

the view. The speed of determining such a binding site, the generation and display of its surface and the surface of its substrate, and the ability to change the conformation of both molecules in real time are significant advantages in drug design. With the methods described in this report, it is possible to examine the steric interaction of many drugs with their receptors efficiently and rapidly. The resultant images are also very beautiful.

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18. We thank K. Davies, I. D. Kuntz, J. McClarin, and S. J. Oatley for discussions. Supported by NIH grant RR-1081 (R.L.), NIH graduate training grant GM-07379 (P.A.B.), and the University of California. P.A.B. is a graduate student in the Biophysics Graduate Group at the University of California, Berkeley.

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Epsilon Carbide: A Low-Temperature Component of Interplanetary Dust Particles

Abstract. *Transmission electron microscope study of a chondritic interplanetary dust particle has revealed the presence of epsilon iron-nickel carbide, a low-temperature carbide previously encountered only in metallurgical studies. In these studies ϵ -carbide was synthesized by carburization of iron or nickel grains in a stream of carbon monoxide or carbon monoxide plus hydrogen. Similar carburization of an iron-nickel metal in situ may have produced ϵ -carbide during particle heating on atmospheric entry or in solar orbit. Alternatively, the ϵ -carbide may be a by-product of Fischer-Tropsch reactions in the solar nebula. Such reactions have been proposed as the mechanism of hydrocarbon formation in the early solar system.*

Interplanetary dust particles (IDP's) collected in the stratosphere have been established as a new family of extraterrestrial materials, of which the subset of particles termed chondritic or C-type (1) shows evidence of containing material from the early solar system (2, 3). Although transmission electron microscope (TEM) studies of C-type particles have revealed some systematic aspects of their mineralogies and microstructures, many features exhibited by specific particles and by the group as a whole remain enigmatic, and new mineralogical problems have appeared frequently in the course of IDP research. We report here TEM observations of ϵ -carbide from a C-type particle. The presence of this phase in IDP's was recently discovered in both our laboratory and that of D. Brownlee (4). This carbide has apparently not been observed previously in extraterrestrial materials, and we believe it represents a significantly new aspect of the mineralogy of chondritic IDP's.

The carbide was identified during a TEM study of particles obtained from the NASA cosmic dust collection. It occurs in a particle (NASA No. U2001B17) approximately 10 μ m in size that is intermediate between the chondritic-porous (CP) and chondritic-smooth (CS) morphological types defined by Brownlee *et al.* (1). The particle has "typical" C-type mineralogy: predominant grains of essentially pure enstatite in an extremely fine-grained, presumably carbonaceous, matrix containing magnetite and iron sulfide. The TEM preparation procedures entailed crushing the particle between clean glass slides and transferring the fragments to a thin-carbon film on a copper grid (5).

The carbide and associated phases were identified by electron diffraction and energy dispersive x-ray spectroscopy (EDS). Single-crystal diffraction patterns were obtained with a focused probe (convergent-beam electron diffraction) as well as by conventional selected-area electron diffraction. Four crystals of ϵ -carbide were identified and occur as dis-

tinct 1000- to 2000-Å grains separated from the matrix material. One of the carbide grains has smaller grains of magnetite around its margin. These do not share grain boundaries with the carbide, but were presumably adjacent to it in the matrix prior to crushing. The EDS spectra from the carbide show major iron and minor nickel in an approximate atomic ratio of 8:1 (6).

Single-crystal electron diffraction patterns of the carbide are shown in Fig. 1. Subsidiary reflections along the 4.0-Å and 4.3-Å rows are characteristic. The periodicities and angles from these patterns and seven others showed good agreement with the published diffraction data for ϵ -carbide (7, 8). Measurements were specifically carried out on successive reciprocal lattice sections obtained on rotation about the 4.0-, 4.3-, and 2.3-Å rows (Fig. 1). The results confirmed that the reciprocal lattice contains only vectors permitted by the ϵ -carbide supercell.

According to Nagakura (8), the ϵ -Fe carbide structure is based on a hexagonal close-packed (hcp) sublattice of iron atoms with one-third of the octahedral sites occupied by carbon. Octahedral vacancies are ordered onto every third atomic plane along unit cell direction a , producing superlattice reflections along $h00$ and a supercell with $a = \sqrt{3} a_{\text{hcp}}$.

