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Carbonaceous Chondritic Material in the Solar System

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Carbonaceous chondritic matrix material (CCMM) appears to be an important planet-forming unit in the mid-solar system, from the orbit of Mars to that of Uranus. The type specimen for CCMM is the lowtemperature (400-500 K) assemblage of clay minerals, organic polymer, magnetite, and Ni-rich iron sulfides which constitutes the black, fine-grained matrix of primitive carbonaceous chondrites. Solar-system objects which appear to be partly or wholly made of CCMM are the satellites of Mars, most asteroids, interplanetary dust, and, perhaps, comets, satellites of the outer planets and the rings of Uranus. CCMM constituents probably formed by low-temperature reactions of higher-temperature condensates with the ambient solar composition gas, or in the case of the organic polymer, by reactions of gaseous species catalyzed by solids.

Carbon is the fourth most abundant element. Its mode of occurrence in the solar system is quite varied; it is found in molecules that occur naturally in atmospheres, oceans, ices, living organisms, rocks and metal alloys. This paper is concerned solely with solid "carbonaceous material" in which the element carbon itself may constitute only a few weight percent of the matter. Nevertheless, the carbonaceous material possesses certain other characteristics in addition to the presence of solid carbon compounds which distinguish it as an unique planet-forming rock unit. Carbonaceous material is recognized as important because of its apparent wide distribution in the solar system and because it is a relatively primitive material. Before proceeding further, it is essential to characterize this "carbonaceous material" so that the distinctions from other carbon-bearing matter are clear. The type-specimens for the carbonaceous material are the carbonaceous chondritic meteorites, in particular the fine-grained matrix in $CM¹$ carbonaceous chondrites.

The major physical and chemical attributes, listed in Tables 1 and 2, of the carbonaceous chondrites have been established by studies spanning centuries, nevertheless, some fundamental gaps in the data remain. In summary carbonaceous material is finegrained and black; it consists largely of sheet-structured hydrated ferromagnesian silicates² with smaller amounts of organic polymer, nickel-bearing sulfides, magnetite, low-iron olivines and pyroxenes, and a near cosmic complement of condensible metals. Hereafter, this material as I have just defined it will be referred to as CCMM for carbonaceous chondritic matrix material. For the purpose of this paper CCMM is *not* $CO₂$ or $CH₄$ ices which exist in extremely cold locations in the solar system, nor is it the extensive deposits of biogenic material (coal, petroleum, carbonates) known on earth. For astronomers and for this paper, a most important characteristic is that CCMM is black. The uniqueness of this attribute is illustrated in Table 3. There are very few naturally occurring materials with albedos less than 0.05, and among these, there are fewer still which are cosmochemically plausible candidates for an independent existence in space.

This paper reviews the occurrence of carbonaceous material (CCMM) in the solar system and briefly describes its probable mode of formation.

Meteorites

Carbonaceous chondrites as type-specimens for CCMM will be given most attention here; however,

¹ There are at present two nomenclature schemes in use for carbonaceous chondrites. The equivalents are as follows: $CI = CI$; $C2 = CM$; $C3 = CV$, CO ; $C4 = CK$ (Karoonda).

² Sheet-structured silicate, layer-lattice silicate, phyllosilicate and clay minerals are used as synonyms in describing the phyllosilicates in meteorites despite certain technical differences among some of the terms.

Table 1. Mineralogy of CI and CM chondrites

^a Minerals formed since the meteorite fell, disputed minerals and unconfirmed minerals which are rare constituents and minerals which occur only in Ca-Al-rich inclusions are omitted. Some minerals which occur in Ca-Al-rich inclusions and matrix are so designated. "Rare" means the presence of the mineral is well-established, but the abundance is much less than 1 wt%. Question marks mean that although the mineral occurrence may not be well-characterized it could nevertheless exceed 1 wt%

Table 2. Densities of meteorites

other carbon-bearing meteorites and their relationship to other carbonaceous materials are discussed briefly at the end of this section.

