* This work was done under contract N7-onr 434 Task Order III, Naval Department, Office of Naval Research.

[1] Cartan, H., "Algebraic Topology," Harvard Univ., 1949; Wallace, A. D. "Outline for Algebraic Topology I," Tulane Univ., 1949–1950; and Wallace A. D., "Map Excision Theorem," *Duke Math. J.*, 19 (1952).

[2] Cf. Tukey, J. W., "Convergence and Uniformity in General Topology," *Ann. Math. Studies*, Princeton, 1940, p. 53.

[3] Cf. Tukey, J. W., *loc. cit.*

[4] See Stone, A. H., "Paracompactness and Product Spaces," *Bull. Am. Math. Soc.*, **54**, 977–982 (1948).

[5] Cf. Spanier, E. H., "Cohomology Theory for General Spaces," *Ann. Math.* (2), **49**, 407–427 (1948).

[6] Cf. Wallace, A. D., *loc. cit.*

[7] See Dowker, C. H., "Čech Cohomology Theory and the Axioms," *Ibid.* (2) **51**, 278–292 (1950).

[8] Cf. Spanier, E. H., *loc. cit.*

[9] Cf. Wallace, A. D., *loc. cit.*

[10] Spanier, E. H., *loc. cit.* and Dowker, C. H., *loc. cit.* (2) **51**, 418.

[11] Cf. Eilenberg, S., "Singular Homology Theory," *Ibid.*, (1944), Cor. 9.3.

[12] $\rho_2 \wedge A = \{U \cap A \mid U \in \rho_2\}$.

[13] Make use of a homotopy lemma similar to Spanier, *loc. cit.*, Lemma 9.1.

ON THE EARLY CHEMICAL HISTORY OF THE EARTH AND THE ORIGIN OF LIFE

BY HAROLD C. UREY

INSTITUTE FOR NUCLEAR STUDIES, UNIVERSITY OF CHICAGO

Communicated January 26, 1952

In the course of an extended study on the origin of the planets[1] I have come to certain definite conclusions relative to the early chemical conditions on the earth and their bearing on the origin of life. Oparin[2] has presented the arguments for the origin of life under anaerobic conditions which seem to me to be very convincing, but in a recent paper Garrison, Morrison, Hamilton, Benson and Calvin,[3] while referring to Oparin, completely ignore his arguments and describe experiments for the reduction of carbon dioxide by 40 m. e. v. helium particles from the Berkeley 60-inch cyclotron. As I believe these experiments, as well as many previous ones using ultra-violet light to reduce carbon dioxide and water and giving similar results to theirs, are quite irrelevant to the problem of the origin of life, I wish to present my views.

During the past years a number of discussions on the spontaneous origin of life have appeared in addition to that by Oparin. One of the most extensive and also the most exact from the standpoint of physical chemistry

is that by Blum.[3a] It seems to me that his discussion meets its greatest difficulty in accounting for organic compounds from inorganic sources. This problem practically disappears if Oparin's assumptions in regard to the early reducing character of the atmosphere are adopted.

In order to estimate the early conditions of the earth, it is necessary to ask and answer the questions of how the earth originated, and how the primitive earth developed into the present earth. The common assumption is that the earth and its atmosphere have always been as they are now, but if this is assumed it is necessary to account for the present highly oxidized condition by some processes taking place early in the earth's history. Briefly, the highly oxidized condition is rare in the cosmos and exists in the surface regions of the earth and probably only in the surface regions of Venus and Mars. Beyond these we know of no highly oxidized regions at all, though undoubtedly other localized regions of this kind exist. This is essentially the argument of Oparin.

The surface of the moon gives us the most direct evidence relative to the origin of the earth. Gilbert[4] called attention to the great system of ridges and grooves radiating from Mare Imbrium, and Baldwin[5] has explained this as due to a colliding planetesimal some hundred kilometers in radius. My own studies show that the object contained metallic iron objects and and silicate materials and that water as such or as hydrated silicates arrived with such objects. This collision occurred during the terminal stage of the moon's formation. Some five other similar objects left their marks on the moon's surface and they all fell within a time span of some 10^5 years. Their temperatures were not high; probably not appreciably higher than present terrestrial temperatures. The arguments for these conclusions are long and detailed and cannot be repeated here.

