References and Notes

1. E. S. Fedorov, *"Simmetriya i struktura kristallov. Osnovniye raboty,"* A. V. Shubnikov and I. I. Shafranovskiĭ, Eds. (Izd. Akad. Nauk SSSR., Moskva, 1949).
2. ———, "Etyudi po analiticheskoi kristallografii," *Gorn. J.*, No. **4**, 87–118 (1885); No. 5, 222–243 (1885); No. 3, 395–425 (1886); No. 12, 407–454 (1886); No. 4, 87–454 (1887); Abstr. in *Z. Kryst.* **17**, 611–615 (1890); *ibid.* **21**, 694–714 (1893); ———, "Simmetriya konechnikh figur," *Zap. Min. Obshch.* **25** (2), 1–52 (1889); Abstr. in *Z. Kryst.* **17**, 617 (1890); ———, "Simmetriya pravilnikh sistem figur," *Zap. Min. Obshch.* **28**(2), 1–146 (1891).
3. ———, "Zusammenstellung der kristallographischen Resultate des Herrn Schoenflies und der meinigen," *Z. Kryst.* **20**, 25–75 (1891).
4. ———, "Theorie der Krystallstructur. I. Theil. Mögliche Structurarten," *Z. Kryst.* **25**, 113–224 (1895).
5. ———, *Symmetry of Crystals*, David and Katherine Harker, Translators, Amer. Cryst. Assoc. Monograph No. 7 (Polycrystal Book Service, P.O. Box 11567, Pittsburgh, 1971).
6. ———, "Reguläre Plan- und Raumtheilung," *Abhandl. kgl. Bayer. Akad. Wiss. II. Cl.* **20**, 1–124 (1900).
7. W. Nowacki, *Homogene Raumteilung und Kristallstruktur*. Doktor-Promotionsarbeit Eidgenoessische Technische Hochschule, Zuerich, 1935 (Druck von A.-G. Gebr. Leemann & Co., 1935), pp. 41–42F.
8. P. Niggli, "Krystallographische und strukturtheoretische Grundbegriffe," *Handb. Exp. Physik*, Bd. 7, Teil 1 (Akadem. Verlagsges., Leipzig, 1928); W. Nowacki, "Der Begriff 'Voronoischer Bereich'," *Z. Krist.* **85**, 331–332 (1933).
9. W. Nowacki, "Die euklidischen, dreidimensionalen, geschlossenen und offenen Raumformen," *Comment. Math. Helv.* **7**, 81 (1934–35).
10. K. Weissenberg, "Dynaden und Inseln im Kristall," *Z. Krist.* **63**, 221 (1926); K. Weissenberg, "Der Aufbau der Kristalle. I. Mitt. Die Systematik der Symmetriegruppen von Punktlagen im Diskontinuum," *Z. Krist.* **62**, 13–51 (1925); and "II. Mitt. Atomgruppen im Kristall und ihre physikalische Bedeutung," *ibid.*, pp. 52–102; "Berichtigungen," *ibid.*, pp. 612–613; A. Schoenflies, "Ueber K. Weissenbergs neuere kristallographische Arbeiten," *Z. Krist.* **63**, 193–220 (1926).
11. E. S. Fedorov, "Simmetriya na ploskosti," *Zap. Min. Obshch.* **28** (2), 345–389 (1891).
12. Contribution 221 from the department of crystallography at the University of Bern.

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Primordial Oil Slick

Abstract. *Calculations and some preliminary experiments suggest that an early methane atmosphere would have been polymerized by solar ultraviolet radiation in geologically short periods of time. An oil slick 1 to 10 meters thick could have been produced in this way and might well have been of considerable importance in the development of life.*

Numerous experiments have shown that amino acids and a large variety of the other building blocks of living organisms can be synthesized in electrical discharges if free oxygen is absent and if some reducing gases are present. These experiments suggest that the earliest terrestrial atmosphere was reducing. Methane and nitrogen may well have been its major components; water vapor, hydrogen, carbon monoxide, and ammonia were probably present in small quantities. A simplified model is presented in Fig. 1. Such an atmosphere would have responded to solar ultraviolet radiation and to lightning discharges quite differently than our present atmosphere. The effects of both energy sources on the chemistry of the present-day atmosphere are relatively small; on the other hand the rather drastic polymerizing effects of electrical discharges on mixtures of reducing gases have been amply demonstrated in a variety of experiments. Measurements suggest (*1*) that an input of electrical energy at the present rate would polymerize a methane atmosphere with an initial pressure of 1 atmosphere in 10^7 to 10^8 years.

