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BIOCHEMICAL FOSSILS[1]

By Professor DENIS L. FOX

SCRIPPS INSTITUTION OF OCEANOGRAPHY

RECENT studies in this laboratory, to be reported in some detail elsewhere, have been concerned with preliminary qualitative and quantitative examinations of carotenoid pigments encountered in marine sediments of hundreds or thousands of years' standing. The preservation of a class of ordinarily highly labile compounds over vast ages of time is less surprising when one considers the special conditions which prevail in the buried strata of the ocean floor, *i.e.*, lack of free oxygen, absence of light and perpetual temperatures of nearly 0° C. The added facts that carotenoids as a class are absorbed in the digestive tract of most animals only at low levels of efficiency, and that they are relatively refractory toward non-oxidative biochemical changes would still further favor their gradual accumulation in the ocean floor.

Pigmentary compounds of the plant and animal porphyrin series have been encountered in petroleum, coal and shale oils.[2,3] Similarly, other chlorophyll derivatives, accompanied by carotenoids, and sometimes also in association with fluorescent pigments common to petroleum, occur in long and deeply buried marine sediments.[4,5] These ancient biochromic compounds, together with other oil-soluble substances in whose presence they occur, may be regarded as diagnostic features in the search for biochemical processes in the origins of petroleum and allied natural deposits.

Carotenoids have been reported in moor soils[6] and

[1] Contributions from the Scripps Institution of Oceanography, New Series No. 232.

[2] R. Lemberg, *Ann. Rev. Biochem.*, 7: 424, 1938.
[3] A. Treibs, *Ann. d. Chem.*, 510: 42, 1934.
[4] D. L. Fox, *Proc. Nat. Acad. Sci.*, 23: 295, 1936.
[5] D. L. Fox and L. J. Anderson, *Proc. Nat. Acad. Sci.*, 27: 333, 1941. (N.B. The published data are in error (p. 335) by a misplaced decimal, thus appearing as 6.0, instead of the correct value of 0.6 mg per cent.)
[6] O. Baudisch and H. v. Euler, *Arkiv. Kemi Mineral Geol.*, 11A, No. 21, 1934.

in muds from lakes,[7,8] marshes[7] and underground caves.[9] Trask[10] has referred to carotenoids in marine sediments, but little or no emphasis has yet been directed toward the probable ages, history and biochemical significance of these pigmentary compounds in natural deposits.

In the current investigations, standard methods of carotenoid analysis were applied to samples of very fine dark mud collected from various water depths between 100 and 1,100 fathoms, both in the Gulf of California and in the open Pacific Ocean off the coast of Southern California. Oceanic muds, of estimated ages from 15 years up to 2,500 years, yielded golden, pale greenish or dirty yellow extracts, some samples containing as much as 0.20 to 0.30 mg carotenoids per 100 g of original vacuum-dried material. Gulf muds were far darker in color; one core section taken from the 16-foot level beneath the mud surface, beneath 364 fathoms of water (estimated age of the deposit being some 6,000 years) yielded about 0.6 mg of total carotenoids per 100 g of dry mud.[5]

An arresting fact was the consistent finding of a great preponderance of the carotene or hydrocarbon type of polyene over the xanthophyll or polyene alcohol class in mud beneath the first few inches of its surface. The finding of 80 per cent. or more of total sedimentary polyene pigments as carotenes is in striking contrast with the relative proportions of carotenoid types in other marine materials. In finely suspended marine detritus, for example, carotenes may represent from 6 per cent. to 14 per cent. of the total carotenoids.[11, 12, 13] Again, microscopic algae, such as *Prorocentrum micans* and *Nitzschia closterium* yield only about 10 per cent. of their total carotenoids as hydrocarbons.[13,14] Species of larger marine plants such as *Fucus, Dictyota* and *Laminaria* contain respectively only 25.7 per cent., 15.4 per cent. and 4.8 per cent. of their carotenoids as carotenes. This list could be extended. Most marine animals which have been analyzed for carotenoids have been found to yield chiefly xanthophylls. Numerous species of fishes and ophiuroids contain xanthophyll esters as the only carotenoids.[8,15–19] Species of tunicates, mollusks, crustaceans, echinoderms and coelenterates may be added to the list of marine fauna whose tissues contain carotenoids chiefly, and in numerous instances solely, of the oxygenated type.[8,13,20,21,22,23]

