Reports

Graphitic Carbon in the Allende Meteorite: A Microstructural Study

Abstract. *High-resolution transmission electron microscopy shows that carbon in the Allende carbonaceous chondrite meteorite is predominantly a poorly crystalline graphite. Such material is of interest as an important carrier of the isotopically anomalous noble gases found in carbonaceous chondrites.*

During the past 10 years there has been much interest in the identification of the carrier phases of noble gases in carbonaceous chondrites. These gases include a "planetary" component, systematically depleted in the lighter noble gases, that is considered to have been trapped in the early stages of condensation of the solar nebula (*1*). It also seems likely from isotopic studies of the noble gases that their hosts include presolar dust grains (*2*). Clearly, the identification of these carrier phases can provide important information on conditions in the early solar system. The bulk of the noble gas content resides in the fine-grained residue obtained after dissolving the meteorite in concentrated HF and HCl (*3*). This residue typically comprises < 0.5 percent of the meteorite and contains ~ 50 percent of the trapped noble gases. Recent efforts have concentrated on the identification of the mineral phases in these carbon-rich "acid residues."

A group at the University of Chicago has reported that the bulk of the gas is contained in a poorly characterized phase, Q, operationally defined by its solubility in oxidizing acids and tentatively identified as an iron-nickel-chromium sulfide (*4*). They also reported that smaller, isotopically different components are present in chromite and amorphous carbon. A group at the University of California, Berkeley (*5, 6*), regards Q, the principal carrier, as carbonaceous and also disputes the role of chromite as a gas carrier. More recently the Chicago group has postulated two additional carbonaceous carriers for two further, isotopically distinct noble gas components (*7*).

Despite the clear importance of the carbon in these residues as a noble-gas carrier, there is no consensus of opinion on its structural form. Carbon from the Allende carbonaceous chondrite has been described as amorphous on the basis of x-ray diffraction (XRD) evidence (*8*) and an electron microscope study (50-Å resolution) (*9*), or as poorly crystalline graphite on the basis of electron diffraction work (*10*). Recently it was reported that ≥ 80 percent of the Allende carbon is in the form of carbynes, a series of polymorphs based on a triply bonded chain structure (*11, 12*); carbynes were also reported to be present in the Murchison carbonaceous chondrite (*11*).

We describe here high-resolution transmission electron microscopy (HRTEM) observations of the carbonaceous material in a density-separated suite of Allende acid residues (*13*). This technique has been used to characterize various morphological forms of synthetic and natural terrestrial carbon (*14*). The capability of electron microscopes to resolve the 3.4-Å spacing of the basal planes in graphite permits a detailed description to be made of the structure of partially graphitized carbon; this proved to be of great use in the present study.

We also examined a series of HNO_3-etched residues (*15*) for possible changes in the carbon microstructure. This etching procedure is known to destroy the principal gas-bearing phase Q.

Samples were dispersed in acetone, with ultrasonic agitation, and one or two drops of the resulting suspension were pipetted onto perforated amorphous carbon support films. Electron microscope images were recorded only from areas that project over holes in the support film.

High-resolution images of the carbon (Fig. 1) show that it consists of a tangled aggregate of somewhat fibrous crystallites, with a prominent lattice fringe spacing of 3.4 to 3.9 Å. This indicates that the material is a poorly ordered graphite, the lattice fringes corresponding to the (002) basal planes of the graphite structure. In most instances these lattice fringes can be traced in the images for no more than 150 Å. However, their true lengths are probably greater since lattice fringes can only be observed where the graphitic basal planes are almost or exactly parallel to the microscope beam axis. A few crystallites were found of rather greater extent, up to a maximum of 1000 Å.

Most of the graphitic crystallites are five fringes or fewer in width, although examples up to 24 fringes were found. The fringe spacings in the graphite were measured to an accuracy of ± 2 percent or better, the error being largely due to the difficulty of measuring a limited number of fringes on a micrograph. Lattice fringes are abundant in HRTEM images of the Allende residue carbon, an indication that this carbon is predominantly crystalline rather than amorphous.

We used two techniques in a search for carbynes in the Allende residues. First, we examined samples at low magnification, looking for grains with the characteristic thin hexagonal flake morphology that has been reported in transmission electron microscope studies of carbynes (*16*). Second, since Whittaker *et al.* (*11*) reported that only a small fraction of the carbyne grains in their Allende residue displayed this morphology, we searched in diffraction space, that is, by translating the specimen with the microscope set to form a diffraction pattern from an area ~ 0.5 μm in diameter. Since the identification of the various carbyne polymorphs depends on accurate measurement of their crystal lattice parameters, we used evaporated gold on the carbon support film for an internal diffraction standard.

