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What Has Caused the Secular Increase in Solar Nitrogen-15?

JOHN F. KERRIDGE

Well-documented variations in the $^{15}N/^{14}N$ ratio in lunar surface samples apparently result from a secular increase in that ratio in the solar wind during the past few billion years. The cause of this change seems to lie in the solar convective zone but is inexplicable within our present understanding of solar processes. This problem therefore ranks with the solar neutrino deficiency as a major challenge to our solar paradigm.

STREAMING OUT FROM THE SUN AT A FEW HUNDRED KILOMETERS per second, the ions of the solar wind possess enough energy to penetrate several hundred angstroms into soil grains lying on the lunar surface. This bombardment results in a population of solar wind atoms in lunar soil that increases with the length of time that the soil is exposed at the surface. The buildup of implanted atoms, and other exposure-related phenomena, is termed "maturation"; maturity is a measure of the duration of that exposure. For elements that are heavily depleted in the moon, resulting concentrations of implanted atoms can be high enough to permit separation of the solar wind signal from the indigenous lunar background. Thus, lunar sample analysis has complemented spacecraft observations as a source of compositional information about the solar wind, and has the added advantage that the record can go back about 4 billion years before the start of the space program. Similar analyses can be done for those meteorites that experienced exposure on the surfaces of their parent bodies, but the data that I discuss in this article were all obtained by analysis of lunar samples collected in the Apollo missions.

The solar wind originates in the solar convective zone, from which gas flows, heated by some poorly understood process, to form the corona. Expansion of the corona generates the solar wind, which therefore samples, apparently with little distortion due to fractionation (*1*), the outermost 1% of the solar mass. According to standard solar models, the composition of the convective zone is not significantly affected by nuclear transformations taking place deeper in the sun (*2*). If correct, this conclusion implies that any observed

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The author is in the Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90024.

compositional anomaly in the solar wind is unlikely to be directly related to the flux of solar neutrinos, which is a manifestation of nuclear processes taking place at depth in the sun (*3*).

The contemporary solar wind, and short-term fluctuations in it, have been assayed by spacecraft for nine elements: H, He, C, N, O, Ne, Mg, Si, and Fe. Except for modest excesses of Mg, Si, and Fe, apparently related to their low first-ionization potentials, their abundances are similar to those in the sun (*1*). Eight elements are sufficiently depleted in the moon to permit their solar wind contributions to be detected in most lunar soil samples: H, He, C, N, Ne, Ar, Kr, and Xe. These elements are depleted because they are volatile, and the moon was apparently extensively outgassed early in its history. Thus, lunar crystalline rocks contain less than 1 μg of N per gram of rock (*4*). When allowance is made for saturation of H and He and apparently mass-dependent diffusive loss of the other noble gases, the relative concentrations of these elements are broadly similar to their solar abundances. The significance of some detailed differences will be touched upon later.

Except for He, present-day spacecraft cannot yield isotopic information about solar wind species, but for most of the elements studied in lunar samples, isotopic compositions can be measured with considerable precision. Resulting values are generally unexceptional, most variations being readily explicable in terms of a modest degree of mass-dependent fractionation. Significant long-term changes in isotopic composition have been inferred for He and Ne, but by far the largest such change involves the isotopes of N: the ratio of ^{15}N to ^{14}N has apparently increased by at least 50% over a time period estimated to be about 3 billion years. This observation is important because the size of the effect exceeds by several orders of magnitude any change in composition of the solar convective zone permitted by current solar models. For that reason, many theories have been put forward that attempt to explain the phenomenon in terms of nonsolar processes. However, I argue in this article that such explanations are not consistent with the observations, implying that the cause lies in the sun, difficult though that is to understand.

In order to reveal the time dependence of the change in isotopic composition of N implanted in lunar soil, we need a measure of when, on average, exposure of a particular sample to the solar wind took place. How do we measure this quantity, commonly referred to as the "antiquity" of a sample?

Measuring Antiquity

We cannot (yet) analyze individual lunar soil grains for the solar wind elements; therefore, we are forced to analyze samples consisting of numerous grains that have experienced a wide range in exposure histories. The physical significance of the resulting average values is not always clear. Most parameters related to exposure duration correlate well with each other, suggesting that they can serve effectively as measures of maturity, but identifying a reliable measure of antiquity is much more difficult: all parameters used so far have serious drawbacks, and none yields a calibrated measure, in units of time, of how long ago exposure took place. Nonetheless, for want of a better chronometer, we have to use one of them.

How antiquity varies with depth in the soil layer, termed the regolith, is a function of the depositional history of the soil at a particular site. The time dependence of that history, however, is highly nonlinear, with excavation and deposition occurring at random intervals and with widely variable magnitude. Although the lower layers in Apollo drill-core samples tend to have been exposed earlier than those higher up, there are many exceptions (for example, Fig. 1). In a few cases, cosmic-ray spallation and neutron-capture effects in a stratigraphic unit can be used to calculate when that unit was deposited, so that lower units must have been exposed earlier than this time.

