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THE CORE STRUCTURE OF PRESOLAR GRAPHITE ONIONS

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ABSTRACT

Of the "presolar particles" extracted from carbonaceous meteorite dissolution residues, i.e., of those particles that show isotopic evidence of formation in the neighborhood of other stars prior to the origin of our solar system, a subset of the onion-like graphite spheres has an interesting concentric graphene core–graphite rim structure. We show here that single graphene sheet defects in the onion cores (e.g., cyclopentane loops) may be observable edge-on by high-resolution electron microscopy. This could allow a better evaluation of models for their formation and in particular could strengthen the possibility that growth of these assemblages proceeds atom by atom with the aid of such in-plane defects, under conditions of growth (e.g., radiation fluxes or grain temperature) that discourage the graphite layering that dominates subsequent formation of the graphite rims.

Subject headings: circumstellar matter — dust, extinction — meteors, meteoroids — molecular processes — stars: carbon — stars: mass loss

1. INTRODUCTION

Dust particles initially formed in the neighborhood of other nucleosynthesis sources, later incorporated without melting during the formation of our solar system into future carbonaceous meteorites, and finally extracted for study in laboratories on Earth are proving to be a useful source of information on various astrophysical objects and processes (Zinner 1998). Along with diamond, silicon carbide, and spinel, condensed phases identified as presolar include several graphite-related particle types. In particular, micron-sized "high-density" and isotopically heavy (i.e., with $^{12}C/^{13}C < \text{solar} = 89$) graphite spheres from the Murchison meteorite (Amari, Zinner, & Lewis 1995) have "carbon black" or "graphite onion" *rims* characterized by the concentric arrangement of 0.34 nm graphite layers. A subset of these rims appears to have nucleated not on the inorganic grains that Bernatowicz et al. (1996) have used to constrain condensation conditions but rather on a spherical *core* comprised of a novel carbon phase with density comparable to graphite.

In addition to being specimens of solid matter each formed in the neighborhood of a single nucleosynthesis source (thus retaining source isotopic signatures), the particles are of interest for the insight they provide into possible causes and effects of precipitation in the atmospheres of asymptotic giant branch (AGB) stars with surface temperatures low compared to our Sun (Winters et al. 2000) as well as into astrophysical observations of cool stellar outflows. Moreover, stars on the AGB appear to be main contributors to the replenishment of the interstellar medium (Sedlmayr 1994) and thus to reservoirs of condensed carbon in the galaxy (Jura 1997).

As shown by reciprocal lattice spacings with "high-frequency tails" in its electron diffraction pattern, the carbonaceous core phase in these presolar onions is comprised of atom-thick "flakes" typically less than 4 nm across, with graphite (hk0) ordering but with no sign of the 0.34 nm (002) graphite layering characteristic of graphite, amorphous carbon, and multiwall carbon nanotubes, i.e., of most solid nondiamond carbon phases (Bernatowicz et al. 1995, 1996). They thus appear to be graphene or polycyclic aromatic hydrocarbon (PAH) aggregates, but with densities comparable to graphite. This raises the questions of extended structure and formation considered below, but also makes contact with astrophysical observations in a larger context as well. That is because the lower size cutoff for expulsion of grains from a star undergoing mass loss is not well defined, and models suggest that cool stellar outflows may be a source of molecule-sized and larger carbon particles (Frenklach & Feigelson 1989; Cherchneff, Barker, & Tielens 1992; Krueger, Patzer, & Sedlmayr 1996). Hence, a significant fraction of the carbon lost to the interstellar medium could be carried by much smaller particles, perhaps made up largely of the novel phase in the core of these presolar onions. The spectral properties of such core-only particles could thus impact interstellar absorption significantly, for example, in the ultraviolet (Sorrell 1990).

One question related to structure and formation is the extent to which cyclopentyl (or other layer defect) groups play a role in facilitating the three-dimensional growth of core material, whose periodicity seems to be dominated by the planar (cyclohexyl) ordering of two-dimensional graphene sheets (Allamandola, Tielens, & Barker 1989). At one extreme, the cores might be formed by the "collisional agglomeration" of previously formed planar PAHs (Bernatowicz & Cowsik 1997). At the other extreme, the cores might form by the addition of one carbon atom at a time, with layer defects added randomly from time to time to lessen entropy loss during the condensation process (Sedlmayr & Kruger 1997). In other words, can the detailed structure of collected onion cores provide further insight into the creation of their disordered three-dimensional form from components with well-defined two-dimensional nearest neighbor order?