We found possible carbyne grains in only one of the six density separates. These grains were readily located either by imaging or by diffraction, and all carbyne-type diffraction patterns could be correlated with euhedral to subhedral hexagonal grains in the image. Figure 2 shows a typical example of one of these grains. All these crystals have a principal interplanar spacing (*d*-spacing) in the hexagonal diffraction pattern of 4.44 ± 0.02 Å, which corresponds to the (110) *d*-spacing of α-carbyne [4.46 Å (*17*)] or possibly chaoite, another carbyne polymorph [4.47 Å (*18*)]. However, since all these flakes lie close to the plane of the carbon support film, it was not possible to measure their *c* cell parameters; for this reason, and in the absence of any chemical data, we regard the identification of carbyne as tentative.

Although it is difficult to estimate volume fractions of phases in dispersed samples, the carbyne-like grains certainly constitute less than 5 percent of the density fraction in which they occur. This density fraction itself constitutes

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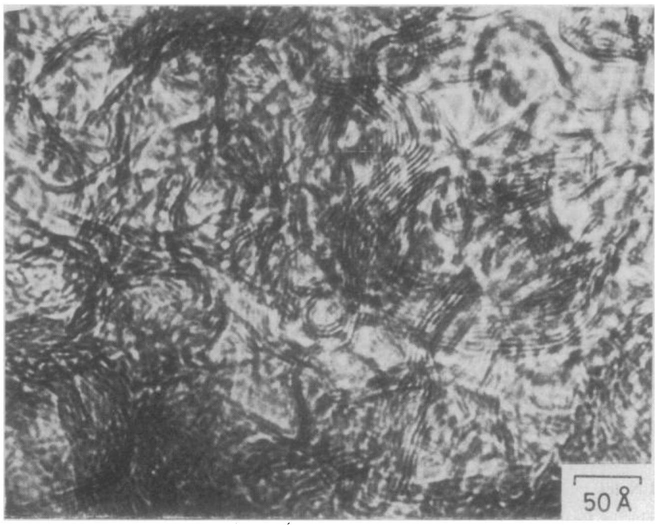
only 40 percent of the initial HF-HCl residue; thus we can set an upper limit of ~ 2 percent on the carbyne content of the initial unseparated residue. Our results thus differ significantly from those of Whittaker *et al.* (*11*), who identified four carbynes, comprising ≥ 80 percent of a nearly pure carbon residue from Allende.

Although it has been reported that some carbynes are susceptible to damage from the electron beam (*11*), this cannot account for the low incidence of carbyne-like material observed in our samples. When searching for carbynes, we defocused the electron beam to cover a wide area, which resulted in an extremely low current density at the specimen. Furthermore, we did not observe amorphous pseudomorphs after carbyne or the hexagonal or rhombohedral graphite crystals that have been reported as transformation products of carbyne (*11*).

Significant changes in the microstructure of the carbon were observed in the sample etched in fuming HNO_3. Much of the carbon appears to be amorphous, although a few graphitic crystallites similar to those of the unetched residues were present. We also observed graphitic particles with a concentric structure, either approximately circular or polygonal, about 100 to 500 Å in diameter (Fig. 3, a and b). The lattice fringe spacing of these particles is 3.4 Å, corresponding to that of partially graphitized carbon (*19*). The graphite basal planes in these particles essentially form a series of concentric cylinders (or prisms in the case of the polygonal type), although extra incomplete layers are found that terminate in dislocations. These crystallites are apparently disk-shaped with thicknesses of < 100 Å, rather than elongated, since crossed fringe patterns are readily observed where adjacent grains overlap.

The imaging of lattice fringes (spacings of 3.4 to 3.9 Å) in the Allende residue carbon clearly demonstrates that it is not amorphous, in contrast to previous XRD results. Very similar HRTEM images have been presented by Ban *et al.* (*20*) for carbonized polyvinylidene chloride (PVDC). The structure that these investigators proposed to account for such images is shown in Fig. 4. It consists of intertwined crystallites comprising ribbon-shaped aggregates of graphitic basal planes. These crystallites are interlinked to form a complex three-dimensional



