

Nitrogen abundances and isotopic compositions in lunar samples

RICHARD H. BECKER and ROBERT N. CLAYTON*

Enrico Fermi Institute, University of Chicago, Chicago, Illinois 60637

Abstract—Nitrogen contents and isotopic compositions have been determined for several lunar rock samples, breccias, and bulk soils by vacuum pyrolysis and mass spectrometry. Such data in addition have been obtained for soil grain-size separates and, in one case, for magnetic separates from a single grain-size fraction, by either total pyrolysis or step-wise heating of the separates. Helium contents of bulk soils and breccias were also determined.

Nitrogen contents of rocks and higher metamorphic-grade breccias are below 5 ppm. Soils and low-grade breccias yielded 40–120-ppm nitrogen. Nitrogen amounts released from soil grain-size fractions below 900°C (surface-situated component) and above 900°C (volume-situated component) both show decreases with increasing grain size. Magnetic particles (agglutinates) contain several times more nitrogen than do non-magnetic particles, particularly in the fraction released above 900°C.

Lunar rocks and nitrogen-poor breccias contain amounts of cosmic-ray produced spallation ^{15}N sufficient to increase markedly their $^{15}\text{N}/^{14}\text{N}$ ratios, except in the case of very low exposure ages. This prevents at the moment a determination of the isotope ratio of indigenous lunar nitrogen.

The $^{15}\text{N}/^{14}\text{N}$ ratio of the nitrogen in grain-size separates from soils increases with increasing grain size. This results from the interplay of several components present. Step-wise heating results indicate the presence of at least three isotopically distinct components in soils. One, released mainly upon melting, is very heavy isotopically, and presumably consists of the indigenous plus spallation nitrogen that is seen as well in rocks. A second component, also relatively heavy isotopically, is released below 900°C, and presumably consists of recently implanted nitrogen in grain surfaces. The third component, released above 900°C but below the melting point, is isotopically light, and represents an earlier generation of surficially implanted nitrogen now present in more retentive sites within agglutinate particles.

The $^{15}\text{N}/^{14}\text{N}$ ratio of nitrogen implanted in lunar soils has increased as a function of time, changing by perhaps 15% over a time span of somewhere between 4.5×10^8 and about 4×10^9 yr. This may be the result of a change in this ratio in the solar wind due to spallation reactions at the solar surface, or it may have resulted from decreasing contributions of an isotopically light, indigenous lunar-nitrogen component outgassed from the interior of the moon and reimplanted by solar-wind ionization and acceleration into the lunar surface. In either case, the isotopic composition of nitrogen in bulk soils provides a measure of how far in the past they received the major part of their surface exposure.

INTRODUCTION

DETERMINATIONS OF THE NITROGEN CONTENTS of lunar rocks and soils have led to the conclusion that the principal source of the nitrogen in these samples is the solar wind. This conclusion derives from such observations as the very low nitrogen contents of rocks compared to soils and breccias (Müller, 1974; Kerridge *et al.*, 1975a), a relationship between grain-size and nitrogen content in soils that implies a surficial component (Goel and Kothari, 1972; Goel *et al.*, 1974; Holland *et al.*, 1972; Müller, 1974), a correlation between nitrogen content and solar-wind

*Also Departments of Chemistry and Geophysical Sciences.

implanted ^{36}Ar (Müller, 1974; Kerridge *et al.*, 1975b), similar correlations with such other measures of surface exposure as agglutinate content (Goel *et al.*, 1974), and the similar release patterns obtained upon heating for the nitrogen in soils and nitrogen implanted experimentally at solar-wind energies (Chang *et al.*, 1973; Bibring *et al.*, 1974). Yet, despite the evidence for essentially a single source of lunar surficial nitrogen, the isotopic ratio of this nitrogen has been shown to vary by almost 20% in bulk soils taken at a single landing site on the lunar surface (Kerridge *et al.*, 1975a), and by as much as 10% in different, thermally derived fractions from a single soil (Chang *et al.*, 1974). Such results are particularly surprising when compared to the terrestrial situation, where the entire range of geological and biological processes available yields a variation in the $^{15}\text{N}/^{14}\text{N}$ ratio of less than 10% (data summarized by Wlotzka, 1972).

In an attempt to determine whether the variation in $^{15}\text{N}/^{14}\text{N}$ ratios might perhaps be due to the presence of unrecognized nitrogen components in the soils other than solar wind, isotopic analyses were carried out on soil separates as well as on the bulk samples themselves. Analyses of nitrogen fractions obtained by step-wise heating of the separates were also done, in recognition of the bimodal release of nitrogen observed upon heating of soils (Gibson and Johnson, 1971; Gibson and Moore, 1972; and subsequent papers), and because of the large isotopic variations seen previously in the step-wise heating of a bulk soil (Chang *et al.*, 1974). We also attempted to obtain a value for the isotopic composition of indigenous lunar nitrogen from analyses of igneous rock samples. Finally, several breccias were also analyzed for their nitrogen isotope ratios.

ANALYTICAL PROCEDURES

Nitrogen is obtained by pyrolysis of the samples under vacuum. Samples are placed in a previously outgassed Al_2O_3 crucible which in turn is put into a platinum crucible. Heating is by induction, with a maximum temperature of about 1350°C attainable. Temperatures are measured with a Pt-Pt + 13%Rh thermocouple, and checked where possible with an optical pyrometer. After introduction to the vacuum system, samples are pumped on overnight under high vacuum at temperatures between 25°C and 200°C to remove adsorbed terrestrial nitrogen before pyrolysis. Sample yields and isotopic compositions and nitrogen blanks are not noticeably affected by the temperature used for this outgassing.

Samples are heated to the desired temperature over a period of 30–60 min. Above the melting point samples are held for 30–60 min. At lower temperatures, in step-wise heating experiments, they are held at each temperature step until gas evolution, as measured on a thermocouple gauge, is negligible, but, in all cases, for at least 90 min. The gases evolved at a given temperature are passed through a liquid-nitrogen trap and collected into a Toepler pump, separating CO_2 , SO_2 , H_2O , and condensible nitrogen compounds from the non-condensable gases. The non-condensable gases are passed over CuO at 850°C to oxidize CO, H_2 , and CH_4 , and the products frozen out in a liquid-nitrogen trap. Oxygen is readsorbed by cooling the CuO furnace, and N_2 and the heavier noble gases are separated from He by adsorption on molecular sieve (5A) at liquid-nitrogen temperatures. The He is collected into a calibrated volume using a second Toepler pump, and its yield measured. After discarding the He, the molecular sieve is heated to 250°C , the nitrogen collected and its yield measured. The initially condensed gases are then processed in a similar manner, to convert any nitrogen originally in a condensible form to N_2 and collect it. In all but a couple of cases, this condensible nitrogen amounted

to less than 5% of the total obtained, and, in all cases, the nitrogen from both collections was combined for isotopic analysis.

