

Total carbon and nitrogen abundances in Apollo 11 lunar samples and selected achondrites and basalts*

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Abstract—Total carbon abundances were determined in lunar samples and related rocks by combusting the samples at 1800°C in an oxygen atmosphere and detecting carbon dioxide produced with a gas chromatograph. Weighted mean analyses for bulk lunar fines were 225 and 140 ppm total carbon. The range was from 110 to 350 ppm total carbon. The weighted mean total carbon in fine breccia (“C”) was 230 ppm; coarse breccia 100 ppm; fine-grained rock (“A”) 70 ppm and medium-grained rock (“B”) 64 ppm. Carbon is concentrated in the finest-grained sieved fraction. Achondrites and terrestrial basalts appear to be higher in carbon than lunar rocks.

Nitrogen was determined after opening the lunar samples at 2400°C in a graphite crucible to produce reducing conditions. Molecular nitrogen was determined in a gas chromatograph. Weighted mean analyses were 150 and 100 ppm for bulk fines. The weighted mean total nitrogen for fine breccia (“C”) was 125 ppm; for coarse breccia 100 ppm; for fine-grained rock (“A”) 115 ppm; and for medium grained rock (“B”) 30 ppm. Achondrites and terrestrial basalts contain from 30 to 50 ppm nitrogen.

The total carbon and nitrogen in fines appear to be mixture of indigenous lunar material together with solar wind components.

INTRODUCTION

TOTAL carbon and nitrogen contents of Apollo 11 lunar samples, basaltic achondrites and terrestrial basalts, were determined utilizing analytical techniques developed for these elements in meteorites (MOORE *et al.*, 1965, 1966, 1967, 1969a, b; GIBSON and MOORE, 1970).

Carbon and nitrogen are important because of their crucial role and organogenic elements. Also, their abundances give an indication of the oxidation-reduction conditions and due to their volatility, thermal conditions near the lunar surface.

EXPERIMENTAL

For the determination of total carbon, samples were burned in a flowing oxygen atmosphere at over 1600°C to form CO₂. After necessary purification and trapping of the effluent gases, the CO₂ was detected utilizing a LECO 589-400 gas chromatographic low-carbon analyzer. Samples were heated to about 2400°C in a graphite crucible in a helium atmosphere to reduce all nitrogen compounds to N₂ which was detected in a LECO Nitrox-6 gas chromatographic analyzer. Differential thermal conductivity is utilized as the detection method in both systems. National Bureau of Standards low carbon (101e) and nitrogen (33d) steel standards were used to construct standard analytical curves for both determinations. The combustion-gas chromatographic detection technique determines total carbon and nitrogen but does not discriminate their chemical state in the analyzed samples.

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Table 1. Total carbon in Apollo 11 lunar rocks

Samples	Sample wt. (g)	Total carbon ($\mu\text{g/g}$)	Weighted mean ($\mu\text{g/g}$)
10086-A Fines	0.3433	130 ± 4	—
	0.3094	162 ± 6	—
	0.0782 Δ	$160 \pm 25 \Delta$	—
	0.1555 Δ	$122 \pm 13 \Delta$	—
	(0.8864)	—	142 ± 10
10086-B Fines	0.1080	190 ± 20	—
	0.2586	181 ± 8	—
	0.2565	109 ± 8	—
	0.3482	353 ± 6	—
	(0.9713)	—	226 ± 10
10002-54 "C" breccia	0.2831	228 ± 7	—
	0.2874	231 ± 7	—
	(0.5705)	—	230 ± 7
10044-37 "C-B" coarse breccia	0.2093	108 ± 9	—
	0.3677	76 ± 6	—
	0.1058	180 ± 18	—
	(0.6828)	—	102 ± 10
10049-23 "A" basalt	0.2268	68 ± 9	—
	0.3464	71 ± 6	—
	(0.5732)	—	70 ± 8
10050-33 "B" basalt	0.2394	152 ± 8	—
	0.3234	15 ± 7	—
	0.3007	47 ± 6	—
	(0.8635)	—	64 ± 8