Galactic cosmic rays interact with the atoms in the upper few meters of the lunar surface to produce a cosmogenic component in certain nuclides, which, if the original natural abundance of those nuclides in a sample is sufficiently low, can be analyzed to give a measure of how long an average constituent grain of the sample has resided in that surface region. This residence time is related in a statistical fashion to the antiquity of the sample: the longer ago that a grain took up residence in the dynamically stirred upper part of the regolith, the longer ago, on average, it first trapped solar wind atoms. Because of the complex and incompletely understood dynamic behavior of a grain in the regolith, this measure of antiquity is not absolutely calibrated. Furthermore, for ^{21}Ne, the most commonly exploited nuclide, loss by diffusion can be significant but difficult to estimate. Thus, we are unable to determine accurately when, relative to either the present or the formation of the moon, the solar wind had a particular composition, even in cases where a clear long-term variation is observed.

Some gaseous radiogenic nuclides, produced by radioactive decay in the lunar interior, escape into the transient lunar atmosphere

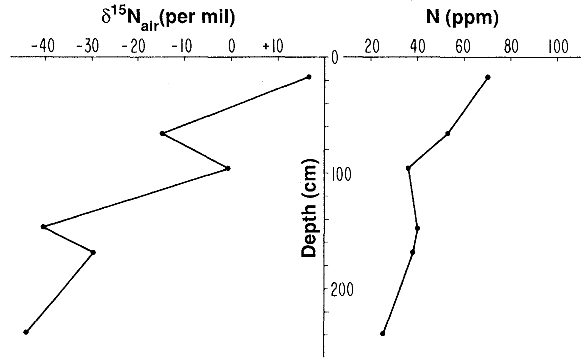


Fig. 1. Nitrogen contents and isotopic ratios for samples from the drill core retrieved from the Apollo 15 landing site. Ratios of ^{15}N to ^{14}N are expressed in the delta notation as deviations in parts per thousand from the terrestrial atmospheric value. There is a general trend for the ^{15}N/^{14}N ratio to decrease with increasing depth, but with local reversals. Within the context of a secular increase in ^{15}N/^{14}N, such reversals correspond to inversions of exposure stratigraphy. The lowest strata in this core were probably exposed on the surface more than 500 million years ago (*40*). [Data from (*44*)]

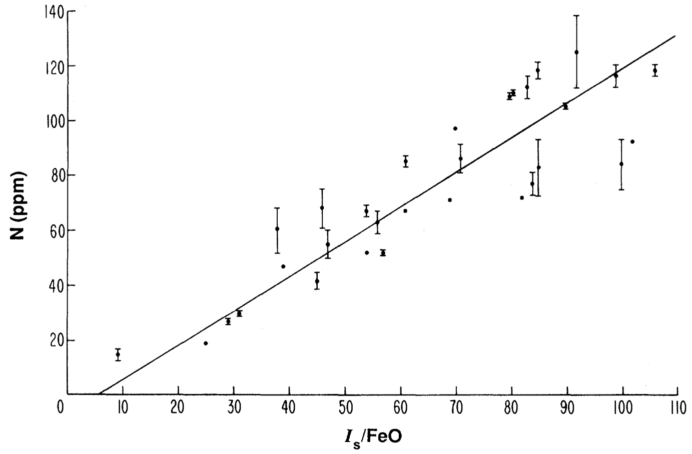


Fig. 2. Close linear relation between N content and intensity of ferromagnetic resonance (FMR) for 31 Apollo 16 soils; FMR intensity is a measure of the proportion of indigenous Fe^{2+} reduced to fine-grained metal by micrometeorite impacts into the solar H-saturated regolith and is therefore also a measure of maturity. [From (*34*)]

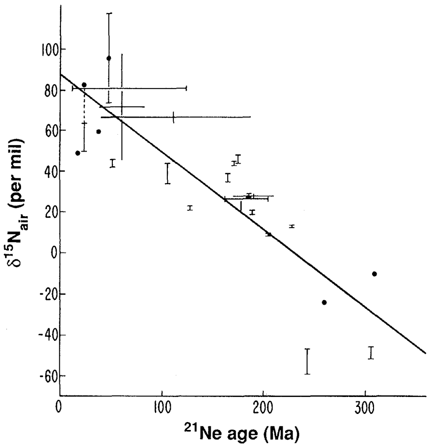


Fig. 3. Nitrogen isotopic composition as a function of cosmic ray–produced ^{21}Ne contents for the Apollo 16 soils. Contents of ^{21}Ne have been corrected for trapped Ne and converted into nominal exposure ages [in millions of years ago (Ma)] based on known production rates and chemical compositions. Those ages are statistically related to the antiquity of the samples but do not give the actual times at which solar wind exposure occurred. [From (*34*)]

whence they may be implanted into the lunar surface layer by ultraviolet ionization and acceleration in the solar wind magnetic field (*5*). Because the abundance of the radioactive parent decreases exponentially with time, the concentration of such an implanted radiogenic daughter nuclide, normalized to constant surface exposure duration, is also a decreasing function of time. The best studied of these species is ^{40}Ar from the decay of ^{40}K, which has a 1.28-billion-year half-life (*6*); others include ^{129}Xe from decay of ^{129}I (17-million-year half-life) and ^{131}Xe to ^{136}Xe from decay of ^{244}Pu (82-million-year half-life). However, attempts to find N with low ^{15}N/^{14}N ratios in samples that are rich in radiogenic Xe, and therefore apparently of great antiquity, have failed (*7*). This failure suggests that, at least in some cases, the solar wind and lunar-atmospheric components are not rigorously coupled.

