Carbynes in Meteorites: Detection, Low-Temperature Origin, and Implications for Interstellar Molecules

Abstract. *Carbon from the Allende meteorite is not graphite but carbyne (triply bonded elemental carbon), inasmuch as on heating to 250° to 330°C it releases mainly triply bonded fragments:* $-(C{\equiv}C)_n-$, *with* $n = 1$ *to 5, and* $-(C{\equiv}C)_n-CN$, *with* $n = 1$ *to 3. Although carbynes have been known to form only by condensation of carbon vapor above 2600 K or by explosive shock of > 600 kilobars, it is found that they also form metastably by the reaction* $2CO \rightarrow CO_2 + C$ *(solid) at 300° to 400°C in the presence of a chromite catalyst. Such low-temperature formation by surface catalysis may be the dominant source of carbynes on the earth and in meteorites, and a major source of interstellar carbynes and cyanopolyacetylenes.*

It is a long-standing paradox in chemistry that carbon, the element with the richest chemistry, has only two elemental forms—diamond and graphite. This monotony has been relieved in recent years with the discovery of rhombohedral graphite, hexagonal diamond, and especially carbynes: a series of at least nine linear polymorphs containing $-(C{\equiv}C)-$ units (*1*, *2*). They fall between diamond and graphite in hardness and density, and are generally colorless.

The first two carbynes were discovered in strongly shocked natural materials: graphite-gneiss from the Ries meteorite crater (*1*) and diamond-graphite aggregates from ureilite meteorites (*3*). Others were made artificially by condensation of carbon vapor above 2600 K (*2*). But carbynes actually seem to be rather common, although well camouflaged, on the earth; Whittaker (*4*) found several carbynes in six terrestrial graphites that on superficial examination would have been dismissed as impure or disordered.

Carbynes may be still more prominent in extraterrestrial settings. According to a tentative phase diagram by Whittaker (*5*), carbynes rather than graphite are the stable low-pressure forms of carbon above 2600 K. Webster (*6*) therefore suggested that carbyne fibers, condensed from cool stars, comprise a major part of interstellar dust, and that the structurally similar interstellar cyanoacetylenes [$H-(C{\equiv}C)_n-CN$, with $n = 1$ to 4 (*7*)] might have formed in a similar way. Lewis *et al.* (*8*) proposed that carbynes might be the host phases of several isotopically anomalous noble-gas components in meteorites, including two suspected of having a presolar origin.

We have therefore looked for carbynes by mass spectrometry in a carbon-rich fraction from the Allende meteorite, prepared by dissolving ~ 99.5 percent of the meteorite in HCl-HF (*9*). The sample was pyrolyzed at increasing temperatures and examined by solid probe time-of-flight mass spectrometry (TOFMS), previously used for analysis of macromolecular material such as coal and meteoritic polymer (*10*), and high-resolution mass spectrometry (HRMS). A similar sample, BK, was studied by electron diffraction and ion microprobe by Whittaker *et al.* (*11*).

About 70 mass spectra were taken by TOFMS between 25° and 750°C. Contaminants, mainly hydrocarbons and reagents used in the preparation of the sample, came off from 25° to 180°C, but were gone by ~ 210°C. The sample itself began to degrade at 245° to 250°C, and gave prominent mass spectra at mass-to-charge ratios, *m*/*e*, between 12 and 132 from 250° to 330°C. The intensity declined sharply between 330° and 400°C, and remained near background levels from 400° to 700°C, except for a large C^+ peak at *m*/*e* 12 (*12*).

To obtain exact elemental compositions of the fragments seen by TOFMS, another portion of the sample was analyzed by HRMS, using a direct probe inlet technique. Representative results are shown in Table 1.

