

# DISTRIBUTION AND ISOTOPIC ABUNDANCE OF BIOGENIC ELEMENTS IN LUNAR SAMPLES\*

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(Received 16 February, 1972)

**Abstract.** A review of the abundance of six biologically important elements (H, C, N, O, P and S) demonstrates that they are present in trace amounts only in lunar matter analysed to date. To the endogenous lunar content, elements are contributed by solar wind irradiation and meteorite impacts. However, it is not yet possible to determine the relative importance of the three sources. Enrichment of the heavy isotopes, C<sup>13</sup>, O<sup>18</sup>, S<sup>34</sup> suggest that these elements may be lost from the lunar surface by 'hydrogen stripping' (from solar wind protons) as volatile gases. The general lack of water, suggests that organic synthesis could not easily be accomplished in lunar rocks. High energy irradiation of the lunar surface may result in rapid destruction of organic matter not protected by a silicate matrix. It is apparent from present data available, that the ambient lunar surface could not support metabolism of known microorganisms.

## 1. Introduction

The elements predominantly associated with terrestrial life are hydrogen, carbon, nitrogen, oxygen, phosphorus and sulfur. Each plays a vital role either in energy transfer, structural integrity, the genetic system or a myriad of other interrelated processes. Other elements are often necessary in trace quantities, however, these are frequently specific to the individual genus (or species) and are therefore classed as second-order elements in terms of biological requirements.

We have no knowledge regarding the distribution of these elements in the Earth's mantle or deeper layers. We know, however, that the Earth's surface has been drastically differentiated. Basement rocks composing the ocean floor (largely tholeiitic basalt) are poor in all the biogenic elements, with the exception, of course, of oxygen which is bound as silicates. Igneous continental rocks are also highly depleted in carbon and nitrogen, except where they have incorporated the elements from pre-formed deposits. Sulfur and phosphorus may, however, occur as localized enrichment in veins or mineralized layers, or may be enriched in specific minerals such as apatite. Table I shows some average values for these elements in the terrestrial biosphere, recent marine sediments and a basalt. It is probable that most analytical values for carbon and nitrogen in igneous rocks are incorrect because of the ease of contamination of these elements and the general lack of care exercised in the past in collecting and storing rocks.

It is apparent that on Earth, concentration of volatile elements occurs in the very surface; either by density diffusion along a temperature gradient or by aqueous

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leaching and subsequent introduction into the ocean. The oceans, and the sediments formed in them, become the repositories for the soluble and volatile elements.

These same processes will also cause isotope effects, either through equilibration among different mineral species or equilibration of gases, solutions and solids, all controlled by temperature. Unidirectional kinetic effects, especially those involving diffusion or evaporation from a gas phase, can markedly influence the distribution of oxygen ( $O^{18}/O^{16}$ ) and hydrogen (D/H) isotopes in water bodies. Superimposed on these physical processes, is the influence of organisms. They will cause isotope separation in association with their metabolic processes, where as a consequence, compounds which are most reduced are enriched in the light isotopes relative to the oxidized compounds of the same element. Thus, methane in sediments is enriched by approximately 50–70‰ in  $C^{12}$  relative to marine carbonate or bicarbonate and hydrogen sulfide is enriched by about 30–50‰ in  $S^{32}$  relative to dissolved sulfate from which it is derived.

TABLE I  
Biogenic elements H, C, N, O, P and S – Concentration (%)

	H	C	N	O	P	S
Biosphere	10.2	6.1	1.5	80	0.13	0.14
Marine Sediments	0.6	3.0	0.015	48	0.07	<1.0
Basalt (Tholeiitic)	<0.09	$2 \times 10^{-3}$	$1 \times 10^{-3}$	44	0.18	$5 \times 10^{-3}$

Because of the dynamic state of the Earth, it has been difficult to determine the distribution of the stable isotopes for most of the biogenic elements in the rocks of the primitive Earth, especially prior to the onset of life. This information would be of great value in evaluating possible losses of volatiles from the Earth's surface and in making a mass balance of these elements in various spheres. Furthermore, accurate knowledge of the isotopic abundance of the light elements in the solar wind which is not available, would permit more accurate predictions of the path taken during element synthesis in the stars. Hope has therefore been placed on lunar return samples as a source of material to help elucidate cosmic and planetary problems concerning elemental distribution and isotopic abundances.

## 2. Distribution of the Elements on Lunar Surfaces

By comparison with terrestrial basaltic rocks, it is apparent that lunar basalts have an approximately similar distribution of the biogenic elements with the possible exception of hydrogen, sulfur and phosphorus. The first is present almost entirely as hydrogen gas in concentrations less than 10 ppm in lunar rock samples. Sulfur appears to be more enriched in the lunar rocks, although values for Apollo 11 rocks appear to be about three times higher than for Apollo 12. Phosphorus is depleted in the crys-

talline rocks by a factor of 3 or 4 compared to terrestrial basalts. Schematic plots of relative distribution have been given for sulfur, phosphorus and other elements by Ganapathy *et al.* (1970).

By contrast, all the six elements discussed here are substantially depleted in comparison to their relative cosmic abundances. This is particularly true of H, C and N. The last two by more than four orders of magnitude. Presently, it is not known whether these elements were lost by volatilization during melting of the lava or whether the original rocks composing the moon were already depleted in them.

#### A. HYDROGEN

Several groups of investigators reported on the distribution of hydrogen in Apollo 11 and Apollo 12 material (D'Amico *et al.*, 1970; Epstein and Taylor, 1970 and 1971; Friedman *et al.*, 1970; Friedman *et al.*, 1971; and Funkhouser *et al.*, 1971). There is little disagreement that hydrogen is present in fines in concentrations averaging 50–100 ppm. However, a concentration below 5 ppm was analysed for the coarse fines, No. 12033, which were obtained in a trench (Epstein and Taylor, 1971). In several breccias, the gaseous hydrogen content for both Apollo 11 and Apollo 12 reached concentrations of 200 ppm. Two basaltic rocks (Friedman *et al.*, 1971; Funkhouser *et al.*, 1971) from Apollo 12 showed the hydrogen gas concentration to be <6 ppm. It is possibly lower, as some hydrogen may have been produced experimentally (see Table II).

It appears that the hydrogen is largely derived from the solar wind. Evidence for this comes from comparison in the same sample of amount of hydrogen with volumes of rare gases on the one hand, or cosmic exposure ages on the other. Samples containing the highest concentration of hydrogen gas have therefore been most favorably exposed to solar wind proton bombardment and have subsequently not been heated beyond 200–300°C. Heating could cause serious loss of the gas by diffusion as has been demonstrated in low temperature vacuum heating experiments during laboratory extraction (Funkhouser *et al.*, 1971).

Additional evidence that the hydrogen has been largely implanted by solar wind proton bombardment comes from the D/H isotope measurements of Epstein and Taylor (1970 and 1971) and from Friedman *et al.* (1970) and Friedman *et al.* (1971). If the only source for the gaseous hydrogen was solar protons, one should expect virtually no deuterium except for D formed as a product of cosmic ray spallation. The D content thus formed should only amount to about 3 ppm and the D/H ratio would be  $\delta D = -980\%$  (Epstein and Taylor, 1971). Such low values for  $\delta D$  have not been measured, but were obtained by extrapolation. However, values around  $\delta D = -850\%$  were found for several fines from Apollo 11 samples (Epstein and Taylor, 1970), and the breccia (No. 10061) which yielded a high hydrogen gas content, was also most depleted in deuterium giving  $\delta D = -873\%$  (Table III). Values obtained by Friedman *et al.* (1970) and Friedman *et al.* (1971) were less depleted in deuterium (Table II).

