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Origins of Interstellar and Solar System

Carbonaceous Materials

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Carbon is a crucial atom in cosmochemistry. It is well-established that carbon is synthesized in stellar interiors after the main sequence, is ejected by red giants as small carbonaceous grains during their 'carbon star' phase, resides in the interstellar medium, and was incorporated into the solar system. The mechanisms of carbon grain formation and later chemical processing are complex because, with only small thermodynamic differences, carbon can take on a bewildering variety of forms: diamond; oxides; carbides; graphite; aliphatic hydrocarbons; polycyclic aromatic hydrocarbons (PAHs); fullerenes, amorphous carbon; and composites like soot, kerogen and coal. These is evidence for many of these forms of carbon in astronomical observations of the carbon stars, interstellar medium and studies of primitive carbonaceous chondritic meteorites.

We seek to understand the possible astrophysical sites and conditions of the origins of different forms of carbon by combining state-of-the-art capabilities of carbon chemistry with astrophysical modeling. The work is a collaboration between Prof. Frenklach, a leading carbon meterials scientist with both laboratory and computer modeling expertise, and Prof. Feigelson, an astrophysicist with interests in star formation. The team has also included two graduate students (one later a post-doc) in materials science, two graduate students in astronomy, and two undergraduates. The findings are briefly reviewed below.

Formation of Carbon Grains in Red Giant Atmospheres

Prior to the initiation of this grant Frenklach & Feigelson (1989; henceforth FF) modeled the conditions necessary for homogeneous condensation of PAHs in the molecular envelopes of carbon-rich red giants, which are thought to be the principal contributors of carbonaceous grains into the interstellar medium. The calculations, confirmed by another group, showed that small amounts of PAHs can condense when temperatures T$\sim$1000 °K. We argued that homogeneous condensation of graphite, a model widely accepted by many astrophysicists, has even lower yields. Thus, it appears that gas-phase chemistry alone is unable to produce significant quantities of carbonaceous material in red giant atmospheres. These results, combined with recent shock tube findings in Frenklach's laboratory, has led us to favor more complex heterogeneous processes. Here, very small particles, such as mineral carbides, condense out at high temperatures near the stellar surface, and grow due to attack by carbon molecules (deposition) and collisions between particles (coagulation). The preliminary laboratory evidence and a conceptual presentation of this model were made by Frenklach, Carmer, and Feigelson (1989, FCF). The work described here is published by Cadwell *et al.* (1994).

The largest effort under this grant was devoted to developing this concept into a comprehensive quantitative model. We named the process 'induced nucleation' of carbon grains, since homogeneous nucleation appears to be too slow to form the carbon grains seen in red giant atmospheres. Our model includes four microphysical processes: an instantaneous nucleation of seed particles close to the surface; growth by deposition of acetylene molecules (the most abundant form of hydrocarbon); growth by homogeneous nucleation of aromatic hydrocarbons; and growth by collision and coagulation of particles.

The initial seed particle production is assumed, as there is no reliable theory for the nuleation of mineral solids in a hydrogen-rich atmosphere. We assume the seed particles are silicon carbide, because silicon is abundant, SiC forms readily in our laboratory experiments in H-rich environments, and SiC spectral bands are widely observed in carbon star infrared spectra. Since we have no model for seed production, we consider a wide range ($\sim 10^6$) in possible seed densities and sizes. Carbon deposition is modeled by the abstraction of hydrogen producing a radical site on a grain, followed by the addition of acetylene. Surface reaction rate coefficients were adopted from recent studies in combustion chemistry. Homogeneous nucleation of large hydrocarbons is calculated using a network of $\sim$100 chemical kinetic reactions. It provides several routes by which acetylene can pyrolyze into an aromatic ring, grows polycyclic molecules by sequences of hydrogen extractions and acetylene additions, and grows a population of large PAHs using a method of moments known as linear lumping. Grain coagulation is described by generalized Smoluchowski equations, formulated in terms of the moments of the grain size distribution.

These four microphysical processes are embedded in a large-scale astrophysical model consisting of a constant velocity stellar wind. A wide range of mass loss rates and wind velocities were considered. The temperature profile of the wind was not calculated self-consistently; we rather adopted the standard assumption of adiabatic cooling. However, the optical depth of the grain-producing wind is computed using Mie scattering theory. The refractive indices of various forms of carbon particles (SiC, soot, graphite and three amorphous carbons) were considered.

