References and Notes

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6. This work is supported by NASA research contract NAS 9-8099.

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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

Table 1. Gas content of pyrolized lunar sample; +++, $\geq$ 20 percent of total ion current; ++, $\geq$ 10 percent; +, 0 to 10 percent for both trapped and untrapped fractions.

Gas	Temperature							
	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_2H_4	+	+	+	++	+			
C_4H_8	++	+	++	+++	+			
C_6H_6	+	+	++	+++	+++	++	+	+
C_7H_8	+	+	+	++	++	+	+	+
C_8H_8				+	+	+		
C_8H_{10}				+	+	+	+	+
C_9H_8					+	+	+	+
C_9H_{10}					+	+	+	+
C_9H_{12}						+	+	+
C_4H_4S		+	+	+	+			

clearly evident from the data (Table 1). The structures of Table 1, assigned by low-resolution mass spectrometry, will be examined in greater detail by high-resolution mass spectrometry. Proper quantitative data are yet to be derived, but the most striking features are:

1) Carbon monoxide and carbon dioxide are continuously evolved, and in especially large amounts at the higher temperatures.

2) Methane appears in substantial quantity. It is accompanied by a variety of unsaturated and aromatic hydrocarbons which may be indigenous. Thermal alteration of indigenous material or contamination would also produce these hydrocarbons. Although evolution of methane virtually ceases at temperatures above 700°C, it is still liberated in quite large quantities by subsequent HF etching of the pyrolyzed sample together with further amounts of the rare gases (other organic compounds liberated would not be seen on account of the trapping system used).

3) The rare gases first appear at temperatures near 300°C, and they continue to be evolved thereafter; there is some variation in the observed isotope ratios, however, presumably due to selective baking out of sites and the presence of terrestrial gases at the lower temperatures.

We have constructed a special, interconnected, glass and Teflon closed system within which to carry out, in a helium atmosphere, the classical geochemical procedures of solvent extraction, separation, evaporation, derivatization, and chromatography, using small volumes of solvent, with brief exposure of samples, extracts, and fractions to the atmosphere and the laboratory environment. We have monitored organic compounds extractable from the lunar fines (14.8 g) with a mixture of benzene and methanol (3:1, 15 ml) during brief sonication (30 minutes). The evaporated extract, a brown oily gum, was dissolved in methanol (2 μl), and a portion (0.5 μl) of the resulting yellow solution was subjected to combined gas chromatography and mass spectrometry (Varian MAT CH7 system; column, 3.6 m × 1.5 mm, stainless steel; 3 percent OV-17 on Chromosorb W), programmed from 120° to 280°C at 4°C per minute, with a helium flow of 5 ml/minute. The minimum level for detection of n-C_{20} alkane was about 25 ng. Control runs with the same volume of solvent, first alone and then, when used for the extraction of a standard hydrocarbon (1-^{14}C-labeled n-octadecane), adsorbed on powdered alumina (grade 1, neutral) as support, demonstrated (i) the background level of contamination (equivalent to no peak > 20 ng) and (ii) the efficiency of recovery (> 70 percent at the 100-ng level) under operating conditions standardized for extraction and evaporation. We conclude that individual alkanes and other relatively nonpolar compounds, if present, do not occur in concentrations higher than 5 parts per billion in the molecular weight range ~ C_{12} to C_{32} which would be revealed by this study. The remaining portion of the extract was derivatized by heating for 45 minutes at 60°C with the reagent $CF_3CON(SiMe_3)_2$. The product, when analyzed by combined gas chromatography and mass spectroscopy, gave only two distinct peaks, which derived from the reagent alone.

We do not know to what extent the carbon compounds herein reported are truly indigenous to the lunar surface. However, we do believe that the methane is present as such in the inorganic matrix. The higher hydrocarbons, observed only in the pyrolysis experiment, might also be in the matrix, but until a refined HF etching experiment is performed we cannot be sure. Methane has been reported in carbonaceous chondrites by Anders *et al.* (*5*), but one analysis of Allende by us did not reveal significant quantities of this component, although the gas-rich chondrite, Kapoeta, which has a very low carbon content, contains appreciable quantities of methane. Thus, our limited data indicate that the quantity of methane is proportional to the solar wind rare gas content but not to the carbon content. There appears to be no previous report of the presence of methane in gas-rich or ordinary chondrites. Methane, in addition to carbon dioxide and carbon monoxide, has also been obtained from terrestrial igneous rocks when baked at 1000°C (*6*).

The preliminary results obtained for the Apollo 11 rocks and fines (*2*) point to an origin from high-temperature melts subsequently exposed on the surface for some millions of years. The presence of biogenic products is therefore extremely improbable, and the predominant sources of carbon are likely to be the solar wind and meteorite impact. However, two factors make it unlikely that meteorite impact contributes much of the carbon: (i) vaporization and consequent loss on impact, and (ii) low frequency of impact.

The rare gas values for lunar material apparently indicate saturation of the outer few hundred angstroms of the crystals and glasses (*2*). The losses by diffusion and shock events are not known but must have been considerable. The loss of carbon compared to that of the low molecular weight rare gases would, of course, be less, owing to 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 indegenous 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		Organic carbon (ppm)*	Comments
Sample number	Type of material		
		Contingency sample	
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
		Documented box	
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)
		Bulk box	
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.