Apart from its gaseous form, there are also reports of water in the samples. The

TABLE II  
Hydrogen and water contents and  $\delta D$  in Apollo 11 and Apollo 12 samples

Sample No.	Epstein and Taylor (1970, 1971)		Friedman <i>et al.</i> (1970)		Friedman <i>et al.</i> (1971)		D'Amico <i>et al.</i> (1970)				
	H ppm	$\delta D$ (‰)	H <sub>2</sub> O ppm	$\delta D$ (‰)	Sample No.	H ppm	$\delta D$ (‰)	H <sub>2</sub> O ppm	$\delta D$ (‰)	Sample No.	H ppm
10084 (1) F	46.0	-853	200	-261	10046, 21 B	50	-830	455	-760	10084 F	110
10084 (2) F	44.7	-830	209	-275	10046, 22 B	60	-970	372	-580	10017 R	44
10084 (3) F	50.6	-850	141	-329	10060, 11 B	66	-870	152	-870	10072 R	69
10061 B	99.8	-873	180	-412	10017, 16 R	~1	-	~25	-	10061 B (Surface)	227
10087 F	100.6	-844	-	-						10061 B (Interior)	127
12070 F	37.8	-784	212	-236	12030 F	13	-430	25	-222		
12033 F	2.0	-523	135	-97	12051 R	6	+341	0.9	-100		
12042 F	40.4	-698	243	-146							

F = fines; B = breccia; = crysatlline rocks

concentrations reported by Epstein and Taylor (1970) and by Friedman *et al.* (1970) are at variance. The former report rather low concentrations ( $<25$  ppm with  $\delta D$  values in the range  $-412$  to  $-260\text{‰}$ , whereas the latter group find as much as 450 ppm  $\text{H}_2\text{O}$  produced by pyrolytic heating of samples of breccia and  $\delta D$  values in the range  $-870$  to  $-580\text{‰}$ . By contrast, much smaller concentrations of water were reported from Apollo 12 samples by Friedman *et al.* (1971) and these were in the range of those reported by Epstein and Taylor.

As the role of water may be crucial for any significant formation of organic matter, it is unfortunate that an accurate evaluation of its concentration does not exist. Whereas, Friedman believes that the water is indigenous to the lunar surface, Epstein believes that it represents a significantly large proportion of terrestrial contamination, probably when the samples were first opened at Houston. Both Epstein and Friedman concede that exchange between hydrogen and water can occur during pyrolysis and extraction, and this is especially seen as the temperature of extraction is increased (see Figure 1).

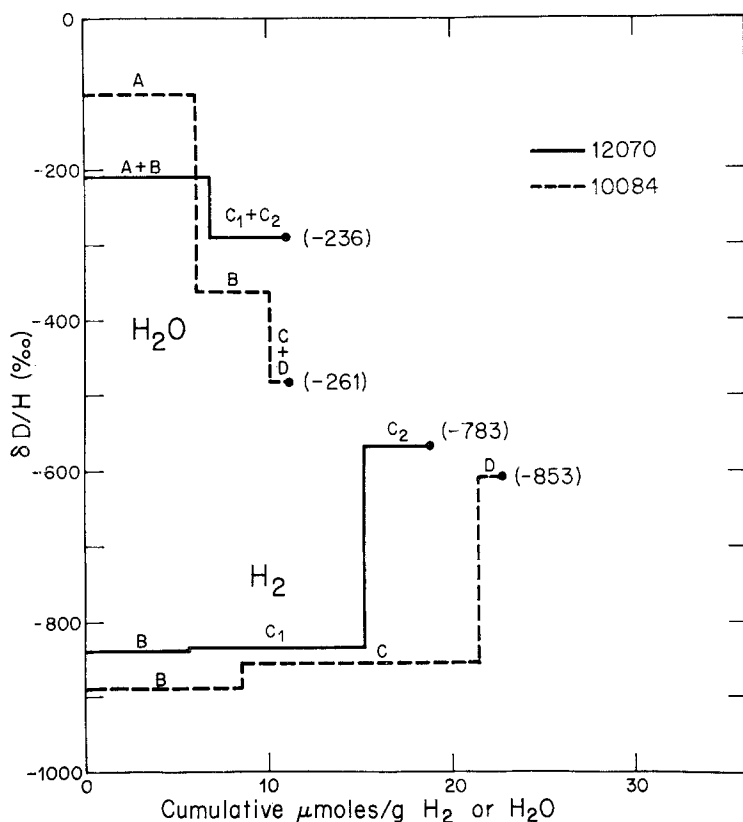


Fig. 1. Data for typical hydrogen (lower two curves) and water (upper curves) extractions from Apollo 11 and Apollo 12 soils, plotted as  $\delta D/H$  vs cumulative  $\mu\text{moles g}^{-1}$ . The letters A, B, C, C<sub>1</sub>, C<sub>2</sub> and D represent the successive fractions extracted during heating (see text). The numbers in parentheses are the weighted average  $\delta D/H$  values of the various fractions from each sample. Figure taken from Epstein and Taylor (1971).

Contamination by terrestrial water is very difficult to eliminate. In experiments by Oró *et al.* (1971), where three consecutive pyrolyses were run on a single sample without withdrawing it from the pyrolysis equipment, but allowing it to cool to room temperature, water peaks always appeared. Water can also have been formed on the lunar surface by combustion of the retrorocket engine fuel, dimethylhydrazine, and by absorption from the atmosphere of the command module, if the sample containers are not totally sealed. Besides contamination, water can be generated by reaction of hydrogen with metal oxides at temperatures above 500°C which occurs during extraction. The decrease in  $\delta D$  during heating, shown in Figure 1, may partly represent water formation from hydrogen and not necessarily exchange.

Apart from a report by Drever *et al.* (1970) for the presence of phyllosilicates in Apollo 11 fines and the surface of one crystalline rock (No. 10017), clay-like minerals have not been reported again. However, hydroxyl containing amphiboles were reported for Apollo 11 (Gray *et al.*, 1970); Apollo 12 (Dence *et al.*, 1971) and recently from Apollo 14 samples (Mason *et al.*, 1972). In all these occurrences, the amphibole minerals were in very low abundance. A significant discovery was made by Agrell *et al.* (1972), who identified goethite in a microbreccia from the Apollo 14 mission (No. 14301). Here again, the abundance of the mineral was low, and it was found surrounding native iron grains to a thickness of 10 to 20  $\mu m$ . Of importance to this discussion, is the report that the goethite-rich minerals contained as much as 0.04%  $H_2O$ , which was only released at temperatures above 105°C by the conventional Penfield tube technique of measurement.

As the lunar surface may reach temperatures approaching 150°C during the lunar day, it is surprising that the water associated with the goethite has not escaped. Agrell *et al.* (1972) believe this is due to protection of the mineral by having it sealed within the lunar rock. In view of the ease of contamination of the lunar samples with small amounts of terrestrial water, caution must still be exercised in assigning a lunar origin for this water.

In view of the isolated reports for hydrated minerals, which apparently occur in very low abundance, it would appear that water must have diffused out of the lunar surface so rapidly that very little survived capture. This would suggest that at the time of formation of these rocks, there was an insignificant partial pressure of water vapor in the lunar atmosphere (Charles *et al.*, 1971). Furthermore, carbonaceous chondrites, which may be assumed to be potential source for most of the biogenic elements, appear to have left no recognizable aqueous component. Boato (1954) has shown that meteoritic water is isotopically heavy ( $\delta D + 300\%$  relative to SMOW) whereas, with the exception of one basalt measured by Friedman *et al.* (1971), all others are highly depleted in deuterium.

