Study of carbon compounds in Apollo 11 and Apollo 12 returned lunar samples

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Abstract—In order to determine the nature and chemical characteristics of the carbon present in the returned lunar materials, several different experimental approaches have been used. Temperature-dependent release of carbonaceous molecules has been examined from ambient to 1000°C. The results indicate that there are at least two different forms of carbon present in the surface fines in addition to terrestrial organic contaminants.

The release of volatile carbon-containing molecules such as CO, CH_4, and CO_2 during acid dissolution has been investigated further, using mass spectrometry for detection and quantitation. A gas chromatographic method of analysis has also been developed to quantitate the release of CO and C_1–C_4 hydrocarbons. The concentrations of these components has been quantitatively determined as CO, less than 1 ppm; C_1–C_4 total hydrocarbons, up to 38 ppm for Apollo 11 and Apollo 12 samples; and CO_2, up to 40 ppm.

Soluble organic compounds obtained upon solvent extraction of the surface fines have been examined; it appears that the possible indigenous organic compounds amount to less than 1 ppm C (wt/wt fines).

Introduction

We have reported previously that, using our techniques, the indigenous organic content of the Apollo 11 fines (10086,A) was < 1.0 ppm and that demineralization of the fines with 20% HF yielded 66 ppm of carbon as carbon monoxide (CO) (Burlingame et al., 1970). Using the same detection and quantitation procedure we confirmed the total carbon content found by other groups (Moore et al., 1970; Kaplan et al., 1970; Abell et al., 1970; Oró et al., 1970). No complete carbon mass balance for the Apollo 11 fines has as yet been reported.

Since then our efforts have been directed towards confirming the concentration of CO obtained, and to obtaining a mass balance for carbon utilizing three different experimental approaches: (1) organic solvent extraction of lunar fines; (2) Carbon analysis at elevated temperatures; (3) HF demineralization of lunar surface and double core materials, and trace gas analysis in closed systems.

Experimental Techniques

Organic solvent extraction

All extractions were carried out in a class 100 organic clean-room facility. [Class 100 clean room as specified by Federal Standard 209a (1966) contains less than 1000 particles of 0.3–0.5 μ size and 100 or less particles of 0.5 μ or greater size per cubic foot.] The fines samples were

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extracted in a mixture (3:1) of redistilled benzene and methanol (Mallinckrodt–nanograde purity) following the procedure of HAN *et al.* (1969) and BURLINGAME *et al.* (1970). For samples 12001 and 12023 (8.5 g of each) 50 ml of solvent mixture was used, and for samples 12032 and 12042 (3.5 g of each) only 30 ml was used. After filtration through a fine fritted filter, the extract was concentrated on a rotary evaporator, followed by further concentration under flowing helium. The extracts were introduced into the MS-902 high-resolution mass spectrometry–computer system via a direct introduction probe. The same on-line operating conditions as reported by BURLINGAME *et al.* (1970) were used.

Carbon analysis at elevated temperatures

All samples were analyzed using a modified Model 185 C, H, and N analyzer equipped with an HP-18 helium purifier (Hewlett-Packard, Palo Alto, California). All modifications to enhance stability and sensitivity have been reported elsewhere (JENSEN *et al.*, 1967). Daily calibration was provided with methyl stearate or $CaCO_3$. At levels of 15–18 μg carbon (as carbonate), measured fluctuations in absolute carbon mass calibration were consistently less than $\pm 2\%$ over the reported experimental period, whether measured before or after sample analyses.

Other standards used included argillaceous limestone (Standard Reference Material 1b, National Bureau of Standards), carbon black, calcined (i.e., heated at 550°C for 12 hours in air) graphite, calcined chromium carbide (ROC/RIC Corporation, Sun Valley, California), and calcined iron carbide (Fe-72, Wilshire Chemical Co., Gardena, California). A low level standard and matrix, calcined at 550°C, was prepared from a sample of crushed Table Mountain latite (from near Sonora, California) to which TiO_2 (7% wt/wt) had been added.

All samples were pyrolyzed in a static helium atmosphere. The pyrolysis cavity was maintained at a constant temperature of 1065°C, the present limit of the instrument. The sample was loaded onto a platinum boat and placed into a holding position at the cold ($\sim 60°$C) end of the pyrolysis tube under helium. Pyrolysis was accomplished by sliding the boat into the hot cavity. The sample was allowed to remain in the hot cavity for 20 or 60 seconds (cf. Table 2) followed by injection of the products through a combustion tube to convert all released carbon compounds to CO_2. The CO_2 was then measured by a sensitive on-line gas chromatograph using a thermal conductivity detector. Differing pyrolysis times resulted in different terminal temperatures (925°–1000°C., cf. see Table 2) with concomitant release of different amounts of carbon.