2. EXPERIMENTAL SETUP

Interstellar graphite onions used for this study are from the Murchison meteorite graphite separate KFC1 (2.15–2.20 g cm^{-3}), whose preparation has been described in detail by Amari, Lewis, & Anders (1994). The onions were microtomed to a thickness of 70 nm and deposited onto 3 mm copper grids with a holey carbon support film by Bernatowicz et al. (1996). Specimens were examined with a 300 kV Philips EM430ST transmission electron microscope (TEM) with point resolution near 0.2 nm.

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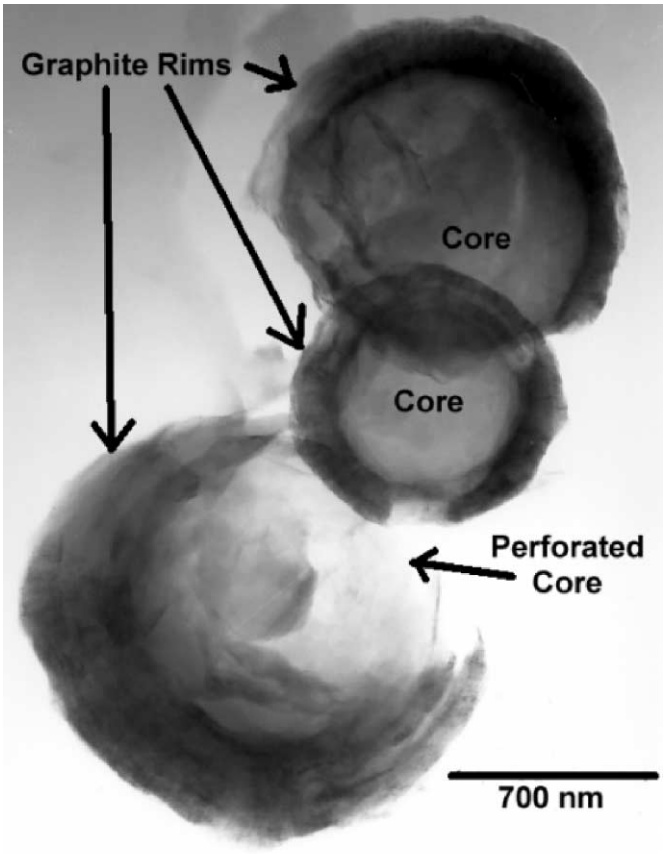

FIG. 1.—Three onion slices, one with a torn core suitable for electron phase contrast study.

Because the sections were generally too thick for electron phase contrast imaging, sliced onions with torn regions of core located over holes in the underlying support film (Fig. 1) were our primary target. Many of the microtome sections on the TEM grid designated KFC1A:E have been surveyed for high-resolution electron microscopy (HREM) suitability and other properties (e.g., their core-rim ratio). The images reported here come from onions on that mount. Electron phase contrast (HREM) images were recorded on Kodak electron image film at 240,000 or 700,000 times and then digitized at 2500 dots inch^{-1} and 12 bits pixel^{-1} with an Agfa DuoScan2500 scanner. Image analyses and simulations were done in Semper, C, Visual Basic, Cerius 2, EMS, and Mathematica.

3. CORE STRUCTURE

HREM images of very thin specimens are *to first order* projections of electron column density in the specimen along the direction of the electron beam, suitably "bandpass" filtered by the complex contrast transfer function of the microscope (Spence 1988). Hence, individual graphene sheets will be difficult to view face-on unless the specimen is no more than a few atoms thick, given that the absence of graphite layer spacings in diffraction argues strongly that the other atoms in the specimen will not be periodically arrayed above or below.

The story is different for atom-thick sheets viewed edge-on. In fact, the properties of lattice fringes from single planes embedded in an otherwise disordered field might be easier to recognize than those of lattice fringes in a crystal, since Fourier ringing from adjacent planes in the latter case may obscure single-column defects. This is borne out by image simulations,

FIG. 2.—Strong phase-object simulation of 0.19 nm resolution HREM image from a collection of randomly oriented atom-thick hexagonal graphene flakes.

such as those shown in Figures 2 and 3. The visual signature of graphene sheets randomly distributed in an otherwise random matrix is therefore in large part a collection of randomly oriented line segments.

