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18. This investigation is part of a continuing study of Precambrian fossils which is being conducted at Harvard University. The hydrocarbon analyses were made in collaboration with Esso Research and Engineering Company, and have been supported by NASA contract No. NASw508. We thank the officials of the White Pine Copper Co. for the samples of the rock used for this study.

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Hydrocarbons of Biological Origin from a One-Billion-Year-Old Sediment

Abstract. *The isoprenoid hydrocarbons, phytane ($C_{20}H_{42}$) and pristane ($C_{19}H_{40}$), are present in the oil seeping from the Precambrian Nonesuch formation at the White Pine Mine, Michigan. Gas-liquid chromatography and mass spectrometry provide the isolation and identification procedures.*

Two experimental methods are now being used to study the origin of terrestrial life and the time of its first appearance. The "primitive atmosphere" experiments (*1*) demonstrate that a wide variety of small molecules of biological significance can be formed in the laboratory from mixtures of extremely simple substances like methane, ammonia, and water. Geologists and geochemists examine ancient sediments for fossil organisms and determine the chemical nature of the imprisoned organic matter (*2–4*). Earlier than about 600 million years ago well-defined morphological remains are scanty, and generally are difficult to relate conclusively to specific living things (*5*). A firm correlation between the morphological evidence and the organic matter present in the same rock would permit a systematic search for chemical evidence of early life in the ancient sediments. Certain classes of organic compounds—the alkanes (*6*), the long-chain fatty acids (*7*), and the porphyrin pigments (*8*)—show promise as biological markers since they are evidently stable for long periods of time under geologic conditions. These compounds are valid as biological markers only insofar as they cannot be synthesized in significant proportions by abiogenic means. For this reason "primitive atmosphere" experiments play an important role. The range of compounds based on the isoprenoid subunit is particularly useful, for here we have a high degree of structural specificity coupled with a widespread distribution in nature. Thus pristane (2,6,10,14-tetramethylpentadecane) and other isoprenoid hydrocarbons have been isolated from crude petroleums of moderate ages (Mesozoic and Paleozoic) in concentrations vastly greater than those anticipated for individual branched alkanes in a thermally derived mixture (*9*). Pristane is a known constituent of living things—zooplankton (*10*), fish and whale oils (*11*), wool wax (*12*), and marine sponges (*13*)—but the original source of the mineralized material may be the phytol portion of chlorophyll degraded either biogenically or abiogenically (*9, 14*). There is every prospect that the isoprenoid hydrocarbons, and the related alcohols and acids, will be useful biological markers.

We now report the isolation and identification of phytane (2,6,10,14-tetramethylhexadecane) and pristane in the oil which seeps in small quantities from the Precambrian Nonesuch shale in Michigan. This rock (*15*) is of Keweenawan age and is in the region of 1 billion (10^9) years old. The identification of these hydrocarbons augurs well for the extension of such analyses to even older Precambrian formations.

We established the conditions for the isolation by processing suitable model mixtures. Thus, the Linde molecular 5 Å sieve (composed of 1.6-mm pellets, dried at 200°C and 10^{-3} mm-Hg, and used at a ratio of 20:1 by weight to the alkanes) quantitatively removed (*16*) the normal isomers from a benzene solution of alkanes from tobacco wax (*17*); the analysis was performed by gas-liquid chromatography at 230°C (3 percent SE-30 silicone gum on Gas Chrom Z, 100-120 mesh, the column being 170 cm × 3 mm). Even after prolonged reflux lasting up to 72 hours, the 2-methyl and 3-methyl substituted *n*-paraffins (C_{25}—C_{35}) were quantitatively retained in the solvent and the necessary solvent washings. A second sieving treatment of the hydrocarbons was found to be unnecessary. The same fractionation quantitatively removed *n*-heptacosane from a mixture containing cholestane, pristane, and squalane. In each case the *n*-alkanes were readily recovered from the sieve by heating in *n*-hexane or by dissolution of the sieve in dilute HF.

In another experiment an oil shale (*18*) from the Green River Formation (Eocene age, about 60 × 10^6 years) at Rifle, Colorado, was extracted for several hours with *n*-hexane under reflux and the extract placed on a washed activated alumina column (the particle size being 2 to 44 μ). The initial hexane eluate contained only the alkane fraction which was then subjected to the sieving process, followed by gas-liquid chromatographic analysis (3 percent SE-30 column, programmed from 100° to 300°C at 6°C per minute). The distribution of the *n*-alkanes closely paralleled that reported for this shale by Cummins and Robinson (*18*), with the marked dominance of the odd-carbon number alkanes, especially C_{27}, C_{29}, and C_{31}, so characteristic of most plants (*19*) and relatively young sediments (*6*). Again, we confirm these workers' prior findings (*18*) that the lower molecular weight range of the branched and cyclic alkane fraction is mainly composed of phytane, pristane, and other terpenoids, since gas-liquid chromatographic fractions collected in capillary tubes from 6-mm columns displayed the appropriate mass spectrometric characteristics (*20*). Thus, the biological history of this Cenozoic rock is evident from both the very uneven distribution of the *n*-alkanes and from the presence of large proportions of isoprenoid alkanes.

