

## CARBYNES IN CARBONACEOUS CHONDRITES: A CAUTIONARY COMMENT

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An interesting controversy has developed recently concerning the structural form of the carbon in carbonaceous chondrites. Whittaker et al. [1] reported that  $\geq 80\%$  of the carbon in a carbon-rich acid-residue from Allende is in the form of carbynes, a series of polymorphs of elemental carbon based on a chain structure with alternating single and triple bonds. Carbynes were also identified in Murchison. However, observations made by Smith and Buseck [2,3] indicate that the carbon in an Allende acid-residue is predominantly a poorly-crystalline graphite.

Carbynes are reported to be carriers of isotopically-anomalous noble gases in carbonaceous chondrites [1], and have been suggested as possible constituents of the interstellar dust [4], the latter theory gaining support from the identification of carbyne in meteorites. In view of these proposed roles for carbyne it is clearly of great importance that the above controversy be resolved. In the present paper we attempt to put this problem into perspective, and we describe some relevant transmission electron microscope (TEM) observations of supposed carbyne grains from glacier microspherules. We also suggest methods by which the TEM may be used to confirm or refute other identifications of carbyne, and we briefly indicate some fundamental questions concerning the nature of carbynes.

Carbon in Allende Whittaker et al.'s [1] identification of carbyne was based on electron diffraction and ion-probe observations. Four carbyne polymorphs were identified by their (110) d-spacing in [0001] hexagonal diffraction patterns. Negative-ion spectra produced in the ion-probe showed a predominance of even-numbered carbon species, a feature reported to be characteristic of carbyne [5]. The identification of graphitic carbon by Smith and Buseck [2,3] was based on high-resolution transmission electron microscopy (HRTEM) observations, which showed a tangled aggregate of crystallites with a lattice-fringe spacing of 3.4-3.9 Å; very similar HRTEM images have previously been published for poorly-ordered graphite produced in the laboratory [6].

Although it would perhaps be possible to reconcile the ion-probe and HRTEM observations by postulating a carbyne-graphite intermediate, there remains a fundamental discrepancy between the electron microscope observations of the two groups: in our study we did not observe any carbon grains that give the hexagonal diffraction patterns characteristic of carbyne. (The small fraction of thin hexagonal flakes that we reported as possible carbynes [2,3] has now been shown by energy-dispersive X-ray spectrometry (EDS) to be kaolinite.) This discrepancy cannot be due to differences in the preparation of the acid-residues as we have now examined the same sample, BK, that was described by Whittaker et al. [1], and we found no carbynes.

Carbynes from glacier spherules Herr et al. [7] reported that certain glassy spherules found in glacier ice contain carbynes. We examined some of this material on two TEM grids provided by A.G. Whittaker, with the aim of familiarising ourselves with the appearance of carbynes. We evaporated gold onto the specimens to provide an internal standard for electron diffraction. The

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chemical compositions of possible carbyne grains were checked qualitatively by EDS.

Two grains considered by Whittaker [8] to be the carbyne carbon VIII ( $d_{110}=4.55 \text{ \AA}$  [9]) were relocated and shown to be talc ( $d_{020}=4.58 \text{ \AA}$ ): electron diffraction results ( $d_{020}=4.59 \pm .02 \text{ \AA}$ ) and EDS spectra are both consistent with this identification. In a search of one of the two TEM grids, we examined 22 more grains that give hexagonal diffraction patterns. Of these grains, 14 were found to be talc, 6 kaolinite, 1 chlorite and 1 biotite; all grains that give hexagonal diffraction patterns proved to be sheet silicate minerals. This TEM grid had been prepared from a glacier spherule shown to be rather pure carbon [8], but the chemistry of individual grains cannot be inferred reliably from the bulk analysis.

Pitfalls in carbyne identification The results described above clearly demonstrate the possibility of mistaking sheet silicates for carbynes in TEM studies. Although most sheet silicates have monoclinic crystal symmetry (kaolinite is triclinic), they give rise to accurately hexagonal diffraction patterns when the electron beam is perpendicular to the cleavage plane [10]; this is the most likely orientation for grains dispersed on a carbon TEM support film. The d-spacing obtained from such patterns corresponds to  $d_{020}$  for the particular sheet silicate and there is considerable overlap between these values and published values for  $d_{110}$  of carbynes.

Since we have not had an opportunity to examine Whittaker et al.'s Allende TEM grids, we cannot offer an explanation for the difference between Whittaker et al.'s observations and our own; it certainly seems unlikely that the  $\geq 80\%$  carbyne reported in [1] could result from contamination of the acid-residue by sheet silicates. However, the figure of 80% was obtained from the ion-probe data rather than electron diffraction; apparently only five carbyne grains were identified by electron diffraction. We therefore feel that further tests are needed to eliminate the possibility that these carbyne grains could be contaminants.

Two precautions should be taken when identifying carbynes by means of TEM: (i) An internal diffraction standard should be used to give the greatest possible accuracy in measuring d-spacings, and (ii) EDS spectra should be recorded from individual grains to eliminate the possibility of confusion with sheet silicates.

Carbynes: some more general problems Although carbynes were first described in 1967 [11], their structure, and conditions of formation are as yet poorly understood. The following points require further investigation:

(i) Kasatochkin et al. [11] suggested a structure for carbyne in which the chains of carbon atoms run parallel to the crystallographic  $c$  axis; this structure does not appear to be consistent with the reported flake-like morphology [12], which suggests a sheet structure.

(ii) Whittaker [9] reported that eight carbyne polymorphs may be distinguished by their  $a$  cell parameters; the structural relationships between these polymorphs are not yet understood.

(iii) Nemoitin et al. [13] recently questioned the very existence of triple-bonded allotropes of carbon. These authors found that some of the X-ray reflections attributed to carbyne forms are found in graphite samples treated at

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a pressure of 10 kb (cold), and suggested that the carbynes have a modified graphite structure rather than a chain structure.

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