

Nanosized carbon-rich grains in carbonaceous chondrite meteorites

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Abstract

Macromolecular carbonaceous material is common in primitive meteorites. Little information exists on its form and composition, and there are no published data on nanometer-scale chemical and structural variations. Transmission electron microscopy (TEM) studies of CM meteorites reveal abundant, previously unrecognized nanosized carbonaceous grains. They have a high aromatic component as revealed by electron energy-loss spectroscopy (EELS), with up to 20 at.% substituted by S, N, and O. They occur as discrete hollow and solid nanospheres and sparse nanotubes. The grains exhibit considerable variations in composition, size, morphology, and abundance among meteorites and may represent materials from multiple reservoirs.

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1. Introduction

The CM carbonaceous chondrites (CC) are ancient meteorites, consisting of a C-rich matrix primarily composed of clays, oxides, and sulfides [1,2]. They record the early stages of the solar system and perhaps of the presolar molecular cloud. Interest in meteoritic carbonaceous material partly stems from its potential to reveal information about prebiotic chemical evolution, although its origin remains controversial [3–6]. Major questions remain regarding the form and composition of the carbonaceous material.

The CC meteorites contain a diverse suite of organic materials, with most of the C bound in an

insoluble, macromolecular, kerogen-like substance [4,5,7]. The CM meteorites contain up to 4 wt.% C. Of particular interest is the Tagish Lake meteorite because of its pristine nature and up to 5.8 wt.% C [8,9]. The macromolecular material has primarily been analyzed in bulk as acid residues, and much information has been provided regarding elemental and isotopic compositions and the nature of the functional groups [3–5,10]. Limitations of acid-residue analyses are that they treat the carbonaceous residue as homogenous, and also the aggressive acid digestion may alter the sample characteristics. Recent studies of CCs suggest a spatial relationship of some carbonaceous materials with products of aqueous alteration [11–15].

Early studies of CCs revealed hollow carbonaceous particles [16–18], although these papers have largely been overlooked in the recent literature. Recent work

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reported unusual nanospheres in the Tagish Lake meteorite [15]. These reports motivated us to reexamine the carbonaceous material in CCs. We studied Tagish Lake and a range of CM carbonaceous chondrites with electron energy-loss spectroscopy (EELS) together with transmission electron microscopy (TEM). These techniques provide unique chemical and crystal-chemical information at high spatial resolution, free of spectral interferences from surrounding materials [19–21].

2. Materials and methods

A range of carbonaceous chondrite meteorites was examined: Tagish Lake (ungrouped), and Bells, Cold Bokkeveld, Mighei, Murchison, and Murray CM meteorites. Samples were prepared by gentle disaggregation of a piece of meteorite and dispersion of a small quantity of powder onto a TEM grid coated with lacey carbon. Most samples were dispersed in $\sim 1 \mu\text{l}$ of water to enhance adherence of the particles to the TEM grid. We ruled out the possibility that the water altered the carbonaceous particles by also examining samples prepared by sprinkling dry disaggregated meteorite onto the grids. We noted no differences between the two preparation methods.

High-resolution TEM (HRTEM) images were acquired with a 002B transmission electron microscope operating at 200-kV accelerating voltage. Single-side-band holographic images [22,23] were recorded by manually shifting the largest objective aperture to obscure half of the image. This method enhances differences in sample thickness [24].

EELS spectra were acquired with a GATAN 766 DigiPEELS spectrometer attached to a Philips 400-ST field emission gun (FEG) TEM operated at an accelerating voltage of 100 keV, and probe currents, I , that ranged from 0.3 to 1.5 nA. The width at half maximum, and hence the energy resolution, of the zero-loss peak was 0.8 eV. Spectra were acquired in diffraction mode, thus allowing control of the collection angle, 2β . Typical values for the beam-convergence semi-angle, α , and collection semi-angle, β , were 16 and 11 mrad, respectively.

