cited at 410 nm. However, on the basis of its behavior in acid and its spectral properties, we do not believe that this compound is a porphyrin. We therefore believe that porphyrins were not present in the lunar sample above the detectability limits of our method—that is, above 10^{-12} mole/g of sample (linear energy spectrofluorometer) or 10^{-13} mole/g of sample (conventional spectrofluorometer).

We have, however, found other fluorescent materials in the lunar sample but not in the solvent control blanks. Thus the benzonitrile and methane sulfonic acid–naphthalene extracts exhibit absorption maxima at 310 and 350 nm with a fluorescence maximum at 410 nm. This material is present in the lunar sample at concentrations of the order of 10 parts per billion (quinine sulfate equivalent). Because of the low concentration of the fluorescent material in the sample we have been unable to identify it by high resolution mass spectrometry. Extraction of an ancient terrestrial sample (Gunflint chert) by the methods outlined above yields a fluorescent material similar in its properties to those of the material present in the lunar sample.

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Search for Organic Material in Lunar Fines by Mass Spectrometry

Abstract. *Three kinds of experiments were performed in an effort to detect and identify organic compounds present in the lunar material (fines 10,086): (i) vaporization of the volatilizable components directly into the ion source of a high-resolution mass spectrometer, and (ii and iii) extraction of the material with organic solvents before and after dissolving most of the inorganic substrate in hydrochloric and hydrofluoric acid. The extracts were investigated by a combination of gas chromatography and mass spectrometry. Although a number of organic compounds or compound types have been detected, none appears to be indigenous to the lunar surface.*

In an effort to characterize the organic compounds present in the surface covering the Apollo 11 landing site, a portion of fines (sample 10,086) has been subjected to mass spectrometric analysis. Three different types of experiments were undertaken: (i) vaporization of organic compounds present in lunar material; (ii) solvent extraction of lunar material; and (iii) dissolution of lunar material in acid followed by extraction of the aqueous phase.

The first experiment involved placing the lunar material (0.4 g) in a small glass bulb mounted directly on the ion source chamber of a high-resolution, double-focusing mass spectrometer (CEC 21-110B). The bulb was positioned in such a manner that any material evolving from the sample would vaporize directly into the ionizing electron beam (*1*). This approach involves the least risk of contamination and provides maximum sensitivity. The mass spectra were recorded in a number of consecutive exposures on a photographic plate (*2*); thus an integrated permanent record was obtained of all ions produced in the 20-minute period during which the sample was heated from ambient temperature to 400°C. Comparison of the resulting exposures with the spectra obtained from known amounts of *n*-decane introduced through the batch-inlet system of the spectrometer indicates that the 0.4 g of lunar material produced about 0.1 to 1.0 μg of organic material—that is, about 0.25 to 2.5 parts per million.

The composition of the ions produced is given in Table 1. Most of the species are hydrocarbon ions of various degrees of unsaturation. In addition to these, a few series of ions were found that contained one, two, or three oxygen atoms (mono-oxygenated ions predominating), and some ions containing one nitrogen atom. Furthermore, a few ions contained nitrogen and oxygen, and some rather abundant ions contained sulfur either alone or in combination with oxygen. The sulfur-containing species were either free of carbon (elemental sulfur, hydrogen sulfide, and sulfur dioxide) or had only one carbon atom (carbon disulfide and carbon oxysulfide).

A few of the ions may represent compositions with three nitrogen atoms, but these differed by only 1.3 millimass units from those having C_2H_2O instead of N_3, and the two species were therefore difficult to resolve. The absence of species with two nitrogens would argue against the presence of molecules containing more than one nitrogen atom.

Although we must emphasize that the species listed in Table 1 represent ions formed in electron impact and do not necessarily indicate molecules present as such, one can draw a number of conclusions from these data. First, there seems to be present a series of hydrocarbons having up to nine carbon atoms and ranging from almost completely saturated species (C_8H_{16} corresponds to a hydrocarbon with one double bond or ring) to more unsaturated ones. The aromatic ions (C_9H_7, C_8H_9, C_7H_8, and C_6H_6, which would correspond to an indenyl ion, styrene, toluene, and benzene) appeared to be present in much lower abundance, despite the high relative intensity of these ions in the mass spectra of the corresponding pure compounds.

