

Organic analysis of the returned Apollo 11 lunar sample

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Abstract—Apollo 11 lunar fines have been examined for organic compounds by solvent extraction, vacuum crushing, programmed heating and hydrofluoric acid etching. Products were examined by low resolution mass spectrometry. Solvent extraction indicated that no single volatile compound was present in excess of 5 ppb. A variety of small organic molecules including methane and other hydrocarbons accompanied the release of carbon monoxide, carbon dioxide and the rare gases when the sample was heated in a stepwise fashion to 900°C under vacuum. Methane is more abundant (ca. 2 ppm) than argon in the gases liberated by hydrofluoric acid etch of the fines. Methane is also liberated from a dark portion of the gas-rich meteorite, Kapoeta but smaller quantities are evolved from the carbonaceous chondrite, Pueblito de Allende.

INTRODUCTION

WE HAVE undertaken analytical procedures for the detection and identification of carbon compounds over a wide molecular weight range.

The preliminary examination of the Apollo 11 rocks and fines (LSPET, 1969) pointed to an origin from high temperature melts subsequently exposed on the surface for some millions of years. This hostile environment makes biogenic products extremely improbable. Sources of carbon apart from indigenous carbon, are likely to include the solar wind and comet and meteorite impact (DRAFFAN *et al.*, 1969).

Preliminary data on the organic carbon content of the fines were available from two experiments carried out at Houston (LSPET, 1969). The results indicated an organic carbon content of between 1 and 10 ppm. A measure of total carbon was subsequently made available by MOORE *et al.* (1970). Weighted mean analyses of two samples (10086 A and 10086 B) of the bulk fines indicated levels of 142 and 226 ppm.

We decided to examine the sample in four main ways:

(1) Extract lipids and polymeric materials soluble in organic solvents and subject these to combined gas chromatography–mass spectrometry (gc–ms) with and without prior derivatisation. Techniques modified to minimize terrestrial contamination were devised.

Although indigenous carbon compounds of biological origin were not expected in the lunar fines (DRAFFAN *et al.*, 1969) a search for such compounds had to be an essential part of the analytical study. The preliminary results from the Lunar Receiving Laboratory (LRL) indicated that a minimum of 10 g of sample would be necessary.

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(2) Pyrolyse a sample under vacuum in a carefully controlled stepwise manner to 900°C and analyse the products by mass spectrometry. A trapping system would be incorporated to permit fractionation. In this way we planned to study temperature and time dependence of the evolution of individual organic compounds, whether occluded or the products of pyrolysis of polymeric materials.

(3) Crush the lunar fines *in vacuo*, trap the head-space gases and examine them by mass spectrometry (GOGUEL, 1963). We hoped to detect occluded low molecular weight organic compounds, the progress of the crushing procedure being monitored by the release of rare gases. This experiment, like that listed below, would allow the detection of compounds such as methane which might conceivably have been formed as a result of solar wind bombardment.

(4) Etch the sample with hydrofluoric acid and again analyse the released gases by mass spectrometry, using a trap system.

The organic content of meteorites that have fallen on the earth would be expected to furnish additional information about extra-terrestrial organic matter. Accordingly, the gas-rich achondritic howardite, Kapoeta and the carbonaceous chondrite, Allende, were selected for comparative analyses.

The low levels of organic compounds reported in the preliminary examination of lunar material (LSPET, 1969) together with the large surface area and presumed highly adsorptive nature of the fines, demanded that stringent measures be taken to avoid organic contamination at all stages of our analyses. These arrangements permitted the classical geochemical procedures of solvent extraction, separation, evaporation, derivatisation and chromatography using only small volumes of solvent and with only brief exposure of samples, extracts and fractions to the atmosphere and the laboratory environment.

EXPERIMENTAL

General

The method of contamination control consisted of a secondary organic barrier in the form of clean filtered air supplied to a clean working station, and a primary organic barrier composed of all-glass and Teflon systems pressurised with inert gas. The gases used were nitrogen (British Oxygen Ltd., white spot grade) and helium (Air Products Ltd. C. P. 99.99%). Normal clean room equipment, apparatus, tools, clothing and procedures were used. Glass apparatus, precleaned with hot chromic acid, was baked at 500°C (12–16 hr) when required for direct contact with lunar fines. Equipment cleaned in this way was stored in glass containers under nitrogen passed through 5 Å molecular sieve. Other glassware was stored in closed glass containers and washed with solvent immediately prior to use. Stainless steel, aluminium and Teflon items were degreased by extraction with solvent in an ultrasonic tank.

Solvents used were either undistilled Nanograde (Mallinkrodt) or distilled Analar grade (Hopkins and Williams).

Establishment of a clean area—secondary organic barrier

The ventilation system of a small (150 ft²) laboratory, reserved for the lunar sample analysis, was modified so that the pressurising supply of fresh air to the room was ducted through the filters of a “class 100” laminar flow bench (Microflow Ltd.). Materials such as lubricants, various plastics, rubber, paper and other substances likely to shed organic particles were, where practical, excluded from the laboratory.

The ambient background was monitored in two ways.

(i) Aliquots (10–20 g) of alumina (Woelm, Grade 1 neutral), previously soxhlet-extracted with benzene–methanol (3:1) and then baked at 500°C for 16 hr in air, were exposed in open vessels for 24 hr. The recovered alumina was eluted with benzene–methanol (30 ml) and the eluate evaporated to dryness under closed conditions (Fig. 1) in a tapered micro-vial (capacity 3 ml). Solvent (1 μ l.) was added and an aliquot (0.5 μ l.) immediately removed for glc. Concentration of solutions of standard mixtures by this method indicates that components more volatile than n-C₁₄ alkane are substantially lost.

