

On the Possible Role of Organic Melanoidin Polymers as Matrices for Prebiotic Activity

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Summary. One of the major diagenetic pathways of organic matter in recent sediments involves the condensation of cellular constituents, particularly amino acids and sugars, into insoluble melanoidin-type polymers. These polymers consist mainly of humic and fulvic acids and make up the major part of the organic carbon reservoir in recent sediments. We suggest that a similar set of reactions between abiotically formed amino acids and sugars, and more generally between aldehydes and amines, occurred on a large scale in the prebiotic hydrosphere. The rapid formation of this insoluble polymeric material would have removed the bulk of the dissolved organic carbon from the primitive oceans and would thus have prevented the formation of an "organic soup".

Melanoidin polymers have several properties which make them attractive hypothetical precursors of contemporary oxidation-reduction coenzymes: 1. they contain heterocyclic nitrogen compounds similar to the nitrogenous bases; 2. they contain a high concentration of stable free radicals; and 3. they tend to concentrate those heavy metals which play prominent roles in contemporary enzymic redox processes. The prebiotic formation of similar polymers could, therefore, have provided the starting point for a basic class of biochemical reactions.

We suggest that the prebiotic scenario involved chemical and proto-enzymic reactions at the sediment-ocean interface in relatively shallow waters and under conditions not much different from those of the recent environment.

Key words: Chemical Evolution - Humic Acids - Kerogen - Melanoidins - Sediments - Amino Acids - Carbohydrates

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INTRODUCTION

The experimental search for understanding the origins of living systems has so far been carried out at two levels of complexity. One of these, initiated by the Miller-Urey experiment, relates to the formation of biologically relevant complex molecules by excitation of simple molecules. This type of experiment is usually made in a confined space, using combinations of reactants and excitation sources which are assumed to simulate the primitive atmosphere. The second approach deals with the later step of the polymerization and/or separation of complex molecules into discrete phases which exhibit morphological and possibly biochemical analogs to some of the properties of simple living cells. The best known examples of such protocell models are "the proteinoid microspheres" of Fox and the "coacervates" of Oparin.

In order to make these types of experiments something more than chemical exercises and make them relevant to the problem of the origin of life, it is customary to use reactants which have some chemical plausibility as naturally occurring precursors for the suggested reactions. Less emphasis has been put on trying to reconcile the experimental conditions of the laboratory experiments with the geological or geochemical environment, as assumed to have occurred at those remote times. A notable exception is the study by Fox & Dose (1972) who described the formation of microspheres in a scenario which involves concentration and subsequent condensation of abiotically formed amino acids (in the dry state!) on hot lava rocks. The products are washed into an aqueous reservoir, and "proteinoid microspheres" separate from the cooling solution. A similar concept is the formation of phosphorylated macromolecules in an "evaporating solar pond" as suggested by Schwartz et al. (1973).

Although it is possible that some of the early prebiotic formation of organic molecules may have occurred under conditions very different from the present geological environment, the adaptation of organisms to the present environment would make it intellectually very satisfying if the initiation of the biosphere occurred under conditions which were not too dissimilar from the present environment (the most notable exceptions would be the lack of oxygen in the primitive atmosphere and the magnitude of UV flux reaching the earth's surface). We assume that the protobiotic scenario included liquid water locked mainly in the oceans, relatively low temperatures (much lower than the boiling point of water), the presence of solid mineral phases similar to those which exist today, and the occurrence of inorganic

erosion-sedimentation processes which are qualitatively (although not necessarily quantitatively) similar to present day processes. This general picture is supported by the fact that most of the ancient rocks known from the early Precambrian are metamorphic analogs of sedimentary rocks that occur throughout the geological record. There is no evidence for the widespread primeval occurrence of any specialized environments, such as have been proposed by some investigators (see for example the criticism of Fox's scenario by Miller & Orgel, 1974).

Therefore, it is clear that any hypothesis which attempts to account for the origin of the biosphere must have not only chemical and morphological plausibility but a high degree of geological plausibility as well. In this paper we suggest a geologically plausible model for the development of certain attributes of protobiotic activity. This model is based on geochemical processes which have occurred in the recent environment, and which, as we have reason to believe, may have occurred throughout the geological record. The approach is highly speculative, but it has, however, many facets which either are supported by geological evidence or which can be experimentally tested.

