

WHAT PREDICTIONS CAN BE MADE ON THE NATURE OF CARBON AND CARBON-BEARING COMPOUNDS (HYDROCARBONS) IN THE INTERSTELLAR MEDIUM BASED ON STUDIES OF INTERPLANETARY DUST PARTICLES?

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The nature of hydrocarbons and properties of elemental carbon in circumstellar, interstellar and interplanetary dust has been a longstanding problem in astronomy and meteorite research. Sagan and Khare [1979] suggested that solid carbon-bearing molecules forming from simple gas mixtures are a major constituent in the interstellar medium, pre-planetary solar nebule, carbonaceous chondrites and comets. This solid material (tholins) forms a fluffy mixture of many carbon-bearing molecules, including carbon chain molecules [Winnewisser and Walmsley, 1979] and polycyclic aromatic hydrocarbons [Sagan and Khare, 1979; Leger and Puget, 1984]. Although the fit is not unique, the spectral characteristics of tholins fit many features in the IR spectra of circumstellar and interstellar dust. The 2175A extinction feature in the UV spectra of circumstellar and interstellar dust has been variously attributed to amorphous, poorly graphitised carbon (=turbostratic carbon) or graphite (=crystalline carbon) [Snow, this volume]. However, spectra for carbon-rich stars suggest the presence of amorphous carbon rather than graphite [Draine, 1984]. In an attempt to unify the observational data Greenberg [1982] proposed a three component dust model of tiny silicate and graphite grains and silicate grains mantled by "yellow stuff" of photo-processed molecules containing C, O, N and H. Greenberg [1982] showed that nonvolatile organic molecules of non-biotic origin are probably common to many comets.

Recently a new set of fine-grained extraterrestrial materials has become available to the scientific community through programs which collect these particles in the Earth's stratosphere [Fraundorf et al., 1982; Clanton et al., 1982]. These fine-grained materials are probably of cometary origin but may also originate in the asteroid belt, or in the interstellar medium [Brownlee et al., 1977]. An important subset of stratospheric dust collections is formed by fluffy aggregates of small-sized grains ranging from $< 100\text{\AA}$ up to $\sim 0.5\mu\text{m}$ in size and which have chondritic bulk composition. The compositions of these Chondritic Porous Aggregates (CPA's) is comparable with the bulk compositions of carbonaceous chondrites [Fraundorf et al., 1982; Mackinnon et al., 1982] and matrices of unequilibrated ordinary chondrites [Rietmeijer and McKay 1985]. The extraterrestrial origin of CPA's is confirmed by their noble gas abundances [Rajan et al., 1977; Hudson et al., 1981] and large D/H fractionation ratios [Zinner et al., 1983; Wood, this volume].

In the past decade many detailed studies have shown that although CPA's have a varied silicate and oxide mineralogy, carbonaceous matter is invariably present [cf. McKay et al., 1985]. The mineralogy of some CPA's tentatively suggest a relationship between these aggregates and carbonaceous chondrites [Rietmeijer, 1985-a; Tomeoka and Buseck, 1985] or matrices of unequilibrated ordinary chondrites [Rietmeijer and McKay, 1985]. The measured D-excesses in many CPA's [Clayton, this volume; Wood, this volume] and inferred $^{12}\text{C}/^{13}\text{C}$ and $^7\text{Li}/^6\text{Li}$ ratios for cometary dust [Fechtig, 1981] suggest that CPA's (a subset of chondritic Interplanetary Dust Particles) may form a class of extraterrestrial materials that is even more primitive than primitive meteorites.

Hydrocarbons are indigenous to carbonaceous chondrites [Nagy, 1975] but the origin of individual molecules is uncertain. The isotopic signature of some

molecules (referred to as kerogen) suggests an origin in the interstellar medium [Kerridge, this volume]. Unfortunately we know little of the mineralogy of carbonaceous matter, including elemental carbon species, in primitive extraterrestrial materials. Analytical Electron Microscope (AEM) studies reveal that poorly graphitised carbon (PGC) is present in the Orgueil, Cold Bokkeveld and Allende meteorites [Lumpkin, 1981; 1983-a; -b; Smith and Buseck, 1981]. A few AEM studies of CPA's show that metastable carbon-2H [Rietmeijer and Mackinnon, 1985-a] and poorly graphitised carbon, similar to meteoritic PGC [Rietmeijer and Mackinnon, 1985-b], are the dominant carbon-bearing species, although "hydrocarbons" [Christoffersen and Buseck, 1984] may be present.

