sponse factors for the pyrolysis products are variable with type of sample. The quantitation is based upon comparison with standard samples (*5*) and is confirmed by agreement with results of classical analyses of many terrestrial soils and rocks. Results showing low amounts are obtained only from very ancient sediments where most of the organic matter is present as intractable graphitic material.

From the first organic analysis it was apparent that the organic content of the lunar samples was extremely low and easily obscured by trace contamination. The samples from the documented box processed in the vacuum chamber were the most heavily contaminated. The remaining samples, which were processed under nitrogen with simpler procedures, were less contaminated. In general the organic content correlated directly with the degree and type of sample processing (*2*). The major sources of contamination appeared to be pump oil, fibers, Teflon, rubber-glove fragments, sterilizing agents, and unclean tools and surfaces.

Five of the samples listed in Table 1 had organic contents of less than 20 parts per million. All were processed under nitrogen with minimal handling. All other samples were treated less carefully during the processing scheme. On this basis we have placed our estimate of the indigenous organic matter at less than 10 ppm, realizing that even much of this may be due to trace contamination. It is not possible from these results to compare the organic content of the different rock types and the fines.

The pyrolysis-hydrogen flame ionization detector method is capable of determining the amount of organic carbon but not its source. The organic mass spectrometer used during the preliminary examination (*1*) can resolve individual organic fragments and permit their identification. The results reported from the mass spectra indicated less than 5 ppm of total organic matter including contamination, and less than 1 ppm of indigenous organics. These results are lower by at least 1 order of magnitude than those reported here. The samples were introduced into the mass spectrometer by gradual heating of the sample in a punctured nickel capsule at 500°C in the vacuum of the inlet system. The quantitation of that method was based upon comparison of the ionization current with that produced by known amounts of *n*-tetracosane (boiling point, 320°C) in clean sand. The use of a relatively low pyrolysis temperature, coupled with a quite volatile calibration standard, seemed inappropriate for accurate quantitation of organic compounds, particularly those that have withstood the thermal and vacuum environment of the moon.

This problem was investigated by heating soil samples low in organic content to 500° ± 50°C at 7×10^{-6} torr for 30 minutes, simulating the inlet system of the mass spectrometer. Using our analytical method to compare the organic contents of these samples with portions of the untreated original sample, we were able to show that up to 90 percent of the organic matter could remain unvolatilized in the inlet of the mass spectrometer. Thus, when based upon a volatile standard, the mass spectrometer results could be low by 1 order of magnitude.

Although we have been unable to do more than place a 10 ppm upper limit on the possible indigenous organic matter, we feel that the values from the mass spectrometric analysis may be too low, and that the true levels of indigenous organic matter may lie between these two results.

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5. The calibration standards consisted of *Serratia marcescens* (43.77 ± 0.67 percent carbon) freeze-dried into incinerated sand at concentrations from 10 to 1000 parts of carbon per million.

5 January 1970

Search for Organic Compounds in the Lunar Dust from the Sea of Tranquillity

Abstract. *A sample of lunar dust was examined for organic compounds. Carbon detected in concentrations of 157 micrograms per gram had a $\delta^{13}C$ per mil (PDB) value of +20. Treatment with hydrochloric acid yielded hydrocarbons of low molecular weight, suggesting the presence of carbides. The gas chromatogram of the acylated and esterified derivatives of the hydrolyzate was similar to that obtained for the Pueblito de Allende meteorite. There were no detectable amounts of extractable high-molecular-weight alkanes, aromatic hydrocarbons, isoprenoid hydrocarbons, normal alkanes, fatty acids, amino acids, sugars, or nucleic acid bases. Traces of porphyrins were found, perhaps arising from rocket exhaust materials.*

A useful approach to the study of chemical evolution is the examination of organic matter in ancient rocks and sediments. The oldest known microfossils are about 3×10^9 years old, indicating that life was already well established at this period (*1*). The possibility, however, of finding rocks on the earth older than 3½ billion years appears to be small. On the other hand, the samples from the moon may give us some clues to prebiotic organic synthesis in the solar system (*2*).

This report contains the results obtained by a group of investigators established as the NASA Ames Research Center Consortium to analyze the sample labeled "10086 bulk A fines." Since this sample consisted of a relatively fine powder, no further grinding was undertaken before analysis.

