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Graphitization of Organic Material In a Progressively Metamorphosed Precambrian Iron Formation

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ABSTRACT

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Organic matter in the sedimentary Biwabik iron formation in northern Minnesota shows a progressive increase in crystallinity where the formation is metamorphosed by the intrusive Duluth gabbro complex. X-ray diffraction studies of acid-insoluble residues show a complete range in crystallinity from amorphous material in the unmetamorphosed sediments to completely crystalline graphite adjacent to the gabbro.

author

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Examination of carbonaceous material from unmetamorphosed Precambrian sediments (1) has shown that such material is not crystalline graphite, It is instead an amorphous aggregate of hydrocarbon compounds of high molecular weight which may be related to the so-called "kerogen" found in younger sedimentary rocks (2).

During a study of progressive metamorphism of the Biwabik iron formation in northern Minnesota (3), the carbonacecus matter from organic-rich layers in the formation was examined by X-ray diffraction to determine the degree of crystallinity at various metamorphic levels and to detect, if possible, the development of crystalline graphite during metamorphism.

The Biwabik iron formation, on the Mesabi Range in northern Minnesota, is a chemical sediment of Middle Precambrian age. It is composed chiefly of quartz, magnetite, hematite, siderite, ankerite, and several hydrous iron silicates (3,4).

On the eastern end of the Mesabi Range, near the town of Babbitt, the sediments were intruded by the Duluth gabbro complex about 1.0 b.y. ago. Progressive changes in the mineralogy of the iron formation occur within a few miles of the contact (3,4,5). The moderately metamorphosed iron formation, 2 to 3 miles (3 to 5 kilometers) from the gabbro is characterized by the presence of the iron-amphibole grunerite; grunerite-ankerite-calcite assemblages are typical. The highly metamorphosed iron formation adjacent to the gabbro is characterized by iron-rich pyroxenes, by reduction of hematite to magnetite, and by the absence of all carbonates except calcite.

The samples studied were collected along the strike of the Biwabik formation from the so-called "Intermediate Slate," a well-known and easily recognized marker bed. The unit is a dark gray to black, fine-grained and finely laminated layer which is generally 5 to 40 feet (2 to 15 meters) thick. Analyses of this unit have shown from 1 to 4 weight per cent carbon (6). Unmetamorphosed "Intermediate Slate" is composed chiefly of siderite and iron-rich chamosite, with minor quartz, stilpnomelane, and magnetite. Grunerite, iron pyroxenes, and fayalite appear where the unit is metamorphosed.

The method of sample preparation was suggested by T. C. Hoering, of the Geophysical Laboratory of the Carnegie Institution of Washington, and has been used by him to separate organic components from sedimentary rocks. About 100 grams of the "Intermediate Slate" sample were ground to minus 230 mesh and then dissolved in hot hydrofluoric acid for about 24 hours to remove silicate and carbonate minerals. It was essential that all quartz be removed, since the strong (101) peak of quartz will completely mask the graphite (002) reflection if even a small amount of quartz is present. The insoluble residue was then treated with hot hydrochloric acid for about 24 hours to remove fluorides and fluosilicates. X-ray diffraction patterns were made to monitor the process at each stage.

The carbon concentrate obtained consisted of from one to 4 grams of a dark gray or black material. Small portions were mounted on a glass slide in an acetone-Duco cement mixture and studied by X-ray diffraction, using Ni-filtered Cu K radiation. Small amounts of original pyrite and tourmaline also survived treatment and were identified in the pattern.

The X-ray diffraction patterns obtained can be divided into four major groups which represent different degrees of crystallinity in the organic matter (Fig. 1):

(1) An amorphous pattern without peaks (Fig. 1, A), which indicates completely noncrystalline material. Such patterns were obtained only from material separated from the unmetamorphosed iron formation.

(2) A very broad peak at a 2θ value of about 25 degrees, corresponding to a d_{002} value of about 3.5 A (Fig. 1, B, C). Such patterns resemble those of coals and asphaltic substances (7). One specimen, which produced this pattern, contained patches of

black, brittle, resinous hydrocarbon in carbonate-bearing iron formation. This material contained a measurable amount of pyridine-extractible organic compounds (8).

(3) A diffuse peak at a 2θ value of 26.0 degrees (d_{002} = 3.43 A), suggestive of poorly-crystalline graphite (Fig. 1, D). Such a pattern may represent graphite with considerable disorder in layer stacking ("turbostratic") (9, p. 79). The term "d-graphite" (for "disordered") is used here to designate such material.

(4) A sharp peak at a 2θ value of 26.5 degrees (d_{002} = 3.36 A) (Fig. 1, 3), corresponding to the (002) reflection of well-crystallized graphite (9,10).

Figure 2 shows the relationship between crystallinity of organic matter and the metamorphic grade as indicated by index minerals in the iron formation. A certain amount of "overlap" of the various types results from the steep thermal gradient in the contact zone and from the fact that the mineralogical zones are not exactly parallel to the surface contact between the iron formation and the gabbro (3). Nevertheless, the results indicate a general increase in crystallinity of organic material with increasing metamorphism. Organic matter from the unmetamorphosed iron formation is amorphous, while both graphite and d-graphite appear to be restricted to the neighborhood of the gabbro. A similar increase in crystallinity with increasing metamorphic grade has been observed in regionally metamorphosed coals (11).

