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Microscopic search for the carrier phase Q of the trapped planetary noble gases in Allende, Leoville and Vigarano

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Abstract–High-resolution transmission electron microscopy micrographs of acid-resistant residues of the Allende, Leoville, and Vigarano meteorites show a great variety of carbon structures: curved and frequently twisted and intertwined graphene sheets, abundant carbon black-like particles, and hollow "sacs". It is suggested that perhaps all of these are carriers for the planetary Q-noble gases in these meteorites. Most of these materials are pyrocarbons that probably formed by the pyrolysis of hydrocarbons either in a gas phase, or on hot surfaces of minerals. An attempt was made to analyze for argon with particle-induced x-ray emission in 143 spots of grains of floating and suspended matter from freeze–dry cycles of an Allende bulk sample in water, and floating "black balls" from sonication in water of samples from the Allende meteorite. The chemical compositions of these particles were obtained, but x-ray signals at the wavelength of argon were obtained on only a few spots.

INTRODUCTION

One of the most enduring enigmas of meteoritics is the nature of carrier phase Q with its associated trapped "planetary Q-gases" (He, Ne, Ar, Kr and Xe), discovered by Gerling and Levskii (1956) and more firmly defined by Lewis *et al.* (1975). Much is already known about Q and its trapped noble gases (see the excellent review by Swindle, 1988). The Q phase is contained within HF-HCl acid-resistant, carbon-rich residues of all chondrites, but its mass fractions in such residues is still unknown. Q is a purely carbonaceous phase (Phinney *et al.*, 1976; Frick and Chang, 1978). Q loses its noble gases quantitatively when acid-resistant residues are intensely treated ("etched") with strongly oxidizing chemicals such as hot concentrated nitric acid (Lewis *et al.*, 1975). Q releases most of its planetary noble gases in the range 1200 to 1600 °C when step-heated *in vacuo* (Srinivasan *et al.*, 1978). Greatly reliable relative abundances and isotopic compositions of the Q noble gases were obtained by Wieler *et al.* (1991).

No investigator of Q has ever firmly identified ("seen") grains or molecules of this carrier phase by ordinary microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), or other methods, which is very different from the discoveries in meteorites of presolar grains of nanodiamond (Lewis *et al.*, 1987), silicon carbide (Bernatowicz *et al.*, 1987), and graphite (Amari *et al.*, 1990) all of which were firmly identified as carriers of their own distinctly different and isotopically anomalous trapped noble gases. Consequently, all discussions about the nature of Q have remained speculative. Among the suggested structural forms of Q were carbynes (Whittaker *et al.*, 1980), various macromolecular carbonaceous substances (Ott *et al.*, 1981), turbostratic carbon (Lumpkin, 1981), graphene sheets (Bernatowicz *et al.*, 1996), adsorption sites in a labyrinth of pores of amorphous carbon (Wacker *et al.*, 1985; Wacker, 1989) as well as three-dimensional, closed carbon structures such as fullerenes, carbon nanotubes, or carbon onions (Heymann, 1986; Becker *et al.*, 1993, 2000; Heymann and Vis, 1998; Vis and Heymann, 1999, 2000; Harris *et al.*, 2000; Poreda and Becker, 2001). Matsuda and Yoshida (2001) have recently suggested that the Q gases were actually trapped by ion implantation in the surfaces of nanodiamonds. We will consider the relative merits of these suggestions in the discussion section of this paper.

Our quest for the nature of Q started with the recognition that a few three-dimensional, closed carbon structures had already been reported in HRTEM micrographs of acid-resistant residues of the Allende meteorite (Smith and Buseck, 1980, 1981a,b; Gilkes and Pillinger, 1999; Harris *et al.*, 2000). We concluded that additional HRTEM studies of acid-resistant residues of Allende and other carbonaceous meteorites were greatly needed to demonstrate that such structures are ubiquitous

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in chondritic meteorites. If that could be demonstrated, there would remain, however, the fundamental issue whether such structures actually contain trapped noble gas atoms, a necessary condition for the structures to be Q. Our estimates suggested that Ar concentrations in such structures could be sufficiently large to be detected by particle-induced x-ray emission (PIXE). We therefore began a program of HRTEM of acid-resistant residues of the Allende, Vigarano, and Leoville meteorites and PIXE analyses of various samples from Allende. We also anticipated that the new microscopic information on carbonaceous matter could yield hitherto unknown structures.

It was intended to study, by the same techniques, residues that were etched with hot nitric acid to monitor whether any significant structural changes could be detected. Unfortunately, our collaborative work came to a grievous halt when Dr. Ronald Vis died in May of 2001 before this could be done. Here we report our results at that time with the hope that they will become useful for other investigators who are attempting to reveal the nature of Q.