The minimum amount of gas measurable in the calibrated volume is about 3×10^{-4} cm³ STP. Blank runs on empty Al₂O₃ crucibles put into the vacuum system gave N₂ yields at the minimum detection limit. Where possible, sample sizes were chosen to yield at least 10^{-2} cm³ STP of N₂ gas, so that contamination of samples by terrestrial nitrogen is in most cases less than a few percent. Uncertainties in the absolute amounts of gases measured are $\pm 3 \times 10^{-4}$ cm³ STP, so that the yields of He and nitrogen, while dependent on sample size, should in most cases be of the order of $\pm 5\%$ of the values given.

Analyses of nitrogen isotope ratios were carried out on a VG Micromass 602C model, double-inlet, double-collecting gas mass spectrometer, using commercially obtained N₂ as a working standard. Analyses are reported in δ notation, as the per mil deviation of the ¹⁵N/¹⁴N ratio in the sample from that of atmospheric N₂, using samples of air from which O₂, CO₂, and H₂O have been removed to fix the value of our working standard relative to the atmospheric N₂ standard. All analyses are corrected for 28 tail in the 29 mass peak, valve leak and spectrometer background, although only the background correction is significant, and only for the very smallest samples. Analytical precision for the mass spectrometer under normal conditions is $\pm 0.03\%$, although most of our analyses, due to the small sample sizes used, have 2 σ errors of about $\pm 0.25\%$. In a few cases, the uncertainties are of the order of several per mil, up to a maximum of $\pm 14\%$ for 14301.

Peak heights at masses 30, 32, and 44, corresponding to NO, O₂, and CO₂, were measured in all samples. No evidence for the presence of nitrogen oxides, contamination of samples by atmosphere or the incomplete removal of gases that might give interferences at masses 28 and 29 was seen in any of the samples reported here. Peak heights for argon at masses 36, 38, and 40 were also measured, for most samples. Using air as a comparison, approximate argon contents in the N₂ samples could be determined. In most cases the argon, which arises from the samples themselves, makes up 1–2% of the nitrogen by volume, though for 14301 and 14321, argon makes up about 10% of the sample. No corrections to the nitrogen yields have been made for this argon contamination.

Argon isotope ratios can also be calculated from the relative peak heights measured, but these are subject to large mass-discrimination effects. If the ³⁶Ar/³⁸Ar ratios in bulk soils are assumed to have the solar-wind value of 5.3 (Eberhardt *et al.*, 1970), then the corrected ⁴⁰Ar/³⁶Ar ratios are found in all cases to agree with those given by other workers to within 0.1 absolute units ($\pm 10\%$ or less in relative terms).

RESULTS

Data obtained on the helium contents of bulk soils and breccias are given in Table 1. Sample weights used are shown, to allow estimation of the uncertainties in the yields. The helium contents of 14301 and 14321 are at the minimum detectable limit, and may actually be zero. No helium was detected in three samples of igneous rock which were analyzed. Reproducibility is seen to be good for all samples with the possible exception of 78501, but our results are generally low with respect to those of other workers. It is possible that helium was lost from our samples during the outgassing prior to pyrolysis, although the temperature of outgassing does not seem to affect the helium content obtained. We have no good explanation for the discrepancy between our results and those in the literature.

Nitrogen contents and isotopic compositions for all bulk samples analyzed are given in Table 2. The reproducibility for nitrogen content is good, as is that for isotopic composition, with the exceptions of samples 12063 and 14313. The latter is a low-grade breccia, and may be internally inhomogeneous. The question of the isotopic composition of sample 12063 will be considered later.

Table 1. He contents of bulk lunar soils and breccias.

Sample	Weight (g)	He content (10 ⁻² cm ³ STP/g)	
		This work	Literature
<i>Soils</i>			
15270,1	0.3452	6.17	7.07(1)
	1.0011	6.50	
	0.4353	6.06	
15600,1	0.4881	5.72	6.19(2); 7.63(3)
	0.4078	5.80	
66041,7	0.3455	3.50	4.21(4)
	0.1281	3.3	
69941,3	0.3036	3.46	4.24(4); 4.7(5)
	0.2388	3.5	
	0.1590	3.4	
75061,8	0.4943	12.7	16.2(6); 10.9(7); 16.5(8)
76501,14	0.4868	10.4	10.0(9); 13.2(6); 13(8)
	0.5197	10.2	
78501,17	0.3942	7.30	9.69(6)
	0.1669	6.4	
<i>Breccias</i>			
14301,92	0.2084	0.05	
14313,34-E	0.2726	4.33	
	0.1404	3.9	
14321,184-4	0.3070	0.03	
70019,10	0.4449	13.8	18.5(8)
	0.2812	12.9	

References: (1) Bogard and Nyquist (1973). (2) Heymann *et al.* (1972). (3) Kirsten *et al.* (1972). (4) Walton *et al.* (1973). (5) Kerridge *et al.* (1975a). (6) Hübner *et al.* (1974). (7) Hintenberger *et al.* (1974). (8) Petrowski *et al.* (1974). (9) Bogard *et al.* (1974).

Nitrogen yields for bulk soils are in good agreement with those obtained elsewhere by vacuum pyrolysis or combustion in oxygen (Petrowski *et al.*, 1974; Kerridge *et al.*, 1975b), and are generally lower than those from neutron activation determinations (Kothari and Goel, 1973; Goel *et al.*, 1974). Agreement with determinations of chemically bound nitrogen (Müller, 1972, 1974) is mixed. A peculiar case is 78501, for which there is disagreement between the bulk content found by Müller (1974) and that found by us, although, in the grain-size fraction below about 25- μ m, our value of 113 ppm N (see below) is in excellent agreement with that given by Müller. The different bulk nitrogen contents observed might have resulted from differing grain-size distributions in the samples measured in the two laboratories, possibly arising from some size sorting having occurred during either sample handling or shipment. It should be noted that our bulk soil value for nitrogen would result in sample 78501 falling on the correlation line for nitrogen content versus trapped ³⁶Ar content given by Müller (1974).

Table 2. Nitrogen contents and isotopic compositions of bulk lunar samples.