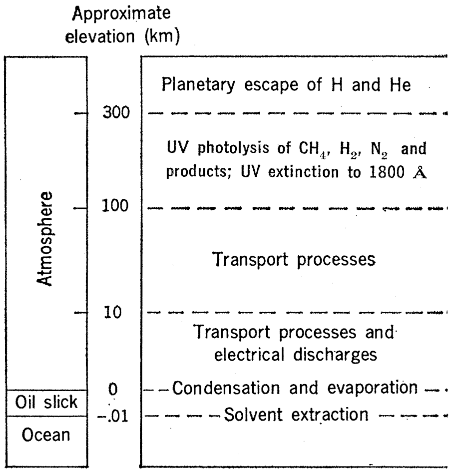

Fig. 1. Locale of some important processes in the primitive atmosphere-ocean system.

The effect of solar ultraviolet radiation on the present-day atmosphere is largely confined to dissociation and ionization reactions. In a predominantly methane-nitrogen atmosphere, methyl and methylene radicals are produced by ultraviolet light of wavelength less than 1450 Å. These radicals can combine to form heavier hydrocarbons. We propose that this process was rapid, that it was followed in the early atmosphere by the downward removal of the reaction products, and that these accumulated in an oil slick which could have been 1 to 10 m thick.

In the primitive atmosphere illustrated in Fig. 1, short-wavelength ultraviolet radiation would be primarily absorbed by methane at an elevation of 100 to 300 km; here methane and hydrogen will be the main reactive species. Figure 2 shows a partial reaction scheme for methane in the presence of ultraviolet light of 1200 to 1800 Å. Methyl and methylene radicals are produced from methane, and ethane is produced most efficiently by the combination of two methyl radicals. The reaction of a C_2H_5 radical with a CH_3 radical leads to the formation of propane, and two C_2H_5 radicals can combine to form butane. As their concentration increases, the photodissociation of the heavier hydrocarbons becomes important. At shorter wavelengths (<1018 Å) photoionization also occurs, but is expected to play a minor role. Ultimately, a steady-state distribution of species is reached in a closed one-phase system. A set of equations was developed to describe the time variation in the composition of such hydrocarbon gas mixtures, and the gas composition was then followed on a computer until a steady state was approached.

The parameters in our theory require a knowledge of the hydrocarbon photodissociation cross sections, P_i, as a function of carbon number, i, as well as the recombination rates, k_{ij}, and the branching matrix, α_{ij}. The rate constant for the recombination of the

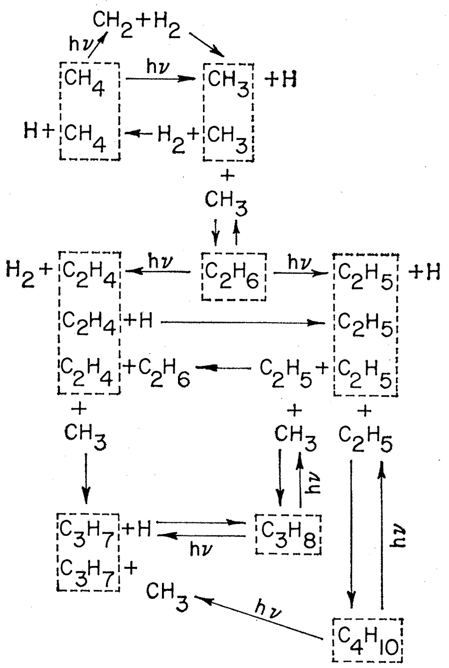

Fig. 2. Partial reaction scheme for polymerization of methane in the presence of 1200 to 1800 Å ultraviolet light (*4, 5, 13*).

Table 1. Reaction rate constants.

Reaction	k (liter mole^{-1} min^{-1})	Refs.
$CH_3 + H \rightleftharpoons CH_4$	6.3×10^{11}	(*10*)
$CH_2 + H_2 \rightleftharpoons CH_3 + H$	1.0×10^{9}	(*11, 12*)
$CH_3 + H_2 \rightleftharpoons CH_4 + H$	1.0×10^{6}	(*10*)
$CH_3 + CH_3 \rightleftharpoons C_2H_6$	4.0×10^{11}	(*2*)
$C_2H_5 + H \rightleftharpoons C_2H_6$	6.0×10^{11}	(*11*)
$C_2H_4 + H \rightleftharpoons C_2H_5$	1.0×10^{8}	(*11*)
$C_2H_5 + C_2H_5 \rightleftharpoons C_4H_{10}$	3.6×10^{11}	(*2*)
$C_2H_5 + C_2H_5 \rightleftharpoons C_2H_6 + C_2H_4$	4.0×10^{10}	(*2, 5*)
$C_2H_5 + CH_3 \rightleftharpoons C_3H_8$	4.0×10^{11}	(*2*)
$C_3H_7 + H \rightleftharpoons C_3H_8$	1.0×10^{11}	*
$CH_3 + C_3H_7 \rightleftharpoons C_4H_{10}$	4.0×10^{11}	(*2*)
$CH_3 + C_2H_4 \rightleftharpoons C_3H_7$	1.0×10^{10}	(*11*)
$C_4H_9 + H \rightleftharpoons C_4H_{10}$	1.0×10^{11}	*