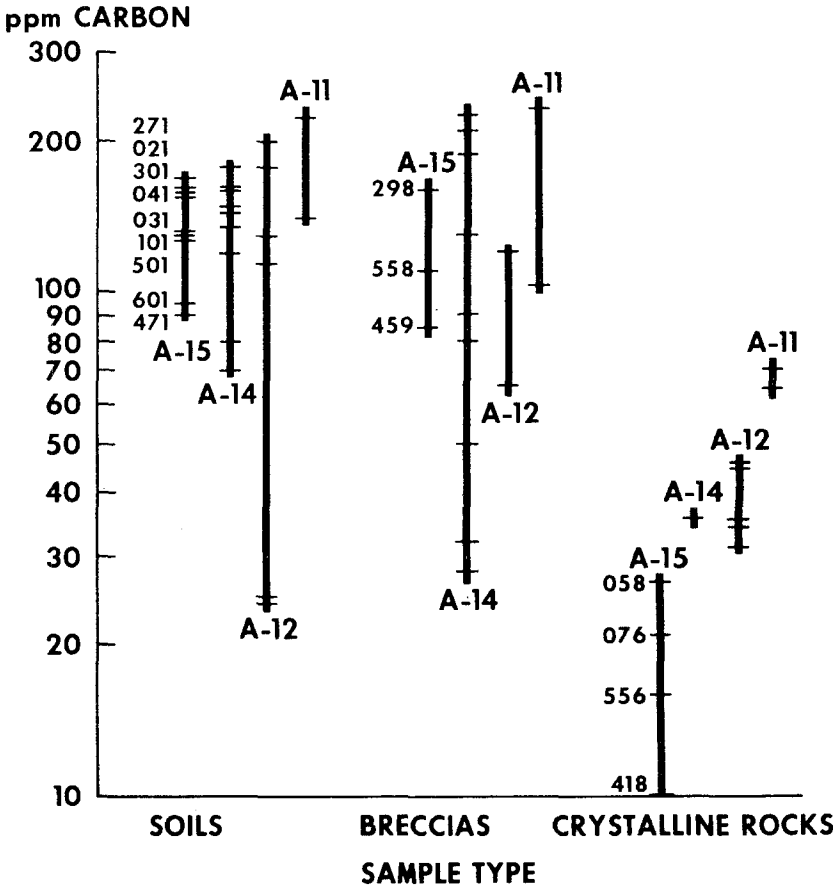
It should be noted, however, that water may be forming on the lunar surface by interaction of high energy solar protons with oxides or silicates (Zeller *et al.*, 1970). Thus, the high surface-area fines would be the effective target and should contain more water than the crystalline rocks from which they form. By analogy, it now appears that as much as 5 ppm methane may be present within lunar samples arising from

interaction of protons with lunar or solar-derived carbon (see Eglinton *et al.*, Gibson and Moore, this issue, pp. 497 and 404).

B. CARBON

The carbon content of fines, breccias and crystalline rocks has been measured by a number of researchers, but mainly by Moore *et al.* (1970), Moore *et al.* (1971), Epstein and Taylor (1970, 1971), Friedman *et al.* (1970), Friedman *et al.* (1971), Nagy *et al.* (1971), Kaplan *et al.* (1970) and Kaplan and Petrowski (1971). A summary of the data obtained by Moore and co-workers is given in Figure 2, which can be considered broadly representative of results by other workers as well. It indicates that the highest concentration of carbon is about 200 ppm.

Fines and breccias have overlapping concentrations which generally fall in the range of 60 to 200 ppm. However, some coarse-grained 'fines' from a trench sample on



Oceanus Procellarum contained relatively low carbon (these same samples also contained little hydrogen as stated earlier) and also displayed low solar wind exposure ages. Similarly low concentrations were measured on coarse breccias with feldspar-rich matrix from Apollo 14 return samples.

Carbon content of crystalline rocks vary from 70 ppm in Apollo 11 basalts to  $\approx 20$  ppm in Apollo 15 rocks. It is probable that the higher values measured on Apollo 11 samples are erroneous, due to contamination. One might suspect that values above 30 or possibly 40 ppm, have had carbon added to them after collection.

This view of contamination, especially on Apollo 11 samples, is also seen from a study of  $C^{13}/C^{12}$  ratios. Kaplan *et al.* (1970) showed that for a series of analyses of bulk fines (10084 and 10086) the lowest carbon content was associated with the highest enrichment in  $C^{13}$  (Figure 3). Common organic components in the laboratory which could act as contaminants are in the range of  $\delta C^{13} = -20$  to  $-30\%$ , and a number of possible contaminants at the Lunar Return Laboratory in Houston are even lighter (see Kaplan and Petrowski, 1971; Table 1). It is logical to deduce that the correct

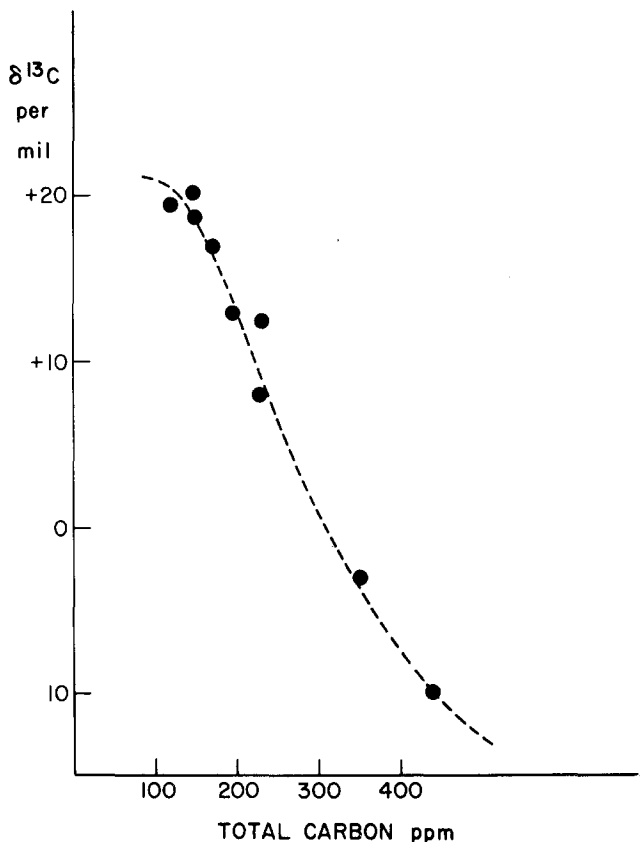


Fig. 3. Relationship between the total carbon content of the bulk fines (10086 and 10084) and  $\delta C^{13}$  of the product  $CO_2$ . From Kaplan *et al.* (1970).



carbon concentration is in the range 116–150 ppm and quoted results for these samples above 200 ppm C includes significant amounts of terrestrial contamination. Differences in concentration are also in part reflected by non-homogeneity of the sample; the finer material contains more carbon and the coarser material contain less than the bulk sample. However, in this case, the finer material is enriched in  $C^{13}$  relative to the remaining coarse fraction (Kaplan *et al.*, 1970).

