

Concentration and Isotopic Composition of Carbon and Sulfur in Apollo 11 Lunar Samples

Abstract. *The concentration of carbon and sulfur in six samples ranged between 20 to 200 and 650 to 2300 parts per million, respectively. Carbon was present in gaseous, volatilizable, and nonvolatile forms, and terrestrial contaminants were recognized. Sulfur appeared to exist only as acid-volatile sulfide. The bulk fines contain a high concentration of carbon and a low concentration of sulfur. They are always enriched in the heavier isotope carbon-13 or sulfur-34. The fine-grained basaltic rocks show the reverse relation; lowest carbon, highest sulfide concentrations, and no apparent enrichment in heavy isotopes. The breccias are of intermediate composition.*

The purpose of this study was to differentiate between the various forms of carbon and sulfur present in the lunar material and to measure the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ ratios of these components. The results presented here relate to six samples, five that were submitted directly to UCLA (10084; 1002,54; 10060,22; 10049 and 10057,40) and one bulk fines submitted through Ames Research Center (10086).

Carbon was analyzed in several ways. Total carbon was measured by combustion of 1-g samples in an atmosphere of oxygen at a pressure of about 700 mm-Hg at 1050°C. The gaseous products were passed over copper oxide catalyst, silver wire, and lead oxide (to remove halogens and oxides of nitrogen and sulfur, respectively). The resulting CO_2 was purified from water by distillation through a trap of acetone and dry ice, and its volume was measured on a manometer. It was recognized after preliminary experiments in which smaller samples were combusted that contamination from handling was seri-

ous and that the gas volumes obtained were so small, as to make them impractical for purposes of mass spectroscopy.

In Fig. 1 the contamination problem in the bulk fines (10084 and 10086) is clearly identified. Samples containing more than 200 ppm of carbon always have $\delta^{13}\text{C}$ of less than +15 per mil. These values probably represent mixtures of lunar carbon (+18 to +20 per mil) and common types of terrestrial carbon (−20 to −30 per mil). The data seem to fall into three groups. Those with $\delta^{13}\text{C}$ values greater than +17 per mil are considered to be largely or entirely of lunar origin. Those with $\delta^{13}\text{C}$ values between +12.5 and +8 have probably been lightly contaminated either at the Lunar Receiving Laboratories or by the lunar module exhaust. The isotopically lightest samples with $\delta^{13}\text{C}$ values smaller than −3.5 per mil are considered to have suffered additional contamination in our laboratory. Samples received from the Lunar Research Laboratory, and stored in the original containers (aluminum or steel) in air, yielded values of the intermediate type.

After degassing the sample under simulated lunar-day conditions by heating to 150°C at 10^{-3} torr for 48 hours, a loss in volatile carbon was detected. The total carbon content decreased and isotopic values increased after this treatment. The values in Tables 1 and 2 were obtained on samples treated in this manner.

In order to determine the nature of the carbon, samples were treated chemically or pyrolyzed. The products were captured, measured quantitatively and their $^{13}\text{C}/^{12}\text{C}$ ratios determined. Some of the results are summarized in Table 2 and will be explained below.

A previously degassed sample (10084) was pyrolyzed under vacuum over three temperature ranges (150 to

250°C, 250 to 500°C, and 500 to 750°C) and the volatile material was frozen out in a liquid nitrogen trap. The products of each pyrolysis step were then volatilized in an atmosphere of oxygen, burnt at 1050°C, passed through the combustion train described earlier, and captured as CO_2 gas. The residue from the pyrolysis experiment was combusted finally, and the released CO_2 also was captured. The total quantity of carbon recovered from the pyrolysis experiment corresponds closely with the total carbon content of the original fines (Table 2); 86 ppm of this carbon was volatilized in this experiment. In a duplicate experiment on the degassed sample of bulk fines 10086, a positive identification of CO_2 in amounts of 48 ppm (minimum), was made by Dr. Sherwood Chang, with a Poropak Q chromatographic column. Thus at least 55 percent of the released volatiles is CO_2 , and the remainder is possibly a mixture of carbon monoxide and hydrocarbon decomposition products (neither positively established). It is apparent from the isotope data that material evolved at the lower temperatures may largely consist of such carbon-hydrogen fragments or compounds (as possible contaminants), whereas the gas evolved at the higher temperature is representative of CO_2 . The isotopic distribution is in accord with that found for reduced and oxidized carbon compounds (1).