Pyrolysis was performed on samples with three different thermal pretreatments: (1) untreated samples were pyrolyzed directly; (2) samples were maintained at 150°C for 12 hours in air to remove most surface adsorbed contaminants and then pyrolyzed; (3) samples were maintained at 550°C for 12 hours in air to remove remaining surface adsorbed materials and all amorphous carbon and then pyrolyzed. When standards were pyrolyzed under these conditions, quantitative recovery was achieved for all organic, amorphous, and carbonate carbon, with nearly quantitative (82%) recovery for graphitic carbon (mixed with an oxidizing catalyst consisting of manganese dioxide and tungsten oxide), but low ($\sim 10\%$) recovery for carbide carbon (as iron carbide and chromium carbide). The comparative recoveries for these carbides appears anomalous; however, the purity of iron carbide as purchased is questionable in that the composition cannot be balanced stoichiometrically. Therefore, the recovery of carbon from iron carbide is likely to be higher than the 10% shown for the Fe-72 standard.

HF demineralization and trace gas analysis

The previously reported experiment (BURLINGAME *et al.*, 1970) on the release and quantitative recovery of CO from lunar fines was repeated with basically similar apparatus and instrumentation. The modifications introduced were a glass reaction and trap system which was greatly reduced in volume (from that previously used), and the G.E.C.–A.E.I. MS 902 instrument was replaced by a C.E.C. 21-110B high-resolution mass spectrometer (BURLINGAME *et al.*, 1968) which was equipped with a micromanometer and an improved gas inlet system. The following spectrometer conditions were used for calibration and sample: resolution 5000 (static), ionizing voltage 70 eV, and ion source temperature 215°C. The system was calibrated for CO as reported by BURLINGAME *et al.*

(1970), except this time the
CO peak and correlated vs.
before (BURLINGAME *et al.*,

A gas chromatographi
hydrocarbons and other g
reaction system consisted o
Cajon fitting with a Teflo
into the dropping funnel a
welded stainless steel man
run, for blanketing the rea
analysis. This transfer wa
through a Dry Ice/isoprop
sieve trap in liquid nitroge
was connected to the gas
instantly transferred from
provided quantitative and
samples used for calibratio

Two gas chromatogra
hydrogen were analyzed o
temperature bath at -22
Los Angeles). Methane a
combination stainless stee
programmed from 50°C t
with a flame ionization
(1 15 μl) of pure gases in
identical to actual run con
using the thermal conduct
detector.

All runs with lunar sa
follows: Purified 20% HI
transferred, still under he
and then heated to 150°C
HF was then added to th
allowed to react for 30 m
sample and HF had cea
were transferred to the
The trap was isolated fro
for 30 seconds and then
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Organic solvent extra

The concentratio
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Samples 12023, the

(1970), except this time the electron multiplier output voltage was measured for the flat topped CO peak and correlated vs. the CO partial pressure. Lunar fines (10086,A, 5 g) were dissolved as before (BURLINGAME et al., 1970) and the contents of the liquid helium trap were analyzed.

A gas chromatographic system was developed for the quantitative determination of the hydrocarbons and other gases released from lunar materials on solution with acid. The glass reaction system consisted of a dropping funnel connected to a removable reaction vessel via a glass Cajon fitting with a Teflon seal. Gas-tight Teflon stopcocks were used for introduction of HF into the dropping funnel and subsequently to the reaction vessel. The reactor was connected to a welded stainless steel manifold with Nupro valves (all stainless steel) for evacuation prior to a run, for blanketing the reaction with helium and for subsequent transfer of gaseous products for analysis. This transfer was made by flushing the reactor with helium and passing the effluent through a Dry Ice/isopropyl alcohol trap to remove HF and H_2O and then on to a 5 Å molecular sieve trap in liquid nitrogen to concentrate the product gases from the stream of helium. This trap was connected to the gas chromatographic system such that the helium carrier gas could be instantly transferred from a by-pass line to the heated trap via two 3-way valves. This system provided quantitative and reproducible injections of the product gases and the standard gas samples used for calibration.

Two gas chromatographic detection systems were used. Carbon monoxide, methane, and hydrogen were analyzed on a 40' × ⅛" stainless steel column packed with Poropak Q in a constant temperature bath at $-22 \pm 0.1°C$ using a micro-thermal conductivity detector (Carle Instruments, Los Angeles). Methane and other hydrocarbons up to C_4 in carbon number were analyzed on a combination stainless steel column (10' × ⅛" Poropak Q and 3' × ⅛" Poropak N), temperature programmed from 50°C to 100°C at 10°C per minute using an Aerograph 665 gas chromatograph with a flame ionization detector. The system was calibrated by injections of known amounts (1–15 μl) of pure gases into the reactor system via a septum followed by a transfer and injection identical to actual run conditions. The minimum detection limits were 0.1 ppm with 100 mg samples using the thermal conductivity detector and 0.1 ppm using 20 mg samples with the flame ionization detector.

