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Express Letter

Fullerene-like carbon nanostructures in the Allende meteorite

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Abstract

Transmission electron microscopy has been used to examine carbon isolated from the Allende meteorite. The structure of the carbon is rather disordered, consisting of curved and faceted graphene sheets with little large scale graphitization, and resembles that of a microporous carbon following high temperature heat treatment. Closed carbon nanoparticles, typically ∼2–10 nm in diameter are commonly observed. These closed particles, which are probably fullerene-like in structure, are strong candidates to be carriers of planetary gases.

Keywords: fullerenes; molecular structure; Allende meteorite; carbonaceous chondrites; transmission electron microscopy; carbon

1. Introduction

The possibility that fullerenes might be present in carbonaceous meteorites was first put forward by Heymann [1], shortly after the discovery of C_{60} in 1985 [2]. This idea attracted much interest, since the closed-shell structures of fullerenes might enable them to act as carriers of noble gases, and of other gaseous atoms and molecules. However, most searches for C_{60} and other fullerenes in meteorites were unsuccessful [3]. Only one group, that of Becker and colleagues, have successfully extracted fullerenes from a meteorite. These workers reported in 1994 that C_{60} was present at a level of approximately 0.1 ppm in the Allende meteorite [4], and subsequently found a distribution of higher fullerenes, from C_{100} to C_{400} in the same meteorite [5]. Recently, this group have shown that fullerenes from the Cretaceous/Tertiary boundary layer contain trapped helium with $^{3}He/^{4}He$ ratios approximately 100× that of atmospheric helium [6]. These results appear to show that fullerenes can indeed carry gases of cosmic origin to the Earth, and give a new impetus to the search for fullerene-related carbons in meteorites. In the present study, which builds on previous work [7], transmission electron microscopy (TEM) is used to examine carbon isolated from a sample of Allende, with the primary aim of seeking evidence for the presence of fullerene-related structures.

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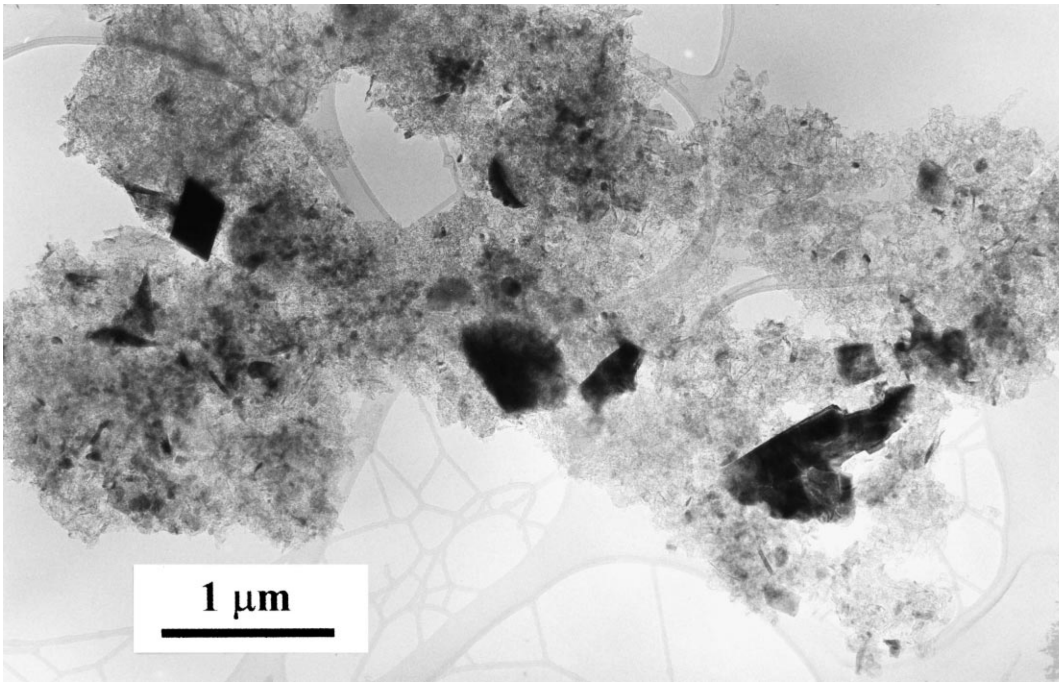

Fig. 1. Intermediate magnification micrograph of Allende acid-resistant residue, showing disordered carbon and inorganic crystallites.

