PAHs, FULLERENES and FULLERANES in the ALLENDE METEORITE

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Introduction The suggestion that the fullerene molecule, C_{60}, might be widely distributed in the universe, particularly in the outflows of carbon stars, was first proposed after the discovery of its exceptional thermal stability and photochemical properties [1]. This hypothesis soon led to the search for C_{60}, or its ions, in carbonaceous meteorites [2] and in further stellar spectra (diffuse interstellar bands (DIBs), infrared (IR) emissions bands etc.) [3,4]. Previous studies of fullerenes in carbonaceous meteorites have led to negative results [2] and the suggestion that the synthesis of fullerenes in the interstellar media (ISM) may be inhibited in such environments, but recently fullerenes (C_{60} and C_{70}) have been detected in trace amounts in the Allende meteorite [5]. Kroto [3] and others [6,7] have suggested that fulleranes ($C_{60}H_x$) might be responsible for certain diffuse interstellar bands (DIBs) in the ISM Recently, slim evidence that two new diffuse interstellar bands may be due to C_{60}^+ in the ISM was reported, but, to date, their is no evidence for fulleranes.

We report here the discovery of fulleranes ($C_{60}H_2$-$C_{60}H_{60}$) and fullerenes (C_{60} and C_{70}) in the Allende meteorite. The fulleranes and fullerenes were detected in separate samples by laser desorption (reflectron) time-of-flight (TOF) mass spectrometry (LDMS). Many polycyclic aromatic hydrocarbons (PAHs) were also observed including benzofluoranthene and corannulene, a cup-shaped molecule that has been proposed as a precursor molecule to the formation of fullerenes in the gas phase [9].

Methods/Analysis We examined several splits of a large reservoir (20 grams) of ground Allende bulk powder. Some of the Allende samples were demineralized while others were crushed and extracted directly without any further sample preparation [10]. Fulleranes were synthesized by a rhodium-catalyzed C_{60} reaction [11] for comparison with the Allende meteorite extracts. The LDMS mass spectrum for the fullerane standard (Fig. 1a) shows a well-resolved series of peaks ranging from m/z=720 amu to m/z=750 amu, corresponding to a distribution of partially hydrogenated products. There is evidence for fragmentation as seen by a strong peak due to C_{60}^+. Another interesting feature of the product distribution is the even-odd intensity alternation with the odd-mass peaks more intense then the adjacent even numbered mass peaks. These even-odd mass distributions are due to facile proton-attachment (proton re-arrangement) during the desorption process. The LDMS mass spectrum of Allende D1A1 (Fig. 1b) shows a distribution of mass peaks up to m/z 760 amu. Both spectra display the same even-odd intensity alternation, with the odd numbered mass peaks more intense than the adjacent even numbered mass peaks. These weaker peaks between m/z 720 amu and m/z 760 amu are likely due to fragmentation to lower molecular weight partially hydrogenated fulleranes.

PAHs in the Allende Meteorite: a possible mechanism for fullerene/fullerane formation in the gas phase Polycyclic aromatic hydrocarbons were also observed in Allende in the m/z 100 to m/z 400 amu mass range (Figure 2). Among the PAHs identified are coronene (m/z 300) and its methyl derivatives, as well as the cations of pyrene (m/z 202) and naphthalene (m/z 128; not shown). This is consistent with PAH analyses of Allende meteorite and interplanetary dust particles (IDPs) reported previously [12]. Like C_{60}, interstellar PAHs are thought to be formed in the outflows of carbon stars. PAH molecules have been postulated as abundant high molecular weight constituents of interstellar space, and many unidentified IR emission features between 3.3 and 11.3 mm have been attributed to PAHs of varying structure [13]. Fullerenes are formed when curvature is introduced by the inclusion of five-membered rings. Curved-PAHs, including benzofluoranthene (m/z 226) and corannulene (m/z 250) are also present in the Allende meteorite. [14]. These PAHs have also been identified as key intermediates in the conversion of planar PAH-type aromatic structures to the curved fullerene-type aromatic structures in flames and carbon vapor systems [9]. Thus, the fullerenes and fulleranes identified in Allende meteorite may have formed in the gas phase by the proposed mechanism based on corannulene and other related five-membered ring PAH structures.

Conclusions The origin of fullerenes/fulleranes in the Allende meteorite is unclear. The observation of these molecules together with PAHs suggests that PAHs may have been involved in fullerene synthesis within circumstellar envelopes or other sites within the ISM. It has been suggested that fullerene formation may be inhibited in the ISM since such environments generally contain a high abundance of atomic and/or molecular hydrogen [2,3]. However, the detection of fullerenes in sooting flames [9] implies that these molecules can be produced under conditions involving many competing processes; even in the presence of hydrogen. In fact, the presence of hydrogen may lead to the conversion of fullerenes, C_{60}, to fulleranes, $C_{60}H_n$. Alternatively, fullerenes may form in the outflows of WC stars which consist mainly of He and C and little or no hydrogen. The most extreme members of this stellar class are known to inject newly formed carbon dust into the interstellar medium (3). Fullerenes might also condense in the high density vapor produced by interstellar hypervelocity carbon-carbon collisions (15). The formation of fullerenes and fulleranes in the solar nebula and/or the Allende parent body cannot be precluded. However, at this time, there are no lines of evidence to tie their origin to the solar system.

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