A Perkin–Elmer F-11 mark 2 gas chromatograph, containing a 10 ft \times $\frac{1}{16}$ in. column (3% OV-17 on Chromosorb W, 100–120 mesh) programmed from 90° to 280° at 5°/min, was used for contamination assays. A major contaminant was consistently recognised in the extracts from the exposed alumina and shown to be absent from control extracts of unexposed alumina. A mass spectrum obtained by gc–ms was consistent with an unresolved mixture. An abundant ion at m/e 149 strongly suggested the presence of phthalate esters. The FID response to the major unidentified

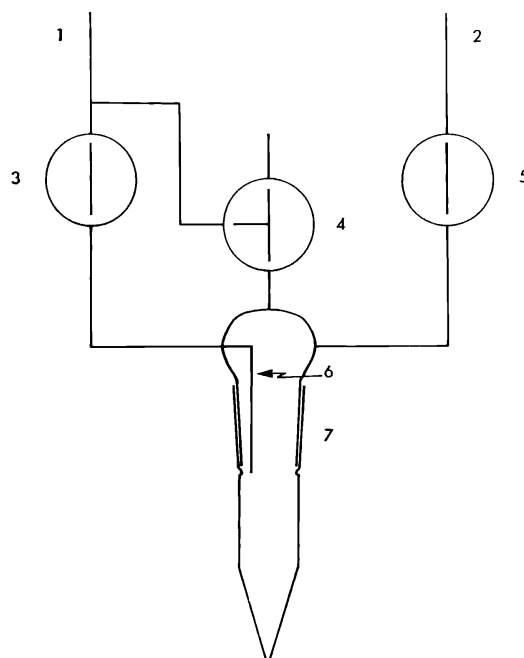


Fig. 1. Diagrammatic representation of a portion of derivatisation closed system for evaporation and derivatisation at ambient temperature. 1. Connection to nitrogen supply *via* pressure-regulated manifold (1–2 psi above atmospheric pressure); 2. Connection to vent manifold; 3, 4, 5. Teflon taps (solvent or reagent may be introduced by syringe needle through the bore of tap 4); 6. Capillary providing a jet of nitrogen; 7. Standard 10 mm ground glass joint on a tapered vessel of 3 ml capacity.

peak (carbon number 22.7) was arbitrarily compared with that of n-C₂₂ alkane. Crude quantitation afforded a spread of results for the principal contaminant in the range $0.3\text{--}2.5 \times 10^{-9}$ g/hr per g of exposed adsorptive material. Thin layers of dispersed alumina gave the highest results. An additional unresolved envelope of peaks from carbon numbers 15–30 was also present at an estimated combined level of $20 \pm 10 \times 10^{-9}$ g/hr per g of adsorptive material.

(ii) Solvent (ether or hexane, 200 ml) was allowed to evaporate to dryness in an open vessel. Concentration of the residue, followed by glc, afforded qualitatively similar results to the alumina exposure assay. Silylation of residues with bis-(trimethylsilyl)-trifluoroacetamide gave no shift in retention time of the major contaminant.

Soxhlet extraction of the following materials with benzene/methanol followed by gas chromatographic analysis of the residues established the main airborne contaminant to be absent: PVC

tubing, polythene gloves, laminar flow bench and central ventilation system filter materials. No contamination attributable to the above materials was detectable in any of the analyses.

Closed analytical systems—Primary organic barrier

Extraction closed system. The major portion of this system is shown schematically in Fig. 2. The complete apparatus permits extraction, evaporation, separation on columns of adsorbents, and collection of fractions—all in a closed apparatus held under a positive pressure of pure inert gas. The relatively large reserve volumes (1 l.) of solvent ensure that a considerable number of experiments, including the necessary blank and control studies, may be performed with a single batch of solvent. Solvent contamination levels therefore remain constant. Calibrated volumes of different solvents can be run under gas pressure into the extraction vessel. Samples are extracted by placing an

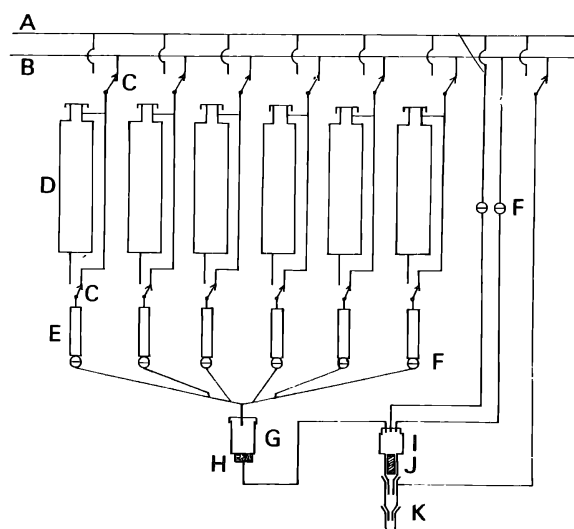


Fig. 2. Diagrammatic representation of extraction closed system. The apparatus as shown allows extraction, evaporation and collection. When required, a chromatographic column and fraction collector replace the collection unit shown. A. Vent manifold; B. Pressure manifold; C. Two way taps (upper Teflon, lower glass); D. Solvent reservoirs (1 l. capacity); E. Calibrated delivery volumes; F. One way taps (upper Teflon, lower glass); G. Extraction vessel; H. Glass sinter; I. Evaporation vessel; J. Magnetic valve; K. Collection vessel.

ultrasonic tank, containing water, around the extraction vessel. Opening and closing of appropriate taps provides a sufficient pressure of gas to transfer solvents and solutions from the extraction vessel to the evaporation vessel, collection vessel or chromatographic column and fraction collector (if present). The magnetic valve permits solutions to be contained in the evaporation vessel while volumes are reduced for collection or for chromatography. The unit for extraction, evaporation and collection is detachable but the remainder of the apparatus, once assembled, is not exposed to air. Teflon taps do not come in contact with liquid solvents and only briefly with solvent vapour; all other taps are greaseless glass taps. Cross contamination between solvents is avoided by flushing taps and lines with gas.

Derivatisation closed system. The possibility of polar material being present in a lunar sample extract required that a chemical derivatisation step be included to increase volatility before gc-ms analysis. A diagrammatic representation of a simple glass unit designed to allow several operations to be carried out under a purified nitrogen stream is shown in Fig. 1. A number of these units are incorporated in the pressure and vent manifolds of the extraction closed system. Dilute solutions containing the material to be derivatized may be concentrated and reagent or solvent introduced to the reaction vessel by syringe while an atmosphere of nitrogen is maintained in the system. Reactions which will

go to completion at room temperature and which employ reagent readily removed under a stream of nitrogen can be conveniently handled in a unit of this type. Silylation with bis-(trimethylsilyl)-trifluoroacetamide is one such procedure. The efficiency of this procedure was determined by treating a mixture of β -naphthol, α -naphthylamine, n -C₁₆ and n -C₁₈ alcohols and n -C₂₂ fatty acid (100 μ g/component) with bis-(trimethylsilyl)-trifluoroacetamide (30 μ l; Applied Science) at ambient temperature for 18 hr under a positive pressure of nitrogen. Gas chromatographic analysis (column 10 ft \times $\frac{1}{16}$ in., 3% OV-17 on Chromosorb W, programmed from 150° to 280°C at 5°/min) showed only peaks arising from the appropriate trimethylsilyl derivatives. No unreacted starting materials were observed. In another experiment to investigate the efficiency of the transfer procedure the same mixture (100 ng/component) containing n -hexadecanoic acid 1-¹⁴C (4 ng) was similarly treated with bis-(trimethylsilyl)-trifluoroacetamide (10 μ l.). A portion (25%) of the radiolabelled material remained in the reaction vessel after evaporation and removal of the products for glc.