The most prominent feature is the (mainly even-numbered) polycarbon series, from C_1^+ to C_{10}^+. Neither graphite nor charcoal produces these fragments in significant abundance, but they would be expected for carbynes. Mass spectra of the smaller homologs of carbynes, polyynes, show a similar even-numbered predominance, reflecting the tendency of a $-C{\equiv}C-C{\equiv}C-$ chain to cleave at the single bond (*13*, *14*). But polyynes also give sizable molecular ion peaks, $H-(C{\equiv}C)_n-H^+$ (*14*), which are missing in the Allende spectra, and they have volatilization temperatures well below 250°C. Thus it seems that the C_{2n}^+ series comes from the degradation of macromolecules containing $-C{\equiv}C-$ units. The low degradation temperature implies that some C–C bonds joining the carbyne units are unusually weak—perhaps due to resonance stabilization of the carbyne fragments, as in the classic case of hexaphenylethane.

Next in abundance and number are the cyanoacetylenes, represented by a molecular ion, $H-(C{\equiv}C)_2-CN^+$, and three fragments, $(C{\equiv}C)_n-CN^+$ ($n = 1$ to 3). The presence of CN groups is not surprising because Allende carbon-chromite residues are known to have substantial nitrogen contents [1600 ppm (*15*)]. Less prominent are methyl- and phenylacetylenes. All may be derived from the terminal groups of carbyne chains. For valence reasons the carbyne chain must be terminated somehow, and

Table 1. Allende meteorite: mass spectrometric evidence for carbynes and cyanoacetylenes. Values are relative intensities.

m/*e*	Fragment	TOFMS 255°C	TOFMS 290°C	TOFMS 330°C	HRMS*
12	C	24	70	59	N.D.†
24‡	$C{\equiv}C$	4	15	10	N.D.
25‡	$C{\equiv}CH$	3	4	3	11
26	$C{\equiv}N$	19	27	21	18?
36‡	$C{\equiv}C-C$	4	6	3	N.D.
39‡	$C{\equiv}C-CH_3$	5	6	2	11
48‡	$(C{\equiv}C)_2$	38	100	21	43
50	$C{\equiv}C-CN$	24	25	15	14
52	$C{\equiv}C-C{=}O$	2	2	< 1	8
63‡	$(C{\equiv}C)_2-CH_3$	3	5	< 1	16?
72‡	$(C{\equiv}C)_3$	6	10	7	33
74	$(C{\equiv}C)_2-CN$	16	8	10	100
75	$H-(C{\equiv}C)_2-CN$	5	< 1	< 1	51
96	$(C{\equiv}C)_4$	22	6	4	12
98	$(C{\equiv}C)_3-CN$	6	5	2	55
101	$C{\equiv}C-C_6H_5$	5	8	< 1	13
105	$C_6H_5-C{=}O$	5	4	< 1	N.D.
120	$(C{\equiv}C)_5$	16	8	2	27

*Composite of spectra taken at 250°, 300°, 320°, and 340°C. Quantitative determination is rather difficult, and therefore the errors may be large. Differences between the two methods may be due to differences in sample handling, degradation methods, and sensitivity. †N.D., not determined. ‡Also seen in synthetic sample (see text).

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Table 2. Gas phase composition during synthesis of carbynes ($CO/H_2 = 1:1, P_0 = 2$ atm, chromite catalyst). Amounts are indicated as follows: +, trace; ++, moderately abundant; and +++, very abundant.

Temperature (°C)	Time (hours)	CO_2	H_2O	Alkanes			
				C_1	C_2	C_3	C_4
200	22	+	+	–	–	–	–
250	96	+	+	–	–	–	–
300	22	+++	+++	?	+	+	–
350	22	+++	++	+	+	+	+
400	96	+++	++	++	++	++	++*

*Also trace of C_5 and higher alkanes, benzene (?), and naphthalene (?). Moderate amounts of toluene, mono- and dimethylnaphthalene, mono- and dimethylindane, but no higher aromatics. At least 75 percent of the initial CO was still present at the end of the experiment.

by analogy with polyynes (*14*) one may expect much greater stabilization from large substituents ($-CN$, $-CH_3$, $-C_6H_5$) than from H. Two oxygenated species are also present in low abundance, and although they may be indigenous, we suspect that they are artifacts, generated by partial oxidation of triple bonds during the isolation procedure.