Table 2. Total nitrogen in Apollo 11 lunar rocks

Sample	Sample weight (g)	Total nitrogen ($\mu\text{g/g}$)	Weighted mean ($\mu\text{g/g}$)
10086-A Fines	0.0971	142 ± 5	—
	0.1822	87 ± 2	—
	0.1239	100 ± 3	—
	0.0749 Δ	$107 \pm 5 \Delta$	—
	0.1192 Δ	$92 \pm 4 \Delta$	—
	(0.5973)	—	102 ± 4
10086-B Fines	0.1969	150 ± 2	—
	0.1299	164 ± 5	—
	0.1024	144 ± 4	—
	(0.4292)	—	153 ± 4
10002-54 "C" breccia	0.0896	113 ± 5	—
	0.1588	135 ± 4	—
	0.1146	119 ± 4	—
	(0.3630)	—	125 ± 4
10044-37 "C-B"	0.1666	135 ± 4	—
	0.1266	95 ± 4	—
	0.1993	69 ± 3	—
	(0.4925)	—	98 ± 4
10049-23 "A" basalt	0.1510	85 ± 3	—
	0.1293	35 ± 4	—
	0.1159	247 ± 5	—
	(0.3962)	—	116 ± 4
10050-33 "B" basalt	0.1888	32 ± 2	—
	0.2067	28 ± 2	—
	(0.3955)	—	30 ± 2

Table 3. Total carbon and nitrogen in basaltic achondrites, basalts and LRL control samples

	C	N
Pasamonte	730 ± 20	33 ± 3
Eucrite	780 ± 20	34 ± 3
	710 ± 20	
	610 ± 20	44
	580 ± 20	45
	700 ± 20	
Sioux Co.	650 ± 20	24 ± 3
Eucrite	690 ± 20	30 ± 3
	690 ± 20	
	640 ± 20	33 ± 3
	580 ± 20	
	440 ± 20	
Haraiya	4250 ± 10	31 ± 3
Eucrite	4460 ± 10	42 ± 3
	4740 ± 10	
	5020 ± 10	43 ± 3
	4620 ± 10	43 ± 3
	4980 ± 10	
Yurtuk	1050 ± 20	66 ± 3
Achondrite	1090 ± 20	57 ± 3
	1190 ± 20	
	790 ± 20	51 ± 3
	830 ± 20	50 ± 3
	830 ± 20	
Columbia River basalt	320 ± 20	31 ± 3
BCR-1	230 ± 20	28 ± 3
	360 ± 20	30 ± 3
	370 ± 20	30 ± 3
	370 ± 20	26 ± 3
Vesicular basalt		
Carbon K-71 (LRL)	1890 ± 20	49 ± 3
Nitrogen K-73 (LRL)	1980 ± 20	58 ± 3
Scoriaceous basalt	360 ± 20	38 ± 3
Mokuopuhi flow	360 ± 20	41 ± 3
Hawaii	420 ± 20	
Dunite	278 ± 20	54 ± 3
LEM exhaust test	323 ± 20	55 ± 3
		48 ± 3
		54 ± 3
Fused quartz	30 ± 10	54 ± 3
F-201 control (F-12)	44 ± 10	56 ± 3
Fused quartz	93 ± 7	57 ± 3
F-201 sample (311010)	36 ± 10	
Fused quartz	38 ± 10	54 ± 3
Control sample (C-7)	21 ± 10	
Fused quartz	90 ± 7	60 ± 3
Crushed sample (311008)	35 ± 10	58 ± 3

The results of the analyses in lunar samples are listed in Table 1 for total carbon and in Table 2 for total nitrogen. Table 3 contains carbon and nitrogen contents of selected basaltic achondrites, terrestrial basalts, and Lunar Receiving Laboratory (LRL) control standards. For each lunar sample the weights of material used for individual analyses are listed together with the concentration of carbon or nitrogen detected. No attempt was made to homogenize individual lunar samples. This minimized the possibility of contamination and also provided a test for sample inhomogeneity. Rock samples were crushed by a single stroke in a clean diamond mortar. All of the rock specimens were crushed quite easily to a moderately fine material. To guard against contamination, they were not sieved or run through a mechanical splitter.