Aside from the large quantities of CO_2, the most abundant oxygen-containing ions consisted of one or two carbons and one or two oxygens, as they may be produced upon ionization of small alcohols or glycols. Such ions might have come from either ethylene oxide or its hydrolysis product, ethylene glycol. (Ethylene oxide was used as a sterilizing agent at the Lunar Receiving Laboratory.) Similarly, the $C_2H_4O_2$ (the elemental composition of acetic acid) may be a reduction product of peracetic acid, also used as a sterilizing agent at LRL, whereas the ions containing three carbon atoms and one oxygen atom may have been derived from acetone which in turn may have been produced by pyrolysis of salts of acetic acid. The $C_8H_5O_3$ ions were probably a small trace of the common laboratory contaminants, dialkyl phthalates.

The nitrogen-containing ions all represent small molecules or fragments thereof, and some of them (indicated in Table 1 by an asterisk) had been previously found in the products of the lunar module retro-rocket exhaust (*3*). Last but not least, there appears to be a considerable amount of sulfur present, in the form of elemental sulfur, hydrogen sulfide, carbon disulfide, and sulfur dioxide.

Table 1. Ions observed upon heating lunar sample (0.4 g) to 400°C and volatilizing the material into the ion source of a high-resolution mass spectrometer. ×, Also present in background;*, found in rocket exhaust (*3*); +, relative intensity.

C,H	
++C_2H_4 ×, *	++C_5H_9 ×
++C_2H_5 ×	++C_5H_{10}
+C_2H_6	++C_5H_{11}
++C_3H	+C_6H_2
++C_3H_2 ×, *	+C_6H_3
+++C_3H_3 ×, *	+C_6H_4 *
++C_3H_4 *	+C_6H_5
++C_3H_5 ×	+C_6H_6 ×
++C_3H_6 ×	+C_6H_7
+++C_3H_7 ×	+C_6H_9
+C_3H_8	+C_6H_{10}
+C_4H	++C_6H_{11}
++C_4H_2 *	+C_6H_{12}
++C_4H_3	+C_6H_{13}
+C_4H_4 *	++C_7H_7
++C_4H_5	+C_7H_8
+C_4H_6	+C_7H_9
+++C_4H_7	+C_7H_{11}
+++C_4H_8 ×	+C_7H_{12}
+++C_4H_9	+C_7H_{13}
+C_5H_2	+C_8H_9
+C_5H_3	+C_8H_{13}
+C_5H_4	+C_8H_{15}
+C_5H_5	+C_8H_{16}
+C_5H_6	+C_9H_7
++C_5H_7	+C_9H_{11}
+C_5H_8	
C,H,O	
+++CO_2 *	+C_3H_5O
++CH_2O	++C_3H_6O
++CH_3O	+C_3H_7O
++CH_4O *	+C_4H_6O
+C_2O	+C_4H_8O
+C_2HO	+C_6H_6O
++C_2H_2O *	+C_7H_4O
+++C_2H_3O ×, *	+C_7H_5O
+++C_2H_4O *	+CH_2O_2
+++C_2H_5O	++$C_2H_4O_2$
+C_3HO	+$C_3H_5O_2$
+C_3H_2O	+$C_8H_3O_2$
++C_3H_3O ×	+$C_4H_2O_3$
+C_3H_4O	+$C_8H_5O_3$
C,H,N,O	
+CH_2N	+C_3H_3N
+CH_4N	+CNO *
+C_2N	+++HCNO *
++C_2HN *	+HNO
++C_2H_2N	+++NO_2 *
+C_2H_3N *	[++HN_3 *]
+C_2H_4N *	[+HCN_3 *]
+C_2H_6N	[+CH_3N_3 *]
C,H,S,O	
+++S	+COS
+HS	+++SO
++H_2S	+++SO_2
++CS	
+CS_2	

Thus it appears that the organic material which can be volatilized out of the sample represents small molecules which are probably of terrestrial origin, with the exception of CO_2, SO_2, H_2S, COS, CS_2, and elemental sulfur. These are probably indigenous to the sample, but it should be noted that a sulfur-base caulking compound was used to seal various partitions within the cabinet system at LRL. It should also be pointed out that most of these species began to appear in the spectra when the sample had reached temperatures of about 150° to 200°C and disappeared in later exposures taken at a sample temperature of 400°C. This makes it unlikely that they are pyrolysis products of otherwise nonvolatile material. Equally significant is the absence of a series of hetero-aromatic systems such as pyridines, furanes, and thiophenes, since they would be produced from the pyrolysis of more complex heteroatom-containing molecules which would be of greater interest to the organic chemist and biochemist. Particularly in view of the high relative intensity of the molecular ion of these types of compounds, it should have been possible to detect them in rather small amounts (a few nanograms).

