Organic Chemistry

Lunar Organic Compounds: Search and Characterization

Abstract. *The carbon concentration in Apollo 11 lunar fine material is of the order of 200 ppm. By far the largest single amount of this carbon appears to be in carbon monoxide. Some of this seems to be in the form of gas bubbles in the glass spheres, but most of it could be in some complex form other than gas. This result would be consistent with the idea that most of the fines passed through a high temperature and that the carbon was oxidized by mineral oxides at that time.*

The search for carbon-containing material on the lunar surface is not only a component part of the study of the origin and history of the moon, but an important step in our understanding of the early stages of chemical evolution leading to the origin of life. It represents the first possibility of examining nonterrestrial material uncontaminated by the biological products found everywhere on earth.

We have therefore proceeded with three sequences of operations: (i) direct pyrolysis into the mass spectrometer at temperatures up to 1150°C; (ii) a preliminary extraction with a clean mixture of benzene and methanol, followed by direct introduction into the mass spectrometer; (iii) solution of the fines in 20 percent HF, purging with helium to trap any volatile materials, then solvent extraction and pyrolysis of the residue.

Two types of direct pyrolysis experiments on moon dust were performed. In the first, the sample was treated at 150°C, and any volatile material was removed (*1*). The sample was then heated directly to fusion at 1150°C for 1 hour. The evolved gases were introduced into a MS-902 high resolution mass spectrometer (*2*) and consisted of CO (156 ppm C), CO_2 (12 ppm C), traces of HCN, H_2S, SO_2, Ne, Ar, C_2H_2, N_2, and O_2 (*3*).

A second experiment involved a preliminary 150°C heating for 30 minutes, followed by direct heating to 500°C for 30 minutes. The gases evolved were CO (9 ppm C), CO_2 (<1 ppm C), and traces of the same series given above, but including some CH_4. A third experiment performed with the same temperature sequence as the second experiment, but involving passage of evolved gases through the GC-MS 12 combination (*4*), confirmed the presence of CH_4.

Because the sample was already so finely divided, we decided that any further reduction in size could only increase possible contamination. An optical examination of the material confirmed that it was a mixture of angular birefringent particles with a small amount of spherical or near-spherical nonbirefringent particles (Fig. 1), as well as some angular glassy particles. In addition, a proportion of the glass spheres appeared to contain vesicles and some optically dense inclusions (Fig. 1, b and c).

Table 1. Composition of the benzene-methanol extract of 19.8 g of lunar fines from Apollo 11 determined by high-resolution mass spectrometry (only ions representing possible molecular species are shown).

Nominal mass	Component	Average ion current (relative)	Observed mass (amu)
17	NH_3 *	260	17.02629
18	H_2O	85,000	
26	C_2H_2	650	
27	HCN *	300	27.01103
28	CO	18,000	27.99490
	N_2	210,000	28.00615
30	NO *	1,100	29.99769
32	CH_2O	1,220	
	O_2	40,300	
42	C_2H_2O	300	
	C_3H_6	420	
43	HCNO *	280	43.00797
	HN_3	40	43.01846
44	CO_2	6,100	
	CH_2NO *	270	44.01581
	C_2H_4O	1,250	
	C_2H_6N *	30	44.05208
46	CH_2O_2	710	
50	C_4H_2	250	
52	C_4H_4	100	
54	C_4H_6	200	
55	CHN_3—C_3H_3O	100	55.01682
56†	C_4H_8	650	
58	CH_4N_3—C_3H_6O	100	58.03816
59	C_2H_5NO *	550	59.03489
60	C_2H_6NO *	110	60.04380
149	$C_8H_5O_3$	3,400	

* Composition attributable to retro-rocket exhaust from lunar module (*5*). † Hydrocarbons were found to C_{10} but were not listed above C_4.

The dust (19.8 g) was extracted in 100 ml of a mixture of benzene and methanol (3:1), following the procedure of Han *et al.* (*4*). A part of this extract, after concentration to 3 μl, was examined by capillary gas chromatography (FID detector), and no organic compounds were detected. The remaining 1.7 μl was introduced into the MS-902 high resolution mass spectrometer (*2*), on-line to a computer; the results are given in Table 1. Materials resulting from retro-rocket exhaust are present (*5*), as are a number of contaminants which are derived from sample handling procedures (*6*). In order to complete the examination of the lunar samples for organic matter, the 19.8 g of cleaned dust were then dissolved in 20 percent HF prepared as described by Han *et al.* (*4*). The resulting residue (12 g) was mostly a white flocculate with some heavy black particles (less than 1 percent of the residue).