The mineral constituents of CI and CM carbonaceous chondrites indicate that these meteorites have been subjected to low-temperature ($T < 400^{\circ}\text{K}$) aqueous alterations [Bunch and Chang, 1980; Clayton and Mayeda, 1984]. The mineralogy of several CPA's shows that low-temperature aqueous, including hydrocryogenic, alterations, may have been operative in these aggregates [Rietmeijer, 1985-b; Rietmeijer and Mackinnon, 1984; 1985-c; Tomeoka and Buseck, 1985]. These observations raise the question to what extent hydrocarbon and elemental carbon phases are indigenous to primitive extraterrestrial materials or how much they have been affected by, or may have formed during, low-temperature alteration processes.

The textures and crystallographical properties of PGC from carbonaceous chondrites and CPA's are comparable with PGC formed by dehydrogenation and carbonisation of hydrocarbon precursors under natural terrestrial and experimental conditions [Rietmeijer and Mackinnon, 1985-b]. The degree of graphitisation of PGC shows a systematic relationship with the heat-treatment temperature or duration of peak-heating. The minimum graphitisation temperature for PGC in the CPA's and carbonaceous chondrites is ca 400°K [Rietmeijer and Mackinnon, 1985-b]. Importantly, in CPA's, but not in carbonaceous chondrites, PGC contains traces of another carbon phase identified as carbon-2H [Rietmeijer and Mackinnon, 1985-a]. Carbon-2H is a metastable product of low-temperature hydrous pyrolysis of a hydrocarbon precursor and itself is a precursor of PGC [Rietmeijer and Mackinnon, 1985-a].

By analogy with terrestrial hydrocarbon and PGC occurrences Rietmeijer and Mackinnon [1985-d] proposed a multi-stage model of hydrocarbon diagenesis in CPA and carbonaceous chondrite (proto-) planetary parent bodies [Rietmeijer, 1985-a; -c] in which hydrocarbons are subjected to low-temperature hydrous pyrolysis. With continued heat-treatment time and temperature the pyrolysis products, e.g. carbon-2H, are graphitised to various degrees of PGC. Hydrous pyrolysis and graphitisation are sensitive to the presence of a catalyst, e.g. certain non-metallic elements, metals, alloys and layer silicates, which contribute to lower the temperatures at which these processes occur [Bradley et al., 1984; Fitzner et al., 1971; Mackinnon et al., 1985; Rietmeijer and Mackinnon, 1985-a; -b; Oya and Marsh, 1982].

In summary, elemental carbon phases in primitive extraterrestrial materials form in situ by low-temperature processes after accumulation of dust into (proto-) planetary parent bodies. Hydrous pyrolysis not only produces soft, well-graphitisable, carbon but may also result in the formation of new hydrocarbon molecules either from heavier hydrocarbon precursors or by reaction between pyrolysis intermediates [Fitzner et al., 1971]. In addition, hydrous pyrolysis may change the deuterium content of hydrocarbons [Hoering, 1982]. Thus, it seems not possible to recognise a priori an unprocessed hydrocarbon

phase in carbonaceous chondrites and CPA's.

Although hydrocarbons in primitive extraterrestrial materials present a complex model, I conclude that hydrocarbons, and not PGC or graphite, dominate the dust around carbon-rich stars and in the interstellar medium. This conclusion, based on observational evidence, supports experimental studies by Dayhoff et al. [1964] and Hayatsu et al. [1980] that vapor phase condensation in carbon-rich environments will produce hydrocarbons rather than graphite because of its high nucleation energy [Czyzak and Santiago, 1973]. We may probably rule out the existence of graphite, and possibly of PGC, in the interstellar medium if chemical processing in the interstellar medium occurs at energie levels comparable with simulation studies [cf. Greenberg, 1982; Sagan and Khare, 1979]. Additional energy sources may be the amorphous to crystalline transitions of silicates [Clayton, 1983] and ices [Smoluchowski and McWilliam, 1984].

In addition, hydrocarbons in primitive extraterrestrial materials may not be pristine interstellar molecules. However, continued efforts to recognise hydrocarbons and elemental carbon phases in Chondritic Porous Aggregates may allow us to understand the multi-stage hydrocarbon/elemental carbon model.

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