High-energy-resolution spectra of the C K edge were acquired with samples cooled to liquid N_2 temperature (77 K). Fluence to the sample was kept

low to acquire data free of beam damage. A typical fluence rate was $< 100 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$.

Spectra were acquired with acquisition times of 1 s. A background of the form $\text{AE}^{-\tau}$ was subtracted from beneath the S $\text{L}_{2,3}$ and C K edges. To remove the background from beneath the N and O K edges, we used modified power-law background subtraction routines [25]. These edges are of weak intensity and sit on the intense tails of the preceding S $\text{L}_{2,3}$ and C K edges, making the standard $\text{AE}^{-\tau}$ power-law background subtraction unsuitable. Following background subtraction, the effects of the tailing of the zero-loss peak were deconvoluted using a point-spread-function spectrum.

A sample of Tagish Lake meteorite was gently crushed and deposited on a Be planchet and imaged with a Hitachi S-4700 scanning electron microscope (SEM). This microscope uses a cold-field-emission gun and has a point-to-point resolution of 1.5 nm. Images were acquired at an accelerating voltage of 15 kV and emission current of $< 9500 \text{ nA}$ from uncoated samples in secondary electron mode. The identities of the particles were confirmed by energy dispersive X-ray spectrometry.

3. Results

3.1. Morphology, size, distribution, and structure of carbonaceous particles

We observed nanosized carbonaceous flakes, spheres, and tubes in the Tagish Lake and CM meteorites. We also obtained carbon EELS signals from clays, carbonates, poorly graphitized carbonaceous mantles on sulfides, and sparse graphite and carbides. We focus our attention on the nanospheres and nanotubes because of their unique nature.

The nanospheres occur as single and clustered particles. Some are solid, and others have hollow or vesicular cores (Fig. 1). The nanotubes are also hollow (Fig. 1h). Nanospheres exhibit a range of sizes, morphologies, aggregations, and are free of foreign mineral grains such as silicates and sulfides (Fig. 1). The surfaces of some nanospheres are bumpy, as revealed by the SEM and single-side-band holographic images (Figs. 2 and 3). It is difficult to measure the concentration of nanospheres in the disaggregated meteorites, although their concentration