SEARCH PROCEDURES AND RESULTS

Transmission Electron Microscopy

Samples for electron microscopy included acid-resistant residues of Allende obtained by treating powdered samples of the meteorite with HF and HCl as described by Lewis *et al.* (1975), followed by treatment with HF-HBO_3 to remove additional inorganic matter by complex formation (Robl and Davis, 1993; see also Vis and Heymann, 1999). After thorough washing with nanopure water and drying in air at 40 °C, elemental sulfur that had formed from sulfides was removed by washing with toluene until S could no longer be detected in the extracts with high-performance liquid chromatography (HPLC). Elemental analysis was performed on the residue with PIXE as described in Vis and Heymann (1999). It showed, apart from the bulk carbon, some chromium and iron from chromite. Additional residues from Leoville and Vigarano were kindly donated by Dr. Gary Huss.

TEM was performed at the National Centre for HREM, Delft, The Netherlands, using a Philips CM30T electron microscope with a LaB_6 filament as the source of electrons, operated at 300 kV. Samples were mounted on a microgrid polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions. Numerous spots on samples of Allende, Vigarano and Leoville were analyzed. Energy dispersive x-ray spectrometry (EDX) elemental analyses were performed using a LINK EDX system. The copper signals in the EDX spectra are due to background radiation striking the copper sample holder grid.

Figure 1 shows the entire Allende AQ1 particle in low magnification. This was one of seven grains of the acid-resistant

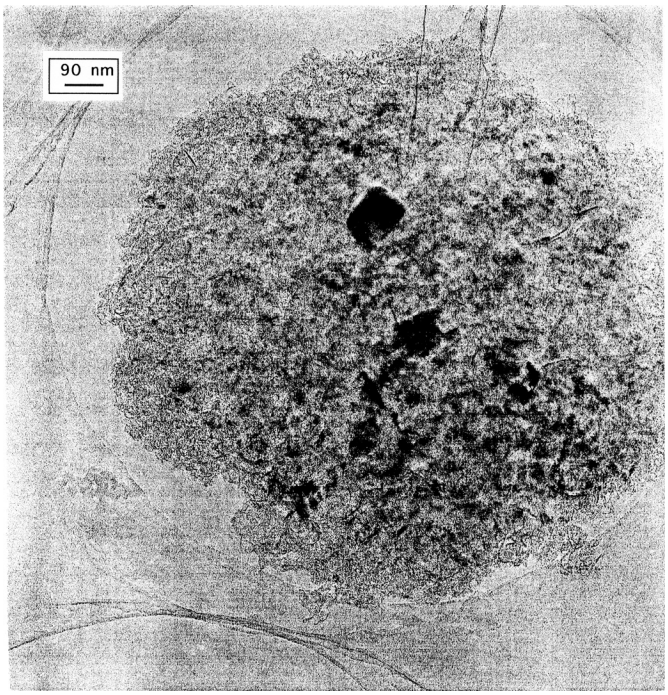

FIG. 1. HRTEM micrograph of a portion of the AQ1 particle of the Allende meteorite. Most of the sample consists of elemental carbon. The dark, blocky areas were identified as chromite grains or crystals by EDX analysis. This material was used for the microscopy study, results of which are presented in the following figures.

residue used for HRTEM. Most of the material is carbonaceous. The dark blocky areas are chromite grains or crystals. The four micrographs of Fig. 2 show structural styles common to all three meteorites, namely regions of curved and frequently twisted and intertwined graphene sheets. Common in all micrographs are also structures resembling carbon onions. However, closer inspection reveals that these are more similar to carbon black particles than to onions (Pontier-Johnson, 1998). Figure 3 shows two portions from still another sample of the Allende meteorite. These appear to be three-dimensional closed structures resembling carbon onions or else carbon black particles. Notice the apparent interior voids in which noble gas atoms could be trapped. A very different type of apparently closed structure, shown in Fig. 4, was found in the Vigarano sample. These sacs resemble the "graphitic hollow calabashes" of Wang and Yin (1998). These could have formed by the pyrolysis of oxygen- or sulfur-bearing hydrocarbon polymers (Oberlin, 1989, 2002). Similar structures were seen in the Allende sample (Fig. 2a, area b). Figure 5 shows an area of the Leoville carbon that contains abundant onion-like structures; possibly carbon-black like particles (labeled (a)). The Leoville carbon is especially interesting in that it contains thin nanocrystals with parallel fringes. Figure 6 presents an area with four such crystals. Two of these have *d*-spacings of 0.29 nm, one has a *d*-spacing of 0.25 nm, and the fourth has a *d*-spacing