Sample	Weight (g)	This work		Literature	
		N content (ppm)	$\delta^{15}\text{N}_{\text{air}}^*$ (‰)	N content (ppm)	$\delta^{15}\text{N}_{\text{air}}$ (‰)
<i>Soils</i>					
15270,1	0.3452	90	+56.5	111(1); 95(2)	
	1.0011	87	+57.9		
	0.4353	83	+54.6		
15600,1	0.4881	52	+33.0	80(3)	
	0.4078	51	+32.9		
66041,7	0.3455	108	+27.7	105(4)	+28(4)
	0.1281	114	+28.0 ^a		
69941,3	0.3036	112	+37.5	140(2); 118(4); 84(5)	+37(4)
	0.2388	112	+36.6		
	0.1590	108	+37.7		
75061,8	0.4943	43	+33.4	49(6); 42(7)	+36.5(6)
76501,14	0.4868	72	+29.2	73(6); 63(7)	+12.0(6)
	0.5197	67	+28.3		
78501,17	0.3942	48	−6.1	73(7); 130(8)	
	0.1669	49	−4.7		
<i>Breccias</i>					
14301,92	0.2084	6.5	+32 ^b	181(1); 16,22(2) 70(6)	−8.5(6)
14313,34-E	0.2726	48	−64.5		
	0.1404	46	−52.8 ^c		
14321,184-4	0.3070	4.3	+30.4 ^d		
70019,10	0.4449	62	+21.7		
	0.2812	57	+22.1		
<i>Rocks</i>					
12063,88	2.1461	0.6	+193 ^c	<10(3)	
12063,113	2.0705	1.0	+171 ^c	<10(3)	
15495,10	0.7566	3.5	+89 ^d		

References: (1) Sakai *et al.* (1972). (2) Kothari and Goel (1973). (3) Müller (1972). (4) Kerridge *et al.* (1975b). (5) Moore and Lewis (1975). (6) Petrowski *et al.* (1974). (7) Müller (1974). (8) Goel *et al.* (1974).

*Values relative to atmospheric N₂. Uncertainties due to mass spectrometer are ±0.25‰ or less (2 σ) unless otherwise indicated.

^aUncertainty less than ±0.5‰.

^bUncertainty is ±14‰.

^cUncertainty is between ±1‰ and ±2‰.

^dUncertainty is ±5‰.

Nitrogen isotope ratios for samples 66041 and 69941 are in perfect agreement with those given by Kerridge *et al.* (1975b). Agreement for 75061 with the value of Petrowski *et al.* (1974) is also reasonable. The value given by them for 76501 may be too low due to atmospheric contamination, so the discrepancy seen for this sample in Table 2 can perhaps be overlooked. The different isotopic ratios

obtained for 70019 cannot be reconciled except by assuming significant isotopic inhomogeneities in the nitrogen contained in this sample. This is probably an acceptable assumption, as the sample is a breccia and not a soil, which in general would be expected to be fairly uniform.

Data on the nitrogen contents and isotopic compositions of grain-size separates from some soils are given in Table 3. For some grain sizes of 69941, step-wise heating rather than total pyrolysis was used, and the values given for the yields are the sums of the various temperature steps. In these cases, isotopic compositions are weighted averages of the values gotten at the individual temperatures. In the case of the 74–140- μm fraction of 69941, a separation into three portions was done using a hand magnet. Only the portions consisting of non-magnetic and very magnetic particles, each making up about 40% of the sample, were analyzed, using step-wise heating. As a result, the data given in Table 3 for this grain-size fraction, which are averages for the two analyzed portions, are much less certain than those for the other grain-size separates, and are therefore given in parentheses. It might be noted in passing that the 60% of magnetic material obtained in the separation of the 74–140- μm fraction of 69941 compares well with the 64% agglutinate content for essentially the same grain-size fraction of this sample observed by McKay and Heiken (1973).

Agreement between total pyrolysis and cumulative step-wise heating results, in cases where both were done on the same size fraction, is good. This increases

Table 3. Nitrogen contents and isotopic compositions of grain-size separates from soils.

Sample	Size fraction (μm)	Weight (g)	N content (ppm)	$\delta^{15}\text{N}_{\text{air}}$ * (‰)
15600,1	< 38	0.1562	86	+24.9 ^a
		0.1895	88	+25.4
69941,3	< 25	0.1331	211	+29.8
		0.0937	213	+30.1
		0.5706	209 ^b	+29.6 ^b
	25–44	0.1293	95	+36.3
	44–74	0.1093	83	+37.5 ^c
		0.2504	80 ^b	+37.3 ^b
	74–140	—	(67) ^d	(+43.5) ^d
	140–1000	0.9429	40 ^b	+45.7 ^b
78501,17	< 25	0.2248	107	–9.4
		0.1988	114	–7.4
		0.9056	119 ^b	–6.4 ^b

*Values relative to atmospheric N_2 . Uncertainties due to mass spectrometer are $\pm 0.25\text{‰}$ or less (2σ) unless otherwise indicated.

^aUncertainty is $\pm 1\text{‰}$.

^bFrom step-wise heating experiment. See text.

^cUncertainty is $\pm 0.6\text{‰}$.

^dIncomplete analysis of this grain-size fraction. See text.

one's confidence in using results obtained solely from step-wise heating, as for the 140–1000- μm fraction of 69941.

The results in Table 3 confirm previous observations of an increase in nitrogen content with decreasing soil grain size (Holland *et al.*, 1972; Goel *et al.*, 1974; Müller, 1974). Interestingly, the results also show a decrease in $^{15}\text{N}/^{14}\text{N}$ ratio with decreasing grain size, most obvious for 69941, but also evident for the other two samples, when the data of Table 3 are compared with the bulk soil isotope ratios in Table 2. The effect for 78501 is much smaller than for the other samples, due undoubtedly to the unusually small mean grain size of 78501 (McKay *et al.*, 1974), which results in about 80% of its total nitrogen being located in the size fraction below 25 μm . The relationship between grain size and nitrogen isotope ratio observed here is in the opposite sense to that seen for sulfur in soils (Thode and Rees, 1972; Rees and Thode, 1974), for carbon (Chang *et al.*, 1974), and claimed for nitrogen in the abstract of Chang *et al.* (1974) although they presented no data. Recently, DesMarais *et al.* (1975) reported a correlation for carbon with grain size in the same direction as ours for nitrogen. Such correlations have been suggested to result from mixing of a surface-situated component of one isotopic composition, in amounts dependent on the surface area present in the size fraction, with a second, isotopically distinct component uniformly distributed (volume-correlated) throughout the soil. This explanation may be reasonable for sulfur, for which there is a significant indigenous lunar component, but for carbon and particularly for nitrogen the contribution from rocks appears negligible, and the “volume-correlated” component, because of the way it results, is potentially variable in both amount and isotopic composition from one grain size to another (see below).

Results of step-wise heating determinations on the <25- μm fractions of 78501 and 69941 are shown in Figs. 1 and 2, respectively. The observed variation of isotopic composition with temperature is similar in both cases to that seen for bulk soil 15012 (Chang *et al.*, 1974), although the actual isotope ratios measured differ for the three soils. The three samples are characterized by a peak in the $^{15}\text{N}/^{14}\text{N}$ ratio at low temperatures, a minimum at temperatures above 800°C, and a second maximum upon melting.

This pattern implies the presence of at least three isotopically distinct components in the soils. The lower isotope ratio in the initial temperature fraction of all three soils may be due to terrestrial nitrogen adsorbed on the samples, rather than a fourth lunar component, although, in our samples, it is just this lowest temperature fraction which consists predominantly of condensible nitrogen compounds rather than N_2 .