One might imagine that a single cyclopentane embedded in a graphene sheet would impose only a gradual curvature effect, diluted by the otherwise large number of hexagons present therein. On the contrary, the effect is quite large, beginning with bond angles for the five-hexagon corannulene molecule bent up from the plane of the pentagon by 26°.8 (Dresselhaus, Dresselhaus, & Eklund 1996). In the asymptotically large molecule limit, the envelope may be approximated by a hyperbolic cone with a half angle of 56°.44, to take into account the 5/6 perimeter mismatch between this structure and that of a disk

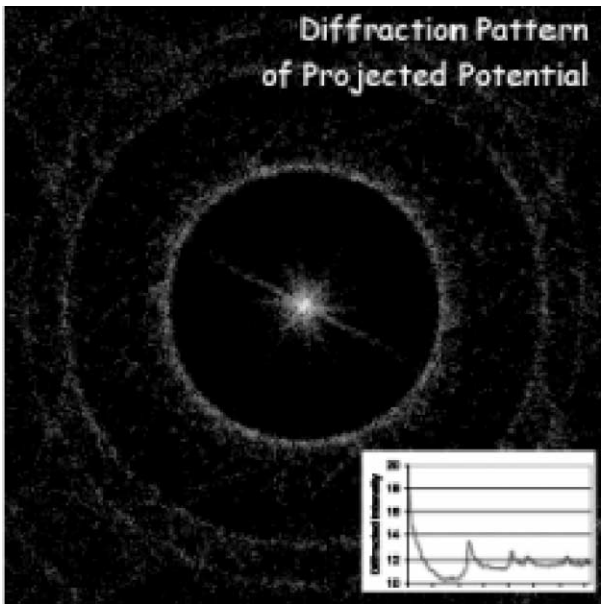

FIG. 3.—Simulated diffraction pattern of image in Fig. 2, showing both the spacings and asymmetric line broadening familiar from experimental electron diffraction patterns of onion cores.

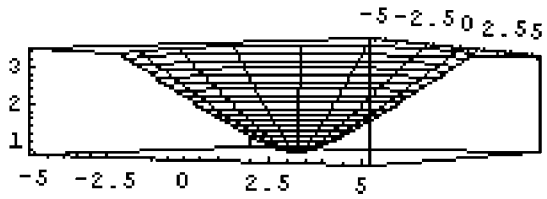

FIG. 4.—Hyperbolic cone with perimeter equal to 5/6 that of a circle at the same distance from the center.

of the same radius (see Fig. 4). This suggests a projected "bend" of as much as 67°.3.

When a simple model of five graphene "flats" intersecting at a central cyclopentane is randomly distributed at near-graphite densities into a 100 nm cube and then sliced for HREM image simulation, the result is shown in Figure 5. As can be seen, the visual signature is subtly perturbed by the addition of line segments that make small angles with one another and that intersect in projection at the cyclopentane site. Future work might show that the statistical distribution of angles between line segments provides information on the details of the in-plane defects. For example, models of graphene with randomly placed cyclopentanes show that each triplet of adjacent pentagons bounds a triangular graphene flat. In the special case of equally spaced pentagons, the projected bend edge-on will look more like the 41°.81 between faces of an icosahedron (McKay, Kroto, & Wales1992). Thus, the qualitative simulations presented here are meant only to suggest features of possible interest in experimental images.

Figure 6 shows experimental HREM images of five specimens. Figures 6*b* and 6*c* are of onion core material. Power spectra of these and/or adjacent image regions show strong 0.21 nm (100) rings, such as those seen in core material electron diffraction and in the simulation shown in Figure 3. Note in particular the nonparallel linear features in these two images, not typical of the others. These features often manifest as an intersection between two line segments, as illustrated in the inset (from the Fig. 6*b* core image) in Figure 7. The line segments involved with this contrast are typically 2–5 nm in length, with all except one of the apparent bends between 39° and 65°. The length observations are consistent with the 4 nm coherence widths suggested by diffraction (Bernatowicz et al. 1996), particularly since we expect our ability to recognize linear features in these images, in the presence of otherwise random superpositions, to be biased toward features larger than 2 nm. The range of edge-on angles is further consistent with those predicted and observed by Kroto & McKay (1988) in images of layered graphene by S. Iijima (1980).

FIG. 5.—Strong phase-object simulation of 0.19 nm resolution HREM image from a collection of randomly oriented atom-thick hexagonal graphene flakes with a cyclopentane at their center.