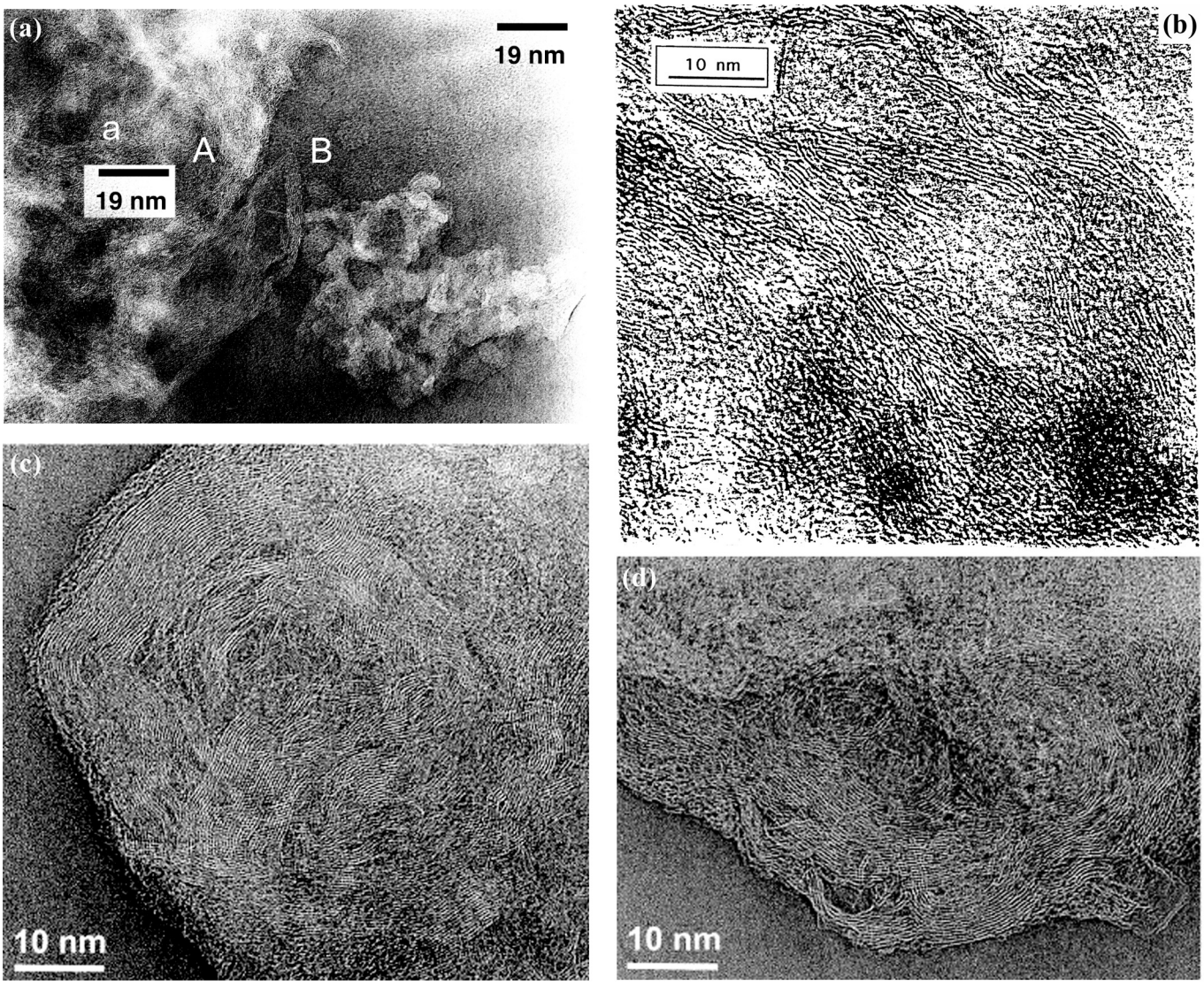

FIG. 2. (a) HRTEM micrograph of Allende carbon. The image was inverted because that yielded better contrast (inverted: fringes which are normally dark are bright here). Curved and tangled graphene sheets in area (a) (see (b)). Apparently closed three-dimensional carbon structures in area (b). There are several spherical particles in this micrograph. (b) Detail of (a) (non-inverted). The figure clearly shows the web of tangled and curved graphene sheets. The fringe distances are extremely constant at 0.385 nm. The increase above the 0.337 nm of the pure graphite stacking is indicative of turbostratic stacking. (c) HRTEM image of a portion of another Allende sample. This material has the appearance of a pyrocarbon (see Oberlin, 2002). The graphene sheets are seldomly longer than 20 nm. The particle has apparent internal "voids" in which noble gas atoms could be trapped. (d) Another HRTEM micrograph of Allende carbon. Notice the tendency of the carbon to form spherical constructs.

of 0.50 nm. Because the crystals occur in the areas of the meteoritic carbon and not in the areas of the backing, they are not contaminants already present on the backing.

A similarly intriguing crystal was found in a spot of the Allende sample (Fig. 7). Its dimensions are roughly 10 × 10 nm. The *d*-spacings are 0.25 nm. A similar crystal nearby had *d*-spacings of 0.48 nm. We are fully aware of the pitfalls of classifying such crystal as a form of carbon without a chemical analysis (Smith and Buseck, 1981a); however, these are remarkably similar to the putative carbyne crystals described by Gilkes *et al.* (1992) and Pillinger (1993). It is, however, entirely conceivable that these are very thin oxide or sulfide crystals that have survived the acid treatment.