At the time such objects were falling on the moon similar objects fell on the earth. The conditions were different because of the greater energy of such objects, 22 times as great if they fell from a great distance and 11 times as great if they fell from the circum surface orbit, and because of the presence of a substantial atmosphere on the earth. The energy was sufficient to completely volatilize the colliding planetesimals and raise the gas to greater than 10,000°K. An object similar to the Imbrium planetesimal would have distributed its material over a region several thousand kilometers in linear dimensions and the explosion cloud would have risen far above the atmosphere. Its materials would have fallen through the atmosphere in the form of iron and silicate rains and would have reacted with the atmosphere in the process. (H. H. Nininger recently showed me spherical iron-nickel objects collected near Meteor Crater, Ariz., which were formed in such a rain.) The objects contained metallic iron-nickel alloy, silicates, graphite, iron carbide, water or water of crystallization, ammonium salts and nitrides, that is substances which would supply the volatile and non-

volatile constituents of the earth. The temperatures produced in these collisions were very high, but unless the accumulation was very rapid indeed the general temperature of the planet was not excessively high. That such objects fell on the moon and earth at the terminal stage of their formation I regard as certain, and it is difficult in this subject to be certain about anything. But regardless of the detailed arguments, those who postulate oxidizing conditions as the initial state of the earth should present some similar argument to justify their assumption.

The reactions taking place at that time of interest to us here are:

$FeO + H_2 = Fe + H_2O$;	$K_{298} = 1.7 \times 10^{-3}$, $K_{1200} = 0.97$
$Fe_3O_4 + H_2 = 3FeO + H_2O$;	$K_{298} = 2.5 \times 10^{-2}$, $K_{1200} = 1.0$
$C + H_2O = CO + H_2$;	$K_{298} = 10^{-16}$, $K_{1200} = 3.8 \times 10^{-6}$
$C + 2H_2 = CH_4$;	$K_{298} = 7.8 \times 10^{8}$, $K_{1200} = 1.6 \times 10^{-2}$
$Fe_3C + 2H_2 = Fe + CH_4$;	$K_{298} = 3.2 \times 10^{11}$, $K_{1200} = 5.9 \times 10^{-3}$
$NH_3 = {}^1/_2N_2 + {}^3/_2H_2$;	$K_{289} = 1.2 \times 10^{-3}$.

From these equilibrium constants one sees that hydrogen was a prominent constituent of the primitive atmosphere and hence that methane was as well. Nitrogen was present as nitrogen gas at high temperatures but may have been present as ammonia or ammonium salts at low temperatures. At high temperatures hydrogen would escape from the planet very rapidly, but if the temperatures were high objects must have arrived rapidly to replenish the lost hydrogen. If the objects arrived slowly then the temperatures were low and hydrogen did not escape rapidly. Thus it is very difficult to see how the primitive atmosphere of the earth contained more than trace amounts of other compounds of carbon, nitrogen, oxygen and hydrogen than CH_4, H_2O, NH_3 (or N_2) and H_2.

We now consider what could reasonably be expected to convert this atmosphere into the present one existing on the earth.* If there was a large

* Poole, J. H. J. (*Proc. Roy. Soc. Dublin*, **22**, 345 (1941)), Harteck, P., and Jensen, J. H. D. (Z. *Naturforschung*, **3a**, 581 (1948)), and Dole, M. (*Science*, **109**, 77 (1949)) have reviewed the modern evidence for the photochemical origin of free oxygen and the evidence against the photosynthetic origin. Their conclusions are accepted here. In a recent paper, Poole, J. H. J. (*Sci. Proc. Roy. Dublin Acad.*, **25**, 201 (1951)) definitely concludes that methane and ammonia were not present in the primitive atmosphere and that it consisted of H_2O, CO_2 and N_2 but contained no oxygen. I cannot accept this conclusion for carbon dioxide and nitrogen are almost as difficult to understand as free oxygen. The interior of the earth and the lavas which reach its surface are highly reducing and are not a likely source of highly oxidized materials. Poole assumes that carbon dioxide was present in large quantities in the primitive atmosphere. How was it produced from methane, graphite or iron carbide? He also assumes that it would remain in the atmosphere, but as is shown in the text and the references cited, carbon dioxide in the presence of water should react rapidly with silicates until its partial pressure reaches values in the neighborhood of those on the earth and Mars.