Carbonaceous chondrites span a large range of compositions, textures and petrographies. It is not possible to review all aspects of carbonaceous chondrites here. For more information the reader is referred to other sources [1, 2]. Carbonaceous chondrites

acquired the name because of a high content of the volatiles, carbon and water, when compared to other meteorites. The content of volatile trace-elements is also high. In fact, CI chondrites are the standard for the cosmic abundances of all non-gaseous elements. The contents of volatile metals is progressively lower in the other types of carbonaceous chondrites: 60% of CI for CM's and 30% of CI for CV,O's [3]. Carbonaceous chondrites are fine-grained rocks. Grain sizes in the matrix extend to the sub-micron level. In the sequence from CI-CK the proportion of coarse-grained components increases. The coarsegrained components include single mineral grains, chondrules, and calcium-aluminum-rich inclusions. The fine-grained nature of the CI chondrites and the matrix material of CM chondrites (material interstitial to the coarse components) has thwarted attempts to complete the mineralogical identification of the

Table 3. Geometric albedos of dark solids (data taken from [10, 19])

Sample	Origin or description	Albedo
Terrestrial		
Peridotite	Quebec, Canada	0.395
Obsidian	Ascension Island	0.239
Basalt	Hawaii	$0.130 - 0.200$
Andesite	Chile	0.136
Ilmenite	Bamle, Norway	0.067
Basalt glass	Hawaii	0.048
Anthracite	Liberia	0.032
Carbon black and amorphous silicate	Laboratory mixture $(1-20\% \text{ C})$	$0.0167 - 0.115$
Candle soot		0.011
Lunar		
Lunar fines		$0.05 - 0.595$
Meteoritic		
CI chondrites	Orgueil	$0.054 - 0.072$
CM chondrites	Murchison, Mighei	$0.043 - 0.061$
CV, O chondrites		$0.089 - 0.135$
СK	Karoonda	0.096-0.098
Ureilite	Kenna	0.077
Enstatite chondrite	Abee	0.087-0.094

constituents of the matrix. Hence, the identities of the major minerals, the layer-lattice silicates, remain controversial. McSween and Richardson have recently suggested that another important constituent of matrix materials is a poorly characterized Fe-Ni-S-O phase [4], which has also been described by Fuchs et al. [5]. The relationship of this phase to Fe-Ni sulfides and magnetite is not clear. Nevertheless, it can be stated with reasonable certainty that the major constituents of the CI and CM meteorites a crystallized layer-lattice silicates bearing essential water and containing Mg as the most abundant cation. Set in this material are the Fe-Ni-S-O phase, organic polymer, magnetite, Ni-rich sulfides, pyroxene and olivine, carbonates and sulfates. Carbonates and sulfates are believed to be alteration products formed by leaching of the original matrix by water and subsequent deposition in veins of CI chondrules. For this reason the sulfate and carbonate salts of Ca and Mg are not considered constituents of CCMM. These salts may be the reason CI's have higher albedos than CM's. CI's and CM's also differ markedly in oxygen-isotope compositions [6]. Pyroxene and olivine may also not belong in original CCMM. However, since they are found in micrometeoroids they may be an ubiquitous, although extraneous, component.

This non-equilibrium assemblage of minerals appears to have been put together at a temperature sufficiently low (less than 500 K) that the iron in the different oxidation states did not equilibrate. Overall, the oxidation state of carbonaceous chondrites is higher than

from [4]

Table 4. Mean elemental abundance ratios for CM meteorite matrix (data taken Elements Ratio Na/Si 0.03 ± 0.02
Mg/Si 0.83 ± 0.05 0.83 ± 0.05 Al/Si 0.12 ± 0.04
S/Si $0.22 + 0.06$ $0.22 + 0.06$ Ca/Si 0.04 ± 0.02
Fe/Si $1.90 + 0.4$

 $1.90 + 0.4$

that of any other chondritic meteorite as is reflected, for example, by the presence of magnetite. For the reasons just outlined a number of meteoriticists [4, 7, 8] feel that the CM matrix is more primitive than CI chondrites. For these same reasons I consider CM matrix a better candidate for the type-carbonaceous material. Element ratios for CM matrix from the work of McSween and Richardson [4] are given in Table 4.

