recorded along the Gulf Coast from cyclonic storms off the Coast of Labrador.

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8 June 1964

Biological Remnants in a Precambrian Sediment

Abstract. *A billion-year-old shale from the Nonesuch formation at White Pine Mine, Michigan, contains microfossils, porphyrins, and optically active alkanes. Pristane and phytane, which are isoprenoid hydrocarbons found in living plants and animals, are constituents of the ancient alkanes in the Nonesuch shale; the presence of porphyrins in this Precambrian sediment suggests that photosynthetic organisms have existed for more than a billion years.*

Most information about the inhabitants, climates, and physical features of prehistoric continents and oceans has been deduced from biological remnants found in sediments. Extensive data have been gathered on the fossils and organic materials of Cambrian to Quaternary age (*1–4*), but publications discussing Precambrian remnants of life are limited in number (*5*).

We are analyzing microfossils and carbon compounds from the Nonesuch shale of upper Precambrian age (Keweenawan, 1.1×10^9 years). This shale is a major sedimentary unit of the late Precambrian sequence of northern Michigan. The dense gray to black shales in the lower part of the formation are copper bearing and are currently being exploited in an extensive mining operation. The shales contain sporadically distributed vugs filled with small amounts of liquid hydrocarbons occurring as crude oil. Petroleum also occurs in fractures in these lower shales.

Micropaleontological study of the acid-insoluble organic fractions of the shale has revealed the presence of abundant, finely divided plant tissue, largely of unorganized morphology, except for occasional filaments and spherical spore-like bodies. The organic and petroliferous content of the shale, and its correspondingly darker color, are positively correlated with the relative abundance of the discrete organic fragments. The presence of fossil microorganisms in the Nonesuch shale lends credence to the interpretation that the petroleum and associated biogenic compounds are indigenous to the shale and represent original organic matter syngenetic with deposition.

Alkanes from the benzene extracts and crude oils of the Nonesuch shale were isolated by silica gel chromatography (*6*). The alkane fractions represent 60 percent (by weight) of the extract and oil samples. Optical activities of these alkanes are (*7*): $[\alpha]^{35°}_{5460} = 0.541$ deg and $[\alpha]^{35°}_{5780} = 1.569$ deg. Liquid-solid and gas-liquid chromatographic, mass spectrometric, and infrared and ultraviolet spectroscopic analyses have been obtained on the saturated and aromatic hydrocarbon fractions of the Nonesuch extracts and crude oil. The extracts and oil resemble certain paraffinic crudes of Paleozoic ages, but the optical activities of alkanes from this Precambrian shale exceed those reported for some Pennsylvanian and Midcontinent oils (*8*).

Pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) have been identified (*9*) in the Nonesuch alkanes. These isoprenoid-type hydrocarbons are commonly found in biological and sedimental lipids (*10*). Identifications of pristane and phytane in the Nonesuch samples were accomplished by gas-liquid chromatography on a series of four capillary columns (0.25 mm × 30 m) which were individually coated with one of four different liquid-solid chromatographic fractions of Apiezon L (*11*). These identifications were confirmed by liquid-solid chromatography on alumina columns and mass spectrometric analyses by previously described methods (*12*). Concentrations of pristane and phytane in Nonesuch alkane fractions approximate 0.5 and 0.3 percent, respectively. Gas-liquid chromatography analyses of these alkanes reveal a slightly greater abundance of odd- than of even-number carbons in *n*-paraffins in the C_{23} to C_{31} range. *n*-Paraffins from living things frequently show a strong "odd carbon preference" in this carbon number range (*3*). The "odd carbon preference" observed in the Nonesuch alkanes is as great as that found in most crude oils and ancient sedimental extracts (*13*), irrespective of the ages of the sediments. The concentrations of pristane and phytane in the Nonesuch oil and the retentions of optical activity and the "odd carbon preference" by the Nonesuch alkanes indicate a remarkable stability of certain plant and animal products in sedimentary environments (*11*). Analyses of the hydrocarbons from the Nonesuch extracts and crude oils reveal that these apparently one-billion-year-old alkanes retain an accurate record of their biological origin just as the hydrocarbons in many geologically young oils do. The capacity of certain organic materials to retain their identities for more than a billion years in some sediments is demonstrated also, by porphyrins from the Nonesuch shales.

Treibs (*4, 14*) first demonstrated the presence of porphyrins in bituminous strata and he presented them as evidence that these strata had experienced a mild thermal history. Calculations based on the activation energy for the degradation of porphyrins have been used to prepare a time-temperature curve from which the maximum temperature of a porphyrin-containing deposit of known age can be estimated (*15*). Extensive investigations have been made of the occurrence of porphyrins in petroleum and sediments and of the relation between them and chlorophyll and hemin (*2, 4, 14, 16*).

Porphyrins isolated from the Nonesuch shale have well-defined peaks at 534 and 573 mμ and they exhibit the typical Soret absorption band near 400 mμ. Polarities of the Nonesuch porphyrins, as demonstrated by their absorption properties on alumina chromatographic column (*17*), and the visual absorption peaks of these compounds establish them as vanadyl porphyrins. The Nonesuch shale appears to be the oldest formation in which the presence of porphyrins has been found. Their presence in these deposits constitutes evidence of the existence of photosynthetic organisms in Precambrian times and that the temperatures for the Nonesuch sediments has never been very high.

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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.

8 June 1964

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