# Conversion of carbonaceous material to graphite during metamorphism

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**Abstract**—Using high-resolution transmission electron microscopy (HRTEM), we have charted some of the structural changes that occur as non-crystalline organic matter in low-grade metamorphic rocks becomes ordered, eventually to form well-crystallized graphite. It has long been known from X-ray studies that the state of crystallization of carbonaceous matter increases with metamorphic grade. Images obtained by HRTEM of samples from a range of metamorphic terranes provide considerable additional detail regarding the process of graphite development. The process is considerably more complex than is suggested by light-optical microscopy and powder X-ray diffraction measurements.

In low-grade metamorphic rocks, the carbon layers are relatively few in number, short in length, and rather contorted. Electron-diffraction patterns show only one or two rings, and they are diffuse. As metamorphic grade increases, the carbon layers progressively increase in length and in number, the number of layers in the crystallite stacks increases, the planarity of the layers increases, and the number of layer terminations decreases. Electron-diffraction patterns show complementary increasing numbers of rings, decreasing diffuseness, and, for well-crystallized graphite, discrete spots. Well-crystallized graphite crystals appear in the chlorite zone but, in contrast to most X-ray measurements, a range of structural order is commonly observed among the various crystallites within a given rock sample. These presumably reflect the chemical and structural character of the carbonaceous precursors, possibly their sedimentary sources, as well as the degree of internal equilibration. The results of our electron microscope observations also have implications for interpreting measurements of carbon-isotope fractionations and the apparent lack of equilibrium reported in many such measurements.

## INTRODUCTION

ELEMENTAL CARBON is widespread in igneous, metamorphic, and sedimentary rocks. Its origin is diverse, but a particularly common source, especially in sedimentary rocks, is organic debris. With time and geological processing this debris is converted into increasingly crystalline and pure material, with graphite as the end product. There are many steps that occur during the conversion of hydrocarbons to graphite. Hydrogen, nitrogen, and oxygen are lost as polymerization proceeds to form larger, more complex, carbon-rich units. Much information is potentially available from these incompletely reacted species, prior to the final development of well-crystallized graphite. Since degree of carbon crystallization is dependent on the extent and intensity of metamorphism, structural studies of such carbonaceous materials hold the promise of providing considerable information regarding metamorphism. Furthermore, graphite commonly influences the partial pressures of $CO_2$, $CO$, $CH_4$, $H_2O$, $H_2$, and $O_2$ in the coexisting vapor phase (FRENCH, 1964, 1966), and for this purpose it is desirable to know the state of crystallization of the carbon.[2]

Many descriptive terms have been used to describe poorly or incompletely crystallized carbon: graphitic, sub-graphitic, pre-graphitic, semi-graphitic, mesophase, semi-crystalline, amorphous, vitreous, glassy, pyrolytic, turbostratic, sooty, disordered, soft, hard, and so forth. Many of these terms have been carried over or, in some cases, have originated in the geological literature. There is much overlap between the terms (and structures), and the distinctions are commonly neither clear nor straightforward.

The goal of this paper is to use high-resolution transmission electron microscopy (HRTEM) to study a variety of carbonaceous materials obtained from low- to middle-grade metamorphic rocks. Wherever possible, we wish to examine systematic changes in samples that had been subjected to different heating histories and thus conversion stages. Our long-range goal is to relate the structures in geological samples to those that have been heat treated under controlled conditions. In a companion paper (BUSECK and HUANG, in preparation), we consider changes that occurred upon heating representative model organic compounds; these have been used in a series of earlier studies of carbonization reactions in the laboratory (EDSTROM and LEWIS, 1969; LEUNG and SAFFORD, 1970). Another companion paper (BUSECK and HUANG, in preparation) examines the development of kerogen and the changes that it undergoes as reflected by a series of acid-insoluble separates from Precambrian rocks.

## PREVIOUS WORK

The conversion of organic carbonaceous material to graphite in metamorphic rocks has been the object of many studies utilizing powder X-ray diffraction (XRD) measurements. The focus of these studies has been on sediments altered either in contact aureoles (FRENCH, 1964) or in regional terranes (e.g., LANDIS, 1971; GREW, 1974; DIESSEL et al., 1978; ITAYA, 1981;

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[2] Carbon, in the context of this paper, refers to carbonaceous materials ranging from the pure element to organic molecules that consist predominantly of carbon, but that also contain other elements such as H, N, O.

WINTSCH et al., 1981). The goal of such research has been to correlate metamorphic grade with degree of carbon crystallinity as measured by the position and peak width of the $d_{002}$ interlayer spacing. Similar studies have been performed on kerogens, which are carbon-rich organic materials found in many sediments (HARRISON, 1976; HAYES et al., 1983).

There is an extensive literature and terminology for the organic constituents of petroleum source rocks (SCHOPF, 1983) and of coals (STACH et al., 1982). For the coals, this includes the major types of macerals—vitrinite, exinite (or liptinite), and inertinite, as well as several dozen subcategories. They are defined on the basis of morphology, and all maceral types may display a range of compositions and physical properties (STACH et al., 1982). Although nominally amorphous, the carbons in these macerals also display varied degrees of ordering as coalification proceeds (QUINN and GLASS, 1958; GRIFFIN, 1967; DIESSEL et al., 1978).