All HRTEM micrographs now available for unetched Allende carbon (this paper; Smith and Buseck, 1980, 1981b; Lumpkin 1981, 1983b) show unambiguously that carbyne crystals, if these occur at all in this material, are very rare. This observation calls into question again what the d_{max} values between 0.44 and 0.48 nm, obtained by electron diffraction on *etched* Allende carbon, represent. Smith and Buseck (1981a)

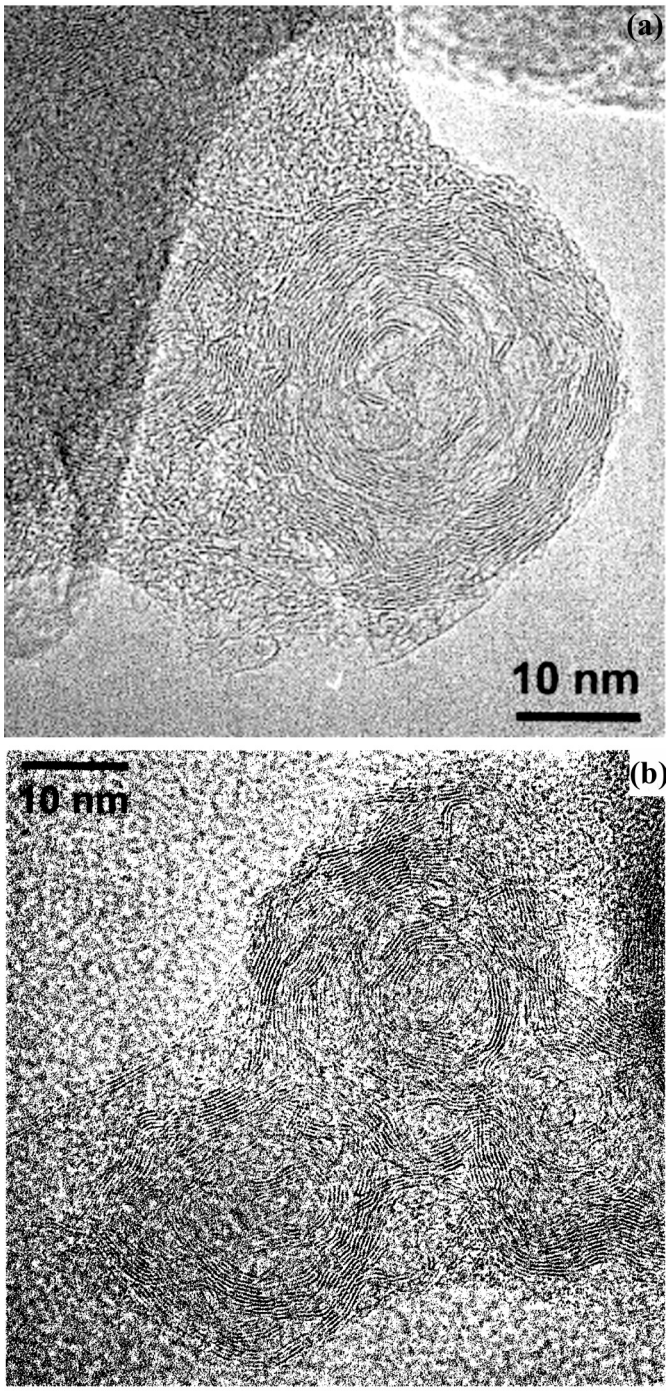

FIG. 3. (a) HRTEM micrograph of an apparently closed carbon structures from Allende sample AQ5. Notice the apparent internal voids in which noble gas atoms could be trapped. (b) A field of several onion-like particles. Such and similar structures occur in the samples from all three meteorites but involve no more than an estimated 10% of all carbon.

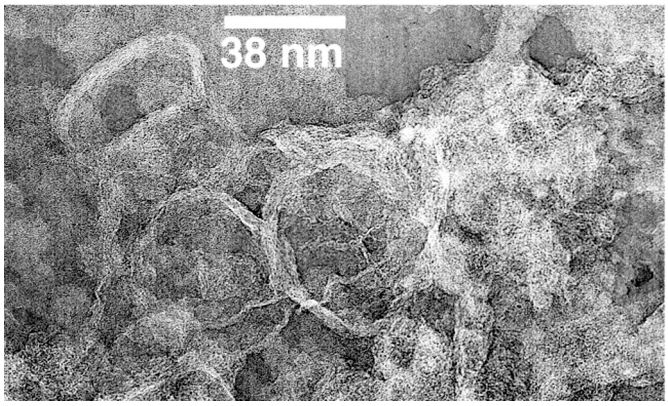

FIG. 4. Detail of a HTREM micrograph (inverted) of carbon from Vigarano. These structures may be carbon sacs similar to the "graphitic hollow calabashes" of Wang and Yin (1998). These could have formed by the pyrolysis of oxygen- or sulfur-bearing hydrocarbon polymers (Oberlin, 2002). They could contain noble gas atoms. The structures in area (b) of Fig. 2a in the Allende carbon appear to be similar. The areas not shown here were rich in carbon-black like carbon spheres.