The precision indicated as \pm is taken from the 90 per cent confidence level on the line of regression for the reference standards. Analytical precision of the nitrogen analyses is superior to that for carbon because the difference between the thermal conductivities of nitrogen and helium is greater than that for carbon dioxide and helium.

RESULTS

The carbon and nitrogen abundances in the lunar samples show some similarities. Both are highest in the fines samples 10086-A and 10086-B and the fine-grained breccia 10002-45. The coarse-grained basalt 10050-33 contained the lowest concentrations of both carbon and nitrogen. With respect to carbon, the fine-grained basalt 10049-23 is similar to the coarse-grained basalt but its nitrogen content is relatively high. The sample of rock 10044-37 provided for our analysis had the macroscopic characteristics of a coarse-grained basalt but was cataloged as a coarse-grained breccia. In terms of both carbon and nitrogen, it is intermediate to the fine-grained breccia 10002-54 and the coarse-grained basalt 10050-33. Both the basaltic achondrites and the terrestrial basalts have higher carbon contents than the lunar samples. The achondrites were carefully selected and prepared and there is little possibility of contamination by our handling. The terrestrial basalts may, of course, have had secondary carbonates added to them from deuteric or groundwater solutions. The unexpected high carbon abundance in the Haraiya eucrite may be from cometary impact during its preterrestrial history or even possibly from immersion in an organic liquid for density determination by an unknown individual. Their nitrogen contents are similar to the lunar rocks in absolute abundance but their nitrogen-carbon ratios are lower.

The lunar rocks like the enstatite chondrites appear to have been formed under high temperature reducing conditions. Unlike the lunar material, the enstatite achondrites have high carbon contents (0.056–0.56 wt. % carbon) indicating a different evolution or initial composition (MOORE and LEWIS, 1966). MOORE *et al.* (1969) showed that enstatite chondrites which do not contain the mineral sinoite, $\text{Si}_2\text{N}_2\text{O}$, have five to ten times the nitrogen concentration present in ordinary chondrites. This relative enrichment in nitrogen in both the lunar rocks and enstatite chondrites may be due to their reducing character.

The carbon and nitrogen in Apollo 11 lunar samples may be from four sources: (1) indigenous, (2) meteorite or comet impact, (3) solar wind, (4) contamination. Contamination may have resulted from the LEM landing, astronaut activity, or subsequent laboratory handling.

The possibilities for contamination from nitrogen in returned lunar samples appear to be greater than for carbon. Possible sources are from the LEM exhaust gases and

from the nitrogen atmosphere to which the fresh lunar rocks were exposed at the Lunar Receiving Laboratory. The control samples show no evidence of extensive carbon or nitrogen contamination in the LRL at the level of significance determined by our analytical technique.

In order to see if nitrogen or carbon could be easily desorbed from lunar fines, a split of sample 10086-A was heated for 24 hr at 300°C in a flowing helium atmosphere. The results of the analyses of this material are identified in Tables 1 and 2 by the symbol Δ . No appreciable carbon or nitrogen appeared to be removed by this treatment. If contamination by atmospheric nitrogen has taken place, it is strongly bonded to the fines material.

The relatively high nitrogen content of fine-grained basalt 10049-23 would then also appear to be indigenous. This supports the idea that the nitrogen has been retained because of the highly reducing state of the lunar igneous environment. Evidence for chemically reduced nitrogen has been given by HINTENBERGER *et al.* (1970) who reported the detection of a major fraction of NH_4^+ in a sulfuric acid leached sample of lunar fines.

Carbon and nitrogen may be indigenous to the moon as elemental carbon, as interstitial atoms of carbon or nitrogen, as organic material, or as inorganic compounds (carbonate, carbides, ammoniacal nitrogen, molecular nitrogen). Meteoritic material apparently arrives with hypervelocity impacts, causing volatilization and atomization of the projectile and part of the target. Solar wind particles presumably arrive as single atoms or ions.