The present study describes a simple method for the identification of crystalline graphite in rocks and for the distinction between graphite and amorphous organic matter. The possible action of graphite as a "buffer" to control oxygen fugacity (3,12) makes the exact identification of such material in igneous and metamorphic rocks of particular significance. It is probable that the presence of amorphous organic material in sediments is significant in fixing low values of P_{O_2} at intermediate levels of metamorphism, although calculations based on crystalline graphite are not rigorously applicable to such material.

Bevan M. French

Department of Geology
The Johns Hopkins University
Baltimore 18, Maryland

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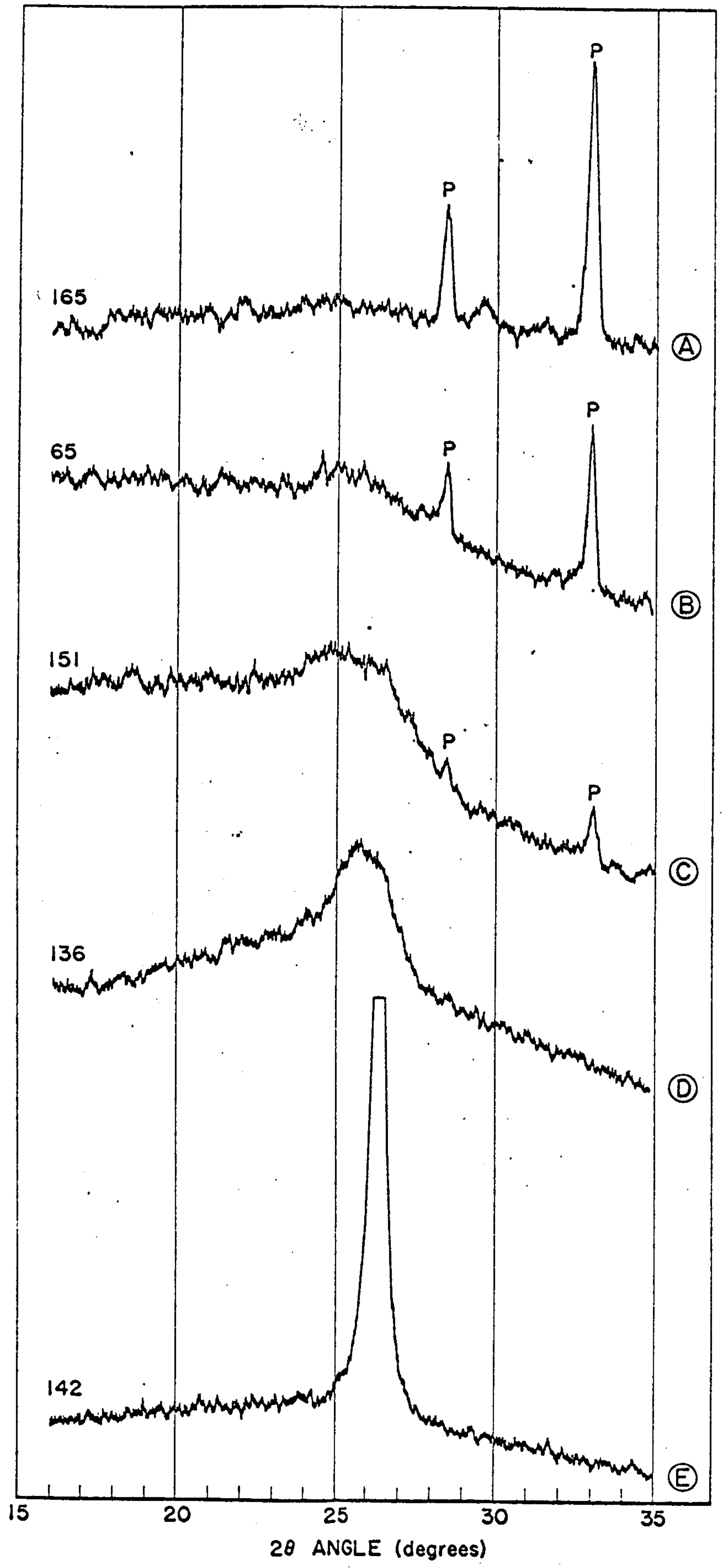
14. The writer is presently with the Theoretical Division, Goddard Space Flight Center, National Aeronautics and Space Administration, Greenbelt, Maryland, as a National Academy of Sciences--National Research Council Research Associate.