RATIONALE

One of the cardinal themes of organic geochemical research involves the transformation of naturally occurring biopolymers into geopolymers. It has been shown (Nissenbaum, 1974) that the major reservoir of organic carbon in recent sediments is in the form of brown or black polymers which are usually referred to as humic substances and kerogen. Humic acids are usually defined as the dark brown polymeric materials which can be extracted from soil or sediments by dilute alkaline solutions. The humic polymers are insoluble in organic solvents. They can be further fractionated into humic acids which are base-soluble and acid-insoluble, and fulvic acids which are acid- and base-soluble. Kerogens are usually defined as that part of the organic matter which is insoluble in any solvent, organic or inorganic, at reasonable temperatures and pressures (up to 400 °C and 1000 torr, respectively).

Studies on humic substances from recent marine and lacustrine environments show that this class of polymers may account for up to 70% of the total amount of organic matter in the sediments (Nissenbaum & Kaplan, 1972; Nissenbaum, 1974; Aizenshtat et al., 1973). Kerogen comprises the

vast majority of the non-humic material (Brown et al., 1972; Aizenshtat et al., 1973). Other classes of organic substances, such as fatty acids, hydrocarbons, pigments, and amino acids, usually account for no more than 1% of the total organic matter.

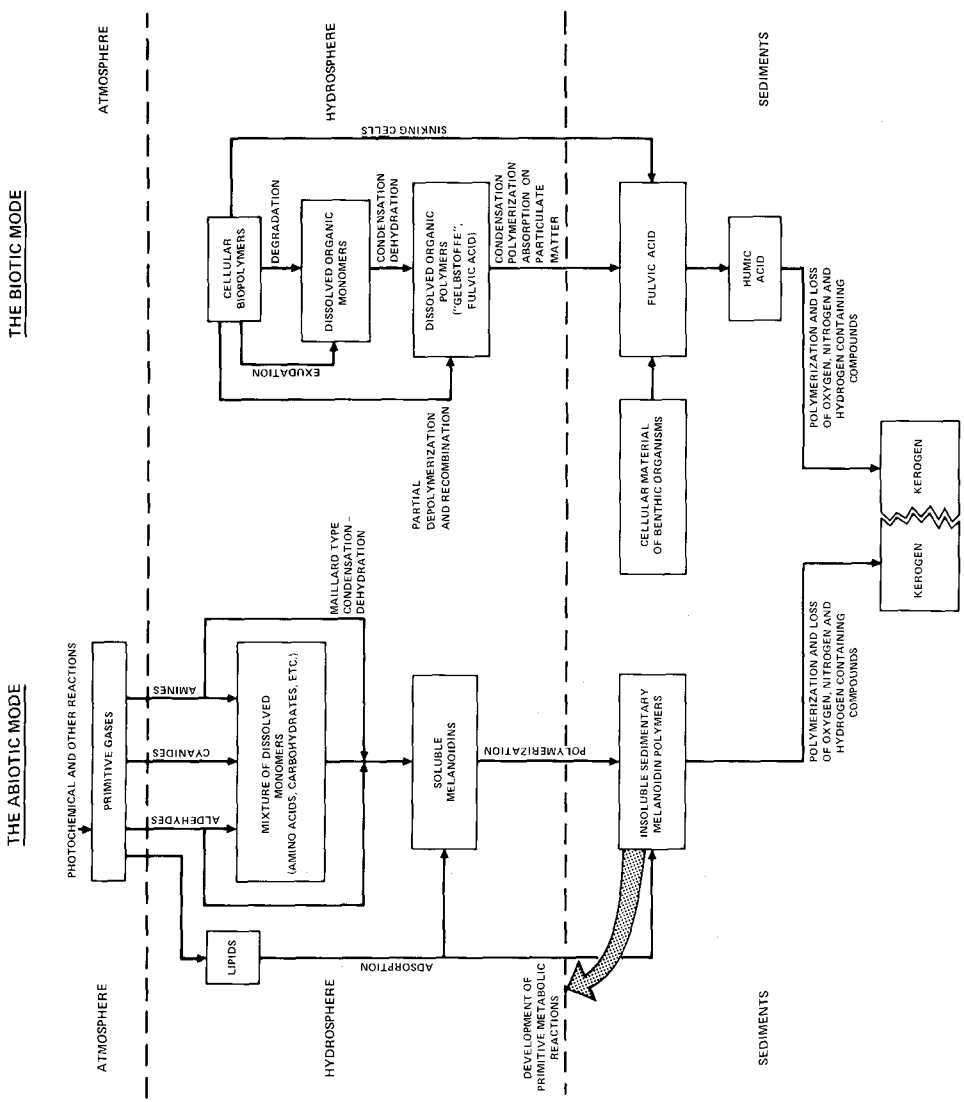
The sheer size of the humic and kerogen reservoirs in sediments indicates that they must originate from some large reservoir of material present in the biosphere. Humic substances do not occur as such in the living world (excluding the secretion of brown phenolic polymers by some fungi, Martin et al., 1972). Since the most commonly available cellular materials in the aquatic environment are carbohydrates and amino acids (Harvey, 1969), it is logical to assume that humic substances, and presumable kerogen, are related to those substances. Chemical, spectroscopic, and isotopic studies on sub-aquatic humates from the marine environment (Nissenbaum & Kaplan, 1972; Nissenbaum, 1974) and the lacustrine environment (Otsuki & Hanya, 1967; Kemp et al., 1973) suggests that humic substances in the subaqueous environment are produced by diagenetic recombination of cellularly derived material, probably through nonbiologically mediated processes. The pathway of formation of biotically derived humic acids and kerogen is modeled in Fig.1 (modified from Nissenbaum, 1974).

