CHEMICAL EVENTS ON THE PRIMITIVE EARTH

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During the past 15 years, many workers employing a variety of energy sources have demonstrated the abiologic production of a large number of biologically interesting substances from many simple starting materials. Most of the experiments, however, have had a curious deficiency. While designed to elucidate origin of life on earth, they do not take into account a body of geologic information.

In this paper the nature of the primitive atmosphere and ocean is considered in the light of geologic and geophysical information. The hypothesis of an early methane-ammonia atmosphere is found to be without solid foundation and indeed is contraindicated. Geologists favor an alternative view—that genesis of air and oceans is a result of planetary outgassing. Some consequences of this view are examined. Volatiles from outgassing interacted with the alkaline crust to form an ocean having a pH 8–9 and to produce an atmosphere consisting of CO, CO_2, N_2, and H_2. Radiation interacting with such a mixture yields HCN as a principal product. Ultraviolet irradiation of HCN solutions at pH 8–9 yields amino acids and other important substances of biologic interest.

The nature of the earth's environment limited the kinds of compounds that might have accumulated in a soup. Arguments concerning feasible components support the view that amino acids and proteins preceded sugars and nucleic acids.

If the methane-ammonia hypothesis were correct, there should be geochemical evidence supporting it. What is the evidence for a primitive methane-ammonia atmosphere on earth? The answer is that there is *no* evidence for it, but much against it. The methane-ammonia hypothesis is in major trouble with respect to the ammonia component, for ammonia on the primitive earth would have quickly disappeared.

The effective threshold for degradation by ultraviolet radiation is 2,250 Å. A quantity of ammonia equivalent to present atmospheric nitrogen would be destroyed in ~30,000 years. Small amounts of ammonia would be reformed, but this process is unimportant in comparison to the destruction.

If large amounts of methane had ever been present in the earth's atmosphere, geologic evidence for it should also be available. Laboratory experiments show that one consequence of irradiating a dense, highly reducing atmosphere is the production of hydrophobic organic molecules which are adsorbed by sedimenting clays. The earliest rocks should contain an unusually large proportion of carbon or organic chemicals. This is not the case.

The composition of the present atmosphere with respect to the gases neon, argon, krypton, and xenon is crucial. Neon is present on earth to an extent about 10^{-10} that of cosmic abundance,[1] and similarly argon, krypton, and xenon are relatively absent. It seems likely that if xenon of atomic weight 130 could not accumulate, other volatile light constituents such as hydrogen, nitrogen, methane, and carbon monoxide would also be lost at the same time. The concept that the earth had a dense methane-ammonia atmosphere is not supported by geochemistry, and it is contraindicated by the scarcity of xenon and krypton in our present atmosphere.

Understanding the evolution of our present atmosphere does not require *ad hoc* assumptions. Geological evidence suggests that the atmosphere evolved as a result of outgassing of the earth. This process has been discussed by a number of investigators, including Rubey,[2, 3] Holland,[4] and Berkner and Marshall.[5]

The geologic record shows that volcanism and associated outgassing have been going on for more than 3,000 million years. Rubey[2] has emphasized that the composition of volcanic gases is similar to that of the volatile substances that must be accounted for at or near the surface of the earth. These major volatile substances are H_2O, $16,700 \times 10^{20}$ gm; C as CO_2, 921×10^{20} gm; and N_2, 43×10^{20} gm.

Studies of the composition of volcanic gases by Shepherd and others have shown that water and CO_2 are the major volatiles produced by outgassing. These gases are accompanied by a significant amount of reducing potential in the form of hydrogen. One can estimate the amount of reducing power brought to the surface of the earth through outgassing by making a balance sheet of the oxidized and reduced chemicals in the atmosphere, biosphere, and sedimentary rocks. This estimate does not take into account gain or loss of hydrogen from the top of the atmosphere.

Most of the carbon is present in sedimentary rocks as carbonate. Part is also present as reduced carbon. Rubey estimates that the organic carbon has a composition 68×10^{20} gm C, 25×10^{20} gm O, and 9.6×10^{20} gm H. To burn this material to $CO_2 + H_2O$ would require 235×10^{20} gm O_2.

