C, N, and Noble Gas Isotopes in Grain Size Separates of Presolar Diamonds from Efremovka

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Nanometer-size presolar diamonds from the Efremovka CV3 chondrite were physically separated into several grain size fractions by ultracentrifugation. The coarsest size fraction is the most enriched in carbon-12; the others have broadly similar carbon isotopic compositions. Measurement of noble gases shows that their concentration decreases with decreasing grain size. This effect is attributed to ion implantation. Such an episode could occur in the envelope of a supernova that produced the diamonds, or in interstellar space; in either case, ions with energies above a certain threshold pass completely through the smaller diamond grains without being captured. Concentrations of nitrogen show only minor variations with grain size, indicating a different mechanism of incorporation into the diamonds.

The origin of nanometer-size diamonds (*1*), the most abundant type of presolar material yet identified (*2*), is less well understood than that of other types of presolar minerals, such as SiC (*3, 4*), graphite (*5*), and refractory oxides (*6, 7*). Theoretical models explaining the occurrence in the diamonds of isotopically anomalous Xe, Xe-HL (*8–11*), suggest type II supernovae as a potential condensation site for the diamonds. However, a satisfactory explanation has not yet been found for the apparent coexistence of Xe-HL with other isotopically normal (solar-like) noble gases and nitrogen that is depleted in ^{15}N. Although the diamonds are not homogeneous in terms of the distribution of trace constituents (*12–15*) and thus may represent several different isotopically distinctive populations, all attempts to fractionate the grains into separates of different physical characteristics have been unsuccessful (*16*).

We separated presolar diamonds from the Efremovka CV3 chondrites into five grain size fractions (Table 1) by ultracentrifugation. In principle, it was considered that nanometer-size diamond particles, consisting of only 1×10^3 to 2×10^3 atoms of carbon, would behave as large organic molecules in solution or suspension—in which case ultracentrifugation could be used to distinguish them according to mass. A diamond-rich residue was prepared from Efremovka by treatment of the bulk sample with various reagents according to previously established techniques (*3*). The recovered residue was separated into a colloid and sediment in NH_4OH and centrifuged at 800*g* for 30 min. Then the colloid was treated with H_3PO_4 to destroy spinel grains and the colloid fraction was again collected, by treatment in NH_4OH with centrifugation at 800*g* for 3.5 hours. This was further treated by ultracentrifugation at 100,000*g* for 4 hours, resulting in ED-3 from the upper half of the solution, ED-2 from the lower half of the solution, and ED-1, the remaining sediment. The ultracentrifugation was repeated on ED-1 to generate three additional samples: ED-4, ED-5, and ED-9, the upper, lower, and sediment parts of the suspension liquid, respectively. We analyzed four of these fractions: ED-2, ED-3, ED-4, and ED-9.

Grain sizes of three samples [ED-2, ED-3, and ED-4 (Table 1)] were determined by transmission electron microscopy (TEM) (*17*). The samples were prepared for TEM by pipetting an acetone-water suspension of diamond onto a perforated carbon film. Electron diffraction patterns confirm that all four samples were composed almost exclusively of diamond. Grain sizes were determined from bright-field images. We only measured those grains in the thinnest regions of the samples where we could be confident that artifacts produced by overlapping grains would be at a minimum. For ED-9 the grain size distribution was determined by a similar technique (*18*) (Table 1). Note that fraction ED-9 is more coarse-grained than the others. A calculated weighted average for all four fractions is 2.9 nm, similar to the average grain size determined for presolar diamonds from other meteorites (*19*). The grain size distribution determined for two of the fractions (ED-3 and ED-9) tends to be log-normal, again similar to unseparated samples from other meteorites (*19*).

We analyzed the concentration and isotopic composition of Ne, Ar, Xe, N, and C (as well as ^{4}He concentrations only) in the four fractions by means of static vacuum gas-source mass spectrometry (*20, 21*) in conjunction with high-resolution stepped pyrolysis and combustion (*20*). The experimental configuration uses three fully automated mass spectrometers fed from a common extraction system (*22*). All the yields and iso-

Table 1. Carbon, nitrogen, and noble gas bulk concentrations and isotopic compositions for four different grain size fractions in Efremovka. Data are the average of two to four parallel measurements for each sample.