As will be discussed in a subsequent section, astronomers have noted that C-type asteroids have albedos lower than any known meteorite. However, the carbonaceous material as defined here is similar to the mixtures of carbon and poorly crystallized hydrated silicates which yielded very low albedos (Table 3) in laboratory experiments [10]. About 70% of the carbon in carbonaceous chondrites is present in the form of high-molecular-weight, highly aromatic or condensed organic polymers, somewhat like kerogen or humic acids [11, 12]. Lower-molecular-weight species are also present in small amounts. Some of the lighter molecules which have been identified include alkanes, olefins, benzene, alkylbenzenes, naphthalene, and related compounds, paraffins, fatty acids, amino acids, and nitrogen bases [1]. Equilibrium chemistry in the C, H, O, system as it relates to observations has been studied by Dayhoff et al. [13]. Considerable controversy raged at one time over the mechanisms by which this assemblage of compounds could be produced in a solar-system setting. At present the most promising process seems to be a series of catalytic reactions known as the Fischer-Tropsch reactions. They are of the following form:

 $nCO + (n + 0.5x)H_2 \longrightarrow \frac{\text{solid}}{2}$ $C_nH_x + nH_2O$

These reactions and their products have been studied and the results compared to meteoritic organic compounds [14-16]. However, uncertainty remains since the high-molecular-weight polymers in carbonaceous chondrites are as yet so poorly characterized.

The source of the carbonaceous chondrites is controversial. Many have supported the idea that comets are the ultimate source of the carbonaceous meteo-

rites. These arguments have been based on compositional grounds, the relatively high volatile content, and dynamical evidence [17]. Carbonaceous chondrites show evidence of having been part of a surficial planetary regolith. They contain solar-windimplanted gases and solar-flare-particle-damaged minerals that could not be acquired by an active comet. Anders [18] has, in fact, argued that these attributes rule comets out entirely. The other probable source is the asteroid belt, and as will be discussed in a subsequent section, astronomical observations show similarities between asteroid surfaces and carbonaceous chondrites which strengthen the possibility of a genetic relationship between the two.

Next to CI chondrites ureilites contain the highest abundance of carbon, an average of 3.0 wt%. The carbon is found in veins in the form of graphite and shock-produced diamond. Graphite is also found in iron meteorites and enstatite chondrites. Albedos of enstatite (E) chondrites and ureilites fall between 0.05 and 0.10 [19]. Aside from containing carbon, none of these meteorites resembles the primitive CCMM. All have low water content. Only the enstatite chondrites are thought to be primitive materials. Their mineral assemblage seems compatible with formation under reducing conditions as will be discussed in a subsequent section.

Small fragments of carbonaceous chondrites which have been found as inclusions in other types of meteorites [8, 20, 21] and on the moon [22] testify to the presence of carbonaceous debris traveling the inner solar system.

Interplanetary Dust

Micrometeoroids, which sample interplanetary dust at 1 A.U., have been successfully collected by Brownlee and co-workers [23-26]. Hundreds of extra-terrestrial particles in the size range 3 to $60 \mu m$ have been collected from the stratosphere by aircraft. Of these roughly 300 have been analyzed for the elements Si, Mg, Fe, A1, Ca, Ti, Cr, Ni, and S. Nearly all fall into one of three compositional groups: chondritic, Ni-bearing iron sulfide, and iron-poor olivine and pyroxene. The majority (60%) are chondritic. Chondritic particles are black, fragile aggregates of grains which may be as small as several angstroms in diameter. The major mineral phase in the aggregates appears to be a poorly crystallized hydrated silicate. Ni-bearing iron sulfides and iron-poor olivines and pyroxenes are, in some cases, among the grains forming an aggregate. Note that all these minerals are constituents of carbonaceous chondrites, CI and CM, discussed in the previous section. In terms of chem-