Most of the organic carbon present in the sediments appears to have been derived from photosynthetic organisms, presumably forming organic matter from $CO_2 + H_2O$. In the process, 235×10^{20} gm O_2 would be liberated. Hutchinson[6] points out that the quantity of atmospheric and fossilized oxygen that can be recognized is much less than this. Assuming that all the sulfate of the sea and the sediment represents oxidized sulfide and that oxygen has been fossilized in the production of ferric from ferrous iron, he calculates the total free and fossil oxygen to be

Free in atmosphere	12×10^{20} gm
Sulfate in sea and sediments	47×10^{20} gm
As ferric iron derived from ferrous	14×10^{20} gm
Total	73×10^{20} gm

This leaves 162×10^{20} gm O_2 to be accounted for. Rubey[2] suggested that the most probable explanation for the discrepancy is that an appreciable amount of the carbon released from volcanoes was in the form of CO. Hutchinson points out that other reducing gases such as H_2 are also possible, and cites Cotton.[7]

One can estimate the nature of the reducing gases. The major amount of magma accompanying volcanism is basaltic in composition and contains ferrous silicates. Holland[4] has provided an estimate of the equilibrium relations between H_2O and basalt, and CO_2 and basalt, using a simplified system which approaches basalt in composition. His calculation is based on the quaternary invariant point in the system MgO-FeO-Fe_2O_3-SiO_2 at $1255°C$. At this temperature and an estimated P_{O_2} of $10^{-7.1}$ atm, $P_{H_2O}/P_{H_2} = 105$ and $P_{CO_2}/P_{CO} = 37$. These ratios correspond to values observed at Kilauea by Eaton and Murata,[8] which were $P_{H_2O}/P_{H_2} = 137$ and $P_{CO_2}/P_{CO} = 31$. Assuming that the discrepancy in the balance sheet for oxygen can be accounted for by H_2 and CO emitted from volcanoes, and using Holland's estimate of the ratios of P_{H_2O}/P_{H_2} and P_{CO_2}/P_{CO}, one can obtain values for

the amounts of these gases which have reached the surface during outgassing. The values are H_2, 19×10^{20} gm, and CO, 17×10^{20} gm.

One can obtain another estimate for the amounts of H_2 and CO using the known amounts of volatiles now at the surface and the ratios of H_2O/H_2 and CO_2/CO quoted by Holland. The values obtained by these different routes are H_2, 16×10^{20} gm, and CO, 14×10^{20} gm. Thus the amounts of H_2 and CO accompanying the water and CO_2 are of the right magnitude to account for the reduced carbonaceous matter found in the sedimentary rocks.

The nature of the primitive atmosphere was to a large degree determined by the ocean-atmosphere interaction, and the pH of the primitive ocean is crucial. Most of the present components of the crust probably reached the surface in the form of basalt. The igneous rocks gradually disintegrate in the presence of water to form partially ionized products. In effect, silicate minerals are salts of strong bases and weak acids, and in dissolving form mildly alkaline solutions. If pulverized basalt is added to water, the pH immediately rises to about 9.6.[9]

Within a short time after outgassing began, there would be sufficient water to form extensive lakes. Rainstorms would begin to occur, accompanied by a weathering process which would bring alkaline waters back to the lakes. These rivers would carry Na^+, Ca^{++}, and clay minerals much as do the rivers of today. These waters would have a pH somewhat less than 9.6, for their pH would be lowered toward 8 by CO_2 and other acid gases. During the initial phases of weathering, the pH of the ocean may have been higher than it is today. At present only about 28 per cent of the surface is available for weathering and most of the continental exposures are sedimentary rocks. These are not so alkaline as are basalts. Sillén[10] has emphasized the buffering capacity of the huge amounts of silicates that have been weathered. The buffering system of weathered silicates and ocean has tended to maintain the pH of the ocean at about 8–9 since outgassing began.

The major products of outgassing were quickly removed from the atmosphere. Water condensed, CO_2 was dissolved in water and converted to carbonate, and other acid gases were converted to nonvolatile salts. The residual gases to be accounted for are CO, N_2, and H_2. The oceanic buffering system affected the distribution of CO. Carbon monoxide is slightly soluble in water and slowly reacts to produce formic acid.[11]

The equilibrium between carbon monoxide in the atmosphere and in the ocean is governed by

$$CO_{(g)} + \overline{OH} \rightleftarrows \overline{HCO_2}_{(aq)} \qquad \Delta F = -9.6 \text{ kcal.}$$
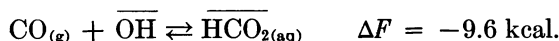
Most CO would be converted to formate.

Assuming that the proportions of volatiles have not changed with time and that $16,600 \times 10^{20}$ gm H_2O and 17×10^{20} gm CO have reached the surface, the concentration of formate would amount to 0.035 M. If the reducing capacity represented by the H_2 were employed in producing CO, the initial concentration of formate might have been as great as 0.6 M. Correspondingly, the partial pressure of CO could have been as high as 0.06 atm.