The value of  $\delta C^{13} = +20.2\%$  is the heaviest so far measured on any sample. Samples from Apollo 12, 14 and 15 reported to the date of writing this report, are all isotopically lighter. The least enriched in  $C^{13}$  relative to PDB, are the trench samples from Oceanus Procellarum (Epstein and Taylor, 1971; Kaplan and Petrowski, 1971). Values for breccias are isotopically lighter than for bulk fines from the same region. They fall intermediate between fines and crystalline rocks, depending on their relative content of each component and the carbon content.

The  $\delta C^{13}$  of a few basaltic rocks with low carbon contents have been measured (Kaplan *et al.*, 1970; Kaplan and Petrowski, 1971; Friedman *et al.*, 1971) and appear to yield values in the range of  $-20$  to  $-25\%$ . Due to the ease of contamination of such samples, it may still be premature to state that these values are authentic. However, if these measured values are correct, then they indicate that the  $C^{13}/C^{12}$  ratio of terrestrial basalt (which also have the same isotopic values) may be representative of primordial carbon of the Earth.

There is some controversy regarding the validity of the heavy  $\delta C^{13}$  data. The results of Epstein and Taylor are generally consistent with those of Kaplan and co-workers for the bulk fines and for the breccias, whereas those obtained by Friedman and co-workers are always isotopically lighter. Figure 4 shows a summary plot of values obtained. It is apparent that Friedman's measurements for  $\delta C^{13}$  are all  $<0\%$  PDB, in fact, for three Apollo 12 samples of bulk fines, his group (Friedman *et al.*, 1971) report  $\delta C^{13} = -8\%$ ,  $-15\%$  and  $-24\%$ . Unfortunately, the same samples have not always been measured by the three groups and some discrepancy may therefore be due to inhomogeneity in the sample containing carbon from different sources. Comments regarding errors in analytical measurements should therefore be reserved until additional measurements have been made. In light of this, and previous remarks on the validity of measurements on basalt, too much stress cannot yet be placed on the agreement between Friedman's and Kaplan's results for crystalline rocks.

Based on isotopic values of carbon products ( $CO$ ,  $CO_2$  and  $CH_4$ ) produced during vacuum pyrolysis or acid hydrolysis, Kaplan and co-workers suggest that the lunar fines contain carbon derived from different sources. There is evidence that small quantities ( $\leq 5$  ppm) of solar wind derived methane is trapped in fractures and voids of bulk fines near the outer surface of particles. Even smaller ( $\leq 1$  ppm) quantities of  $CO_2$  or  $CO$  may also be trapped, as well as minute (1–10 ppb) quantities of more complex organic molecules. However, the predominant carbon components are non-volatile. Heavy metal carbides are recognized as composing a significant proportion of this carbon, but a complete mass balance has not yet been established. During heating of a lunar sample,  $CO$  and  $CO_2$  are released at a range of temperatures,

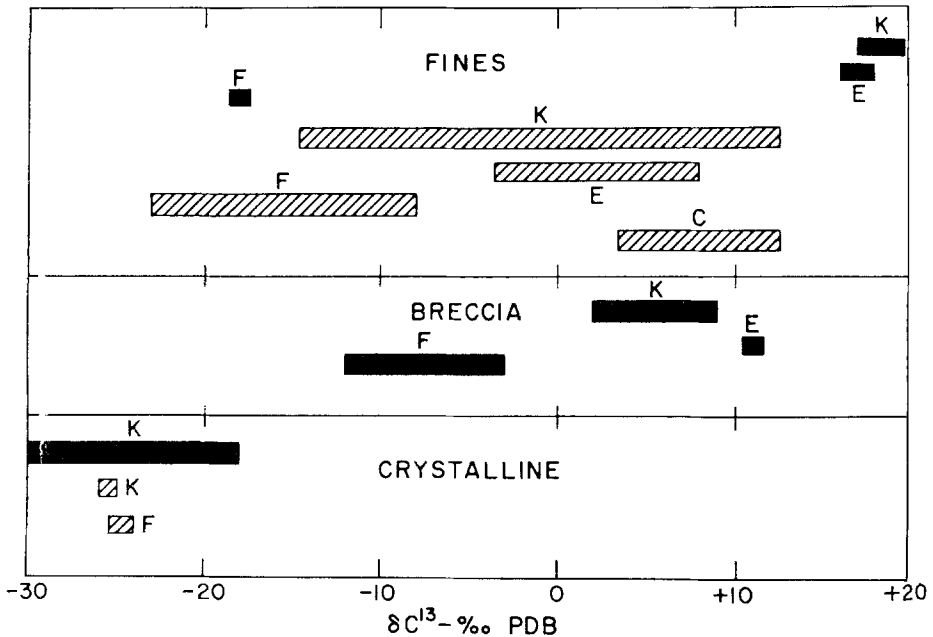


Fig. 4. Relative abundances of the stable isotopes of carbon in lunar materials. The analyses are given in ‰ deviation from the PDB standard. Solid bars = Apollo 12; diagonal lined bars = Apollo 11. C = Chang *et al.* (1971); E = Epstein and Taylor (1970, 1971); F = Friedman *et al.* (1970); K = Kaplan *et al.* (1970) and Kaplan and Petrowski (1971). Taken from Friedman *et al.* (1971).

suggesting that oxidation of reduced carbon has occurred within the sample by solid-solid reactions (see Gibson and Moore, this issue, p. 404. More detailed discussion on the distribution of carbon compounds will appear elsewhere in this issue.

### C. NITROGEN

Most of the nitrogen measurements have been made by Moore *et al.* (1970) and Moore *et al.* (1971). In general, it appears that the nitrogen content is proportional to the carbon content as seen in Figure 5 for Apollo 11 and Apollo 12 samples. It is apparent that most of the values for total N fall in the range from 50–150 ppm. Little is yet known about the nature of this nitrogen.

In hydrolysis experiments undertaken by Hinterberger *et al.* (1970), 56 ppm ammonia was detected in a sample of bulk fines 10084 which had been treated with 1:10H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O. Other hydrolyses experiments yielded ammonia concentrations only slightly above background. The authors therefore caution against accepting their published results as accurate. However, they indicate that decomposition of the rock by sulfuric acid yielded only small quantities of gaseous nitrogen (10% of the total) and therefore suggest that the nitrogen is implanted by solar wind as ammonia or nitrides.

Confirmation of these studies was presented at the *Third Lunar Science Conference* by Müller (1972) and by Sakai *et al.* (1972). It is apparent from the results of both

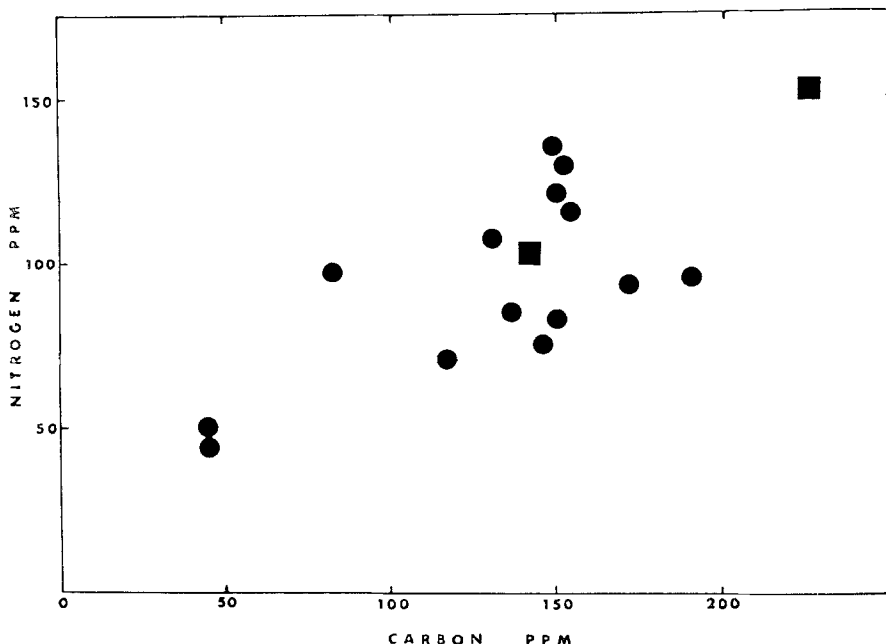


Fig. 5. Correlation of total carbon and nitrogen in lunar fines Apollo 11, Apollo 12.