We cannot tell from our experiments what fraction of the sample consists of carbynes, because only a minor part volatilized; the major part remained as a black residue of carbon and chromite. However, ion microprobe as well as electron and x-ray diffraction data of Whittaker *et al.* (*11*) show that ≥ 80 percent of the Allende carbon was initially present as carbynes. Some of these carbynes readily graphitize on heating (*11*), and may have been the main source of the fragments seen.

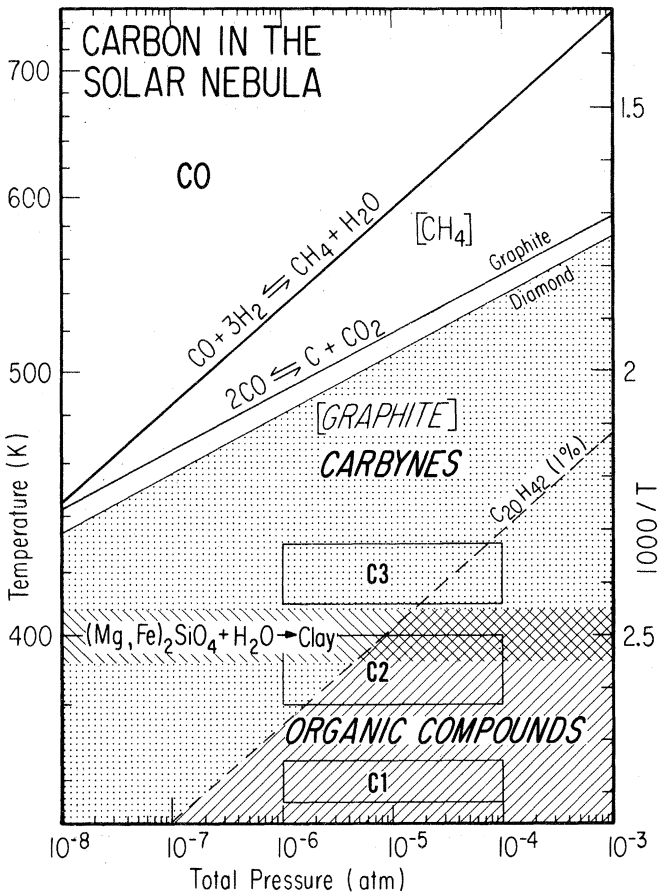

Fig. 1. Chemical state of carbon in the solar nebula. Solid lines give the temperatures at which 50 percent of the CO should have reacted according to the equilibrium shown (the 0.1 percent lines would be typically 100 to 200 K higher). In each field, principal stable products are shown in roman type and metastable products in italics; those that do not form for kinetic reasons are enclosed in brackets. For example, at 10^{-5} atm, 50 percent of the CO should have transformed to CH_4 at 590 K, but this reaction is very slow in the absence of catalysts and so CO may instead disproportionate to CO_2 and elemental carbon. This reaction should be 50 percent complete at 520 K. It yields carbynes rather than graphite, if a chromite catalyst is present. At 400 K, clays form from anhydrous silicates, catalyzing hydrogenation of CO to complex organic compounds (*23*). The dashed line shows the temperatures at which 1 percent of the CO transforms to a typical alkane, $C_{20}H_{42}$, under metastable conditions (the lines for most other alkanes, from C_3H_8 upward, are very similar). Chemical state of carbon in carbonaceous chondrites agrees with that predicted from their formation conditions (indicated by boxes), as inferred from isotopic fractionation of O and C, or abundances of volatile metals (*20, 24*). The C1 and C2 chondrites, having formed between 360 and 400 K, contain mainly organic compounds with only traces of carbynes (*11*). The C3 chondrites contain mainly elemental carbon, which, at least in the case of Allende, is present as carbynes rather than graphite.

Allende represents the first extraterrestrial occurrence of natural (as opposed to shock-produced) carbynes. That this identification has been so long delayed, despite the intensive study of Allende carbon by many authors, is further evidence for the elusiveness of carbynes. X-ray and electron diffraction of Allende carbon suggested "amorphous carbon" (*9, 16*) or "poorly crystalline graphite" (*17*), and although spark source mass spectrometry and differential thermal analysis (*18*) pointed to a "nongraphitic" nature, no positive identification had been obtained until now. In the light of the results reported here and by Whittaker *et al.* (*11*) and Whittaker's study of terrestrial graphites (*4*), it would seem necessary to reexamine natural occurrences of "amorphous carbon" as well as crystalline graphite to determine the actual abundance of carbynes on the earth.