Maillard (1913) was one of the first to point out that natural humic acids may be similar to the condensation products of sugars and amino acids, which he named melanoidins. Hoering (1973) has investigated the spectroscopic behavior and the degradation products of marine humic acids and melanoidins, and has shown the similarity between the two types of polymers.

The formation of melanoidins, by what has been termed the Maillard or browning reaction, has been the subject of numerous investigations, especially by food scientists, and comprehensive reviews of this reaction are given by Hodge (1953), Ellis (1959), and Reynolds (1969).

The condensation of amino acids and sugars takes place over a wide range of environmental conditions. The reaction would occur essentially between any reducing sugar and any amino acid, although at different rates for different reactants. The condensation has been shown to occur at temperatures from -20°C to 100°C (Lea & Hannan, 1949; Buttkus, 1967), although the reaction rate increases with increasing temperature. These condensations can proceed at low pH, but are favored by slightly alkaline pH's (8-10). The condensations can occur at almost any moisture content, including nearly dry state. (Reaction of glucose and glycine

Fig. 1
Schematic modeling of the pathways by which organic matter of biotic and abiotic origin may be transformed into melanoidins, humic substances, and kerogen



occurs at 2% water content, as shown by Ellis, 1959.) The effect of oxygen on the condensation is unclear, but there is evidence that the reaction can take place under anaerobic as well as aerobic conditions (Reynolds, 1969; Ellis, 1959). The reaction is known to proceed even at very low reactant concentrations. The exact mechanisms by which the melanoidin polymers are formed are not known. The primary steps include the formation of Schiff bases between the α -amino nitrogen of the amino acid and the carbonyl group of the reducing sugars. The Schiff base then undergoes cyclization to N-substituted glycosylamine. Further isomerization follows the Amadori rearrangement. The formation of pigments from the Amadori rearrangement product of N-substituted 1-amino-1-deoxy-2-ketose probably proceeds via two pathways, one involving dicarbonyls and one through 3-deoxy-hexosones (Reynolds, 1969; Ellis, 1959). The important point for our discussion is the fact that the condensation-polymerization sequence involves dehydration in aqueous systems at low temperatures.

Experimental evidence on the formation of melanoidins and observations on the nature of humic substances in the recent environment lead to the conclusion that sugar-amino acid condensations are geologically very rapid, in some cases essentially instantaneous (in the geological sense), and inevitable if the proper precursors are available. The implications of this process for several prebiotic processes are discussed in the following paragraphs.

We would like to emphasize at this point that most of the discussion in previous and in forthcoming paragraphs deals with the condensation products of amino acids and carbohydrates. This is being done because most of the experimental studies reported in the literature relate to this reaction. However, the amino acid-sugar condensation is only a specialized case of the aldehyde-amine condensation, and the arguments marshalled in support of the melanoidin hypothesis may apply to the aldaminoins as well. (We suggest the use of the term aldaminoins to describe the insoluble polymers formed by the *aldehyde-amino* acids condensation.)

MELANOIDIN AND THE PREBIOTIC SOUP

A basic feature of most theories of chemical evolution is the assumption that abiogenic production of organic monomers led to the accumulation of simple molecules in the primitive water bodies which could have been either oceanic or lacustrine. The resulting organic-rich solution has been given

various names such as "nutrient broth", "primordial soup", "prebiotic soup", etc. Recently Lasaga et al. (1973) suggested that most of the organic matter occurred as a layer of hydrocarbons several meters thick, floating on the surface of the oceans. Miller & Orgel (1974) pointed out that if all the carbon present today on the surface of the earth was dissolved in the primitive oceans, the size of the present oceans, the resulting solution would contain about 10,000 mg/l dissolved organic carbon. If only 1-5% of the present surface carbon was dissolved as organic matter, the result would be a solution of about 100-500 mg/l organic carbon. Of course, if the prebiotic oceans were smaller than the present oceans, the concentration of organic carbon would increase correspondingly. These hypothetical values can be compared with the 0.5 mg/l dissolved organic carbon typical for the present-day oceans.

