

the COOH-terminal region are missing in the proteins that are smaller than the largest cell-free product (peak A). This can arise from initiation of mRNA translation at one point followed by premature termination of translation at several discrete points. Premature termination resulting in the synthesis of discrete protein bands was observed in the cell-free translation of encephalomyocarditis virus mRNA (12). The above reasoning may explain the peptide map of the tryptic digest of the cell-free products, which contained 27 of 28 L-chain peptides plus 4 additional peptides (1). The additional peptides might come from the extra piece as well as from new tryptic peptides generated at the COOH-terminus as a result of incomplete synthesis of the L chain. The apparent loss of one peptide is probably due to a modified NH₂-terminus in the precursor (13).

The synthesis of hemoglobin (14), and perhaps that of immunoglobulin L chain (10), is initiated by a specific methionyl-tRNA. The finding that all L-chain cell-free products share an identical NH₂-terminal sequence (Fig. 1) provides further evidence that in eukaryotes, as in prokaryotes (15), there is one major point for the initiation of mRNA translation.

Although the sequence of the extra piece is incomplete, the fact that 30 percent of it is composed of leucine residues indicates that it would be quite hydrophobic. Indeed experiments on the sequence of M-321 and M-41 precursors labeled with six ³H-labeled amino acids show that in both cases at least 60 percent of the extra piece is composed of hydrophobic amino acids. The marked hydrophobicity suggests that the role of the extra piece is to favor interaction of the precursor with the endoplasmic membranes or the cell wall (or both). Furthermore, the NH₂-terminal extra piece in the M-321 and M-41 L-chain precursors differs both in size and in amino acid sequence (16).

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Solar Nitrogen: Evidence for a Secular Increase in the Ratio of Nitrogen-15 to Nitrogen-14

Abstract. *Solar wind nitrogen, implanted in lunar soil samples, exhibits isotopic variations that are related to the time, although not to the duration, of implantation, with earlier samples characterized by lower ratios of nitrogen-15 to nitrogen-14. An increase in the solar nitrogen-15 content during the lifetime of the lunar regolith is probably caused by spallation of oxygen-16 in the surface regions of the sun.*

Interaction between the solar wind and the moon leads to the implantation of solar wind species in the surfaces of lunar grains (1, 2). This effect is revealed by the presence within lunar soils of such elements as carbon, nitrogen, hydrogen, and the noble gases, which are effectively absent from lunar rocks. Although virtually all lunar soils are enriched in these elements, there is considerable intersample variation in the elemental abundance ratios and isotopic compositions. These variations have generally been associated with lunar fractionation mechanisms (3). No evidence has been found for any change in the composition of the solar wind over the lifetime of the lunar regolith, although short-term variations in the ratio of hydrogen to helium have been observed and related to solar flare activity (4).

Elemental and isotopic fractionations on the lunar surface reflect primarily the preferential loss of light species as a result of mass-dependent mechanisms such as thermally activated diffusion (1, 3, 5). Thus, the hydrogen content of lunar soils is depleted below the solar proportion relative to helium (5), and similar effects have been observed for other solar wind elements. Figure 1a shows the relationship between car-

bon and nitrogen abundances for soils from the Apollo 16 landing site (6). The strong correlation suggests a common origin for both elements, and the slope of the line for the Apollo 16 soils differs from that representative of the solar abundances, yielding a value for the ratio of carbon to nitrogen (atomic) of 1.5 ± 0.1 , as compared with the solar value of 3.2 (7). Similar relationships exist between the nitrogen abundance and the abundance of hydrogen or of those noble gas isotopes of solar rather than spallogenic origin, and all show depletion relative to nitrogen in comparison with solar abundances, thus suggesting that nitrogen is the most efficiently retained solar wind element. This efficiency may approach 100 percent as a result of the reactivity of atomic nitrogen and the stability of bonds formed between nitrogen and the prevalent lunar cations (8). Calculations based upon the solar wind flux and nitrogen abundances in regolith of known thickness are consistent with 100 percent efficiency (9).