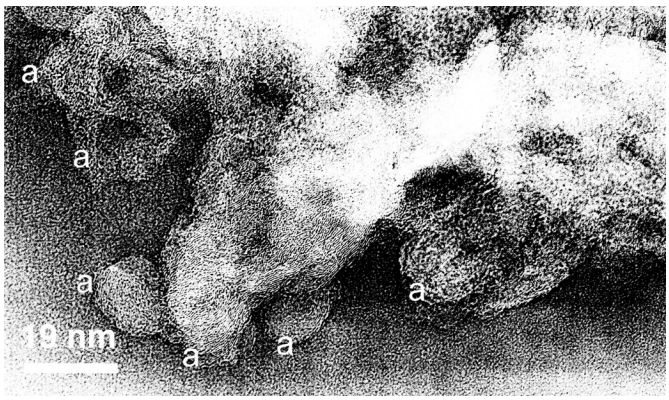

FIG. 5. HRTEM micrograph of carbon from the Leoville meteorite. This sample is rich in carbon spheres (a).

suggested that these were layer-lattice silicates which had contaminated the sample. We suggest that a systematic HRTEM study of *d*-spacings of an etched sample of Allende carbon is necessary to resolve this issue.

Close inspection of all micrographs reveals a fundamental property of these carbons, namely that they contain very few long graphene ribbons. The sheets are typically 10 to 20 nm long, but numerous segments are even shorter than 10 nm. There are also numerous offsets ("faults") between stacks of sheets. One could call these structures "nanocrystalline". It is perhaps at these imperfections that the etching chemicals attack and remove C atoms as CO or CO_2, thereby opening channels for the Q-gases to escape.

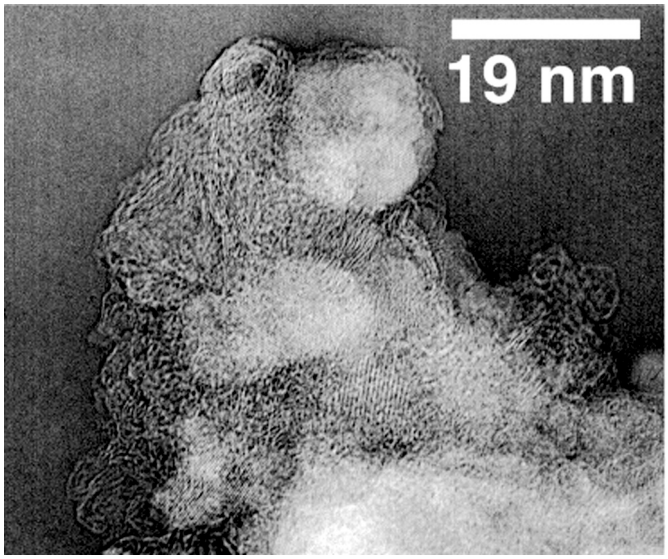

FIG. 6. HRTEM micrograph of another spot of the carbon of Leoville. This spot contains four microcrystals with parallel lattice fringes. These show *d*-spacings of 0.25, 0.29, and 0.50 nm.

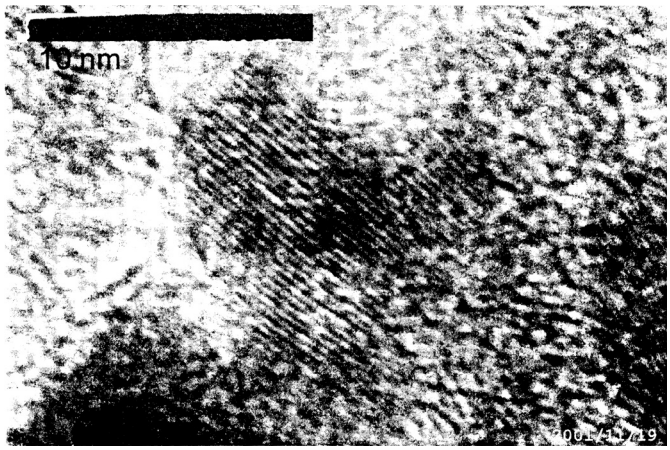

FIG. 7. Crystal with *d*-spacings of 0.48 nm in the Allende sample.

TABLE 1. Energies of the characteristic x-rays of S, Cl, Ar, K, and Ca.

Energy (eV)	Element	Line	Relative intensity*
2306.6	S	K_{α_2}	50
2307.8	S	K_{α_1}	100
2464.0	S	K_{β_1}	5
2620.8	Cl	K_{α_2}	50
2622.4	Cl	K_{α_1}	100
2815.6	Cl	K_{β_1}	6
2955.6	Ar	K_{α_2}	50
2957.7	Ar	K_{α_1}	100
3311.1	K	K_{α_2}	50
3313.8	K	K_{α_1}	100
3688.1	Ca	K_{α_2}	50
3691.7	Ca	K_{α_1}	100

*An intensity of 100 is assigned to the strongest line in each shell for each element.
Source: x-ray data booklet, Center for x-ray optics and advanced light source, Lawrence Berkeley National Laboratory.

