(*Petalostemum*) and wild onion (*Allium*).

Fossil and sedimentological evidence suggest a five-phase history at the Seibold Site.

1) During phase 1, a depression formed as underlying glacial ice melted during the late Wisconsinan (about 12,000 or 11,000 years B.P.). Meltwater flowed into the depression, depositing units 1 and 2 in a cool, oligotrophic lake, here called Paleolake Seibold (*2*). Ostracod evidence (*17*), from the upper part of unit 2, suggests that a permanent stream entered the lake; the maximum temperature of the summer air was about 30°C, and precipitation exceeded evaporation. Fish and other organisms probably entered the lake from the west via a tributary of the Missouri River.

2) During phase 2 (represented by units 3 and 4), latest Wisconsinan and earliest Holocene time or about 10,500 years B.P. and later, a eutrophic lake or permanent pond existed at the Seibold Site and shallowed gradually. Ostracod evidence from unit 3 (fish bed) suggests a maximum water depth of about 6 m during the deposition of that unit. Dissolved solids were lower at the outset of phase 2 than during phase 1 and fluctuated considerably during deposition of the fish bed. Aquatic vegetation was abundant during deposition of most of the fish bed. The lake was flanked by a spruce-dominated forest during the early stage of fish bed deposition and later was surrounded by prairie with tree groves. Ostracod evidence suggests that maximum air temperature during the later stages probably approached 32°C, accompanied by a decrease in precipitation. Continued shallowing of water resulted in the deposition of calcareous unit 4.

3) By phase 3 (early Holocene, about 8500 years B.P. and earlier) all of the ice in the area had melted and a shallow pond, with high concentrations of dissolved solids (represented by unit 5), replaced the lake phases. This phase marked the beginning of Seibold Slough deposition. Branchiate gastropods gave way to pulmonate gastropods.

4) During phase 4 (middle Holocene, about 8500 to 4500 years B.P.) the climate became drier still, and less protective vegetative cover resulted in increased hillslope erosion (represented by sandy unit 6 at the south edge of the basin and by parts of units 5 and 7 near its center). During part of this phase a prolonged dry period is reflected by a complete absence of aquatic gastropods in the sedimentary sequence.

5) Phase 5 (represented by unit 7) was a time (late Holocene, 4500 years B.P. to the present) of reversal to a relatively more moist climate, essentially similar to that of phase 3; it continues as the present-day slough.

