Reports

A Striking Nitrogen Isotope Anomaly in the Bencubbin and Weatherford Meteorites

Abstract. *The stony-iron meteorites Bencubbin and Weatherford contain nitrogen with a ratio of nitrogen-15 to nitrogen-14 larger than normal by as much as a factor of 2. The excess nitrogen-15 may be due either to a nucleosynthetic origin or to extreme isotopic fractionation. In the former case, it may reflect failure to homogenize nitrogen-15 produced in nova explosions. In the latter case, it may reflect chemical processing at temperatures below 40 K in a presolar molecular cloud.*

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Since different nucleosynthetic processes occur in different astrophysical settings, each producing its own characteristic pattern of nuclear abundances, it is expected that matter in the interstellar medium should be isotopically heterogeneous. If such heterogeneities survived the physical and chemical processing associated with the formation of the solar system, they may be recognizable as "isotopic anomalies" in various constituents of primitive meteorites.

The two stable nitrogen isotopes, ^{14}N and ^{15}N, are synthesized in different astrophysical processes—^{14}N during hydrostatic hydrogen burning, and ^{15}N during explosive hydrogen and helium burning. ^{14}N is ejected into the interstellar medium by red giants and supernovae. Red giants are thought to be the principal sources of ^{14}N and ^{13}C (*1*). Explosive sites of ^{15}N production include novae (*2*) and the outward shock of supernovae (*3*); however, novae are considered to be the dominant source of ^{15}N (*4*) and are also sites of ^{13}C production. Novae have also been suggested as a source of ^{26}Al in the interstellar medium and of the extinct ^{26}Al inferred from the presence of excess ^{26}Mg in meteorites (*5*). The fact that residual isotopic heterogeneity is present in meteorites for ^{26}Al, which may have had a nova origin, suggests that at least some of the heterogeneity for ^{15}N in meteorites may be caused by incomplete mixing of material produced in novae.

Previous whole-rock nitrogen isotopic measurements in meteorites [expressed as $\delta^{15}N$ (*6*)] range from −90 per mil for IIAB iron meteorites (*7*) to +190 per mil for the C2R carbonaceous chondrite Renazzo (*8, 9*); however, whole-rock $\delta^{15}N$ values for the vast majority of meteorites fall between −90 and +50 per mil.

Some of the analytical data suggest that the observed isotopic variations result from the mixing of components with more extreme abundance variations. Evidence for both ^{15}N-rich and ^{15}N-poor nitrogen components has been found. A component of composition between −400 and −1000 per mil (that is, pure ^{14}N) was inferred by comparing vacuum pyrolysis and sealed-tube Kjeldahl analyses of an Allende acid residue (*9*). The lowest $\delta^{15}N$ value directly measured so far is −326 per mil (*10*) in a fraction of an Allende acid residue.

Renazzo has an ^{15}N-rich component—bulk $\delta^{15}N$ values range from +170 to +190 per mil (*8, 9*)—and ^{13}C-rich carbon is found in high-temperature combustion steps of Renazzo whole rock (*11*). A stepped combustion of the C2M chondrite Murray produced nitrogen with a $\delta^{15}N$ value of +93 per mil, which may be associated with carbon with a $\delta^{13}C$ value of +108 per mil (*12*). The highest $\delta^{15}N$ value measured in a C2M chondrite is +335 per mil for a bulk meteorite analysis of the Bells meteorite (*13*).

The Bencubbin stony-iron meteorite is a polymict breccia containing metal clasts, silicate clasts, and chondritic xenoliths cemented together by a glass-metal matrix (*14, 15*). Host silicate clasts consist mainly of clinoenstatite, forsterite, and interstitial glass (*15*). Weatherford is also a stony-iron breccia consisting of metal, silicates, and carbonaceous chondritic clasts. Its similarity to Bencubbin was noted by Mason and Nelen (*16*). That Bencubbin and Weatherford have essentially identical (but different compared to other meteorites) oxygen isotopic abundances suggests that they are from the same parent body (*17*). Bencubbin and Weatherford appear to be related to some carbonaceous chondrites. Their oxygen isotopic compositions are similar to those of the olivine and pyroxene of the C2R chondrites Renazzo and Al Rais, so that they may be derived from a common precursor material. Their oxygen isotopic compositions also lie on the mass-fractionation line defined by the matrix of CM meteorites. Whether this implies a common precursor is unclear, but it suggests that other connections between Bencubbin/Weatherford and CM meteorites should be sought. On the basis of trace element chemistry, it has been proposed that Bencubbin silicates were formed from an impact melt produced from an asteroidal regolith of carbonaceous chondritic composition (*14*).