amount of hydrogen, the outer parts of the atmosphere beyond the convection zone would become highly enriched in hydrogen. Hydrogen would absorb light from the sun in the far ultra-violet[6] and since it does not radiate in the infra-red would become a high-temperature atmosphere just as exists on the earth at present, and hydrogen would be lost very rapidly. As hydrogen was depleted, the atmosphere would become a methane one and since methane and its photochemical disintegration products absorb a wide band of energy in the ultra-violet and radiate in the infra-red, the temperature of the high atmosphere would fall far below the present temperature of 1500° or 2000°C.[7] In fact, it might well approach present terrestrial surface or even lower temperatures. The loss of hydrogen would be decreased, but since an oxidized atmosphere is present on the earth it can be assumed that it escaped at some appropriate rate. The net process was the dissociation of water into hydrogen which escaped, and into oxygen which oxidized reduced carbon compounds to carbon dioxide, ammonia to nitrogen, and reduced iron to more oxidized states. When the methane and ammonia were oxidized free oxygen appeared and the present atmospheric conditions were established. As carbon dioxide was formed it reacted with silicates to form limestones, i.e.,

$$CaSiO_3 + CO_2 = CaCO_3 + SiO_2, \qquad K_{298} = 10^8.$$

Of course the silicates may have been a variety of minerals but the pressure of CO_2 was always kept at a low level by this reaction or similar reactions just as it is now. Plutonic activities reverse the reaction from time to time, but on the average the reaction probably proceeds to the right as carbon compounds come from the earth's interior,[8] and in fact no evidence for the deposition of calcium silicate in sediments seems to exist.†

The histories of Mars and Venus should be similar to that of the earth. Mars has no mountains higher than 750 meters. Thus the initial lunar type mountains were probably eroded by water and no folded mountains have been formed. The oxidation of methane to carbon dioxide and the

† The alternative to this course of events would be the production of carbon dioxide from the earth's interior and there is evidence that at least some oxidized carbon is so produced. Gases escaping from lava lakes of Hawaiian volcanoes are highly oxidized, so much so that it is difficult to account for the high states of oxidation (Day, A. L., and Shepherd, E. S., *J. Wash. Acad. Sci.*, **3**, 457 (1913); Shepherd, E. S., *Bull. Hawaiian Volcano Obs.*, **VII**, 97 (1919); *Ibid.*, **VIII**, 65 (1920).) It seems probable to the writer that atmospheric oxygen directly or indirectly is responsible for the oxidation. Observers report burning gases as escaping from lavas, thus indicating the escape of reduced gases from the lava. Also surface oxidation of the lava pool must occur, as is shown by the high temperatures in the surfaces of such pools. Ferric oxide is probably produced and this in turn would oxidize carbon within the magma. (See *Bull. Hawaiian Volcano Obs.*, **IX**, 113 (1921).) If atmospheric oxygen is the source, then the carbon dioxide does not represent oxidized carbon being supplied to the atmosphere, but on the contrary it represents reduced carbon being so supplied.

formation of limestone proceeded as on earth, but oxygen atoms or water molecules were lost from the planet. In an atmosphere containing oxygen and nitrogen, a high temperature should have existed on Mars just as exists on the earth, and due to the smaller gravitational field atoms of atomic weight, 16, should escape if atoms of atomic weight, 4, i.e. He, escape from the earth now, as they do Finally, there results a desert planet with very small amounts of water and a pressure of carbon dioxide in its atmosphere about equal to that on the earth,[9] the excess carbon dioxide having reacted with the silicates to form limestones until its partial pressure was reduced to a low value. Since mountains are absent, volcanic activity must be small or non-existent and carbon dioxide has not been generated from limestone and silicon dioxide.