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References and Notes

1. S. H. Richards (Disease Research Biologist, North Dakota Game and Fish Department) recognized the possible scientific importance of the fossil assemblage and notified the Department of Geology, University of North Dakota. W. B. Bickley, Jr., L. Clayton, A. M. Cvancara, *Proc. N. Dakota Acad. Sci.* **24** (pt. 1) (abstr.) 2 (1970); W. B. Bickley, Jr., and A. M. Cvancara, *Geol. Soc. Amer. Abstr. with Programs* **2**(6), 377 (1970).
2. The Seibold Slough, Seibold Site, and Paleolake Seibold are named after Mr. and Mrs. Vernon Seibold, on whose property the slough is located. They allowed free access to study and collect fossils and sediments and donated several specimens.
3. L. Clayton, in *Glacial Geology of the Missouri Coteau and Adjacent Areas*, L. Clayton and T. F. Freers, Eds. (North Dakota Geological Survey, Grand Forks, 1967), Misc. Ser. 30, pp. 25–46.
4. H. A. Winters, *N. Dakota Geol. Surv. Bull.* **41** (pt. 1), 67 (1963).
5. R. R. Miller and T. M. Cavender (University of Michigan) identified the fish.
6. N. R. Sherrod, *Proc. N. Dakota Acad. Sci.* **17**, 32 (1963).
7. D. G. Frey, *Arch. Hydrobiol.* **2**, whole issue (1964).
8. J. H. McAndrews, R. E. Stewart, Jr., R. C. Bright, in *Glacial Geology of the Missouri Coteau*, L. Clayton and T. F. Freers, Eds. (North Dakota Geological Survey, Grand Forks, 1967), Misc. Ser. 30, p. 101.
9. D. R. Moir, in *Guidebook, Ninth Annual Field Conference Mid-Western Friends of the Pleistocene*, W. M. Laird, R. W. Lemke, M. Hansen, Eds. (North Dakota Geological Survey, Grand Forks, 1958), Misc. Ser. 10, pp. 108–114.
10. L. Clayton, *Proc. N. Dakota Acad. Sci.* **15**, 11 (1961).
11. S. J. Tuthill, *ibid.*, p. 19; thesis, University of North Dakota (1963); in *Glacial Geology of the Missouri Coteau and Adjacent Areas*, L. Clayton and T. F. Freers, Eds. (North Dakota Geological Survey, Grand Forks, 1967), Misc. Ser. 30, pp. 73–82; thesis, University of North Dakota (1969).
12. S. J. Tuthill, L. Clayton, W. M. Laird, *Amer. Midland Natur.* **71**, 344 (1964).
13. G. G. Thompson, *Proc. N. Dakota Acad. Sci.* **16**, 16 (1962).
14. J. G. Ogden, in *Quaternary Paleoecology*, E. J. Cushing and H. E. Wright, Jr., Eds. (Yale Univ. Press, New Haven, 1967), p. 117.
15. W. A. Watts and R. C. Bright, *Bull. Geol. Soc. Amer.* **79**, 885 (1968).
16. J. C. Ritchie and S. Lichti-Federovich, *Can. J. Earth Sci.* **5**, 873 (1968).
17. L. D. Delorme, *ibid.* **6**, 1471 (1969).

22 June 1970; revised 20 August 1970

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Kinetics of Single-Layer Graphite Oxidation: Evaluation by Electron Microscopy

Abstract. *Etch-decoration reveals that the rate of removal of carbon atoms exposed at monolayer steps on graphite surfaces is very different from the rate of removal, under identical conditions, at multilayer steps. At 1113°K and a pressure of 1.33 newtons per square meter of oxygen, the rate of oxidation (along the layer planes) is less by a factor of nearly 100 than that at multilayer steps.*

For over a century investigators have measured the kinetics of the oxidation of carbon by recording either the rate of change of the mass of the solid (the procedure still widely used for metals and alloys) or the rate of production of gaseous oxides. Within the last decade (*1, 2*) it has proved possible to measure oxidation rates along all the principal crystallographic axes of graphite by following, with optical microscopy, the rate of growth of dislocation etch pits on the (0001) face of single crystals. Anisotropy factors as large as 10^{13} (for the *a*- and *c*-directions) have been shown (*3*) to occur. It is apparent from optical micrographs (see Fig. 1) (*4, 5*) of partially oxidized basal faces that oxidation in directions parallel to the basal planes (that is, in the *c*-plane along either the $\langle 10\bar{1}0\rangle$ or $\langle 11\bar{2}0\rangle$ direction involves the uniform recession of multilayers, the step heights being as much as 10 μm. This means that, under steady-state conditions, many thousands of individual basal layers are oxidized cooperatively from their peripheries. The activation energy (*4*) for the recession (*6*) in molecular oxygen in the temperature range 1085° to 1145°K is 268 ± 17 kjoule/mole. We now report a direct method of measuring the rate of recession of individual layers—that is, the lateral movement, by combustion in O_2, of 0.335-nm steps—and