The metal clasts of Bencubbin do not have a unique composition, and they contain chromium-enriched troilite; some contain up to 2.3 weight percent silicon (*15*). On the basis of trace element variations, Newsom and Drake (*15*) concluded that these clasts are probably nebular condensates and that they were incorporated into the breccia as solids.

Table 1 lists the nitrogen contents and isotopic compositions of metal and silicate portions of Bencubbin and of the silicates of Weatherford (*18*). Matrix material was not analyzed separately. The nitrogen contents of both metal and silicates are high in comparison with most iron and achondritic meteorites. All phases are highly enriched in ^{15}N, with maximum values for the ratio ^{15}N:^{14}N that are almost double the ratio for terrestrial nitrogen species. The $\delta^{15}N$ values are the highest measured for any bulk meteorite, separated phase, or temperature step from a meteorite. That the ^{15}N:^{14}N ratio in the bulk meteorite is greater than that in any of the separated components analyzed implies the existence of another component with an even higher ^{15}N:^{14}N ratio.

Nitrogen in carbonaceous chondrites generally has higher ^{15}N:^{14}N ratios than nitrogen in other stony meteorites. This has previously been interpreted as a chemical isotope effect associated with

Table 1. Nitrogen isotopic compositions and contents for Bencubbin and Weatherford.

Description	Content of nitrogen*	$\delta^{15}N$ (per mil)	Mass of sample (grams)
		Bencubbin	
Metal	53.3	+829.3 ± 0.7	0.772
		+819.2 ± 0.1†	
Silicate clast 1	5.7	+414.3 ± 0.9	0.44
Silicate clast 2	44.0	+489.1 ± 0.1	1.217
		+479.1 ± 0.03†	
Whole rock	48.0	+973‡	2.10
Whole rock	59.3	+923‡	0.85
		Weatherford	
Silicate	34.7	+462.5 ± 0.1	0.20

*In micrograms per gram of sample. †After recycling sample gas through the purification procedure. ‡Mass analyzed in single beam mode (*18*); errors are estimated to be about ±30 per mil.

production of organic compounds (*9*). The present result suggests an alternative interpretation: addition of various degrees of a component especially rich in ^{15}N. The metal phase of Bencubbin may then provide a lower limit for the ^{15}N:^{14}N ratio in this component. The difference in isotopic composition between metal and silicates in Bencubbin would require dilution by "normal" nitrogen ($\delta^{15}N$ near 0 per mil) by a factor of about 2 in the silicates. In the C2M and C2R meteorites, nitrogen concentrations are higher and $\delta^{15}N$ values are lower, possibly as a result of increased dilution associated with aqueous alteration and production of nitrogen-containing compounds.

The association between Bencubbin/Weatherford and Renazzo (and other C2R meteorites) is especially close. As noted above, their oxygen isotopic compositions are consistent with derivation of their primary silicates from a common reservoir. They are metal-rich [Renazzo, 12 percent (*19*); Bencubbin/Weatherford, 50 to 60 percent (*15, 16, 20*)], and they contain silicon-bearing metal. They are the most enriched in ^{15}N of the known meteorites. The C2M meteorites such as Murchison probably had different initial isotopic compositions of oxygen and nitrogen (*21*).

The origin of the large ^{15}N:^{14}N ratio in the Bencubbin metal is of special interest. Isotopic variations in meteorites can be due to physical and chemical fractionation effects, decay of primordial radionuclides, spallation reactions in the solar system, and addition of solar-wind particles with different isotopic abundances. Isotopic variations not explainable by the operation of these processes in the solar system are considered to be due to primordial inhomogeneity. This primordial inhomogeneity can be of nucleosynthetic origin, but it can also be the result of compositions modified by fractionation processes occurring in interstellar clouds.