Water vapor was another important component of the atmosphere. Its partial pressure at low altitudes was determined largely by the atmospheric temperature at the surface of the earth. The amount of water vapor at high altitudes was gov-

erned by the temperature profile above the earth. It is likely that the temperature of the primitive atmosphere decreased rapidly with height to reach a minimum. In the present atmosphere the temperature distribution is complicated by the effects of oxygen and ozone. The temperature drops from 289°K at the surface to 214°K at 14 km, then rises due to effects of ozone before dropping again to 178°K at 86 km.[12] In the primitive atmosphere with little oxygen present, there was only one temperature minimum. Very low temperatures might have been reached at altitudes not much greater than 20 km. This low-temperature region would limit the fraction of moisture in the region above the temperature minimum.

Most of the nitrogen that has reached the surface of earth is now in the atmosphere. From a small value the nitrogen content has gradually increased to its present amount.

Hydrogen is an important component of volcanic gases. Its abundance in the atmosphere would be governed in part by hydrogen escape, which is sharply dependent on the temperature at the top of the atmosphere. The abundance of hydrogen would also be governed by chemistry occurring at the top of the atmosphere. This too is influenced by temperature. A well-considered calculation of the temperature of the ionosphere of the primitive earth would be an important contribution. However, that is beyond the scope of this paper. Crude guidance is obtained from measurements of the present atmosphere. Above the minimum at 86 km, temperatures rise to 800°K at 140 km, 1200°K at 180 km, and to higher temperatures, e.g., $\sim$1500°K, above that. In a primitive atmosphere possessing a different composition, the temperature would not be the same. However, at the top of the atmosphere where energetic radiations from the sun impinge and where chemical events of interest occur, the temperature would have been elevated.

The reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ is of importance. At 25°C this reaction has a $\Delta F = +6.831$ kcal.[13] However, at such temperatures the equilibrium time is about 10^{20} years. At 1200°K the reaction proceeds rapidly[14] and $\Delta F = \sim$0.

The composition of gases at the top of the atmosphere was governed by thermodynamic relationships existing at the higher temperatures. It was also influenced by the action of the cold trap in limiting the partial pressure of H_2O. These conditions combined to favor production of CO from $CO_2 + H_2$. As a result, carbon monoxide was at one time a major component of the earth's atmosphere.

Above the earth the principal agent causing radiation-induced transformations is ultraviolet radiation and this acts at the top of the atmosphere where temperatures are high. An electric discharge producing high temperatures and short ultraviolet radiation provides a situation qualitatively similar to the terrestrial circumstances. By conducting the discharge in a vessel with a cold trap, one can improve the similarity to nature. The cold trap maintains a low partial pressure of H_2O and serves to remove complex molecules produced by radiation.

To obtain an indication of the kinds of chemicals that might be synthesized, Dr. T. C. Hoering and I have conducted experiments under such conditions. Starting mixtures, with pressures measured in centimeters of Hg, were (1) N_2, 8; CO, 8; H_2, 2; (2) N_2, 4; CO, 4; H_2, 4; (3) N_2, 2; CO, 4; H_2, 6; (4) N_2, 2; CO, 4; H_2, 24. The principal product formed in the last three mixtures was HCN and H_2O. Small amounts of CH_4 and CO_2 were also made. In the first mixture, CO_2 was the major

product, with HCN and H_2O second. The products were analyzed by T. C. Hoering in a mass spectrometer. Thus it was simple to look for formaldehyde and for the unexpected. No formaldehyde was detected, which meant that if made, it was present in amounts no more than about 10^{-3} those of HCN. Similarly, other products such as nitriles, acids, and hydrocarbons would have been seen. When hydrogen is not present, the principal products from N_2 + CO or CO alone are CO_2 and C_3O_2. This reaction was studied by Harteck, Groth, and Faltings.[15] We also studied other mixtures. If the cold finger is not refrigerated, water is present in the gas phase. Yields of interesting products such as HCN are small. In summary, irradiation of a variety of mixtures of CO, N_2, H_2 produces HCN as the major product and little else except C_3O_2, CO_2, and H_2O.

