B relative to counter A may have been dependent on wavelength and, therefore, significantly greater at the longest x-ray wavelengths. Some evidence to this effect is apparent in the data of Table 1.

4. L. Woltjer, "X-rays and type I supernova remnants," preprint (1964).
5. I. S. Shklovsky, "On the energy spectrum of relativistic electrons in the Crab Nebula," private communication.
6. W. L. H. Shuter and G. L. Verschuur, *Monthly Notices Roy. Astron. Soc.* **127**, 387 (1964).
7. A. G. W. Cameron, *Astrophys. J.* **129**, 676 (1959).
8. B. L. Henke, R. White, B. Lundberg, *J. Appl. Phys.* **28**, 98 (1957).
9. F. Hoyle and W. A. Fowler, *Astrophys. J.* **132**, 565 (1960).
10. E. M. Burbidge, G. R. Burbidge, W. A. Fowler, F. Hoyle, *Rev. Mod. Phys.* **29**, 547 (1957).
11. L. Woltjer, *Bull. Astron. Inpt. Netherlands* **14**, 39 (1958).
12. C. Heiles, *Astrophys. J.* **140**, 470 (1964).
13. C. O'Dell, *ibid.* **136**, 809 (1962).
14. J. W. Overbeck, "Small-angle scattering by interstellar grains as a source of angular broadening of celestial x-ray sources," preprint (1964).
15. S. Colgate, private communication.
16. I. S. Shklovsky, *Astron. Tzirkulyar* No. 304 U.S.S.R. (1964).
17. R. H. Brown, R. D. Davies, C. Hazard, *Observatory* **80**, 191 (1960).
18. The attitude control system used to stabilize the Aerobee Rocket was furnished by NASA. We thank Dr. W. Nicholson, of the Royal Greenwich Observatory, for supplying the occultation predictions upon which the observational program was based. Sponsored jointly by the Office of Naval Research and the National Science Foundation.

1 October 1964

Graphitization of Organic Material in a Progressively Metamorphosed Precambrian Iron Formation

Abstract. *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 of acid-insoluble residues shows that there is a complete range in crystallinity, from amorphous material in the unmetamorphosed sediments to completely crystalline graphite adjacent to the gabbro.*

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

During a study of progressive metamorphism of the Biwabik iron formation in northern Minnesota (*3*), carbonaceous 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, development of 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 (*3–5*).

On the eastern end of the Mesabi Range, near the town of Babbitt, the sediments were intruded by the Duluth gabbro complex about 10^9 years ago. Progressive changes in the mineralogy of the iron formation occur within a few miles of the contact (*3–6*). The moderately metamorphosed iron formation, 3 to 5 kilometers (2 to 3 miles) from the gabbro, is characterized by 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, generally 2 to 15 meters (5 to 40 feet) thick. Analyses of this unit have shown from 1 to 4 percent carbon by weight (*4*, pp. 54–62). 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 g of the "Intermediate Slate" sample were ground to minus 230 mesh and treated with hot hydrofluoric acid for about 24 hours to remove silicate and carbonate minerals. It was essential that all quartz be removed, because 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 1 to 4 g 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, with Ni-filtered CuKα radiation. Small amounts

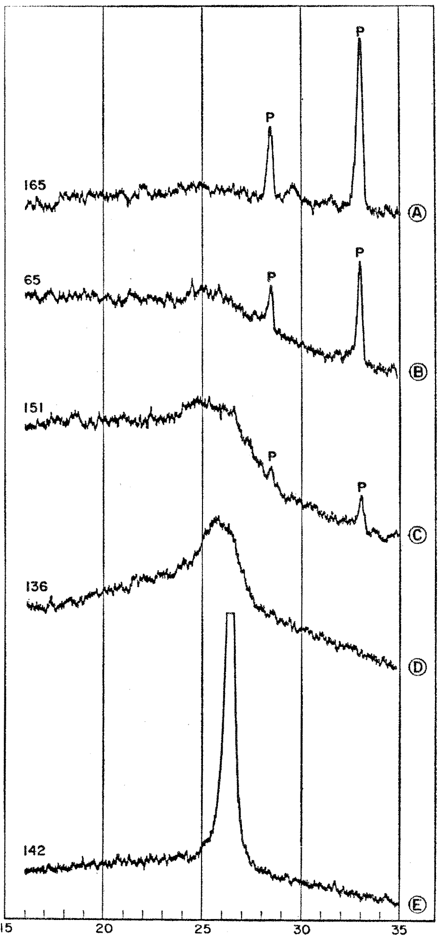

Fig. 1. X-ray diffraction patterns of organic matter extracted from samples of the "Intermediate Slate" member of the Biwabik iron formation. Sample numbers are shown at the left-hand side of the traces; the peaks designated "P" in patterns, *A*, *B*, and *C* are produced by small amounts of pyrite. 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 graphite. The height of the peak in pattern *E* has been reduced by one-half relative to the other patterns.