Lunar Nitrogen Systematics

A mature lunar soil can contain more than 100 μg of N per gram of soil, that is, more than 100 times as much as in the crystalline rocks from which it was made by impact-induced comminution. Analyses of grain-sized fractions and etching of grain surfaces demonstrate that much of this excess N in the regolith is located on grain surfaces (*8*). The remainder has either diffused into the interiors of grains (*9*) or has been occluded in aggregate particles welded together by impact-generated glass on the lunar surface (*8*). Clearly, as is the case for solar noble gases, the surficial N has been implanted in the grains subsequent to regolith formation. An obvious possible source for regolith N is the solar wind, but whether it is the only source is controversial. The amount of N in the regolith as a whole exceeds by a factor of 3 to 10 what could have been implanted during the life of the regolith at the present solar wind flux, but this can readily be interpreted in terms of a higher flux in the past (*10*), for which there is independent evidence (*11*).

Nitrogen contents of bulk soils correlate strongly with measures of maturity, including contents of other elements believed to be of solar wind origin, consistent with such an origin for the N. A convenient measure of maturity is the intensity of ferromagnetic resonance, I_s, which records the presence in a soil of very fine-grained metallic Fe particles produced by reduction of indigenous lunar Fe^{2+} during micrometeorite impacts; implanted solar wind H serves as the reducing agent (*12*). A plot of N content versus I_s, normalized to FeO content (Fig. 2) reveals a strong linear relationship. Equivalent plots for the solar wind–derived noble gases give similar trends, but with slopes corresponding to marked depletions of the noble gases relative to their solar abundances. These depletions, relative to the abundances tabulated by Cameron (*13*), range from ~0.5 for the Xe/N ratio to ~10^{-3} for the He/N ratio. These values suggest that the noble gases are lost preferentially by a mass-dependent process such as diffusion. Such a loss process would be consistent with the evidence for mass fractionation observed in the noble gas isotopes (*9, 14*). However, the large apparent enrichment of N relative to the noble gases has led to suggestions that an additional, non–solar wind N component may be present on the lunar surface (*15, 16*). Presence of such a component cannot be rigorously ruled out but seems unlikely as a major contributor to regolith N (*9*). Frick *et al.* have suggested (*9*) that the ratios of solar noble gases to N may be about an order of magnitude less than previously assumed; if correct, the need for excess lunar surface N is eliminated. The question of non–solar wind N is discussed further below.

In bulk samples, lunar-regolith N exhibits an enormous range of ^{15}N/^{14}N values, from 17% below (*10*) to 10% above (*17*) the terrestrial atmospheric value of 3.67×10^{-3}. This range is an order of magnitude greater than that observed among natural samples on Earth. Indigenous lunar N, sampled in crystalline rocks, is not well characterized isotopically but appears to be close to the terrestrial value, after correction for spallogenic ^{15}N (*4, 8*). The ^{15}N/^{14}N ratios of regolith samples do not vary appreciably with maturity but tend to decrease with increasing antiquity (*17, 18*), whether measured by depth in a drill core (Fig. 1), content of spallogenic ^{21}Ne (Fig. 3), or proportion of radiogenic ^{40}Ar (Fig. 4). Similarly, ilmenite grains separated from ancient regolith breccias have much lower ^{15}N/^{14}N ratios than equivalent grains from a recent soil (*19*).

During stepwise release from a regolith sample, ^{15}N/^{14}N values generally exhibit a characteristic U-shaped pattern (Fig. 5), and partial fluorination initially releases a ^{15}N-enriched component that is apparently in the readily fluorinated surfaces of grains (*8*). Extreme values observed during stepwise release, relative to the value for terrestrial atmospheric N_2, range from >20% below for the intermediate-temperature release (*10*) to >20% above for the low-temperature release (*20*). All these observations are consistent with a situation in which recently implanted N is enriched in ^{15}N relative to that which was implanted earlier. However, composite particles, termed agglutinates, separated from a mature soil, which might be thought to contain N of greater antiquity than the bulk, are not relatively depleted in ^{15}N (*21, 22*). This observation has been construed as evidence against the notion that there has been a secular increase in the ^{15}N/^{14}N ratio of implanted N (*21, 22*) but, in that the constituents of composite particles on the lunar surface have had a complex history, this question needs to be explored further.