Figure 3 shows the result of step-wise heating on the 140–1000- μm fraction of 69941. The three isotopic components are again in evidence, although relative amounts have obviously changed. The same is seen for both the magnetic and non-magnetic portions of the 74–140- μm size fraction of 69941, although they were done in fewer temperature steps for analytical reasons. Their release patterns are shown in Figs. 4 and 5, respectively.

Finally, Table 4 shows cumulative results for temperature steps up to and above 900°C, for the grain-size fractions of 69941. It includes the 44–74- μm

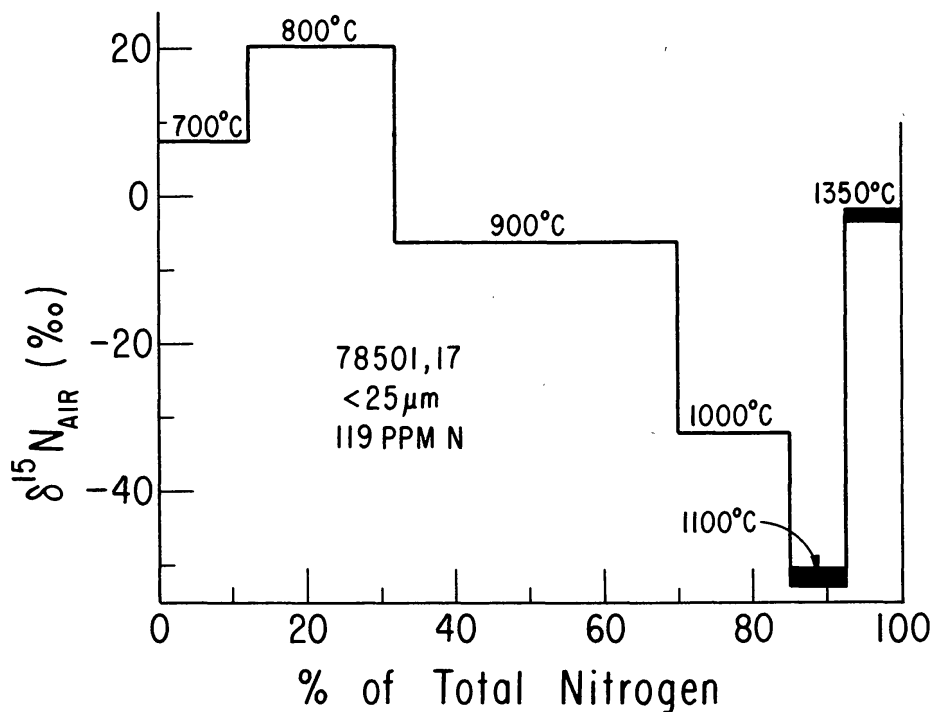


Fig. 1. Isotopic compositions of nitrogen fractions released from $<25\text{-}\mu\text{m}$ grain-size fraction of soil 78501,17 during step-wise heating, as a function of amount of nitrogen released. Total nitrogen yield is 119 ppm. Temperatures shown are approximate. Uncertainties in $\delta^{15}\text{N}$ values are indicated by the thicknesses of the horizontal lines.

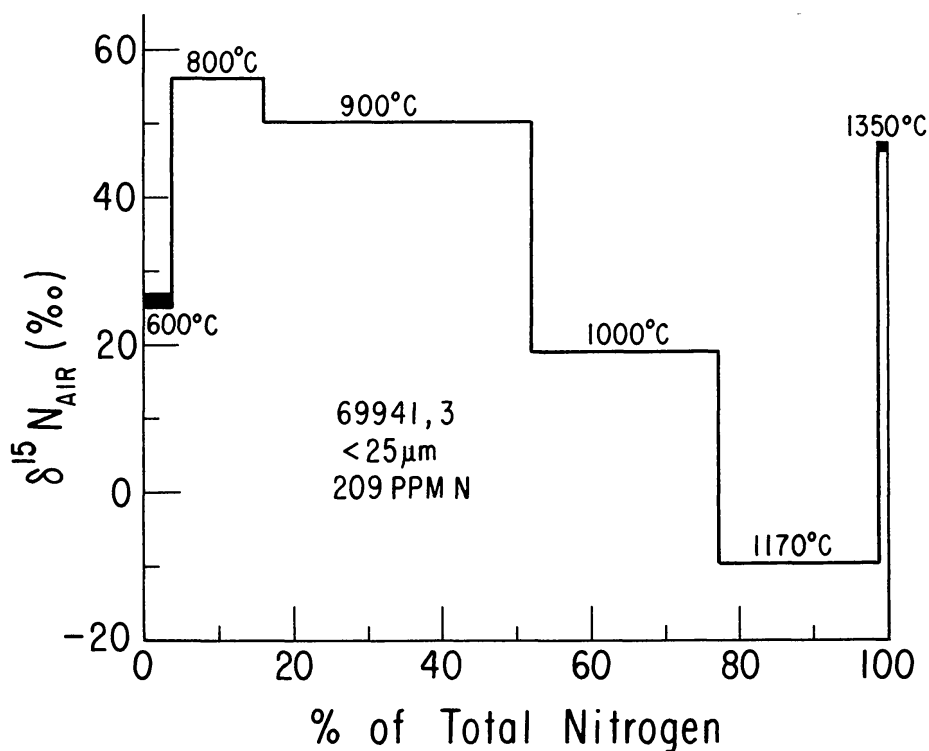


Fig. 2. Isotopic compositions of nitrogen fractions released from $<25\text{-}\mu\text{m}$ grain-size fraction of soil 69941,3 during step-wise heating. Total nitrogen yield is 209 ppm.

