Technical Papers

Biochemical Limnology[1]

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A major part of limnological research has centered about the relationship between the chemical composition of lake waters and sediments on the one hand, and the physiology of phytoplankton and rooted plants on the other hand. A limited amount of success has been achieved in this direction, largely from the study of inorganic ions such as phosphate, nitrate, and ammonia. Few serious attempts have been made to include organic compounds in such studies (*1–6*). Yet it is well known (*1*) that the dispersed organic matter (dissolved plus colloidal) of lake water generaly exceeds the particulate (seston) by a factor of 5–10. The dispersed organic matter constitutes an important part of the chemical environment, one whose biological significance is uncertain because the analyses have been for elements rather than for molecules. This is no less true for the organic matter of sediments.

This article gives a general account of results obtained during the 4 years of my study. More detailed treatments will be published elsewhere.

Acid hydrolysates of the dispersed organic matter from Lower Linsley Pond, Conn., and Lake Opinicon, Ont., were qualitatively examined for amino acids. Amino acids were separated on paper using butanol-acetic acid and phenol as solvents. In both lakes, the following amino acids predominated: aspartic, glutamic, alanine, leucine and/or isoleucine, and a fifth that occupied a position not quite identical to that of methionine. The same amino acids predominated in seston from both lakes and also in sediment from Lower Linsley Pond, suggesting a qualitative similarity in the amino acid composition of seston, water, and sediment. The relative abundance of acidic and neutral amino acids is dissimilar to the data for Wisconsin lakes (*2*).

A second phase of biochemical limnology has been developed in conjunction with R. G. S. Bidwell, of Queen's University: a study of the free sugar contents of Connecticut lake sediments. Free sugars were found in all sediments studied (Lower Linsley Pond, Lake Waramaug, Lake Quassapaug, Lake Quonnipaug, and East Twin Lake). The total amount of free sugar varied from 24 to 72 mg/kg dry weight of ethanol insoluble sediment (92 to 300 mg/kg ignitible matter). With the exception of one sample, glucose comprised more than half of the total free sugar. Other free sugars found in lesser quantity were galactose, arabinose, xylose, and ribose. The amounts of free sugars found in Connecticut lake sediments were surprisingly high, approaching the figures given by Bidwell, Krotkov, and Reed (*7*) for fresh algae, Chlorophyta excluded. This suggests that free sugars are not so quickly decomposed in sediments as has hitherto been assumed for all simple organic nutrients in lakes. This suggestion is strengthened by results of sugar analyses on sediments from Bethany Bog, Conn., known to be 5000 to 9000 yr old (age was estimated by comparing pollen zonations from Bethany Bog with those from Upper Linsley Pond which have been dated by C^{14}). Free glucose was found in these samples, the concentrations varying from 1 to 11 mg/kg dry weight of ethanol insoluble sediment (3 to 24 mg/kg ignitible matter). It can be shown by indirect means that some diagenetic destruction of glucose occurred in these relatively old sediments.

Another biochemical approach to limnology stemmed from a study of the carotenoids and chlorophylls of sediments. Carotenoids were first found in lake sediments by Trask (*8*) and later by Baudisch and von Euler (*3*). The carotenoids of sediments appear to resemble those of fresh plant tissues (*9*), but the chlorophylls differ (*10, 11*). The acetone-soluble green pigments of sediments are called chlorophylls here; however, it should be realized that there is no basic evidence to indicate that this is the correct terminology.

Although carotenoids are highly labile in the laboratory, Fox, Updegraff, and Novelli (*10*) found that they resisted complete destruction in marine sediments estimated to be 8000 yr old. These workers realized that it might be possible to use carotenoids as biochemical fossils in marine sediments. I have extended this approach to fresh-water sediments. Using paper chromatography (*12*), a semiquantitative method has been developed for the separation and estimation of the carotenoids and chlorophylls of sediments. The chief importance of the method is that it provides a new measure of plant abundance in lake sediments, one that does not require the preservation of biological form.

The most interesting result of this work concerns the epiphasic carotenoid, myxoxanthin, which has been tentatively identified in acetone extracts of lake sediments. The only fresh-water organisms known to contain this compound are the blue-green algae. Examination of the sediments of Bethany Bog revealed the presence of myxoxanthin throughout the eutrophic phase of development, but when the sediments recorded a change to a dystrophic (acid, bog water) lake, myxoxanthin was no longer found. This suggests a decrease in populations of blue-green algae coupled with the onset of dystrophy. This conclusion, suggestive at best, could not have been derived from "morphological" paleontology. Microscopic examination of the samples failed to reveal the presence of blue-green algae. In another lake, Upper Linsley Pond, myxo-

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xanthin was found both in the bottom and near-surface samples. This lake is not yet truly dystrophic.

