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CARBON IN COMET DUST

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Comets are small, cold bodies that are likely to contain chemical, mineralogical and isotopic records of conditions and processes that existed in the outer regions of the solar nebula as well as interstellar and circumstellar environments that predate the planetary system. Carbon and carbon compounds in comet dust are of particular importance because of the rather broad and interesting range of processes that can form and alter solid carbonaceous matter. Many of the compounds may have formed by nonequilibrium processes such as catalysis and radiation processing. Carbon in cometary "solids" could range from refractory phases like elemental carbon and silicon carbide to comparatively volatile polymers. Detailed knowledge of the abundance, distribution and chemical forms of carbon in comet dust is fundamental to an understanding of the origin and evolution of comets.

The only direct measurements of carbon in comet dust came from the three particle impact mass spectrometers flown to Halley by the Giotto and Vega spacecraft [1,2]. These instruments measured thousands of mass spectra from individual micron and submicron particles. The detected particles fall into three major groups; pure silicate, mixtures of C, O, Mg, Si and Fe , and pure low atomic weight elements (the CHON particles [3]).The nature of carbon in Halley dust and its association with other elements are discussed in this volume by Ben Clark. The present paper will concentrate on the association of Halley particle results with data from existing meteoritic materials that can be analyzed in the laboratory. Comet samples must exist in present collections of meteoritic materials and the Halley results provide clues for identifying them. Although it is not presently possible to positively identify cometary meteorites or cometary interplanetary dust (IDP) samples, it is possible to determine which materials are similar to Halley dust and which ones are distinctly unlike Halley. The properties of these existing "Halley-compatible" samples provide insight into the possible properties of cometary material. Positive identification of meteoritic comet samples or direct samples returned from a comet nucleus would of course revolutionize our ability to study carbonaceous matter in comets. Modern analytical techniques are very powerful and it is possible to perform elemental, chemical, mineralogical and even limited isotopic analysis on micron-size particles.

The bulk composition of Halley dust appears to be chondritic [4,5] for the majority of elements but uncertainties in conversion of experiment data to element ratios does not allow association of the bulk heavy element composition with any particular chondrite class. Jessberger *et al.* [4] estimate that the abundances of Na, Mg, Al, Si, S, Ca, and Mn in Halley are within a factor of two of their relative abundances in C I chondrites. The carbon and nitrogen abundances in the Halley material appear to be much higher than in any of the chondrites. Jessberger et al estimate that the C/Mg and N/Mg in Halley dust are enhanced relative to C I by factors of 6 to 12 and 6 to 8 respectively. These numbers are uncertain because ion production in the mass spectrometers is not well understood, but it is reasonably certain that the carbon and nitrogen abundances in Halley dust are much higher than in any chondrite. The clearest indication of this is the finding that roughly a third of the particles are dominated by C, H, O and N [5]. This result is rather insensitive to uncertainties in ion production. If the carbon and nitrogen in Halley dust are in stable forms capable of surviving storage in the interplanetary medium and meteorite parent bodies, then the high abundance of these elements implies that Halley dust is different from all chondritic meteorites. Carbon and nitrogen are strongly fractionated among the chondrite groups, varying by a factor of 100 between the C I and ordinary chondrites but in most cases they are minor elements [6]. The atomic abundance of carbon in C I's approaches that of silicon but this is still significantly smaller than found in Halley. Chondrites do not have high carbon abundances and their lack of appreciable porosity rules out the possibility that they could have contained transient carbon that was lost solely by gentle sublimation. Production of rocks from Halley dust that would even crudely approximate the elemental composition and structure of chondrites would require loss of carbon and nitrogen followed by compaction to solid,nonporous matter.

Carbon and nitrogen are more abundant in Halley dust than in chondrites but it is not presently known if they are more abundant than in interplanetary dust. There are experimental difficulties with carbon analysis of small particles and the first carbon determinations are just being published. Early measurements indicate that at least some on the collected particles have high carbon abundances that are intermediate between C I and the estimated abundance in Halley [7,8].

