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High-resolution transmission electron microscopy of carbon and nanocrystals in the Allende meteorite

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Transmission electron microscopy has been used to examine carbon extracted from the Allende meteorite. The structure of the carbon is rather disordered, consisting of curved and faceted graphitic sheets which often enclose voids of the order of 2–10 nm in size. Completely closed fullerene particles are quite commonly observed. This carbon is a strong candidate to be a carrier of planetary gases. Carbon-coated crystallites, which appear to be iron sulphide, are also found in the carbon.

Keywords: TEM; meteorite; carbon; fullerenes; iron sulphide

1. Introduction

Carbonaceous chondrites are stony meteorites which contain up to 5% by weight of carbon. The majority of this carbon occurs in the form of insoluble, disordered material, whose precise nature appears to depend on the class of chondrite (Mullie & Reisse 1987; Rietmeijer 1988; Henning & Salama 1998). Thus, in CM chondrites, named after the meteorite which fell at Mighei, much of the carbon seems to be an organic polymer (Hayatsu *et al.* 1977), while for CV chondrites, named after the Vigarano meteorite, the carbon is partly graphitized (see, for example, Lumpkin 1981; Vis *et al.* 2002). Transmission electron microscopy (TEM) is undoubtedly the most powerful method for probing the structure of meteoritic carbons, since it enables direct images of the carbon to be recorded, potentially at atomic resolution. In the present study, TEM is used to examine carbon extracted from the Allende meteorite, an important CV3 carbonaceous chondrite. It is hoped that a better understanding of the structure of this carbon might provide clues to the thermal history of the material, and therefore give an insight into the conditions under which the meteorite formed, *ca.* 4.56 billion years ago. It might also help to explain the way in which the carbon can act as a carrier for noble gases.

Carbon from Allende has been the subject of a number of TEM studies. One of the earliest was carried out by Green *et al.* (1971), who reported that much of the carbon

† Deceased 9 May 2001.

resembled 'poorly crystalline graphite'. In 1981, work by Lumpkin confirmed that the carbon phase contained large amounts of randomly stacked sp^2-hybridized carbon layers which gave diffraction patterns similar to those from carbon black and glassy carbon (Lumpkin 1981). Smith & Buseck (1981) came to a similar conclusion using lattice-imaging techniques. These authors also reported finding well-ordered graphitic nanoparticles in the Allende carbon. In these particles, which had outer diameters of *ca.* 50 nm, a small hollow core was surrounded by many layers of graphitic carbon. Subsequent work has shown that nanoparticles of this kind are sometimes found in the carbon support films used for TEM (Harris 1997*a*, 2001). Therefore, the particles observed by Smith and Buseck may not have been part of the meteoritic carbon, but a contaminant. In support of this idea, it should be noted that well-ordered nanoparticles of this kind, with many rather perfect graphitic layers, are usually formed at exceptionally high temperatures (perhaps 3000 °C), and it is not believed that Allende has experienced such high temperatures. Of course, the possibility that the particles are genuine Allende material cannot be ruled out.

The present study builds on previous work which has shown that carbon isolated from the Allende meteorite resembles heat-treated charcoal, and contains many fullerene-related elements (Harris *et al.* 2000). This fullerene-like carbon is a strong candidate to be the carrier of the planetary noble gases, known as phase Q (Vis & Heymann 1999). The planetary noble gases are thought to have been incorporated into the meteoritic material during the birth of the Solar System (Ozima & Podosek 2002). They have lower abundances of He and Ne compared with the noble gases present in the Sun. Recent work has shown that the gases are contained in a 'minor combustible constituent' of the carbon in chondritic meteorites, but the precise nature of this constituent has not yet been firmly established (Verchovsky *et al.* 2002). As well as investigating the structure of the carbon in more detail, this work also focuses on some of the inorganic nanocrystals which are found distributed throughout the meteoritic carbon. Detailed studies of these crystallites may also provide insights into the history of the material.

2. Experimental

To prepare TEM samples from the raw meteorite, a fragment was broken open to reveal a fresh surface, and material was scraped away using a scalpel. This was then ground gently in a pestle and mortar under isopropanol, and a small amount of the suspension was pipetted onto holey carbon films.

The acid residue was prepared as follows. Firstly, *ca.* 80 g of the powdered meteorite was treated with HF and HCl, as described in Lewis *et al.* (1975), to remove most of the inorganic minerals. The residue was further treated with HF–H_3BO_3 (Robl & Davis 1993) to remove additional matter by complex formation. After washing with nanopure water and drying in air at 40 °C, elemental sulphur, which had formed from sulphides, was removed by washing with toluene. Again, TEM samples were prepared by suspending some of the material in isopropanol and pipetting a small amount onto holey carbon films.