Graphite is also important in electrodes and in a wide variety of materials having high tensile strengths and light weights. As a consequence, there have been a large number of papers on the formation of graphite in the laboratory and in industrial processes. A productive approach has been to take organic compounds that have known structures and chemistries and then thermally to convert them (pyrolysis or coking) into graphite or graphite-like materials (e.g., FRANKLIN, 1951; RULAND, 1965; EDSTROM and LEWIS, 1969). A parallel approach has been to take a variety of types of coals and similarly convert them in the laboratory (e.g., MARSH, 1973; ÖYA et al., 1983).

A wide variety of experimental techniques have been used to study the poorly crystallized states of carbon. While powder XRD measurements have been the most prominent, correlative measurements on geological samples have been made by isotopic and spectral studies (RUMBLE et al., 1977; WEIS, 1980; SCHOPF, 1983; DUKE and RUMBLE, 1983). Synthetic samples have been investigated by an even wider range of spectral and diffraction measurements; these are well outlined in a recent review by LEWIS (1982).

There have been a large number of extensive and sophisticated treatments of X-ray data to interpret structures of pregraphitic carbon (e.g., FRANKLIN, 1951; RULAND, 1968; ERGUN, 1968). Parameters such as $L_a$ and $L_c$ (the average nominal widths and heights of graphite crystallites, parallel to the crystallographic $a$ and $c$ axes), $a_3$ (the graphite (002) interlayer spacing), and $\sigma_{12}$ (the defect concentration) have been measured and published for many synthetic samples. However, they are all based on powder diffraction data and thus are indirect. Furthermore, there is no simple way of distinguishing between the effects of crystallite sizes and structural disorder, because both can affect the X-ray peaks and positions in similar ways; there is thus an inherent ambiguity in such X-ray data (RULAND, 1968).

A limited number of papers have used electron-microscope images to study graphite and its precursors, both from natural samples (MILLWARD and JEFFERSON, 1978; OBERLIN et al., 1980; BOULMIER et al., 1982) and from synthetic materials (BAN et al., 1975; MILLWARD et al., 1978). There is both great complexity and much information in such images.

## SYNTHETIC STUDIES

The pyrolytic conversion of organic compounds into graphite has received much attention. Temperature and time of heating are of major importance, as are the total pressure and partial pressures of various gaseous species and the presence of catalysts. The chemical and structural features of the reactants and products are also significant. The hydrocarbon precursors strongly influence the structural character of the resulting carbon and the ease with which graphite forms.

FRANKLIN (1951), in an XRD study of laboratory-heated compounds, distinguishes between "graphitizing" and "non-graphitizing" carbons. The latter show no evidence of "homogeneous development of a graphite structure", even after heating to 3000°C for 15 to 20 minutes (prior to that, these samples had been heated for two hours at 1000°C). The sharp distinction between graphitizing and non-graphitizing carbons depends largely on the structures and compositions of their hydrocarbon precursors. If the precursors are aliphatic, then they must first be aromatized before they can be polymerized into more graphite-like molecules. If the precursors are aromatic, then the basic hexagonal, benzene-ring structure that characterizes graphite already exists, greatly facilitating graphitization. Materials from the natural environment typically are more complex than the above, and they commonly have mixed character. An example, shown in Fig. 1a, is acenaphthylene. (This and other compounds that are selected as examples, are considered in greater detail by BUSECK and HUANG (in preparation); the samples were prepared by I. C. Lewis, and the material in this section is largely described by LEWIS (1982) and papers cited therein.)

The process of graphitization is simple in concept but complex in detail. It requires a large number of steps, most of which include the release of hydrogen, oxygen, and other foreign atoms (heteroatoms), as well as the development of ordered, planar layers of carbon that can be stacked into the parallel layers that characterize the graphite structure. The process is largely one of ordering and removal of structural defects, but many of the details are not well understood. The diffusion-controlled elimination of bonding vacancies is of major importance, whereas nucleation and growth processes seem of lesser or even negligible importance (FISCHBACH, 1971).

Graphite layers, of course, are planar, and there are many aromatic compounds that either are not planar
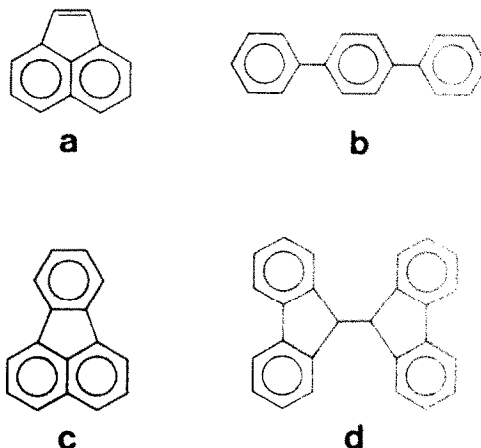


**a**     **b**

**c**     **d**

FIG. 1. Schematic structures of representative model hydrocarbon precursors of graphite. (a) acenaphthylene. (b) paraterphenyl, (c) fluoranthene, and (d) bifluorenyl.