Demonstrating or refuting a nucleosynthetic origin for the Bencubbin ^{15}N-rich composition is not clear-cut. However, since the nitrogen isotopes are formed in different stellar environments and may, as a consequence, exist in different chemical forms in the interstellar medium, it is possible that the nitrogen isotopic composition of Bencubbin reflects primordial inhomogeneity due to stellar nucleosynthesis. An excess of ^{15}N originating from novae is a possibility. Novae are possible sources for the extinct ^{26}Al observed in meteorites (*5*), for neon-E (*22*), and for the ^{13}C excesses found in small quantities in Murchison and other C2M, C2R, and CI chondrites (*12, 23, 24*). The carbon component called Cα has a twofold enrichment in ^{13}C and is a carrier phase for neon-E and for xenon and krypton resulting from neutron capture processes (*23*). These anomalies have been found in C2M chondrites, to which Bencubbin may be related. Proton reactions on oxygen in the early solar system may also produce ^{15}N-rich compositions (*25*). However, this does not seem to be a likely explanation for the Bencubbin ^{15}N-rich component, since it is more abundant in the metal than in the silicate.

The possibility of the origin of the ^{15}N-rich composition by extreme chemical or photochemical enrichment is an open question. A factor of 2 isotopic enrichment in a thermally activated process would require temperatures of 40 K or less. However, special mechanisms involving photochemistry or vibrational excitation may produce large isotope effects. Basov and co-workers (*26*) have reported ^{15}N enrichments by a factor of 100 in reactions of nitrogen excited by laser or electrical discharge. In similar electric discharge experiments, however, Manuccia and Clark (*27*) achieved ^{15}N enrichments of only a factor of 1.2. Nevertheless, it may be that chemical enhancements of ^{15}N by a factor of 2 are plausible, but they probably require temperatures well below 100 K. For example, laboratory experiments suggest that a factor of 2 enrichment of ^{15}N can occur by isotopic equilibration between N_2 and N_2H^+ at temperatures less than 20 K (*28*). This ion-molecule reaction is rapid enough to establish equilibrium in a cold molecular cloud. Thus chemical enhancements could occur in prenebular molecular clouds or in colder parts of the solar nebula.

One possible mass-dependent process that can result in a ^{15}N enrichment is preferential loss of the lighter isotope, enriching the residue in ^{15}N. For example, this process combined with photochemical dissociation of N_2 molecules is postulated to be the explanation for the measured $\delta^{15}N$ value of 680 per mil for the Martian atmosphere (*29*). Neon and argon cannot be fractionated by photochemical or chemical processes, but they should have been affected if a process such as diffusion was the origin of the ^{15}N-rich composition. Begemann and colleagues (*30*) found primordial and spallation neon and argon in both metal and silicate portions of Bencubbin. Weatherford also contains primordial argon and neon in "planetary" proportions (*31*). The noble gases show no enrichment of the heavy isotopes, as would be expected if the nitrogen isotopic composition is the result of diffusional enrichment of ^{15}N.

To understand the origin of this ^{15}N-rich composition, it will be necessary to see what other anomalous or normal isotopic compositions will be found. The discovery of ^{13}C-rich compositions would suggest a nuclear origin but would also be consistent with some fractionation mechanisms. An initial study (*32*) found only isotopically normal carbon associated with "heavy" nitrogen in Bencubbin. Discovery of radiogenic ^{26}Mg would also strengthen the case for a nucleosynthetic origin, but this isotope is not likely to be measurable even if present because minerals with high Al:Mg ratios are absent.

Finally, the observation of nitrogen in meteorites with both extreme ^{15}N enrichment described here and extreme ^{15}N-depletion (*10*) raises the question of the degree of isotopic heterogeneity within the solar nebula. It has not been possible to identify specific reservoirs with fairly uniform isotopic compositions, as has been done for the noble gases (*33*). The large variability of the ^{15}N:^{14}N ratio in meteoritic, planetary, and solar nitrogen may result from incompletely homogenized residual heterogeneities rather than from solar system processes operating on an initially homogeneous reservoir. This suggestion is qualitatively similar to the two-component model of Geiss and Bochsler (*34*).