In the natural situation any formaldehyde would tend to be destroyed. CH_2O is unstable and it decomposes to CO + H_2. The reaction is rapid at 500°C.[16] Formaldehyde if produced at the top of the atmosphere would not survive the temperatures or radiation there; CH_2O is decomposed by quanta of wavelengths as long as 3650 Å.[17]

Any surviving formaldehyde which reached the alkaline ocean would be subject to further attenuation. Formaldehyde undergoes disproportionation to methyl alcohol plus formic acid. In addition, CH_2O reacts rapidly with HCN, amines, and amino acids at room temperatures at pH 8–9. Experiments made in the last century showed that formaldehyde in lime water yields sugarlike substances. Suppose that a small amount of a carbohydrate were formed. This product would also be subject to rapid degradation and attenuation. First there is the well-known browning reaction. In addition, carbohydrates such as glucose combine readily with amino acids to form nonbiologic products. This reaction proceeds at room temperature, and even at 0°C there is a noticeable reaction in a week. At pH 8–9, amino acids and free carbohydrates are simply incompatible. Reaction between them leaves whatever is present in excess. As will be seen, synthesis of amino acids is relatively much more favored than synthesis of carbohydrates. In addition, substances such as glycine and alanine are very stable and hence could accumulate. Thus it is unlikely that the primitive ocean ever contained more than traces of free glucose, free ribose, or deoxyribose.

This discussion of limitations on the production and preservation is illustrative of similar arguments which can be made with respect to important constituents of any primitive "thick soup." For instance, arginine is adsorbed by sedimentary clay as are chlorophyll and porphyrins. Fatty acids form insoluble salts with magnesium and calcium, and hence would be removed from the soup. At least five major factors limit the kinds of compounds that might have accumulated in the primitive ocean.

First, there are limitations on what can be made by inorganic means; second, all organic matter degrades spontaneously with time; third, some substances are readily destroyed by radiation; fourth, many compounds would have been removed from the ocean by precipitation or adsorption; fifth, there are serious chemical incompatibilities among the constituents of living matter, and some of the components of the soup would react to form nonbiologic substances. In view of these limitations, one is challenged to seek a series of steps toward life that are compatible with the environment.

What kind of prebiologic chemistry is there that can occur at ordinary temperatures, in dilute solutions at pH 8.0? How can one form carbon-carbon bonds under these circumstances? Among simple substances, three methods are notably feasible. One is condensation of aldehydes. A second is condensation of aldehydes with HCN. A third is polymerization of HCN. I have indicated that formaldehyde would not be produced in quantity and it is easily destroyed. In contrast HCN can be readily produced and is stable at high temperatures. In slightly alkaline solution, HCN combines with itself to yield a number of interesting compounds.

The reactions involved are importantly sensitive to pH. Thus a 1 M solution of HCN having a pH 4.6 will not polymerize. Polymerization does not occur at very high pH. However, the reaction proceeds well at pH 8–9. Thus the range of pH likely in the primitive ocean is also a favorable one for polymerization of HCN. With solutions 0.1 M in HCN + cyanide, the reaction occurs rapidly at 100°C, more slowly at 25°C. A major product is the tetramer:

$$\begin{array}{ccc} NH_2 & & CN \\ & \diagdown \diagup & \\ & C & \\ & \| & \\ & C & \\ & \diagup \diagdown & \\ NH_2 & & CN \end{array}$$
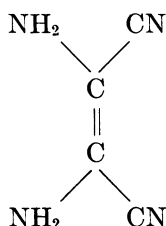
This reaction has long been known, and it has further been found that on hydrolysis this tetramer gives small yields of glycine. Oró and Kamat[18] have also noted production of small amounts of alanine and aspartic acid when 2.2 M cyanide solutions were heated at 70°C for 25 days.

Production of glycine from HCN has been noted in this laboratory. However, yields can be strikingly improved by radiation, and polymerization of dilute cyanide solutions can be made to occur at ambient temperatures. When solutions containing HCN at pH 8–9 are irradiated with 2,536-Å radiation and the product mixture is hydrolyzed, glycine, alanine, serine, aspartic acid, and glutamic acid result. The relative yields of the acids depend on time of irradiation. With short irradiations, yields are low and glycine is prominent. With longer times, yields are better and the larger amino acids are more prominent. At very long times, yields decrease. The ultraviolet radiation speeds the polymerization of HCN and, in view of the products obtained, must cause internal rearrangements including disproportionation. Production of amino acids from solutions 0.002–0.10 M in cyanide have been noted. After irradiation the solutions were hydrolyzed with 6 M HCl. The resultant amino acids were determined by E. Hare using an amino acid analyzer. In one instance, 1 mmole HCN gave rise to the following amounts of amino acids (μmole): 30.0 gly, 3.5 ser, 0.9 ala, 0.8 asp.