Contrary to the earlier suggestion that essentially all stages of chemical evolution occurred in the open seas, it is now generally accepted that the concentration of the "soup" was probably too small for efficient synthesis, particularly of biopolymers (Miller & Orgel, 1974). Among the concentration mechanisms which have been suggested are: 1. adsorption onto clays (Bernal, 1967; Anderson & Banin, 1975); 2. evaporation of water from shallow ponds and lagoons (Fox & Dose, 1972); and 3. freezing of water to form eutectic mixtures (Miller & Orgel, 1974). Other suggestions (see Matthews, 1975) envisaged the land surface of the Earth to be covered by proteinaceous material and other products of atmospheric photochemistry. Even this terrestrial model assumes that at some stage the polymers were washed into the oceans where the evolution of enzyme reaction chains occurred.

Considering the discussion in the previous section, it is reasonable to assume that concomitant with the production of simple organic molecules and their accumulation in the oceans there would have been an opposing mechanism of condensation of the accumulating amino acids and carbohydrates, or generally speaking, of amines and aldehydes, to form insoluble polymers of the melanoidin type. It is important to note that the formation of these polymers would cause not only the removal of hydrophilic molecules, such as carbohydrates and amino acids (Abelson & Hare, 1970), but also of hydrophobic molecules, such as fatty acids and hydrocarbons, which are known to occur in natural humic polymers (Ogner & Schnitzer, 1970; Neyroud & Schnitzer, 1975). This scavenging of dissolved organic matter from the oceans by polymerization and sedimentation would have left the

oceans much more depleted in abiotically formed organic matter than is usually assumed.

It is difficult to see how, under such conditions, the "primordial soup" could have existed at all. One kinetic possibility would be that the rate of production of organic molecules in the primitive hydrosphere exceeded the rate of removal by polymerization into the sediments. The rate of production of organic matter by abiotic synthesis is unknown but it presumably occurred through a period of at least several million years. Neither is the rate of formation of melanoidin (under natural conditions) known. However, dissolved organic matter in the recent oceans is mostly of the humic type (Nissenbaum, 1974; Steurmer & Harvey, 1974). ^{14}C age determination of the dissolved organic matter in the northeast Pacific ocean gives values of around 3500 years (Williams et al., 1969). This material is highly refractory to biological activity, and its removal from the oceans is by condensation and/or adsorption on clays or other suspended minerals (see Fig.1). Such mechanisms of removal could have occurred in prebiotic times as well, and we can conclude, therefore, that the removal of dissolved organic carbon from the oceans into the sediments is probably of much shorter duration than the period necessary for the accumulation of the primordial soup.

We suggest that the concentration of dissolved organic matter in prebiotic open oceans may have been of the same order of magnitude as it is in the present oceans, and the locus for processes which led to life phenomena must be sought in other places.

THE POSSIBLE ROLE OF MELANOIDINS AS PROTO-ENZYMATIC EXTERNAL ELECTRON ACCEPTORS

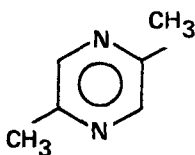
Considering the presumed anoxic nature of the prebiotic environment, it is very frequently assumed that the most primitive metabolic systems were capable of obtaining energy through reactions in which organic matter, rather than oxygen, acted as the terminal electron acceptors. Such an example would be conversion of an alcohol to an aldehyde or ketone, or the conversion of lactate to pyruvate. Generally speaking, the universal occurrence of the glycolytic pathway in organisms testifies to its primitive nature.

Most of the coenzymes utilized in anaerobic oxidation-reduction processes contain heterocyclic nitrogen bases as

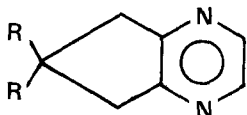
part of their structure. The most typical coenzymes are the nicotinamide derivatives (NAD and NADP) and the flavins (FMN or FAD).