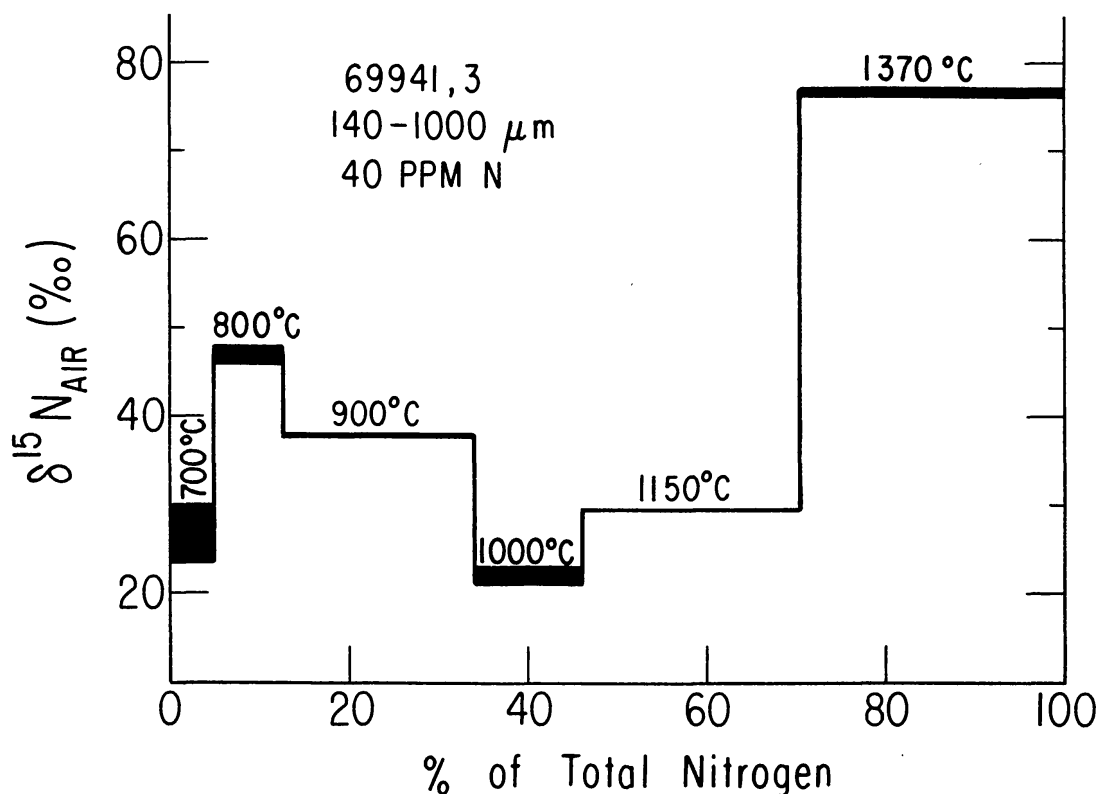


Fig. 3. Isotopic compositions of nitrogen fractions released from 140-1000- μm grain-size fraction of soil 69941,3 during step-wise heating. Total nitrogen yield is 40 ppm.

fraction, done in just two steps and thus not shown in any figure. The 74-140- μm fraction again is an incomplete analysis, as previously noted. A temperature of 900°C was used because it has been suggested as a possible, though imperfect, dividing line for surface and volume-related nitrogen components (Wszolek *et al.*, 1974). 900°C also separates the two components released in continuous-heating experiments (Gibson and Johnson, 1971) and falls between the release temperatures of two of the isotopically distinct nitrogen components observed in Figs. 1-5.

DISCUSSION

The nitrogen isotope ratios in Table 2 include the two most extreme values yet reported for lunar samples. The value of about -60‰ found for 14313, and similar extremely negative values found for soil 65500 (Kerridge *et al.*, 1975a), for the deeper levels in the Apollo 15 drill stem fines (Smith *et al.*, 1973) and for the 1100°C fraction of 78501 (Fig. 1), must represent a source of nitrogen which is itself low in ^{15}N abundance. This is so because there are no obvious ways to decrease the isotope ratio of nitrogen once it has entered the soil. On theoretical

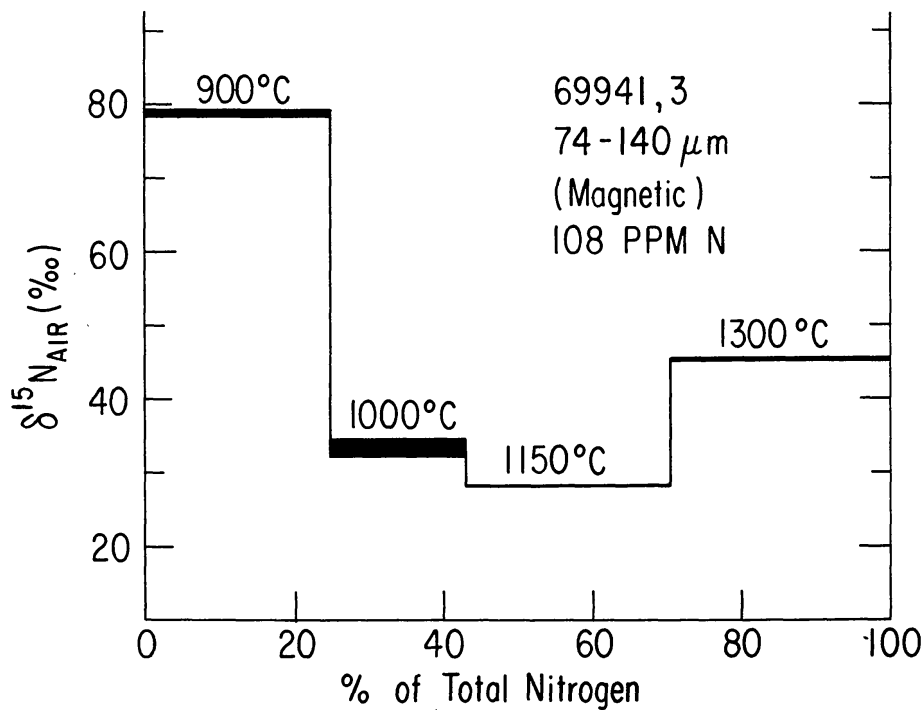


Fig. 4. Isotopic compositions of nitrogen fractions released from a magnetic separate out of the 74-140- μm grain-size fraction of soil 69941,3 during step-wise heating. Total nitrogen yield is 108 ppm.

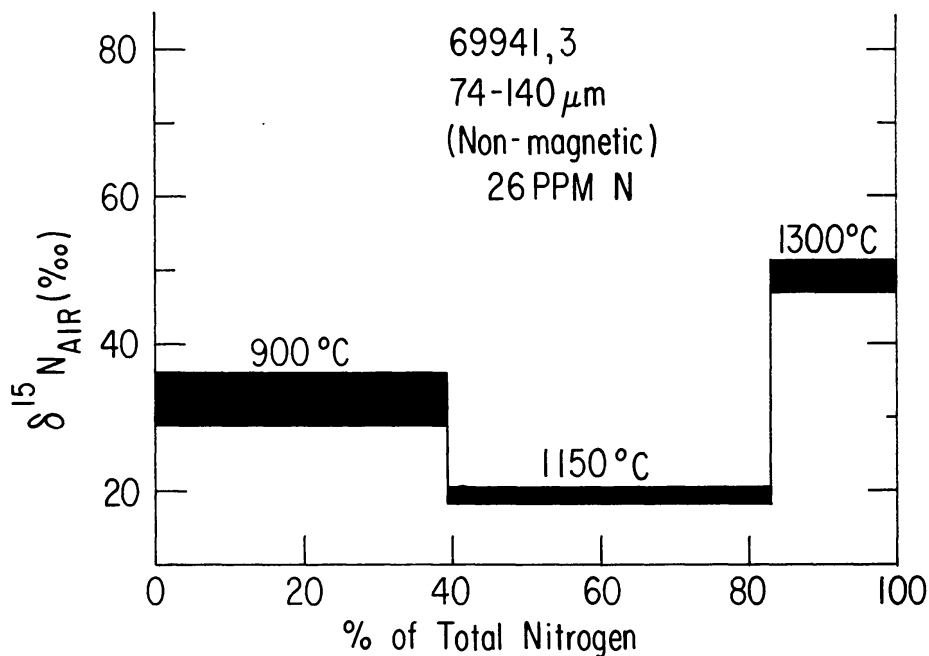


Fig. 5. Isotopic compositions of nitrogen fractions released from a non-magnetic separate out of the 74-140- μm grain-size fraction of soil 69941,3 during step-wise heating. Total nitrogen yield is 26 ppm.