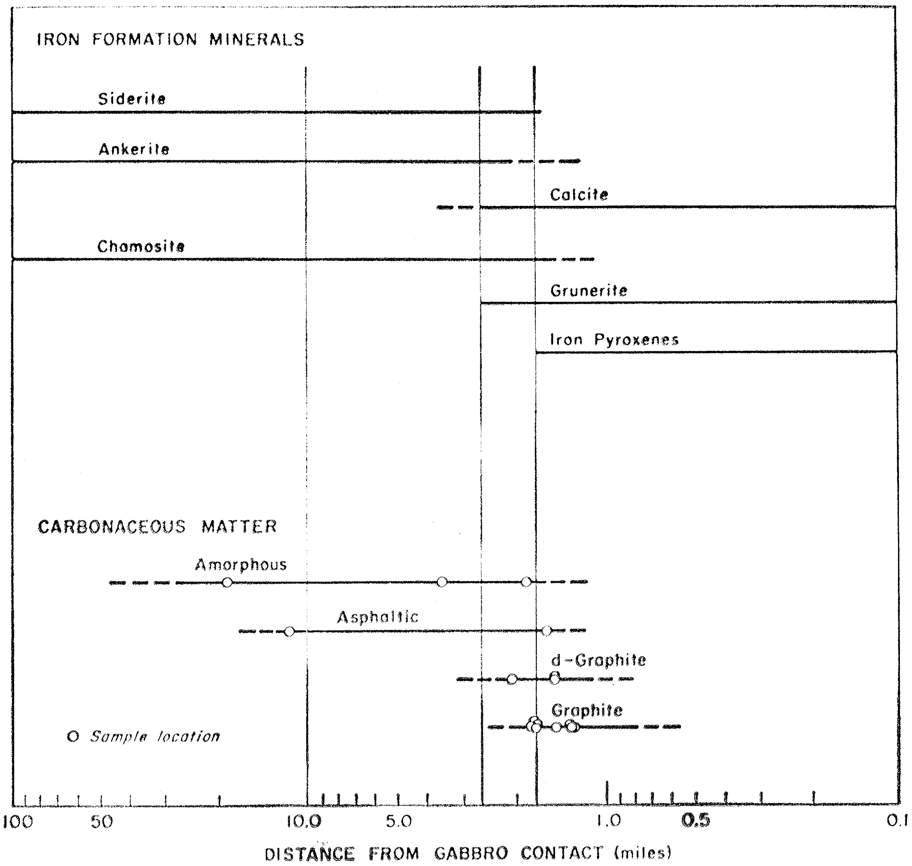

Fig. 2. Crystallinity of organic matter in the "Intermediate Slate" member as a function of distance from the Duluth gabbro complex. The metamorphic grade of the Biwabik iron formation is indicated by the index minerals (calcite, grunerite, and iron pyroxenes) which have developed from original minerals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

of pyrite and tourmaline survived treatment.

The x-ray diffraction patterns 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 Å (Fig. 1, *B* and *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-extractable organic compounds (*8*).

3) A diffuse peak at a 2θ value of 26.0 degrees ($d_{002} = 3.43$ Å), 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 ($d_{002} = 3.36$ Å) (Fig. 1*E*), 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 isolation and identification of trace amounts of organic matter in sedimentary and metamorphic rocks have been largely neglected in the past. Such investigations, which can be carried out by the methods used in the present study, are of great petrologic importance in view of the ability of graphite to control the partial pressure of oxygen in the vapor phase with which it coexists (*3, 12*). Although thermodynamic calculations based on graphite cannot be rigorously applied to noncrystalline carbonaceous matter, such material may be significant in producing reducing conditions during metamorphism. The gradual change in the crystalline character of the organic matter with metamorphism would also be of interest for comparison with other mineralogical "isograds."

BEVAN M. FRENCH*

Department of Geology,
Johns Hopkins University,
Baltimore 18, Maryland

References and Notes

1. F. M. Swain, A. Blumentals, N. Prokopovich, *Bull. Am. Assoc. Petrol. Geologists* **42**, 173 (1958); T. C. Hoering, *Carnegie Inst. Wash. Year Book* **61**, 184 (1962).
2. J. P. Forsman, in *Organic Geochemistry*, I. A. Breger, Ed. (Pergamon, New York, 1963), pp. 148–182.
3. B. M. French, dissertation, Johns Hopkins University (1964).
4. J. W. Gruner, *The Mineralogy and Geology of the Taconites and Iron Ores of the Mesabi Range, Minnesota* (Office of the Commissioner of the Iron Range Resources and Rehabilitation, St. Paul, Minnesota, 1946).
5. D. A. White, *Minn. Geol. Surv. Bull.* **38** (1954).
6. J. N. Gundersen and G. M. Schwartz, *Minn. Geol. Surv. Bull.* **43** (1962).
7. D. W. Van Krevelen, *Coal: Typology, Chemistry, Physics, and Constitution* (Elsevier, New York, 1961), pp. 324–342; J. F. Weiler, in *Chemistry of Coal Utilization: Supplementary Volume*, H. H. Lowry, Ed. (Wiley, New York, 1963), pp. 580–628.
8. T. C. Hoering, personal communication (1962).
9. A. R. Ubbelohde and F. A. Lewis, *Graphite and Its Crystal Compounds* (Clarendon, Oxford, 1960).
10. L. G. Berry and R. M. Thompson, *Geol. Soc. Am. Mem.* **85**, 23 (1962).
11. A. W. Quinn and H. D. Glass, *Econ. Geol.* **53**, 563 (1958).
12. E. Zen, *Am. J. Sci.* **261**, 929 (1963); A. Miyashiro, *Geochim. Cosmochim. Acta* **28**, 717; B. M. French and H. P. Eugster, in preparation.
13. This research was part of a doctoral dissertation completed under the supervision of Prof. H. P. Eugster, department of geology, Johns Hopkins University. Supported in part by a grant from the Penrose Fund of the Geological Society of America. I thank Dr. T. C. Hoering, of the Geophysical Laboratory of the Carnegie Institution of Washington, for many helpful suggestions on sample preparation and interpretation of the x-ray diffraction patterns. I have also benefited greatly from discussions with Dr. H. J. Greenwood and Dr. D. R. Wones.

* Present address: Theoretical Division, Goddard Space Flight Center, NASA, Greenbelt, Md.

3 September 1964