The benzene-methanol extract of this residue, after vacuum drying at 120°C for 12 hours, yielded no detectable material above solvent background either by gas chromatography or by direct introduction into the MS-902 ionization chamber. A 22-mg sample of this residue was subjected to sequential pyrolysis at 150°, 500°, and 1100°C. The principal product in each case was CO at 18 ppm C, 13 ppm C, and 88 ppm C, respectively, by weight of the original dust, adding up to a total of 119 ppm C.

The relatively low value of carbon, together with the presence of vesicles in the glass spheres, suggested that the dust might contain volatile material which would be liberated and lost upon solution in HF. We therefore designed an apparatus which would allow the dissolution of the sample with simultaneous trapping of any liberated gases. This involved a dissolver followed by a sequence of cold traps at the temperatures of Dry Ice–acetone, liquid nitrogen, and liquid helium, respectively. After dissolved and absorbed gases were eliminated, the apparatus was calibrated by dissolving approximately 20 g of silica gel, to which had been added 1 ml (3.5×10^{-5} mole), at standard temperature and pressure, of CO. Carbon monoxide (2×10^{-5} mole) was recovered from the liquid helium trap, indicating a 58 percent efficiency of recovery. When 17.8 g of moon dust as received from the Lunar Receiving Laboratory was dissolved in this equipment, a total of 66 ppm C was recovered as CO from the liquid helium trap. When added to the 119 ppm C as CO obtained by pyrolysis of residual silica after HF digestion, this totaled 185 ppm C, which can be compared with the value of 168 ppm C (CO value plus CO_2 value) found in the dust by direct pyrolysis at 1150°C. There remains the possibility that a small amount of volatile C has been lost during preliminary drying of the residual silica.

It is of interest to estimate the amount of gaseous CO which might be present in the vesicles of the glass spheres. A rough statistical analysis of their distribution would require that they contain 10^4 atmospheres partial pressure CO in order to be equivalent to the 66 ppm C liberated upon solution. This seems excessive, and we therefore feel a considerable amount of CO liberated by HF must be in other than gaseous form in the original moon dust, for example as carbonyls.