The contamination level in the system as operated in purified inert gas was determined by attaching vessels containing aliquots (6 g) of alumina and leaving them for four hours under a pressure of nitrogen. Gas chromatographic analysis of the extracts of the alumina revealed no detectable contamination at the FID setting used (detection level equivalent to less than 5 ng/component). However, if the nitrogen pressure was shut off and the alumina left in the system for a further 16 hr to allow equilibration via joints and taps with the air in the laminar flow bench the ubiquitous phthalate esters contamination appeared at a level of ca. 0.5×10^{-9} g/hr per g alumina. This indicated that the two closed systems were indeed necessary as primary organic barriers.

Sample handling and storage

The lunar sample container (sample No. 10,086.19, bulk fines D, 105 g) was opened and aliquots of the sample transferred, to glass tubes which were then attached to a unit of the derivatisation closed system and sealed off under nitrogen with a hydrogen/oxygen torch. Exposure time was kept to a minimum. The soxhlet extracted (benzene/methanol) samples of alumina (heated to 550°C for 16 hr) needed for blank experiments were exposed, handled and stored in the same way as the lunar fines.

The sample of Pueblito de Allende meteorite, which had been received in a Teflon bag, was stored in a desiccator until required. The exterior surface (ca. 2 mm) was removed and the sample (5 g) pulverised in a porcelain mortar and pestle to pass 22 mesh. The Kapoeta meteorite sample (4.3 g after removal of outer surface), was handled in the same way. All operations, prior to the pyrolysis and the hydrofluoric acid etching procedure, were carried out in the clean area.

Mass spectrometry

Mass spectra were determined on a Varian-MAT CH-7 single focussing mass spectrometer. Gas mixtures were admitted from the appropriate reaction system, by means of a variable leak (valve: Hoke Engineering, 413-HT). The sensitivity of the mass spectrometer was sufficient to detect a flow of 0.1 ng/sec of methane.

The response was calibrated with aliquots of a gas mixture (British Oxygen Ltd, Grade X purity) comprising neon 80.7%, argon 7.5%, krypton 1.9%, methane 7.8% and ethane 2.1%. The ion current in coulombs/g was measured for an individual calibrant gas by calculating the percentage contribution to the total ionisation produced by the mixture using the ten most abundant peaks in its mass spectrum. Peak heights were converted to absolute peak heights using the relationship between the height of the base peak and that of the ion m/e 43 of n -butane (CORNU and MASSOT, 1966). The sensitivity of detection and the accuracy of the isotopic abundance measurements for rare gases are inferior to those obtainable by the static method normally used in rare gas analysis. The amounts of krypton and xenon in the lunar fines are insufficient for detection at the sample sizes and sensitivities employed. Quantitative data for low molecular weight species (H₂, ³He, ⁴He) were not feasible under the ion-focussing conditions used.

Solvent extraction of lunar fines

An aliquot (14.8 g) of the lunar sample was added to the extraction chamber (G) of the detachable unit (Fig. 2). This unit was then re-attached to the extraction closed system with the minimum

exposure of the sample to the air (ca. 2 min). Benzene/methanol (3:1, 9 ml) was added from the appropriate reservoir and the sample extracted (15 min.) in an ultrasonic tank. The extract was passed under helium pressure (2 psi) to the evaporation chamber (I) and the solvent evaporated at ambient temperature under a flow of helium. The extraction was repeated (4.5 ml benzene/methanol) and the extract again evaporated. The magnetic valve (J) was lowered and benzene/methanol (3 ml) was passed through the system under helium pressure and the washings collected. This washing procedure was repeated (2 ml benzene/methanol) and the washings collected separately.

The extracts were centrifuged in stoppered tubes, to remove any lunar fines which had passed through the sinter (H) in the extraction chamber, and the supernatant removed. Evaporation of the supernatant and washings to dryness in the derivatisation closed system (Fig. 1) afforded the extract as a yellow gum (ca. 2 μ l). The extract did not dissolve appreciably in benzene/methanol (6 μ l) but dissolved in methanol (2 μ l). An aliquot (0.6 μ l) of the yellow methanolic solution was injected into the gc-ms instrument. No peaks were detected in the total ion current gas chromatogram at the minimum level of detection (equivalent to 25 ng of n-C₂₀ alkane). The remainder of the extract was silylated by heating (45 min, 60°C) with 5 μ l of reagent drawn from a freshly-opened ampoule of bis-(trimethylsilyl)-trifluoroacetamide. The gas chromatogram of the total product, when injected into the gc-ms, showed only two distinct peaks, which were also present in the product of a blank

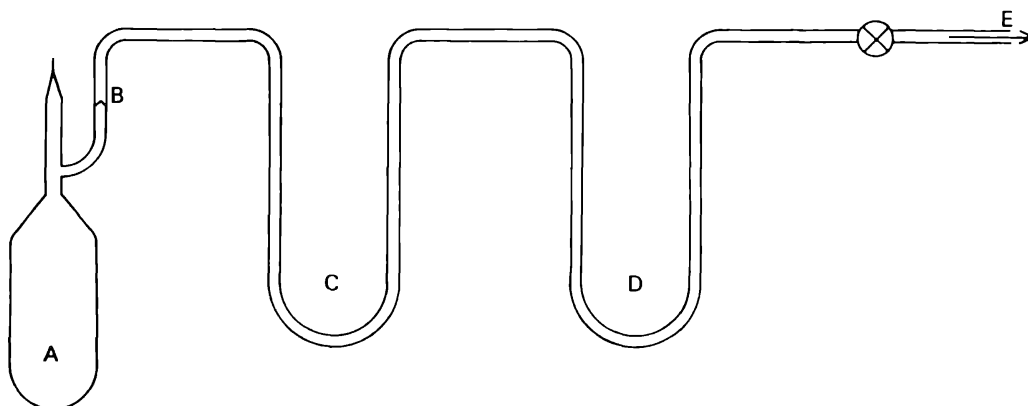


Fig. 3. Lunar sample pyrolysis system. A. Pyrolysis vessel; B. Break seal; C. Trap cooled in solid carbon dioxide/acetone; D. Trap cooled in liquid nitrogen; E. Entry valve to mass spectrometer ion source.