Table 4. Amount and isotopic composition of nitrogen released above and below 900°C from grain-size separates of soil 69941.

Grain size (μm)	Below 900°C		Above 900°C	
	ppm N	$\delta^{15}\text{N}_{\text{air}}^*$	ppm N	$\delta^{15}\text{N}_{\text{air}}^*$
< 25	109	+ 50.2	100	+ 7.1
44–74	27	+ 40.7	54	+ 35.7
74–140 ^a	(18)	(+ 66.3)	(48)	(+ 34.8)
(magnetic)	27	+ 79.0	81	+ 36.2
(non-magnetic)	10	+ 32.6	16	+ 27.8
140–1000	14	+ 38.4	27	+ 49.5

*Values relative to atmospheric N_2 .^aIncomplete analysis. See text.

grounds, partial removal of the light elements by vaporization or as the result of diffusion is expected to be mass dependent, with preferential loss of lighter isotopes. The observed variations of light-element isotope ratios in lunar soils seem to confirm the fact that such fractionation processes as vaporization and transport or hydrogen stripping, with subsequent incorporation of residues enriched in heavier isotopes onto or into the soil grains (Clayton *et al.*, 1974; Kerridge *et al.*, 1974), are operating. In addition, production of nitrogen in lunar soils by cosmic-ray spallation reactions would also act to increase the $^{15}\text{N}/^{14}\text{N}$ ratios (see below). Thus, there must be one component in lunar soils whose source has a $\delta^{15}\text{N}$ value at least as low as -60% . As will be discussed later, this component is also very old.

The second extreme nitrogen isotope ratio is found in the igneous rock 12063. One might expect the nitrogen contained in igneous rocks to be the most representative example of any indigenous lunar-nitrogen component. However, the facts that rock 15495 differs by 100% from 12063, even though it might be expected that early large-scale differentiation would have homogenized lunar nitrogen, and that the +190% measured in 12063 lies far outside the range reported for other extraterrestrial bodies (Injerd and Kaplan, 1974) or the earth, suggests that spallation production of nitrogen must be taken into account.

That production by spallation occurs at a measurable rate for such isotopes as ^{21}Ne in lunar surface samples is well known, as it provides the basis for surface-exposure age determinations. Oxygen, the principal target element for nitrogen production, is several times more abundant than any other element in lunar samples, so that production of nitrogen should be greater than that for ^{21}Ne . From Fig. 2 of Armstrong and Alsmiller (1971), production rates of both nitrogen isotopes are estimated to be about ten times that of ^{21}Ne . Using measured spallation neon contents and exposure ages for two Apollo 11 rocks (Eberhardt *et al.*, 1974) with elemental compositions similar to that used in the calculation of Armstrong and Alsmiller (1971), approximate production rates per 10^6 yr for each

isotope of 7×10^{-6} - $\mu\text{g N/g}$ sample are obtained. These rates are relatively insensitive to chemistry, because oxygen contents of lunar samples are fairly constant.

It is clear that the amount of total nitrogen that can be produced during the lunar lifetime is negligible, even when compared to the small amounts in rocks. However, since the $^{15}\text{N}/^{14}\text{N}$ ratio in ordinary nitrogen is about 3.7×10^{-3} , it is also clear that, for long exposure ages and for low nitrogen contents, the amount of spallation ^{15}N produced is comparable to the ^{15}N present in the samples. Increases of up to a few hundred per mil could be expected under optimum conditions, as in rock samples with long surface exposures. It should be noted that the statements above in no way conflict with the observation of Kerridge (1975) that the $\delta^{15}\text{N}$ values of Apollo 16 soils decrease with increasing ^{21}Ne exposure ages, an effect that is apparent for Apollo 17 soils (Fig. 6) as well. Since soils have 50–100 times the nitrogen contents of rocks, spallation will only cause $\delta^{15}\text{N}$ increases of a couple of per mil, which will be overwhelmed by other effects.

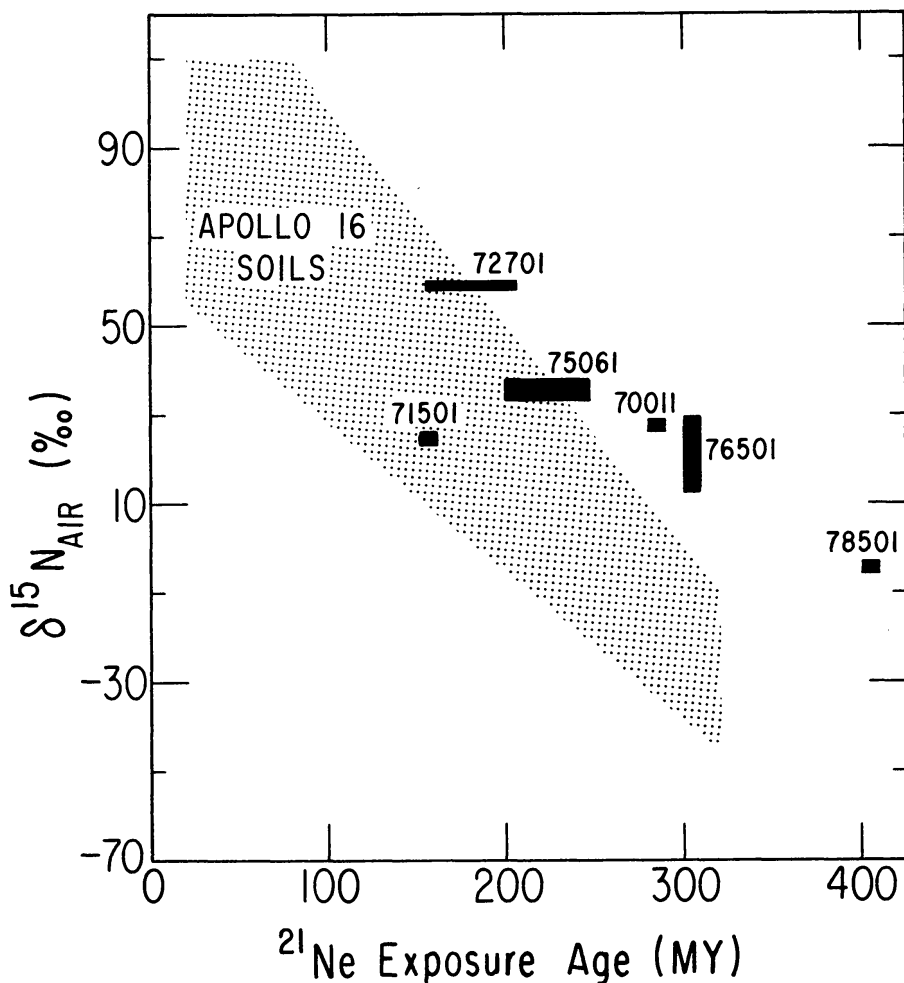


Fig. 6. Nitrogen isotope ratios and ^{21}Ne exposure ages for Apollo 16 and 17 bulk soil samples. Apollo 16 data from Kerridge (1975). Apollo 17 nitrogen data from Petrowski *et al.* (1974) and this work; Apollo 17 exposure ages from Hübner *et al.* (1974) and Hintenberger *et al.* (1974).