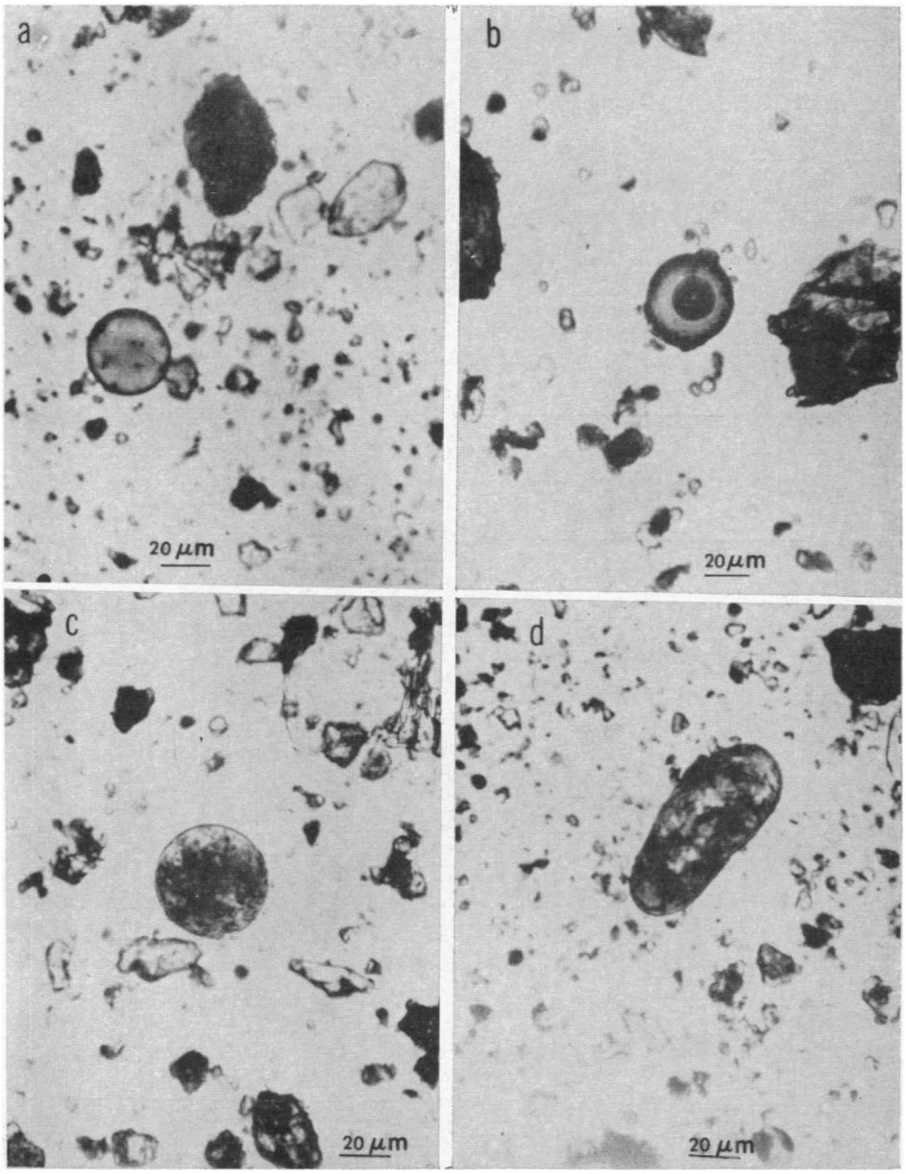

Fig. 1. Oil mounts ($n = 1.569$) of Apollo 11 dust. (a) Clear glass sphere with minor dark inclusions; (b) clear glass sphere containing vesicle; (c) cloudy glass sphere showing granular dark inclusions; (d) cloudy elongate glass "spherule" showing granular dark inclusions, and vesicle.

Calibration of the method with a Hawaiian basalt containing 120 to 150 ppm C by combustion (*7*) produces the corresponding amount of CO, whereas the addition of graphite to the fused fines, followed by pyrolysis, does not convert more than 3 percent of that graphite to CO. We therefore conclude that there will be only a small amount, if any, of graphite present in the fines.

The largest chemical component form of carbon in the lunar fines which we have so far analyzed is carbon monoxide. This could be the result of the oxidation of any reduced carbon by the heat of meteorite impact or other sources of energy available to the lunar surface, mineral oxides being the oxidizing agent. Most of the carbon monoxide so formed would have escaped the lunar gravitational field, thus accounting for the extremely low concentrations of total carbon in any of the samples yet analyzed (<0.02 percent). We might expect much more carbon in those lunar materials which have never been molten. These would be either the primordial aggregates from which the moon might have been formed, or the collection of infall of meteorites at low energy.

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References and Notes

1. This consisted of air, water, CO, CO_2, and some methane.
2. A. L. Burlingame, D. H. Smith, T. O. Merren, R. W. Olsen in *Computers in Analytical Chemistry,* C. H. Orr and J. Norris, Eds. (Plenum Press, New York, 1969), p. 13; A. L. Burlingame, D. H. Smith, F. C. Walls, R. W. Olsen, *Proceedings of the 17th Annual Conference on Mass Spectrometry and Allied Topics* (Dallas, Texas, 18–23 May 1969), p. 28.
3. Nitrogen is 20 times more abundant than oxygen.
4. J. Han, B. R. Simoneit, A. L. Burlingame, M. Calvin, *Nature* **222**, 364 (1969).
5. B. R. Simoneit, A. L. Burlingame, D. A. Flory, I. D. Smith, *Science* **166**, 733 (1969).
6. Lunar Sample Preliminary Examination Team, *Science* **165**, 1211 (1969); D. A. Flory, B. R. Simoneit, D. H. Smith, *Apollo 11 Organic Contamination History*, NASA Manned Spacecraft Center Report, August 1969.
7. Samples obtained from I. Kaplan, University of California, Los Angeles.
8. We acknowledge the contributions of G. Thomas (metallurgy), T. Eberhart (electrical engineering), T. Hayes (medical physics) for electron microscopy; G. Somorjai (chemistry) for auger spectroscopy; D. H. Smith, M. Petrie, F. C. Walls, P. Harsanyi, C. Sprowls (Space Sciences Laboratory) for technical assistance in high resolution mass spectrometry and computation. Supported by NASA MSC contract NAS 9-7889.

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