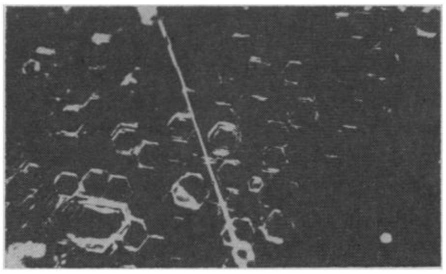
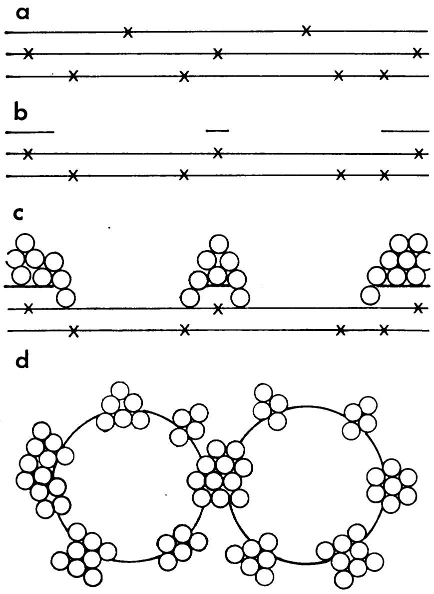


Fig. 1 (above). Typical optical micrograph of the basal surface of graphite after oxidation for 90 minutes in O_2 at 1110°K and a pressure of 1.33 newton/m^2. The step heights of the etch pits are in the range 0.1 to 10 μm, and step recession rates are evaluated from a series of micrographs [see (*4*)] (magnification, × 88). Fig. 2 (right). (a) Schematic diagram of a graphite crystal normal to the *c*-direction. The crosses signify the location of lattice vacancies that are randomly distributed in each layer. (b) Graphite crystal normal to the *c*-direction after oxidation by O_2. Vacancies in the top layer are expanded but, because of the marked anistropy of the oxidation process, the second and succeeding layers are not punctured. (c) Graphite crystal normal to the *c*-direction after preferential gold decoration of expanded vacancies (gold denoted by small circles). (d) Schematic diagram of the basal surface of a graphite crystal after gold decoration of expanded vacancies.



show that the activation energy and rate coefficient of this recession are very different from those that apply to multilayers.

The principle of the method is that of etch-decoration, a technique that has proved valuable for the study of inherent point defects (*1*) and radiation damage (*7*) in graphite, as well as for the investigation of defects in molybdenite (*8*). Residual vacancies present in a (cleaved) single crystal of natural graphite (thickness less than 100 nm) are expanded by oxidation (with O_2 at a pressure of 1.33 newton/m^2) for a fixed length of time (Fig. 2, a and b). Gold is then evaporated under vacuum onto the surface, which is maintained at 520°K to assist migration and subsequent nucleation of the condensate on the graphite (Fig. 2, c and d). As a result of preferential nucleation (*1, 9*) a circle of gold particles (which are electron-opaque) is revealed when the oxidized and decorated flake is examined by transmission electron microscopy (Fig. 3). The radii of the circles "developed" by oxidation on a large number of graphite slivers are recorded as a function of the time of oxidation. The plots are linear in the temperature range 973° to 1113°K; and the activation energy is 148 ± 8 kjoule/mole. It is not meaningful in this context to use a specific rate coefficient that refers to the unit area of interface, as is the custom for gas-solid reactions. Instead, it is instructive to employ a rate coefficient that is a measure of the ease of oxidation of carbon atoms exposed at the interface, which itself is but a monolayer deep. Somewhat surprisingly, the specific rate at which such an interface recedes is nearly a hundredth of the corresponding rate for multilayer interfaces, the specific coefficients at 1113°K in O_2 at a pressure of 1.33 newton/m^2 being 1.45 and 137 atoms oxidized per exposed carbon atom per second. These results are of considerable significance in the chemistry of carbon. They suggest (*10*) that there are hitherto unsuspected structures (*11*) for the peripheral oxide formed on graphite, and that there is more than one mechanism for the oxidation of edge carbon. It is apparent that oxides at the edge of single layers affect the kinetics of oxidation in a way radically different from oxides formed between the edges of two contiguous layers.