The total carbon trends seem to support the idea that the values of 70 and 64 $\mu\text{g/g}$ (ppm) found in the lunar basaltic rocks are primarily due to indigenous carbon. The close agreement for the two splits of the fine-grained basalt 10049-23 indicates some degree of homogeneity with respect to the analyzed sample, whereas, the variation between the splits of the coarse-grained basalt 10050-33 indicates a more sporadic distribution of carbon among or between the large crystalline phases.

The two fines samples 10086-A and 10086-B and the fine dark breccia 10002-54 are significantly higher in total carbon than are the basalts. Sample 10086-A received less handling than sample 10086-B in the Lunar Receiving Laboratory and its lower carbon values may be attributed to this. There is no evidence to support this assumption, and the overlap in the range of values in 10086-A and 10086-B together with a constant carbon-nitrogen ratio, suggests a normal sample variation. In order to investigate the distribution with respect to particle size, a split of sample 10086-A was sieved and analyzed for carbon. Material greater than 60 mesh had $70 \mu\text{g/g} \pm 15$ total carbon; from 60 to 140 mesh had $115 \pm 20 \mu\text{g/g}$; from 140 to 300 mesh, $210 \pm 10 \mu\text{g/g}$; and minus 300 mesh, $500 \pm 20 \mu\text{g/g}$. Evidently the carbon is concentrated in the finest sized material. Microscopic examination of the material larger than 60 mesh and the 60-140 mesh fraction indicated that it is made up primarily of fine-grained basalt, glassy impactite material, and some crystal fragments. Samples 10086-A and 10086-B may contain different proportions of coarse and fine fragments and hence, have different total carbon abundances. The fine-grained breccia appears to consist primarily of compacted fines and apparently lost no carbon during lithification.

DISCUSSION

In our initial report (MOORE *et al.*, 1970) we noted that the rare-gas analyses reported in the preliminary examination of lunar samples from Apollo 11 (LSPET, 1969) also showed enrichment in the fines and breccia. Assuming that all of the rare-gas content is due to solar wind, some rough calculations were made to indicate how much of the carbon might be attributed to the solar wind. The major unknown in the calculation was a "sticking" or retention factor relating the relative retention on the lunar fines to each of the rare gases. A comparison of Apollo 11 rare-gas abundances with CAMERON's (1968) table of abundances in the solar system, indicated a fractionation in the lunar materials favoring the retention of higher atomic weight gases. If the solar carbon/neon is normalized to the neon in the lunar samples, the solar wind contribution of carbon to the lunar fines is $6 \mu\text{g/g}$ or about 4 per cent of the total carbon. If the carbon abundance is calculated from the krypton abundance, the solar wind contribution is about $50 \mu\text{g/g}$, and if it is calculated from xenon, the solar wind contribution would be $300 \mu\text{g/g}$. Assuming similar "sticking" factors, the solar wind contribution would be about five times lower for nitrogen than for carbon.

A general calculation was also made to estimate the possible meteoritic and cometary contribution to the lunar fines. The major unknown in this case was the composition of the meteoritic influx. Carbonaceous chondrites were selected as representative of impact material. This choice was supported by comparing the increase in nickel from the lunar igneous rocks to the lunar breccia and fines as reported in the preliminary examination of samples from Apollo 11 (LSPET, 1970). Nickel and carbon both showed significant increases, and nickel, like carbon, has a much higher concentration in carbonaceous chondrites than in lunar rocks. KEAYS *et al.* (1970) work on trace elements in Apollo 11 rocks also indicated that carbonaceous chondrite-like material is being added to the lunar surface.

MASON's (1963) review of carbonaceous chondrites gives typical concentrations of 2% carbon and 1% nickel in these meteorites. Using these values to calculate the approximate contribution of meteoritic extralunar material indicated that about 0.5–2 per cent has been mixed with lunar material. The nitrogen contribution of meteorites is about 10 per cent that of carbon and again this element did not give an apparent satisfactory material balance. Based on our simplifying assumptions, both solar wind and meteorite influx failed to account for the relatively high nitrogen abundances. They were explained by the possibility that indigenous nitrogen is high in the lunar rocks, as indicated by the fine-grained basalt 10049-23, or that solar wind or meteoritic nitrogen is retained to a greater degree than carbon.