When the lunar fines (10086) were treated with hydrochloric and hydrofluoric acids, the residues from duplicate extractions contained 30 and 42 ppm, respectively, relative to the original sample. The $\delta^{13}\text{C}$ value and car-

Table 1. Concentration and isotopic composition of carbon and sulfur.

Sample No.	Carbon		Sulfur	
	Conc. (ppm)	$\delta^{13}\text{C}^*$ (per mil)	Conc. (ppm)	$\delta^{34}\text{S}^\dagger$ (per mil)
<i>Bulk fines</i>				
10086	143	+20.2	680	+5.4
10086	170	+17.2	640‡	+8.2‡
10084	147	+18.8	770	+4.7
10084	116	+19.5		+4.4
<i>Breccia</i>				
10002,54	198	+8.4	1070	+3.5
10002,54	181	+9.2		+3.4
10060,22	137	+1.6	1120	+3.6
10060,22	132	+2.7		+3.3
<i>Fine-grained rock</i>				
10049	63	−18.8	2200	+1.2
10049	77	−21.4		+1.3
10057,40	21	−25.6	2280	+1.2
10057,40	11	−29.8		+1.2

* Relative to PDB standard. † Relative to Canyon Diablo standard. ‡ Total sulfur by aqua regia oxidation.

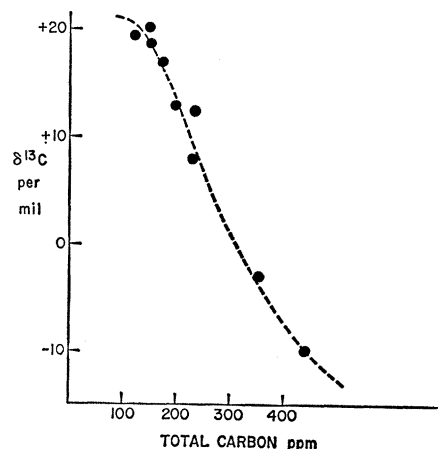


Fig. 1. Relation between the total carbon content of the bulk fines (10084 and 10086) and the carbon isotope abundance.

Table 2. $\delta^{13}\text{C}$ of carbon fractions resulting from pyrolysis and hydrolysis.

Experiment	Sample	Carbon content (ppm)	$\delta^{13}\text{C}$ (per mil)
Combustion of intact sample	10086	157*	+ 18.7*
	10084	132*	+ 19.1*
Combustion of residue from HCl-HF treatment	10086	30	- 7.9
	10086	42	- 4.3
Pyrolysis† at 150° to 250°C	10084	27	- 25.1
Pyrolysis at 250° to 500°C	10084	19	- 12.0
Pyrolysis at 500° to 750°C	10084	40	+ 23.4
Combustion of residue	10084	59	+ 9.4

* Average of values, in Table 1. † Refers to pyrolysis at the temperature given followed by combustion of volatile products.

bon concentration of this residue are considerably lower than their corresponding values in the residue resulting from pyrolysis. This, therefore, suggests that the nonvolatile carbon from the pyrolysis experiment is composed of two carbon phases, one being soluble in acid. This could be either a carbonate, or carbon dioxide captured within minerals that melt at high temperatures, or a carbide. There was little, if any, chemical evidence for carbonate resulting from acid treatment of the untreated bulk fines, but acid hydrolysis (6*N* HCl) at 105°C for 24 hours yielded measurable quantities of low-molecular-weight hydrocarbons from C_1 to C_4 .

Experiments in collaboration with the Ames Research Center on cohenite (Fe_3C from an iron meteorite) indicate that some 20 ppm of carbide carbon would be required to produce the quantities of hydrocarbon gases measured. This carbide would need to have an isotopic composition of $\delta^{13}\text{C}$ greater than +20 per mil in order to be balanced by the residual carbon with a $\delta^{13}\text{C}$ of -4 to -8 per mil. Although the residue remaining after treatment with hydrochloric and hydrofluoric acids has not been identified, it seems logical to assume it is some form of elemental carbon.

The results of our investigation on carbon compounds can be summarized as follows. The highest concentration of carbon is in the bulk fines and in the breccias. There seems to be a somewhat heterogeneous distribution in the samples. Some of the scatter in the data on total carbon may be due to terrestrial contamination. The indigenous carbon is in three or four possible forms; elemental carbon, metal carbide, carbon dioxide (and possibly carbon monoxide and carbon-hydrogen compounds). The samples with the lowest carbon content are the fine-grained basaltic rocks, which also contained the isotopically lightest carbon. This may indicate that either heavier carbon (as

CO_2) escaped during crushing and sample preparation or else that these samples contain only traces of indigenous carbon and are influenced most by terrestrial contamination.