Quantity	Sample				
	ED-3	ED-2	ED-4	ED-9	Bulk‡
Grain size* (nm)	1.5 (0.7–3.1)	1.8 (1.5–2.7)	2.0 (1.2–2.7)	3.7 (1.5–9.0)	~2.9
Fraction yield (%)	10	28	4	50	92§
C (wt %)	76	73	61	80	
δ^{13}C (per mil)	–26.0	–26.3	–26.3	–32.8	–29.5
C_{pyr}† (wt %)	12.9	11.9	12.3	8.6	
N/C	0.00921	0.00712	0.00948	0.00872	0.00841
δ^{15}N (per mil)	–204	–225	–239	–282	–253
^{4}He (cm^3/g C)	0.00847	0.00982	0.0105	0.0194	0.0146
^{20}Ne (cm^3/g C)	6.92×10^{-5}	9.89×10^{-5}	8.08×10^{-5}	1.30×10^{-4}	1.09×10^{-4}
^{20}Ne/^{22}Ne	8.74 ± 0.10	8.39 ± 0.10	8.44 ± 0.10	8.26 ± 0.10	8.37
^{21}Ne/^{22}Ne	0.0304 ± 0.002	0.0311 ± 0.001	0.0320 ± 0.001	0.0398 ± 0.003	0.0355
^{36}Ar (cm^3/g C)	7.06×10^{-6}	9.97×10^{-6}	1.27×10^{-5}	3.32×10^{-5}	2.16×10^{-5}
^{38}Ar/^{36}Ar	0.216 ± 0.003	0.208 ± 0.002	0.217 ± 0.005	0.196 ± 0.004	0.204
^{132}Xe (cm^3/g C)	1.59×10^{-7}	1.58×10^{-7}	1.89×10^{-7}	4.00×10^{-7}	2.83×10^{-7}
^{136}Xe/^{132}Xe	0.678 ± 0.008	0.671 ± 0.010	0.659 ± 0.010	0.609 ± 0.007	0.639
^{134}Xe/^{132}Xe	0.637 ± 0.009	0.609 ± 0.010	0.614 ± 0.010	0.572 ± 0.009	0.594
^{129}Xe/^{132}Xe	1.030 ± 0.010	1.051 ± 0.010	1.015 ± 0.010	1.080 ± 0.010	1.059

*Range of grain sizes is shown in parentheses. †Amount of carbon released by pyrolysis (300° to 700°C). ‡Calculations made with the assumption that ED-5 is similar to ED-4. §Fraction ED-5, which has not been analyzed, has a yield of ~8%.

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topic data were obtained simultaneously from samples treated by a single temperature program: Each specimen was pyrolyzed from 300° to 700°C in 100° increments and then combusted from 300° to 1300°C with variable temperature steps [that is, 100° at the beginning and end, but during the major combustion phase (450° to 500°C) with 5° resolution].

The bulk concentrations of noble gases, C, and N in the four size fractions from Efremovka indicate that concentrations of ^{4}He, ^{36}Ar, ^{132}Xe, and ^{20}Ne decrease as the grain size decreases (Table 1). Unlike the noble gases, the nitrogen content does not change systematically as a function of grain size.

For each size fraction, the concentrations of the noble gases follow the sequence Ne > He = Xe > Ar (Fig. 1). This sequence is not compatible with the incorporation of noble gases from a single reservoir or in a single process, because in such cases the trapping efficiency should change gradually according to noble gas mass (either increasing or decreasing, depending on the specific mechanism of incorporation). There are systematic isotope variations in Ne, Ar, and Xe; Ar and Xe become isotopically more normal (solar-like) with increasing grain size [that is, the contributions of the so-called P3 and P6 components increase (*12*)], whereas Ne becomes enriched in ^{21}Ne and ^{22}Ne (Table 1). The Ne enrichment may indicate (Fig. 2A) that Ne-A2 is not a pure component but represents a mixture of Ne-P3 and Ne from another source enriched in heavy Ne isotopes, but not of cosmogenic origin. The largest difference for any of the noble gases is observed for Xe: ^{136}Xe/^{132}Xe is different in the coarse and fine fractions, with values of 0.61 and 0.68, respectively. Although the precision of Xe isotopic analyses (±1 to 3%) is insufficient to resolve different components on three-isotope diagrams, a plot of ^{136}Xe/^{132}Xe versus 1/^{132}Xe (Fig. 2B) indicates that different relative contributions of P6 and HL components are possibly responsible for the Xe isotope variations.

In each case, the noble gas concentrations across the entire temperature range are lowest in the finer fractions. It is possible that grains with the smallest sizes (<2 nm) do not contain any noble gases at all; these grains would act to dilute the noble gas concentrations in the fractions to produce the observed variations between the release profiles.