Carotenoids and chlorophylls have been found in Connecticut lake sediments that are up to 11,000 yr old. Concentrations of all carotenoids and chlorophylls do not progressively decline with depth. In the Bethany Bog core, a carotenoid tentatively identified as rhodoviolascin reached maximal values in the uppermost sediments, carotene (alpha plus beta) in the middle section of the core, whereas a third carotenoid (not yet identified) had maximal values in the lowermost part of the core.

Such results indicate the promise of the approach, even though the interpretation may be difficult. It is unlikely that much reliable information will come from the study of plant pigments in lake sediments until a great deal more is known about their destruction in lake waters and sediments.

References

1. E. A. Birge and C. Juday, *Bull. Bur. Fisheries* **42**, 185 (1926).
2. W. H. Peterson, E. B. Fred, and B. P. Domogalla, *J. Biol. Chem.* **63**, 287 (1925).
3. O. Baudisch and H. von Euler, *Arkiv. Kemi, Mineral. Geol.* **11A**, No. 21, 1 (1934).
4. G. E. Hutchinson, *Arch. Biochem.* **2**, 143 (1943).
5. W. J. Robbins, A. Harvey, and M. E. Stebbins, *Bull. Torrey Botan. Club* **77**, 423 (1950).
6. P. J. Wangersky, *Science* **115**, 685 (1952).
7. R. G. S. Bidwell, G. Krotkov, and G. B. Reed, *Can. J. Botany* **30**, 291 (1952).
8. P. D. Trask, *Origin and Environment of Source Sediments of Petroleum* (1932).
9. E. Lederer, *Bull. soc. chim. biol.* **20**, 611 (1938).
10. D. L. Fox, D. M. Updegraff, and G. D. Novelli, *Arch. Biochem.* **5**, 1 (1944).
11. H. K. Phinney, *Am. Midland Naturalist* **35**, 453 (1946).
12. L. Bauer, *Naturwissenschaften* **39**, 88 (1952).

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Occurrence of Structurally Preserved Plants in Pre-Cambrian Rocks of the Canadian Shield

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A small but varied assemblage of primitive lower plants, representing both blue-green algae and simple forms of fungi was discovered recently by the writers in nonferruginous cherts of the Gunflint iron formation of southern Ontario. The plant fossils were first observed in dense black cherts collected from the lower "algal" members of the Gunflint formation near Schrieber, Ontario, but additional material has been secured from widely separated localities along the strike of the formation. The collective plant remains thus far studied constitute a small, but significant, flora of remarkably ancient plant life.

As far as we are aware, these plants are the oldest structurally preserved organisms that clearly exhibit cellular differentiation and original carbon complexes which have yet been discovered in pre-Cambrian sediments and, as such, are of great interest in the evolutionary scheme of primitive life. Their discovery likewise appears to validate the somewhat questionable organisms described by Gruner (*1–3*) from the pre-Cambrian of northern Minnesota and tend to support the evidence presented by Rankama (*4*) regarding the organic origin of *Corycium enigmaticum,* a supposed organism of pre-Cambrian age.

Although detailed studies of the plants and comparisons with existing forms among lower groups of algae, fungi, and protophyta are being carried out, it seems desirable at this time to present a preliminary

FIG. 1. Globose colony showing actinomorphic central mass of filaments surrounded by the remains of what is interpreted as a gelatinous ''sheath.'' ''Sheath'' is outlined by mineral stain, partially ground away in lower quadrant of colony. Thin section, ×725.

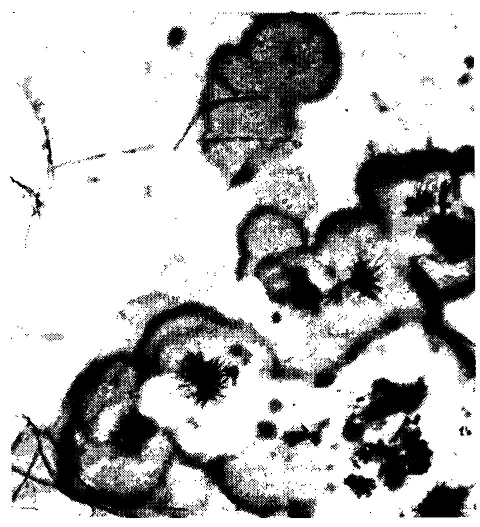

FIG. 2. Aggregation of colonies similar to that shown in Fig. 1. Black threads at upper and lower left are unbranched free filaments, not associated with the globose colonies. Thin section, ×325.