Nitrogen is clearly retained more efficiently than carbon and should therefore show a smaller range of isotopic fractionation than carbon if such fractionations are caused by loss from the lunar surface. Actually the ob-

served range in $\delta^{15}\text{N}$ is from -50 to $+100$ per mil, whereas the corresponding range in $\delta^{13}\text{C}$ is only from -17 to $+20$ per mil (10). In addition, despite the strong correlation between carbon and nitrogen abundances, a plot of $\delta^{13}\text{C}$ as a function of $\delta^{15}\text{N}$ (Fig. 1b) shows no significant trend, a result which suggests that different mechanisms were responsible for isotopic fractionation in the two cases. Kerridge *et al.* have shown (11) that the accumulation of carbon in the lunar regolith is accompanied by enrichment in ^{13}C as a result of the diffusive loss of CH_4 produced by reaction between solar wind hydrogen and implanted carbon. Although a similar process might have been anticipated for the fractionation of nitrogen via the formation of NH_3 , Fig. 1b indicates that this has not occurred. In fact, if $\delta^{15}\text{N}$ is plotted against a measure of soil maturity, such as agglutinate content (12) (Fig. 1c), a weak negative correlation is observed, unlike the positive correlation found for the corresponding $\delta^{13}\text{C}$ plot.

If, however, $\delta^{15}\text{N}$ is plotted against cosmic-ray exposure age calculated from the spallogenic ^{21}Ne content (13), a strong negative correlation is observed (Fig. 1d). The ^{21}Ne age is a measure of the time that a sample has spent within ~ 2 m of the lunar surface (14). For ejecta from a recent cratering event this age corresponds to the age of the crater, but for older samples it is the average of many events spread over a period which may be as long as the age of the regolith, that is, about 4×10^9 years. Although often referred to as a surface exposure age, the ^{21}Ne age is related to solar wind exposure only in a statistical sense, in that the longer a lunar grain spends within ~ 2 m of the surface, the greater its probability of exposure to the solar wind. Because the ^{21}Ne age is a measure, not of the duration of surface residence but of the time when, on the average, that residence occurred, I conclude that the earlier the date of implantation of a nitrogen sample, the lower is its $^{15}\text{N}/^{14}\text{N}$ ratio (15). Does this reflect a lunar fractionation acting in the sense of relatively enriching the light isotope, or does it signify a secular increase in the solar $^{15}\text{N}/^{14}\text{N}$ ratio?

The former explanation is unlikely because the weakness of the correlation with surface exposure (Fig. 1c) and the accompanying trend toward the lighter nitrogen isotope argue against a diffusive loss mechanism. Although oxidation of NH_4^+ to molecular N_2

selects ^{15}N preferentially, thus enriching the residue in ^{14}N (16), such a reaction is improbable in the reducing and nitrogen-deficient environment of the moon. The only other known mechanism for modifying the ^{15}N content of implanted nitrogen is spallation of ^{16}O by cosmic rays, which would act in the direction of increasing ^{15}N with time, contrary to Fig. 1d.

I conclude that the $^{15}\text{N}/^{14}\text{N}$ ratio of the solar wind, and hence of the solar photosphere (4), has increased during the time interval represented by the spread in ^{21}Ne ages. Because the ^{21}Ne age of an old, reworked sample does not date a unique event, it is difficult

to place a lunar ^{21}Ne date on a solar time scale. In fact, both $\delta^{15}\text{N}$ and the ^{21}Ne content of a sample represent averages derived from lunar grains with differing values of these quantities. Whether these averages correspond to the same moment in solar system history cannot be decided without further information on secular variations in cosmic-ray intensity, solar wind flux, and turnover rates of grains in the regolith. One may assign tentative limits to the actual ages of the oldest samples in Fig. 1d by taking the apparent ^{21}Ne age, 300×10^6 years, as a reasonable minimum and a value of about 800×10^6 years as a maximum (17). Thus,

