Reports

Carbynes: Carriers of Primordial Noble Gases in Meteorites

Abstract. *Five carbynes (triply bonded allotropes of carbon) have been found by electron diffraction in the Allende and Murchison carbonaceous chondrites: carbon VI, VIII, X, XI, and (tentatively) XII. From the isotopic composition of the associated noble-gas components, it appears that the carbynes in Allende (C3V chondrite) are local condensates from the solar nebula, whereas at least two carbynes in Murchison (C2 chondrite) are of exotic, presolar origin. They may be dust grains that condensed in stellar envelopes and trapped isotopically anomalous matter from stellar nucleosynthesis.*

Among the noble-gas components in primitive meteorites, there are several whose isotopic composition cannot be explained by known solar-system processes. They are attributed either to speculative processes (such as fission of a superheavy element) or to presolar, stellar sources (*1–6*). To establish the true nature of these gas components, their carriers must be isolated and characterized. This is more easily said than done, because these carriers comprise only 0.1 to 1 percent of the meteorite and are fine-grained (0.01 to 10 μm) and often intergrown (*1, 3, 4*).

At least four of these carriers seem to be carbonaceous on the basis of direct or circumstantial evidence, but only one of them is a known material: the organic polymer comprising most of the carbon in C1 and C2 chondrites (*1, 7*). The other three do not match any of the known forms of carbon, and have therefore been designated by the noncommittal terms amorphous carbon, Cα, and Cβ (*1, 2*). Lewis *et al.* (*2*) suggested that Cα and Cβ might be carbynes, a proliferating series of carbon polymorphs containing triply bonded carbon (*8*). According to a phase diagram by Whittaker (*9*), carbynes are the stable low-pressure forms of carbon above 2600 K, which has led Webster (*10*) to suggest that carbynes rather than graphite dominate in stellar condensates and interstellar dust. Sclar and Squiller (*11*) had previously speculated that two carbynes—carbon VI and VII—might occur in C1 and C2 chondrites.

We have looked for carbynes by electron diffraction in three samples from the Allende (C3V) and Murchison (C2) carbonaceous chondrites. All samples were prepared by dissolving the meteorite in HCl-HF, and treating the 0.5 to 2 percent residue (chromite, spinel, carbonaceous matter) with additional reagents (*1, 4, 12*) to etch off ordinary gases, while leaving the anomalous gas components behind. The Allende BK sample was nearly pure carbon, whereas the Murchison 2C10 samples consisted mainly of spinel ($MgAl_2O_4$) and chromite ($FeCr_2O_4$), with smaller amounts of hibonite ($CaAl_{12}O_{19}$).

All three samples turned out to contain carbynes, which, according to their maximum lattice spacing on a *c*-axis pattern (d_{max}), more or less match five known carbynes: carbon VI, VIII, X, XI, and XII (Fig. 1).

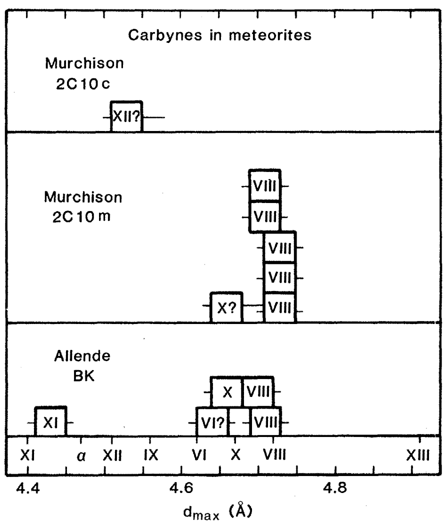

Fig. 1. Five carbynes are present in the Murchison and Allende meteorites, according to electron diffraction data. Identifications are based on the match of the observed d_{max} (on a *c*-axis pattern) with the values for known carbynes, as indicated on the abscissa (*8, 11, 28*); α = α-carbyne or chaoite). Where such identifications were ambiguous, owing to the error of the meteoritic values, they generally were checked by other criteria, such as radiation damage or transformation under the electron beam. Graphite, diamond, lonsdaleite, β-carbyne, and carbon VII are off scale to the left.

The Murchison carbyne grains were dense solids (~ 0.04 to 0.75 μm in size) of irregular, angular shape, often showing conchoidal fracture. The Allende grains were of similar size, but had a porous and loose structure (Fig. 2A). Only two faceted crystals, of typical carbyne morphology, were found; one of them (Fig. 2B) showed radiation damage and gave a rapidly fading diffraction pattern.