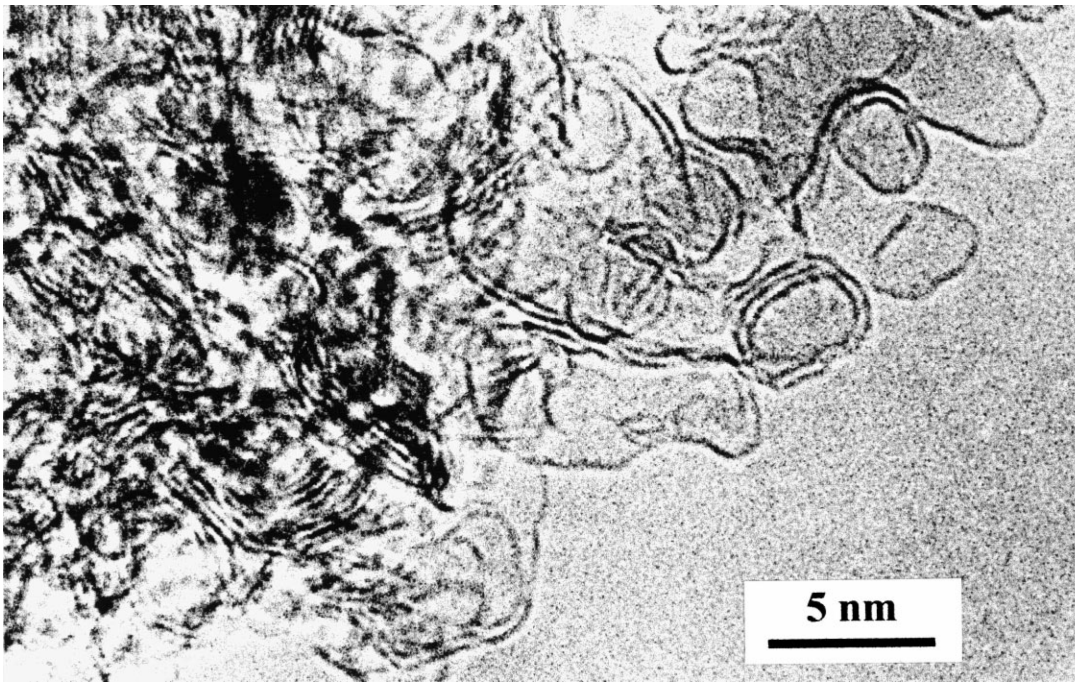

Fig. 2. Higher magnification image showing structure of carbon.

2. Materials and methods

The following treatment was carried out to remove the majority of silicates and other minerals from the meteorite sample. Firstly, about 80 g of the powdered meteorite was treated with HF and HCl as described in Lewis et al. [8] to remove most of the inorganic minerals. The residue was further treated with HF–H_3BO_3 [9] to remove additional matter by complex formation. After washing with nanopure water and drying in air at 40°C, elemental sulfur which had formed from sulphides was removed by washing with toluene. This left 320 mg of residue.

For electron microscopy, the material was deposited directly onto holey carbon films (Agar Scientific Ltd), without the use of solvents. The carbon support films were checked for contamination before use, as discussed further below. The microscope employed was a Philips CM20 TEM, operated at 200 kV, and equipped with an energy dispersive X-ray (EDX) spectrometer capable of detecting elements with $z > 11$.

3. Results

Fig. 1 shows a typical region of the meteorite sample at intermediate magnification. The regions of low contrast are mainly carbon, while the dark regions are inorganic crystallites. EDX analysis showed that these dark particles contained Cr and Fe, suggesting that they were crystals of chromite ($FeCr_2O_4$). Fine grained chromite is commonly found in the acid residues of carbonaceous chondrites [10]. Other elements detected, in minor amounts, were Si, Al and S. Higher magnification images of the carbon, such as that reproduced in Fig. 2, showed the material to be rather disordered, with only very small areas of graphitic structure. The spacing of the graphite layers was generally in the range 0.34–0.36 nm. Images of extremely thin areas, such as at the right hand side of Fig. 2 show that the carbon contained many curved carbon layers enclosing voids of the order of 2–10 nm in size. In some cases these structures constituted discrete nanoparticles; examples are shown in Fig. 3. It seems very likely