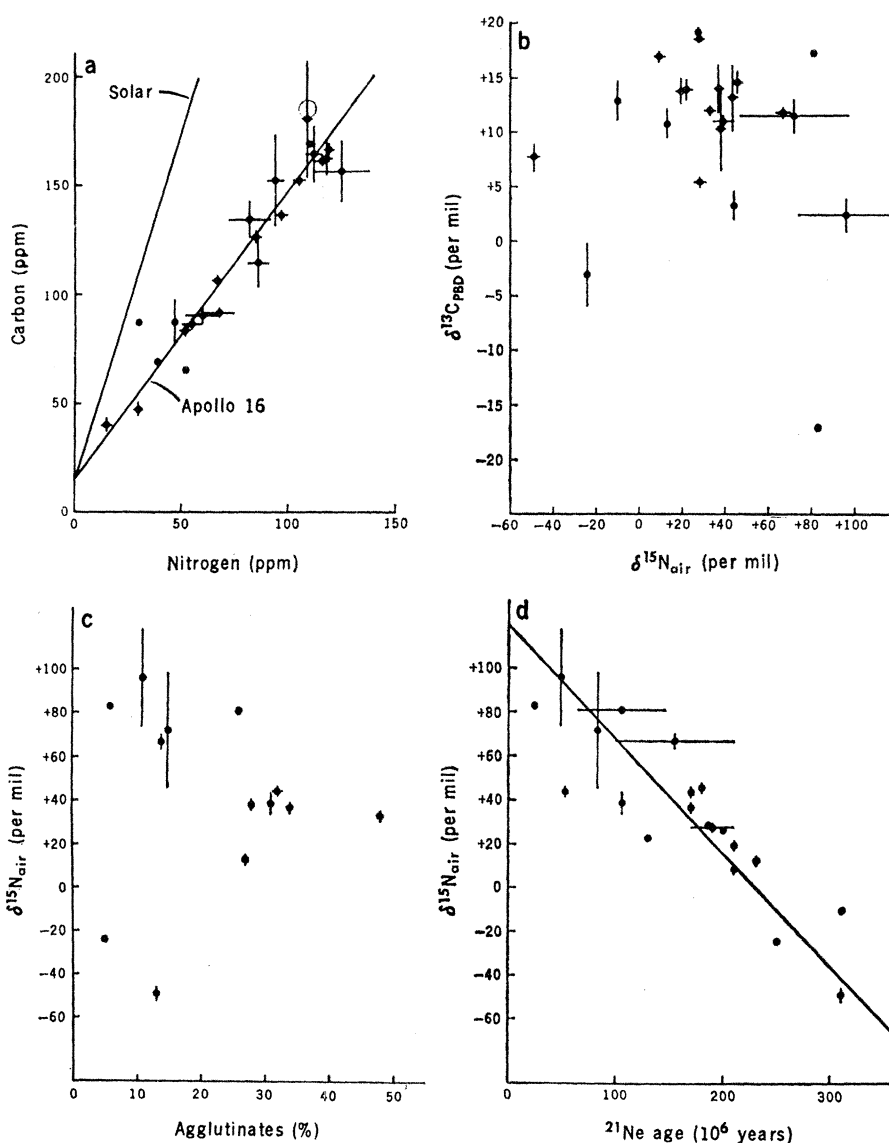


Fig. 1. (a) Carbon and nitrogen abundances correlate strongly for Apollo 16 soil samples, with an average carbon/nitrogen ratio significantly below the solar value. (b) Carbon and nitrogen isotopic data for Apollo 16 soil samples show no systematic trend. (c) The $\delta^{15}\text{N}$ values for Apollo 16 soil samples exhibit a weak negative correlation with agglutinate contents. (d) The $\delta^{15}\text{N}$ values for Apollo 16 soil samples show a strong negative correlation with cosmic-ray exposure age. The ^{21}Ne ages are taken from (13). Uncertainty limits on the ^{21}Ne ages represent analyses from different laboratories. All other uncertainty estimates are based upon replicate analyses where available.

the solar abundance of ^{15}N has increased by about 15 percent in the time period between 300×10^6 and 800×10^6 years. The possibility that the change is due to a relative loss of ^{14}N by some mass-dependent process, such as preferential acceleration of light ions into the solar wind, may be discounted for two reasons. First, an excessive amount of nitrogen would have to be processed in order to achieve such a large fractionation. Second, such a process would produce a 20 percent larger increase in $^{13}\text{C}/^{12}\text{C}$ than in $^{15}\text{N}/^{14}\text{N}$, a result that is not observed, and would generate a sevenfold larger increase in $^4\text{He}/^3\text{He}$, whereas Geiss (4) has shown that this ratio has actually decreased with time.