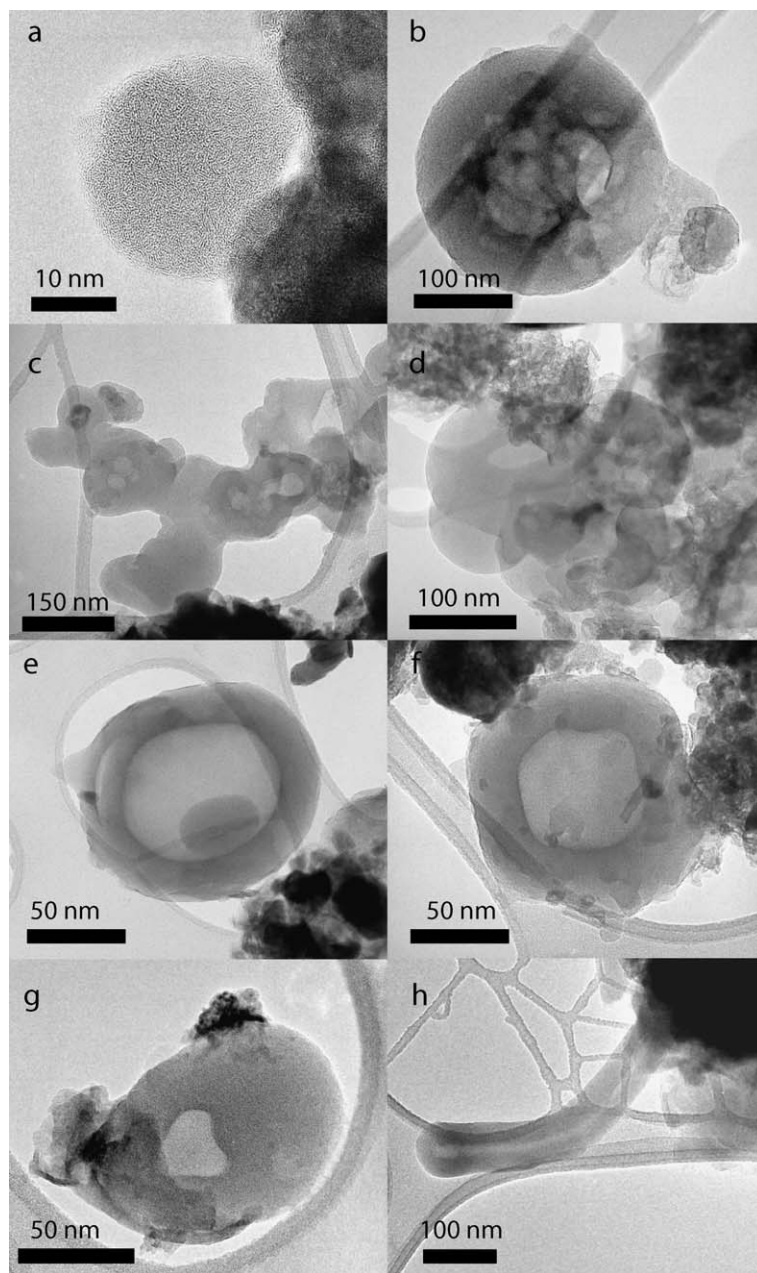


Fig. 1. TEM images of nanosized carbonaceous grains from the Tagish Lake and CM meteorites. (a) Typical nanosphere adhering to clay particles (Bells meteorite). (b) Nanosphere with a vesicular core (Cold Bokkeveld meteorite); the diagonal band is part of the supporting substrate. (c) Cluster of agglomerated nanospheres (Tagish Lake meteorite), some of which have vesicular cores. (d) Three agglomerated nanospheres (Murray meteorite). (e) Hollow nanosphere with solid nanosphere (Tagish Lake meteorite). The width and intensity of the Fresnel fringe of the solid nanosphere shows that it is enclosed in the hollow globule. (f) Hollow nanosphere (Mighei meteorite). (g) Irregularly shaped nanosphere with a small hollow core (Bells meteorite). (h) Nanotube (Tagish Lake meteorite) on lacey substrate.

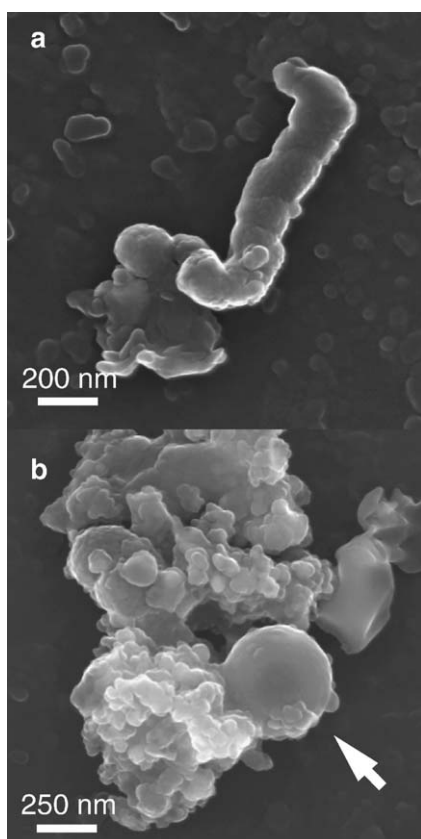


Fig. 2. Scanning electron microscope images of nanosized carbonaceous grains from the Tagish Lake meteorite. (a) Single vermiform particle, and (b) one carbonaceous sphere (arrowed) protruding from an aggregate of magnetite, sulfides, and clay.

in the HF/HCl residues allows a visual estimate of up to 10% of the macromolecular materials [26].