* Inferred from similar reactions.

free radical C_iH_{2i+1} with the radical C_jH_{2j+1} is k_{ij}, and α_{ij} is the branching ratio of the photochemical production of C_jH_{2j+1} radicals from the hydrocarbon C_iH_{2i+2}. When plotted against carbon number, the cross sections, P_i, approximate a straight line in the wavelength region of principal interest. Recombination rates of the various free radicals appear to be similar, 4×10^{13} to 6×10^{13} cm^3 mole^{-1} sec^{-1} at 300°K, because steric effects are minimized by a long C–C bond in the transition state of the free radicals (*2*). This similarity decouples many of the simultaneous equations, and simplifies the computational scheme so that the constant k' can be used for all the various k_{ij}. It can be shown (*3*) that at steady state the ratio of the concentration of C_nH_{2n+2} to that of CH_4 is given by the expression:

$$\frac{[C_nH_{2n+2}]}{[CH_4]} = \frac{\phi k' \sum_r K_r K_{n-r}}{P_n}$$

where

$$K_r = \frac{\sum_j \alpha_{r+j,r} P_{r+j} D_{r+j}}{\sum_i \alpha_{i,o} P_i D_i}$$

$$D_k = \frac{[C_kH_{2k+2}]}{[CH_4]}$$

and $\phi = [H]^2/2[CH_4]$. The value of ϕ is defined by the initial ratio of ethane to methane.

The rate of attainment of a steady state was studied by obtaining numerical solutions with the aid of the Runge-Kutta method for the differential equations describing the behavior of the concentration of each of the components in Fig. 2, as well as for C_2H_4 and C_2H_2. The flux of solar ultraviolet was assumed to be identical to the present flux. The photodissociation constants, P_i, are known (*4, 5*) for CH_4, C_2H_6, C_3H_8, and C_4H_{10}; values of P_i for heavier hydrocarbons were obtained by extrapolation. Three-body effects, which lower the recombination coefficients by approximately two orders of magnitude, were taken into account (*6*). The rate constants used to define the reaction kinetics are shown in Table 1. The α_{ij} matrix was based on the assumption that all C–C bonds were equally likely to break, and that all C–H bonds were equally likely to break. The probability of C–H bond rupture is less than that of C–C bond rupture (*5, 7*).

Our computations indicate that the atmosphere in the 100- to 300-km region will reach a steady state under the influence of the solar ultraviolet flux in 1 to 50 years. Saturated hydrocarbons are the dominant products; their abundance decreases with increasing carbon number (Fig. 3). Surprisingly, the decrease in steady-state abundance relative to methane is relatively slow for hydrocarbons beyond butane. The ratio of hexane to methane, for example, is predicted to be $\sim 2 \times 10^{-4}$.

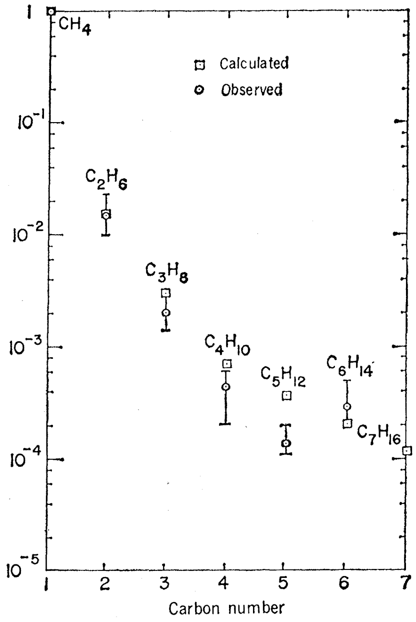

Fig. 3. Calculated and observed variations in the ratio of the pressure, *P*, of the lighter *n*-alkanes to the pressure of methane in a photochemical steady state. The limitations of our analytical scheme prevented the detection of hydrocarbons beyond C_6.