Venus started with a reduced atmosphere, which was oxidized to carbon dioxide and limestone by photochemical action. It cannot lose water, however, and the absence of water means that much less water was present initially than in the case of the earth, probably due to having been formed nearer to the sun and thus at a higher temperature. Assuming plutonic activity on Venus, the carbon dioxide has been regenerated by processes similar to those of the earth. In the absence of water the reaction of carbon dioxide with silicates is very slow and hence a dense atmosphere of carbon dioxide is possible. Thus a reasonable course of events can be postulated for this planet.‡

The Origin of Life.—The problem of the origin of life involves three separate questions in our present discussion: (1) the spontaneous formation of the chemical compounds which form the physical bodies of living organisms; (2) the evolution of the complex chemical reactions which are the dynamic basis of life; and (3) the source of free energy which alone can maintain the chemical reactions and synthesize the chemical compounds. It is only the first and third questions which will be discussed here. At present the source of free energy is sunlight through photosynthesis, but how were primitive living organisms maintained through a long enough period of time for the evolution of photosynthesis to occur?

It is suggested here that life evolved during the period of oxidation of highly reduced compounds to the highly oxidized ones of today. During

‡ The discussion up to this point, together with the suggestion that life originated during the period of oxidation of reduced carbon compounds to oxidized ones, was presented before the Geological Society of America, Washington, November, 1950. It was thought that there might be some condition of pressure, temperature and composition such that organic compounds became stable, thus making the synthesis of complex compounds possible. The general ideas were discussed with Dr. H. E. Suess, who was a Fellow at the Institute for Nuclear Studies. He made some studies relative to this problem which did not appear to be promising of positive results. The present paper follows a somewhat different approach to the problem by assuming the synthesis of organic compounds by means of ultra-violet light in the high atmosphere,

this period compounds of carbon, oxygen, hydrogen, and nitrogen were present in substantial amounts. It is also suggested that the source of free energy was the absorption of ultra-violet light in the high atmosphere by methane and water and other compounds produced from them by this photochemical action. This process also protected primitive organisms from ultra-violet light in the absence of an ozone layer as exists now.

Organic compounds are generally unstable relative to completely reduced or completely oxidized compounds throughout the entire range of hydrogen and oxygen pressures in chemical equilibrium with water at ordinary temperatures, but photochemical processes should produce such compounds. The exact conditions obtaining in a methane atmosphere can only be roughly estimated. Convection to higher altitudes than now occur on the earth should have been present, since a methane atmosphere radiates in the infra-red while an oxygen-nitrogen atmosphere does not. The atmosphere should have been cooler at high altitudes so that convection extended to higher levels than now, and water vapor should have been carried to high altitudes and photochemical products of the high atmosphere should have been moved rapidly downward.

The photochemical processes in a pure methane atmosphere can be estimated qualitatively. Methane absorbs in the ultra-violet below 1450 A. The total energy of the present solar spectrum below this wave-length is about 5×10^{-6} of the total energy. Methane dissociates into methyl and atomic hydrogen. Methyl probably absorbs at much longer wave-lengths and probably repulsive states exist resulting in the formation of methylene. This compound likewise would be dissociated into CH. Thus the reactions

$$\begin{aligned} CH_4 + h\nu\ (\lambda < 1500) &= CH_3 + H \\ CH_3 + h\nu\ (\lambda < 2800) &= CH_2 + H \\ CH_2 + h\nu\ (\lambda < 2800) &= CH + H \\ CH + h\nu\ (\lambda < 2800) &= C + H \end{aligned}$$

will occur and with their reversal and the reaction of the primary products with each other and with secondary products a steady state of great complexity will be established, the details of which cannot be estimated because of many unknown factors. The absorption spectra of CH_3 and CH_2 and the kinetics of the back reactions and other reactions are unknown. The fraction of the sun's energy below 2000 A is 3.3×10^{-4} and below 2500 A is 2.2×10^{-3}, so that very appreciable dissociation of CH_3 and CH_2 may be expected. The energies per year cm.$^{-2}$ of the earth's surface for complete absorption of the sun's spectrum at the earth below 1500 A, 2000 A and 2500 A are:

	Cal. yr.$^{-1}$ cm.$^{-2}$
1500	1.6
2000	85
2500	570

Not much methyl would be produced directly but secondary reactions such as $CH + CH_4 = CH_3 + CH_2$ could be expected to produce more of this radical. Altogether a very considerable absorption of solar energy would be expected.

In a pure water atmosphere dissociation of water into hydroxyl and atomic hydrogen would occur by absorption of light below 1900 A. Also dissociation of hydroxyl should occur giving atomic oxygen. Secondary reactions should produce O_2, H_2O_2, HO_2 and O_3 in amounts very difficult to estimate.

A combined methane and water atmosphere quite obviously would give a great variety of compounds of carbon, hydrogen and oxygen. In particular the reaction

$$CH_4 + OH = CH_3 + H_2O$$

would occur, thus producing larger quantities of methyl. These compounds would move by convection to lower levels in some quantities, dissolve in rain water and produce solutions of organic compounds in the oceans. Here ammonium salts should have been present (see below), and and the formation of nitrogen-containing compounds would occur. Given time, some natural catalysts and very slow destruction of organic compounds because of the absence of living organisms, a large number of organic compounds would be expected. If all the present surface carbon were dissolved in the present oceans as organic compounds, the oceans would become approximately a one per cent solution of these compounds. Thus compounds suitable for living organisms were possible and probably abundant.

Though the conditions postulated above are not approximated in any past experiments so far as I have been able to determine, the extensive studies on photochemistry, free radicals produced by various methods and the effects of electrical discharges on chemical substances[10] leave no doubt that many compounds would be formed due to the absorption of ultraviolet light.

A free energy supply for primitive living organisms is necessary, for only in this way can an active metabolism be supported and in the absence of such metabolism only dead and not living organic substance is possible. Rabinowitch[11] estimates that the present annual energy from photosynthesis is 600 cal. cm.$^{-2}$ of the earth's surface. The following table shows the standard free energies for three types of reactions of carbon-hydrogen-oxygen compounds of different oxidation states of the carbon atom.

COMPOUND	DISPROPORTION TO CH_4, CO_2 AND H_2O	OXIDATION TO CO_2 AND H_2O	REDUCTION TO CH_4 AND H_2O
CH_4	0	−195.50	0
CH_3OH	−22.31	−168.94	−30.13
CH_2O	−27.0	−124.75	−42.63
CH_2O_2	−21.83	−70.71	−45.28
CO_2	0	0	−31.26
$^1/_6C_6H_{12}O_6$	−17.23	−114.97	−32.85

It is apparent from this table that substantial quantities of free energy are available from the disproportion and reduction reactions of organic compounds, i.e., reactions possible under reducing conditions, though the free energies of the oxidation reactions possible in the present oxidizing atmosphere are much larger. It is not intended to infer that the reactions listed are necessarily the ones used by primitive life, but only that they indicate the order of magnitude of the free energies available from similar reactions. (Yeast uses a disproportion reaction,

$$^1/_6C_6H_{12}O_6(\text{aq.}) = {}^1/_3C_2H_5OH + {}^1/_3CO_2, \qquad \Delta F^\circ_{298} = -8.68$$

as a source of its free energy.) The high energy photochemical reactions of the reducing atmosphere at high altitudes could not be highly effective because of back reactions and because of the high energy used for the elementary processes (~150,000 cal.). Hence, the free energy supply for the primitive life processes was much less than that of the present time probably not more than 10^{-3} or 10^{-4} as much. However, experimentation on metabolic processes was possible and probably proceeded on a substantial scale. Also, a great advantage accrued to the mutations producing photosynthesis, thus ensuring survival of these processes.