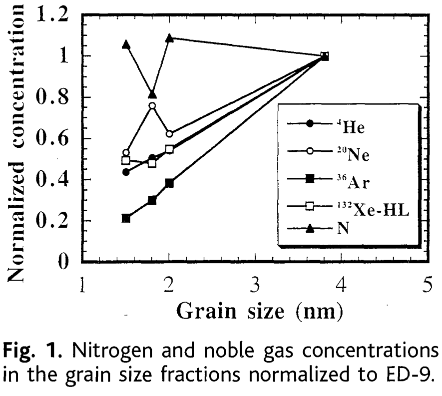

Fig. 1. Nitrogen and noble gas concentrations in the grain size fractions normalized to ED-9.

The bulk C data (Table 1) indicate that the overall isotopic concentrations for ED-2, ED-3, and ED-4 are similar (δ^{13}C ≈ –26 per mil), which suggests a single component; in contrast, a δ^{13}C value of –32.7 per mil was measured for ED-9. Isotopically light (^{12}C-enriched) carbon like that observed in ED-9 has been observed in many carbonaceous chondrite acid residues, believed to be dominated by presolar diamonds (*13, 14*). The C isotopic results from Efremovka would suggest predominantly one form of diamond in residues ED-2, ED-3, and ED-4, and perhaps a mixture of this and an additional component in ED-9. We make this assessment given that the minimum δ^{13}C values seen in stepped combustions of presolar diamonds are < –40 per mil (*13, 14*) and on this basis ED-9 is not a pure end-member. We cannot yet say whether Efremovka diamonds consist of only two main populations or represent a continuum of isotopically different components. However, the C isotope data suggest that the diamonds do not represent a single population. Also, the N isotopic composition becomes progressively ^{14}N-enriched in the larger grains (Table 1), indicating that there must be at least two N components present. Variations of carbon content in the samples (Table 1) are also related to their grain size (*23*).

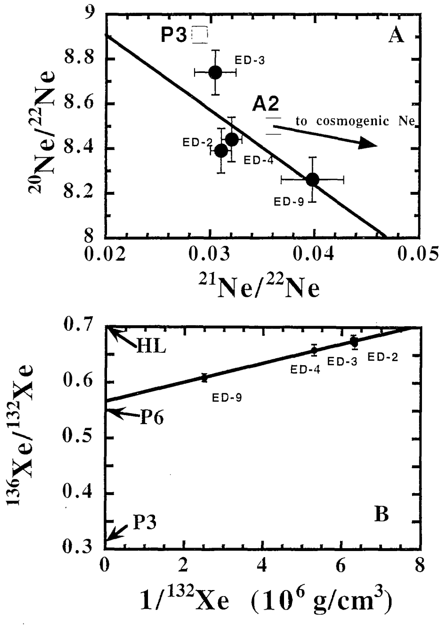

Fig. 2. Ne (**A**) and Xe (**B**) isotope variations in the grain size fractions. For both plots, the lines are the best fits through the experimental data points. P3, P6, and A2 are specific noble gas components of presolar diamonds [for details see (*12*)].

If our samples were whole diamond crystals of a uniform size, it is possible that combustion would proceed contemporaneously in each constituent grain on a layer-by-layer basis; thus, data from the lower temperature steps would represent material combusted from the exterior of a grain, whereas high temperature steps would represent material combusted from the core (*24*). In other words, for combustion of a single diamond, or crystals of uniform size, the type of information displayed in Fig. 3 (*25*) would repre-