Small nanospheres, <50-nm diameter, are common in Tagish Lake and CM meteorites, whereas larger globules and clusters are rare. Single carbonaceous spheres up to 200 nm in diameter occur, and agglomerated clusters up to 2300 nm across are found. The largest clusters are in the Tagish Lake and Murray meteorites. The nanotubes are <100 nm in diameter, with internal diameters of 20 nm.

Hollow nanospheres occur in Tagish Lake and all CM meteorites. The distribution of nanospheres is heterogeneous among and within different pieces of meteorite examined. The hollow cores range from single and spherical to complex and vesicular. There is a continuum in core morphology, from small nano-

spheres with vesicular cores to larger particles with single hollow cores. Hollow nanospheres are spherical to subrounded, <1000 nm in diameter, with wall thicknesses >14 nm and void volumes to $3.3 \times 10^5 \text{ nm}^3$ (Table 1). Nanotubes occur only in the Tagish Lake meteorite, and they are far less abundant than the hollow nanospheres.

Most nanosized carbonaceous grains are amorphous as revealed by electron-diffraction patterns, HRTEM images, and shape of the C K edge. A subset of the nanospheres exhibits weak ring diffraction patterns that indicate a poorly crystalline structure.

3.2. EELS data

We determined the average compositions of nanosized carbonaceous grains using EELS; they fall

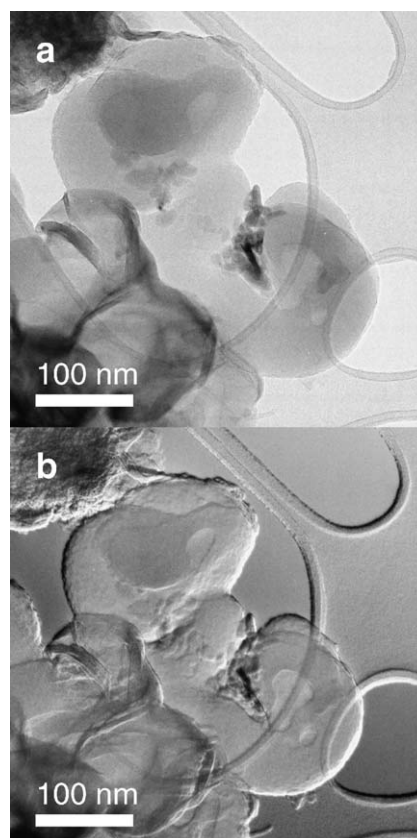


Fig. 3. Comparison between (a) conventional bright-field TEM image and (b) single-side-band holographic image of a cluster of nanosized carbonaceous grains from the Tagish Lake meteorite.

Table 1
Dimensions of single hollow nanospheres from the Tagish Lake meteorite

Particle	Diameter (nm)	Internal diameter (nm)	Wall thickness (nm)	Void volume (nm ³)
1	166	104	31	8.5×10^3
2	193	166	14	2.2×10^4
3	270	120	75	1.1×10^4
4	300	175	63	2.4×10^4
5	306	94	106	6.9×10^3
6	319	200	60	3.1×10^4
7	388	175	107	2.4×10^4
8	500	167	167	2.2×10^4
9	830	644	93	3.3×10^5

within the range of bulk macromolecular material from CCs [9,27]. The average results show minor differences among meteorites but with significant particle-to-particle heterogeneities. The average compositions of the nanosized carbonaceous grains have a narrow range with S, N, and O as the only adatoms detected (Fig. 4, Table 2). Hydrogen is excluded from the analyses since EELS cannot detect bonded H.