Particle-Induced X-Ray Emission

PIXE is analogous to electron microprobe analysis, except that high-energy ions, 2.5 MeV protons in our case, are used to generate the characteristic x-rays of the elements in the target material. Table 1 lists the characteristic wavelengths of significant elements near argon. Potentially the most serious interference can be due to the K_{β_1} line of Cl that is not resolved from the major Ar lines. Potassium and calcium interfere only when present in large concentrations. Carbon contents, however, were estimated with proton recoil.

Four different kinds of samples were used for this analysis: (1) selected particles from an Allende residue ranging in size from 20 to 50 mm that were attached to hostaphane foil of 4 mm thickness and mounted in the nuclear microprobe sample-chamber. (2) Floating matter produced from the Allende meteorite *via* the freeze–thaw method described by Matsuda *et al.* (1999). Its carbon content was ~1%. A sample of this material was also studied with the electron microprobe and SEM of the Department of Earth Science at the Vrije Universiteit (Amsterdam). It contained olivine, enstatite, clinopyroxene, pentlandite and other minerals with carbonaceous material dispersed between them. (3) Suspended matter obtained by the same method. Its carbon content was estimated ~3%. (4) "Black balls" generated by ultrasonification of Allende powder in water, as reported by Vis *et al.* (2001). Their carbon content was determined at 1.5%. The bulk of the last three materials consisted of silicates, oxides, and sulfides. They were mounted on a silicon-rich backing. Single spots on all samples were irradiated with a 2.5 MeV proton beam of 10 μm diameter generated by the NEC Pelletron accelerator and beam focusing system of the Vrije Universiteit. The x-ray signals were detected with a liquid nitrogen-cooled Ortec IGLET X HPGe detector (active diameter 11 mm; Be window 25 mm; resolution 145 eV at 5.9 keV and 1000 cps) whose wavelength range of interest was calibrated with radioactive x-ray emitters.

A vexing problem of this analysis was that all signals due to elements in the spot under the proton beam other than Ar continued to grow during the course of an analysis, whereas x-ray signals at the wavelength of Ar were only observed during the first 10 to 30 s of the measurement. For longer collection times, any Ar signal present became masked by the non-Ar "noise". This phenomenon probably means that the proton beam swiftly destroyed the Ar carrier on which it impinged, thereby allowing the Ar atoms to escape into the vacuum of the accelerator's sample chamber and removing them from

detection. Consequently, the number of counts collected at the Ar K_α lines was nearly always in the range 10–100. It was not known whether the Ar loss was due to local heating or to wholesale rupture of carbon bonds. With beam currents in the range 1 to 10 nA, the beam's power was in the range 1 to 10 mW, perhaps insufficient to engender substantial heating. However, the ions must have produced "latent tracks", semi-cylindrical channels along which the C-atoms are pushed radially outward by the ionization through which the Ar atoms might have escaped. It is this Ar loss rather than the presence of traces of K and Ca that make the detection of Ar by PIXE difficult, if not problematic.

Sixty spots on the acid-resistant residue of Allende were investigated. Of these, six revealed Ar x-ray signals above the detection limit which means that the Ar concentration in the beam, normalized to C, was at least Ar/C = 1:10 000 atoms/atom. Figure 8 presents the strongest case. The largest signal of 74 ± 9 counts occurs at 2.956 keV. The spectrum contains significant contributions from S, Cl, K, Ca, Fe, and possibly small contributions from heavier transition elements. However, the contribution of the K_{β_1} line of Cl to 2.956 keV can be only a small fraction of the Ar-line. Radiogenic ^{40}Ar contents should be very small in these measurements.

The PIXE spectra of the "floats", "suspended particles", and "black balls" show three clusters of strong lines: S + Cl, K + Ca, and the Fe-group. Of the 83 spots analyzed, only four showed possible Ar signals above the detection limit and some 19 contained marginal evidence for Ar. The fundamental uncertainty of these results is that one cannot know whether this is Q-Ar or radiogenic ^{40}Ar sited in a K-bearing phase of these inorganic mineral-rich samples when significant K is detected.

DISCUSSION

The bulk of the carbon in the Allende meteorite has been called "poorly graphitized carbon" (Smith and Buseck, 1981a) or "turbostratic carbon" (Lumpkin, 1981). The carbons in the three meteorites of our study fit these generic names but are more complex. Many particles in our HRTEM images are spherical objects, usually not much larger than 10–20 nm across. These resemble "nested fullerenes" (*i.e.*, the "carbon onions" of Ugarte, 1992), but could also be carbon black particles. These carbon spheres probably formed in the gas phase, perhaps by direct carbon condensation, or else by dehydrogenation of polyaromatic hydrocarbons (PAHs). The bulk of the carbon