One of the most perplexing aspects of the N-isotope issue is the lack of any associated effects in other solar wind–derived elements implanted along with the N in the lunar regolith, despite evidence for systematic variations in several of those elements. Thus, over essentially the same time interval as for the increase in the ^{15}N/^{14}N ratio, decreases of about 20% in the ^{4}He/^{3}He ratio (*11, 19, 23*) and of a factor of 2 in the ^{4}He/N (*19*) and Xe/N (*18, 19*) ratios have been observed, together with an increase of about 3% in the ^{20}Ne/^{22}Ne ratio (*19, 24*), but none of these are apparently associated with the change in the ^{15}N/^{14}N ratio. The first three observations most likely reflect a decrease in Coulomb-drag efficiency of the solar wind acceleration process (*25*), caused by an apparent decrease in solar wind intensity (*18*). The cause of the apparent increase in the ^{20}Ne/^{22}Ne ratio is not known, but it may be significant that the ^{20}Ne/^{22}Ne ratio measured by spacecraft in contemporary solar flares is roughly 30% lower than the solar wind value (*26*). Also, lunar soil grains contain a deep-seated Ne component with a ^{20}Ne/^{22}Ne ratio about 15% lower than the solar wind value; this Ne may have been implanted with greater energy than that provided by the solar wind

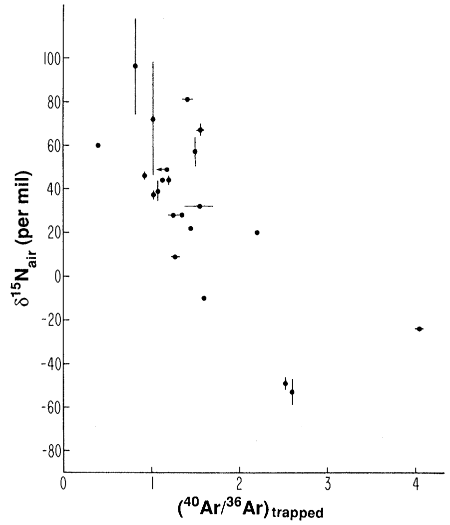


Fig. 4. Nitrogen isotopic composition as a function of trapped ^{40}Ar in the Apollo 16 soils; ^{40}Ar contents have been corrected for in situ production from ^{40}K and normalized to ^{36}Ar contents to allow for differences in maturity. [From (*18*)]

(*27*). These variations are apparently unrelated to the change in the ^{15}N/^{14}N ratio, however.

Attempts have been made to isolate implanted ancient solar wind N from certain meteorites believed to have experienced irradiation in a regolith setting on their parent bodies, but so far, any possible solar wind signature has been swamped by relatively abundant indigenous N (*28*). To date, lunar samples provide the best record of solar wind N.

The apparent long-term trend in the ^{15}N/^{14}N ratio of N implanted in the lunar regolith is summarized in Fig. 6A. Most observations are consistent with a picture in which that ratio has increased by more than 50% over a period of approximately 3 billion years. Has this increase been caused by a change in the composition of a single component, the solar wind, or does it represent a change in the mixing ratio of a second, non–solar wind component?

Nonsolar Nitrogen?

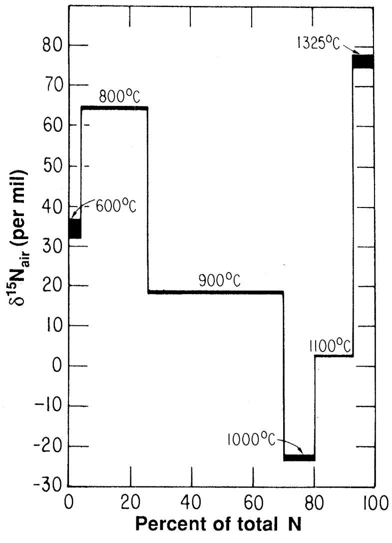
The mixing model approach implies that the isotopic composition of each component has remained constant through time. The merit of such an approach is that it obviates the need to postulate a large change in composition of a major isotopic reservoir such as the solar convective zone; its drawbacks are explored below. Because we lack independent, a priori knowledge of the ^{15}N/^{14}N ratio in the contemporary or any other solar wind, interpretation of the trend in Fig. 6A as a mixing line can place the solar component at either end of the line, with the corresponding hypothetical nonsolar component at the other. Two separate sets of arguments are therefore needed to address this question.

The more common variant is to identify the ^{15}N-enriched component with the solar wind and to invoke a heavily ^{15}N-depleted nonsolar component (*15, 21, 22, 29*). Physically, this component is identified as either outgassed indigenous lunar N (*15, 29*) or N contained in refractory carbonaceous material brought to the lunar surface by meteorite impact (*22*). The actual ^{15}N/^{14}N ratio of such a hypothetical component, which has been termed "light planetary N" (*15*), is obviously highly uncertain, but for modeling purposes it may be taken as pure ^{14}N. (Any less extreme value would make these arguments more constraining, not less.) The presence of such a component must affect both the isotopic ratio and N content of a sample. Therefore, any model of this kind can be tested by determining whether observed variations in N content and ^{15}N/^{14}N ratio are consistent with admixture of variable proportions of this component. This calculation proceeds as follows.