Sulfur was analyzed by reacting samples (approximately 3 g) under vacuum with 85 percent phosphoric acid (10 ml). The reaction mixture was heated at intervals of a few hours to boiling and left standing overnight at 60°C. Evolved hydrogen sulfide was captured in side arms containing a 5 percent solution of silver nitrate and precipitated as silver sulfide. The Ag_2S was separated and then combusted with CuO to evolve SO_2 gas, which was purified by distillation from dry ice in preparation for mass spectroscopy. After the reaction had been completed, the residue was washed to remove excess H_3PO_4 and oxidized with aqua regia. No sulfate could be detected on addition of barium chloride to these solutions. In a separate experiment conducted at the Ames Research Center (2), 55 g of lunar sample was extracted with a mixture of methanol and benzene; elemental sulfur could not be detected in this extract. Likewise, no soluble sulfur was found either in the aqueous or acid-hydrolyzed products from this experiment. It is therefore concluded that all the sulfur is in the form of acid-volatile metal sulfides. The concentration of sulfide was inversely related to that of the carbon, highest in the fine-grained basalt and lowest in the bulk fines, the maximum being 2280 ppm as S (or 0.62 percent FeS).

The most surprising result is the enrichment of $\delta^{34}\text{S}$ (Table 1). The samples containing the highest sulfur approximate average meteoritic sulfur (3), whereas the bulk fines are enriched by 5 per mil or more.

There appears some inconsistency in the results, which have not yet been checked owing to lack of sample. A larger sample (55 g of 10086) on treatment with boiling hydrochloric acid (2) yielded H_2S which gave an aver-

age measured value for $\delta^{34}\text{S}$ of +8 per mil, oxidation of the same fines sample with aqua regia gave a similar $\delta^{34}\text{S}$ value of +8.2. However, treatment with phosphoric acid as described above yielded hydrogen sulfide with a $\delta^{34}\text{S}$ of only +5.4 per mil. In all cases the total sulfur content varied by only a few ppm. Comparative analyses of HCl and H_3PO_4 treatment of meteorites show $\delta^{34}\text{S}$ values for released sulfides that fall within ± 1 per mil.

The results of analyses on a large number of meteorites show the isotopic spread rarely to exceed ± 3 per mil for a variety of sulfur compounds. Troilite sulfur in iron meteorites, for instance, did not vary beyond the range of ± 1 per mil relative to Canyon Diablo troilite.

The isotopic values for $\delta^{13}\text{C}$ in the breccias and fines are also anomalously heavy compared to total meteoritic carbon range -4 to -25 per mil (4) and to terrestrial carbon with a normal range of +2 to -30 per mil. They are, however, not as enriched in $\delta^{13}\text{C}$ as the carbonate phase of meteorites, which appears to lie in the range of +40 to +70 per mil (5).

Therefore, it appears that the lunar fines are anomalously enriched in heavy isotopes, relative to the compacted fine-grained rocks, and to terrestrial volcanic rocks and meteorites.

What process is responsible? It must be either one preferentially enriching the heavy isotopes or one preferentially removing the light isotopes. Equilibration fractionation can probably be ruled out in the case of sulfur, as probably only one major phase exists—troilite. In any case, equilibrium effects in a closed system could not account for an enrichment of the total system.

This would therefore suggest addition of heavy isotopes to the fine material and brecciated rocks or removal of light isotopes. In the absence of any evidence for the former (6), we prefer to speculate that isotopically light carbon has been preferentially lost from the unconsolidated or weakly consolidated rocks. One possible mechanism for this behavior could be the stripping of carbon and sulfur by protons from the solar wind. Kinetically, this may favor the conversion of ^{12}C to methane and ^{32}S to hydrogen sulfide, which would be lost from the moon's surface.