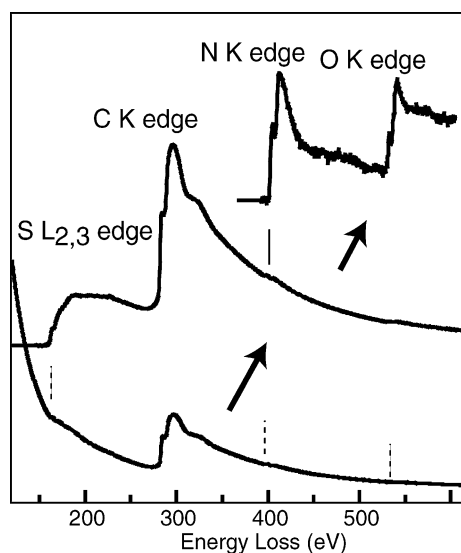


Fig. 4. Electron energy-loss spectra of a S-rich Tagish Lake meteorite nanosphere. The bottom spectrum illustrates the edges on the sloping background. Subtraction of the background from beneath the S edge reveals the relative intensities of the major elements (middle spectrum). The weak N and O K edges are clearly visible after subtracting the background from beneath the N K edge (top spectrum).

Table 2
Average and representative compositions of nanosized carbon-rich grains in the meteorites examined

Form	Composition ^a	Atom percent			
		C	S	N	O
<i>Tagish Lake</i>					
Bulk ^b	C ₁₀₀ N ₁₀ O ₁₅	80.0	—	8.0	12.0
Globules (<i>n</i> = 16)	C ₁₀₀ S _{1.8} N _{2.8} O _{3.1}	92.8	1.6	2.6	2.9
Globule	C ₁₀₀ S _{10.5} N _{3.1} O _{4.8}	84.5	8.9	2.6	4.1
Globule	C ₁₀₀ S _{2.7} N _{5.0} O _{10.0}	85.0	2.3	4.3	8.5
Globule	C ₁₀₀ S _{0.8} N _{13.6} O _{2.5}	85.5	0.7	11.6	2.1
Globule	C ₁₀₀ S _{5.0} N _{10.2} O _{5.7}	82.7	4.1	8.4	4.7
<i>Murchison</i>					
Bulk ^c	C ₁₀₀ S ₂ N _{1.8} O ₁₂	86.4	1.7	1.6	10.4
Globules (<i>n</i> = 10)	C ₁₀₀ S _{1.9} N _{2.6} O _{6.3}	90.3	1.7	2.4	5.7
Globule	C ₁₀₀ S _{4.6} N _{4.2} O _{2.0}	90.3	4.2	3.8	1.8
Globule	C ₁₀₀ S _{0.9} N _{5.6} O _{7.1}	88.0	0.8	4.9	6.3
<i>Murray</i>					
Globules (<i>n</i> = 12)	C ₁₀₀ S _{1.7} N _{2.2} O _{2.2}	94.3	1.6	2.1	2.1
Flake	C ₁₀₀ S _{5.9} N _{3.3} O _{5.2}	87.4	5.2	2.9	4.6
Globule	C ₁₀₀ S _{0.7} N _{7.7} O _{5.3}	88.0	0.6	6.8	4.7
Flake	C ₁₀₀ S _{1.5}	98.5	1.5	—	—
<i>Mighei</i>					
Spheres (<i>n</i> = 11)	C ₁₀₀ S _{1.8} N _{4.5} O _{3.0}	91.5	1.7	4.1	2.8
Globule	C ₁₀₀ S _{2.9} N _{2.9} O _{7.7}	88.1	2.6	2.6	6.8
Globule	C ₁₀₀ S _{4.3} N _{4.0} O _{4.0}	89.1	3.8	3.6	3.6
<i>Bells</i>					
Globules (<i>n</i> = 11)	C ₁₀₀ S _{2.4} N _{1.9} O _{4.0}	92.3	2.2	1.8	3.7
Globule	C ₁₀₀ S _{8.0} N _{6.1} O _{5.1}	83.9	6.7	5.1	4.3
Globule	C ₁₀₀ S _{5.6} O _{3.5}	91.7	5.1	—	3.2
<i>Cold Bokkeveld</i>					
Globules (<i>n</i> = 10)	C ₁₀₀ S _{1.7} N _{5.6} O _{5.6}	88.6	1.5	5.0	5.0
Globule	C ₁₀₀ S _{1.0} N _{16.1} O _{7.1}	80.5	0.8	13.0	5.7
Flake	C ₁₀₀ S _{1.7} O _{6.7}	92.3	1.6	—	6.2

Except for bulk analyses [9,27], H is neglected because of analytical limitations.

