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CARBON PETROLOGY IN COMETARY DUST

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INTRODUCTION

Chondritic porous [CP] interplanetary dust particles [IDPs] are collected in the Earth's stratosphere. There exists an extensive database on major and minor element chemistry, stable isotopes, noble gas abundances and mineralogy of many CP IDPs, as well as infrared and Raman spectroscopic properties. For details on the mineralogy, chemistry and physical properties of IDPs, I refer to the reviews by *Mackinnon and Rietmeijer* [1987], *Bradley et al.* [1988] and *Sandford* [1987]. Texture, mineralogy [*Mackinnon and Rietmeijer, 1987*] and chemistry [*Schramm et al., 1989; Flynn and Sutton, 1991*] support the notion that CP IDPs are a unique group of ultrafine-grained extraterrestrial materials that are distinct from any known meteorite class. Their fluffy, or porous, morphology suggests that CP IDPs probably endured minimal alteration by protoplanetary processes since their formation. It is generally accepted that CP IDPs are solid debris from short-period comets. The evidence is mostly circumstantial but this notion gained significant support based on the comet Halley dust data [*Brownlee, 1990*]. In this paper, I will accept that CP IDPs are indeed cometary dust.

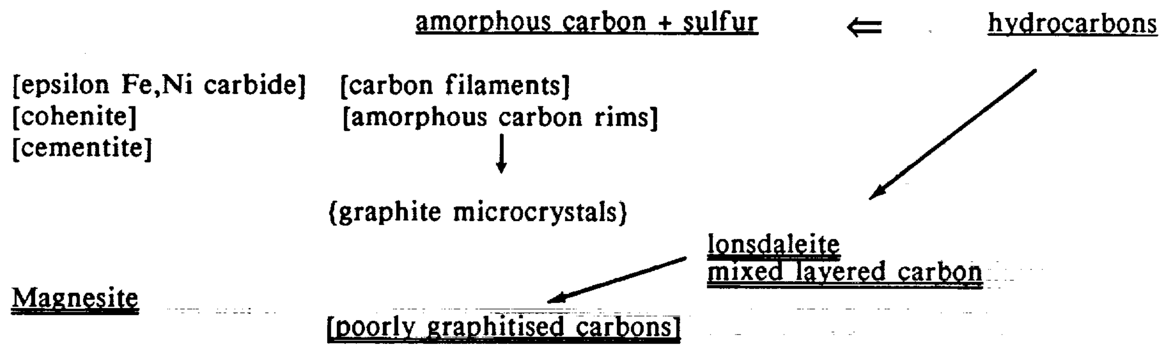
The C/Si ratio in CP IDPs is 3.3 times higher than in CI carbonaceous chondrites [*Schramm et al., 1989*]. The intraparticle carbon distribution is heterogeneous [*Rietmeijer and McKay, 1986*]. Carbon occurs both in oxidised and reduced forms. Analytical electron microscope [AEM] and Raman spectroscopic analyses have shown the presence of several carbon forms in CP IDPs but the data are scattered in the literature. Carbons in cometary CP IDPs are among the most pristine Solar System carbons available for laboratory study. Similar to a recently developed petrological model for the diversity of layer silicates in CP IDPs [*Zolensky, 1991*] that is useful to constrain *in situ* aqueous alteration in comets [*Rietmeijer and Mackinnon, 1987a*], I here present the first effort to develop a petrological concept of carbons in CP IDPs. This concept is useful to constrain comet evolution. I also present the philosophical constraint facing Earth Scientists in studies of protoplanets that require a new approach to cometary dust studies.

CLASSIFICATION

This paper uses published data on carbons in CP IDPs that are presented in TABLE 1. This table should be perused with some caution as only a few CP IDPs reported contain more than two or three carbons listed in the table. It is presently not clear whether this situation is an experimental artifact (AEM analyses of CP IDPs are quite time-consuming) or whether it carries genetic information. In the table, carbon types are listed according to various stages in the lifetime of cometary dust from its formation in the early solar system to collection in the Earth's stratosphere. This approach is chosen because it might assist to "see through" the various processes that affected CP IDPs and the resulting carbons. For this purpose, I define three types of carbon in cometary dust:

(1) *indigenous carbons* are pre-accretion solar nebula materials,
(2) *metamorphic carbons* form during protoplanet alteration, and
(3) *neoformed carbons* form during a transient (heating) event.

TABLE 1: CARBONS IN COMETARY DUST



Carbons are indigenous (underlined) or metamorphic (double underlined). Neoformed carbons form during transient events such as heterogeneous catalysis in the solar nebula and dynamic pyrometamorphism on atmospheric entry (brackets) or via solid-state grain boundary nucleation (braces).

The neoformed carbons form a diffuse group wherein individual carbons cannot yet be linked to a particular transient event. Two orthorhombic forms of Fe_3C, cementite and cohenite [*Fraundorf, 1981*; *Bradley et al., 1984*], and ϵ-$(Fe,Ni)_3C$ crystals [*Christoffersen and Buseck, 1983*] could form during dynamic pyrometamorphism of IDPs due to atmospheric entry flash-heating, or could be products of Fischer-Tropsch synthesis in the solar nebula. The same uncertainty surrounds rare carbon filaments in these particles. Whatever environment is conducive to carbide and filamentous carbon formation, these carbons indicate that carburization reactions are important during CP IDP evolution which again shows the uniqueness of CP IDPs [*Bradley et al., 1984*].