research teams that hydrolysable nitrogen is the dominant component in the lunar samples. Grain size separation of the fines indicate that the highest concentration of hydrolysable nitrogen resides in the particles with greatest total surface area, or smallest size (see Table III). Müller interprets this as evidence for a solar wind origin of the nitrogen. The incoming nitrogen (probably as atoms) is thought to react with the lunar matrix or with solar wind protons, forming chemically-bound nitrides or ammonia.

Funkhouser *et al.* (1971) question the presence of molecular nitrogen within lunar samples. By heating a variety of samples at temperatures of 225° and 300°C they were unable to measure any N<sub>2</sub> released. However, when a basalt (No. 12063, 112) was crushed at room temperature, very small amounts of N<sub>2</sub> was detected, amounting to 0.1–1 ppm. These results were essentially confirmed by Müller (1972) on Apollo 14 and 15 samples while heating to 500°C.

In pyrolysis experiments, nitrogen has been observed to evolve at both low and high temperatures (Wachi *et al.* 1971). As samples have been packed in dry nitrogen, it is probable that low temperature evolution represents removal of adsorbed gas, and possibly some trapped N<sub>2</sub> at temperatures approaching 500°C. Stronger heating caused nitrides to oxidize to NO fragments which were observed. It is puzzling why a strong nitrogen peak appeared at temperatures above 1150°C (Figure 6). It is possible that this may represent ammonia within a structural lattice position, such as a cation in a silicate, which has been oxidized by metal oxides at the point the sample melts and crystalline integrity of minerals disappears.

TABLE III

Chemically bound nitrogen (chem. b.N) concentrations in lunar bulk fines and grain size fractions, breccia and crystalline rocks determined as ammoniacal nitrogen by the Kjeldahl method.<sup>a</sup> Error:  $\pm 5$  ppm

Sample type and number	Chem. b.N (ppm)
Fines 10084,31-bulk	93
< 48 $\mu$ m	148
Fines 12070,76-bulk	80
Fines 14003,24-bulk	92
< 48 $\mu$ m	194
Grain < 24 $\mu$ m	226
size 24–48 $\mu$ m	149
fract. 48–60 $\mu$ m	73
60–109 $\mu$ m	60
Breccia 10046,1	131
Fragmental rock 14303,13	31
Fines 15101,59-bulk	109
Grain < 24 $\mu$ m	272
size 24–48 $\mu$ m	113
fract. 48–60 $\mu$ m	86
60–109 $\mu$ m	65
Fines 15601,63-bulk	80
Grain < 24 $\mu$ m	157
fract. 24–48 $\mu$ m	83
Vesicular basalt 10057,80	64
Microgabbro 12063,112	< 10
Basalt 12075,13	< 10
Vesicular basalt 15556,25	< 10

<sup>a</sup>From: Müller (1972)

By analogy with carbon, one may expect that nitrides are present as a lunar component and ammonia may be formed by solar wind impact. Hydrolysis of lunar samples will result in ammonia formation and possibly supply  $-\text{NH}_2$  fragments as necessary precursors for amino acid synthesis. The status of present results on nitrogen analysis, requires additional measurements before any conclusions can be drawn.

#### D. OXYGEN

It is well recognized that lunar rocks are depleted in oxygen relative to terrestrial igneous rocks. They contain troilite and apparently no measurable quantities of  $\text{Fe}^{+++}$ . Sato and Helz (1971) estimated the oxygen fugacity under which Apollo 12 rocks formed to be  $10^{-12}$  to  $10^{-14}$ , several orders of magnitude smaller than for terrestrial basalts. Ehmann and Morgan (1970, 1971) have related oxygen content to silicon content. Their plot shown in Figure 7 indicates that oxygen is depleted relative to terrestrial igneous rocks for which the O–Si regression line is  $\text{O}\% = 0.415 \text{ Si}\% + 35.0$ . The closest to this relationship is that measured on rock No. 12013 where  $\text{O}\% = 0.43$

Si% + 33.0, some 2% depleted in O. The regression line for Apollo 11 rocks is  $O\% = 0.96 Si\% + 19.6$  and for Apollo 12 rocks  $O\% = 0.98 Si\% + 20.8$ . The low O/Si ratio in the lunar rocks is in part due to the presence of illmenite with a relatively low oxygen content (31.6%O) and reduced species such as  $Cr^{+2}$ , but the difference in the slopes of the terrestrial and lunar regression line is not simply explained.

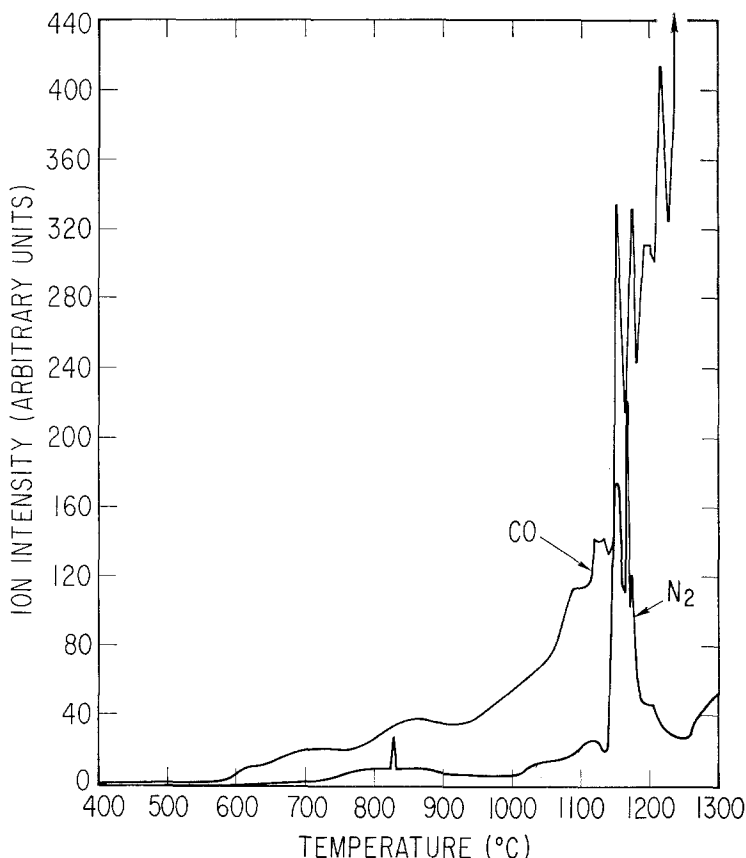


Fig. 6. Evolution curves for CO and N<sub>2</sub> for Apollo 11 lunar fines. From Wachi *et al.* (1971).