The diffraction patterns in Fig. 1 are indexed according to this supercell. The appearance of faint forbidden $00l$ ($l = \text{odd}$) reflections is consistent with multiple diffraction effects. There is apparently complete solid solution between ϵ -Fe₃C and ϵ -Ni₃C with little change in overall structure or lattice parameters (8, 9). Jack (7) reports that the metal/carbon ratio can vary between 2 and 3. This ratio for the present phase is unknown.

Carbides with the epsilon structure have been identified in martensite after low-temperature ($\sim 200^\circ\text{C}$) tempering (7) and have been synthesized from metal films and powders under CO or CO + H₂ gas streams (8-10). Conversion of magnetite and iron metal cata-

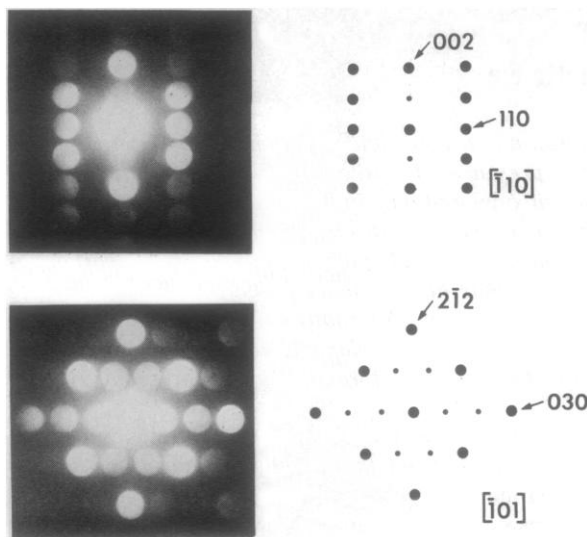


Fig. 1. Convergent-beam electron diffraction patterns for $[110]$ and $[101]$ zones. Indexing is based on a hexagonal supercell (space group $P6_322$) for iron ϵ -carbide with dimensions $a = 4.767 \text{ \AA}$ and $c = 4.354 \text{ \AA}$ (7). For our sample the interplane spacing $d_{(010)} = 4.0 \text{ \AA}$, $d_{(001)} = 4.3 \text{ \AA}$, and $d_{(110)} = 2.3 \text{ \AA}$.

lysts to ϵ -carbide during Fischer-Tropsch (F-T) synthesis has also been reported (11, 12). Nagakura's (8, 9) synthesis experiments show production of both the iron and nickel end-member phases on carburization of iron and nickel films in pure CO below 250° and 450°C , respectively. Annealing was done for several hours, and synthesis for shorter times was not attempted. Under vacuum, the iron end-member was stable up to 380°C , where after a few minutes it transformed irreversibly to χ -carbide, an orthorhombic polymorph. These results are consistent with the synthesis temperatures of ϵ -carbide in the other studies mentioned above.

Beyond Nagakura's (8, 9) experiments there is no additional more detailed information on the thermal stability relations of ϵ -carbide. The stability of ϵ -carbide under various $p\text{H}_2/p\text{CO}$ ratios has also not been studied precisely, but results with iron F-T catalysts suggest that ϵ -carbide can form at H_2/CO volume ratios as high as 1 (12). Given the relatively low temperature of the ϵ -to- χ transformation, ϵ -carbide may provide constraints on the thermal history of its host particle during atmospheric entry.

By analogy with terrestrial synthesis processes, it is possible that ϵ -carbide in the present sample formed by carburization of an iron-nickel metal phase, possibly kamacite. The presence of appreciable nickel in the ϵ -carbide seems to rule out an iron-oxide starting material. Some circumstances under which such a carburizing process might take place are (i) heating and reaction within the particle on atmospheric entry or during solar orbit or (ii) gas-solid reaction during condensation in the early solar nebula. We also considered the possibility that the ϵ -carbide formed on an IDP parent body.

This was considered unlikely, however, since comet nuclei are the most probable repositories for C-type IDP's (13), and they remain well below the temperature interval for ϵ -carbide formation, even on close approach to the sun (14).