I. R. KAPLAN
J. W. SMITH*

*Institute of Geophysics
and Planetary Physics,
University of California, Los Angeles*

References and Notes

1. Y. Bottinga, *Geochim. Cosmochim. Acta* **33**, 49 (1969).
2. C. Ponnampuruma, E. Barghoorn, I. Breger, S. Chang, A. Duffield, C. Gehrke, B. Halpern, G. Hodgson, H. Holland, R. Johnson, I. Kaplan, K. Keil, K. Krauskopf, K. Kvenvolden, D. Philpott, G. Pollock, W. Schopf, J. Smith, *Science*, this issue.
3. I. R. Kaplan and J. R. Hulston, *Geochim. Cosmochim. Acta* **30**, 479 (1966).
4. G. Boato, *ibid.* **6**, 209 (1954); T. Belsky and I. R. Kaplan *ibid.*, in press.
5. R. N. Clayton, *Science* **140**, 192 (1963); J. W. Smith, I. R. Kaplan, E. Ruth, unpublished data.
6. Lunar module exhaust from a simulated pre-flight experiment yielded a value for $\delta^{13}\text{C}$ of -34.7 per mil.
7. Supported by NASA contract NAS 9-8843. We thank E. Ruth for valuable assistance, and Drs. C. Ponnampuruma, S. Chang, J. Lawless and K. Kvenvolden for collaboration.

* Permanent address: Division of Mineral Chemistry, C.S.I.R.O., P.O. Box 175, Chatswood, New South Wales, Australia.

4 January 1970

Rare Gases, Hydrogen, and Nitrogen: Concentrations and Isotopic Composition in Lunar Material

Abstract. *The concentrations and isotopic abundances of the rare gases have been investigated in fines and three types of rocks. The results obtained from different grain-size fractions and from samples etched to different degrees with nitric and hydrofluoric acids demonstrate the strong concentrations of the solar-wind component in the surface layers of the grains. Exposure ages as well as gas retention ages have been determined in different types of Apollo 11 material. Hydrogen, nitrogen, and other gases have been analyzed by a high-resolution mass spectrometer. As compared with that in terrestrial water, deuterium is depleted by at least a factor of 3 in the investigated type C rocks.*

We have investigated the concentrations and isotopic abundances of the rare gases in fines and in three types of rocks. The results obtained are listed in Table 1.

A systematic decrease of the concentrations of all rare gases has been found with increasing grain size and with increasing loss of material in the etching experiments (Table 1; Figs. 1, 2). The rare gases in the fines are obviously concentrated predominantly in the outer grain layers. Among the light rare gases, Ar shows the greatest and He the smallest decrease of concentration with increasing weight of removed ma-

terial (Fig. 2), which may be due either to a different distribution or different losses of these nuclides by diffusion or to different penetration depths for He, Ne, and Ar solar wind particles. On the basis of our experience with gas-rich stone meteorites, where the metal fraction invariably shows the least (or no) loss by diffusion, and of a comparison of the $^4\text{He}/^{20}\text{Ne}$ or $^4\text{He}/^{36}\text{Ar}$ ratios in these etched samples with ratios found in the selected iron grains, we believe that preferential loss of the He and Ne by diffusion is responsible. The Kr and Xe concentrations depend similarly on

the grain size and on the amount of material removed by etching.

The abundance ratios with one nuclide abundantly formed by spallation and the other abundantly occurring in the solar wind (for instance, $^3\text{He}/^4\text{He}$, $^{21}\text{Ne}/^{20}\text{Ne}$, and $^{38}\text{Ar}/^{36}\text{Ar}$) show a strong increase with increasing grain size and with increasing degree of etching (Fig. 3).

In the 1 percent residuum of the strongly etched sample the ^{21}Ne is almost purely spallogenic. The amount, together with a production rate of $P_{21} = 0.2 \times 10^{-8} \text{ cm}^3/\text{g}$ (at standard temperature and pressure) times 10^6 years yields an exposure age of $T_{21} = 215 \times 10^6$ years. Furthermore, as the ^4He in this fraction is almost pure solar wind helium, the ^3He can be corrected to obtain the spallogenic component, which is $2.7 \times 10^{-6} \text{ cm}^3/\text{g}$ at standard temperature and pressure. Hence, using a production rate of $P_3 = 1.3 \times 10^{-8} \text{ cm}^3/\text{g}$ (at standard temperature and pressure) times 10^6 years, we obtain the ^3He exposure age of $T_3 = 207 \times 10^6$ years, in good agreement with the ^{21}Ne exposure age.