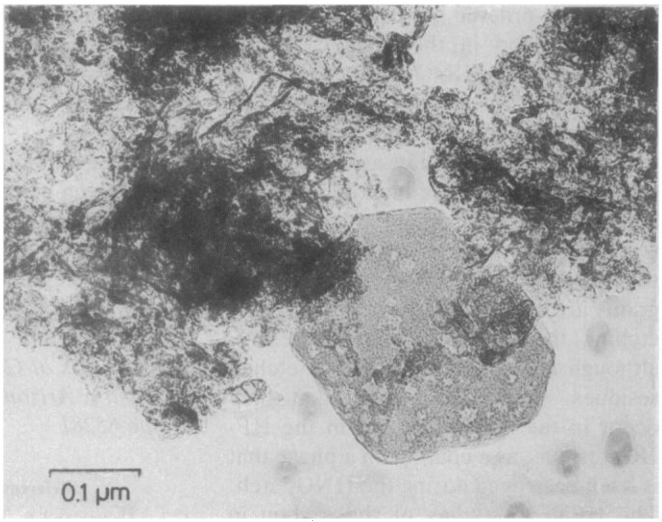


Fig. 1 (left). Typical high-resolution transmission electron microscope (HRTEM) image of carbon from an Allende acid residue. The crystal lattice fringes have spacings of 3.4 to 3.9 Å, corresponding to the interlayer spacing of graphitic carbon. Fig. 2 (right). Electron micrograph of a possible carbyne, showing the hexagonal shape characteristic of such grains. The surrounding material, which appears amorphous in this low-magnification image, shows graphitic crystal lattice fringes in HRTEM images.

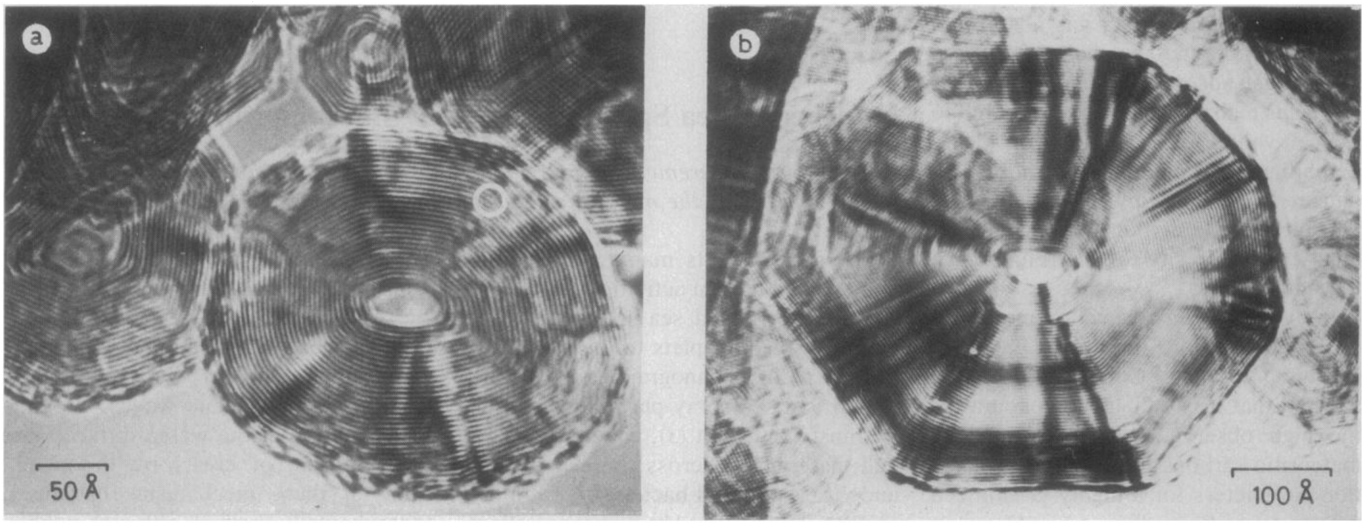


Fig. 3. (a and b) HRTEM images of graphitic crystallites with a concentric structure, found in a residue sample that had been etched in fuming HNO_3. The circle in (a) encloses a dislocation, indicated by the termination of a lattice fringe.

structure. The HRTEM images described here suggest that this structure is also appropriate to the Allende residue carbon.

The HF-HCl residues have been severely processed relative to the original carbon in the meteorite; this processing could have affected the carbon microstructures. For this reason we are now commencing a study of the carbon in situ in the meteorite. Preliminary results indicate the presence of graphitic carbon, similar in appearance to that in the acid residues, occurring interstitially to the silicate grains. This observation is consistent with the results of Green *et al.* (*10*), who reported poorly crystalline graphite located at grain boundaries in Allende. Thus it appears likely that the microstructure of at least some of the carbon is not affected by the HF-HCl treatment.