Porphyrins probably appeared during the reducing period as important constituents of enzymes. Also during this time, photosynthesis evolved, and as oxidizing conditions were established green plants became the fundamental, even if they are not the dominant, type of life. In this way the evolution of photosynthesis was possible before the free energy due to it was available to living organisms.

Time and Conditions of Transition Period.—The order in which reduced substances were oxidized depends on the free energies of the oxidation reactions,

$$^1/_2CH_4(\text{g.}) + O_2 = {}^1/_2CO_2 + H_2O, \qquad \Delta F^\circ_{298}\ \text{kcal.} = -\ 97.75$$
$$^4/_3NH_3(\text{g.}) + O_2 = {}^2/_3N_2 + 2H_2O, \qquad \Delta F^\circ_{298}\ \text{kcal.} = -110.73$$
$$^1/_2H_2S + O_2 = {}^1/_2H_2SO_4\ (1\ \text{molar}), \qquad \Delta F^\circ_{298}\ \text{kcal.} = -\ 84.72$$
$$^1/_2FeS + O_2 = {}^1/_2\ FeSO_4\ (\text{aq.}), \qquad \Delta F^\circ_{298}\ \text{kcal.} = -\ 86.7.$$

Thus ammonia should oxidize first, then methane, and hydrogen sulfide third. However, if ammonium salts of organic acids are possible the stability of reduced nitrogen is greatly increased, and thus methane and ammonium ion

would be oxidized more or less together. This is shown by the reaction,

$$^4/_3NH_4OOCCH_3+O_2 = {}^2/_3N_2+2H_2O+{}^4/_3CH_3COOH, \ \Delta F^\circ_{298} = -97.83.$$

The last two reactions show that sulfide sulfur will be oxidized after the methane and ammonium ion have been oxidized. This conclusion is supported by other oxidation-reduction reactions of sulfur and carbon.

The amount of carbon on the earth's surface is about 350 g. atoms cm.$^{-2}$ equivalent to 1.4×10^3 moles cm.$^{-2}$ or 2.5×10^4 g. cm.$^{-2}$ of water, if all carbon was initially present as CH_4 and all had been oxidized to CO_2. But carbon is produced from the earth's interior and its state of reduction is less than that of methane and part of the surface carbon is not now oxidized to carbon dioxide. Hence the total amount of water which has been decomposed in order to oxidize the carbon is more nearly half of the above value, or 700 moles cm.$^{-2}$ of water. Using the energy per year absorbed by the atmosphere in wave-lengths below 1500 A, i.e., 1.6 cal. yr.$^{-1}$ cm.$^{-2}$, and assuming that every quantum produces a hydrogen atom with 200,000 cal. per/gram atom and that the hydrogen atom escaped from the earth, 10^8 years would be required for the oxidation process. If effectively all the energy below 2000 A is utilized in this way, the time would be 2.5×10^6 years. Neither assumption is realistic and no estimate can be made in this way except that the time might be either very long or comparatively short.

The hydrogen must escape in order for an oxidized atmosphere to be established, and if the methane-water atmosphere is cold, escape will be difficult. Interpolating from Spitzer's calculations[12] the escape of the required amount of hydrogen would require about 2×10^9 years, if atomic hydrogen escaped at 325°K. with an effective surface partial pressure of 10^{-3} atmosphere and 2×10^6 years if the surface pressure was one atmosphere. In the latter case the escape formula is not a good approximation but the time would be short nevertheless. If escape was by molecular hydrogen the temperature must be 650°K. for the same times of escape. The temperature of the methane water atmosphere at high altitudes was probably less than 325°K. and hence a long time for the escape of hydrogen from the reducing atmosphere is indicated.