silylation procedure. The efficiency of the extraction and isolation procedures was determined by adding a solution of n-octadecane I-¹⁴C (100 ng) in hexane (100 μ l) to activated alumina (10 g Grade I neutral) contained in the extraction closed system. Extraction of this material and subsequent evaporation and collection in a manner similar to that used for the lunar sample gave a 70 per cent recovery of n-octadecane I-¹⁴C. Immediately prior to each extraction and isolation procedure a blank experiment was carried out in the apparatus with the same volumes of solvent alone. Alumina (15 g) which had been exposed, handled and stored with the lunar fines was also used as a blank in the analytical system. No peaks were detectable in the gas chromatograms of the products from the blank experiments.

Vacuum crushing

A stainless steel (type EN58BM; C, 0.1%) capsule (volume ca. 35 ml), equipped with a stainless steel ball and two glass break-seals, and previously baked out (36 hr, 550°C) under vacuum (10⁻⁶ torr) was used in this experiment. The capsule containing an aliquot (2–5 g) of lunar sample was baked out (30 min, 150°C) under the mass spectrometer vacuum (10⁻⁶ torr) to remove adsorbed terrestrial gases, as far as possible, from the sample. Heating was continued until the background had diminished to the level observed prior to break-seal opening. After cooling, the capsule, sealed under vacuum, was removed from the trap system and the sample crushed by subjecting the capsule to 4 min of intermittent shaking (Glen Creston Pulverizer, catalogue No. 8000). The capsule was then reconnected to the trap system, the system evacuated, the second break-seal broken and the gases

allowed to flow into a molecular sieve (5 Å)/liquid nitrogen trap. A mass spectrum of the non-condensed gases was recorded. Cooling of an unpacked trap to liquid nitrogen temperature and warming of the molecular sieve trap to ambient allowed a spectrum of sieve-trapped gases to be recorded. Finally, a spectrum of the remaining gases was obtained when the unpacked trap was warmed to ambient temperature.

Blank experiments were carried out with the capsule and ball alone.

Vacuum pyrolysis

The system used is shown in Fig. 3. The pyrolysis vessel (ca. 30 ml) was baked out before use (12 hr 550°C) and was constructed of pyrex or quartz, depending on the maximum temperature required (500° or 900°C, respectively). Baking (130°C) of the entire system, containing an aliquot (ca. 2 g) of lunar fines, was carried out under the mass spectrometer vacuum until the background spectrum reached a constant low intensity. The temperature in the pyrolysis vessel was raised in

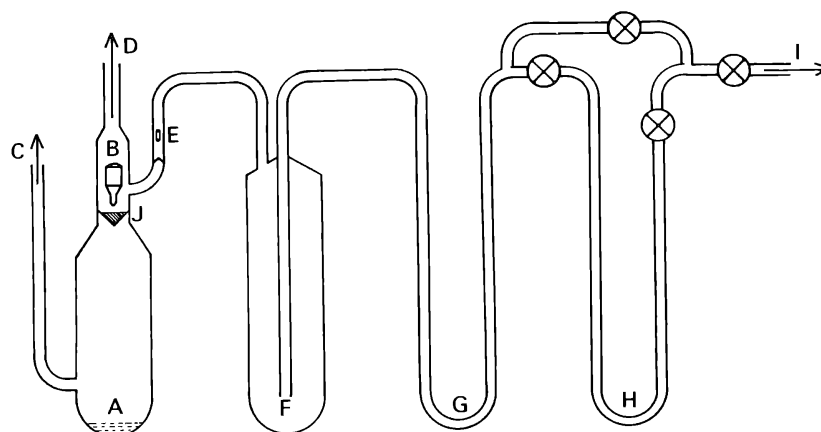


Fig. 4. Hydrofluoric acid etching apparatus. A. Reaction vessel containing hydrofluoric acid; B. Sample vessel; C. Hydrofluoric acid degas exit; D. Sample degas exit; E. Break seal; F, G. Liquid nitrogen traps; H. Molecular sieve/liquid nitrogen trap; I. Entry valve to mass spectrometer ion source; J. Dump seal.

100° steps (heating time ca. 5 min) and the baked-out gases examined after the temperature had been held steady (ca. 15 min) at the end of each temperature increment. The untrapped, non-condensable gases were metered into the mass spectrometer. The total ion current was recorded continuously and spectra recorded repeatedly over a period of up to 30 min. Similarly, mass spectra of the trapped gases were subsequently recorded by raising the liquid nitrogen trap to ambient temperature and metering the gases into the mass spectrometer over a further period of time (up to 10 min). A blank experiment was also carried out with empty pyrolysis vessels.

Hydrofluoric acid etching

The apparatus shown in Fig. 4 was used for all etching experiments. The molecular sieve trap was baked (220°C) under vacuum (10^{-6} torr) prior to each experiment. After removal of adsorbed gases from the sample vessel and the reaction vessel under vacuum (150°C, 10^{-6} torr), an aliquot (ca. 0.2 g) of the sample was added to the sample vessel and the adsorbed gases again removed. The sample vessel was then sealed under vacuum. Hydrofluoric acid (ca. 1 ml, 40%, Hopkin and Williams, "Analar" grade) was added to the reaction vessel and this then sealed on to a vacuum line. Gases dissolved in the hydrofluoric acid were removed by several freeze (liquid nitrogen)/pump/thaw cycles. Reaction of the hydrofluoric acid with the pyrex glass of the reaction vessel was evidently slow since no gas evolution was visible, either before or after degassing. The reaction vessel was next cooled in liquid nitrogen, sealed off under vacuum, removed from the vacuum line and the dump-seal broken by shaking the vessel. When all of the sample was in contact with the hydrofluoric acid the reaction

vessel was warmed to ambient and the reaction allowed to proceed (30 min). Copious evolution of gases occurred. The mixture was then cooled to liquid nitrogen temperature, the reaction vessel sealed on to the trap system, and the system pumped down. Only when the background in the mass spectrometer was at an acceptable low level was the trapping system cooled to liquid nitrogen temperature and the break-seal broken. The reaction vessel was allowed to warm to ambient and the mass spectra of untrapped gases (H_2 , He, Ne) recorded. Hydrofluoric acid gas, silicon tetrafluoride and water were retained in the two preliminary traps, along with any high molecular weight organic compounds. Gases trapped in the molecular sieve/liquid nitrogen trap (Ar , CH_4 , O_2 and N_2) were analysed by warming the trap to ambient.