In the Murchison samples, most of the grains were inorganic; the seven points plotted in Fig. 1 represent all the carbyne grains that could be clearly identified among some 50 grains examined in the diffraction mode. The actual abundance of carbyne grains was probably somewhat higher, because we did not photograph several additional carbyne patterns that were confused by diffraction from neighboring grains. In Allende, on the other hand, many single-crystal carbyne patterns were seen, but only those likely to yield accurate data were photographed. A typical pattern for carbon VIII is shown in Fig. 2C.

The assignments to known carbynes (Fig. 1) vary in reliability. For Allende, where only the best patterns were chosen, it was possible to measure five orders of reflection, and the errors of d_{max} are correspondingly small (± 0.03 Å). Where the match was ambiguous, a clear choice could usually be made on the basis of radiation damage or heat-induced structural transformations caused by the 60-kV electron beam. For example, two Allende crystals of very similar d_{max} (4.64 and 4.66 Å), falling between CVI and CX, differed markedly in their response to the electron beam: the former reacted more slowly and yielded rhombohedral rather than hexagonal graphite. Formation of rhombohedral graphite from a carbyne is unprecedented, but the lower radiation sensitivity and d_{max} are suggestive of CVI. (However, the particle was less stable than normal CVI, transforming at 60 rather than 80 kV, and we therefore regard the identification as tentative.) Similarly, the particle of d_{max} = 4.43 Å fell between CXI and α-carbyne (chaoite), but its radiation sensitivity to 80-kV electrons was strongly suggestive of CXI.

For Murchison, the patterns were fewer and of poorer quality, measurable to only two to four orders of reflection. Most were based on slightly tilted crystals, and therefore gave somewhat too low d_{max} values. Still, only the "CXII" and "CX" particles at 4.53 and 4.66 Å

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remain ambiguous; the former could be α-carbyne, and the latter, CVIII.

Ion probe analysis of the Allende particles showed that they were very pure carbon, with only traces of Fe and Cr. The relative intensities of negative carbon ions showed the preponderance of even-numbered species characteristic of carbynes, with little if any graphitic carbon (*13*). The proportion of carbyne was estimated from the intensity ratio of monatomic and diatomic carbon (C_1/C_2), using pure graphite and one of the hard carbynes for reference. Three grains examined had carbyne contents of 91 ± 2, 80 ± 3, and 80 ± 3 percent, all averaged over the 20-μm diameter of the ion beam.

The ion beam produced a remarkable etch pattern on the initially smooth surface (Fig. 2D, right), showing the presence of two carbon forms of very different etch resistance (Fig. 2D, left). A stereo view of the etched region (Fig. 3) shows the more resistant of the two phases in high relief, separated by deep pits where the less resistant phase used to be.

Let us compare the noble-gas components of each sample with the observed carbyne distribution (Table 1). The isotopic ratios characteristic of each component are shown, as well as the previously postulated carriers.

Table 1. Noble-gas components and carriers in Murchison and Allende (*1*, *2*, *14*).

Component*	Diagnostic ratio	Carrier (*2*)	Allende BK	Murchison 2C10c	Murchison 2C10m
Ne-E(L)	$^{20}Ne/^{22}Ne \leq 0.01$	Cα	−	++	++
Ne-A2	$^{20}Ne/^{22}Ne \simeq 8.7$	C amorphous	+++	−	−
CCFXe	$^{136}Xe/^{132}Xe \gg 0.31$	C amorphous	+++	−	−
s-Xe	$^{130}Xe/^{132}Xe > 0.162$	Cβ	−	+	++
Carbon VI			+		
Carbon VIII			++		++
Carbon X			+		+
Carbon XI			+		
Carbon XII				+	

*Ne-E(L) is an apparently presolar component of very low $^{20}Ne/^{22}Ne$ ratio, probably derived from β^+ decay of ^{22}Na (*3*); Ne-A2 is ordinary "planetary" Ne, common in primitive meteorites and presumably derived from solar Ne ($^{20}Ne/^{22}Ne \simeq 13$) by mass fractionation (*1*, *6*, *24*); CCFXe (= carbonaceous chondrite fission Xe) is a controversial component enriched in the heavy isotopes that may be derived from fission of an extinct heavy element or from nucleosynthetic processes (*5*, *6*, *14*, *22*); and *s*-Xe is an apparently presolar component showing the signature of the *s*-process: high abundance of intermediate-mass isotopes 128 to 132, especially the even-numbered ones (*1*, *26*).