All runs with lunar samples, including HF alone and HF plus glass blanks, were performed as follows: Purified 20% HF (HAN et al., 1969) was degassed under helium with ultrasonication and transferred, still under helium, to the dropping funnel. The sample was added to the reaction flask and then heated to 150°C for 5 minutes under vacuum to remove adsorbed gas from the sample. HF was then added to the sample (5 ml of HF solution per 100 mg of sample) under helium and allowed to react for 30 minutes at 50 C. Visual observation indicated that the reaction between the sample and HF had ceased after 20 minutes, often with complete dissolution. All evolved gases were transferred to the molecular sieve/liquid nitrogen trap by flushing with 250 ml of helium. The trap was isolated from the reactor by closing off the inlet valve, followed by heating to 350°C for 30 seconds and then injecting the trap contents into the gas chromatograph by rerouting the helium carrier gas from a bypass line through the trap.

RESULTS AND DISCUSSION

Organic solvent extraction of lunar fines

The concentrations of extractable organic compounds were low as determined by high resolution mass spectrometry only. The main results are shown in Table 1. The levels of contamination from sample handling procedures (SIMONEIT and FLORY, 1971) and from the LM retro-rocket exhaust (SIMONEIT et al., 1969) are low, especially in the Special Environment Sample Container (SESC) sample. Sample 12001 contains the largest amount of extractable material, consisting mainly of the more common saturated hydrocarbons and significant amounts of LM engine exhaust products. Samples 12023, the SESC sample, and 12032 show the lowest amounts of extractable

W. Henderson *et al.*

Table 1. Composition of the benzene-methanol extracts of lunar fines from Apollo 12, as determined by high-resolution mass spectrometry.

Nominal Mass	Species	Blank	Samples			
			12011	12023(SESC)	12032	12042
27	HCN[c]	30[a] (4)[b]	3200[a] (7)[b]	20[a] (1)[b]	20[a] (1)[b]	200[a] (8)[b]
30	NO[c]	—	3150 (8)	25 (1)	—	3200 (7)
31	HNO[c]	—	720 (1)	—	—	1500 (1)
41	CH₃CN[c]	—	—	—	—	100 (4)
43	C₂H₃O	1200 (10)	7200 (10)	350 (10)	400 (9)	1500 (10)
	HCNO[c]	—	700 (1)	—	—	150 (4)
44	C₂H₆N[c]	—	1380 (4)	—	60 (1)	200 (5)
45	CHO₂	—	5700 (9)	—	—	2500 (9)
	CH₃NO[c]	—	100 (1)	20 (1)	—	200 (2)
46	CH₂O₂	—	4500 (9)	—	—	1900 (9)
	CH₄NO[c]	—	650 (1)	—	—	300 (2)
57	C₄H₉[d]	5500 (10)	9800 (10)	2000 (10)	2500 (10)	2000 (10)
104	C₈H₈	50 (4)	550 (3)	—	—	100 (6)
149	C₈H₅O₃	4000 (10)	5500 (9)	550 (10)	320 (10)	500 (8)

[a] Average ion current (relative).
[b] Occurrence number per 10 scans.
[c] Composition attributable to LM retro-rocket exhaust (SIMONEIT *et al.*, 1969).
[d] Hydrocarbons of the series C_nH_{2n+2} to C_nH_{2n-6}, but mainly the more saturated series, were found in the mass spectral data for $n = 1$ to 14 in the extracts of the samples and the blank.

Table 2. Carbon content
det

Sample	In Treatme (°C)/T
Surface fines 10086A	Am
	15(
	55(
	Am
Interior chip Rock 10059	Am
	15
	55

[a] Probably removes mo:
[b] Removes amorphous c
[c] 100% recovery of o:
carbonates; 65% recovery o:
carbide.
[d] 82% recovery of gra
carbide.

material observed to date, with essentially no compounds attributable to the LM engine exhaust.

Carbon analysis at elevated temperatures

Results obtained for the temperature/time dependent release of carbon from Apollo 11 samples are summarized in Table 2. Surface adsorbed contaminants released by treatment in air at 150°C for 12 hours amount to 1–2 ppm C. Additional carbon amounting to 16 ppm and 20 ppm for the fines and the rock respectively is released upon treatment at 550 C for 12 hours. Under these conditions, recovery of amorphous carbon and carbonate carbon was 100% and 0%, respectively. The recovery (5 ppm) of extractable organic contaminants (BURLINGAME *et al.*, 1970) accounts for only 25–33% of this material. Therefore, the remainder of this carbon could be surface adsorbed CO_2 and possibly amorphous carbon. Between the 550°C/12 hour treatment and 925°C/20 second pyrolysis, the fines and the rock release additional carbon amounting to 36 ppm and 55 ppm, respectively. Under these conditions carbonate recovery is 100%, graphite recovery is 65%, and carbide recovery, as iron carbide or chromium carbide is less than 10%. Therefore, should carbonate or graphite carbon be present, all of the carbonate, most of the graphite, and only a little of the carbide would be recovered. An additional 24 ppm carbon from the fines results from increasing the terminal pyrolysis temperature and time from 925°C/20 seconds to 1000°C/60 seconds. The latter conditions providing 82% recovery of graphite but only approximately 10% for carbide. Therefore, this 24 ppm could be predominantly graphitic carbon.