From examination of the parameter space of this model, we find that the range of plausible microphysical and astronomical conditions can reproduce the observed range of properties of carbon stars. Models with fast winds, low mass loss rates, low carbon abundance, and/or steep temperature gradients do not produce many large grains or high-optical depth dust shells. Astronomically, these are seen as Class 1 and 2 carbon stars, as classified by Willems from *IRAS* spectroscopy. Class 3 stars, showing the 11.5 μm SiC emission feature and mid-infrared excess but not much optical band opacity, are well represented by our standard case with wind velocity $v = 1$ km/s and mass loss M$= 1 \times 10^{-5}$ $M_\odot$/yr. Class 4 stars, with opaque dust shells, are cases where the grain growth is very efficient, perhaps depleting all carbon (except that trapped in CO molecules) in the atmosphere.

In addition to explaining the astronomical properties of red giants producing carbonaceous grains, our model also can incorporate recent meteoritic findings. The large SiC grains, 1-25 μm in size, may represent seed particles that grow without carbon deposition in stellar atmospheres with intermediate carbon abundances. A group of compositie 'graphitic' pre-solar grains are round and exhibit depositional layers as expected from our model. Mineral carbide particles are found embedded within a carbon matrix, again consistent with our heterogeneous model. Their large sizes implies they are formed in Class 4 carbon stars with very slow winds or quasi-static envelopes.

Finally, our induced nucleation grain formation model provides a natural explanation for the widespread presence of PAH emission bands in the Galactic interstellar medium. Whereas homogeneous PAH formation was inefficient, the deposition of aromatic layers onto pre-existing grains in carbon star atmospheres can be very efficient. A typical grain may have a SiC seed core, a layer of amorphous carbon and a coating of aromatic hydrocarbon molecules. After the grains are ejected into the interstellar medium, the outer PAH molecules can be sputtered off or excited *in situ* by stellar ultraviolet light, giving rise to the prominent complex of mid-infrared emission bands often attributed to PAHs.

Other Activities

The group conducted a series of laboratory experiments to measure empirically the rates of carbon grain nucleation and growth in a variety of hydrogen-rich gases. The experiments were conducted in Prof. Frenklach's shock tube facility. Unlike the homogeneous formation of PAHs, which is slow under these conditions, we found that the formation of SiC and amorphous carbon grains is very rapid, and occurs at higher temperatures than predicted by equilibrium theory. A typical run produces both small particles of SiC around 5–20 nm and large 100–200nm depositional structures (probably) of amorphous carbon. These represent experimental evidence for the seed particles and depositional growth process in our induced nucleation grain formation model described above. Due to a personnel problem (the graduate student performing the experiments left the University abruptly and is only now returning to complete his academic program and this project), this effort was not published. As a result, we return to the government some unspent funds.

The team completed a paper started before the arrival of this grant applying our ideas to the solar nebula. We showed that the then-dominant model for for formation of meteoritic kerogen, based on the Fischer-Tropsch mechanism for polymerizing carbon monoxide, is probably incorrect. We established instead that the aromatization of acetylene, as developed by FF, can produce signficant aromatic carbon in the solar nebula. Given the isotopic heterogeneity of the kerogen matrix of carbonaceous chondrites, we suspect that some of the aromatic and aliphatic carbon was inherited from interstellar grains, while other fractions were produced in the nebula as we describe. This paper was published by Morgan *et al.* (1991).

The group presented and discussed its findings at several conferences. The PI attended the first NASA Workshop on Isotopic Anomalies at Clemson University, while co-I Frenklach attended the second Workshop at Washington University. Graduate student Morgan presented his paper at the international Meteoritical Society meeting in Monterey CA. Graduate student Cadwell presented the carbon star grain formation model at an international conference on stellar winds and dust shells at Royal Greenwich Observatory in Sussex England. The PI gave invited lectures on the subject at the University of New South Wales and University of Sydney, Australia. Co-I Frenklach gave a plenary talk at the Americal Association of Aerosol Research on particle nucleation, which featured our red giant grain formation model.

The grant partially supported the education of three students: a female undergraduate, who later pursued graduate training in the biological sciences; an Afro-American astronomy graduate student, now an Assistant Professor at Dickinson College; and a male astronomy graduate student, now engaged in dissertation research in a related field.

Publications under this Grant

Cadwell, B. J., Wang, H., Feigelson, E. D. and Frenklach, M., 1994, Induced nucleation of carbon dust in red giant stars, *Astrophysical Journal* 429, 285-299.

Morgan, W. A. Jr., Feigelson, E. D., Wang, H. and Frenklach, M., 1991, A new mechanism for the formation of meteoritic kerogen-like material, *Science* 252, 109-112.