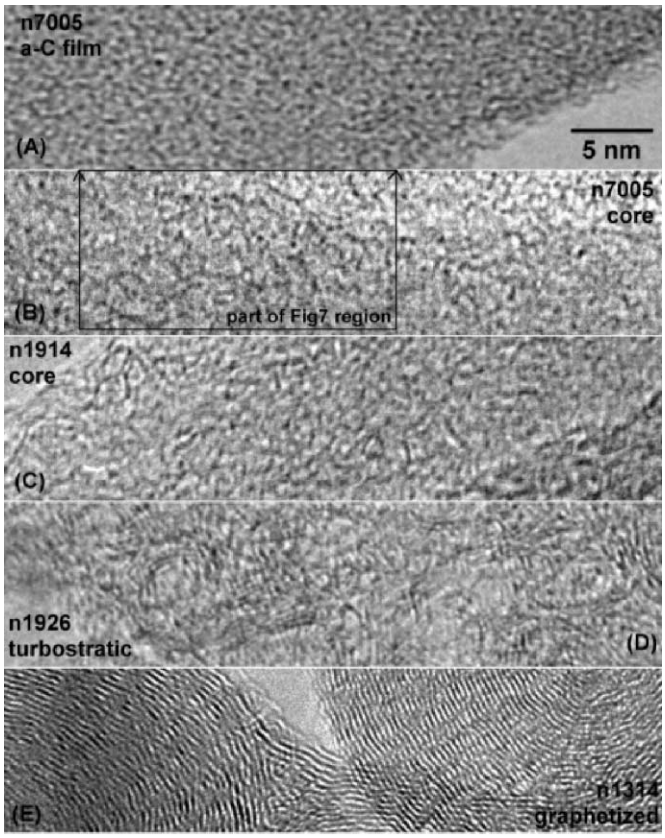

FIG. 6.—Experimental HREM images of five specimens arranged in order of increased order in their electron diffraction patterns: (*a*) amorphous support material from TEM negative 7005, (*b*) thin onion core material recorded in that same exposure, (*c*) core material from a different onion in negative 1914, (*d*) turbostratic graphite, and (*e*) terrestrial graphetized carbon.

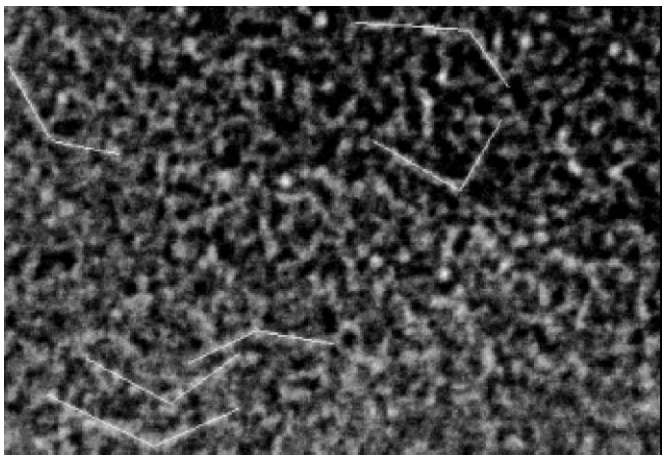

FIG. 7.—Inset of part of the core image B region from Fig. 6, in negative contrast with some intersecting linear features highlighted in white.

A caution is in order for those who wish to associate specific features in the experimental images with model structures. Contrast depends on both specimen thickness and microscope defocus. We have selected relatively sharp images, that do not show signs of global anisotropy, e.g., due to drift or astigmatism. However, detailed information on specimen thickness or defocus is not yet available.

4. SUMMARY

We report simulations that suggest that the signature of a solid comprised of randomly oriented 2–4 nm graphene sheets, in electron phase contrast images, will be images peppered with line segments due to those sheets that the beam encounters nearly edge-on and with otherwise disordered contrast nonetheless showing power spectrum *rings* characteristic of the graphene 0.21 nm (100) and smaller in-plane *d*-spacings. We further provide evidence, through simulations, that planar defects in these sheets will manifest as a pattern of line segment pairs intersecting at the sheet defect connecting them. Lastly, we show that experimental HREM images of material found in the cores of interstellar graphite onions have a pattern of linear features consistent with these simulations. These preliminary observations support the possibility that these presolar graphene cores manage three-dimensional growth atom by atom with help from sheet defects (e.g., cyclopentane or cycloheptane inserts randomly placed within sheets of predominantly hexagonal graphene rings).

The observations suggest possibilities for several types of future work. (1) Microscopy techniques that compensate for aberrations with the help of simulation and thereby push the point resolution of the images down toward 0.1 nm, combined with further molecular modeling and image simulation of possible graphene sheet structures, might enable the kinds of analyses hinted at here to provide a more detailed picture of the structure and properties of this novel material, as well as of the processes involved in its formation. (2) The initial growth of these cores might have taken place around a corannulene icospiral shell that is relatively ordered and less dense than the remainder of the core (Kroto & McKay 1988). Careful HREM searches of the center of these onion cores might be able to identify its presence. (3) The transition between core and rim in these particles (Fig. 1) is abrupt. Models of circumstellar condensation that can account for the assembly of dense graphene structures with graphite's (002) 0.34 nm Van der Waals layering suppressed must also allow for an abrupt transition to layered growth. What inequality undergoes reversal at this point? (4) Is unlayered graphene of this sort found on Earth, can it be made in the laboratory, and what are its properties? (5) What fraction of the mass loss in cool carbon-rich stellar outflows is likely to be comprised of core material only, and what observational consequences (e.g., to interstellar absorption) are likely to result?

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