istry and mineralogy, the resemblance of these micrometeoroids to carbonaceous chondrites, CI or CM types, is strong; however, the physical structure is quite different. The interplanetary grains have a fragile, porous structure whereas on a similar scale the meteorites have a compacted fibrous or platey texture. Brownlee and co-workers [26] have argued on the basis of the differences in textures that interplanetary dust and the carbonaceous chondrites cannot have a common origin. In their view the fragile structure of interplanetary dust seems incompatible with a prior existence in a regolith, and hence, they believe active short-period comets are the source of the interplanetary dust which they have collected. The case for micrometeoroids having their origin in comets has been made on other evidence by a number of people $[27-29]$. From trace-element contents of lunar soils it appears the micrometeroid flux has been nearly constant in time in the inner solar system [30].

Comets

A cometary source for micrometeoroids would mean comets are composed in part of dark carbonaceous material. Aside from the indirect link via micrometeorites between CCMM and comets, there is scant observational evidence bearing on the composition of the dust emitted by comets. A silicate-emission feature at 10µm has been observed in dust tails within 2.0 A.U. of the sun [31]. Its disappearance beyond 2.0 A.U. is attributed to a coating of ices or clathrates. The silicate-grain material in the dust appears similar to that in the interstellar medium. Day [32] has produced analogs to interstellar grains in the laboratory. The analogs are poorly crystallized hydrated magnesian silicates similar in some respects to certain terrestrial clay minerals and very much like CI and CM matrix, i.e., CCMM [33]. Possibly conflicting with this is the observation that the albedo of the dust grains in Comet Kohoutek (1973f) is relatively high, and did not change over the interval 0.37 to 1.9 A.U. Rieke [34] has suggested that water-ice cement between silicate grains might account for these observations. However, the equilibrium temperature at perihelion, 0.15 A.U., is 720 K. At this temperature water would be lost from the structure of hydrated silicates and the spectral signature should change [33]. The molecular and atomic species observed in cometary atmospheres and tails are consistent with the presence of CCMM. Molecular fragments such as C_2 , C_3 , CH, CN, etc. could be UV-decomposition products of organic polymer. They could also be fragments of much lighter, simpler parent molecules. Not enough is known about comets to be more specific at this time.

Asteroids

Spectral-reflectivity studies of asteroids were already documenting compositional differences among the asteroids [35] when it was discovered that some asteroids were much darker and, hence, much larger than previously suspected [36]. With two observational techniques, polarimetry and radiometry, yielding albedo data, it soon was clear that a major fraction of the asteroids were covered with a dark material of albedo=0.02-0.06 [37-40]. In their synthesis of asteroid data Chapman et al. [41] dubbed these dark asteroids, C-type, for carbonaceous type, because carbon seemed to be the only cosmically abundant material capable of producing such low albedos. In addition to their low albedos C-type asteroids are characterized by spectra which are relatively flat in the wavelength region $0.5-1.1 \mu m$ and which fall off sharply in the ultraviolet [42]. Such spectra are well-reproduced by CM meteorites [42, 43]. The other types of asteroids: S-type for silicace0us or stony-iron, E-type for enstatite, M-type for metal-rich, and O-type for ordinary chondritic are discussed by Chapman et al. [41] and Zellner and Bowell [44].

The prevalence of C-types among the asteroids is quite clear. After correcting for observational bias Zellner and Bowell [44] concluded that 76% of 560 main-belt asteroids with diameters > 50 km are Ctype. C-type asteroids become more abundant relative to S-types with increasing distance from the sun.

It should be noted that there is variability in physical properties within the C-type group of asteroids. While the albedo-frequency distribution is strongly peaked at 0.035, well-established albedos for asteroids such as Ceres are near 0.05 [45]. Morrison [45] concludes the probable spread in albedos among C-type asteroids is at least a factor of two. Spectral reflectance also varies among the C-type asteroids as it does for the carbonaceous chondrites. Some asteroids show an absorption feature near 0.65 µm, others do not. The CM chondrite, Mighei, shows such a feature whereas the CM chondrite, Murchison, does not. Nevertheless, it has been argued by Chapman et al. [41] that the higher-albedo, large asteroids such as 1 Ceres and 2 Pallas and others are made of materials more like the metamorphosed carbonaceous chondrite, Karoonda. It is also possible that the actions of water, leaching, and redeposition of salts, are the reason for higher albedos. Finally, a possibility that was also suggested is that the surfaces of these slightly-higher-albedo objects are covered with opaquerich basalts or opaque-rich glasses.