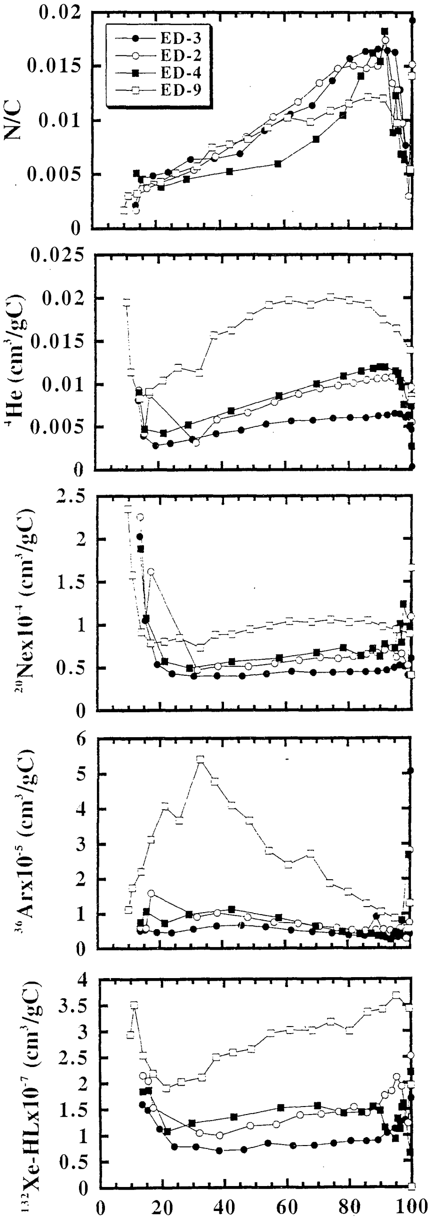

Fig. 3. Concentration profiles of nitrogen and noble gases obtained during stepped combustion of the grain size fractions. Because some carbon has already been lost in the pyrolysis steps, the plots do not commence at zero on the cumulative yield axis.

sent concentration profiles across the grain from the rim to the core. However for a heterogeneous mixed population, such as we are considering here, finer grains will become oxidized at lower temperatures than coarser grains, so the data in Fig. 3 can be interpreted as representing a grain size versus temperature effect.

The concentrations of noble gases do not remain constant as a function of temperature throughout the experiments; minor changes are observed. In the case of N this effect is more pronounced, with the highest N/C ratios seen for the latter steps in the combustion. These observations indicate that the noble gas and N locations are different within or between grains (or both). Note that within an individual residue, profiles for different noble gases are not always the same, hence the distribution of these species is also variable within the diamonds. The similarities in the ^{20}Ne and ^{132}Xe-HL profiles for ED-2, ED-3, and ED-4 suggest a common origin and location of these components. In contrast, the He profiles seem more variable, showing increasing concentrations toward higher temperatures, which might indicate that there could be another He component in addition to that related to Xe-HL. The ^{36}Ar profile for ED-9 is quite different from any other profile, suggesting that this species is the subject of some special effect.

The variations in isotopic composition of N and C versus temperature reached during stepped combustion of ED-2, ED-3, and ED-4 are similar (Fig. 4). The profile for ED-9 is different from the other three, in that δ^{15}N values of ~ -250 per mil are reached before 10% of the sample has been combusted. Irrespective of the differences, each sample has a small amount of N (δ^{15}N of $\sim$0 per mil) at the start of the extraction (atmospheric contamination), and thereafter the results demonstrate mixing between indigenous isotopically heavy and light components (δ^{15}N < -250 per mil and > -290 per mil down to -350 per mil, respectively). The proportion of the heavier component is highest in ED-2, ED-3, and ED-4.

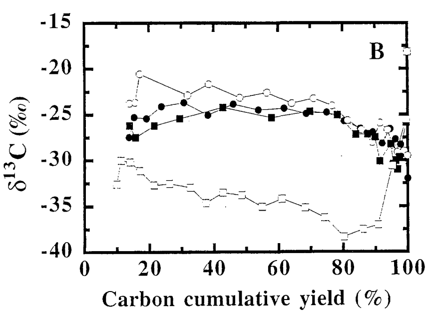

Fig. 4. Nitrogen (**A**) and carbon (**B**) isotope profiles observed during stepped combustion of the grain size fractions.

The C data (Fig. 4B) do not show such obvious internal isotope variations as those of N. The first 80% of the C released from ED-2, ED-3, and ED-4 during stepped combustion has a rather monotonous δ^{13}C of ~ -25 per mil. The final 20% shows a mixing between this low-temperature C and an isotopically lighter component, presumably from coarser grains (measured δ^{13}C values are down to ~ -30 per mil). Terrestrial organic contamination generally has δ^{13}C of ~ -25 per mil; however, it is improbable that much of the carbon in ED-2, ED-3, and ED-4 samples could be from such a provenance. Furthermore, all samples were exposed to highly corrosive oxidizing acids early in their handling that should have destroyed everything of an organic nature. However, to minimize handling losses, we did not reexpose the samples to acids after the ultracentrifugation, and so there is a possibility that some small quantities of contamination could have been added (we estimate <5% of total C).