Formation of ϵ -carbide by heating on atmospheric entry could involve solid-solid reaction between metal grains and carbonaceous matrix material, or reaction between metal and a carburizing gas (CO ?) produced internally by heating of the matrix. Iron-nickel metal is rare in C-type particles but has been reported by Fraundorf (2). These grains exhibited rims of cementite, an orthorhombic iron-carbide polymorph that forms at higher temperatures ($\sim 550^\circ\text{C}$) than ϵ -carbide (8). We found one grain that appears to be kamacite in the present particle, but this shows no associated carbide. Brownlee (15) has noted that carburization, rather than oxidation, could be an important reaction on atmospheric entry if the interior of the particle were internally buffered at a high $p\text{CO}/p\text{O}_2$ ratio.

A principal uncertainty of the atmospheric entry hypothesis concerns the time for diffusion-controlled carburization reactions to occur compared to the duration of particle heating, which is only a few seconds (16). At present there are no data to indicate whether the carbon self-diffusion rate would be high enough, and the size of the starting grains small enough, for ϵ -carbide to be formed in the allotted time. We note that the rate of carbon diffusion should also control the kinetics of the ϵ -to- χ transformation, and hence determine whether ϵ -carbide is an effective thermometer for atmospheric entry.

The special circumstances necessary to form ϵ -carbide in the atmosphere, in addition to the time constraints, make us favor a preatmospheric origin. Longer

particle heating during solar orbit might have been sufficient to induce ϵ -carbide formation in situ by reactions similar to those proposed for atmospheric heating. In this case the particle, regardless of initial size, would need to have had an orbital trajectory that brought it between 0.4 to 0.8 astronomical units (17) of the sun prior to capture by the earth.

Alternatively, origin in the early solar system represents the most interesting and complex circumstance for ϵ -carbide formation. Anders and co-workers [see Hayatsu and Anders (18)] have suggested for some years that condensation in the solar nebula below approximately 400 K involved reaction of H_2 and CO to form the array of hydrocarbons now seen in the C1 chondrites. The process is thought to be analogous to F-T synthesis and would have used magnetite, hydrated silicate, or possibly iron-nickel metal grains as catalysts.

The possibility of F-T synthesis in the early solar system and the presence of ϵ -carbide in some earthly F-T synthesis products (11) suggest an intriguing connection. The broad implication is that ϵ -carbide formed as a by-product of nebular hydrocarbon synthesis through carburization of iron-nickel "catalyst" grains. There are, however, several unanswered questions associated with such a proposition. For example, although ϵ -carbide can apparently form in a 1:1 H_2/CO mixture (12), whether it could form under the much higher (~ 1000) H_2/CO ratios and lower (for instance, 10^{-3} atm) total pressures of the nebula is not known. The ϵ -carbide grains might also be expected to be embedded in or otherwise intimately associated with the hydrocarbon products. Such a relation has not been seen by us or by Bradley and Brownlee (15), although they report uncarburized magnetite embedded in carbonaceous filaments in some particles (4). Alternatively, ϵ -carbide might have formed in a cosmic carburizing reaction unassociated with hydrocarbon formation.

Further attention to the systematics of the occurrence of ϵ -carbide in IDP's and to its relation to other IDP constituents, especially carbonaceous ones, may decide the question of its origin as a primitive phase. If this could be demonstrated, then ϵ -carbide provides a unique insight into important early solar system processes.

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Membrane Lipid from Deep-Sea Hydrothermal Vent Methanogen: a New Macrocyclic Glycerol Diether

Abstract. *The membrane lipid of a new deep-sea hydrothermal vent methanogen, Methanococcus jannaschii, has been structurally characterized. The hydrolyzed polar lipid of this archaeobacterium is primarily (95 percent) a macrocyclic glycerol diether, which has not been described previously. The structure was elucidated by a combination of chemical and spectroscopic techniques. An initial survey of selected methanogens failed to indicate the presence of this membrane lipid in any microorganism other than Methanococcus jannaschii.*

As part of an effort to determine source markers for biogenic organic matter in hydrothermal vent fluids, we have characterized the lipids of the newly discovered methanogenic bacterium *Methanococcus jannaschii* which was recently isolated from deep-sea hydrothermal vent sediment (1). The lipids of methanogens (2–6), as well as of other archaeobacteria (7–19), consist primarily of (i) isoprenoid hydrocarbons and (ii) alkylglycerol ethers. The latter are stable ether-linked analogs of the ester-linked glycolipids and phospholipids found in other organisms, and thus fulfill our requirement of being new, source-specific markers for microbial input to organic matter at hydrothermal vent sites (20).