FIGURE CAPTIONS

Fig. 1. X-ray diffraction patterns of organic matter extracted from samples of the "Intermediate Slate" member of the Biwabik iron formation. Sample numbers are shown at the left-hand side of the traces; the peaks designated "P" in patterns A, B, and C are produced by small amounts of pyrite. Increasing graphitization is indicated by the gradual development of the strong (002) graphite reflection at about 26 degrees. Pattern A represents amorphous material from unmetamorphosed iron formation. Patterns B and C show the gradual appearance of a broad peak indicative of asphaltic substances. Pattern D is a disordered graphite, and Pattern E represents crystalline graphite. The height of the peak in Pattern E has been reduced by one-half relative to the other patterns.

Fig. 2. Crystallinity of organic matter in the "Intermediate Slate" member as a function of distance from the Duluth gabbro complex. The metamorphic grade of the Biwabik iron formation is indicated by the index minerals (calcite, grunerite, and iron pyroxenes) which have developed from original minerals during metamorphism. Graphite and d-graphite appear restricted to the highly metamorphosed iron formation.


165
65
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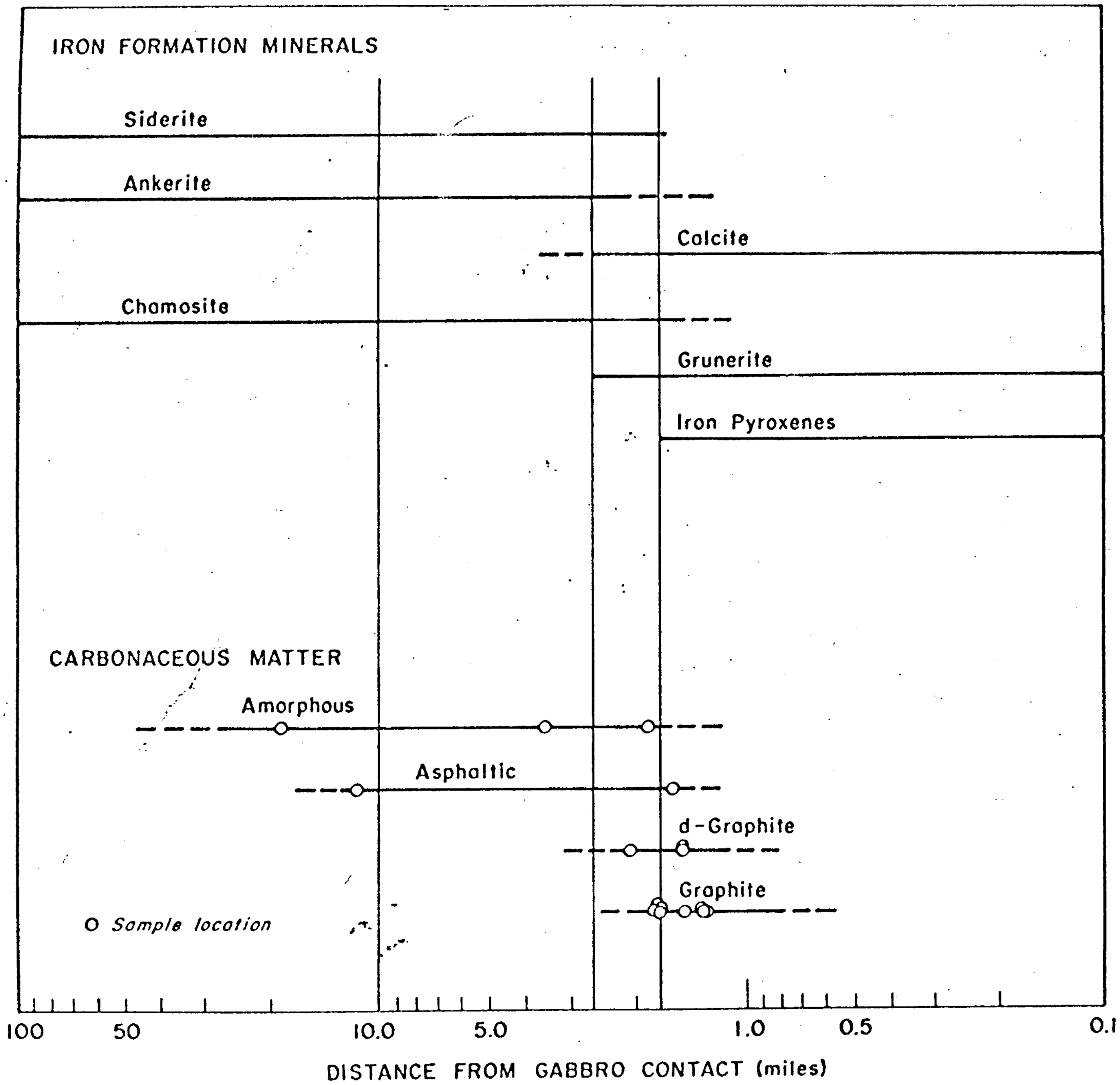
IRON FORMATION MINERALS
Siderite
Ankerite
Calcite
Chamosite
Grunerite
Iron Pyroxenes
CARBONACEOUS MATTER
Amorphous
Asphaltic
d-Graphite
Graphite
O Sample location
100
50
10.0
5.0
1.0
0.5
0.1
DISTANCE FROM GABBRO CONTACT (miles)