Some preliminary experiments were done to check the results of our calculations (Fig. 3). We irradiated methane at a pressure of 5 mm-Hg in an 84-cm-long glass container fitted with MgF_2 windows 4 mm thick. Our source of high-intensity short wavelength ultraviolet light—approximating the solar flux at wavelengths shorter than 1200 Å—was the 17-kw argon plasma vortex at the Ames Research Center. The irradiation products were collected in both gas expansion bulbs and an N_2 cold trap, and were then analyzed by gas chromatography. The products of a first run of 4 hours differed only slightly from those of a second run of 42 hours. The composition of the gases in the second run was determined after 6, 22, and 34 hours of irradiation as well as at the end of the run. The observed changes with time are probably within the uncertainties in the measurements; this suggests that a steady state was reached within the first few hours of irradiation. The error bars cover the entire range of the abundance ratios found in our experiments. We therefore believe that the results of our calculations are reliable. The argon lamp had not been calibrated for some time, and transmission through our 4-mm MgF_2 window is known only approximately. We estimate that 1 hour of irradiation in our experiments corresponds to approximately 1 year of solar ultraviolet radiation (assuming a 10 percent window transmission). The rather rapid approach to radiative equilibrium is therefore consistent with the results of our calculations. However, the effects of wall reactions are not known; and a window polymer was formed, which outweighed the other products by a factor of 4 or 5 after an irradiation time of 42 hours. A method of drastically reducing polymer formation has been devised, and we are planning experiments to clarify the matter. Experiments employing different pressures of methane, nitrogen, and hydrogen and different ultraviolet intensities are also planned to confirm other assumptions implicit in our calulations.

It is likely, then, that rather large hydrocarbons were produced in the early atmosphere by the solar flux if methane and hydrogen were major atmospheric constituents. Short-wavelength ultraviolet radiation probably penetrated the atmosphere to a level at which the pressure of methane was 10^{-5} atmosphere. Transport processes and transport rates in the early atmosphere are not well known but should have been fast below the mesopause. A small fraction of the hydrocarbon products may also have been subjected to further reactions while passing through the lower atmosphere.

Condensation probably occurred near ground level and ultimately led to the development of an oil slick. Ultraviolet absorption calculations were related to the temperature and transport model of McGovern (*8*); the calculations indicate that the important formation of hydrocarbons would occur anywhere from just above the mesopause to tens of kilometers below it. If we assume that a steady state is reached in about 10 years and that the irradiation products are transported into the lower atmosphere within a few years, the methane atmosphere could have been polymerized by solar ultraviolet radiation in 10^6 to 10^7 years.

If 1 atmosphere of methane is polymerized, a universal oil slick some 1 to 10 m thick would be produced. It is not known whether or how fast this material would be removed from the surface of the early oceans by adhering to mineral or rock particles, but the continued presence of an oil slick would have had some rather intriguing consequences. The dilute "prebiotic soup" would have been covered with a very rich hydrocarbon layer that could have acted as a host for prebiotic compounds. These would have been exposed to longer wavelength solar ultraviolet light and lightning discharges as well as to solvent extraction processes at the water-oil interface. Thus the effects of an oil slick on the chemistry of the prebiologic and earliest biologic periods could well have been important and deserve careful evaluation.

The photodissociation rate of molecular nitrogen is negligible at wavelengths longer than 1000 Å. Only a very small fraction of the energy of the solar ultraviolet spectrum is therefore available for N_2 dissociation, and the photochemistry of an early CH_4-H_2-N_2 atmosphere was probably quite similar to that of a CH_4-H_2 atmosphere. The photochemistry of a more oxidizing atmosphere would probably have been quite different.

If the temperature structure of the early atmosphere was similar to that of the present day, water vapor would have been a rare constituent of the upper atmosphere, but CO and CO_2 may have been present, and were surely there during the transition from an early reducing to a later, more oxidizing atmosphere. The effects of these gases on the appearance and composition of an oil slick remains to be determined.

Polymerization reactions similar to those discussed above are surely in progress on the major planets. However, comparable oil slicks are probably not formed, because the large excess of hydrogen and the high temperatures ($\sim 900°K$) at the base of the atmospheres of these planets favor the thermal decomposition reactions of larger hydrocarbons with hydrogen to form methane (*9*).