These data suggest the existence of several forms of carbon in the lunar fines—adsorbed terrestrial contamination (5 ppm), endogenous organic compounds, adsorbed CO_2 or amorphous carbon (11–15 ppm), graphite (≥ 24 ppm), and possible

carbonate (≤ 36 ppm). In addition able (see below), would account fo experiments (76–80 ppm) and th reported for total carbon content

HF demineralization and trace gas

A new experimental system w carbons released from lunar fine (CHANG *et al.*, 1971). This system v the same reaction conditions. A li was used to collect effluent comp dual gas chromatographic detect ionization detectors). The system surface materials for dual detect detector alone. The results from tl tive chromatograms are shown in not detected by the micro-therma tion limit of 0.1 ppm carbon as (exhibit a significantly higher prod (10059) yields approximately twice of CH_4 production with depth i material obtained by pyrolysis-ma noted (BURLINGAME *et al.*, 1971) significantly more CH_4 than the c 11 cm depth exhibited an indicati GAME *et al.*, 1971)]; and (6) large : The total gas mixture from tl

Table 2. Carbon content of lunar samples by total organic carbon determination technique.

Sample	Initial Treatment Temp. (°C)/Time(hr)	Pyrolysis Terminal Temp. (°C)/Time(sec)	Carbon Content (ppm)
Surface fines 10086A	Ambient	925/20[c]	53.9
	150/12[a]	925/20[c]	52.0
	550/12[b]	925/20[c]	36.4
	Ambient	1000/60[d]	78.3
Interior chip Rock 10059	Ambient	925/20[c]	74.0
	150/12[a]	925/20[c]	73.1
	550/12[b]	925/20[c]	53.3

[a] Probably removes most surface adsorbed contaminants in 12 hrs.
[b] Removes amorphous carbon.
[c] 100% recovery of organic compounds, amorphous carbon, and carbonates; 65% recovery of graphite, < 10% recovery of iron and chromium carbide.
[d] 82% recovery of graphite, ~10% recovery of iron and chromium carbide.

carbonate (≤ 36 ppm). In addition, carbide carbon, at least part of which is hydrolyzable (see below), would account for the difference between the total recovered in these experiments (76–80 ppm) and the much higher values (140–200 ppm) previously reported for total carbon content (for example, MOORE et al., 1970).

HF demineralization and trace gas analysis

A new experimental system was devised to investigate and quantify the hydrocarbons released from lunar fines, probably by HF acid reaction with carbides (CHANG et al., 1971). This system was also designed to investigate CO evolution under the same reaction conditions. A liquid nitrogen trap packed with 5 Å molecular sieve was used to collect effluent components. Quantitative results were obtained using a dual gas chromatographic detection system (microthermal conductivity and flame ionization detectors). The system sensitivity allowed the use of 100 mg aliquots of surface materials for dual detection and 20 mg aliquots using a flame ionization detector alone. The results from these analyses are shown in Table 3, and representative chromatograms are shown in Figs. 1, 2, and 3. The main findings are: (1) CO was not detected by the micro-thermal conductivity system, which has a minimum detection limit of 0.1 ppm carbon as CO per 100 mg of sample; (2) the Apollo 11 fines exhibit a significantly higher production of CH_4 than Apollo 12 fines; (3) the breccia (10059) yields approximately twice as much CH_4 as the fines; (4) there is no correlation of CH_4 production with depth in the core (12028) [the noncorrelation of organic material obtained by pyrolysis-mass spectrometry with depth in the double core was noted (BURLINGAME et al., 1971)]; (5) the core sample at 11–12 cm depth exhibits significantly more CH_4 than the other core aliquots (cf. Fig. 3) [the sample from the 11 cm depth exhibited an indication of possible indigenous organic matter (BURLINGAME et al., 1971)]; and (6) large amounts of hydrogen are evolved during hydrolysis. The total gas mixture from the molecular sieve trap was also analyzed by high

W. HENDERSON et al.

Table 3. Gaseous hydrocarbons released on demineralization of lunar surface materials.

	Carbon Content (ppm C)				
	Total	CH$_4$	Total C$_2$	Total C$_3$	Total C$_4$
Apollo 11 Fines (10086,A)	21.7	13.2	2.9	4.5	1.1
Apollo 11 Rock (10059) Interior	32.1	23.3	5.3	2.5	0.9
Apollo 11 Rock (10059) Exterior	38.2	24.2	5.7	5.9	2.4
Apollo 12 Fines					
(12001,23)	14.0	10.1	2.1	1.2	0.6
(12023,6)	17.6	11.4	3.0	2.1	1.2
(12032,7)	3.7	1.9	0.7	0.8	0.3
(12033,14)	9.3	3.5	2.5	2.5	0.8
(12042,6)	32.2	13.3	3.6	9.9	5.3
Apollo 12 Core (12028,12)					
166 (11–12 cm) (12028,24)	19.2	9.3	4.5	3.5	1.9
172 (20.8–21.8 cm) (12028,29)	7.0	3.7	1.7	1.1	0.5
175 (25.4–26.1 cm) (12028,33)	8.5	6.4	1.3	0.5	0.3
179 (28.8–30.0 cm) (12028,35)	9.0	5.6	1.8	1.2	0.4
184 (30.6–31.2 cm)	7.2	4.2	1.1	1.0	0.9

resolution mass spectrometry (G.E.C.–A.E.I. MS–902). The results shown in Table 4 indicate that the most abundant species are H$_2$S, CO$_2$, CO, CS$_2$, and CH$_4$. Hydrocarbons in the C$_1$–C$_6$ carbon number range and traces of benzene and tropylium ion are present.