The thermal release of organic material from an inorganic matrix is a simple, but drastic and sometimes inefficient, technique. Solvent extraction or removal of the inorganic material by dissolution in acid, followed by extraction of the liberated organic substances, is a commonly employed alternative to the direct volatilization described above. A 50-g portion of the fines (10,086) was extracted with 50 ml of benzene-methanol (1 : 1) in a sealed ampule by shaking in an ultrasonic bath for 48 hours at 60°C. After settling, the solvent was decanted and the residue was stirred with more solvent, then combined with the first batch and evaporated in a stream of purified helium to a fraction of a milliliter.

The insoluble residue was dissolved in (i) hydrochloric acid and (ii) hydrofluoric acid. The respective acid solutions were diluted, neutralized, and extracted with dichloromethane (*4*). These extracts were dried with magnesium sulfate and concentrated in a stream of helium to 0.1 to 0.2 ml each. Another aliquot (30 g) of the sample was treated with hydrochloric acid only, without prior extraction with benzene-methanol. The acidic solution was neutralized and extracted with dichloromethane. This extract was dried and concentrated as described above. It should be noted that, during the treatment of the sample with acids, hydrogen sulfide is evolved.

Since it was our major aim in these experiments to detect the presence of various types of organic compounds other than hydrocarbons, the resulting extracts were subjected to gas chromatography in which a general-purpose column (OV-17) was utilized rather than one that is specifically suited for a certain compound type. The gas chromatograph is operated in conjunction with a low-resolution mass spectrometer coupled to a computer, to enable one to permanently record all data in a form that then can be analyzed with the help of the computer (*5*). In none of the extracts discussed above, with the exception of elemental sulfur (from sulfides) were there any significant peaks in the gas chromatogram that could be attributed to material indigenous to the lunar sample. A number of compounds were identified, such as toluene, isopropylbenzene, diisopropyl disulfide, ethyl isopropyl disulfide, methyl isopropyl disulfide, phenol, diethyl phthalate, dibutyl phthalate, biphenyl, styrene, naphthalene, dihydronaphthalene, indane and anthracene. However, with the possible exception of the last six aromatic hydrocarbons, these compounds appear to be traces of contaminants introduced during the analytical procedure. The detection of the dialkyl disulfides is somewhat surprising, but these may be reaction products of the solvent (perhaps traces of higher alcohols in the methanol) with free sulfur or metal sulfides that were indigenous to the lunar sample. This possibility should be further investigated, but the relatively high volatility of these disulfides and their absence in the direct vaporization experiment (Table 1) seem to eliminate the possibility that they are indigenous to the moon. High-resolution mass spectra of the extracts discussed above have been obtained and are in process of being analyzed.

From our experiments we conclude that there are no volatile or extractable organic compounds exceeding the part-per-billion amounts region in the surface material returned from the Sea of Tranquillity by the Apollo 11 mission.

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Organic Analysis of the Returned Lunar Sample

Abstract. *Lunar fines have been examined for organic compounds by crushing, programmed heating, hydrofluoric acid etching, and solvent extraction. Products were examined by mass spectroscopy. A variety of small organic molecules, including methane and other hydrocarbons, accompanied the release of the rare gases when the sample was heated in a stepwise fashion to 900°C under vacuum. Methane is more abundant (abundance on the order of 1 part per million) than argon in the matrix-entrapped gases liberated by hydrofluoric acid etching of lunar fines. Methane is also present in a dark portion of the gas-rich meteorite Kapoeta.*

We have undertaken an analytical procedure for detecting and identifying carbon compounds over a wide range of molecular weights. In particular we have attempted to locate any compounds of carbon formed as a result of bombardment of the surface of the moon by solar wind and cosmic rays (*1*). The solar-wind flux of hydrogen, carbon, nitrogen, oxygen, and other elements might be expected to result in the formation of organic compounds in the shallow surface layer of the exposed particles in the lunar fines and surface rocks. We have made approximate calculations of the ratios of the amounts of the elements that might be expected, but it seems impossible at this stage to judge the extent of the interaction between them on implantation in the mineral matrix. Methane is one possible product.