Thode[13] and his coworkers have found that the ratios of the sulfur isotopes in the sulfides, elementary sulfur and sulfates are closely the same as this ratio in meteoritic sulfur until about 8×10^8 years ago, and after this time the sulfur and sulfides contain increasing amounts of S^{32} with time while the sulfates contain less amounts of this isotope. They ascribe this to the action of living organisms in promoting the oxidation and reduction of sulfur compounds, thus leading to a progressive separation of the isotopes, and suggest that life evolved about 8×10^8 years ago. This is a very interesting suggestion and may be a correct conclusion. It does

not give a very long time for the evolution of the very comlpex organisms whose remains are found in the Cambrian rocks.

On the other hand, this date might mark the transition from the reducing to the oxidizing atmospheric conditions. The oxidation of sulfur and sulfides to sulfates would probably not occur to any large extent until free oxygen appeared or until photosynthesis was well developed. But limestones were deposited in large quantities early in the earth's history and graphite was not. The two reactions,

$$CaCO_3 + SiO_2 + 4H_2(g.) = CH_4 + 2H_2O + CaSiO_3, \qquad K = 3 \times 10^{16}$$

and

$$C + 2H_2(g.) = CH_4(g.), \qquad K = 8 \times 10^8,$$

make possible an estimate of the pressure of hydrogen and methane that would make these two events possible at the same time. The pressure of methane would only be 5 atmospheres if all the present surface carbon were methane and if part of this carbon were dissolved as organic compounds in the oceans, the partial pressure might well be about one atmosphere. Then, if limestones were deposited, the hydrogen partial pressure was less than 10^{-4} atmosphere if equilibrium existed, but was probably higher since complete equilibrium cannot be expected. The second equation shows that graphite would not be stable under these conditions. As the methane was consumed the hydrogen pressure must have decreased. The partial pressure of carbon dioxide was 10^{-8} atmosphere if calcium carbonate was present, and may have been higher than this as it is today. If the hydrogen pressure fluctuated and for brief periods exceeded some critical pressure, massive deposits of limestones would be possible, but organisms which experimented with calcareous shells would have had great difficulty in preventing the dissolution of their shells during these periods and the extinction of their species, and indeed no certain calcareous fossils have been found in the Precambrian.

It seems just barely possible that reducing conditions were maintained until some 8×10^8 years ago. Limestones could be deposited, graphite need not have been formed, living organisms might find some 10^{-3} atmosphere or even less of hydrogen with photochemically oxidized organic compounds sufficient for their metabolic processes, and the methane pressure could not have been above 5 atmospheres and was maintained at lower pressures by the solubility of the oxidized organic compounds in water. The precipitation of limestones in great quantities presents a difficulty to the hypothesis of a long period during which a reducing atmosphere was present. The presence of highly oxidized iron in "red beds" and hematite (Fe_2O_3) iron ores are justly regarded as evidence for atmospheric oxygen. Red beds apparently are unknown earlier than the late Precambrian.

Most of the great bodies of iron ore were laid down in the late Precambrian (Huronian) or were extensively eroded during this time. The iron ore of the Vermillion range of Minnesota is much earlier (Keewatin) and thus oxidation of ferrous iron to ferric oxide took place early in the earth's history.[14] It should be noted that ferrous oxide should be oxidized to magnetic iron oxide by water if the temperature is sufficiently high to make the reaction fast enough with respect to the time available. However, magnetic iron oxide cannot be oxidized to ferric oxide by water unless the hydrogen is removed. The relations are shown by the reactions,

$$3FeO + H_2O = Fe_3O_4 + H_2; \quad K_{298} = 10^8, \; K_{500} = 10^4$$
$$2Fe_3O_4 + H_2O = 3Fe_2O_3 + H_2; \quad K_{298} = 10^{-6}, \; K_{500} = 10^{-5}$$

Thus circulating hot water could produce ferric oxide even in the absence of free oxygen, but it would probably be a rare event. The magnetic iron oxide is formed when iron is corroded by water in boilers. The conditions of deposition of these ores of the Precambrian are not well understood, though as stated above the presence of highly oxidized iron justifies a strong presumption of an oxidizing atmosphere. Thoughout the calculations it has been assumed that thermodynamic equilibria will be attained except for photochemical effects. This need not be the case and the presence of living organisms almost certainly would lead to important deviations from such equilibrium.