We treated a small sample (4.1 g) of

the black viscous oil which oozes from the Precambrian Nonesuch shale (*15*) using the procedures described and found that the members of the *n*-alkane series range from C_{11} to about C_{35}. The distribution reaches a maximum around C_{19} and there is a very slight, but quite definite, predominance of odd-numbered members. The branched-cyclic fraction (2.5 g), which still contains small amounts of aromatic hydrocarbon, is very complex, but is characterized by several prominent peaks in the region corresponding in retention time to that between *n*-C_{14} and *n*-C_{18} on the silicone gum column. We collected amounts of the order of a milligram for each of these peaks by successive sampling on a 6-mm column and then by rechromatographing these at 90°C upon a strongly polar substrate—5 percent tetracyanoethylated pentaerythritol on Gas-Chrom RA, 80–100 mesh, the column being 170 cm × 6 mm—that provided a particularly effective separation. Two of the fractions so obtained when chromatographed on a variety of substrates (Apiezon 'L', fluorosilicone QF-1, silicone gum SE-30, Carbowax-20M, and tetracyanoethylated pentaerythritol) gave single peaks of the same retention times as phytane and pristane. These identifications were then confirmed by direct comparison on the mass spectrometer (*20*).

The mass spectrometric data on incompletely separated fractions show that other compounds with isoprenoid skeletons are present; these fractions may represent geologic breakdown products from the more abundant phytane and pristane. Studies on a capillary column (with Apiezon 'L', 45 m × 0.25 mm at 170°C) of cuts taken from the packed columns show that the branched fraction is an extremely complex mixture: even so, the phytane and pristane comprise approximately 0.6 and 1.2 percent, respectively, of the branched-cyclic fraction.

If one accepts the presence of these hydrocarbons as evidence of life in Precambrian times, there remains the question of the relation between the oil and the rock. We believe that the oil is indigenous to the rock, since we have found an almost identical pattern for the normal and the branched-cyclic alkane fractions (about 3 mg total) isolated from carefully washed (water, HF, and benzene-methanol) and pulverized Nonesuch shale (18 g) taken from the so-called "marker bed" situated above the stratum from which the oil had been collected. No method for the dating of ancient organic matter exists as yet, so that some doubt must remain concerning the precise age of this oil; however, the geologic evidence (*15*) favors the viewpoint that the organic matter and the associated copper are sedimentary or early diagenetic in origin.

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Shape of the Recorded Area in Precession Photographs and Its Application in Orienting Crystals

Abstract. *The equation of the perimeter of the recorded area of zero-level precession photographs as a function of the orientation error is derived in polar coordinates. The angle between the tangent to the perimeter and the radius vector is also derived. How these relations can be conveniently applied to determining the orientation error of a crystal mounted on the precession instrument is discussed.*

The recorded region of a zero-level precession photograph is marked out by general-radiation streaks (*1*). When the crystal is properly oriented this shaded region is circular with its center at the location of the 000 reflection. If the crystal is somewhat misoriented the edges of the recorded region shift in the direction of the setting error. This is the basis for various methods of correcting an orientation error (*1, 2, 3*).

The knowledge of the shape of the recorded area for precession photographs made with a somewhat misoriented crystal is in a confused state. Fisher (*2*) considers the area to coincide with a "circle of precession" on the side of error, but shortened on the opposite side (*2*, p. 1039). Furthermore, although the feature is not discussed, a central region without a record is evident in his Fig. 34*a*. Evans (*3*) illustrates such a region in a drawing, but also without discussion and, as will be seen subsequently, the shapes of the bounding curves are misleading.

In the first publication on the precession method (*1*) the change in radius due to an orientation error was derived. When the law of sines is applied to the triangle *OWJ* of Fig. 13 (*1*, p. 24) of that article it is seen that

$$\frac{\xi_{\max}}{2\sin(\bar{\mu}+\varepsilon)}=\frac{\sin(90^\circ+\bar{\mu}+\varepsilon)}{\sin(90^\circ-\bar{\mu}-2\varepsilon)}. \qquad (1)$$

which can be solved for $\xi_{\max}$ to give

$$\xi_{\max}=\frac{\sin 2(\bar{\mu}+\varepsilon)}{\cos(\bar{\mu}+2\varepsilon)}. \qquad (2)$$

The maximum radius vector $\xi_{\max}$ occurs when the phase of the precession motion brings the angle $\bar{\mu}$ in the same direction as the error angle ε. For present purposes let the phase τ of the precession cycle be measured from the position where the plane of $\bar{\mu}$ is parallel to the plane of ε, the angles increasing in the same sense. In the general case the angular separation in the plane of