The increase in $\delta^{15}\text{N}$ due to spallation depends directly on exposure age and inversely on nitrogen content. The much lower $\delta^{15}\text{N}$ value of 15495 compared to 12063 thus results from the difference in nitrogen contents of the samples, although differing exposure ages may also play a part. The exposure age of 12063 is 95 ± 5 m.y. (Marti and Lugmair, 1971), that of 15495 has not been determined. Without knowing the $^{15}\text{N}/^{14}\text{N}$ ratio of indigenous lunar nitrogen, it is not possible to say what the relative exposure ages of the samples are on the basis of nitrogen isotope ratios. Determinations on igneous rocks of very low cosmic-ray exposure ages, or with high nitrogen contents, are required to determine the indigenous nitrogen isotope ratio, and are planned.

The difference in $\delta^{15}\text{N}$ of the two samples of 12063 is rather large, although in the direction expected when it is considered that a higher yield for 12063,113 would imply a greater dilution of spallation nitrogen by other nitrogen components, of either indigenous lunar or terrestrial contaminant origin. Due to the small samples of N_2 obtained in these two analyses, both the uncertainties in the yield and the possible contributions from terrestrial contamination are large in a relative sense. We believe that the yields for the two samples are the same within the uncertainty, and that the lower isotope ratio of 12063,113 results from a slightly larger contribution of terrestrial contamination in this sample.

The presence of spallation ^{15}N provides an explanation for the isotopically heavy nitrogen component released upon melting in the step-wise heating experiments. Formed essentially uniformly throughout all grains, spallation nitrogen is a true volume-correlated component, and might be expected to show a greater effective retentivity than nitrogen implanted in surfaces or otherwise taken up during soil maturation. It will thus be relatively concentrated in the highest temperature fractions, particularly the fraction released on melting. As the soils analyzed here have cosmic-ray exposure ages of about 100–400 m.y., the spallation ^{15}N produced, if concentrated into temperature fractions containing only a few ppm nitrogen, would be expected to have noticeable effects on $\delta^{15}\text{N}$.

A volume-correlated spallation component would account, at least qualitatively, for the grain size versus $\delta^{15}\text{N}$ effect illustrated in Table 3, and could also cause the trend in the $>900^\circ\text{C}$ data of Table 4, although we believe the situation in the soils is actually quite complicated, and requires some further discussion.

Models describing the build-up of carbon, and by analogy nitrogen, in soils are discussed by DesMarais *et al.* (1973) and Kerridge *et al.* (1974). They involve implantation of the element into the outer surfaces of grains by solar-wind bombardment, yielding a component varying directly in concentration with the surface area of the grain size considered, followed by incorporation of some of this component into a "volume-correlated" component during formation of glassy agglutinates. Element concentrations in grain surfaces are limited by saturation or through a balance between implantation and loss of the surface by erosion. Total concentrations may presumably increase indefinitely as agglutinates are formed, broken down and reformed.

Experiments on artificial implantation of nitrogen (Chang *et al.*, 1973) suggest that solar-wind implanted nitrogen which has not been modified by lunar regolith

processes such as agglutinate formation will be released almost completely below 950°C in heating experiments. It thus seems reasonable to associate the nitrogen released up to 900°C (Table 4) with the surface-correlated component mentioned above, and the nitrogen released above 900°C then corresponds to the volume-correlated component. Indeed, results of Wszolek *et al.* (1974) and this work on magnetic (agglutinate-rich) and non-magnetic (agglutinate-poor) separates from individual grain-size fractions show that the nitrogen released above 900°C is strongly concentrated in agglutinate particles. Finally, the data presented in Figs. 1–5 require that nitrogen released in temperature fractions above and below 900°C be distinct components, as these temperature fractions have differing isotopic compositions.

One consequence of this interpretation is that, from the yields given in Table 4, both the surface-situated and the internally-situated nitrogen decrease in abundance with increasing grain size. If the carbon situation is analogous, then the assumption of a volume-correlated component independent of grain size, used in the carbon-accumulation models cited above, is invalid. This will influence the concentrations calculated for the grain surfaces from grain-size data (DesMarais *et al.*, 1973), among other things.

The observed variation of higher-temperature nitrogen yields with grain size may be due to a corresponding variation in agglutinate content, to higher concentrations of nitrogen within smaller agglutinate particles than in larger ones, or to a combination of the two. Our yield data do not allow us to distinguish among these possibilities. The trend in nitrogen yields at temperatures up to 900°C (Table 4) goes approximately as expected for a surface-correlated component, with the difference between magnetic and non-magnetic particles of nominally the same grain size arising from the highly irregular shapes of agglutinate particles, resulting in greater surface areas for these particles compared to non-agglutinate particles.

The isotopic data in Table 4 may be considered in light of the following. As noted above, nitrogen released above 900°C presumably was originally surface-implanted nitrogen which became fixed in more retentive sites as a result of agglutinate formation. It thus represents, on the average, an earlier generation of nitrogen than that now at the surfaces of grains. As was also pointed out earlier, fractionation effects during agglutinate formation as well as spallation production of ^{15}N will only serve to increase the $\delta^{15}\text{N}$ value of the higher-temperature nitrogen component. Therefore, the observation that high-temperature nitrogen is isotopically lighter than low-temperature nitrogen in the finer grain sizes of soils implies that earlier generations of surface-implanted nitrogen were lower in ^{15}N than more recently implanted nitrogen. This is consistent with the available data on other low- $\delta^{15}\text{N}$ samples. For example, breccia 14313, with the lowest $\delta^{15}\text{N}$ found, appears related to breccias 14301 and 14318 on the basis of the presence of parentless Xe from decay of extinct nuclides (Behrmann *et al.*, 1973; Reynolds *et al.*, 1974), although the case for 14313 may still be in doubt (Reynolds *et al.*, 1974). Also, Warner (1972) has suggested that the Apollo 14 breccias all formed during the Imbrium impact, although Floran *et al.* (1972) prefer a later lithification in the

case of 14313. The formation of 14318 is dated at 3.7×10^9 yr ago (Reynolds *et al.*, 1974). Its affinities with 14318 may imply a similar age for 14313. Lead isotope data (Church and Tilton, 1975) suggest that agglutinate formation in 78501, which has a very low- $\delta^{15}\text{N}$ value in its high-temperature component (Fig. 1), may have occurred a relatively long time ago. The Apollo 15 drill stem fines were last exposed to solar wind 450 m.y. ago or earlier (Pepin *et al.*, 1974). The evidence strongly implies an increase in $\delta^{15}\text{N}$ values for surficially implanted nitrogen with time, from values below -60% possibly as long ago as 3.7×10^9 yr to values of perhaps $+100\%$ today, based on the Apollo 16 soil data of Kerridge *et al.* (1975a).