Among the polyene hydrocarbons encountered in marine muds, the preponderant member was β-carotene, with compounds resembling α-carotene in secondary prominence. These were often accompanied by other carotenes with properties closely resembling those of torulene from red yeasts, leprotene from certain acid-fast pathogenic bacteria, or rhodopurpurin and flavorhodin from bacteria of the *Rhodovibrio* group. Small quantities of carotenes with previously undescribed absorption spectra were occasionally found.

Chief among the polyene alcohols were xanthophylls closely resembling zeaxanthin and the spectroscopically similar diatom pigment diatoxanthin described by Strain *et al.*,[23] fucoxanthin and lutein (or perhaps more probably diadinoxanthin from diatoms and dinoflagellates)[23] and small quantities of pigments resembling taraxanthin or dinoxanthin. Prominent in hypophasic fractions also were xanthophylls spectroscopically similar to sulcatoxanthin (peridinin[23]) petaloxanthin and antheraxanthin, while other carotenoids having a single absorption maximum similar to those of glycymerin or astacene were occasionally detected. Xanthophyllic counterparts of the bacterial carotenoids rhodopurpurin and flavorhodin, reported as occurring with the latter in *Rhodovibrio,* were not encountered in marine muds.

Concentrations of total organic matter tend to decrease with age, *i.e.,* depth of burial, of marine sediments.[24] Our preliminary studies indicate that lipids and carotenoids likewise so decrease, the quantities of carotenes undergoing degradation at a rate somewhat parallel to that of total lipids.

Trask[24] estimates that, of the organic matter synthesized annually in a column of sea water 2,000 fathoms deep, the proportion deposited in each square meter of the ocean floor amounts to only some 2 per cent. Trask's computed loss of 98 per cent. of total organic matter is estimated by us to be accompanied by a decrease of some 83 per cent. of the original total lipids,

[7] B. K. Klimov and E. I. Kazakov, *C.R. Acad. Sci. U.R.S.S., N.S,* 16: 321, 1937.

[8] E. Lederer, "Recherches sur les caroténoides des animaux inferieurs et des cryptogames." Lons-le-Saunier, Paris, 1938.

[9] R. A. Beatty, *Jour. Exp. Biol.,* 18: 144, 1941.

[10] P. D. Trask *et al.,* "Origin and Development of Source Sediments of Petroleum," p. 177. Houston, Texas. Gulf Publishing Company. 1932.

[11] D. L. Fox *et al., Bull. Scripps Inst. of Oceanography,* 4: 1, 1936.

[12] Unpublished.

[13] B. T. Scheer, *Jour. Biol. Chem.,* 136: 275, 1940.

[14] N. Pace, *Jour. Biol. Chem.,* 140: 483, 1941.

[15] F. B. Sumner and D. L. Fox, *Jour. Exp. Zool.,* 66: 263, 1933.

[16] F. B. Sumner and D. L. Fox, *Proc. Nat. Acad. Sci.,* 21: 330, 1935.

[17] F. B. Sumner and D. L. Fox, *Jour. Exp. Zool.,* 71: 101, 1935.

[18] D. L. Fox, *Proc. Nat. Acad. Sci.,* 22: 50, 1936.

[19] R. T. Young and D. L. Fox, *Biol. Bull.,* 71: 217, 1936.

[20] D. L. Fox and B. T. Scheer, *Biol. Bull.,* 80: 441, 1941.

[21] I. M. Heilbron, H. Jackson and R. N. Jones, *Biochem. Jour.,* 29: 1384, 1935.

[22] D. L. Fox and C. F. A. Pantin, *Phil. Trans. Roy. Soc. London, Ser. B.,* 574: 415, 1941.

[23] H. H. Strain, W. M. Manning and G. Hardin, *Biol. Bull.* In press.