In another experiment the molecular sieve trap was by-passed and the gases examined directly by the mass spectrometer. Blank experiments with hydrofluoric acid alone and with alumina were also carried out.

RESULTS

Contamination control

Calibration of the FID response allowed background contamination to be expressed in semi-quantitative terms. The results indicated that the system of contamination control is adequate for measurement of low levels of organic compounds. The level of contamination of the principal contaminant within the secondary barrier, that is within the laminar flow bench in the clean area, ranged from 0.3 to 2.5×10^{-9} g/hr per g of exposed adsorptive material. Over a period of three months the qualitative reproducibility of these results was satisfactory.

Within the main primary barrier, that is the extraction and derivatisation closed systems, no contaminant was observed using the experimental procedures outlined above.

The double barrier approach described herein should have wide applicability in organic geochemistry; difficulties and limitations associated with glove box working are avoided.

Solvent extraction

Gc-ms examination of an aliquot of the benzene methanol extract and the silylated residue from 15 g of fines afforded no indication of any peaks assignable to the lunar sample. From these data we infer that individual compounds in the approximate volatility range corresponding to $n\text{-C}_{14}$ to $n\text{-C}_{32}$ alkanes are not present in excess of ca. 5 ppb. A wide variety of common classes of carbon compounds would be revealed by these procedures, including hydrocarbons, esters, alcohols, amines, phenols and carboxylic acids. Some handling losses are inherent at the nanogram level and have been studied in the extraction closed system. They do not greatly affect these qualitative estimates. Low molecular weight compounds, highly polar compounds, polymeric materials and matrix-bound or trapped compounds would not be detected by this experiment. It is noteworthy that there was a yellow gum remaining after evaporation of the extraction solvent. This gum gave no volatile materials either by direct injection, or after silylation on gc-ms but cannot be ascribed to elemental sulphur (KAPLAN and SMITH, 1970).

Vacuum crushing

Rare gases, including ^{20}Ne and ^{22}Ne , ^{36}Ar , ^{38}Ar and ^{40}Ar , in the isotope abundances observed by LSPET (1969), were liberated in this experiment, indicating that the

crushing was at least partially effective. However, electron microscope studies, both scanning and transmission, carried out before and after the crushing showed little change in the overall appearance of the sample (at magnifications of 500 to 12,000 times), but some fractured bubble-filled fragments were seen. Other gases including CO, CH₄, C₂H₆ and C₃H₈ were observed in this experiment but comparable amounts of the same gases were observed in blank experiments when the capsule and ball were subjected to the shaking procedure. Metal carbides and other carbon inclusions in the steel are the likely sources of these gases (ROBINSON, 1960).

Vacuum pyrolysis

Vacuum pyrolysis (Fig. 3) of the lunar fines indicated that approximately 150 ppm of carbon (based on ion monitor response) can be released as low molecular weight

Table 1. Gas content of pyrolysed lunar sample

	130– 200°C	200– 300°C	300– 400°C	400– 500°C	500– 600°C	600– 700°C	700– 800°C	800– 900°C
H ₂	+	+	++	++	++	++	+	+
⁴ He	+	+	+	+	+	+	+	+
²⁰ Ne				+	+	+	+	+
²² Ne				+	+	+	+	+
³⁶ Ar				+	+	+	+	+
³⁸ Ar				+	+	+	+	+
⁴⁰ Ar				+	+	+	+	+
N ₂	+	+	+	+	+	+	+	+
O ₂	+	+						
CO	+++	+++	+++	+++	+++	+++	+++	+++
CO ₂	+++	+++	+++	+++	+++	+++	+++	+++
NH ₃		+	++	++	+			
CH ₄	+	+	++	++	++	+		
C ₂ H ₄	+	+	+	++	+			
C ₄ H ₈	++	+	++	+++	+			
C ₆ H ₆	+	+	++	+++	+++	++	+	+
C ₇ H ₈	+	+	+	++	++	+	+	+
C ₈ H ₈				+	+	+		
C ₈ H ₁₀				+	+	+	+	+
C ₉ H ₈					+	+	+	+
C ₉ H ₁₀					+	+	+	+
C ₉ H ₁₂						+	+	+
C ₄ H ₄ S		+	+	+	+			

pyrolysis products. The major components of the total pyrolysate were CO and CO₂, especially at the higher temperatures. The untrapped gases proved to be H₂, He, CH₄, Ne, CO and Ar (Table 1), all of which were present in the mass spectrum of the 500°C pyrolysate (Fig. 5A, 5B). The rare gases first appear near 300°C and continue to be evolved thereafter, but with some variation in observed isotope ratios, presumably due to selective baking out of different sites and the presence of terrestrial gases at the lower temperatures. Methane appears predominantly between 300 and 600°C. Analysis of the condensed gases liberated from the traps indicated the presence of (Table 1) NH₃, CO₂ and unsaturated and aromatic hydrocarbons, including benzene and alkylbenzenes (Fig. 5C, 5D). The compounds identified from their principal ions were NH₃, CO₂, C₂H₄, C₄H₈, C₆H₆, C₇H₈, C₈H₁₀, C₉H₈, C₉H₁₀, C₄H₄S. A pyrolysis to 500°C in a pyrex vessel without the dry ice/acetone trap, also indicated the presence