The microscopes employed were a Philips CM20 TEM, equipped with an energy-dispersive X-ray (EDX) spectrometer and a JEOL 2010 high-resolution TEM (HRTEM), both operated at 200 kV.

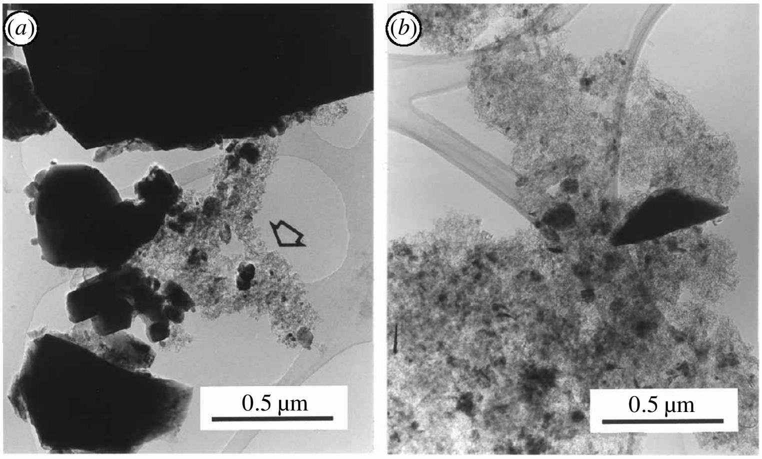

Figure 1. Low-magnification TEM images of (*a*) an unprocessed Allende sample, with the arrow indicating carbon, and (*b*) an Allende sample after acid treatment.

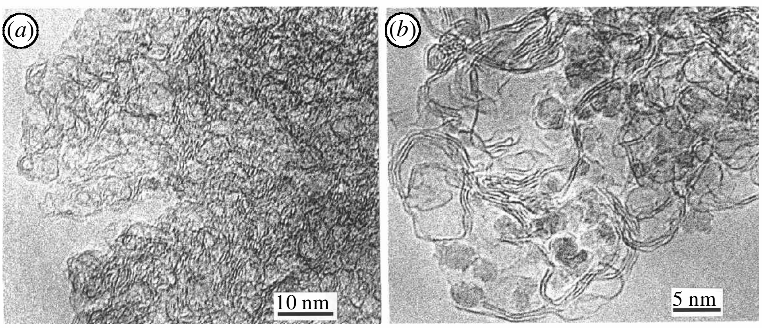

Figure 2. Micrographs of carbon in an acid-treated Allende sample.

3. Results

Figure 1*a*,*b* shows typical micrographs of the raw and acid-treated meteorite samples at low magnification. More than 95% of the raw meteorite consists of inorganic crystallites such as olivine or pyroxene, which appear as dark or opaque regions in TEM micrographs. The carbon, which is mainly disordered, gives much lower contrast, as can be seen in figure 1*a*. The carbon was intimately mixed with the mineral matrix, and no large areas containing carbon alone were found. In the acid-treated sample, shown in figure 1*b*, the large crystallites have been removed, facilitating study of the carbon structure. Of the crystals which remain in the acid-treated material, the larger ones are mostly chromite ($FeCr_2O_4$). Smaller crystals of iron sulphide are also commonly found, as discussed further below.

Images of the carbon at intermediate and high magnification are reproduced in figure 2. These show the material to be rather disordered, with small areas of randomly oriented graphitic layer planes. The overall appearance of the carbon is rather similar to that of non-graphitizing carbon following high-temperature heat treatment, as discussed in the next section. In some regions, such as that shown in figure 2*b*, it can clearly be seen that the curved carbon layers enclose voids of the order of 2–10 nm in size. Some small inorganic crystallites can also be seen in this image. While much