The well-ordered concentric graphitic particles found in the residue sample etched in fuming HNO_3 (Fig. 3) provide an interesting problem of interpretation, since such grains were not seen in any unetched samples. They are irregularly distributed in the etched material, and so it is difficult to estimate their volume fraction, but they appear to constitute several percent of this sample. If these grains are not created during the HNO_3 etching, then they must also be present, although not observed, in the unetched residues. One possibility is that they occur in the meteorite, and in the HF-HCl residue, as a coating on a phase that is itself destroyed during the HNO_3 etch. The HRTEM studies of the carbon in situ in the meteorite may shed further light on this matter.

If poorly graphitized carbon such as carbonized PVDC is an approximate model for the Allende residue carbon, then it is interesting that such materials have an extremely high gas adsorption capacity (*21*). The specific surface area for nitrogen adsorption in PVDC carbons can be as high as 1400 m^2/g, compared to typical values of < 1 m^2/g for highly graphitized carbons such as those produced from polyvinyl chloride. The Allende residue carbon thus provides a highly plausible site for the retention of the noble gases.

In discussing an adsorption model for the incorporation of noble gases in graphitic carbon, Göbel *et al.* (*22*) showed that it is difficult to account for the high observed gas abundances in meteoritic carbons by using the adsorption parameters for a highly graphitized carbon (specific surface area, 13 m^2/g). This problem is clearly reduced if the specific surface area is two orders of magnitude greater, as seems likely for the Allende carbon. However, simple physical adsorption alone cannot account for the highest release temperatures reported for the noble gases in carbonaceous chondrite acid residues (*5*, *23*); it is necessary to appeal also to a more powerful form of binding, such as solution or occlusion within growing crystallites.

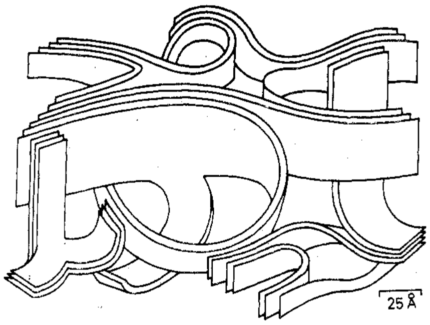


Fig. 4. Schematic diagram of the tangled graphitic structure of the Allende residue carbon, modeled after that of Ban *et al.* (*20*) for carbonized polyvinylidene chloride.

Future evaluation of models for noble-gas retention in carbonaceous chondrite meteorites could be refined by the incorporation of microstructural observations of the kind reported here.

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13. Six density fractions from an Allende HF-HCl residue were provided by S. Chang of NASA's Ames Research Center. All the results described are from one density fraction (specific gravity < 2.25); no significant differences were observed in the carbon of the other five separates. An analysis of this sample (in percentages), provided by Chang, is as follows: carbon, 60; sulfur, 2.4; chromium, 3.7; iron, 2.6; hydrogen, 1.1; nitrogen, 0.30; nickel and cobalt were present in trace amounts.
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24. We thank S. Chang, U. Ott, and J. H. Reynolds for supplying samples; S. Turner for helpful discussions; and E. Anders, S. Chang, and R. S. Lewis for critical reviews of the manuscript. The electron microscopy was performed in the Facility for High Resolution Electron Microscopy, Arizona State University, established with support from the NSF Regional Instrumentation Facilities Program (grant CHE-7916098). The work was supported by NASA grant NAG 9-4.

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Evidence of Sea Spray Produced by Bursting Bubbles

Abstract. *Measurements of air bubbles and sea spray are compared, showing that bubble bursting is the major mechanism for producing spray.*

Sea spray affects many natural phenomena and human activities. Meteorologists have related sea salt carried upward by small droplets to the formation of rain (*1*, *2*). Oceanographers have suggested that sea spray plays a major role in transferring heat (*3*), water vapor (*4*), and material (*5*) across the sea surface and viruses (*6*) and bacteria (*7*) from the surface. Icing caused by spray can affect a ship's stability, and the salt damages turbines. In remote sensing with microwave radiation, spray can attenuate backscattering and radiation signals from the sea surface (*8*).

It has been suggested that sea spray is produced through aerodynamic suction at the crests of capillary waves, bursting of air bubbles at the water surface, and direct tearing of crests by the wind. None of these mechanisms has been experimentally verified, although bubble bursting has received the most attention (*9*). In this report, recent measurements