There are conflicting results regarding CO liberated on HF treatment from the mass spectrometric experiments on Apollo 11 fines (BURLINGAME et al., 1970), and the mass spectrometric and gas chromatographic experiments reported here. The previous result of 66 ppm carbon as CO from fines sample 10086,A seemed to be corroborated within experimental error by utilizing the CEC 21–110B mass spectrometer and inlet system as described in the experimental section. Hence two possibilities should be considered to explain the carbon monoxide anomalies: (a) instrumental artifacts, and (b) sorption-desorption phenomena on the lunar fines as suggested by ORÓ et al. (1971).

There are two possible instrumental sources which could introduce the observed CO signal. First, oxygen in the evolved gases could react with carbon previously deposited on various ion source surfaces. Second, amplifier "ringing" after intense peaks was noted in the high resolution mass spectrometric data, particularly after the large nitrogen peak. The synthesis of CO in the ion source of the MS–902 on hot surfaces such as the filament was investigated by introducing oxygen-18 gas (10 cm^3 at 80 mm) to the source via a doser and a gold leak (Fig. 4). There is indeed a generation of C^{18}O as well as C^{18}O$_2$ and CO^{18}O. The C^{18}O intensity ranges from 1 to 13% on the increasing ^{18}O$_2$ intensity. The CO^{18}O and C^{18}O$_2$ generated amounts to less than 0.1%
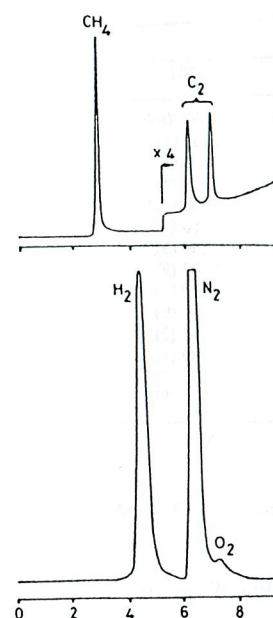

Fig. 1. Gas chromatograms (F.I.D. and demineralization. (Conditions: (a) F.I. ½" packed with Poropak Q and 3' × grammed from 50°–100°C at 10°C per n (b) T.C. 40' × ⅛" stainless steel column ture bath at −22° ± 0.1°C, usi

of the ^{18}O$_2$ intensity. The "ringing" o 0.7–1.0% of the nitrogen peak intensity summed peak area in the high resoluti

Correcting for the generation of C effect, the level of CO released by HF t This value is corroborated by the gas

The presence of CO as an artifact. terminations of total carbon as CO by (BURLINGAME et al., 1970). In contra (1971), the generation of CO by the CO + Fe is well known and used i minerals such as SiO$_2$ analogously fo ments, the oxygen and nitrogen conce at instrument background levels, thu electron multiplier amplifier "ringing."
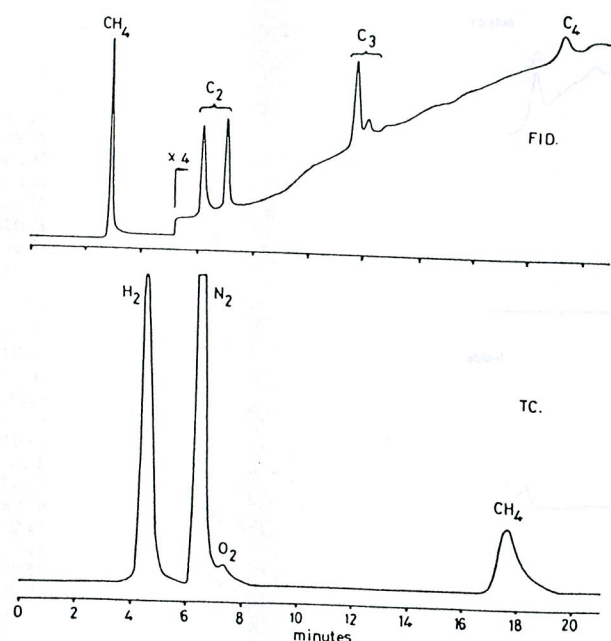
The possibility of adsorption of g

Fig. 1. Gas chromatograms (F.I.D. and T.C.) for Apollo 12 bulk fines 12023 after HF demineralization. (Conditions: (a) F.I.D. combination stainless steel column, 10′ × ⅛″ packed with Poropak Q and 3′ × ⅛″ packed with Poropak N, temperature programmed from 50°–100°C at 10°C per minute, using helium at a flow rate of 40 ml/min. (b) T.C. 40′ × ⅛″ stainless steel column packed with Poropak Q in a constant temperature bath at −22° ± 0.1°C, using helium at a flow rate of 40 ml/min.)

of the $^{18}O_2$ intensity. The "ringing" of the electron-multiplier amplifier amounts to 0.7–1.0% of the nitrogen peak intensity and tails into the CO peak. The net effect is a summed peak area in the high resolution mass spectral calculations.