We describe here the structure of the major alkylglycerol ether, **1a** (Fig. 1), of *Methanococcus jannaschii*. This structure had been tentatively proposed for an isolated glycerol ether from another species of archaeobacteria (13, 15), but more detailed studies have shown that the compound for which this structure had been proposed was actually the high molecular weight bis-(diphytanyl)diglycerol tetraether (2) (2–6, 10–12).

Methanococcus jannaschii was grown on hydrogen and carbon dioxide optimal-

ly at 85°C (1). Freeze-dried cells of the microorganism were suspended in a mixture of methylene chloride (CH₂Cl₂), methanol, and water and were sonicated. The total lipid extract (TLE) was then partitioned between CH₂Cl₂ and water, and subsequently the CH₂Cl₂ fraction was evaporated to dryness below 35°C. This resulted in 32.2 µg of TLE per milligram (dry cell weight), in approximate agreement with reported values for methanogenic bacteria (2–6).

The TLE was separated into individual compound classes by adsorption chromatography on silica gel. Elution with a series of solvents of increasing polarity separated the TLE into a neutral lipid fraction (NLF) and polar lipid fraction (PLF). The PLF, eluted by ethyl acetate and methanol fractions, yielded 8.4 mg/g (dry cell weight). This fraction was hydrolyzed for 5 hours at 100°C with a mixture of 4.0M methanolic HCl. The hydrolyzate was neutralized and extracted with hexane, and the resulting hydrolyzed PLF (HPLF) was studied spectroscopically.

Infrared spectra of the HPLF showed absorptions corresponding to a hydroxyl group (3200 to 3600 cm⁻¹, 1258 cm⁻¹), and a carbon-oxygen single bond (1060

to 1140 cm⁻¹) (21). The infrared spectrum is nearly identical to that of authentic bis-(phytanyl)glycerol diether (**3a**) and bis-(diphytanyl)diglycerol tetraether (2) (3, 5, 9, 11, 17, 18).

High-field proton nuclear magnetic resonance (NMR) spectra of the HPLF ethers were taken with a Bruker 250 MHz instrument (21). The chemical shift data show resonances consistent with a glycerol ether structure. The methyl resonances are doublets, showing coupling to one proton, as would be expected for a methyl group in an isoprenoid alkyl chain. The ¹H-NMR spectrum of this substance closely matched that of authentic **2** and **3a**.

Field desorption mass spectroscopy was performed on the HPLF (Varian MAT 731 double-focusing mass spectrometer). Field desorption mass spectra of authentic **3a** and the HPLF differ by two mass units with a m/z of 653 for the protonated molecular ion of **3a** and m/z of 651 for the protonated molecular ion of the HPLF molecule. Authentic tetraether **2** exhibits an ion cluster in the molecular ion region of 1292 to 1300. This ion cluster, with a maximum at 1296, is not present in the HPLF molecule, thus clearly indicating that the glycerol ether in the HPLF is not **2**.

High-resolution glass capillary gas chromatography (GC) of the acetate and trimethylsilyl derivatives of the HPLF was accomplished with the use of a deactivated, cross-linked SE-52-coated (25.5 m by 0.32 mm inside diameter) column. Two components were present in the HPLF. The minor component (5 mole percent) elutes, both as the acetate and the trimethylsilyl ether, with authentic bis-(phytanyl)glycerol diether acetate (**3b**) and trimethylsilyl ether (**3c**), respectively. GC-mass spectrometry (MS) of the HPLF shows that the minor component has identical fragmentation patterns as the authentic **3b** and **3c**. The major component (**1a**) of the HPLF (95 mole percent) has a different fragmentation pattern, both as the acetate and trimethylsilyl derivative (21). Quantitative data for the amounts of the alkylglycerol ethers in the NLF and PLF are displayed in Table 1.

The HPLF ethers were converted to bromides by heating with boron tribromide (BBr₃) at 90°C for 4 hours (Fig. 2). This reaction for the HPLF takes place in 95 percent yield (by weight) and results in two compounds. The major component (mole fraction 0.87) coelutes with diphytanyl dibromide (**4**), and its mass fragmentation pattern is identical to that of (**4**). The minor component (mole fraction 0.13) coelutes with phytanyl bro-