Others have studied the production of interesting substances from cyanide. These include Oró,[19] who produced adenine. Additional important roles involving cyanide and its products have been discovered. From irradiation of aqueous HCN, cyanamide is produced.[20] Cyanamide in turn has the important facility of bringing about peptide synthesis from amino acids in dilute solution under the influence of

ultraviolet radiation.[21, 22]   Other dehydrating reactions of great biologic interest are also facilitated in a similar way.[23]

One difficulty that must be considered is that HCN is subject to hydrolysis.   The rate of reaction is such that HCN decomposes to $NH_4OH + HCOOH$ in about 10 years at 25°C and about 70 years at 15°C.[24]   At the same time, the production of HCN is limited.   Assuming formation of cyanide requires photolysis of nitrogen, and assuming an over-all efficiency of 10 per cent of the quanta available, one obtains a production rate of the order of 4×10^{14} gm/year.   Even in the early stages of the ocean when the volume was less than, e.g., 10^{22} ml, the resultant solution would be quite dilute ($\sim 10^{-4}$ M in HCN).

A dehydrating mechanism for resynthesis of HCN might have been available. We have already seen one example.   It is possible that silicates could do the job even better.   The energy involved in dehydration reactions is in the range 0 to perhaps 10 kcal/mole.   On the other hand, typical quanta of visible light represent ~ 50 kcal/mole.   If visible light were harnessed to reform HCN from NH_4COOH, a large amount of HCN would be available for synthetic activities.

Formate would be a consequence of volcanic outgassing.   The ammonia produced by hydrolysis of HCN would be available for recycling.   As an example, let us examine the production of serine.   The net chemical reaction is

$$5HCN + 7H_2O \rightarrow C_3H_7O_3N + 4NH_3 + 2CO_2.$$
$$\text{Serine}$$
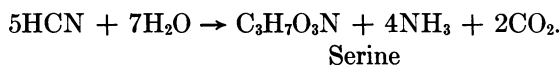
If the dehydration system were working, the product ammonia would be combined with more formate.

Given a dehydration mechanism utilizing cyanamide or some other agent, the step to an enzyme is relatively short.   Eck and Dayhoff[25] have developed some interesting arguments about ferredoxin which are relevant.

Ferredoxin is an unusually simple protein containing only 55 amino acid residues. It occurs in primitive anaerobic organisms, both photosynthetic and nonphotosynthetic.   The functions of ferredoxin are basic to cell chemistry.   The enzyme participates in oxidation, reduction, energy transfer, fixation of nitrogen, formation of ATP, and synthesis of pyruvate.[26]

Eck and Dayhoff have made an analysis of amino acid content and structure of the enzyme.   They find that it contains an unusual proportion of glycine, alanine, serine, aspartic acid, and cysteine.   From a study of the sequence of amino acids in ferredoxin, the authors are led to the conclusion that the original molecule was based on a repeating sequence of alanine, serine, aspartic acid, and glycine.   These amino acids are those which are produced most readily from HCN.

When one examines the processes of biosynthesis, he is impressed by how few mechanisms and basic building blocks are involved.   Pyruvate, acetate, and carbonate are key chemicals in the synthesis of amino acids.   In some microorganisms these three sources can furnish almost all the carbon in

Serine, glycine, cysteine, alanine, valine, leucine, isoleucine, lysine, aspartic acid, threonine, methionine, glutamic acid, proline, arginine.

All three of these carbon sources were present in the primitive ocean.   Pyruvate and acetate result from degradation of serine.   Snell[27] points out that the reaction

$$CH_2OHCHNH_2COOH + H_2O \rightarrow CH_3COCOOH + NH_3$$

Serine   Pyruvate
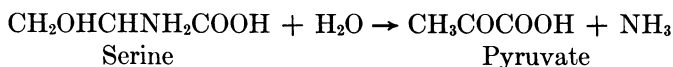
proceeds to the right. From pyruvate and from malonic acid, acetate can be derived.

The principal processes required to synthesize the 14 amino acids are condensations (such as those involving pyruvate, carbonate, and acetate in the Krebs cycle), hydrogenation, and transfer of NH_3. Furthermore, given condensation and hydrogenation, one has a mechanism for producing fatty acids. Formate would be a convenient source of hydrogen. Simple receptors for solar radiation might have helped speed the condensation reactions. Thus one can visualize that natural conditions might have favored synthesis of increasingly complex molecules from the simple but versatile substances available.

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