What is the origin of Allende carbynes? They can hardly have formed as equilibrium condensates of carbon vapor, because the required conditions [> 2600 K, C/O > 0.9 (*5, 19*)] differ radically from those inferred for Allende matrix [~ 420 K, C/O < 0.9 (*20*)], which apparently formed in the solar nebula. Under equilibrium conditions, carbon in a hot solar gas occurs as CO, and on cooling yields methane, as well as graphite if the pressure, $P(H_2)$, is less than $10^{-7.6}$ atm (*21*):

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \quad (1)$$

$$CO + H_2 \rightarrow C(s) + H_2O \quad (2)$$

Estimated pressures in the solar nebula (~ 10^{-6} to 10^{-3} atm) are too high for equilibrium formation of graphite. But although methane should be the equilibrium product under these conditions (heavy line in Fig. 1), the reaction rate is very low (*22, 23*), and so nothing happens until the temperature has fallen enough (~ 400 K) for catalytically active clays to form by the hydration of ferromagnesian silicates (*23*). At that point, the rate of hydrogenation rises > 10^8 times (*23*). But at this low temperature many complex organic compounds are stable relative to CO, and for mechanistic reasons, they form metastably in preference to methane, by a Fischer-Tropsch reaction (*23*):

$$20\,CO + 41\,H_2 \rightarrow C_{20}H_{42} + 20\,H_2O \quad (3)$$

The dashed line labeled $C_{20}H_{42}$ in Fig. 1 corresponds to 1 percent conversion of CO by reaction 3. Of course, such conversion is feasible only when clay minerals are present, and so the approximate formation region for organic compounds is the hatched trapezoidal field at the bottom (Fig. 1), bounded by the clay formation threshold at ~ 400 K and the $C_{20}H_{42}$ line. The formation temperatures of carbonaceous chondrites, as determined by O- or C-isotope fractionations or abundances of volatile metals (*20, 23, 24*), fit well in this picture. The C1 and C2 chondrites, which contain clays and organic compounds, fall within the field of organic compounds, whereas C3 chondrites such as Allende, which lack both but have elemental carbon, fall above this field.

In principle, elemental carbon also could form metastably from CO. Lewis *et al.* (*25*) proposed two specific reactions for the formation of Allende carbon, involving disproportionation or reduction of CO

$$2\,CO \rightarrow CO_2 + C(s) \qquad (4)$$

$$Fe(s) + 2Cr(s) + 4CO \rightarrow FeCr_2O_4(s) + 4\,C(s) \qquad (5)$$

Let us consider reaction 4, as the more general of the two. [Reaction 5, designed to explain the carriers of noble gases in Allende, will be discussed elsewhere (*26*).] This reaction becomes thermodynamically feasible at rather high temperatures, well above the clay formation threshold at 400 K (50 percent conversion at the "Graphite" line in Fig. 1; 0.1 percent conversion about 90 to 160 K higher). Two points remain to be checked, however: first, that this reaction dominates over the hydrogenation of CO when only poor catalysts (anhydrous minerals) are present, and second, that it yields carbynes rather than graphite (*27*).

In an early attempt to check the first point (*28*), we carried out reaction 4 in competition with reactions 1 and 3 by heating 150 ml of a 1:1 mixture of CO and H_2 in a silica tube (initial pressure, 2 atm) with 297 mg of terrestrial chromite. The gas phase was examined periodically by TOFMS (Table 2). Up to 400°C, CO_2 strongly dominated over hydrocarbons, indicating that CO indeed mainly disproportionates rather than hydrogenates under these conditions. Both reactions are very slow, however, and left more than 75 percent of the CO unreacted.