Our analysis included an examination of the lunar material for total carbon, organic carbon, isotope fractionation, microfossils, and mineralogy. Sequential treatment of the sample by a benzene-methanol mixture, water, and hydrochloric acid provided extracts for examination by chromatographic and spectrometric methods (Fig. 1).

To monitor every stage of the analysis, parallel experiments were conducted on an interior sample from a 6-kg piece of the Pueblito de Allende meteorite (*3*), and a sand blank was prepared by heating a sample of Ottawa sand for 48 hours at 1000°C. To minimize contamination, the analyses were carried out in a clean laboratory ventilated with filtered air, and the entire sequence of solvent extractions of the lunar dust was accomplished in a single glass vessel.

Total carbon was determined by measuring the volume of CO_2 evolved when a 1-g sample was outgassed at

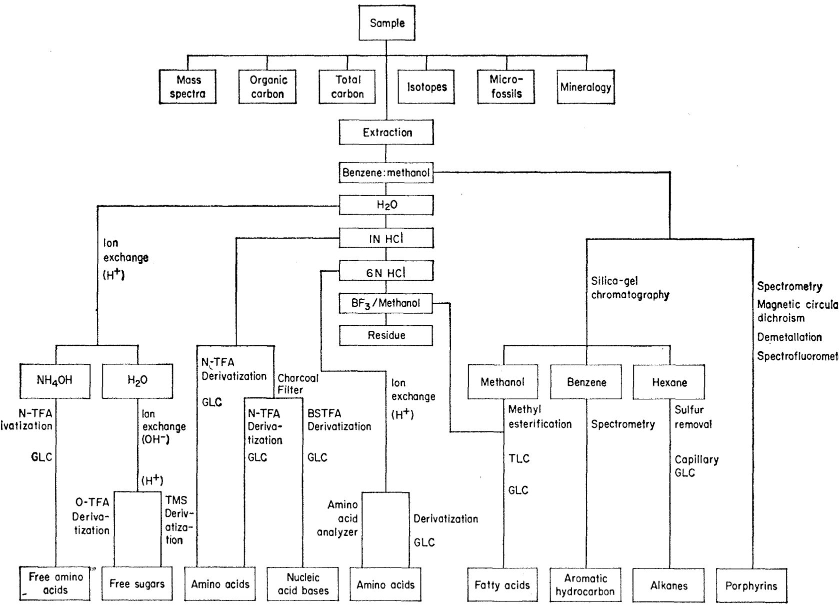


Fig. 1. Scheme of analysis.

150°C at a pressure of less than 1 μm-Hg and burned at 1050°C. The values ranged from 140 μg/g to 200 μg/g. The most consistent values were between 140 and 160 μg/g. The comparable figure for a sample of the Pueblito de Allende meteorite was 3000 μg/g. The sand blank showed no detectable carbon.

The amount of carbon that could be converted into volatile carbon-hydrogen compounds was determined by pyrolyzing about 30 mg of the dust at 800°C in an atmosphere of hydrogen and helium (*4*). The resulting volatile compounds were estimated by a hydrogen flame ionization detector. The average value obtained was 40 μg/g. For a sample of the Pueblito de Allende meteorite this amounted to approximately 14 μg/g, and for the sand blank, 1 μg/g.

Isotope measurements on the total sample resulted in a $\delta^{13}C$ value of +20 relative to the PDB standard and the $\delta^{34}S$ of +8.2 relative to the Canyon Diablo meteorite. These figures are considerably higher than those generally reported for intact meteorites ($\delta^{13}C$, −4 to −20; $\delta^{34}S$, −2 to +2). A detailed account of these findings and their significance are described by Kaplan and Smith (*5*).

A portion (20 mg) of the sample was pyrolyzed from 80° to 300°C in the ion source of a CEC 110 high-resolution mass spectrometer. The analysis was repeated at 700°C with the high-resolution mass spectrometer (MS 9) at the Jet Propulsion Laboratory in Pasadena. Ions indicating the possible presence of formic acid, acetic acid, and SO_2 were found above the background concentration. However, no conclusive identification was possible. Carbon dioxide was identified in the pyrolysis products at 250°C to 750°C. Observations of dust, surfaces of the microbreccias, and thin sections of microbreccias made by light and electron microscopy yielded no evidence of indigenous biological structures (*6*).