Allende. We are faced with an embarrassment of riches: four carbynes where only a single carrier, amorphous carbon, had been postulated. The sample indeed is nearly pure carbon, as confirmed by ion microprobe and neutron activation analysis (Cr = 0.27 ± 0.14 percent; Fe = 0.04 ± 0.02 percent), but on x-ray diffraction (XRD) it shows no evidence for amorphous (graphitic) carbon or other carbon polymorphs. Any such polymorph comprises less than 10 percent of the material, judging from the absence of lines or even diffuse features at the appropriate spacings. It is not surprising that carbynes were missed in previous XRD work (*1*, *14*), because XRD is rather insensitive for carbynes, especially when strong patterns from minerals of higher atomic number are present.

Taken at face value, the ion-etching pattern (Figs. 2D and 3) suggests that at least two of the four carbynes in Allende formed simultaneously, and hence probably share the same gas component. The interlocking, vermicular texture suggests that these two carbynes grew together in situ, but we cannot rule out the possibility that this texture is an artifact of sample preparation, caused by aggregation of thin films. Of course, only one carbyne can be thermodynamically stable at a given set of conditions, but carbynes seem to have an unusual ability to form and persist metastably. In six terrestrial graphites studied by Whittaker (*15*), at least two different carbynes have persisted side by side for $> 6 \times 10^7$ years.

We cannot yet tell whether all Allende carbynes contain the same gas component. Because Allende carbon occurs in two morphologies, surface coatings and spherical aggregates (*16*), some differences might be expected. But existing data shed no light on this question: density separations on Allende residues (*17*) did not take small enough cuts to separate individual carbynes, and stepped heating experiments (*18*) could not have resolved four additional phases, most of which transform to graphite on heating.

Allende carbon contains about 0.4 percent N (*19*), and at least some of it seems to occur as CN groups. The ion probe data showed peaks corresponding to CN^-, C_2N^-, C_3N^-, and C_5N^-, but not C_4N^-, confirming the more detailed mass spectrometric analysis of Hayatsu *et al.* (*20*). The presence of C_3N^- and C_5N^- is of interest, in the view of the prominence of cyanopolyacetylenes, $H-(C{\equiv}C)_n-CN$, among interstellar molecules (*21*).

Murchison. There is considerable overlap with Allende, all but one of the carbynes in Murchison (carbon XII) also being present in Allende (Fig. 1 and Table 1). The noble-gas data seem to re-

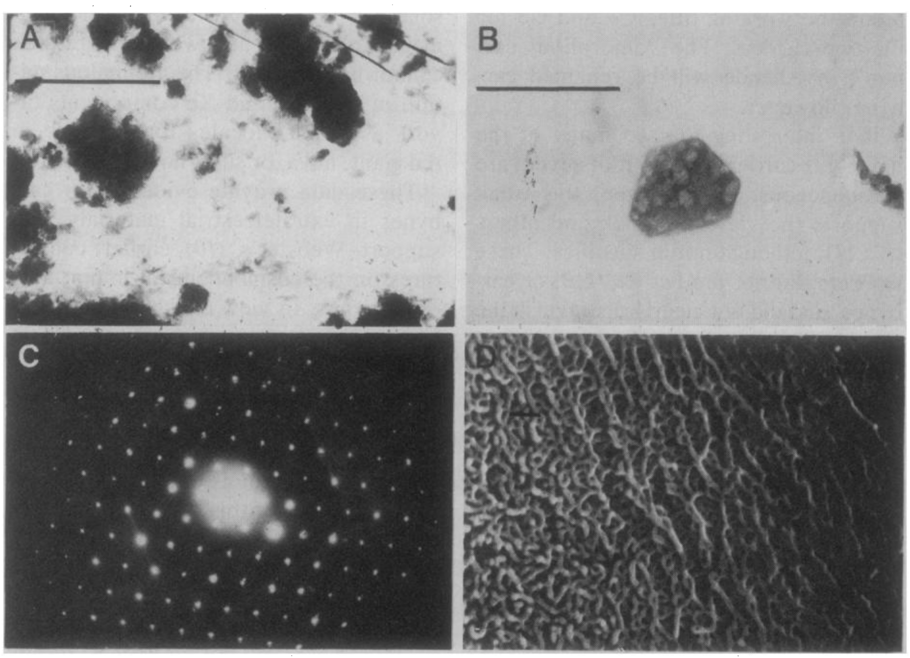

Fig. 2. Carbynes in Allende. Scale bars, 1 μm. (A) Typical irregular carbyne grains. (B) One of two euhedral carbyne crystals found. It shows radiation damage and gave a rapidly fading diffraction pattern. (C) Electron diffraction pattern of a carbon VIII grain. (D) Edge of ion-etched area. The initially smooth surface (right) develops a striking relief pattern (center and left) on ion bombardment, showing that two carbynes with greatly different etching rates are present.