Correcting for the generation of CO by oxygen, as well as the minor amplifier effect, the level of CO released by HF treatment of fines appears to be less than 1 ppm. This value is corroborated by the gas chromatographic results reported above.

The presence of CO as an artifact, as discussed above, in no way affects the determinations of total carbon as CO by vacuum pyrolysis at 1150°C in this laboratory (BURLINGAME et al., 1970). In contrast to the statements of GIBSON and JOHNSON (1971), the generation of CO by the reaction FeO + C (any form of carbon) → CO + Fe is well known and used in commercial blast furnace processes (other minerals such as SiO_2 analogously form CO). During the vacuum pyrolysis experiments, the oxygen and nitrogen concentrations in the mass spectrometer source were at instrument background levels, thus eliminating the possible synthesis of CO and electron multiplier amplifier "ringing."

The possibility of adsorption of gases on the lunar fines should be considered, since the major LM exhaust products are NH_3, H_2O, HCN, CO, NO, O_2, CO_2, and
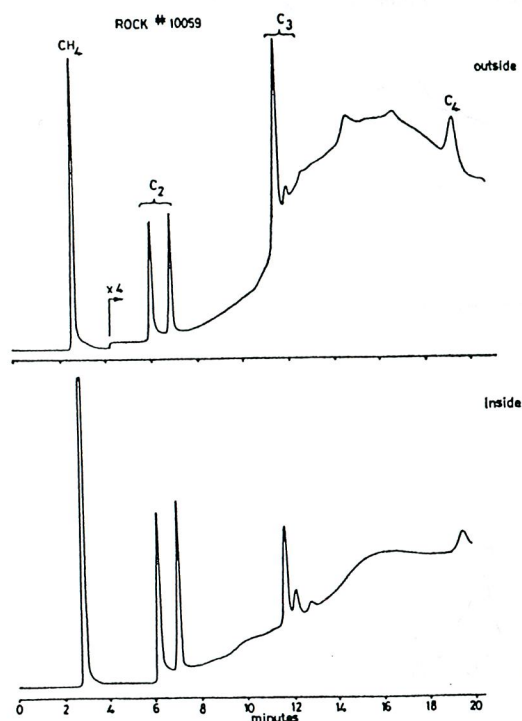
W. Henderson *et al.*

Fig. 2. Gas chromatograms (F.I.D.) after HF demineralization of interior and exterior chips (Breccia 10059). (Conditions as cited in Fig. 1).
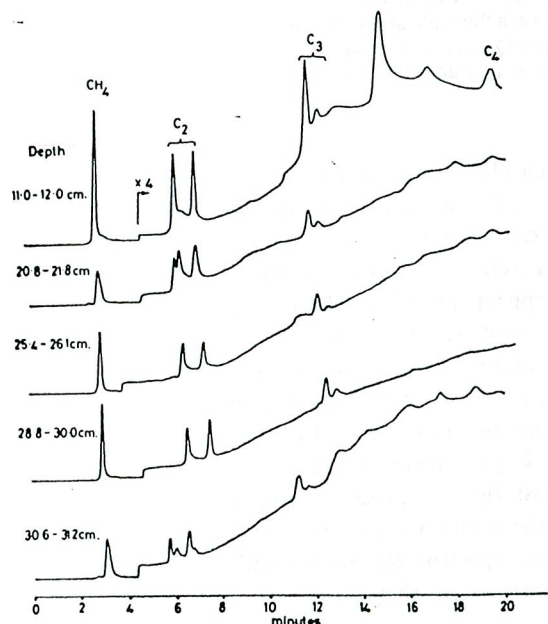

Fig. 3. Gas chromatograms (F.I.D.) of the hydrocarbons from HF demineralization of the 12028 lunar core tube aliquots. (Conditions as cited in Fig. 1).

Table 4. High resolution mass sp
HF den

Observed Mass	Mass error (
16.03092	1.14
27.99498	−0.02
28.00615	0.00
28.03124	0.06
29.00315	−0.41
29.03896	0.04
30.04695	0.00
31.01834	−0.37
31.97227	−0.20
31.99001	−0.18
32.98012	−0.22
33.98800	−0.23
40.03164	−0.34
41.03927	−0.15
42.04708	−0.14
43.01684	0.07
43.05463	−0.07
43.97208	0.02
43.98988	−0.15
44.02638	−0.17
45.03435	−0.35
45.99348	−1.35
46.99627	0.40/−
47.96672	0.27
52.03084	0.46
53.03920	−0.40
54.04664	0.30
55.05589	−0.21
56.06329	0.13
57.07061	−0.19
59.05062	0.20
59.96874	−0.05
62.97040	0.07
63.94387	0.27
63.96374	0.14
65.99134	0.37
67.05514	−0.37
69.06938	−0.08
70.07703	0.98
75.94413	0.09
77.04013	−1.01
78.04474	0.78
91.05414	0.63

* mmu = millimass unit.
† Ten scans averaged and co

NO_2 (SIMONEIT *et al.*, 1969). Some
lunar landing, then desorbed duri
It should also be noted that th
than its atmospheric abundance a
Furthermore, the concentration o
completely contradicts the previo
high resolution mass spectromet
have essentially equal ionization

Table 4. High resolution mass spectral data for the Apollo 11 lunar fines (10086,A)
HF demineralization total gases.