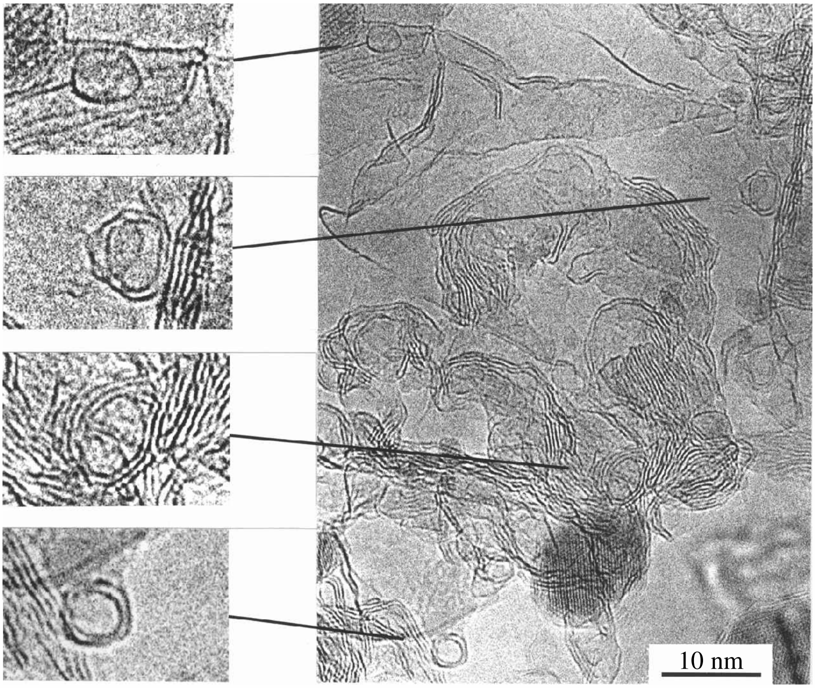

Figure 3. High-magnification micrograph of carbon in an acid-treated Allende sample, with enlarged areas showing individual closed carbon nanostructures.

of the carbon was relatively thick, obscuring its detailed structure, some extremely thin regions could be found. An example is shown in figure 3, with enlarged regions showing discrete closed carbon nanoparticles. These closed structures could be either single-walled, as in the particle shown at the upper left, or multilayered, as in the other particles, and were typically *ca.* 2–5 nm in diameter. The presence of at least four closed particles in such a small region of the carbon suggests that they are quite abundant. It seems very likely that the particles are fullerene-like, since it is difficult to envisage any other explanation for their closed structures.

Of the small inorganic crystallites found in the carbon, some were found to be coated with a graphitic layer or layers. A group of such structures is shown in figure 4, while individual particles are shown in figure 5*a*,*b*. Energy-dispersive X-ray microanalysis indicated that the coated crystallites were probably iron sulphide, but the precise form of iron sulphide has not yet been established. In high-resolution images the largest lattice spacings observed were 0.58 nm, with an error of *ca.* ±0.01 nm. This would appear to rule out pyrite (FeS_2), for which the largest lattice spacing is 0.313 nm. The lattice images also do not appear to be consistent with troilite, FeS. It is possible that the crystallites could be either greigite (Fe_3S_4) or pyrrhotite (Fe_7S_8), but further HRTEM studies will be needed to determine their exact structure. An alternative possibility would be the iron–nickel sulphide pentlandite $(Fe, Ni)_9S_8$, although EDX analysis did not show a clear nickel signal. Brearley has reported finding carbon-coated crystals of pentlandite within the olivine matrix of Allende (Brearley 1999).

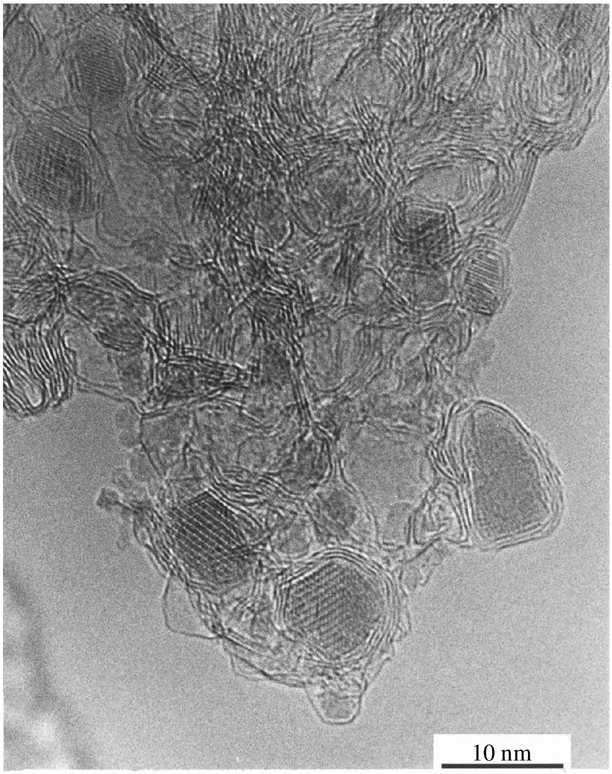

Figure 4. Micrograph showing a cluster of coated inorganic crystallites in Allende carbon.

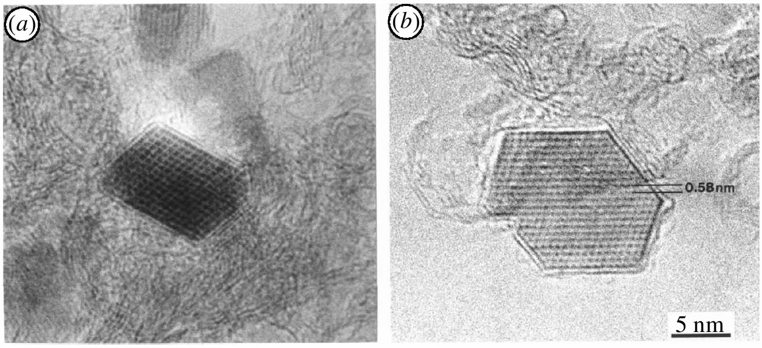

Figure 5. Individual coated crystallites, probably iron sulphide.