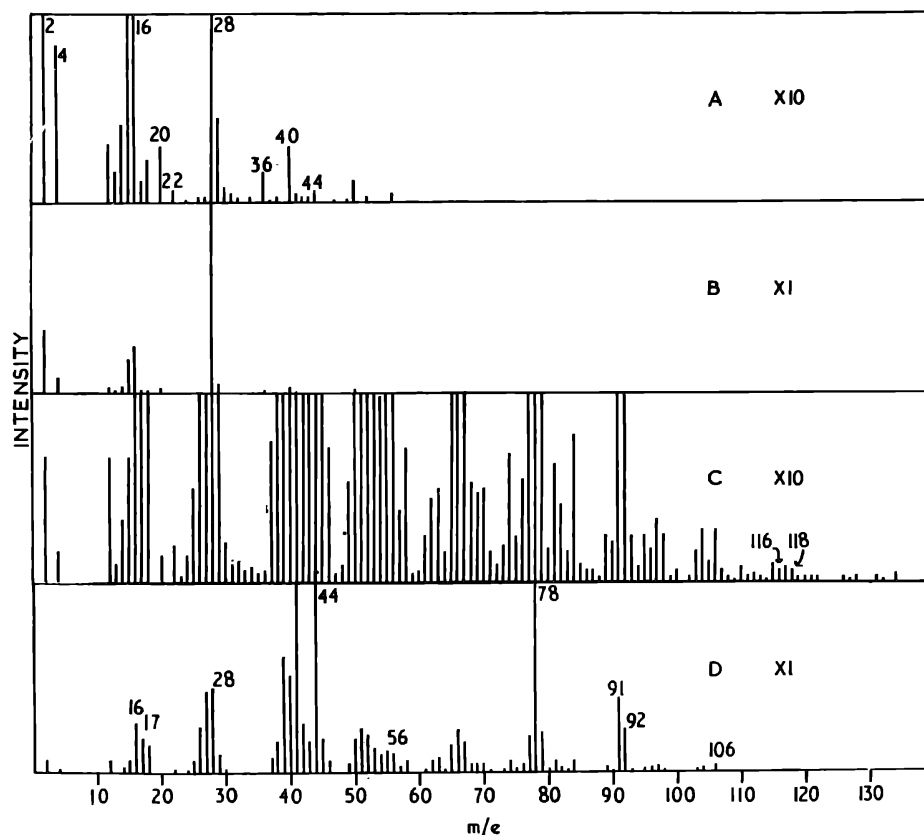


Fig. 5. Mass spectra (sensitivities $\times 1$ and $\times 10$) of the non-condensable (A + B) and the condensable (C + D) gases released during the 400°–500°C pyrolysis step.

of $C_{10}H_8$ and $C_{11}H_{10}$ compounds. Otherwise, the results of this pyrolysis were comparable with most from the earlier stages of the 900°C pyrolysis.

It should be noted that the identifications are based on low resolution mass spectra and some heteroatomic species may contribute to the observed ion abundances. The relative amounts indicated by +, ++ and +++ in Table 1 refer to each temperature increment only and do not allow comparisons between temperature increments. The only carbon-containing compound present in a blank pyrolysis (900°C) conducted on the empty quartz capsule was carbon dioxide. This component was present in very small quantities and probably arose from desorption of atmospheric gases from the capsule. Nitrogen, oxygen and nitric oxide were also identified.

Hydrofluoric acid etching

Utilization of the molecular sieve trap in the system (Fig. 4) permitted a fractionation step, Ar, CH_4 , O_2 and N_2 being retained at liquid nitrogen temperatures, but not when the sieve was warmed to 20°C. Methane was the most abundant non-atmospheric gas (Fig. 6) and was present at a level of ca. 2 ppm by weight ($3\text{--}4 \times 10^{-3} \text{ cm}^3/\text{g}$) of the fines (Table 2). The CH_4 was identified by its fragmentation pattern and was distinguished from ^{16}O at a resolving power of 1000 (10% valley) in the mass spectrometer. The etching procedure also released H_2 and the rare gases, He, Ne and Ar.

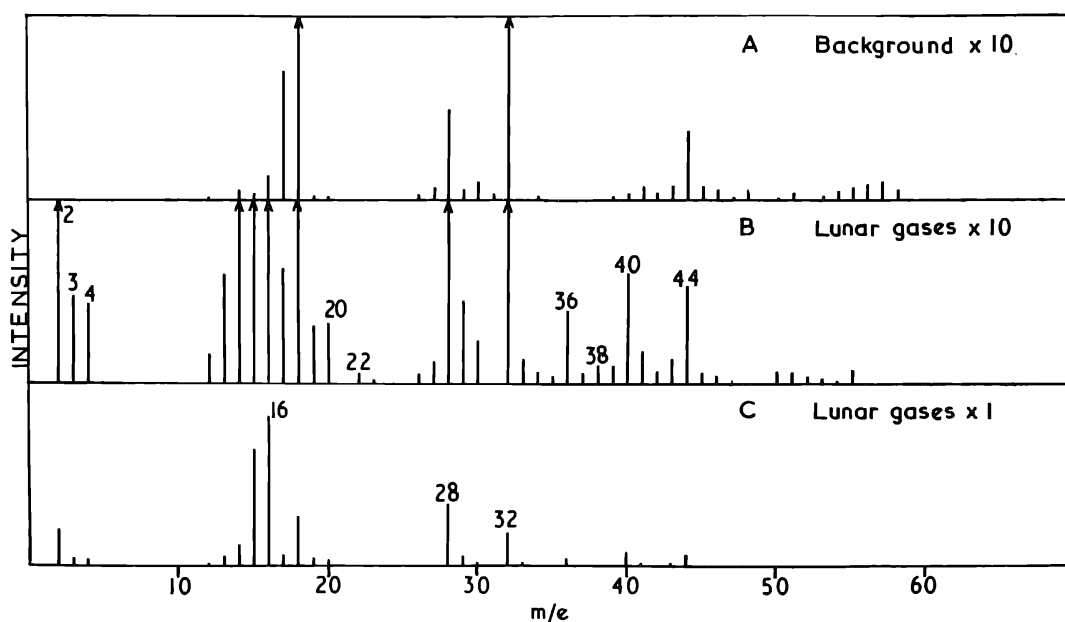


Fig. 6. Mass spectra (sensitivities $\times 1$ and $\times 10$) of total lunar gases (B + C) released by hydrofluoric acid etching. Mass spectrum (sensitivity $\times 10$) of the analysis system residual gas background (A).

The amount (Table 2) of ^{36}Ar ($7\text{--}9 \times 10^{-4} \text{ cm}^3/\text{g}$) is similar to that measured for the lunar fines at the LRL (LSPET, 1969). Precise quantitation was not feasible with the techniques used: variables include the extent and rate of dissolution of the samples.