First, the position of a sample on a trend line such as that in Fig. 6A yields directly a measure of the proportions of the two putative end members by application of the lever rule (upper scale in Fig. 6A). Second, addition of a pure ^{14}N component is equivalent, of course, to addition of elemental N. Consequently, a ^{15}N-depleted sample should contain excess N, compared with an otherwise equivalent ^{15}N-rich one, and such excess N would perturb the correlation between maturity and content of (solar wind) N (Fig. 2). The possible amount of such excess N in each sample can be calculated (Fig. 6B). The exact slope of the "solar wind loading" line is not known a priori, but all plausible values give essentially equivalent results. For convenience, I use a line through the origin tangential to the lower bound of the data. For the data in Fig. 2, the height of each measured point above such a loading line yields "excess" N contents for the same Apollo 16 soil samples whose isotopic data (Figs. 3 and 4) can yield values for the light planetary component. These two measures of what is nominally the same quantity, expressed as percentage of the total N in each sample, can then be plotted against each other (Fig. 6C). Clearly, the Apollo 16 data do not match the model prediction. Unless uncertainties in the data are obscuring the record (*15*), this type of mixing model cannot account for the apparent secular increase in ^{15}N.

In the second type of mixing model, an isotopically light solar wind is mixed with a hypothetical nonsolar component with a ^{15}N/^{14}N ratio higher than the highest measured value (*30*). Because the composition of that component is not known, even roughly, we cannot quantitatively test such models. Arguments based on the apparent absence of excess N, as employed above, can be used to rule out a component with a composition not far removed from the highest measured value, say a ^{15}N/^{14}N ratio within a factor of 2 of the terrestrial value. That there could be a more highly ^{15}N-enriched reservoir of N cannot be ruled out but is unlikely. The most ^{15}N-enriched solar system N yet observed is about a factor of 2 enriched relative to terrestrial values and occurs only in a couple of rare meteorites (*31*); there are no grounds for postulating a more widespread distribution. Generally, ^{15}N-rich material is rare in the cosmos because the nucleosynthetic sources of ^{14}N apparently greatly outweigh those of ^{15}N (*32*). Also, hypothetical production of a suitably ^{15}N-enriched component by drastic mass fractionation of solar N would necessitate loss of colossal amounts of N and would lead to comparable isotopic fractionations in C and the noble gases that are not observed (*17, 33*). Unless a highly ^{15}N-enriched reservoir accessible to the lunar surface can be found, this type of mixing model is most likely not correct.

Fig. 5. Isotopic composition of N released at different temperatures during a stepwise extraction from a typical lunar soil (sample 70011, 23). After an initial step containing a small amount of atmospheric contamination, the major low-temperature release is enriched in ^{15}N, corresponding apparently to recently implanted solar wind. At higher temperatures, ^{15}N-depleted N is evolved, corresponding to N implanted at an earlier epoch. At the highest temperature, enrichment of ^{15}N reflects the presence of a small quantity of ^{15}N produced by cosmic-ray spallation. [Reproduced from (*42*) with permission]



A special case of the mixing model is one in which the hypothetical non–solar wind component is identified as solar flare–implanted N, so that the isotopic change in N would reflect a change in the relative proportions of solar wind and solar energetic particles. The appeal of such a model lies in the documented difference, of an appropriate magnitude, in the $^{20}Ne/^{22}Ne$ ratio between solar wind and solar flares (*26*) (although the $^{15}N/^{14}N$ ratio has not been measured with sufficient precision in either source). However, the arguments given above against mixing models probably apply to this case as well, with the additional argument that for lunar regolith samples, the change in $^{15}N/^{14}N$ is not correlated with that in $^{20}Ne/^{22}Ne$. This conclusion is based on rather few observations and perhaps additional data are needed.

The general conclusion is that the presence in lunar regolith samples of a non–solar wind N component capable of generating, by means of a variable mixing ratio, the apparent secular increase in the $^{15}N/^{14}N$ ratio is unlikely and that models based upon such a component are therefore similarly implausible. Other models advanced to account for the isotopic systematics of N in the lunar regolith are summarized below [see (*15, 18, 34*) for details].

Other Models Assessed

Explanations for a change with time in the $^{15}N/^{14}N$ ratio of an assumed single-source, that is, solar wind, N component fall into two categories: nuclear mechanisms, and mass-dependent fractionations. These categories may be further subdivided on the basis of whether the process is supposed to have taken place on the lunar surface or in the sun.