4. Discussion

The insoluble carbon in carbonaceous chondrites has been variously compared with coal, kerogen, carbon black and glassy carbon. This study suggests that, at least in the case of Allende, a better model for the meteoritic carbon would be charcoal, or char, following high-temperature heat treatment. It is well known that heating the carbons to temperatures above *ca.* 2200 °C produces a structure consisting largely of curved or faceted two- or three-layer graphitic sheets (Jenkins & Kawamura 1976; Oberlin 1989). Studies by Harris and colleagues have shown the presence of closed particles, which are believed to have a fullerene-like structure, in these heat-treated carbons (Harris 1997*b*; Harris & Tsang 1997). The structures observed are very similar to those seen in the Allende carbon.

An alternative model for the Allende carbon might be fullerene soot, the low-density, disordered material which forms on walls of the arc-evaporation vessel during C_{60} synthesis. This has a structure made up of curved fragments of carbon, containing pentagons and other non-six-membered rings in addition to hexagons, very similar to recent models for the structure of char. Heat treatment of fullerene soot produces a structure rather similar to that of heated chars, which contains many closed nanoparticles (de Heer & Ugarte 1993; Ugarte 1994). By comparing the Allende carbon with char, or with fullerene soot which has been exposed to various heat treatments, it is possible to arrive at an estimate of the temperature which the meteoritic carbon may have experienced. The best match appears to be with chars heated for *ca.* 1 h at temperatures in the range 2000–2200 °C. However, the sulphide particles which are present in the meteoritic carbon could not survive such high temperatures. It is possible that the material experienced rather lower temperatures for a much longer period, although this can only be speculation at this stage.

As noted in § 1, the present programme of work was partly motivated by a desire to identify phase Q, the carrier of the planetary noble gases (Vis & Heymann 1999). The fullerene-related carbon described here certainly seems capable of acting as such a carrier. Micrographs, such as that shown in figure 3, indicate that closed particles are relatively common in the carbon. It is well established that fullerenes can act as receptacles for noble gases (see, for example, Saunders *et al.* 1994). The idea that the noble gases are contained in fullerene-related nanoparticles is also consistent with the fact that the gases can be released by treatment with oxidizing acids (Lewis *et al.* 1975). It has been shown that carbon nanotubes and nanoparticles can be selectively opened by acid treatment, as a result of selective attack on the pentagonal rings (see, for example, Tsang *et al.* 1994). In addition to the completely closed particles, the curved and faceted microstructure of much of the carbon contains many other closed pores which could potentially carry trapped gases (Vis *et al.* 2002). It seems reasonable to assume, therefore, that this carbon is indeed phase Q.

If much of the carbon in Allende has a fullerene-related structure, this may suggest that small fullerenes such as C_{60} are also present. Such fullerenes were not seen in the present TEM study, but they may have been removed during the toluene treatment (large fullerenes and fullerene-like structures are not soluble in toluene). Several groups have searched for C_{60} and other fullerenes in meteorites, by using chemical-extraction techniques, but most have been unsuccessful (Heymann 1997; Buseck 2002). Only one group, that of Becker and colleagues, has successfully extracted fullerenes from a meteorite. These workers reported in 1994 that C_{60} was present at a level of *ca.* 0.1 ppm in the Allende meteorite (Becker *et al.* 1994), and subsequently found a distribution of higher fullerenes, from C_{100} to C_{400} in the same meteorite (Becker *et al.* 1999). Recently, this group have shown that fullerenes from both the Cretaceous–Tertiary and the Permian–Triassic boundary layers contain trapped helium and argon with isotope ratios consistent with an extraterrestrial origin (Becker *et al.* 2000, 2001). It was suggested that the fullerenes were carried to Earth as a result of impact events. However, questions have been raised about certain aspects of this work (Braun *et al.* 2001; Farley & Mukhopadhyay 2001; Isozaki 2001).

In addition to the carbon itself, the present study has looked at the structure of sulphide crystallites supported on the carbon. Interestingly, these were almost always covered with one or more layers of graphitic carbon. There are a number of possible mechanisms whereby inorganic particles could become coated in this way. Heat treatments of microporous carbon impregnated with a salt can produce nanoparticles covered with multilayered graphitic carbon (Harris & Tsang 1998). This requires very high temperatures (typically 2000 °C), however, and invariably converts the metal salt to a carbide. Perhaps a more likely mechanism, therefore, is catalytic deposition of carbon onto the particle surfaces from the vapour phase (see, for example, Oberlin 1989), which can occur at much lower temperatures.

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