Methane and ^{36}Ar were released at the levels of $6 \times 10^{-5} \text{ cm}^3/\text{g}$ (0.04 ppm) and $7 \times 10^{-6} \text{ cm}^3/\text{g}$, respectively, from the gas-rich achondrite Kapoeta which has a low total carbon content (0.07 per cent). (MASON and WILK, 1966). On the contrary, the type C-3 chondrite Pueblito de Allende, which has a total carbon content of 0.35 per cent HAN *et al.* (1969), released $2 \times 10^{-5} \text{ cm}^3/\text{g}$ (0.02 ppm) methane under the hydrofluoric acid etching conditions (Table 2), but no ^{36}Ar was detected.

The quantities of CH_4 and ^{36}Ar released from an aliquot of the exposed alumina

Table 2. Argon-36 and methane content by 40% aqueous HF etch

Sample	Wt. of sample (g)	Etch	Yield in $10^{-8} \text{ cm}^3/\text{g}$	
			Argon-36	Methane
Lunar fines	0.270	--	90,000	300,000
Lunar fines	0.201	--	70,000	400,000
Lunar fines after pyrolysis at 900°C	0.213	--	5000	100,000
Packaging blank (Al_2O_3)	0.200	-	Below detection limit	
System blank	0	0	Below detection limit	
Allende	0.234	---	Below detection level	2000
Kapoeta	0.312	--	700	6000

Degree of etch indicated by number of dashes.

Minimum detectable: $100 \times 10^{-8} \text{ cm}^3/\text{g}$.

blank and from empty reaction vessels were below the detection limits of the experiment. Methane was not detected when a fresh sample of fines was heated to 150°C at 10^{-6} torr: we presume that measurable quantities of this gas are not present on the surface of the sample. The LM exhaust studies make no mention of CH₄ as a component of the exhaust gases (SIMONEIT *et al.*, 1969).

The isotope ratios of Ne and Ar observed in the HF etch experiments (and the pyrolysis experiments) of the lunar material and Kapoeta meteorite are approximately those observed in the LSPET experiment (LSPET, 1969) and the data on Kapoeta reported by ZHRINGER (1963). The argon isotope ratios we observe for the Apollo 11 lunar fines ($^{36}\text{Ar}:^{38}\text{Ar}:^{40}\text{Ar} \cong 3:1:5$) are not terrestrial ($1:0.2:300$); terrestrial argon is highly depleted in the lighter isotopes. The results we find for Kapoeta ($^{36}\text{Ar}:^{40}\text{Ar} = 1:10$) are comparable to ZHRINGER's data (1:15). ^{38}Ar was not detected. These ratios are obviously different from those obtained for terrestrial argon and for argon from the Apollo 11 lunar fines.

DISCUSSION

Carbon content of lunar fines and rocks

The results reported by MOORE *et al.* (1970) show that the largest quantities of total carbon (500 ppm) occur in the finest fractions of the fines and the smallest (64 ppm) in the interior of the igneous rocks. Similarly, the lunar fines have the highest rare gas content; therefore, the content of total carbon broadly parallels that of the solar wind rare gases. It is unlikely that these large differences are to be explained by contamination. The elemental composition of the solar corona is known from spectroscopic evidence and consideration of solar abundance tables (UNSÖLD, 1969) leads to the conclusion that carbon, nitrogen and other important organogenic elements must accompany hydrogen, helium, argon, etc. in the solar wind flux. Although it is possible that rare gases could be primordial, cosmogenic or radiogenic it is widely accepted that the hydrogen and the rare gases in the lunar fines derive predominantly from the solar wind. If so certainly some of the carbon in the fines must also be derived from that source.

The question is, how much? The rare gas values for lunar material indicate saturation of the surface layers of the particles (HINTENBERGER *et al.*, 1970; HEYMANN *et al.*, 1970). Losses by diffusion and shock events are not known but the observed depletion of light rare gases and the difference from solar isotope composition indicate that these must have been considerable. Comparing solar and lunar abundances of nuclides, the observed depletion factors relative to ^{84}Kr are of the order of 10, 50 and 300 for ^{36}Ar , ^{20}Ne and ^4He , respectively. But the loss of carbon compared to that of the lower molecular weight rare gases should be less owing to retention by reaction with the matrix. Making some rough allowance for this factor by assuming a carbon depletion factor more like those of ^{36}Ar or ^{84}Kr than of ^{20}Ne or ^4He , the figure for carbon implanted by the solar wind in the Apollo 11 surface fines should be around 50 ppm. Similar arguments have been advanced by MOORE *et al.* (1970). Precise calculations are not as yet possible for little is known of the diffusion losses, the surface exposure ages, lunar gardening processes, etc.

Two other sources for the lunar carbon merit discussion: carbonaceous chondrites and the igneous rocks themselves. KEAYS *et al.* (1970), using the proportions of certain elements as an indication, have suggested that the contribution of carbonaceous chondrites to the regolith approximates to about 2 per cent. The amount of carbon provided from this source must therefore be very small, bearing in mind both the low carbon content (approximately 2 per cent) of such meteorites and the extremely high temperatures following impact which should vapourize most of the carbon, partially as carbon monoxide. The parent igneous rocks of the moon, like their terrestrial counterparts (BARKER, 1965), could well contain a small abundance of truly indigenous primordial carbon, but the results of our own and of other investigations (BURLINGAME *et al.*, 1970; ORÓ *et al.*, 1970) show that much of the carbon present in the Apollo 11 rocks and fines is very rapidly lost, mainly as CO, on heating to high temperatures of 700°C and over. The vesicular nature of some of the rocks may have resulted from just such outgassing at the time of crystallization.

Since the bulk of the "lunar soil" has been derived from the crystalline rocks, it seems difficult to escape the conclusion that the higher carbon content of the fines is to be ascribed to additional quantities provided from an outside source, namely the solar wind.

Major organic contaminants which we had anticipated might be present in the sample from collection, handling in the biopreparation facility at the LRL, and packaging, include butyl rubber, plasticizers, hydrocarbon oils, Teflon, cellulose fibres, contingency bag contaminants, peracetic acid and ethylene oxide and their reaction products. Further, the bulk fines had been collected over an area within about 30 feet of the LM engine, where they must certainly have received considerable effluent during the final few seconds of the descent. The oxidizer, N₂O₄, was also vented on that side of the craft. We were unable to positively identify any of these contaminants in our sample of fines, but high resolution mass spectrometric studies of the products of controlled heating by MURPHY *et al.* (1970), BURLINGAME *et al.* (1970), revealed hydrocarbons and heteroatomic species known to be present in the LM exhaust, and the presence of phthalate contaminants. MURPHY *et al.* (1970), are of the opinion that most of the ions seen in the M.S. analysis of the products of pyrolysis of the fines are derived from contaminants, such as ethylene oxide and peracetic acid. However, the high positive $\delta^{13}\text{C}$ values found by KAPLAN and SMITH (1970), ORÓ *et al.* (1970) and EPSTEIN and TAYLOR (1970) preclude a terrestrial origin for most of the carbon in the lunar samples.