All models based on enrichment of ^{15}N by mass-dependent isotopic fractionation may be ruled out because the other implanted solar wind elements that accompany N in lunar regolith samples fail to show evidence for the comparable mass fractionation that would also have affected them. This argument is particularly strong for C; the C abundance shows a strong linear relationship with that of N (*17, 35*) but the $^{13}C/^{12}C$ ratio shows only a hint of a relation with the $^{15}N/^{14}N$ ratio (*33, 35*), and the range in C-isotopic composition is only a tenth that in N (Fig. 7). Modest degrees of mass fractionation may be seen in the isotopes of Kr and Xe [for example (*14*)], but this fractionation appears to be due to diffusive separation and loss relative to N, and those fractionations show no relation to the change in the $^{15}N/^{14}N$ ratio. In that the Coulomb-drag coefficients for ^{14}N and ^{15}N are similar (*25, 34*), a change in acceleration conditions for the solar wind is unlikely to effect significant fractionation of the N isotopes.

A "lunar-nuclear" process would result in either production of ^{14}N or destruction of ^{15}N during residence on the lunar surface. The only known process capable of producing ^{14}N is spallation of ^{16}O, but that would produce ^{15}N in comparable abundance, thereby increasing the $^{15}N/^{14}N$ ratio, an effect opposite to that desired. [Spallogenic ^{15}N can actually be observed in lunar samples, in the highest temperature steps of a stepwise extraction (Fig. 5), but in amounts too small to obscure the secular change, which has an opposite effect (*8, 10*).] The cross sections of ^{15}N for any radiation that it might encounter in the lunar regolith are far too small to produce any perceptible change by destruction during the life of the regolith. Therefore, no nuclear process acting on the lunar surface is apparently capable of generating the change in $^{15}N/^{14}N$.

Finally, in "solar-nuclear" models, the composition of the solar wind reservoir is thought to be changed by admixture of a nucleogenetically distinct component or by either production of ^{15}N or