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References and Notes

1. C. Ponnamperuma and F. Woeller, *Nature* **203**, 272 (1964).
2. S. W. Benson, *Adv. Photochem.* **2**, 1 (1963).
3. A. C. Lasaga, thesis, Princeton University (1971).
4. Data from H. Okabe and D. A. Becker, *J. Chem. Phys.* **39**, 2549 (1963); R. I. Schoen, *ibid.* **37**, 2032 (1962).
5. J. B. Calvert and J. N. Pitts, *Photochemistry* (Wiley, New York, 1966).
6. G. B. Kistiakowsky and E. K. Roberts, *J. Chem. Phys.* **21**, 1637 (1953).
7. Data from D. J. Peters, *ibid.* **41**, 1046 (1964); S. Karplus and R. Berschn, *ibid.* **51**, 2040 (1961); S. Rice, I. McLaughlin, J. Jortner, *ibid.* **49**, 2756 (1968).
8. W. E. McGovern, *J. Atmos. Sci.* **26**, 623 (1969).
9. D. F. Strobel, *ibid.* **26**, 906 (1969); J. R. McNesby, *ibid.*, p. 594.
10. J. C. Polanyi, *J. Chem. Phys.* **23**, 1505 (1955); F. C. Majury and E. W. R. Steacie, *Disc. Faraday Soc.* **14**, 45 (1953).
11. E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold, New York, ed. 2, 1954).
12. C. Rosenblum, *J. Am. Chem. Soc.* **63**, 3322 (1941).
13. H. Akimoto, K. Obi, I. Tanaka, *J. Chem. Phys.* **42**, 3864 (1965); C. A. Heller, *ibid.* **28**, 1255 (1958); A. H. Laufer and J. R. McNesby, *ibid.* **49**, 2272 (1968); H. Okabe and D. A. Becker, *ibid.* **39**, 2549 (1963); H. Okabe and J. R. McNesby, *ibid.* **36**, 601 (1962); *ibid.* **37**, 1340 (1962); L. S. Stief, V. J. Decarlo, R. J. Mataloni, *ibid.* **42**, 3113 (1965); W. B. DeMore and S. W. Benson, *Adv. Photochem.* **2**, 219 (1963); J. R. McNesby and H. Okabi, *ibid.* **3**, 157 (1964); B. S. Rabinovitch and D. W. Setser, *ibid.* **2**, 1 (1963); G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, Princeton, N.J., 1964), vol. 2.
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Fecal Pellets: Role in Sedimentation of Pelagic Diatoms

Abstract. *Membrane-enclosed fecal pellets of planktonic herbivores were sampled at several depths in the Baltic Sea (459 meters deep) and off Portugal (4000 meters deep) by means of a Simonsen multinet. Pellets contained mainly empty shells of planktonic diatoms and silicoflagellates. Two kinds of fecal pellets were found, those with the remains of one species (for example,* Thalassiosira baltica*) and those with the remains of several species (for example,* Chaetoceros, Achnanthes, *and* Thalassiosira*). Siliceous skeletons were protected from dissolution during settling by a membrane around the pellet.*

Pelagic diatoms are a major factor in the biology, chemistry, and sedimentation of the oceans (*1*). They are the most important primary producers at the base of the food chain (*2*) and may be responsible for the general undersaturation of seawater with silica (*3*), because the rate at which they deposit silica exceeds the influx of dissolved silica. The excess supply of silica demanded by diatom frustules necessitates re-solution of sedimented diatom frustules to maintain the geochemical balance of silica in the water column (*4*). Evidence for dissolution in the upper centimeters of sediment has been presented (*5–7*). In addition to their important role in the modern ocean, diatoms are a diversified group of shelled plankton potentially useful in the reconstruction of ancient ocean conditions (*8*).

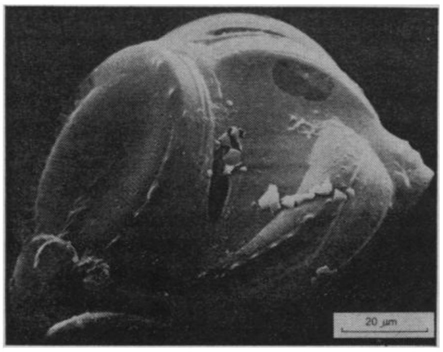

Fig. 1. Fecal pellet of *Calanus finmarchicus* Gunnerus with the centric diatom *T. baltica* enclosed within. The damage to the fecal pellet membrane occurred during coating with metal in a vacuum (scanning electron micrograph).

In discussions of the biochemical and geological aspects of diatom sedimentation, the role of fecal pellets, although occasionally mentioned (*9–11*), until recently has not received the attention it deserves (*12–14*). Membranes surrounding the fecal pellets of planktonic