Cuttitta *et al.* (1971), Ehmann and Morgan (1971) and others found that the total reducing capacity for Apollo 11 samples was greater than for Apollo 12 samples. An excess reducing capacity ( $\Delta RC$ ) of 0.8 to 4.1% in Apollo 11 and 0.0 to 1.6% in Apollo 12 samples, defines the lack of oxygen relative to iron calculated as FeO. This non-stoichiometry is generally ascribed to competition for O by Ti (and possibly  $Cr^{+2}$ ). The greatest oxygen deficiency occurs in the fines and breccias. Ehman and Morgan (1971) suggest that reaction of oxygen with solar wind hydrogen may be removing oxygen. Interestingly, trench sample 12033 showed least  $\Delta RC$  (0.2 to 0.3%), in line with other evidence suggesting it had only a brief history of solar exposure.

In view of this oxygen deficiency, it is interesting to note the recent claim of Agrell

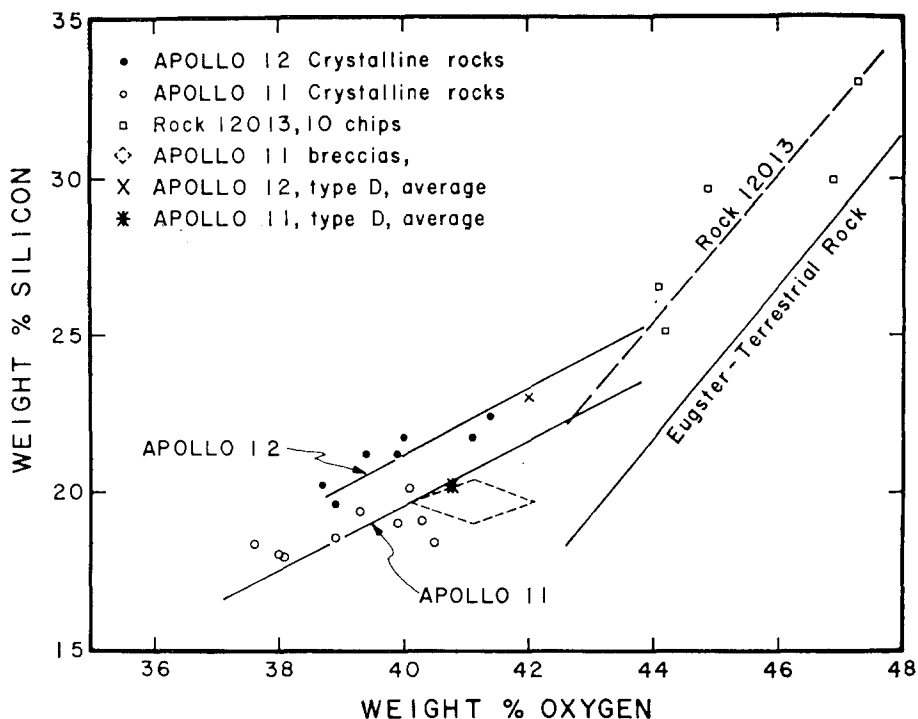
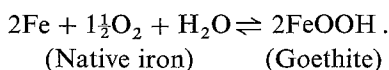


Fig. 7. Relation of Si and O in lunar materials. From Ehmman and Morgan (1971).

*et al.* (1972) that trace amounts of goethite are present in microbreccia No. 14301, surrounding native iron grains. Of equal significance is their suggestion that some troilite may also have been oxidized to iron sulfate. These oxidized minerals indicate that molecular oxygen may also have been present, as native iron does not readily oxidize to goethite at low temperatures unless dissolved oxygen is present.



Oxidation may have occurred at high temperature with resulting escape of hydrogen, but at present insufficient information is available for interpretation.

If the presence of oxidized iron is confirmed, the probability of finding greater enrichments of oxidized phases at depth, away from the highly reducing environment at the regolith, is significantly high. However, it is possible that the water was derived through impact of a carbonaceous chondrite at the lunar surface. In such an event, the oxidized phases would have local significance only.

Values for  $\text{O}^{18}/\text{O}^{16}$  isotope ratios (see Figure 8) indicate that they fall in the range of igneous terrestrial rocks. The total spread for  $\delta\text{O}^{18}$  is +5.6 to +6.8‰ relative to SMOW standard. At the heavy end of the range are bulk fines and breccias from Apollo 11 which had the highest solar wind exposure. These same samples are the most depleted in oxygen as explained above.

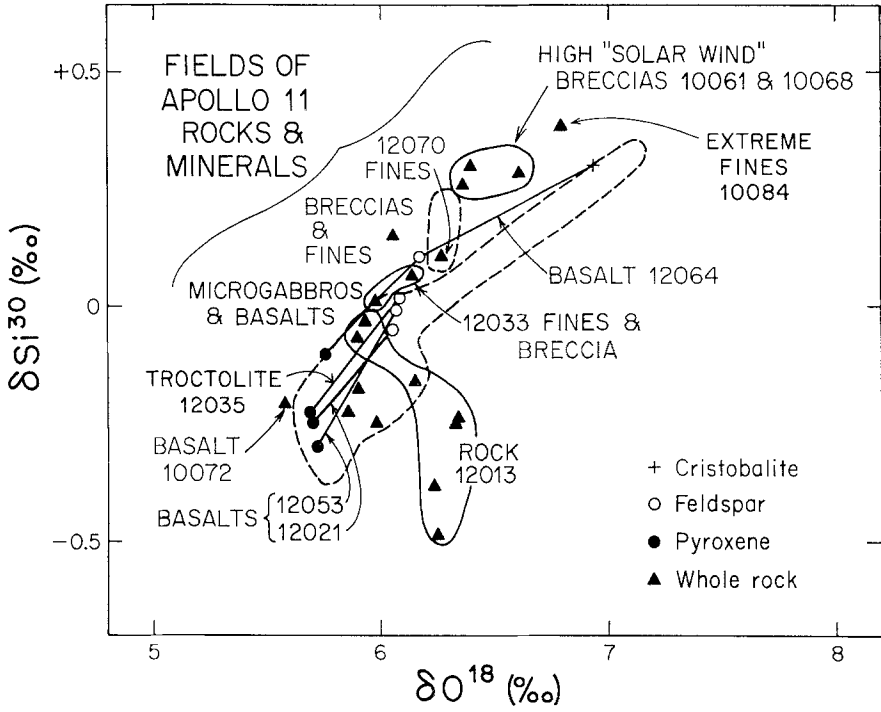


Fig. 8. Plot of  $\delta Si^{30}$  as  $O^{18}$  for Apollo 11 and Apollo 12 lunar samples. Note that the long extension of Apollo 11 field toward the upper right-hand corner of the diagram is due solely to a single analysis of cristobalite from 10044. From Epstein and Taylor (1971).