After the reaction, the catalyst was extracted with benzene-methanol (3:1) and ether. The extracts gave only a trace of organic matter. The residue (C = 1.16 percent, corresponding to 4.7 percent of the initial C in the system) was examined by TOFMS over the temperature range 25° to 680°C. Between 110° and 215°C, small amounts of aliphatic (C_2 to C_8) and aromatic hydrocarbons were seen, apparently degradation products or strongly adsorbed contaminants. Between 240° and 290°C, sizable peaks appeared at m/e 24, 25, 36, 39, 48, 63, and 72. These peaks, marked by ‡ in Table 1, remained uninterpreted in the original work, but now that Allende carbyne data are available for comparison, it is clear that they correspond to essentially all the triply bonded C and CH species in Allende up to mass 72, and appear in the same temperature range. Unfortunately, the sample was too small for analysis by HRMS. Nitrogen-containing species were absent, of course, because no N had been included in the initial gas mixture.

These results show that the disproportionation of CO is indeed faster than hydrogenation when chromite is the only catalyst present, and that carbyne rather than graphite forms under these conditions. To be sure, there are flaws in this experiment: chromite alone was used instead of the complete mineral assemblage of the meteorite, $P(H_2)$ and CO/H_2 were 10^5 and 10^3 times higher than those of the solar nebula, the mixture was heated rather than cooled, there was no NH_3 in the system, and so on. But some of these points have already been checked in earlier work: for instance, use of a complete chondrite as catalyst, or CO/H_2 ratios approaching the solar value (*23*).

In any event, this experiment shows that carbynes can indeed form metastably at low temperatures, by disproportionation of CO. It seems likely that such a process in the solar nebula produced the carbynes in Allende. Perhaps carbynes formed in this manner are also responsible for the C_2 and C_3 bands in comet spectra, whose parent molecules have thus far remained unidentified (*29*).

These results also have obvious implications for interstellar molecules. We showed in 1974 (*30*) that a Fischer-Tropsch reaction on a clay catalyst made essentially all the interstellar molecules then known and a number of others, six of which have since then been discovered in interstellar space (*31*). The only significant discrepancy has arisen for cyanopolyacetylenes, $H{-}(C{\equiv}C)_nCN$, which have been seen up to $n = 4$ in interstellar space (*7*), but only up to $n = 1$ in the syntheses. An obvious excuse is the much higher pressure in the laboratory experiments, which strongly favors polymerization of reactive molecules such as cyanoacetylenes (*30*). The present study certainly supports this idea: the fragments released from Allende (Table 1) and the synthetic sample apparently are not single molecules, but degradation products of a polymeric material.

A further argument for a surface-catalytic origin of interstellar cyanoacetylenes (*30, 32*) is the slow decline in abundance of successive homologs: on the average, 0.38 times per C_2 unit (*7*) or 0.62 times per C atom, which is within the observed range of 0.6 to 0.9 for the Fischer-Tropsch reaction (*30*). It seems doubtful that gas phase mechanisms, such as association or ion-molecule reactions, can make such molecules. Although several ingenious mechanisms have been proposed (*33*), none has convincingly solved the basic problem: how to build large, hydrogen-poor molecules in a medium where the H/C ratio is ~ 10^3.

Of course, the low-temperature, metastable formation path emphasized in this report is only one alternative for the formation of carbynes and cyanopolyacetylenes; the other is equilibrium condensation from a carbon-rich gas above 2600 K (*5, 34*). But the latter may be hard to achieve in cool stars, as their carbon condensation temperatures generally are below 2600 K (*35*), where carbynes are unstable. And kinetic arguments show that the major species at these lower temperatures will not be elemental carbon, but highly unsaturated molecules, such as C_2H or C_4H_2 (*36*). Conceivably these may react further to yield carbynes and cyanoacetylenes as metastable products, by gas phase or grain-catalyzed reactions. [For interstellar molecules, condensation and/or polymerization on dust grains may be necessary soon after formation, to protect them from the star's radiation field (*37*).] Apparently, equilibrium formation of carbynes is hard to achieve in nature. Thus metastable formation mechanisms may be the principal source of interstellar polycyanoacetylenes, as well as meteoritic and terrestrial carbynes.