For ED-9, δ^{13}C starts at ~ -30 per mil and trends down to ~ -38 per mil with increasing temperature. At the highest temperatures of the experiment, δ^{13}C begins to rise (up to -17 per mil), demonstrating the presence of an additional C component [possibly ^{13}C-enriched SiC (*4*)]. The results suggest that coarse grains in ED-9 are enriched in ^{12}C compared to the finer grains of ED-2, ED-3, and ED-4.

In summary, there is a certain correlation between diamond grain size on one hand and concentrations (except for nitrogen) and isotopic compositions on the other, for all minor and major components. To understand the origin of the diamonds in Efremovka, we need first to address the issue of why noble gas concentrations increase with increasing grain size while N does not. One explanation is that most of the N was incorporated during diamond growth, whereas the noble gases were subsequently added by implantation.

With respect to incorporating structural N into diamond, we can speculate that the mechanism does not depend on grain size, but instead is determined by the localized partial pressure of N or N-bearing molecules such as HCN (that is, at the time and place of diamond formation). This is compatible with a chemical vapor deposition (CVD) process, proposed as a mechanism of presolar diamond formation (*19*). Because diamond grains are so small, any ions impinging on the crystals after their formation, even at low implantation energy (a few electron volts per nucleon), will tend to pass straight through them. Assuming at least some energy spread, ions could potentially be captured, but the smaller the size of the individual grain, the lower the probability. Thus, the concentration of noble gases in a collection of diamond grains will depend mostly on two parameters: the energy distribution of primary ions (*26*) and the size distribution of the grains being irradiated. Qualitatively, the notion of formation followed by implantation is in agreement with the chemical evidence presented herein (*27*).

The processes described above are compatible with the hypothesis (*9, 10*) that diamonds condensed in the expanding He shell of a type II supernova and that Xe-H and Xe-L were subsequently implanted as energetic ions formed in the He and O shells, respectively. The variations in Xe isotopic composition measured between different grain size fractions imply different mixing ratios of normal Xe and Xe-H. In other words, normal Xe was probably implanted at different energy from that of Xe-H. This in turn suggests a separate event for the implantation of the normal Xe component; we speculate that this could occur some time after formation, when the diamonds were resident in the interstellar medium. Perhaps what we call "normal Xe" is a mixture of Xe from many sources with somewhat variable isotopic compositions. If so, and if the implantation energies of the "pure" components were different, it may be possible to resolve them by high-resolution grain size analysis. The same should also be true for the supernova ejecta such as Xe-HL and other associated noble gas components, if several different supernovae contributed to the diamond populations. In that case, it may be possible to discern variations in the Xe-H/Xe-L ratio and also subtle variations within Xe-H and Xe-L, resulting from differences in either primary neutron production (*8, 9*) or separation times of radioactive Xe precursors (*28*). The correlation of C and N isotopic compositions with grain size suggests the existence of an isotopic gradient during diamond growth (*11*). Alternatively, a contribution of implanted N and C with variable isotopic composition and implantation energy is possible. However, in this case, the source of the implanted N and C remains to be found (*29*).