References and Notes

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18. Each result in Table 1 is the product of a single nitrogen extraction and isotopic analysis. The errors quoted for $\delta^{15}N$ are the statistical errors (1σ) in the mass spectrometry only. Heterogeneity in the meteorite is indicated by differences in nitrogen contents and isotopic composition between clast 1 and clast 2. In the normal procedure for isotope ratio measurement with the Micromass 602C spectrometer, the ion beams ${}^{14}N^{14}N^{+}$ and ${}^{14}N^{15}N^{+}$ are collected simultaneously, and their ratio is compared with that for a N_2 reference gas. In the present work, the sample ratios were beyond the range of the instrument, so that modified procedures were required. In particular, the values for "Whole rock" in Table 1 were determined by a single-beam method, in which *m/e* values of 28 and 29 were measured separately, and then $\delta^{15}N$ was calculated. This procedure results in poorer precision. Verification that the large excesses at *m/e* = 29 were due to ${}^{14}N^{15}N^{+}$ ions rather than an isobaric contamination was accomplished in two ways. First, the gas samples were recycled through the chemical purification procedure to ensure complete oxidation and removal of hydrocarbons and carbon monoxide. Second, the intensity of the ion beam at *m/e* = 30 was measured (in two different mass spectrometers) and found to be exactly that expected for ${}^{15}N^{15}N^{+}$ calculated on the basis of the ratio of *m/e* = 29 to *m/e* = 28. That similar nitrogen contents and isotopic compositions were found for two meteorites that fell on opposite sides of Earth (Australia and the United States) proves that the results are properties of the meteorite parent body, not the consequence of any terrestrial alteration process.
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Crystal Axes in Recent and Fossil Adult Echinoids Indicate Trophic Mode in Larval Development

Abstract. *The type of larval development in echinoids (Phylum Echinodermata) was found to determine crystal patterns in adult apical skeletal plates. This relation between larvae and adults will allow fossil species to be examined to determine the effects of developmental mode on evolutionary patterns, such as species longevity and speciation rate. Independent tests of hypotheses of such patterns now shown among fossil mollusks with and without feeding larvae can thus be performed.*

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Developmental mode has been linked to geographic distribution, species longevity, and speciation rate in benthic marine organisms (*1*). This connection is based on a varying opportunity for dispersal, and contrasts species having long-lived, planktonic, feeding larvae that can disperse over great distances with species having nonfeeding larvae that develop more quickly and have limited or no dispersal. Species with feeding larvae are predicted to be geographically widely distributed and geologically long-lived and to speciate infrequently. Species with nonfeeding larvae are predicted to be geographically narrowly distributed, geologically short-lived, and prone to speciation and extinction events (*1, 2*). These predictions are supported by patterns among fossil gastropod mollusks (*3*). To date, developmental mode has been inferred for gastropods and bivalves because adult shells include a larval shell that indicates the mode of larval development (*4*).

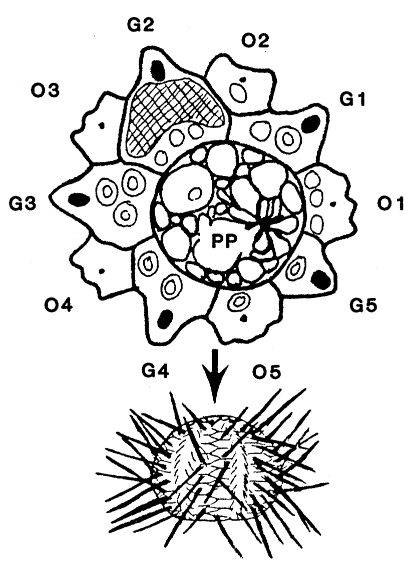

Fig. 1. Camera lucida drawing of the apical system of an echinoid. Five genital (G) and five ocular (O) plates surround the periproct (PP). The arrow indicates the location of the apical system on the aboral surface of an adult echinoid.

Here I show that type of larval development can be inferred from Recent and fossil adult skeletons in another taxon, the echinoderm class Echinoidea, from crystal orientations in adult apical plates (Fig. 1). Echinoid larvae have skeletal rods and postmetamorphic juveniles have skeletal plates, but crystal axes of the rods determine crystal axes of some of the plates.

The echinopluteus larva of echinoids (Fig. 2A) feeds and swims with a ciliated band on epidermal projections called arms (*5*). Each arm contains a skeletal rod composed of calcite, like adult spines and test plates. Each rod behaves optically like a single crystal (*6*). In species with nonfeeding larvae, the pluteus form does not develop; the larvae lack arms, rods, an elaborate ciliated band, and a larval gut (*7, 8*).

Rearrangement of the pluteus at metamorphosis leaves the larval rods on the aboral surface of the settled juvenile.