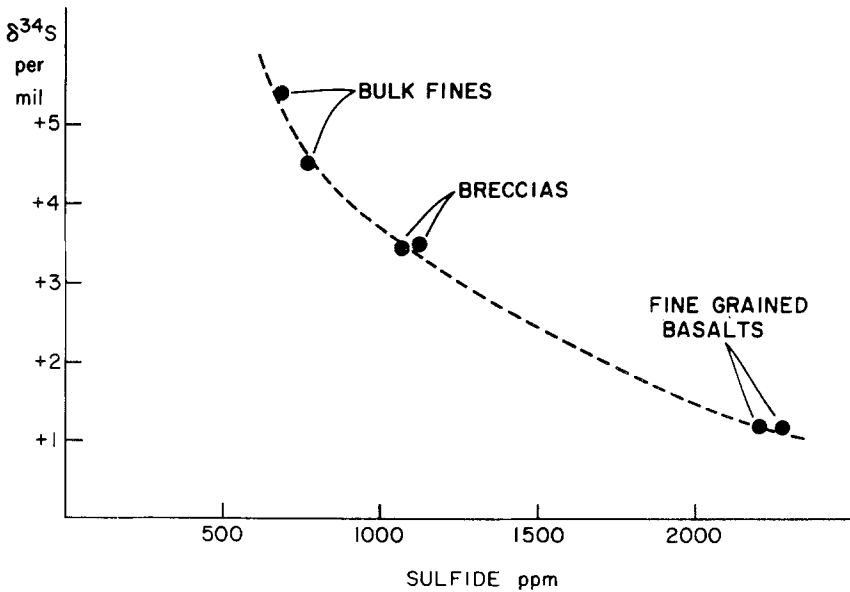


Fig. 9. Variation of  $\delta S^{34}$  with total sulfur content in fines, breccias and fine-grained basalt of Apollo 11. From Kaplan *et al.* (1970).

## E. PHOSPHORUS

Phosphorus shows a wide range of concentrations. It was found to be particularly abundant in the bulk fines from Oceanus Procellarum, which also displayed relative enrichment of potassium and rare earth elements and then became known as KREEP. Phosphorus also appears to be enriched in a sample of bulk fines (14163) and basalt (14310) reported by LRL (1971) for Apollo 14. However, concentrations in Apollo 15 material were equal to, or lower than, for Apollo 11 (see Table IV).

TABLE IV  
Phosphorus content of Apollo rocks and fines (ppm)

Apollo 11			Apollo 12		Apollo 14		Apollo 15			
basalts	breccias	fines	basalts	fines	basalts (No. 14310)	fines (No. 14163)	basalts	breccias	fines	basaltic achondrites
630	630	570	470	1950	1400	1930	300	700	630	830

Lunar concentrations appear to be lower than terrestrial concentrations by a factor of 5 or more. Phosphorus is distributed mainly in the three minerals – apatite, whitlockite and schreibersite. Factors controlling its distribution are not known. It is apparent, however, that differentiation must occur during crystallization of basalt or in formation of the initial melt, in order to explain the distribution range. From a biogenic standpoint it is probably not a limiting element.

## F. SULFUR

Sulfur contents of crystalline rocks, breccias and bulk fines have been reported for Apollo 11 and Apollo 12 samples. The data indicate that the dominant sulfur form is stoichiometric troilite, FeS, although trace quantities of other metal sulfides have also been reported by El Gorse *et al.* (1971). The metal sulfides are observed as discrete inclusions both in the bulk fines and in the crystalline rocks. In Apollo 11 fines, most metal inclusions were surrounded by troilite (Agrell *et al.*, 1970) and a significantly important meteorite contribution was recognized. In Apollo 12 fines, much less meteoritic contribution was found (Goldstein and Yakowitz, 1971), and troilite and native metals were not always associated. As troilite has been observed in the crystalline rocks, it therefore also has a lunar origin.

The distribution of sulfur in Apollo 11 samples is shown in Figure 9. It can readily be seen here that the highest concentration of sulfur is in the rocks, the least in the fines, and the breccias are intermediate. However, in Apollo 12 analysed samples (see Table V), there appears to be little difference between the concentration in rocks and



in bulk fines. In this case, the sulfur content of the rocks at Oceanus Procellarum is about one-third that at Mare Tranquillitatis, whereas the content of sulfur in the fines at the two areas is about the same. Preliminary results from Apollo 14 and Apollo 15 return samples suggest that concentrations <400 ppm to >900 ppm are present in the fines. This heterogeneous occurrence of sulfur suggests that selective processes must exist in distributing sulfide minerals on the lunar surface.

TABLE V

Sulphur isotope ratios (relative to Canyon Diablo) and sulphur concentrations in Apollo 12 samples (from Thode and Rees, 1971)

NASA sample number	McMaster fraction number <sup>a</sup>	Sulphur content ppm <sup>b</sup>	$\delta S^{34}$ ‰	$\delta S^{33}$ ‰	$\delta S^{36}$ ‰	$\Delta S^{33c}$ ‰	$\Delta S^{36d}$ ‰
120530-71	1	730	0.68	0.24	1.28	-0.11	-0.01
12021-60	2	895	0.38	0.23	-0.76	+0.04	-1.48
12022-50	1	903	0.37	0.20	0.59	+0.01	-0.11
12018-33	1	550	0.68	0.40	0.61	+0.05	-0.68
12002A	1	633	0.46	0.18	0.43	-0.06	-0.44
12070-57	(entire sample used)	700	8.70	4.31	14.95	-0.17	-1.58
Mean value						-0.06	-0.7
Standard deviation of mean						$\pm 0.04$	$\pm 0.3$

<sup>a</sup> Chips of the rock samples have been saved for future duplicate analyses

<sup>b</sup> Error estimated as  $\pm 3\%$

<sup>c</sup>  $\Delta S^{33} = \delta S^{33} - 0.515 \delta S^{34}$

<sup>d</sup>  $\Delta S^{36} = \delta S^{36} - 1.90 \delta S^{34}$

Additional evidence for selective concentration processes comes from  $\delta S^{34}$  isotope measurements of crystalline rocks. Kaplan and Petrowski (1971) found one Apollo 12 basalt (12022) to have  $\delta S^{34} = -0.2\%$  compared with  $\delta S^{34} = +1.2\%$  for two basaltic rocks from Apollo 11. Thode and Rees (1971) obtained somewhat higher enrichment in  $S^{34}$  as seen in Table V, however, none of their measured values reached the value of  $\delta S^{34} = +1.3\%$  measured by Kaplan *et al.* (1970) for Apollo 11 sample 10049. This difference in  $\delta S^{34}$  in troilite in crystalline rocks suggests that differentiation has occurred near the lunar surface resulting in isotopic fractionation.

Sulfur also displays an enrichment in the heavy isotope in the bulk fines (see Figure 5 and Table V). The maximum values measured for  $\delta S^{34}$  range from  $+8.2\%$  for 10086,  $+8.7\%$  for 12070,  $8.8\%$  for 12023,  $+9.7\%$  for 14298 and  $+9.4\%$  for 15271. It is, therefore, apparent that some external process is causing this effect. Thode and Rees (1971) also measured  $S^{33}/S^{32}$  and  $S^{36}/S^{32}$  ratios in order to determine if the isotope effects measured may have resulted from addition of sulfur by cosmic ray spallation. Spallation products were measured in meteorites by Hulston and Thode (1965). The data shown in Table V indicate that isotopic fractionation is the result of mass discrimination and not spallation products.

## G. LUNAR ISOTOPE FRACTIONATION PROCESSES

It can be seen from Figure 10 that the lunar fines show an anomalously high enrichment of  $C^{13}$  and  $S^{34}$ , compared to reduced compounds in meteorites or terrestrial samples. Initial interpretations, after results of the Apollo 11 samples analyses became available, was that the isotopically heavy carbon and sulfur in the fines was derived from the solar wind. As the sulfur content is depleted in Apollo 11 bulk fines relative to the crystalline rocks, Kaplan *et al.* (1970) suggested that enrichment of heavy isotopes was due to 'hydrogen stripping' through solar wind action of protons on the lunar surface.