In addition to bulk elemental composition, the compositional variability seen in the Halley data provides a means of investigating similarities between Halley and meteoritic material. The Halley data shows considerable variation among the elemental composition of submicron particles. If Halley dust is dominated by mineral grains then the observed variability suggests that the fundamental grain size is in the submicron to micron range. Even with uncertainties in instrument calibration, the observed compositional variations provide a powerful method for comparing Halley with meteoritic materials. The distribution of Fe, Mg, and Si in the Halley material is distinctly different from that seen in any of the carbonaceous chondrites or in matrix of the unequilibrated ordinary chondrites at the micron and submicron size scale [9]. A straight forward distinction is that Halley contains abundant submicron grains of pure Mg silicates and Fe rich material while the meteorites do not. The meteorites are more homogeneous at the submicron scale than Halley. In a way this is evidence that Halley is more "primitive" than the chondrites. The term primitive is used here in the sense that Halley solids could be modified by alteration processes to produce the chondrites, which are coarser grained and more homogeneous, but it is unlikely that chondrites could be modified by simple processing to form Halley dust, a more complex and heterogenous material.

The dispersion of abundances in Halley dust is also distinct from some of the hydrated types of interplantary dust samples collected in the stratosphere. Interplanetary particles can be grouped into two major mineralogical classes, those dominated by hydrated silicates and those that are composed entirely of anhydrous phases [10,11,12]. A subclass of the hydrated IDP's, predominately composed of serpentine, is very similar to the carbonaceous chondrites. Like the C chondrites their fine scale compositional variability is much less than in seen in the Halley data. For example less than 1% of the micron grains in the serpentine particles are Mg silicates, a factor of ten lower frequency than seen in Halley. A second subclass of hydrated particles contain smectite minerals. These particles are more heterogenous than the serpentine IDP's and the C chondrites but are not the best "match" to Halley. The compositional dispersion of the major elements in Halley best resembles that seen in the anhydrous interplanetary particles. This particle type is also the most porous meteoritic material and for this reason it has previously been speculated that the anhydrous porous particles might be cometary [13]. The anhydrous IDP's are open aggregates of rather equidimensional submicron grains of silicates, sulfides and carbonaceous matter. Like Halley dust the major submicron components are pure silicate, mixed silicate and carbonaceous matter and pure carbonaceous matter.

The tentative best "match" between Halley dust and the anhydrous class of interplanetary dust, gives special importance to laboratory studies of carbon that have been performed on particles in this group. Transmission electron microscope (TEM) studies of microtome thin sections of these particles show that carbon exists as grains of pure low atomic weight material, "tar balls" (mixtures of <1000A silicates, metal, sulfides and carbon) and grain coatings [10,13]. The chemical forms and quantitative distribution of carbon in these particles are poorly known but they are subjects of intense investigation at the present time. A question of major interest is whether or not the submicron lumps of organic matter in these particles resemble the CHON particles seen at Halley. This will be partly answered when C, N and O measurements are made on submicron grains in the laboratory samples. As viewed in the electron microscope, most of the low atomic weight grains appear to be amorphous and it is evident that the bulk of the total carbon in typical particle types is either amorphous or highly disordered. Although 3.4A fringes from graphite are seen, they are rare and an important result from examination of typical interplanetary particles is the observation that well crystallized graphite is only a trace constituent. Rare IDP's do contain abundant well ordered elemental carbon. TEM observations on two hydrated particles revealed that carbon-2H (lonsdaleite) was an important constituent [14]. Lonsdaleite is metastable and its existence places constraints of the thermal processing of the particles. Reitmeijer and Mackinnon [14] suggest that the carbon-2H detected in the particles was produced by hydrous pryolysis below 350C. The abundant elemental and polymeric carbon in anhydrous particles has been studied by laser Raman spectroscopy of individual particles. The shape of the carbon Raman bands agree with the TEM studies showing that well ordered graphite is not a significant phase [15]. The shape of the first order Raman lines provides information on the sizes of aromatic domains. Many of the particles have domain sizes smaller than 25A showing that they are less ordered than commercial "glassy" amphorous carbon. The Raman bands are similar in position and strength to interstellar IR features that have been attributed to molecular-size polycyclic aromatic hydrocarbons (PAH's) [15]. The Raman studies have also detected luminescence that is similar to excess red emission in some astronomical sources that has been attributed to PAH's or hydrogenated amorphous carbon.

The IDP's contain a several carbon compounds other than polymers. A minor but unique constituent IDP's is epsilon FeNi carbide, a mineral not found elsewhere in nature [16,17]. The carbide is seen as micron and smaller grains occuring in association with with amorphous carbon, metal and magnetite. The existence and distribution of this carbide is evidence for formation by hetereogenous catalysis from CO on grain surfaces. The amorphous carbon adjacent to the carbide may be a product of Fischer-Tropsch-like surface catalysis reactions also evolving CO. Fegley [18] has estimated that F-T reactions could have occured on submicron nebular grains at temperatures as low as 440K. Another minor carbon bearing phase in IDP's is Mg, Ca carbonate [19], a phase also seen in carbonaceous chondrites. A 6.8um absorption feature seen in the IR spectra of hydrated particles has been demonstrated, by electron microscopy and chemical etching, to be carbonate [20]. The IDP absorption may be related to the 6.8um feature seen in young stellar objects.