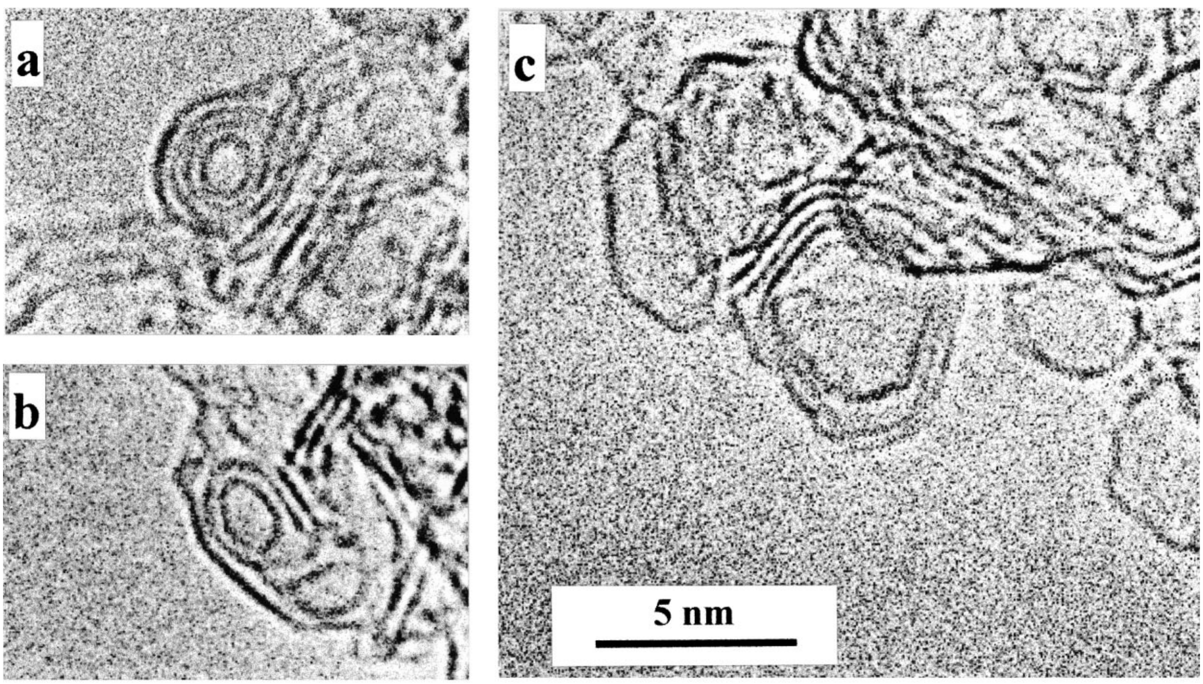

Fig. 3. a, b, c: Examples of individual closed carbon nanostructures.

that particles such as these have fullerene-like structures, as discussed below. Most of the carbon nanoparticles observed were empty, but particles were also found which were apparently filled with crystalline material. A detailed analysis of the filled particles has not been made, but in some cases the enclosed crystallites displayed lattice fringes in the range 0.30–0.33 nm. This rules out the possibility that they could be diamond, for which the maximum lattice spacing is 0.206 nm. Diamond particles are known to be a component of carbonaceous meteorites [11], and may have been present in the samples studied here, but they were not the focus of this work.

As well as the multi-layered particles shown in Fig. 3, single-walled particles were also commonly observed. In most cases these particles were similar in size to the multi-layered ones, i.e. approximately 2–10 nm. However, smaller single-layered particles, comparable in diameter with C_{60} and C_{70} were sometimes seen. Unfortunately, these particles were difficult to photograph as they tended to be mobile in the electron beam, and were susceptible to beam damage.

4. Discussion

When studying carbon isolated from meteorites, it is essential to ensure that the sample examined is genuinely meteoritic material, and not some form of contamination. A particular problem with TEM studies is that a wide range of carbon structures, including poorly graphitized carbon [12], carbon nanotubes and nanoparticles [13], and carbynes [14], can be present as contaminants on the carbon film supports used for TEM. This problem was not widely appreciated until quite recently, and as a result certain TEM studies of meteoritic carbon should be treated with caution. In 1981 Smith and Buseck reported finding graphitic carbon nanoparticles in material isolated from the Allende meteorite [15]. However, these nanoparticles differed from those found in the present study in that they had many more layers and much larger outer diameters ($\sim$50 nm). The particles are very similar to those which are found as contaminants on TEM carbon support films. Also, the Smith/Buseck nanoparticles were only found in a sample which had been etched in fuming HNO_3, a treatment which is known to destroy the gas-bearing carbon phase. This supports the view that they may have been an artefact. In the present study, the carbon support films were checked before use, as mentioned above, and those containing significant amounts of contamination were discarded. We can therefore be confident that the micrographs recorded showed genuine sample material.

The overall appearance of the carbon described here is very similar to that observed in studies of microporous, non-graphitizing carbons which have been subjected to high temperature heat treatments [16,17]. In these studies it was shown that heating the carbons to temperatures in the range 2000–2800°C produced a structure made up of curved or faceted 2- or 3-layer graphitic sheets enclosing voids typically 5–15 nm in size, with many discrete, closed nanoparticles. Heat treatment of fullerene soot at temperatures around 2000°C produces a similar structure [18]. Comparison of the carbon structures observed in the present work with the laboratory-heated carbons suggests that the meteoritic carbon has experienced temperatures of the order of 2000–2200°C.

It seems very likely that particles such as those shown in Fig. 3 contain pentagonal carbon rings, as in fullerenes, since it is difficult to envisage any other explanation for their closed structures. The general appearance of the particles is also consistent with their having fullerene-like structures. Thus, the particles shown in Fig. 3a and b have rounded shapes, while the larger particle shown in Fig. 3c is more obviously faceted. This is consistent with the belief that the sphericity of fullerenes decreases as their diameter increases [19]. The pentagonal shape of the particle in Fig. 3c provides further evidence for a fullerene-like structure.

In summary, our results show that significant numbers of fullerene-like, closed carbon nanoparticles are present in carbon isolated from the Allende meteorite. As discussed elsewhere, we believe that carbon nanoparticles of this kind are likely carriers of the planetary noble gases in meteorites [6,20], and they could also be carriers of pre-solar gases. In this connection we note that the absorption spectra of fullerene-like carbon nanoparticles contain features which resemble those from interstellar dust [18].***[FA]***

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