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23. It is known from previous studies (*30*) that both the total carbon yield and the yield of carbon at pyrolysis depends on the amount of oxygen chemically adsorbed on diamond grains. This oxygen could derive from exposure to the atmosphere or from reagents used in sample preparation, and there is even a remote chance that it is extraterrestrial. Because the diamond grains are so small and therefore have high surface area, the amount of adsorbed oxygen is substantial, giving the maximum yield of carbon for the most pure diamond sample (that is, ~80%, which corresponds to ~15% of carbon yield at pyrolysis in the form of $CO + CO_2$). Three Efremovka samples (ED-2, ED-3, and ED-4) with similar and relatively heavy carbon isotopic composition ($\delta^{13}C \approx -26$ per mil) have similar total and pyrolysis carbon yields (Table 1) except for the total carbon yields for ED-4. The latter seems to be contaminated with a non-carbonaceous component. In contrast, sample ED-9, having substantially lighter carbon ($\delta^{13}C = -32.7$ per mil), also has considerably higher total and lower pyrolysis carbon yields. Apart from that, these data are also in agreement with ED-9 being the coarsest fraction.
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25. When considering N and noble gas abundances released by stepped combustion, it is necessary to normalize the yields of these species to the overall C content of each sample. This has been done for each step of the four extractions, and the results are presented as element-to-C ratios versus proportion of total C removed (Fig. 3).
26. We cannot exclude the possibility that the primary ion energies could be modified because of ion collisions with dust particles and gas, present along with diamonds in the place where implantation has occurred, making the ion energies just enough to stop within diamond grains.
27. An implantation mechanism was suggested earlier (*3*) on the basis of the relative abundance of ^{129}Xe in Xe-HL, which does not show any excess due to ^{129}I decay (as would be expected if Xe and I were trapped during diamond growth). In addition, the abundance of ^{4}He, ^{20}Ne, and ^{36}Ar in the individual fractions (Table 1) indicates that the smaller the grain size, the higher the relative concentration of lighter noble gases (that is, the $^{4}He/^{36}Ar$ and $^{20}Ne/^{36}Ar$ ratios decrease with increasing grain size). This is clearly not compatible with preferential noble gas losses from smaller grains (as may accompany postformational heating, for instance) but is in agreement with an implantation mechanism at which small, light ions have a shorter projected range (*31*).
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29. For implantation to have caused the C isotopic composition to have changed by 7 per mil between fine and coarse fractions (Table 1), we need to suggest a fluence of pure ^{12}C (or strongly enriched by ^{12}C) ions providing 7 atoms of ^{12}C per 1000 C atoms of diamond. Because of the difference in the diamond grain size, the effectiveness of implantation is relatively greater in the coarse grains. The maximum difference in relative concentration of implanted species observed in this study for noble gases is about a factor of 5 (see Table 1). A similar difference translated to the isotopes of C would result in the actual measured difference in δ^{13}C between fine and coarse grain size fractions at $^{12}C_{impl}/^{12}C_{diam} = 0.01$. In this case the calculated $^{12}C/^{4}He$ ratio in the ion flux would be ~10^3. Such a high ratio is predicted to exist in the O/Ne shell of a 25 M_o supernova (*32*) where a strong enrichment by ^{12}C is also predicted. This shell also contains a substantial fraction of ^{12}C of the star. However, there would need to be a mechanism that prevented implantation of He into diamonds from other shells (for instance, O/C, He/C, and He/N) containing relatively much more He than the O/Ne shell. Applying the same sort of logic to explain N isotope variations between the grain size fractions, we are faced with a more serious problem, as variations of δ^{15}N are an order of magnitude larger than that for δ^{13}C (Table 1). Both high $^{14}N/^{4}He$ and enrichment of ^{14}N would be required at the same time, and that is not predicted in any of the supernova shells (*32*).
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Biogeochemical Evidence for Dinoflagellate Ancestors in the Early Cambrian

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Dinoflagellates are single-celled organisms that reflect the ecological conditions in modern oceans and lakes. Ultrastructural data and molecular phylogeny suggest that they originated in the Neoproterozoic, yet dinoflagellate ancestors are classified only to the Middle Triassic (~240 million years ago). Examination of dinoflagellate-specific biological markers (dinosteranes and 4α-methyl-24-ethylcholestane) in concentrated microfossils with known morphology identified ancient dinoflagellate ancestors from the Early Cambrian (~520 million years ago).

Dinoflagellates are single-celled organisms, protists, that are found in most aquatic environments and form a major part of the modern plankton. Many genera are sensitive to such conditions as water salinity and nutrients, and some genera are characteristic of latitudinal oceanic temperature zones; hence, the geographic distributions of dinoflagellates can be important indicators of environmental conditions (*1*), not only for present-day environments but also for ancient ones. Fossilized dinoflagellate cysts are widespread in Mesozoic-Cenozoic sedimentary rocks (*2*). Here we examined certain morphotypes of segregated microfossils from Lower Cambrian formations for biological markers and determined that dinoflagellates originated much earlier, at least as early as the Early Cambrian.

Several lines of evidence have indicated that dinoflagellates originated in the Neoproterozoic (*3*). RNA molecular sequencing and examination of mitochondrial cristae of modern organisms (*4*) suggest that dinoflagellates are older than Foraminifera and Radiolaria, which have been found in Cambrian rocks.

Organic-walled, acid-resistant microfossils of uncertain biological affinities that are classified on the basis of their morphology (acritarchs) are widely distributed in sedimentary rocks from the Proterozoic and Phanerozoic. Some acritarchs resemble dinoflagellate cysts (*5, 6*), but they do not show paratabulation and they have excystments that are different from classical archeopyles of recognized Mesozoic and younger dinocysts. Many acritarch specimens have no excystment structure. However, most modern dinocysts reach sediments before germination (*7*), and some of these can fossilize without excystment structure formation. Some Ordovician acanthomorphic acritarchs have a double-wall structure (*8*) comparable with that of dinoflagellate cysts. Certain cysts of living dinoflagellates from the

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