^a Compositions are recast with respect to 100 C atoms.

^b From Ref. [9].

^c From Ref. [27].

Sulfur ranges between 1.5 and 2.2 at.%, N from 1.8 to 5.0 at.%, and O from 2.1 to 5.1 at.%. Despite the similar average compositions, individual particles show large elemental variations. For example, one particle from Cold Bokkeveld contains 13 at.% N, and one from Tagish Lake has 11.6 at.% N. These results reveal the extreme compositions of a subset of the

nanosized carbonaceous grains, with up to 20 at.% of the C replaced by S, N, and O.

The C EELS spectra (the C K edge) of the nanosized carbonaceous grains exhibit similar shapes, with a sharp rise in intensity and a maximum at 285 eV. This maximum represents transitions to unoccupied π^* states (π^* peak) and indicates C=C ring bonds (Fig. 5). There are significant spectral variations that show differences in bonding and structure. For example, the spectrum labeled Bells1 (Fig. 5) resembles that of poorly ordered graphite, whereas Bells2 has a similar shape to that of amorphous C [20], but with a double-peaked π^* maximum.

The spectral features at the C K edge (Fig. 6) show the high degree of aromaticity of the nanosized

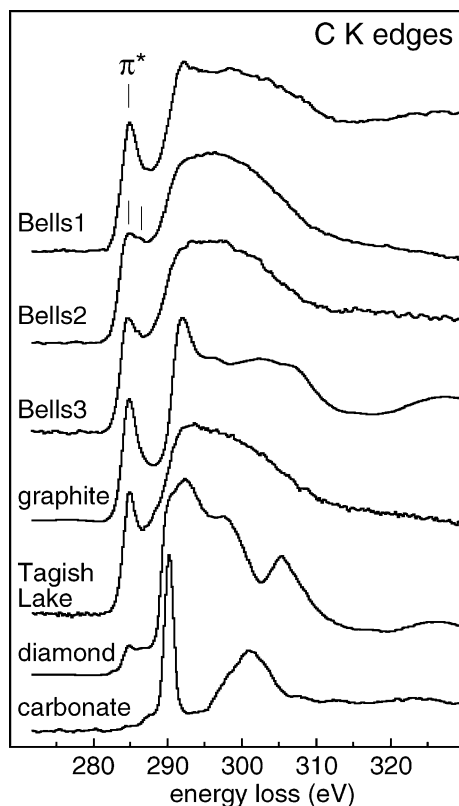


Fig. 5. Representative C K edges from the nanosized carbonaceous grains. The C K edges from other forms of C in the carbonaceous chondrites are shown for comparison. The diamond spectrum is from the Allende meteorite. The carbonate spectrum is from a Mg carbonate from the Bells meteorite. The vertical lines above the spectra reveal the positions of the π^* peaks.

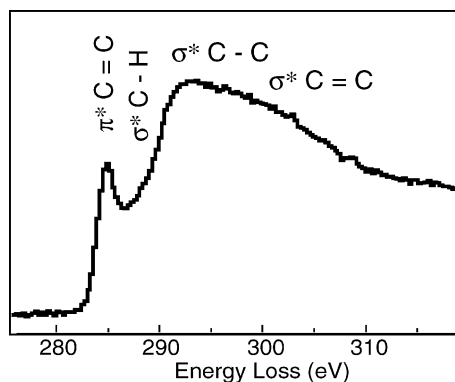


Fig. 6. Representative high-energy-resolution C K edge from a nanosized carbonaceous grain from the Tagish Lake meteorite. Spectrum was acquired under low-dose conditions, with the sample cooled to 77 K.

carbonaceous grains, consistent with previous studies of the macromolecular material [4,5,9]. The shapes of the C K edges of most carbonaceous grains are consistent with lack of long-range order. The N and O K edges are similar in shape and show bonding to C. Prominent features are the sharp edge onsets, indicative of C=O and C=N groups. Spectral features at both the C and O K edges suggest bonded H [28]. The shapes of the S $L_{2,3}$ and C K edges show that the S in the S-rich globules is bonded to C.