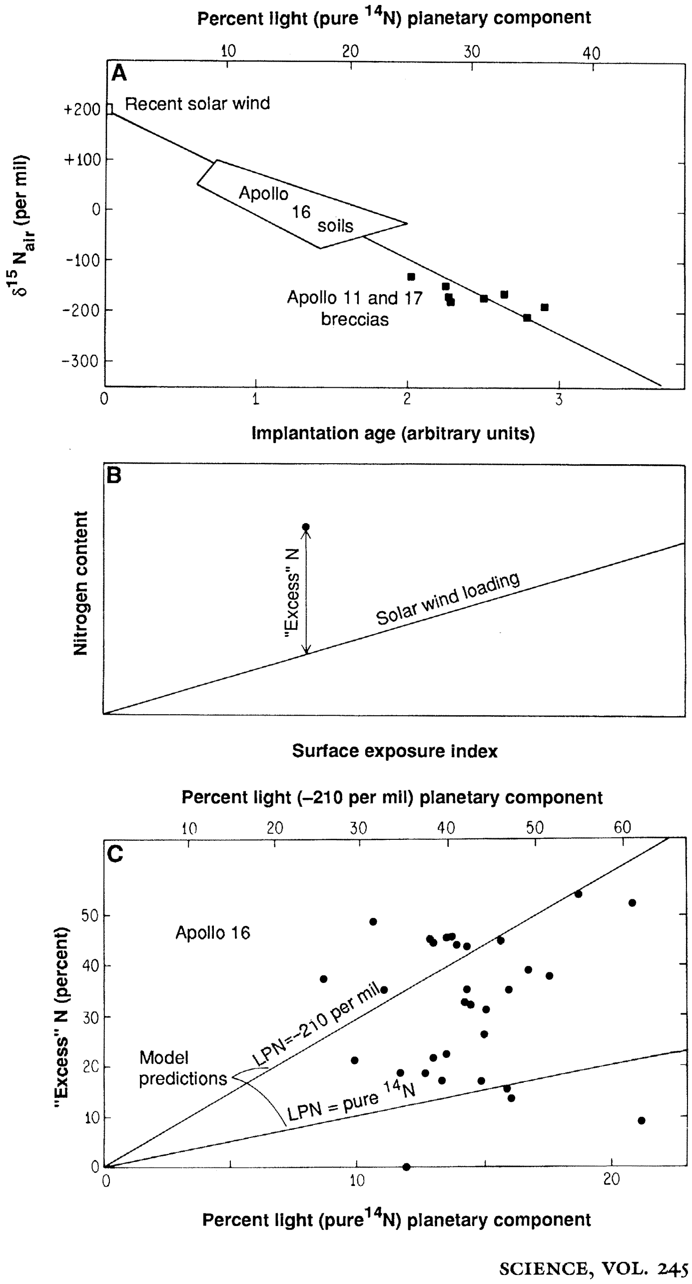


Fig. 6. (**A**) Summary of dependence of the $^{15}N/^{14}N$ ratio on antiquity. The measure of antiquity represents a rather loose synthesis of the various lines of evidence available and is given in arbitrary age units. Those units are estimated to correspond roughly to billions of years, but this is not reliably calibrated, particularly for the Apollo 16 samples, which have been positioned by bringing their internal trend line into coincidence with that for the other data. On the upper scale, the positions of the data are interpreted in terms of the proportion of a hypothetical pure ^{14}N planetary component. [Recent solar wind datum from (*20*), Apollo 16 data from (*18*), and Apollo 11 and 17 data from (*10*).] (**B**) Calculation of "excess," that is, non–solar wind, N in regolith samples. Addition of a hypothetical ^{14}N-rich component to solar wind N would perturb the linear relation between N content and a surface exposure index, such as the I_s/FeO ratio (Fig. 2). The magnitude of any such perturbation can be calculated for each sample as N in excess of a linear solar wind loading trend. (**C**) Test of the light planetary component hypothesis. Application of the approach illustrated in (A) and (B) to the data in Figs. 2, 3, and 4 yields estimates of the light planetary component and excess N, expressed as percentage of total N in each sample, that should equal each other if the hypothesis is correct. Proportion of the light planetary component is calculated for both the case where light planetary N (LPN) = pure ^{14}N, as in (A), and for the other limiting case in which LPN = −210 per mil, the lowest observed lunar value. Not only do the data fail to follow either predicted trend, but they also reveal no significant linear relationship. The results therefore appear not to support the hypothesis.

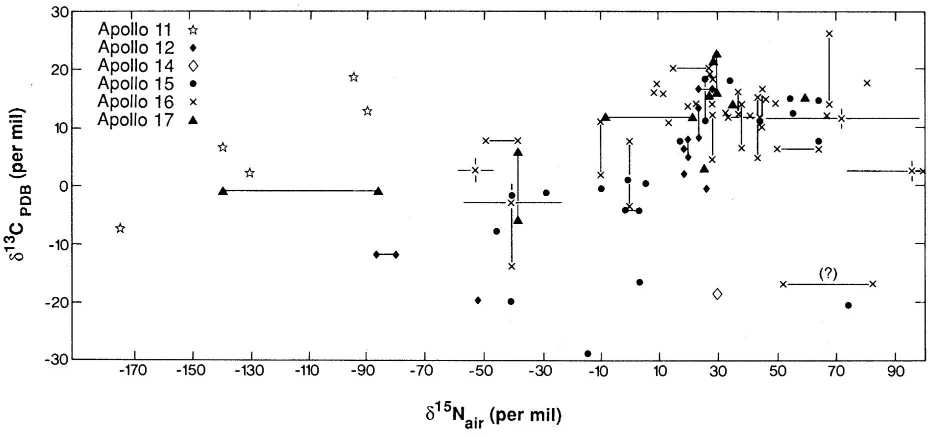


Fig. 7. Isotopic compositions of C and N in a comprehensive collection of regolith samples. A hint of a positive trend may be present (*33*), but variations in the $^{13}C/^{12}C$ ratio are obviously not closely coupled to those in the $^{15}N/^{14}N$ ratio and are typically only a tenth as large; PDB is a C isotopic standard. [After (*33*) with additional data from (*43*)]

destruction of ^{14}N in the reservoir itself. Two variants of the nucleogenetic mixture type of model have been considered that involve either an early transient addition of ^{14}N-rich material or long-term addition of ^{15}N-rich material.

The suggestion that the solar convective zone might have been contaminated by ^{14}N-rich material from outside the solar system is attractive because such material is abundant in the galaxy, notably in planetary nebulae (*36*). Although the probability that the early sun intersected enough material is low, it cannot be ruled out. A major problem with the model lies in the size of the convective zone required, which is two to three orders of magnitude smaller than present estimates based on solar observations (*18, 37*). Furthermore, stellar material substantially enriched in ^{14}N would also have C and Ne, among other elements, with nonsolar isotopic composition (*15*). However, there is no relation between the variations in the $^{15}N/^{14}N$ ratio and those in the $^{20}Ne/^{22}Ne$ ratio, and if there is any sympathetic variation in the $^{13}C/^{12}C$ ratio it is much smaller than that in the $^{15}N/^{14}N$ ratio. Finally, the time scale for restoration of the original composition in an initially perturbed convective zone would be less than 10^7 years, whereas the lunar data imply that a change took place over a time scale of the order of 10^9 years (*15*).

Long-term accretion of ^{15}N-rich material by the sun, as for the lunar surface, cannot be rigorously ruled out but suffers similarly from the rarity of such material in the cosmos. Furthermore, if such material were entering the solar system in sufficient quantity, it would probably also contaminate the lunar surface directly, leading to an effect larger than the putative solar wind change and of opposite sign (*15, 18*). Mixing of nucleogenetically distinct components in the solar wind reservoir does not appear to constitute a viable explanation of the N-isotope data.