In agreement with most other bioscience investigators, we were unable to detect any of the conventional biolipids. Our levels of detection, arrived at by solvent extraction of the 15-g sample of fines, were equivalent to putting an upper limit of ca. 5 ppb on any single component in the volatility range studied. Thus the anhydrous state of the lunar fines and rocks, their high temperature history, the low abundance of carbon and the non-detectability of biolipids, the extremes of the lunar environment in terms of radiation, temperature and lack of atmosphere, all parallel the anticipated and confirmed absence of viable lunar organisms (LSPET, 1969; OYAMA *et al.*, 1970).

However, pyrolysis of the lunar sample (150–900°) did give evidence of a variety of aromatic compounds (Table 1). These compounds are probably not present as such in the lunar fines and they most likely have been formed by pyrolysis of polymeric material. Thermal equilibration in a C, H, O ternary system produces a variety of aliphatic and aromatic compounds (DAYHOFF *et al.*, 1964; ECK *et al.*, 1966). Calculations of thermal equilibrium concentrations for a variety of compounds at selected regions of the CHO ternary diagrams have been largely verified by experimental studies of equilibria in plasma (WEIFFENBACH *et al.*, 1969; GRIFFITHS *et al.*, 1969). Aromatics may constitute as much as 70% volatiles in an equilibrium mixture. Aromatic products similar to those reported herein have been recognized in the pyrolyses products of carbonaceous chondrites (HAYES and BIEMANN, 1968), and the Onverwacht chert (SCOTT, 1970). In the case of the lunar fines it is difficult at this stage to rule out pyrolysis of contaminants as at least a partial source. Pyrolysis of the methane in the sample, even if present as such, is insufficient to produce the quantity of aromatics detected (HAN and ORÓ 1967).

Carbon monoxide is certainly the major carbon containing molecule evolved on heating the lunar fines. Our figures, and those of other workers (BURLINGAME *et al.*, 1970; ORÓ *et al.*, 1970), show that most of the carbon in the sample is eventually released in the form of carbon monoxide as the temperature is raised to 900°C and beyond. We do not as yet know the form, bound or unbound, of most of this carbon—that is prior to heating of the fines or the dissolution in acid. We have been unable to confirm the release of large quantities, equivalent to 66 ppm, of carbon monoxide on HF treatment of the fines (BURLINGAME *et al.*, 1970). Some of the carbon is evidently present as graphite, for one fragment has been reported in the fines (ARRHENIUS *et al.*, 1970). The presence of small amounts of calcium carbonate (calcite and aragonite) (AGRELL, 1970) has been reported. Iron nickel carbide (Fe, Ni)₃C (cohenite) has been recognized in meteorites (BRETT, 1967) and meteoritic fragments from the lunar soil (FRONDEL *et al.*, 1970). Carbon-containing materials may also be present in the opaque portion of the rocks and fines, since these are difficult to characterize.

Methane and lunar rare gases

The impressive quantities of the lunar rare gases, first reported in the preliminary analyses (LSPET, 1969), prompted our search for methane and other likely products of solar wind implantation, for the vast excess of hydrogen (as H⁺ and H^{*}) over carbon reaching the surface of the moon might reasonably be expected to give rise to hydrogenated products. Thus, proton bombardment of glasses in the laboratory produces hydroxyl groups (ZELLER *et al.*, 1966). Model solar wind experiments involving bombardment of glass and of other silicate materials with mixtures of nuclei (hydrogen, carbon, etc.) are clearly desirable. The situation on the lunar surface is further complicated by the existence of the intense u.v. radiation, the thermal regime of the lunar day and night, and of the cosmic ray bombardment. High energies released spallogically provide further means for alteration of the carbon content of the lunar fines through 'hot atom' chemistry (MACKAY and WOLFGANG, 1965). Hence, we believe our most significant finding to be the release of approximately

2 ppm of methane when the lunar sample is etched with hydrofluoric acid. The lunar rare gases are concomitantly released. Again, methane and rare gases are liberated when the sample alone is heated above 300°C, but here the methane might have a pyrolytic origin. Methane and other hydrocarbons have been reported by PONNAMPERUMA *et al.* (1970), in the gaseous products evolved on dissolution of the sample in 6 N-hydrochloric acid. They ascribe the formation of these hydrocarbons to hydrolysis of indigenous metal carbides. Our present trapping techniques unfortunately preclude study of hydrocarbons other than methane, but acidic hydrolysis of carbides could conceivably account for some of the methane evolved in our hydrofluoric etching experiments. A modification of the crushing experiment may well provide a non-chemical method which would test our belief that the methane is present as such in the fines.

If methane is indeed present as such in the lunar fines, then it could well have one or more of the following origins: (1) it could be primordial; (2) it could have been entrapped during formation of the fines; (3) it could be a primary product of the solar wind; or (4) a secondary product of indigenous carbon or of solar wind carbon. We hope to distinguish between these possibilities in due course, but we have sought information from two meteorites. Methane has been reported in carbonaceous chondrites by STUDIER *et al.* (1965), but analyses of Allende by us revealed only small quantities of this component. The gas-rich achondrite Kapoeta which consists of aggregated interplanetary dust bombarded by the solar wind (MULLER and ZAHRINGER, 1966) and has a very low carbon content, contains approximately three times as much methane. The cosmic ray exposure ages are presumably similar for both meteorites. Thus, our limited data indicate that the quantity of methane is approximately proportional to the rare gas content, but not to the carbon content. We have no information on the carbide content (if any) of these meteorites. There appears to be no previous report of the presence of methane in gas-rich achondrites or in ordinary chondrites.

We anticipate that new information on the solar wind implantation and cosmic ray irradiation of the moon and of meteorites will become available by the kind of approach herein described. The compounds of carbon and other elements liberated from the sample simultaneously with the rare gases should be identified and quantitatively measured. In particular, it will be important to do this by careful etching studies designed to reveal precise locations and state of the carbon compounds trapped and bound to the matrix.

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