The $\delta^{15}\text{N}$ values for nitrogen fractions obtained below 900°C from separates of 69941 (Table 4) are higher for agglutinates than for non-agglutinates, and, excepting the $74\text{--}140\text{-}\mu\text{m}$ size fraction, are higher for fine than for coarse particles. For agglutinates, if it is assumed that their formation involves either outgassing of old surfaces or production of new ones by glass splashing, their surface nitrogen might be expected to represent on the average a more recently implanted nitrogen than for non-agglutinates. This is so because nitrogen at agglutinate surfaces would date from the time of formation of the agglutinates, whereas that at the surfaces of non-agglutinates would contain earlier nitrogen as well. If high-diffusion rates in the amorphous coatings of soil grains, suggested by Maurette and Price (1975), allow the surfaces to act as well-mixed layers, then removal of old nitrogen by sputtering of non-agglutinate grain surfaces should proceed more slowly than the build-up of surface concentration to equilibrium values in newly formed surfaces. The difference seen in $\delta^{15}\text{N}$ for magnetic and non-magnetic grains in 69941 would then be consistent with the secular change in the $^{15}\text{N}/^{14}\text{N}$ ratio of implanted nitrogen.

The grain-size variation of $\delta^{15}\text{N}$ for the nitrogen released below 900°C might then reflect a variation in the ratio of agglutinates to non-agglutinates with grain size. Petrological data so far available on Apollo 16 soils, not including 69941 however, do not show the increase in agglutinate percentage with decreasing grain size which is required (Butler *et al.*, 1973), although grain sizes below about $30\text{ }\mu\text{m}$ were not included. It may in any case be true that, for small grain sizes, the breakdown products of agglutinates might not be recognized petrologically as such.

The isotopic variation for the higher-temperature nitrogen fraction is partially explainable by an increasing effect of spallation ^{15}N for large grains, but probably also results from the secular change in the isotope ratio of implanted nitrogen. As heavier nitrogen is added to interior sites during agglutinate formation, it would be expected to show up first in larger grains, and then as these get broken up, the new nitrogen is added to the higher-temperature fraction of the finer grains. As a result, the finer grains in a soil contain a greater portion of early relative to late nitrogen in retentive sites than do the coarser grains, and their high-temperature nitrogen is isotopically lighter.

This secular change in the isotopic composition of implanted nitrogen has been proposed on the basis of somewhat different considerations by Kerridge (1975). He proposed spallation reactions on the sun resulting in a changing solar-wind

isotopic ratio as the cause. We would like to suggest, in the absence of any data at the moment on indigenous lunar nitrogen, a possible alternative explanation. The presence of so-called parentless ^{40}Ar in lunar soils has been attributed to outgassing of radiogenic ^{40}Ar , in amounts which decrease with time, from the lunar interior, followed by solar-wind ionization and acceleration into the lunar surface (Yaniv and Heymann, 1972). An indigenous lunar-nitrogen component, present initially in the moon at a level of 1–2 ppm and with a $\delta^{15}\text{N}$ value below -60% , could have accompanied this ^{40}Ar and have been implanted in the same manner in the primitive lunar regolith, in decreasing amounts as time progressed (nitrogen outgassing would presumably decrease at a faster rate than that for ^{40}Ar , as it would not be replenished by radioactive decay). The secular trend in $^{15}\text{N}/^{14}\text{N}$ ratios for implanted nitrogen would then be the consequence of a constant solar-wind isotope ratio and a decreasing contribution of lunar nitrogen with time. A lunar interior source for nitrogen, and presumably other volatiles as well, would perhaps negate the need for much higher solar-wind fluxes in the past to account for the quantities of these elements in the lunar regolith (Geiss, 1974). Possible supporting evidence for our suggestion comes from the relatively high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios for trapped argon of 2.7 for 14313 (Alexander and Kahl, 1974) and 2.5 for 65501 (Bogard and Nyquist, 1973), the two samples with the lowest total-nitrogen $\delta^{15}\text{N}$ values. (Breccia 14301, also reported to have a high $^{40}\text{Ar}/^{36}\text{Ar}$ ratio, has a low-nitrogen content, and may have been affected by spallation ^{15}N .) Arguing against our suggestion, however, is the fact that no other solar-system bodies have been found to have indigenous nitrogen with such a low $^{15}\text{N}/^{14}\text{N}$ ratio, and this makes it important for us to determine the isotopic ratio for lunar nitrogen.

A consequence of the observation that the isotope ratio of implanted nitrogen varies with time is that the bulk $\delta^{15}\text{N}$ values of soils are not related to their maturities, as has been argued for carbon (Kerridge *et al.*, 1974), but rather to the time in the past at which they were exposed on the surface. The relationship is presumably a complex one, involving both the amount of time spent by soil particles on the surface and when the exposure occurred. The data in Fig. 6, for example, show that soils at the Apollo 16 site tend to contain more old nitrogen than soils at the Apollo 17 site, for apparently equal lengths of time spent in the upper few meters of the regolith. This could result from the regolith at the Apollo 16 site simply being older than that at Apollo 17, and thus having started with lower isotope ratios, or it could be the result of a difference in cycling rates at the two sites, so that soil grains at the Apollo 17 site spend more time at the surface or come there more often than do grains at the Apollo 16 site. Comparisons with other sites would be useful, in attempting to understand the relationships shown in Fig. 6.

CONCLUSIONS

Several lines of evidence point to the conclusion that the isotope ratio of the nitrogen being implanted into the lunar regolith has increased by some 15% over a period of at least 4.5×10^8 yr and possibly as long as 3.7×10^9 yr or more. This may

be the result of changes in the nitrogen isotope ratio of the solar wind with time, or it may be due to outgassing and subsequent reimplantation of an isotopically light indigenous lunar nitrogen from the lunar interior in the early history of the moon. Attempts to show the presence of such an indigenous lunar component in lunar igneous rocks are hampered by the presence of significant amounts of spallation-produced ^{15}N in these rock samples.

The lunar soils contain at least three isotopically distinct components of nitrogen, when analyzed by step-wise heating methods. These are the indigenous plus spallation-produced component and two different generations of implanted nitrogen, a recent one located at grain surfaces and a second, earlier one located within agglutinate particles. The bulk isotopic composition of a soil is determined by the relative amounts and the isotopic compositions of these components, which are in turn dependent on the history of the particular soil at and near the lunar surface. The bulk nitrogen content of a soil is determined essentially by the amounts of the latter two components, both of which may vary with the grain size of the soil.

Acknowledgment—This research was supported by NASA grant NGL-14-001-169.

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