Evidence of this stripping effect was elegantly demonstrated by Epstein and Taylor (1971) by fluoridation of fines and collection of the products ( $O_2$  and  $SiF_4$ ). Figure 11 shows that when such time-controlled etching experiments are carried out, the products first obtained (interpreted as coming from the outer surfaces) are highly enriched in  $O^{18}$  and  $Si^{30}$ . This process would, therefore, be responsible for enrichment in  $O^{18}$  in the fines of Apollo 11 with a long history of solar wind exposure. As the sulfur content of the fines is substantially lower than that from the crystalline rocks, it would appear that processes of removal must be more important than processes of addition.

In the simplest case, isotope fractionation would then result from escape of the products formed by diffusion. As a first approximation, this would be controlled by the inverse square root of the masses. Thus:

$$k_1/k_2 = (M_2/M_1)^{1/2}.$$

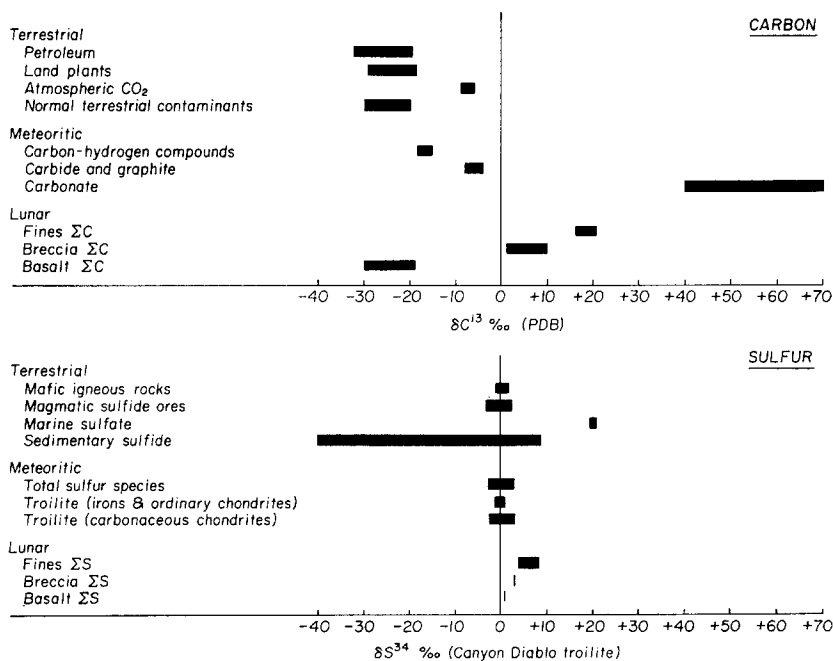


Fig. 10. Distribution diagram of  $\delta C^{13}$  and  $\delta S^{34}$  among various phases of terrestrial, meteoritic and lunar components. From Kaplan *et al.* (1970).

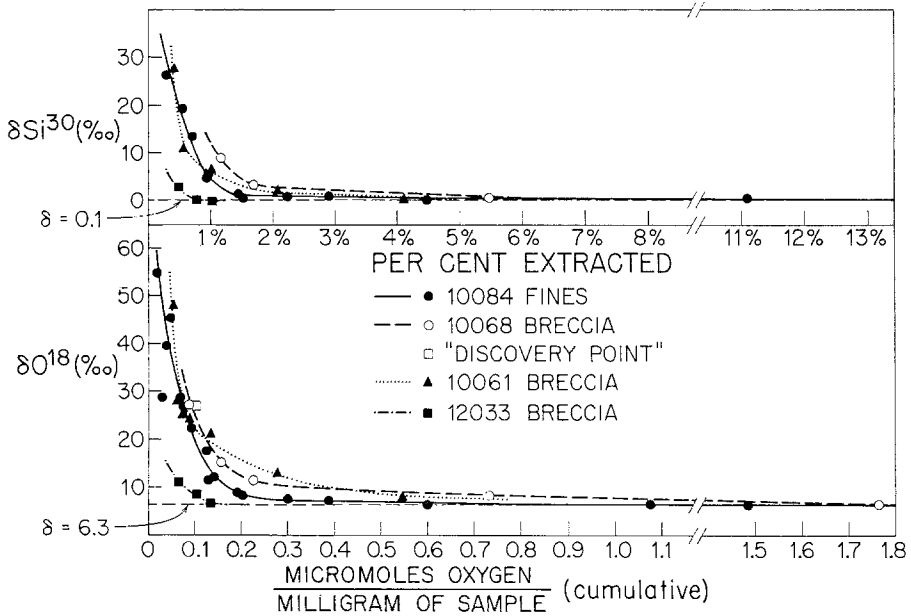


Fig. 11. Variation of  $\delta O^{18}$  and  $\delta Si^{30}$  in the gases from 10084 fines, 10068 breccia, 10061 breccia and 12033 breccia by partial fluorination experiments. The  $\delta Si^{30}$  and  $\delta O^{18}$  values are both plotted against the cumulative  $\mu\text{moles/g}^{-1}$  of oxygen extracted during the fluorination experiments. The 'per cent extracted' refers to per cent of oxygen extracted relative to that present in the bulk sample. The  $\delta Si^{30}$  values of the initial 2 or 3 fractions extracted from 10084 and 10068 probably should be lowered by about 4 to 9 ‰. From Epstein and Taylor (1971).

### 3. Summary

The information so far gleaned from studies on biogenic elements in lunar rocks and bulk fines can be summarized below:

(1) The six elements considered in this study (H, C, N, O, P and S) are present either as minor or trace elements, with the exception of oxygen. However, oxygen is largely bound as silicates, and is depleted in terms of its stoichiometry in relation to the transition metals.

(2) Three sources can be ascribed to these elements in breccias and in the bulk fines (i) endogenous to Moon (ii) solar wind (iii) meteorites, comets or planetary dust. The elements in the crystalline rocks almost entirely arise from (i). It is probable that nearly all of H and a significant proportion of C and N in fines may be derived from (ii). Most of the measured P and S has a (i) origin, although a small component of (iii)-derived elements are also present. Although oxygen in silicates undoubtedly have a predominantly (i) origin, it is difficult to determine any other source. Spallation elements may form by cosmic ray activity, but are probably not important in terms of abundance.

(3) Exposure to solar wind irradiation will also cause removal of elements by hydrogenation. Thus, carbon may escape as  $CH_4$  and other light hydrocarbons,

oxygen, nitrogen and sulfur may diffuse out of the lunar gravitational field as water, ammonia or hydrogen sulfide.

(4) This 'hydrogen stripping' appears to be responsible for enrichment of the heavy isotopes  $C^{13}$ ,  $O^{18}$  and  $S^{34}$  in the bulk fines, which have a history of long exposure to the solar wind. Gaseous hydrogen is greatly depleted in deuterium, pointing to its origin as solar wind protons.

(5) Mineralogical evidence argues for lack of water in the magma from which the rocks in maria have crystallized. Any water present on the lunar regolith should only be in the fines (or breccias) and has probably formed by high energy ( $>1$  MeV) proton reaction causing oxygen bond breakage.

(6) General lack of a concentration mechanism for the water; potent destructive processes by proton, cosmic ray and UV, radiation; volatilization by high day-time temperatures and low atmospheric pressures, all suggest a steady state condition in which rate of destruction and removal of organic molecules is much greater than the rate of synthesis and concentration.

(7) Phosphorus, sulfur and possibly nitrogen are present in quantities in lunar fines sufficient to support some terrestrial type microbiological forms. However, carbon, hydrogen and available oxygen are all in critically short supply on the lunar surface, insufficient for any active energy transfer or protein synthesizing processes.

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