Broad-band photometry of asteroids and meteorites [46] yields the result that no meteorites can reasonably be matched to C-type asteroids because the meteorites are too red in B-V. Since this is a likely result of terrestrial weathering of meteorites (limonite will form within hours, if not minutes on freshly cut surfaces of carbonaceous chondrites), no real significance has been attached to this observation. Recent infrared studies by Lebofsky in the region, $1-2$ and $3-4\,\mu$ m indicate the presence of bound water in both CM meteorites and the C-type asteroid, Ceres [47]. This would seem to rule out the basalts and glasses, and lend more support to the primitive-materials hypothesis.

Aside from the possible presence of water no other compositional inferences have been made for C-type asteroids owing to the difficulties engendered by the presence of the low-albedo material. It has been demonstrated that most diagnostic spectral features in mineral mixtures are completely wiped out by the addition of 5% carbon black [43]. However, water should be detectable. The black material out of which many asteroids are made would seem to be a primitive material. However, heating of some asteroids, e.g., 4 Vesta, must have certainly taken place [35, 48]. No satisfactory explanation exists for the observations, i.e., some objects and not others were heated to melting.

The question has been raised whether the dark asteroidal surfaces could be merely a coating rather than representative of the composition of the asteroids as a whole. Three arguments counter this suggestion. First, not all asteroids have the C-type surfaces, and it would be difficult to imagine a process of coating with something like "cosmic" dust that would not be universal for all asteroids. Secondly, many of the smaller asteroids must therefore have exposed internal portions of asteroids. The majority of these smaller asteroids are C-type. Finally, it has been effectively argued by Morrison [49] that there is a real difference in density between 4 Vesta, a high-albedo asteroid, and 1 Ceres, a C-type, with Ceres being the less dense of the two.

In summary, it seems that CCMM is the best match to the material on surfaces of C-type asteroids.

Planetary Satellites and Rings

Other low-albedo objects which could be composed of CCMM include Phobos and Deimos, the satellites of Mars, which have albedos near 0.065 [50J. Recent close passage of Phobos by Viking Orbiter has permitted an accurate determination of the mass and, hence, the density, which is $2.2 + 0.4$ g/cm³ [51]. Similar measurements are planned for Deimos. This density is identical to that of CI chondrites as can be seen by referring to Table 2. As both the albedo and density **are** closer to CI's than CM's, this could reflect chemical action by transient liquid water.

From cosmochemical considerations, the satellites of the giant planets would be expected to consist of cores similar in composition to carbonaceous chondrites and partially or entirely covered by ice crusts [52, 53]. Under certain conditions liquid water could exist on the satellites and cause chemical changes. Because of the high albedo of ices the presence of even a moderate amount of ice will raise the albedo and influence spectral properties to the extent that dark CCMM would be very difficult to recognize even if it had not been altered. Indeed, the larger, inner satellites of Jupiter have high albedos, ranging from 0.17 to 0.68 (the high albedo of Io, 0.63 is not due to ice) [54]. But the smaller satellites, J6 and J7, have radiometric albedos of 0.03 identical to those of the C-type asteroids [55]. It should also be noted that the Trojan asteroids, which are objects trapped in the Jovian Lagrangian points, have similarly low albedos [55]. The argument has been made, as it has been for the asteroids, that the dark surfaces of Phobos, Deimos, J6 and J7, and the Trojans **are** covered with a thin coating of black dust (over ice?). The source of the dust is a problem for objects in such different orbits. Why were not all of Jupiter's satellites covered with the coating? The problem is similar to that of the asteroids. Although thin coatings seem unlikely, that possibility still exists for the Jovian satellites and the Trojan asteroids.