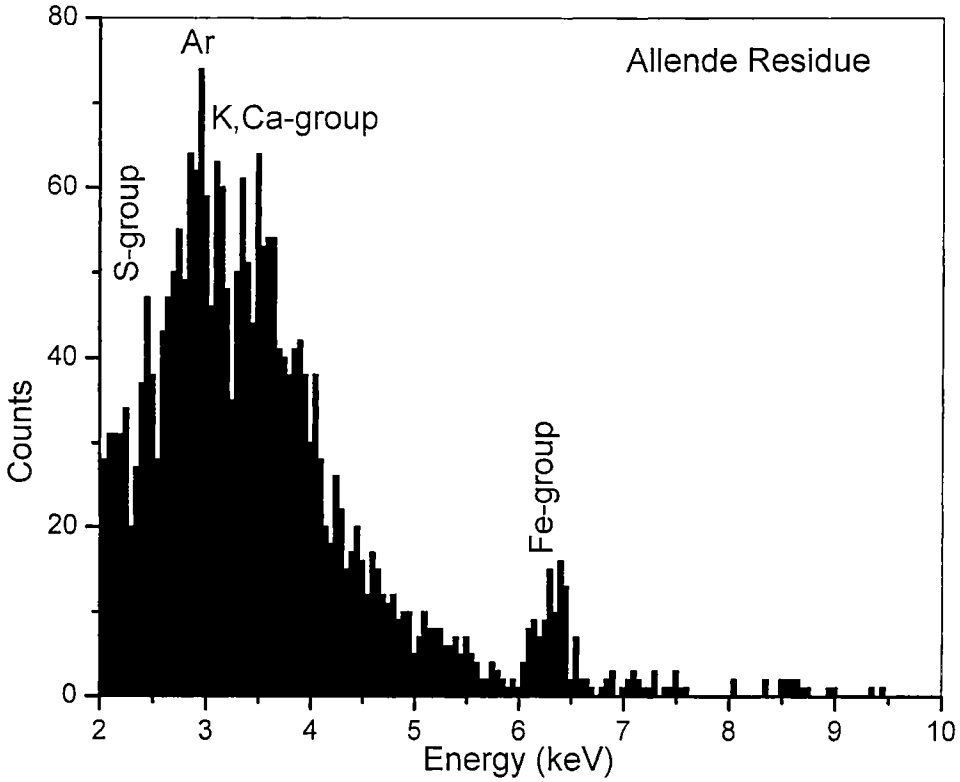

FIG. 8. PIXE spectrum from a spot on acid-resistant residue AQ1 of Allende. Sixty spots were analyzed. This was one of six spots that showed an Ar line at 2.956 keV. Data below 2 keV are omitted from this figure because of the occurrence of strong Si lines of backings, or strong Si and Al lines from inorganic minerals. In this figure, S-group stands for K_α lines of sulfur and chlorine; K,Ca-group for lines of potassium and calcium; and Fe-group for lines of chromium, manganese, iron, and cobalt.

and the remarkable structures of Figs. 4 and 5, although reminiscent of the "graphitic hollow calabashes" of Wang and Yin (1998), are reminiscent of pyrocarbons (see, for example, Figs. 25, 26, and 27 in Oberlin 1989). Pyrocarbon is a generic term for a variety of carbon deposits formed on hot substrates by the pyrolytic dehydrogenation of gaseous hydrocarbons. The clan of pyrocarbons includes so-called "glassy carbon", a term used by Smith and Buseck (1981a) and "turbostratic carbon", the term used by Lumpkin (Lumpkin, 1981). The meteoritic pyrocarbons could have formed on hot surfaces of inorganic minerals, which dovetails with observations that much carbon in Allende occurs as films or micromounds on such minerals (Bauman and Devaney, 1973; Bauman *et al.*, 1973; Bunch and Chang, 1980). However, the formation of the bulk of the carbon by "condensation" in a very carbon-rich atmosphere cannot be ruled out.

Which of these carbon structures could be the elusive Q? Perhaps all! The tangled web of graphene sheets could be the labyrinth of pores of amorphous carbon as suggested by Wacker *et al.* (1985) and Wacker (1989) but it is not yet clear exactly how the Q-gases could be lost from this web by etching with, for example, hot nitric acid. Closed three-dimensional structures such as the spherules and the carbon "sacs" could be gas containers much more vulnerable to etching (R. D. Smalley, pers. comm.). If all of these are, indeed, carriers of the Q-gases, then these gases could be widely dispersed in the carbonaceous matter, with only spotty concentrations of Q-Ar, rendering the detection of Q-Ar by PIXE or any other detection method a matter of hit-and-miss.