The sample container was opened and the aliquots of sample 10086.19 were transferred, in the flow of a clean air cabinet, to glass ampules which were then sealed under purified nitrogen. Standard clean room equipment, tools, and apparatus were used throughout. All the equipment had been previously cleaned through treatment with hot concentrated chromic acid, followed by washing with a solvent or by heating to 500°C and cooling under nitrogen. Exposure times were kept as brief as possible in order to minimize laboratory contamination.

We brought about partial dissolution of lunar fines as follows. A vacuum-degassed sample of 40 percent aqueous HF (about 1 ml) and a sample of lunar fines (about 200 mg), both under vacuum, were mixed by breaking a thin glass diaphragm. The reaction was allowed to proceed at room temperature for about 30 minutes, after which time the breakseal connecting the reaction vessel with the thoroughly evacuated and degassed fractionating system was broken. The fractionating system consisted of two traps in series, cooled in liquid nitrogen, followed by a 5-Å molecular-sieve trap and an open U-tube trap, sealed onto the inlet valve of the mass spectrometer (Varian MAT CH-7). The molecular sieve trap could be bypassed. The two traps cooled by liquid nitrogen retained the reactants and the reaction products, and all organics other than methane. Incorporation of the molecular-sieve trap into the system permitted a fractionation step, with argon, methane, oxygen, and nitrogen being retained at liquid-nitrogen temperatures, but not when the sieve was warmed to 20°C. Portions of a standard gas mixture (80.7 percent Ne; 7.5 percent Ar; 1.9 percent Kr; 7.8 percent CH_4, and 2.1 percent C_2H_6) were admitted in order to check sensitivity and to obtain a calibration point for approximate quantitation of sample gases. The minimum detectable quantity of any single gas was about 10^{-6} cm^3 STP. Methane was conclusively identified by the fragmentation pattern and by the m/e value at the resolution available (1000, 10 percent valley).

The etching procedure released 3×10^{-3} cm^3 of methane (1 ppm by weight) and about 9×10^{-4} cm^3 of ^{36}Ar from 1 g of the lunar fines, while about 6×10^{-5} cm^3 of methane and 7×10^{-6} cm^3 of ^{36}Ar were released from 1 g of gas-rich chondrite, Kapoeta. Smaller amounts of methane were observed in the Pueblito de Allende C3 chondrite. No methane was observed in an apparatus and reagent blank. A sample of baked out alumina which had been handled in parallel with the lunar sample since its arrival in Bristol yielded no methane. Nonterrestrial rare gases were observed from the meteorites and from the lunar sample. Amounts and isotopic abundances of hydrogen, helium, neon, and argon observed in the lunar fines were of the same order as those already measured (*2*).

Our initial studies with the lunar fines were directed toward pulverizing them under high vacuum and examining liberated gases by mass spectrometry (*3*). Solar gases were indeed liberated (for example, ^{36}Ar, ^{38}Ar, ^{40}Ar, ^{20}Ne, ^{22}Ne) but we were unable to degas the stainless steel capsule sufficiently to achieve a good blank for organic gases.

The Burlingame-Biemann experiment, which was part of the preliminary examination conducted at the Lunar Receiving Laboratory, involved the stepwise heating of small amounts (~ 100 mg) of lunar samples, the products being evolved directly into the ion source of a sensitive, fast-scanning mass spectrometer (*2*). These investigators announced the low levels (less than 1 ppm) of organic compounds in the Apollo 11 samples and also emphasized the variation in results which would arise from particulate contamination of small samples.

We have carried out a similar pyrolysis but on a larger scale, and with the introduction of two traps (solid carbon dioxide and acetone, and liquid nitrogen) to effect preliminary fractionation in a fashion similar to that described for the etching experiment. The temperature of the sample (2.6 g), which was contained in a quartz vessel held at 10^{-6} torr, was raised in 100°C steps (of ~ 5 minutes each) and then held for about 15 minutes; the baked-out head-space gases, both untrapped and trapped in liquid nitrogen, were examined at each step by opening the system to the mass spectrometer. The total ion current was recorded continuously, and mass spectra were taken at frequent intervals. The system blank gave N_2, O_2, CO_2, and NO (mass-to-charge ratio, 30). Gas evolution was incomplete at each step, but trends are