The recently discovered rings of Uranus [56, 57] seem to have very low albedos. Upper limits set by the failure to photograph the rings from earth-based observatories indicate an albedo of a few percent [58]. It is surprising to find the ring particles are not coated with ice. Much remains to be learned about the cosmochemical processes in the outer solar system.

Formation of Carbonaceous Material

Extensive theoretical studies have been made of the chemical behavior of a cooling gas of solar composition $[59-61]$. With respect to carbon the results of these studies can be simplified as follows. On cooling initially gaseous systems where C/O is at or below the solar value of 0.6, major carbon compounds condense, under strict equilibrium conditions, only at very low temperatures, less than 100 K. Catalytic conversion of CO and H_2 by a Fischer-Tropsch-type reaction to carbon compounds which would condense at higher temperatures (\approx 400 K) has been demonstrated to be a possible alternative [14-16]. In a system **where** C/O approaches 1, major carbon species in the form of graphite and carbides are high-temperature condensates [62]. In both cases it is possible a fraction of the carbon condensed in solid solution in iron [63].

The solar nebula was probably heterogeneous in composition to an as yet undetermined degree. Although **there were** regions in the early solar system **where** C/O approached 1, e.g., formation location of the enstatite chondrites, it appears that C/O near the solar value was the dominant condition during the hightemperature stages of solar-system formation. This implies that the carbon compounds in carbonaceous matter formed at low temperatures, 400-500K. This temperature range is compatible with the presence of layer-lattice silicates, iron in the ferric oxidation state and the cosmic complement of volatile metals in CCMM. At these low temperatures most of the phases **are** formed by reactions of the ambient gas and previously formed minerals. Major reacting species **are** olivine, pyroxene and metal. Near 700 K metal reacts with H_2S in the nebula to form another reactant, FeS. Plagioclase feldspar may supply some cations (Ca, Na, A1) to the layer-lattice silicate. A simplified schematic of this process is given in Figure 1. Kinetic barriers in diffusion, reaction rates, and so forth, will be more important under these circumstances than would be the case in initial condensation from a gas (leaving aside the problem of nucleation). In summary, it seems quite likely that CCMM could be a primordial "condensate" bearing in mind that it is a mixture which is not an equilibrium assemblage. Interstellar dust could form a small component of this mixture and have remained unchanged since its

Fig. l. This is a highly schematic picture of the reactions which could have produced CCMM as a "primordial condensate." Olivine, pyroxene, metal, and troilite (feldspar, another likely reactant, is omitted for clarity) are the reactants formed by condensation processes at higher temperatures. These species react with the solar composition gas in which water has become an important constituent because of failing temperature. Products are shown below the "nebular cloud." Arrows by-passing the cloud indicate that all reactions did not go to completion or some material did not participate in the reactions (taken from [61])

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initial formation if it did not experience higher-temperature regions of the solar system. Although the chemistry in the formation of CCMM is not known in great detail, the observed mineralogy and chemical composition are in general accord with what are perceived to be the important chemical and physical constraints on its formation.

Conclusion

I have described a set of minerals and compounds which occur in carbonaceous chondritic meteorites and in interplanetary dust. This material, which I have called CCMM, is composed largely of layerlattice silicates, organic polymer, magnetite, and ironnickel sulfides. Physical properties, such as albedo, spectral reflectance, and density, of CCMM seem to match the properties, insofar as they have been determined, of a number of objects in the solar system, namely the satellites of Mars, the asteroids, some satellites of Jupiter, and the rings of Uranus. Chemical properties of CCMM seem compatible with its presence in comets. It is noteworthy that there is no evidence for the presence of substantial CCMM on any object closer to the sun than Mars.

The assemblage of minerals constituting CCMM could be formed by partial reaction of cosmically abundant minerals, olivine, pyroxene, metal, and troilite, with a gas of solar composition at 400-500 K and low pressure. A likely setting, but not the only possible setting, for these reactions could be a dusty solar nebula.

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