4. Discussion

The ranges in composition, size, and morphology of the carbonaceous grains suggest differences in their origin and mode of formation, and they may represent particles from multiple reservoirs. Possible sources of meteoritic carbonaceous material include stellar outflows, reactions in the interstellar medium, and hydrothermal processing on the parent asteroids [6,29]. Evidence suggesting a preaccretionary origin for a significant proportion of the macromolecular carbonaceous material in CCs is revealed by enrichment of deuterium and N and C isotopic fractionation [3,7,10]. Refractory carbonaceous material is a component of interstellar dust and is believed to have formed as a residue from energetic processing of interstellar ices [30], although the main sources of C in the interstellar medium are red giants and supergiant stars [29]. Spectroscopic evidence sug-

gests the presence of carbonaceous material in the form of nanosized C grains in the interstellar medium [31]. Some may have formed in a similar fashion to soot formation in hydrocarbon flames in the outflows of C-rich stars [32].

The hollow character of a subset of carbonaceous grains remains intriguing. Nakamura et al. [15] suggest that those in the Tagish Lake meteorite formed on the primitive asteroid by hydrothermal processing of UV-irradiated organics in interstellar ices. Laboratory experiments of UV-irradiated interstellar ice analogues show the formation of amphiphilic molecules that can self-assemble into vesicular structures [33]. It is also possible that the hollow particles formed through a heating event of interstellar ices. Heating would cause the ices to melt, with coagulation of the UV-irradiated organics into insoluble droplets [33]. The lack of significant crystallinity of the carbonaceous particles reveals the low-temperature nature of this process.

Hollow nanospheres have also been synthesized for industrial uses such as controlled release of medicines, dyes, inks, and the protection of enzymes, proteins, and DNA. Such syntheses have been accomplished through a wide range of procedures involving core templates such as organic surfactants or block copolymers that are subsequently removed, self-assembly of organic materials, and multilayered emulsions [34–36]. It is unlikely that any of those synthetic methods would have occurred in the primitive natural environment in which the meteoritic nanospheres formed. However, the rich variety of synthesis methods suggests that nanospheres can form through a range of mechanisms. An additional possibility is a combustion origin analogous to the cenospheres that occur in atmospheric emissions [37].

An intriguing aspect of the nanosized C grains is their potential as hosts of primordial noble gases such as the planetary noble gases (PNG). The carrier of the PNGs is commonly called Q and is thought to be carbonaceous [38–41]. PNGs occur in many primitive and differentiated meteorites and are thought to have been widely distributed in the asteroid-forming region of the solar system, in the protosolar molecular cloud, or to be presolar [38, 40]. These gases were postulated to be absorbed on interior surfaces of a pore labyrinth network within

amorphous C [42]. The hollow and vesicular cores of the nanospheres in the CM and Tagish Lake meteorites provide high surface areas suitable for gas absorption, although recent ^{129}Xe NMR studies show that Xe adsorption primarily occurs on quasi-graphitic crystallites and strong heteroatom-adsorption sites [43].

5. Conclusions

The chemical heterogeneity of the carbonaceous particles argues strongly for a preaccretionary origin for at least a subset. If this assumption proves true, then their structures and composition will provide important new information on the identity of the interstellar UV ‘bump’ at 217.5 nm, which is believed to be carbon dust [44]. Some of the nanosized carbonaceous grains may therefore represent a previously unrecognized type of presolar grain. Finally, if the nanospheres prove to be Q and thus carriers of the PNGs, increased knowledge of the nanosphere characteristics and origin will provide new constraints on the sources of the PNGs.

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