

retention by reaction with the matrix; bearing in mind the solar corona proportions, one arrives at a rough estimate of something of the order of 1 to 1000 ppm for carbon attributable to solar-wind implantation. On the basis of these calculations, one might even conjecture that all the carbon, as measured by Moore's experiments (4)—that is, of the order of 100 ppm—is provided by the solar wind.

Major organic contaminants expected in the sample from collection, handling in the Biopreparation Facility, and packaging are likely to be (1, 2, 7) butyl rubber, plasticizers, hydrocarbon oils, Teflon, cellulose fibers, contingency-bag contaminants, peracetic acid, and ethylene oxide and its products from sterilization. However, we have not yet detected these contaminants in our experiments. The bulk fines were collected over a fairly wide area within about 9 meters of the module engine, where they must certainly have received considerable effluent during the final few seconds of the descent of the spacecraft. Oxidizer (N_2O_4) was also vented on that side of the craft. No evidence of rocket exhaust products could be detected on baking a sample at 150°C under vacuum (10^{-6} torr) and examining the trapped gases by mass spectrometry.

Aromatic products similar to those reported here have been obtained from carbonaceous chondrites when heated (8). Despite the possibility of contamination both of the lunar samples and of the carbonaceous chondrites, the occurrence of aromatic compounds in the pyrolysis products of both materials may indicate that these compounds or their precursors are truly extraterrestrial.

The indigenous lunar methane could have one or more origins: (i) primordial, (ii) entrapped during crystallization of the rocks, (iii) a primary product of the solar wind, (iv) a secondary product of indigenous or solar wind carbon arising from "hot atom" chemistry (9) induced by high energy cosmic rays. We hope to distinguish between some of the above possibilities by more detailed work. The reaction between the solar wind and the inorganic matrix to give matrix-O-C products remains to be studied.

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Pyrolysis-Hydrogen Flame Ionization Detection of Organic Carbon in a Lunar Sample

Abstract. *The lunar samples were analyzed for total organic carbon content by pyrolysis at 850°C and subsequent detection of the resulting volatilized organic compounds in a hydrogen flame ionization detector. The organic content ranged from 10 to 126 parts per million, depending primarily upon the handling in the sample processing. No correlation of organic content with rock type has been shown. The small quantities of organic matter are primarily contamination, and the indigenous organic content is estimated to be less than 10 parts per million.*

During the preliminary examination of the Apollo 11 lunar samples at the Lunar Receiving Laboratory, 14 different specimens of lunar material were analyzed for total organic carbon content (1, 2). One additional related sample was analyzed as part of the subsequent lunar sample distribution (3). The results of these analyses are given in Table 1.

The analytical method is based upon the response of the hydrogen flame

ionization detector (4) to the volatile products arising from pyrolysis of the solid sample at 800° to 900°C. Inorganic compounds, including those with carbon as carbonate, graphite, and carbides (silicon and zirconium), give essentially no response under the conditions of the analysis. While the detector is sensitive and specific to organic compounds, the overall analysis is approximate, since both the degree of char formation and the exact re-

Table 1. Organic carbon content of Apollo 11 lunar samples.

Sample number	Sample Type of material	Organic carbon (ppm)*	Comments
<i>Contingency sample</i>			
10,5	Fines	16 ± 7	Sampled immediately
10,26	Fines	48 ± 18	Sampled after 11 days
21,21	Aggregate	44 ± 31	Handled extensively
24,4	Crystalline	17 ± 6	Handled moderately
32,1	Crystalline	10 ± 9	Unhandled previously
<i>Documented box</i>			
15,10	Fines	126 ± 64	From gas reaction cell
61,4	Aggregate	62 ± 19	Vacuum chamber
64,4	Aggregate	96 ± 30	Vacuum chamber
68,3	Aggregate	39 ± 18	Vacuum chamber (handled specially)
<i>Bulk box</i>			
02,73	Fines	18 ± 8	Unhandled
86,A	Fines	40 ± 8	Distributed to investigators
46,3	Aggregate	80 ± 26	Handled routinely
48,3	Aggregate	88 ± 43	Handled routinely
49,7	Crystalline	54 ± 23	Handled routinely
50,3	Crystalline	28 ± 19	Handled routinely
56,12	Aggregate	10 ± 4	Handled specially

* The values are obtained from fitting to the log-log calibration plot. The errors quoted are derived from 90 percent confidence limits.

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.

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 $\delta^{13}\text{C}$ 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 × 10⁹ 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,

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

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 CO₂ evolved when a 1-g sample was outgassed at