One mechanism for the production of ^{15}N in the sun is spallation of ^{16}O by high-energy events near the solar surface. However, calculations by Fowler (18) suggest that the present level of solar flare activity fails by a factor of at least 40 to account for the magnitude of the effect observed. In the absence of any other mechanism for the production of ^{15}N , a discrepancy therefore exists between theory and observation. A potential means of testing the interpretation given above lies in the accurate determination of the solar abundance of boron which should have been produced by spallation of ^{12}C in about the same proportion as nitrogen from ^{16}O . This would lead to a present-day solar abundance of boron equal to 1500 (normalized to a silicon abundance of 10^6) as distinct from the primordial value of 350 derived from meteorite data (7).

Spallation of ^{16}O may also have added to the solar ^{13}C reservoir; however, this effect would be much smaller than that for nitrogen and would be masked in lunar samples by the higher initial abundance of ^{13}C relative to ^{15}N and the pronounced lunar fractionation of carbon. In addition, it is possible that spallation has increased the solar proportion of ^{21}Ne during the age of the regolith, which would have the effect of increasing the actual ages shown in Fig. 1d (19).

Nitrogen-15 is burned before ^{14}N in the solar interior. The observation that the abundance of ^{15}N has increased with time in the surface of the sun shows that convective mixing involving the deep interior of the sun has been insignificant and this is in agreement with the conclusion of Bochsler and Geiss (20).

Finally, the apparent lack of lunar

fractionation in nitrogen is consistent with highly efficient retention of this element on the lunar surface. It is known from vacuum pyrolysis experiments (21) that carbon and nitrogen are volatilized over the same temperature range (800° to 1200°C); thus the efficient retention of nitrogen indicates that the bulk of the carbon lost from the moon is not volatilized at high temperatures but is lost by diffusion as CH_4 at relatively low temperatures, as Kerridge *et al.* have proposed (11).