The red bacteria and some species of algae are able to use hydrogen and carbon dioxide in photosynthesis. This ability to use hydrogen is especially interesting because they do not find hydrogen available in their natural habitats. They appear to be living fossils from some former time and would live under conditions outlined above, though they prefer higher pressures of hydrogen than 10^{-3} atmosphere. Incidentally, modern plants prefer higher concentrations of carbon dioxide than those available in nature.§ If the present atmosphere should slowly change to a reducing one, it is certain that a substantial flora and fauna would survive. The flora would surely include many green plants and the fauna most of the principal orders of animals with the exception of the mammals and birds, i.e., the warm-blooded animals, for whom the reduced free energy supply would probably be fatal. A few aerobes would probably survive wherever photosynthesis was very intense. Aerobic organisms must naturally be most abundant under aerobic conditions, but mutations would surely supply anaerobic ones for life in a reducing atmosphere.[15]

Poole[16] thinks that oxygen may have been absent from the earth's atmosphere for some 10^9 years of the earth's history, but according to the evidence given here his model of the primitive atmosphere is not correct and hence his conclusion does not substantiate the present work. He shows that Tammann's thermal dissociation is not correct and that photo-

chemical dissociation and the escape of hydrogen are necessary for the formation of free oxygen. It is contended here that this mechanism is necessary to account for carbon dioxide as well. Lane[17] has argued that free oxygen did not appear until late Precambrian times because of the reduced condition of the Keewatin Greenstone schists. MacGregor[18] comes to similar conclusions from the Precambrian rocks of Rhodesia. He suggests that the Precambrian iron deposits were concentrated from igneous surface rocks by solution of iron in the absence of free oxygen as ferrous carbonate which was precipitated as ferric oxide by the action of green plants in a lake or sea into which the rivers ran. The plants may have been diatoms and hence the well-known banded structure of hematite and jasper may have been produced. As indicated above, the origin of these deposits is not well understood and therefore these suggestions, while worthy of consideration, cannot be regarded as conclusive.

The general course of events and the favorable condition for the origin of life outlined in this paper in no way depend on the time of transition from reducing to oxidizing conditions being exactly some 8×10^8 years ago. However, the evolution from inanimate systems of biochemical compounds, e.g., the proteins, carbohydrates, enzymes and many others, of the intricate systems of reactions characteristic of living organisms, and of the truly remarkable ability of molecules to reproduce themselves seems to those most expert in the field to be almost impossible. Thus a time from the beginning to photosynthesis of two billion years may help many to accept the hypothesis of the spontaneous generation of life. On the other hand, our judgment of an approximate time for the origin of life certainly is not so precise that we can say that 2×10^9 years are sufficient but 2×10^8 years are not.

It seems to me that experimentation on the production of organic compounds from water and methane in the presence of ultra-violet light of approximately the spectral distribution estimated for sunlight would be most profitable. The investigation of possible effects of electric discharges on the reactions should also be tried since electric storms in the reducing atmosphere can be postulated reasonably.

Also theoretical investigations on hydrogen and methane-water atmospheres would be most helpful in estimating the time of transition from the reducing to the oxidizing atmosphere. Most interesting in this connection would be more experimental data such as those of Dr. Thode and his coworkers on the abundance of the sulfur isotopes. The time of transition should be recorded in the rocks, and some such indication as that observed, by Thode, or some change in the state of oxidation of some elements should occur and should be detectable providing the time of transition was not too early in the earth's history.

I have profited greatly from discussions of this subject with Professor

James Franck, who has often pointed out to me and others that complex organic compounds, even porphyrins, may have originated under approximately the conditions outlined in this paper.

Note added in proof: Since this paper was written an interesting paper by J. D. Bernal on the Physical Basis of Life (London, Routledge and Kegan Paul, 1951) has come to my attention, in which very similar suggestions have been made, but there are differences in details and the arguments used. His paper is worthy of serious study.

§ I am indebted to Dr. H. Gaffron for information relative to these bacteria and algae.

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