To detect extractable organic compounds, 54.6 g of the lunar dust were treated with a mixture of benzene and methanol (9 : 1). Twenty-three percent of the extract was examined for porphyrins (*7*). Fluorescence excitation and emission spectra of these extracts are suggestive of porphyrins. Since similar spectral responses were observed in exhaust products from tests of the lunar descent rocket engines, it is possible that these pigments were formed from components of the rocket exhaust (*8*). The amount of porphyrins detected was approximately 10^{-4} μg/g.

The remainder of the benzene-methanol extract was chromatographed on a silica-gel column and eluted with hexane, benzene, and methanol. Capillary gas-liquid chromatography of the hexane fraction showed that no single *n*-alkane from C_{12} to C_{32} was present at concentrations of 2×10^{-5} μg/g. The absorption spectrum of the benzene eluate showed bands at 224, 274, and 280 nm. Since these absorption bands were also present in the sand and solvent blanks, the presence of aromatics in the lunar sample cannot be inferred. The methanol eluate from the silica-gel chromatography was esterified and examined for fatty acids by gas-liquid chromatography. The C_{12} to C_{32} fatty acids were not detected at levels of 10^{-2} μg/g.

After treatment with benzene-methanol, the bulk fines were dried in a rotary evaporator and extracted with water. This extract was desalted and analyzed for free amino acids and carbohydrates by gas-liquid chromatography as *N*-trifluoroacetyl-*n*-butyl esters of amino acids, as trimethylsilyl derivatives of sugars, and as trifluoroacetyl derivatives of sugar alcohols. In the water extracts, the amino acids were not detected at a concentration of 10^{-5} μg per gram of sample. Sugars were not present at concentrations of 6×10^{-4} μg/g.

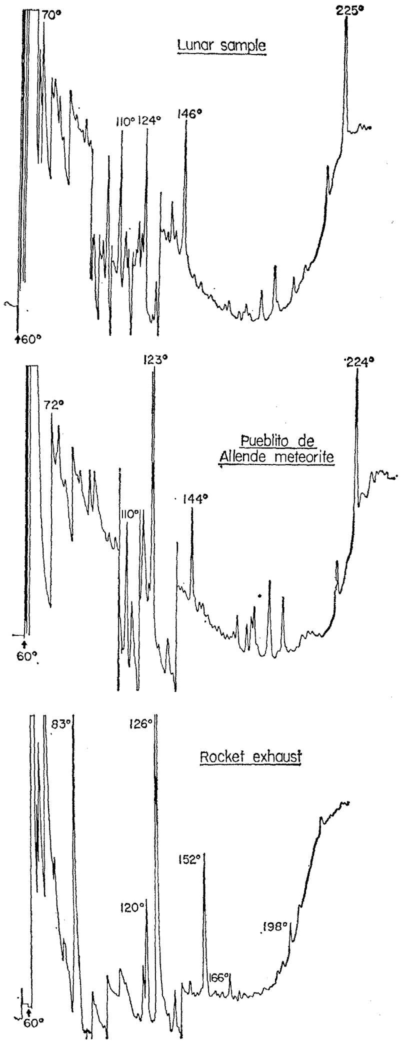
The residue, after the water extraction, was hydrolyzed with HCl. Hydrogen sulfide evolved during the hydrolysis was collected. The concentration was about 700 μg/g, with an average $\delta^{34}S$ value of +8.0. The 1*N* hydrolyzate was treated with Norite charcoal to absorb any bases that may have been present. The charcoal was extracted with formic acid, and the extract was treated with bis(trimethylsilyl)trifluoroacetamide and analyzed for the bases as trimethylsilyl derivatives. Purines and pyrimidine bases were not present at concentrations of 4×10^{-3} μg/g.

The hydrolyzate obtained after refluxing the sample with 6*N* HCl at 125°C for 19 hours was desalted and examined for amino acids by ion-exchange chromatography and gas chromatography of the *N*-trifluoroacetyl-*n*-butyl ester derivatives. Although as little as 2×10^{-3} μg/g could be detected by this method, none of the amino acids commonly found in protein appeared to be present.

However, in the HCl hydrolyzates several compounds were found which did not appear on the gas chromatogram unless the hydrolyzates were both esterified and acylated. These molecules were present in a similarly treated acid hydrolyzate of the Pueblito de Allende meteorite but not in the sand blank or the rocket exhaust material (Fig. 2). Organic compounds, as derivatives, appear to be present in both samples.