Observed Mass	Mass error (mmu*)	Relative Average Intensity†	Elemental Composition
16.03092	1.14	1482	CH_4
27.99498	−0.02	1200	CO
28.00615	0.00	42300	N_2
28.03124	0.06	400	C_2H_4
29.00315	−0.41	354	CHO
29.03896	0.04	158	C_2H_5
30.04695	0.00	85	C_2H_6
31.01834	−0.37	115	CH_3O
31.97227	−0.20	7206	S
31.99001	−0.18	2576	O_2
32.98012	−0.22	6850	HS
33.98800	−0.23	18130	H_2S
40.03164	−0.34	105	C_3H_4
41.03927	−0.15	245	C_3H_5
42.04708	−0.14	131	C_3H_6
43.01684	0.07	6	C_2H_3O
43.05463	−0.07	101	C_3H_7
43.97208	0.02	108	CS^+
43.98988	−0.15	14865	CO_2
44.02638	−0.17	65	C_2H_4O
45.03435	−0.35	88	C_2H_5O
45.99348	−1.35	90	NO_2
46.99627	0.40/−1.83	72	CH_3S/COF
47.96672	0.27	84	SO
52.03084	0.46	65	C_4H_4
53.03920	−0.40	67	C_4H_5
54.04664	0.30	54	C_4H_6
55.05589	−0.21	158	C_4H_7
56.06329	0.13	87	C_4H_8
57.07061	−0.19	69	C_4H_9
59.05062	0.20	112	C_3H_7O
59.96874	−0.05	137	COS
62.97040	0.07	146	CFS
63.94387	0.27	65	S_2
63.96374	0.14	148	SO_2
65.99134	0.37	50	COF_2
67.05514	−0.37	62	C_5H_7
69.06938	−0.08	81	C_5H_9
70.07703	0.98	76	C_5H_{10}
75.94413	0.09	833	CS_2
77.04013	−1.01	73	C_6H_5
78.04474	0.78	98	C_6H_6
91.05414	0.63	40	C_7H_7

* mmu = millimass unit.
† Ten scans averaged and corrected for instrument background.

NO_2 (SIMONEIT et al., 1969). Some of these gases could have been adsorbed during the lunar landing, then desorbed during long storage of the samples.

It should also be noted that the CO_2 abundance (cf. Table 4) is significantly higher than its atmospheric abundance and therefore cannot be attributed to occluded air. Furthermore, the concentration of CO is six times lower than that of the CO_2. This completely contradicts the previous results obtained using the liquid helium trap and high resolution mass spectrometry (BURLINGAME et al., 1970). Methane and CO_2 have essentially equal ionization potentials. By taking their respective fragmentation
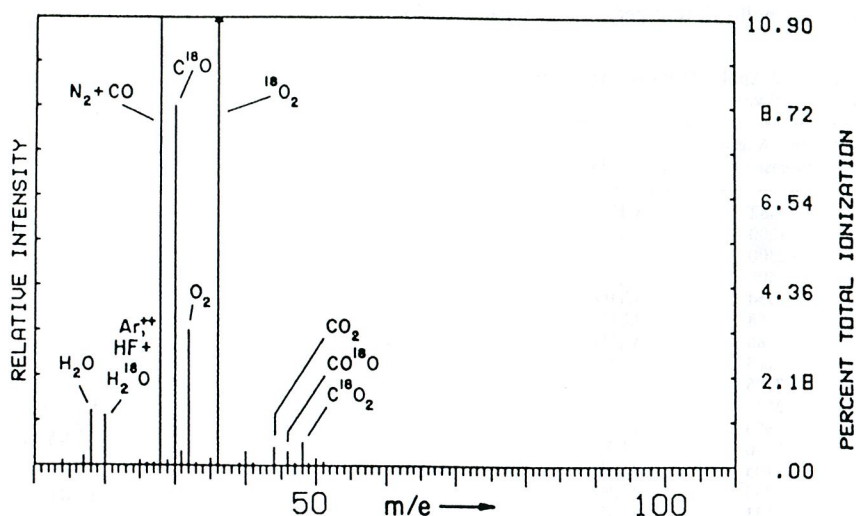
Fig. 4. Low resolution mass spectrum of the products from oxygen-18 gas in the ion source of an MS–902 (the $^{18}O_2$ peak at m/e 36 has a relative intensity of 650, assuming 100 as full scale).