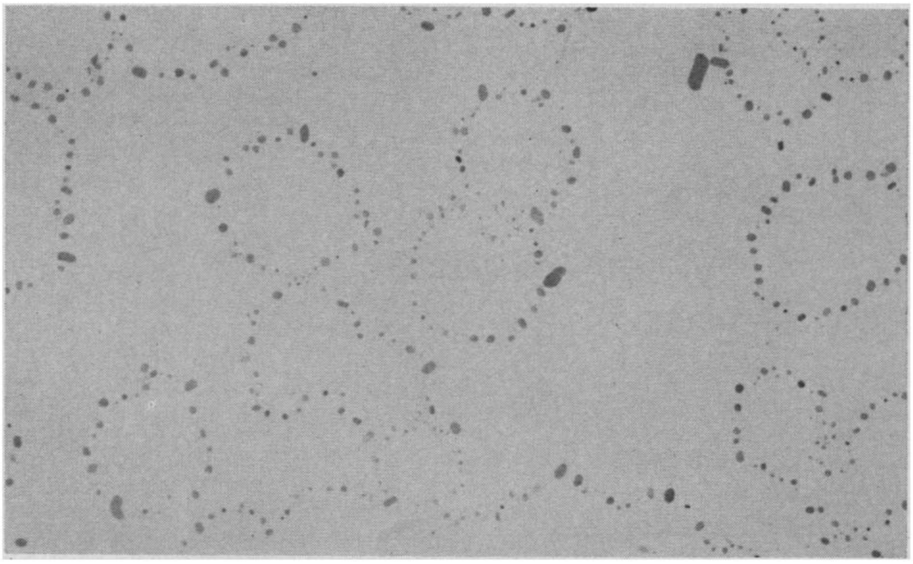


Fig. 3. Typical electron micrograph of the basal surface of graphite after oxidation for 10 minutes in O_2 at 1110°K and a pressure of 1.33 newton/m^2, followed by gold decoration to reveal the extent of monolayer recession (magnification, × 50,700).

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References and Notes

1. G. R. Hennig, in *Chemistry and Physics of Carbon*, P. L. Walker, Jr., Ed. (Arnold, Leeds, England, 1966), vol. **2**, p. 1.
2. J. M. Thomas, *ibid.*, vol. 1, p. 121.
3. G. R. Hennig, *Science* **147**, 733 (196 C. Roscoe and J. M. Thomas, *Proc. Roy. Soc. Ser. A Math. Phys. Sci.* **297**, 397 (1967).
4. J. M. Thomas and E. E. Glenda Hughes, *Carbon* (*Oxford*) **1**, 209 (1964).
5. E. E. Glenda Hughes and J. M. Thomas, *Nature* **193**, 838 (1962); B. McCarroll and D. W. McKee, *ibid.* **225**, 722 (1970).
6. There is a slight difference (amounting to approximately 17 kjoule/mole) between the activation energy for multilayer step recession in the $\langle 10\bar{1}0\rangle$ and $\langle 11\bar{2}0\rangle$ directions.
7. F. S. Feates, *Trans. Faraday Soc.* **64**, 3093 (1968).

). P. Bahl, E. L. Evans, J. M. Thomas, *Proc. Roy. Soc. Ser. A Math. Phys. Sci.* **306**, 53 (1968); G. L. Montet, *Appl. Phys. Lett.* **11**, 223 (1967).

9. G. A. Bassett, J. W. Menter, D. W. Pashley, *Discuss. Faraday Soc.* **28**, 7 (1959).
10. E. L. Evans, R. J. M. Griffiths, J. M. Thomas, in preparation.
11. P. L. Walker, Jr., *Amer. Sci.* **50**, 259 (1962); H. P. Boehm, *Advan. Catalysis Relat. Subj.* **16**, 179 (1966).

12. We gratefully acknowledge discussions with R. Lind, J. Wright, and their colleagues. Supported by the United Kingdom Atomic Energy Authority.

19 May 1970; revised 8 September 1970