One of the most important findings in IDP studies has been the discovery of small regions within particles that have very large D/H excesses [21]. The highest observed enhancement is 10,000 per mil excess D/H, a value that exceeds the highest D/H seen in chondrites and approaches the level of fractionation observed in molecular clouds. The high degree of fractionation seen in molecular clouds is widely believed to be the result of ion-molecule reactions [22]. The deuterium rich material in IDP's is contained in micron or smaller "nuggets" giving the particles a highly heterogenous and unequilibrated distribution of D/H. Although there is a general positive correlation of D with C/O it is not a precise correlation and it has not been proven that the high D anomaly is carried by carbon rich matter [21]. The lack of correlation of excess D with OH is however strongly suggestive that enhanced deuterium is associated with carbonaceous matter [23].

The observed properties of interplantary dust provide insight, but perhaps features that are not observed provide some of most important constraints on the nature of carbon in cometary dust. Hundreds of IDP's have been studied in the laboratory and surely the most common types of cometary grains have been seen. The previously discussed abundance of amorphous carbon and scarcity of well ordered graphite strongly implies that graphite is not an important phase in comets. The complex distribution of carbon implies that carbon in comets is not a simple interstitial filling material as one might expect if it had been extensively mobilized on the parent body. Carbon also does not form thick mantles on silicate grains similar to those proposed by Greenberg [24] for interstellar and cometary grains. Grains do have carbonaceous coatings but typical coatings are thin, in the 100A thickness range or less. With pure carbonaceous grains, "tar balls" and grain coatings the distribution of carbon is more complex than predicted by the model. While the collected samples do not match a literal interpretation of the Greenberg model there are possible grounds for reconciliation. One possibility is that comet dust does have a core-mantle structure in the comet but the collected samples are modified either in the comet, in the interplanetary medium or during entry into the atmosphere. Another possibility is that instead of a simple core mantle structure, comet grains actually are mixtures of many smaller silicate cores imbedded in a carbonaceous matrix. This type of plum-pudding structure would better match the "tar balls" seen in anhydrous IDP's.

Taking into account the interplanetary dust data and the Halley results it is interesting to speculate on the true nature of carbon in Halley-like comets. The author's best conjecture is that the Halley dust is very similar to many of the anhydrous IDP's. A comet made from this material would be an ice-dust conglomerate with ice filling many of the voids between the largely submicron silicate grains. The material would be very fine grained, heterogenous at the submicron scale but rather homogenous for scales greater than 10um. Like the IDP's the ice-dust material would be black even for pieces as small as 3um. Some carbon would be in volatile constituents of ice phases but a substantial fraction would be less volatile and remain as a component of the dust. Elemental carbon, carbides, and some polymeric material would permanently remain with the silicates but intermediate volatility compounds would sublime on time scales of days to millennia. Evidence for the presence of intermediate material comes from the observed CN jets [25] and grain fragmentation [26]. Carbonates and hydrated silicate minerals would be rare and the IR spectral features of these minerals should be absent or at least minor. The silicates would be anhydrous phases that include well preserved high temperature minerals such as pure magnesium pyroxene and olivine. The silicates have not interacted with water in the parent body or via gas phase reactions in the nebula and is likely that carbon compounds would also not be affected by such processes. Like carbonaceous chondrites the cometary solids would contain minor amounts of diamond, silicon carbide and other carbon bearing phases that preserve large isotopic effects that predate the formation of the solar system.

There is an important synergism between the laboratory studies of collected samples and astronomical data from comets and interstellar grains. However to fully interpret results however there must be convincing methods for associating a particular class or classes of meteoritic material with comets. Ultimately this will be done by direct comet sample return such as the Rosetta mission under development by ESA. At the present time the only "links" that can be made involve comparison with sample properties and measurable properties of comets. Unfortunately there is at present no known unique property of cometary dust that allows its absolute identification in the laboratory. The results from Halley encounters and observations do however provide much new information on cometary grains. The Halley grain compositions, density, size distribution and scattering properties all provide a basis for future investigations. Other Halley properties such as the presence of polyoxymethylene [27] and the 3.4um emission feature [28] could play key roles for making convincing links in the future.

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