Amorphous carbon forms thin coatings (up to 30 nm) on many submicron metal, carbide and metal-oxide grains in CP IDPs [*Mackinnon and Rietmeijer, 1987*; *Bradley et al.*, 1988]. The amorphous coatings often have graphite microcrystals (up to 30 nm thick) at the interface with the enclosed grain. If these graphite microcrystals form via grain boundary nucleation to relieve grain boundary energy, they could form during dynamic pyrometamorphism. It is hard to understand that both amorphous carbon coatings and graphite microcrystals could form during this 10-15 second transient heating event. Thus, these microcrystals indirectly support a notion that the amorphous coatings are a 'pre-terrestrial' carbon. Unquestionably, neoformed carbons contain important information about the evolution of cometary dust. But unless it is possible to constrain their formation, this information cannot be placed in a proper context. Still, it seems possible to study the remainder of CP IDP carbons without concerns that they are seriously affected by the processes that produced neoformed carbons.

INDIGENOUS and METAMORPHIC CARBONS

The CP IDPs are loosely-bound aggregates of 'granular units' (or tar balls) with embedded micometer-sized silicate crystals, *e.g.* pyroxene whiskers. A 'granular unit' consists of carbon material with embedded, heterogeneously-distributed, nanometer-sized olivines, pyroxenes and sulfides. Within a single 'granular unit' it is possible to find areas of almost pure carbon material and areas that have abundant silicates and sulfides. It is still an open question whether 'granular units' represent an accretion [*Bradley, 1988*] or an annealing [*Rietmeijer, 1989*] event. In each scenario the carbon material, which includes hydrocarbons and amorphous carbon, is the solar nebula dust that accreted into CP IDPs. Evidence to support (as yet unidentified) hydrocarbons is slim [*cf. Mackinnon and Rietmeijer, 1987*]. The best evidence is from Raman spectroscopy [*Wopenka, 1988*] and ion microprobe analyses [*cf. Bradley et al.*, 1988]. The hydrocarbons are the loci of D/H enrichments including a "hot spot" with $\delta D > 9000$ pro mille that possibly indicates an interstellar grain [*McKeegan et al., 1987*]. Some sulfur is associated with amorphous carbon in 'granular units' [*Rietmeijer, 1989*]. The modes of hydrocarbon and amorphous carbon occurrence in the units suggest that they could be the carbonaceous dust in the solar nebula prior to accretion. Whether both carbons in cometary dust are related is not yet known but volatile (H,O,N) loss from hydrocarbons conceivably produces amorphous carbon, either during protoplanet accretion or alteration.

The formation of metamorphic carbons during protoplanet alteration is a challenging field of CP IDP research. If lonsdaleite, mixed layered carbon and poorly graphitised carbons (PGCs) are metamorphic carbons, they indicate considerable mineralogical activity in comet nuclei. These platey and fluffy carbons co-occur in individual CP IDPs, both separately and as individual grains. Crystalline lonsdaleite (or carbon-2H) forms thin (< 10 nm) lobate submicron sheets that probably contain a small amount of volatiles [*Rietmeijer and Mackinnon, 1987b*]. Another platey CP IDP carbon occurs as thin, sub-micron (up to 4.5 μm x 1.3 μm) sheets that have turbostratic layer stacking. This mixed layered carbon has considerable three-dimensional order of its pre-graphitic carbon layers that contain alicyclic and aromatic structures with variable C/[C+H+O+N] ratio between 0.35-0.75 [*Rietmeijer, 1991*]. A third metamorphic carbon has a distinct fluffy morphology. This PGC occurs as domains associated with both platey carbons and as discrete particles up to ~1.5 μm [*Rietmeijer and Mackinnon, 1985*] and it has a distinct microstructure of tangled loops and concentric subcircular to polygonal rings of graphite.

All three metamorphic carbons have natural terrestrial or synthetic analogs and we can understand the conditions and processes that lead to their formation. Layer silicates and magnesite ($MgCO_3$) [TABLE 1] that co-occur with metamorphic carbons support aqueous alteration in comets. Lonsdaleite formed via hydrocarbon hydrous pyrolysis at T< 350°C supported on catalytically-activated layer silicates [*Rietmeijer and Mackinnon, 1987b*]. Mixed layer carbon formation does not require the presence of water. This carbon supports kinetically controlled, early stages of hydrocarbon carbonisation. If the platey carbons are so-called graphitisable carbon, thermal annealing will (partially) transform these carbons into PGCs. If temperature is the only active parameter for PGC formation in CP IDPs, the thermal regime was at ~315°C [*Rietmeijer and Mackinnon, 1985*]. A thermal regime of this magnitude in active short-period comet nuclei (or protoplanets) is unlikely. Temporal and spatial variations in the water/rock ratio during aqueous alteration gives some degree of freedom but it probably requires temperatures at least similar to those for CI carbonaceous chondrite alteration (~125°C) and efficient catalysis supported by co-occurring layer silicates.

The principle of uniformitarianism states that the same processes and natural laws prevailed in the past as processes that we can presently observe, infer from direct observation, or derive from laboratory experiment. The only known natural terrestrial environment to serve as a comet nucleus analog is the Antarctic Dry Valley permafrost but its thermal regime and time scales differ significantly and its carbon content is very low [*Rietmeijer, 1985*]. Martian permafrost soils might be a better natural analog but an opportunity to study these soils is remote. The alternative is to develop an experimental program to constrain the hydrocryogenic (T< 0°C) thermal regime that produces the metamorphic CP IDP carbons, the carbon reaction rates and paths and layer silicate - carbon catalytic interactions.

CONCLUSIONS

A listing of carbons in CP IDPs, that are solid debris of short-period comets, proves useful to discuss interrelations among these carbons and to define areas for IDP research. Carbons are listed as indigenous, metamorphic or neoformed. Natural analogs for studies of cometary carbons and carbon - silicate petrology are not readily available. I suggest the development of experiments based on our knowledge of the physical environment of evolving short-period comets.

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