What about other carriers that were suggested in the literature? We have not observed any single- or multi-walled carbon nanotubes. If carbyne crystals occur at all, these seem to be too rare to qualify. Carbon onions, in the sense of perfectly nested fullerenes, were not observed. Fullerenes can be eliminated on the following grounds. The compilation of He, Ne, and Ar contents of numerous chondrite samples, either bulk samples or acid-resistant residues, by Schultz and Kruse (1989) demonstrates that all ordinary chondrites, with the possible exception of the very gas-rich ones in which the Q-gases are totally masked by trapped solar wind He, Ne, and Ar, contain Q-gases. Consequently all chondrite samples, either bulk samples or acid-resistant residues, must contain fullerenes, which is not the case (Heymann, 1995). Ion implantation into surfaces of diamonds (Matsuda and Yoshida, 2001) is an intriguing alternative because it could be a low-temperature process and because of the well-established proportionality of diamond and Q-gas contents of chondritic meteorites.

A salient issue is the trapping of the Q-gases by the carrier. The literature of adsorption of gases by carbonaceous materials is vast and it includes numerous recent studies of adsorption of gases on carbon nanotubes, mostly of molecular hydrogen but also of He (Wang *et al.*, 1999; Teizer *et al.*, 1999; Cole *et al.*, 2000; Gordillo *et al.*, 2000; Stan *et al.*, 2000; Challa *et al.*, 2001), Kr (Muris *et al.*, 2000), and Xe (Kutznetsova *et al.*, 2000; Simonyan *et al.*, 2001). We do not suggest that carbon nanotubes occur in meteoritic carbonaceous matter, these have not been found, or were parent materials for the carbonaceous matter. The significance of these studies is that they demonstrate conclusively that the adsorptive power of concave carbon surfaces is much greater than that of flat or convex carbon surfaces. Hence, adsorption into narrow, carbon-lined channels, especially when the diameter of the channel is commensurate with the diameter of the noble gas atom, should be strong because inside such channels, the noble gas atom interacts by van der Waals bonding, closely with a significantly larger number of carbon atoms than for adsorption on flat graphene sheets. Consequently, the adsorptive strength for noble gas atoms inside the porous carbon suggested by Wacker *et al.* (1985) and Wacker (1989) for the carrier of the Q-gases is greater than on other surfaces of elemental carbon. Furthermore, temperature programmed desorption (TPD) of Xe, initially absorbed at 95 K in open, single-walled nanotubes, revealed that most of the gas was released into high vacuum between 100 and 120 K (Kuznetsova *et al.*, 2000). Helium can become trapped in the interstitial channels of nanotube bundles from which it is released between ~15 and 100 K (Teizer *et al.*, 1999). When one compares these observations with the known thermal release pattern of the Q-gases, mentioned in the introduction, one deduces that the firm entrapment of the Q gases probably occurred by adsorption at low temperatures on concave carbonaceous surfaces while these structures formed, grew, and closed. An attractive feature of this adsorption variant is that the well-known enrichment of the heavier isotopes of He, Ne, and Ar in the Q-gases relative to solar He, Ne, and Ar is explained in that case by the known process of "quantum sieving" (Wang *et al.*, 1999; Challa *et al.*, 2001). Once again, we do not suggest that carbon nanotubes occur in or were parent materials for meteoritic carbonaceous matter.

This variant of trapping by adsorption accepts fullerenes, end-capped carbon nanotubes, carbon onions (nested fullerenes), graphitic hollow calabashes, and any other three-dimensional closed carbon structures as carriers of the Q-gases. Fullerenes were eliminated above. With regards to the remaining suggested structures, the most likely to be closed are the absorption sites in a labyrinth of narrow (~2 nm diameter) pores of amorphous carbon (Wacker *et al.*, 1985; Wacker, 1989) although it is not obvious from all available HRTEM micrographs (Smith and Buseck, 1980, 1981a,b; Lumpkin, 1981, 1983a,b; Harris *et al.*, 2000; this paper) exactly what this labyrinth is.

While this paper was in review, there was published a new concept of the trapping of noble gases on carbon surfaces by Hohenberg *et al.* (2002). The concept proposes the incorporation of heavy noble gases into growing solids by a two-step process. First, a noble gas atom, say Xe, is bound to especially active surficial sites by "anomalous" (*i.e.*, very tenacious) adsorption. Then, as the solid continues to grow, the atom cannot get out of the way and becomes occluded. The

authors even suggested that such bonding of Kr and Xe is due "more to chemical than Van der Waals forces", hence that "Kr and Xe temporarily lose their labels as 'inert' gases". One of us has discovered by theoretical, semi-empirical calculations that the "especially active surficial sites" of growing graphene sheets are most likely the so-called "dangling carbon bonds", which are actually greatly shortened, originally aromatic C–C bonds to bonds with double- and even triple-bond character at the edges of such sheets. These are the locations of very strong chemical activity on growing graphene sheets. The new hypothesis, combined with the suggested identification of the sites of anomalous absorption, revive the suggestion that the heavy Q-gases could become trapped between graphene sheets (Bernatowicz *et al.*, 1996).

There remains the issue of how the combination of HRTEM and Ar analysis might pin down the nature of Q. Judging from what we have learned, the diameters of PIXE beams are likely to always remain much larger than the closed structures seen in our HRTEM prints. One is therefore left with comparing the Ar x-ray response of areas rich in suspected Q against areas poor in suspected Q structures.

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