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6. The abundances of carbon and nitrogen were obtained either by combustion in O_2 or by vacuum pyrolysis at 1220°C with subsequent combustion, and separation and measurement of the evolved gases. Carbon and nitrogen fractions, as CO_2 and N_2 , respectively, were collected and analyzed mass spectrometrically against Pee Dee belemnite (PDB) (CO_2) and air (N_2) standards (10, 21).
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9. The regolith at North Ray Crater close to the Apollo 16 landing site is "a few centimeters" thick [Apollo 16 Preliminary Science Report, *NASA SP-315* (1972)]. If we take 10 cm as the thickness of this regolith and assume that it has been thoroughly stirred since deposition 50×10^6 years ago [K. Marti, B. D. Lightner, T. W. Osborn, in *Proceedings of the Fourth Lunar Science Conference*, W. A. Gose, Ed. (Pergamon, New York, 1974), vol. 2, pp. 2037-2048], a solar nitrogen/hydrogen ratio of 1.2×10^{-4} (7), a solar wind flux of 2×10^8 hydrogen atoms per square centimeter per second (4), and a specific density for lunar soil of 2 g cm^{-3} [W. D. Carrier, J. K. Mitchell, A. Mahmood, in *Proceedings of the Fourth Lunar Science Conference*, W. A. Gose, Ed. (Pergamon, New York, 1974), vol. 3, pp. 2403-2411] lead to a predicted nitrogen content of 43 parts per million (ppm), compared to an actual value of 47 ppm found for a typical North Ray soil, sample 67701 (10).
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12. Agglutinates consist of soil particles that have been welded together by glass apparently produced by micrometeorite impact. The agglutinate content of a sample is therefore governed by its exposure to the micrometeorite flux and correlates well with other measures of surface exposure [D. S. McKay, G. H. Heiken, R. M. Taylor, U. S. Clanton, D. A. Morrison, G. H. Ladle, in *Proceedings of the Third Lunar Science Conference*, E. A. King, Jr., Ed. (MIT Press, Cambridge, Mass., 1972), vol. 1, pp. 983-994].
13. The ^{21}Ne data are from the following sources: D. D. Bogard, L. E. Nyquist, W. C. Hirsch, D. R. Moore, in *Lunar Science IV* (Lunar Science Institute, Houston, 1973), pp. 79-81; H. Hintenberger and H. W. Weber, in *Proceedings of the Fourth Lunar Science Conference*, W. A. Gose, Ed. (Pergamon, New York, 1974), vol. 2, pp. 2003-2019; T. Kirsten, P. Horn, J. Kilo, in *ibid.*, pp. 1757-1784; J. R. Walton, S. Lakatos, D. Heymann, in *ibid.*, pp. 2079-2095. Using the procedure of Walton *et al.*, I calculated the ages in cases where this group of investigators had not already carried out such calculations.
14. Calculations of ages from the ^{21}Ne content involves correction for implanted solar wind ^{21}Ne and computation of the ^{21}Ne production rate for each sample on the basis of its bulk chemical composition. Because of possible uncertainties both in the empirical constants employed in the production rate calculations and in the analytical data used, it is preferable to consider only data from a single, reasonably homogeneous landing site, and Kerridge *et al.* have argued (10) that the Apollo 16 site satisfies this condition.
15. Although the data are scanty, the $\delta^{15}\text{N}$ values in the Apollo 15 drill stem show a tendency to decrease with increasing depth, a finding that is consistent with this conclusion [J. W. Smith, I. R. Kaplan, C. Petrowski, in *Proceedings of the Fourth Lunar Science Conference*, W. A. Gose, Ed. (Pergamon, New York, 1974), vol. 2, pp. 1651-1656].
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17. If the ^{21}Ne production depth is taken as 2 m [W. Hübner, D. Heymann, T. Kirsten, in *Proceedings of the Fourth Lunar Science Conference*, W. A. Gose, Ed. (Pergamon, New York, 1974), vol. 2, pp. 2021-2036], the lower limit of $\sim 10 \text{ m}$ placed on the average thickness of the regolith at the Apollo 16 site, based on geological evidence [Apollo 16 Preliminary Science Report, *NASA SP-315* (1972)], implies a maximum ^{21}Ne age of about one-fifth the age of the regolith, that is, about 800×10^6 years. The possibility that the oldest points in Fig. 1d correspond to the actual age of the regolith, 4×10^9 years, cannot be excluded but is considered unlikely.
18. In large solar flares, $^3\text{He}/^4\text{He} \approx 3 \times 10^{-2}$. Because the cross section for ^{15}N production from ^{16}O spallation is close to that for ^3He production from ^4He , in solar flare material $^{15}\text{N}/^{14}\text{N} \approx 3 \times 10^{-2}$. If we take 10^{18} g as the mass involved in each major flare and $5 \times 10^{31} \text{ g}$ as the mass of the solar convective layer, then one large solar flare per year for 4×10^9 years will convert 2.4×10^{-6} of the ^{16}O in the solar wind reservoir. Because the $^{15}\text{N}/^{14}\text{N}$ ratio in the sun equals 6×10^{-4} (7), the 15 percent increase observed in ^{15}N corresponds to the conversion of 10^{-4} of the available ^{16}O , that is, a factor of 40 more than predicted for the lifetime of the regolith (W. A. Fowler, personal communication).
19. Spallogenic ^{21}Ne is calculated by subtracting a solar wind component from the total value of ^{21}Ne . If the proportion of ^{21}Ne in the solar wind were smaller in the past, the calculated ages would be erroneously short. The possibility of an effect at the mass number ^{21}Ne was pointed out by K. Marti (personal communication).
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