The rare gas contents of type A, B, and C rocks are compiled in Table 2. For type C rock 10021.20, similar values have been found as for fines. In type A and B rocks all three components (solar wind, radiogenic, and spallogenic) have been detected. The results for radiogenic ^4H and ^{40}Ar , as well as for spallogenic ^3H and ^{21}Ne , are shown in the table. Exposure ages have been calculated, with production rates $P_3 = 1 \times 10^{-8} \text{ cm}^3/\text{g}$ times 10^6 years and $P_{21} = 0.12 \times 10^{-8} \text{ cm}^3/\text{g}$

Table 1. Concentrations of rare gas in cubic centimeters per gram at standard temperature and pressure in the bulk material in various grain-size fractions and in acid-etched fractions of fines of sample 10084.18. The concentrations in acid-treated fines are given after 40 percent of the weight has been removed by HNO_3 , 93 percent has been removed by HNO_3 and HF , and 99 percent has been removed by acid treatment. The concentrations in a few large grains ($>250 \mu\text{m}$) selected from the residuum of an acid-etched sample and those in a few milligrams of iron grains selected with a hand magnet are also listed.

Nuclide and ratios	Original fines	Grain-size fractions (μm)			Acid-etched fractions (removed weight in %)			Large grains	Iron grains
		30	30-100	100-250	40	93	99		
^3He	7.88×10^{-5}	1.06×10^{-4}	3.98×10^{-5}	1.80×10^{-5}	3.13×10^{-5}	5.83×10^{-6}	3.07×10^{-6}	2.75×10^{-6}	3.87×10^{-5}
^4He	2.01×10^{-1}	2.78×10^{-1}	1.02×10^{-1}	4.70×10^{-2}	8.72×10^{-2}	1.02×10^{-2}	9.51×10^{-4}	6.84×10^{-3}	9.80×10^{-2}
^{20}Ne	2.21×10^{-3}	3.34×10^{-3}	1.18×10^{-3}	5.85×10^{-4}	5.28×10^{-4}	4.04×10^{-5}	3.14×10^{-6}	3.35×10^{-5}	3.34×10^{-4}
^{21}Ne	5.65×10^{-6}	8.78×10^{-6}	3.42×10^{-6}	1.93×10^{-6}	1.76×10^{-6}	3.59×10^{-7}	4.37×10^{-7}	2.04×10^{-7}	9.44×10^{-7}
^{22}Ne	1.74×10^{-4}	2.69×10^{-4}	2.44×10^{-4}	4.77×10^{-5}	4.31×10^{-5}	3.57×10^{-6}	7.29×10^{-7}	2.82×10^{-6}	2.73×10^{-5}
^{36}Ar	3.71×10^{-4}	6.22×10^{-4}	2.36×10^{-4}	1.63×10^{-4}	3.05×10^{-5}	1.73×10^{-6}	9.46×10^{-7}	1.71×10^{-6}	5.11×10^{-5}
^{38}Ar	7.21×10^{-5}	1.20×10^{-4}	4.72×10^{-5}	3.22×10^{-5}	6.44×10^{-6}	6.96×10^{-7}	5.69×10^{-7}	4.46×10^{-7}	1.03×10^{-5}
^{40}Ar	4.09×10^{-4}	6.48×10^{-4}	3.04×10^{-4}	2.36×10^{-4}	6.60×10^{-5}	4.33×10^{-6}	2.76×10^{-6}	9.09×10^{-6}	7.69×10^{-5}
^{84}Kr	2.11×10^{-7}	3.34×10^{-7}	1.26×10^{-7}	8.87×10^{-8}	2.53×10^{-9}	2.3×10^{-9}	4.96×10^{-9}	1.62×10^{-9}	3.07×10^{-8}
^{136}Xe	2.87×10^{-8}	3.97×10^{-7}	1.82×10^{-7}	1.59×10^{-8}	6.09×10^{-9}	5.7×10^{-10}	1.13×10^{-9}	7.0×10^{-10}	5.5×10^{-9}
$^4\text{He}/^3\text{He}$	2550	2620	2560	2480	2790	1760	310	2450	2530
$^{20}\text{Ne}/^{22}\text{Ne}$	12.7	12.4	12.5	12.3	12.2	11.3	4.31	11.9	12.4
$^{22}\text{Ne}/^{21}\text{Ne}$	30.0	30.6	27.6	24.7	24.5	10.0	1.67	13.8	28.9
$^{36}\text{Ar}/^{38}\text{Ar}$	5.15	5.18	5.00	5.06	4.74	2.43	1.66	3.83	4.96
$^{40}\text{Ar}/^{36}\text{Ar}$	1.10	1.04	1.29	1.45	2.16	25	29.2	5.32	1.50