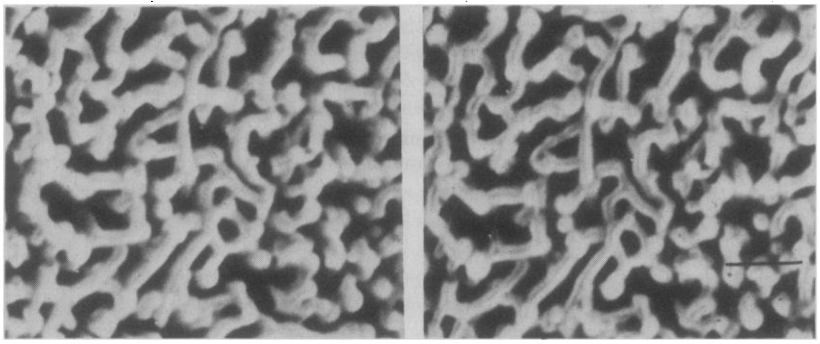

Fig. 3. Stereo view of ion-etched carbyne grain from Fig. 2D. The C_2/C_1 ratio rose slightly as etching progressed, showing that the more resistant phase has a higher carbyne content (91 versus 80 percent). Scale bar, 1 μm.

quire at least two such divergences, because two of the gas components [Ne-E(L) and *s*-process Xe] and their postulated carriers (Cα and Cβ) have been detected only in Murchison, not Allende. The overlap may reflect nothing more than incompleteness of the search for carbynes; indeed, even the two Murchison fractions have no carbynes in common, although both contain the same gas components (in somewhat different proportions): Ne-E as well as *s*-process Xe. But it may not be necessary to have different carriers for different gas components. Identical minerals condensing from two different gas phases would obviously trap two different gas components. Anyhow, until we get more comprehensive data, it would be premature to match up specific carbynes and gas components, and we therefore retain the working titles Cα and Cβ for the two carriers. The "amorphous carbon" in Allende will be renamed carbyne, however.

It is interesting that so many of the noble-gas carriers (four out of seven) are carbonaceous. To a degree, this trend supports the views of Frick and others (*17, 22*), although not in specifics. These workers did not predict Cα, Cβ, or carbynes, and did not clearly distinguish the organic polymer from Q (the principal carrier of ordinary planetary gases), regarding both, as well as "amorphous carbon," as variants of kerogen rather than elemental carbon. But now that carbynes have turned out to be present, it will be necessary to reassess earlier interpretations of Q, based on release temperature, oxidizability, and density (*4, 18*). It could be a carbyne rather than an inorganic mineral, although an organic polymer still seems unlikely.

Carbynes may also be present in other meteorite classes. One interesting candidate is a small, fibrous inclusion from the Abee E4 chondrite, which turned out to be 10- to 10^4-fold enriched in volatile elements such as Br, Hg, and Sb relative to nonvolatiles such as Fe, Ir, and Co (*23*).

At this early stage, very little can be said about the formation conditions of these carbynes. Three of the four Allende carbynes transform to graphite or (true) amorphous C on heating, and hence must have formed at low temperatures—presumably by reduction or disproportionation of CO (*20*). The place of origin of Allende carbynes probably was the solar nebula, judging from the prevalence of their Ne component, Ne-A2, in various meteorites (*1, 6, 24*). So abundant a component (~ 60 percent of the total Ne) can hardly be presolar.

The Murchison carbynes are thermally more stable, and hence may have formed as high-temperature condensates from a solar gas of C/O > 0.9 (*9, 25*), although a metastable origin at lower temperatures cannot be ruled out. The anomalous nature of their Ne and Xe components favors a presolar locale—for example, a red giant, nova, or supernova (*2, 26, 27*).

These data provide evidence for carbynes in extraterrestrial materials, and support Webster's (*10*) earlier conjectures on the cosmochemical importance of carbynes. In view of the evidence for carbynes in terrestrial graphites (*15*), it appears that carbynes can form and persist in a wide variety of environments, and play an important role in nature. It is remarkable that so abundant and so well-studied an element as carbon should still yield surprises of this sort.

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29. We thank L. Alaerts and J. Matsuda for preparation of the samples, K. Wrightsel for the scanning electron microscope work, and N. Marquez for the ion microprobe examination. This work was supported in part by NASA grant NGL-14-001-010.

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