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Radioactive Waste Storage Materials: Their α-Recoil Aging

Abstract. *Ion implantation experiments suggest that the accumulation of α-recoil damage in radioactive waste storage materials, which behave like solid-state track detectors, plays a drastic role in their long-term degradation. The understanding of α-recoil "aging," overlooked in earlier studies, offers new guidelines for improving waste storage conditions.*

The leach resistance of solidified radioactive waste materials in groundwaters is often invoked as a critical factor for the long-term isolation of high-level radioactive wastes in the environment (*1*). Many phenomena influence leach resistance. This work is concerned with the effects of radiation on the chemical reactivity of solid waste glasses (*2*).

In earlier work designed to evaluate the importance of irradiation effects, the role of α, β, and γ radiation was investigated primarily by loading short-lived radionuclides into the material under evaluation. The experiments simulated in a few years the radiation damage that would occur in the high-level waste form in ~ 1000 years (*3*). Results were reported showing that α, β, and γ radiation do not markedly decrease the materials' leach resistance (*4*). In this report we argue that these simulation experiments clearly overlooked the drastic effects due to heavy recoils emitted during the α-decay of actinide elements (α-recoils) that suddenly appear after ~ 2000 years of storage.

The new consideration underlying our work stems from the realization that most storage materials that have been investigated so far (glasses, ceramics, cements) also register particle tracks, like dielectric minerals exemplified by mica. When such materials are used for the storage of high-level radioactive wastes, most of the damage should result from the accumulation of the very short damage paths of α-recoils. This premise, which neglects the contribution of α, β, and γ radiation, is indeed supported by both experimental observations (*5*) and the predictions of our new model of etchable tracks in dielectric minerals (*6*). Consequently, the alteration of the bulk properties of the α-recoil–irradiated material can be described in terms of the stability of α-recoil damage paths against various environmental parameters. Our predictions are based on our new track model and the results of ion implantation experiments.

These experiments may be schematically described as follows.

1) Over the storage periods of interest (~ 100,000 years), actinide atoms, trapped in the storage material, decay by emitting a single low-energy ($E \sim 0.5$ keV per atomic mass unit), heavy (mass ~ 240 amu) α recoil. This triggers an "internal" ion implantation of the storage material, which should be well simulated by an external beam of 0.5 keV/amu ^{238}U ions. However, in the present work we used lead ions of higher energy ($E \sim 1$ keV/amu). Indeed, these lead ions are much more easily accelerated than uranium nuclei, and we have verified that the increased incident ion energy affects only the depth of the implanted layers and not their etching rates.

2) A polished section of the material under evaluation is covered with an electron microscope grid and then exposed to the beam of lead ions, thus delineating a periodic succession of irradiated and nonirradiated areas. The irradiated areas extending up to a depth of ~ 500 Å (Fig. 1), should be similar to an internal ultrathin slice of the real storage material, where waste elements are homogeneously dispersed. By varying the incident ion fluence (Φ_i) from 10^{10} up to 10^{14} ion cm^{-2}, storage periods (T_s) ranging from 1 to 10^6 years can be continuously simulated (*3*).

3) After a given chemical etching, one can measure depth differences between the two types of areas with an accuracy of ~ 10 Å by probing the etched surface with a diamond stylus device (Fig. 1) and averaging the measurements for a large number of individual areas. These depth differences directly scale the increase in the chemical reactivity of the irradiated material, $\Delta v^* = v^* - v_0$, where v^* and v_0 are the etching rates of the irradiated and nonirradiated material, respectively. The variation in Δv^* can be investigated as a function of several parameters (for example, Φ_i or leaching conditions), that define specific storage conditions.

4) One can then evaluate the variations of v_0 with the leaching conditions by observing with a high-voltage electron microscope the shrinking of micrometer-sized crushed grains or glass fibers, or both, upon chemical etching.

In this work we applied this microscopic approach to three types of glasses: (i) "low" silica (64 percent SiO_2) borate glass, similar to a type already in use; (ii) "intermediate" silica (75 percent SiO_2) glass; and (iii) "high" silica (100 percent SiO_2) glass. The last two of these types of glasses have not as yet been