patterns into account and then relating the molecular ion intensities (corrected for both instrument and blank run backgrounds) to the observed CH_4 concentration (GC method), we calculate 62 ppm of CO_2 liberated on HF treatment. (In 70 eV mass spectra of the individual gases, the CH_4 peak is 50% of the total methane ionization and the CO_2 peak is 80% of the total carbon dioxide ionization.) Since we have previously set an upper limit of 36 ppm for CO_2 derived from carbonate in the lunar fines, this suggests that, during the handling procedures at MSC and during the 18 months storage and handling in our laboratories, approximately 15 to 26 ppm of atmospheric CO_2 could have been adsorbed on the surface of the fines. This is supported by the fact that when we first analyzed the evolved gases upon acid dissolution of the fines, the CO_2 concentration found was of the order of 10 ppm (BURLINGAME *et al.*, 1970).

All solution experiments with lunar samples, but none of the standardization or calibration experiments, exhibit a peak in the thermal conductivity chromatographic record which elutes 2 minutes before nitrogen. This peak has been identified as hydrogen on the basis of its retention characteristics and low resolution mass spectrometry. Preliminary quantitation for H_2 indicates a concentration of approximately 4 cc STP/g of lunar fines. Just what proportion of the evolved hydrogen is endogenous to the lunar materials or results from reduction of the acid on contact with those materials is not known at the present time. The use of deuterated acids in dissolution experiments, currently underway in this laboratory, should resolve this question.

FRIEDMAN *et al.* (1970) reported 150 to 450 ppm hydrogen for three breccias (10046,21; 10046,22; and 10060,11), while HINTENBERGER *et al.* (1970) estimate 92 ppm for breccia 10021,20. Therefore, our value of 350 ppm H_2 obtained in HF dissolution

experiments, although from lunar pyrolysis experiments.

(1) Trace gas analysis by high the release of CO from lunar fin followed by mass spectrometry di then found that the carbon on the mately a minimum of 1% conversic from the nitrogen peak overshoot the net amount of CO detected by could be less than 1 ppm. (2) The pyrolysis at 1150°C in this labo (3) A range of hydrocarbons, inclu number are evolved during HF d different forms of carbides. (4) A concentrations of hydrocarbons tl appears to be no correlation of hy the Apollo 12 double core (12028) released predominantly more hy analytical techniques allow us to carbon present in the lunar fines surface contamination (≤ 5 ppm). (cf. GAY *et al.*, 1970), graphite (2 carbides (≤ 25 ppm) nonhydrolyz: for above (10–50 ppm).

ABELL P. I., DRAFFAN C. H., EGLIN1 (1970) Organic analysis of the ret *Conf., Geochim. Cosmochim. Acta* ARRHENIUS G., ASUNMAA S., DREVER H., HANOR J. S., LAL D., LIANG WILKENING L. (1970) Phase chemi 167, 659–661. BURLINGAME A. L., SMITH D. H., an molecular structure studies, XIV. resolution mass spectral data. *An* BURLINGAME A. L., CALVIN M., H/ Study of carbon compounds in *Geochim. Cosmochim. Acta* Supp therein.

experiments, although from lunar fines, corroborates the data obtained in vacuum pyrolysis experiments.

CONCLUSIONS

(1) Trace gas analysis by high resolution mass spectrometry appeared to confirm the release of CO from lunar fines by HF dissolution while gas chromatography followed by mass spectrometry did not detect CO above background levels. It was then found that the carbon on the ion source filament reacts with oxygen (approximately a minimum of 1% conversion) yielding CO. Furthermore, the amplifier bounce from the nitrogen peak overshoot makes a minor contribution to the CO peak. Thus, the net amount of CO detected by mass spectrometry of HF dissolution of the fines could be less than 1 ppm. (2) The determinations of total carbon as CO by vacuum pyrolysis at 1150°C in this laboratory are not affected by instrumental artifacts. (3) A range of hydrocarbons, including CH_4, C_2H_4, C_2H_6, C_3H_8, up to C_6 in carbon number are evolved during HF demineralization. These probably are derived from different forms of carbides. (4) Apollo 11 lunar materials yield significantly higher concentrations of hydrocarbons than Apollo 12 materials on HF treatment. (5) There appears to be no correlation of hydrocarbon release upon HF treatment with depth in the Apollo 12 double core (12028), except that sample 12028,12 (closest to the surface) released predominantly more hydrocarbons. (6) Preliminary results from several analytical techniques allow us to tentatively set maximum limits for the categories of carbon present in the lunar fines as follows: endogenous organic carbon ($\ll 1$ ppm), surface contamination (≤ 5 ppm), adsorbed CO_2 (15–26 ppm), carbonate (≤ 40 ppm) (cf. GAY et al., 1970), graphite (25–50 ppm) (cf. ARRHENIUS et al., 1970), hydrolyzable carbides (≤ 25 ppm) nonhydrolyzable carbides and other forms of carbon not accounted for above (10–50 ppm).

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