Tests of models that postulate nuclear reactions in the sun are based on other predictable effects that the necessary radiation fluence would produce. Conditions needed to destroy sufficient ^{14}N are more extreme (*34*) than for producing ^{15}N, so that only the latter hypothesis needs to be tested. As on the lunar surface, ^{15}N would be made in the sun by spallation of ^{16}O (*17*). A suitable level of spallation in the outermost convective zone can be ruled out for the contemporary sun by the low levels of nuclear gamma activity observed, either in the steady state or during solar flares (*15, 34, 38*). Similarly, the relative constancy of the solar flare track record in lunar rocks of different age is a strong argument against much greater surficial activity in the past (*15*). What neither observation constrains is nuclear activity at depth in the sun. However, such activity would produce ^{11}B comparably to ^{15}N, which would have led to a present-day solar abundance of B at least two orders of magnitude greater than that observed spectroscopically (*15, 34*). Thermonuclear burning could, in principle, have eliminated this excess if the B were mixed to a sufficiently great depth in the sun (*33, 34*), but operation of such a process to just the degree that the contemporary photospheric value matches, to within ±60%, the meteoritic or cosmic abundance seems implausible (*15*).

Obviously, none of the models advanced so far constitutes a satisfactory explanation for the apparent secular change of the $^{15}N/^{14}N$ ratio in the solar wind. In addition, few of them lead to useful experiments that might be performed in order to resolve the question. What lines of inquiry might therefore be productive?

Future Directions

Several categories of model could be eliminated if the $^{15}N/^{14}N$ ratio in the present-day solar wind were known. For example, in many models, a value substantially enriched in ^{15}N compared with the terrestrial value is required. Fortunately, direct determination of this quantity by spacecraft observations should be feasible within a decade or so.

Another issue that may well be resolved by spacecraft measurements is whether the protosolar system had everywhere a single $^{15}N/^{14}N$ ratio that was uniformly distributed on a planetary scale, and if so, what that value was. This information should be provided by the Galileo mission to Jupiter, which will obtain, among other parameters, the $^{15}N/^{14}N$ ratio for the Jovian atmosphere. The general run of isotopic values in that atmosphere, when compared with those for other solar-system objects, should indicate whether Jupiter is representative of nebular gas. Nitrogen should have been accreted quantitatively, that is, without isotopic fractionation, during formation of Jupiter. Uncertainties in current estimates of the Jovian $^{15}N/^{14}N$ ratio by means of remote spectral measurements (*39*) are too large for those estimates to be used to assess different models.

The solar-nuclear models are strongly constrained by the various observations discussed above, but, unlike the case for most other models, these observations represent indirect evidence, in that they are based on phenomena that might be decoupled from the solar wind. A better, more direct, test would be one based on a similar effect in another implanted solar wind element from the same population in which the N-isotope effect is observed. Such a direct test is potentially available. Any nuclear reaction capable of generating a 50% change in the $^{15}N/^{14}N$ ratio would produce enough neutrons to cause an approximately 0.5% decrease in the $^{131}Xe/^{132}Xe$ ratio through neutron capture on ^{131}Xe. This change should show up as a systematic difference in the $^{131}Xe/^{132}Xe$ ratio between ancient and modern solar wind samples, after correcting for any mass fractionation such as is observed in solar wind–implanted Xe. Resolution of such a variation is currently beyond the state of the art, but progress in that area could render this measurement feasible.

The observational and experimental studies described above are all worth performing but the most useful contribution to resolving the solar wind nitrogen problem at this time may be a model that satisifies all existing observational constraints. It does not seem far-fetched to compare the ^{15}N problem with the celebrated solar neutrino deficiency (*3*), even though they probably originate in different regions of the sun. Both represent fundamental challenges to our solar paradigm; as long as both remain unresolved we cannot claim to understand fully how the sun functions. Given the level of cerebral effort devoted to the neutrino problem it would be nice to see a comparable effort aimed at the N isotopes in the solar wind. Readers of this article should regard it as a challenge.

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Drugs from Emasculated Hormones: The Principle of Syntopic Antagonism

JAMES BLACK

This lecture illustrates the early stages in the planning and discovery of propranolol, an adrenaline β-adrenergic receptor antagonist, and cimetidine, a histamine H_2-receptor antagonist—the first examples of clinically useful drugs from each of these classes. The significance of selective agonists, partial agonists, and syntopic antagonists and the importance of the bioassay and the use of molar models in the drug discovery process are discussed. For the future, an outline of potential developments in hormone-receptor concepts is offered leading to the conclusion that progress may depend on improvements in bioassays and related molar modeling.

THE WORK THAT IS THE THEME OF THIS LECTURE BEGAN IN the early summer of 1958 when I joined Imperial Chemical Industries' Pharmaceuticals Division. I had gone there to pursue a very clear project that had been developing in my mind for several years. The idea had clinical, therapeutic, physiological, and pharmacological elements.

The author is professor of the Department of Analytical Pharmacology, Rayne Institute, King's College Hospital School of Medicine and Dentistry, 123 Coldharbour Lane, London SE5 9NU, United Kingdom. This article is taken from the lecture he delivered in Stockholm, Sweden, 8 December 1988, when he received the Nobel Prize for Physiology or Medicine, which he shared with Gertrude B. Elion and George Hitchings. It is published here with the permission of the Nobel Foundation.