On the basis of the sulfur abundances in the lunar samples by KAPLAN and SMITH (1970) it now appears that carbonaceous chondrite and/or cometary material may not be a major source of carbon and nitrogen in the lunar fines. Sulfur, like carbon and nickel, is much more abundant in the carbonaceous chondrites than in the lunar basalts. An influx of carbonaceous chondrite-like material should then increase the sulfur content in the lunar fines with respect to the lunar basalts. KAPLAN and SMITH (1970) noted the opposite effect. Sulfur in the fine-grained rocks was about $2200 \mu\text{g/g}$ and in the fines about $700 \mu\text{g/g}$. In order for an element to be depleted in the lunar soil, it must be either (1) volatile and lost from the surface by some mechanism or

(2) diluted by the addition of a material depleted in that element. This material may be either extra-lunar or from a different area on the moon. The mixture of anorthosite with Apollo 11 site bedrock as reported by WOOD *et al.* (1970) would be an example of such a mixing effect. It appears that this specific mixing has added aluminum to the Apollo 11 fines. In order to cut the sulfur abundance by more than one-half, greater than a one to one mixture of anorthosite and basalt would be required. WOOD *et al.*'s (1970) data on the distribution of rock types in the soil do not support such a model. Impact vaporization is a more likely mechanism. That meteorite impact is catastrophic enough to destroy the impacting material is supported by the fact that no complex carbonaceous compounds or water have been found in the lunar soil (LSPET, 1969) and that no magnetite has been identified (JEDWAB *et al.*, 1970). Water, organic compounds, and magnetite are abundant in the carbonaceous chondrites. It appears that most of the meteoritic impact material is atomized, reconstituted or severely shocked with the resultant loss of volatile species. The target material of either bedrock and/or regolith must also undergo a similar process. The preliminary examination of the lunar fines (LSPET, 1969) indicated that about half of it was glassy. This estimate together with the fact that the fines have half the sulfur content of the lunar rocks has led us to estimate that about half of the material making up the lunar fines has been heated enough to expel its volatile elements.

Utilizing a model based upon the assumptions that (1) the average proton flux on the lunar surface has been $2 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ (KEAYS *et al.*, 1970); (2) there is a 100 per cent retention factor for carbon, nitrogen, and sulfur accumulated; (3) half the indigenous volatiles from lunar rocks and solar wind volatiles in the lunar regolith were lost by impact; (4) all meteoritic volatiles are lost on impact; the expected total concentration of carbon, nitrogen, and sulfur in lunar fines may be estimated. The results of such a set of calculations are given in Table 4. The solar wind is assumed to have an elemental distribution similar to CAMERON's (1968) solar abundance table.

Table 4. Calculated and experimental concentrations of volatile elements in lunar fines

Element	Maximum solar wind ($\times \frac{1}{2}$) ($\mu\text{g/g}$)	Lunar basalt (type A) ($\times \frac{1}{2}$) ($\mu\text{g/g}$)	Theoretical fines ($\mu\text{g/g}$)	Reported fines	Reported breccia	Reference
C	150	35	185	142-226	230	a
N	32	55	87	102-153	125	a
S	15	1100	1100	640-770 1400 1200	1070-1120 1500	b c d

References:

a. This paper.

b. KAPLAN and SMITH (1970).

c. PECK and SMITH (1970).

d. AGRELL *et al.* (1970).

The agreement may be considered satisfactory in view of the poor sampling and gross assumptions. According to this model a major amount of the volatile elements carbon and nitrogen in the lunar fines appears to have been derived from solar wind. Solar wind contributions of carbon and nitrogen would not be concentrated in separate mineral phases but would most likely attach themselves to a nearest neighbor on a

particle surface. Since the most abundant element available is oxygen, carbon—oxygen and nitrogen—oxygen bonds would be expected to be common. Also solar wind protons would contribute to carbon—hydrogen bonds. Evidence for carbon compounds of both types have been presented by BURLINGAME *et al.* (1970) and ABELL *et al.* (1970) who have reported that the species CO, CO₂ and a minor amount of CH₄ have been released from lunar fines by pyrolysis.

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