[24] P. D. Trask, "Recent Marine Sediments," 440 *et seq.,* Tulsa, Okla. Amer. Assoc. Petrol. Geol., 1939.

and of nearly 87 per cent. of the original carotenoids, *i.e.,* 97 per cent. of the xanthophylls and about 33 per cent. of the carotenes.

Analyses of a core of ocean mud revealed lipids in concentrations of 0.06 per cent., 0.05 per cent. and 0.04 per cent. by dry weight at the 6-inch, 74-inch and 80-inch levels (estimated to be about 600, 7,000 and 8,000 years in respective ages). All three sections yielded chlorophyll degradation products and carotenoids; but an intermediate section taken from the 44-inch level of the same core (4,000 years) yielded similar greenish cleavage products of chlorophyll but no carotenoids. Instead it contained a pigment with blue-green fluorescence, identical in chromatographic behavior and spectral absorption maxima with a pigment recovered from a sample of California crude petroleum,[5] and similar to a porphyrin isolated by Treibs[3] from a California asphalt. This section of the core yielded tenfold the concentration of lipid-soluble substances found at the other levels.

The general preponderance of carotenes over xanthophylls in muds of the ocean floor may arise from several factors: (1) Xanthophylls are more readily degraded than are carotenes by atmospheric or dissolved oxygen;[25] this is especially true of the prominent marine xanthophyll, fucoxanthin and its isomers, which are also especially susceptible to alteration by heat or alkalies.[23] While the foregoing factors would find less application at the bottom of the sea, two other general processes might well contribute to the situation, both there and in overlying waters, namely: (2) The majority of marine animals so far investigated store chiefly xanthophylls rather than carotenes in their tissues; their storing and partial oxidation of polyene alcohols, with fecal rejection of carotenes could bring about a gradual preponderance of the latter class of carotenoid in bottom sediments. Finally (3) there are indications that some microorganisms living in marine muds may contribute polyene hydrocarbons of their own synthesis, and that other such flora may be capable of reducing xanthophylls to compounds of lower oxygen content, or perhaps even to carotenes.

MODERN EVIDENCES FOR DIFFERENTIAL MOVEMENT OF CERTAIN POINTS ON THE EARTH'S SURFACE. II

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Shortly after the publication of Kawasaki's paper, Professor Schlesinger, after correspondence with me, undertook to make the necessary calculations to see if the known variation in the position of the pole that caused the annual term in the variation of latitude could not also introduce an appreciable variation in longitude for geometrical reasons. Professor Schlesinger's deductions were published in 1937 in the *Monthly Notices* of the Royal Astronomical Society,[13] and did indicate that a large part of the variation in longitude that we had attributed to changing positions of the moon could and should be accounted for on the basis of this annual term. Since that time I have corrected all our previously published data by applying this annual term. Though not yet published, the resultant curve still persists in showing a maximum and minimum change in longitude across the Atlantic with the hour angle of the moon. This shows up in the exchange of time signals between the Naval Observatory and both Greenwich and Paris, but not across the English Channel. The magnitude of the variation with the lunar day, however, is reduced in amplitude by the correction to about one half the former value assigned by Mr. Loomis and myself. If the remaining variations therefore are translated into linear values there remains a variation of about 32 feet to be accounted for in the distance across the Atlantic that correlates with the position of the moon.

To add zest to the controversy a publication was shortly forthcoming from the Jesuit Observatory at Zi-ka-wei, China, showing that a study of the intercomparison of time signals between Shanghai and the European stations at Nauan and Bordeaux, revealed periodic variations in longitude between Berlin and Zi-ka-wei, dependent upon the moon's position. The explanation advanced was an earth tide causing a linear variation in distance of 60 feet between central Europe and the east coast of China. The amount of the variation given was several times larger than any probable error of the observations.

Unfortunately after June, 1934, shortly after the publication of our original papers, the daily intercomparisons of the 17.6 Kc. transatlantic time signals between our own Naval Observatory and the observa-

[13] F. Schlesinger, "Note on Annual Change in Longitude." MNRS 97: 696, 1937, 98: 203, 1938.

[25] L. Zechmeister, "Carotinoide," J. Springer, Berlin, 1934.