Since approximately 100 μg of carbon per gram of sample still remained to be accounted for, an attempt was made to determine whether some of the residual carbon was present as carbides. A fresh sample, outgassed in a vacuum at 150°C, was therefore hydrolyzed with 6*N* HCl in a sealed tube, and the resulting gases were distilled or extracted with *n*-hexane. Analysis by gas-liquid chromatography and mass spectrometry revealed the presence of C_1, C_2, C_3, and C_4 hydrocarbons. The total added up to almost 20 μg per gram of the lunar sample. A sample of Mighei meteorite and cohenite (Fe_3C) from the Canyon Diablo meteorite were similarly analyzed (Fig. 3), hydrocarbons being identified in each case.

Our examination of the Apollo 11 sample from the Sea of Tranquillity leads us to conclude that the concentration of carbon is about 157 μg per gram of sample. If we assume that the hydrocarbons generated from the acid hydrolysis come from carbides, the amount of carbon accounted for is approximately 20 μg/g. The isotopic compositions of carbon and sulfur are significantly different from the composition determined for other extraterrestrial samples. The $\delta^{13}C$ value of +20 relative to the PDB standard and the $\delta^{34}S$ value of +8.2 relative to the Canyon Diablo meteorite are unusual by comparison with both terrestrial and meteorite samples. Although the limits of detectability of our techniques were in the nanogram range, normal alkanes, isoprenoids, hydrocarbons, aromatic hydrocarbons, fatty acids, amino acids, sugars, and nucleic acid bases were not present at this level of concentration. There is a striking but yet unexplained similarity between the chromatogram of the compound that formed the derivative in the acid hydrolyzates of the lunar sample and of the Pueblito de Allende meteorite. These findings should be considered to be specific for a single surface sample from the Sea of Tranquillity. Samples from the highlands, or core samples, may be expected to yield different results.



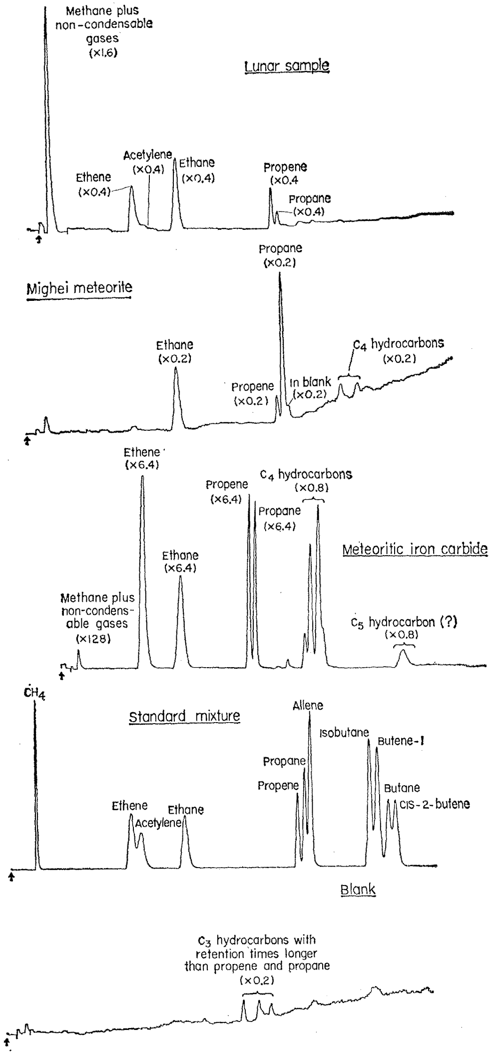


Fig. 2 (left). Gas chromatograms of *N*-trifluoroacetyl-*n*-butyl esters of 1*N* hydrolyzates of the Pueblito de Allende meteorite and the lunar sample, on a glass column (1 m by 6 mm), packed with 1.5 percent (by weight) OV-17, on heat-treated 80/100 mesh Chromosorb G, temperature programmed from 60°C to 250°C, at 4°C per minute. Vertical lines represent attenuation changes. Fig. 3 (right). Gas chromatograms of hydrocarbons from 6*N* HCl treatment of the lunar sample (0.1 g), Mighei meteorite (0.05 g), and Fe_3C (0.0014 g), on a stainless steel column (2 m by 3 m), packed with 150 mesh Poropack Q, programmed from ambient temperature to 150°C, at 10°C per minute. Standard mixture attenuated at × 160.

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