron.* **4**, 704–708 (*Chem. Abstr.* **57**, 6932)
- KVENVOLDEN K. A., CHANG S., SMITH J. W., FLORES J., PERING K., SAXINGER C., WOELLER F., KEIL K., BREGER I. A., and PONNAMPERUMA C. (1970) Carbon compounds in lunar fines from Mare Tranquillitatis, I. Search for molecules of biological significance. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2, pp. 1813–1828. Pergamon.
- LAL D., MACDOUGALL D., WILKENING L., and ARRHENIUS G. (1970) Mixing of lunar regolith and cosmic ray spectra: Evidence from particle track studies. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 3, pp. 2295–2303. Pergamon.
- LAL D., MURALLI A. V., RAJAN R. S., TAMHANE A. S., LORIN J. C., and PELLAS P. (1968) Techniques for proper revelation and viewing of etch tracks in meteoritic and terrestrial minerals. *Earth Planet. Sci. Lett.* **5**, 111–119.
- LSPET (Lunar Sample Preliminary Examination Team) (1970) Preliminary examination of lunar samples from Apollo 12. *Science* **167**, 1325–1339.
- MEINSCHEN W. G., JACKSON T. J., MITCHELL J. M., CORDES E., and SHINER V. J. JR. (1970) Search for alkanes of 15–30 carbon atom length in lunar fines. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2, pp. 1875–1877. Pergamon.
- MOORE C. B., GIBSON E. K., LARIMER J. W., LEWIS C. F., and NICHIPORUK W. (1970) Total carbon and nitrogen abundances in Apollo 11 lunar samples and selected achondrites and basalts. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2, pp. 1375–1382. Pergamon.
- MOORE C. B., LEWIS C. F., DELLES F. M., GOOLEY R. C., and GIBSON E. K., JR. (1971) Total carbon and nitrogen abundances in Apollo 12 lunar samples. Second Lunar Science Conference (unpublished proceedings).
- MURPHY Sister M. E., MODZELESKI V. E., NAGY B., SCOTT W. M., YOUNG M., DREW C. M., HAMILTON P. B., and UREY H. C. (1970) Analysis of Apollo 11 lunar samples by chromatography and mass spectrometry: Pyrolysis products, hydrocarbons, sulfur, amino acids. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2, pp. 1879–1890. Pergamon.
- MURPHY R. C., PRETI G., NAFISSI V. M. M., and BIEMANN K. (1970) Search for organic material in lunar fines by mass spectrometry. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2, pp. 1891–1900. Pergamon.
- ORÓ J., UPDEGROVE W. S., GIBERT J., MCREYNOLDS J., GIL-AY E., IBANEZ J., ZLATKIS A., FLORY D. A., LEVY R. L., and WOLF C. J. (1970) Organogenic elements and compounds in types C & D lunar samples from Apollo 11. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2, pp. 1901–1920. Pergamon.
- ORÓ J., FLORY D. A., GIBERT J. W., MCREYNOLDS J., LICHTENSTEIN H. A., and WIKSTROM S. (1971) Abundances and distribution of organogenic elements and compounds in Apollo 12 lunar samples. Second Lunar Science Conference (unpublished proceedings).
- PEPIN R. O., NYQUIST L. E., PHINNEY D., and BLACK D. C. (1970) Rare gases in Apollo 11 lunar material. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2, pp. 1435–1454. Pergamon.
- PEPIN R. O. (1971) Personal communication.
- REID A. M., MEYER C., JR., HARMON R. S., and BRETT R. (1970) Metal grains in Apollo 12 igneous rocks. *Earth Planet. Sci. Lett.* **9**, 1–5.
- RHO J. H., BAUMAN A. J., YEN T. F., and BONNER J. (1970) Fluorometric examination of the returned lunar fines from Apollo 11. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 1, Vol. 2, pp. 1929–1932. Pergamon.
- SHAHIN M. M. (1962) Reaction of elementary carbon and hydrogen in high frequency discharge. *Nature* **195**, 992.
- ZELLER E. J. and DRESCHOFF G. (1968) Chemical reactions resulting from heavy particle bombardment of diamond. *Z. Naturforsch.* **23a**, 953–954.