We suggest that under prebiotic conditions, melanoidins may have acted as primitive coenzymes, where the apoenzymes could be either amino acids or peptides adsorbed on the polymer, or even some of the amino acid residues of the polymer itself. In the latter case, the melanoidin itself, or certain regions of it, would be the holoenzyme. Some of the characteristic properties of the flavine enzymes can be paralleled by some properties of melanoidins. We will discuss the following points: 1. the role of certain metal ions in the redox processes; 2. the participation of free radicals in electron transport systems; and 3. the possible presence of the pyrimidine-based isoalloxazine structure or the pyridine ring.

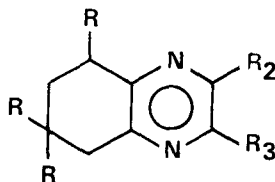
The Presence of Heterocyclic Nitrogen in Melanoidins. It has been known for some time that in the case of melanoidins synthesized from aliphatic amino acids and carbohydrates, a large part of the nitrogen in the polymer cannot be solubilized by acid hydrolysis. The situation is similar in naturally occurring humic substances, where only about 50% of the nitrogen in the polymer can be solubilized by hydrolysis (Schnitzer & Khan, 1972). The nature of the nonhydrolyzable nitrogen is unknown. However, a clue to the fate of the amino nitrogen can be inferred from studies of the steam-volatile products of amino acid-carbohydrate condensations. According to Hodge (1953) a 4(5)-methylimidazole, tetraphenyl pyrrole, and several substituted pyrazines are detectable in the reaction mixture. Dawes & Edwards (1966) isolated methyl-substituted pyrazines [I] from heated aldose-amino acid aqueous mixtures. Koehler et al. (1969) described the formation of pyrazines in sugar-amino acid model systems. The volatile products of roasted peanuts, which are assumed to be related to the browning reaction, contain alkyl derivatives of compounds related to 6,7-dihydro-5H-cyclopentane-pyrazine [II] and 5,6,7,8-tetrahydroquinoxaline [III] (Pittet et al., 1974).



[I]

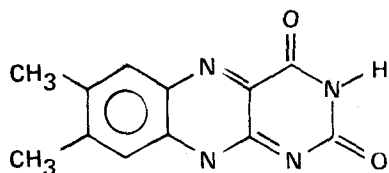


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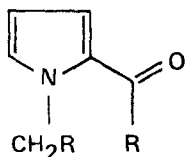


[III]

These compounds are assumed to form through condensation of α,β -alicyclic diketones. 1,2-diketones are important products of the first stages of amino acid-carbohydrate condensation (Reynolds, 1969). These bicyclic heterocyclic compounds are similar to the isoalloxazine moiety of the flavine coenzymes [IV].



[IV]



[V]

It has to be emphasized that all the heterocyclic compounds were isolated from *volatile* products of the condensation, and there is no information available on the state of nitrogen in the polymers. However, these data support the view that heterocyclic nitrogenous compounds can be formed from aliphatic amines, and it is possible that the polymer contains moieties even more closely related to pyridine and flavine coenzymes than the volatile products. In addition to the heterocyclic nitrogen compounds, oxygenated compounds such as N-alkyl-2-acyl-pyrroles [V] were isolated from the reaction of furfural and L-amino acids (Rizzi, 1974). The presence of quinoid-type molecules in melanoidin has not been demonstrated as yet, although condensations involving compounds having the skeleton of [V] could lead to quinone-type compounds. Although there has been some controversy as to the presence of quinone groups in natural humic substances, recent studies by Rashid (1972) have shown the presence of high concentrations of such groups in humic substances isolated from the marine environment. We conclude that although rigorous evidence is still lacking there are good reasons to believe that melanoidins and humic substances contain large amounts of heterocyclic nitrogen and quinone groups, suggesting their similarity to some of the oxidation-reduction coenzymes.

Free Radicals in Melanoidins. It has been shown recently that natural humic substances contain appreciable concentrations of stable free radicals (Schnitzer & Raffaldi, 1972). The exact nature of these free radicals is unknown, but they have been related to quinone-like groups. Nissenbaum & Kaplan (1972) and Hoering (1973) have also shown the presence of free radicals in melanoidins made from carbohydrates and amino acids. One of the characteristics of the flavine co-

enzymes is their ability to form semi-quinones. The formation of free radicals by the semi-quinone structure is one of the intermediate steps in electron transport systems. In this context the presence of quinone groups in marine humates has been mentioned in the previous paragraph. Therefore, we suggest that free radicals resulting from quinonoid groups may give melanoidins a role in some primitive oxidation-reduction systems.

Association with Metals. Soil humic substances are considered to be among the best chelating agents in the recent environment (Schnitzer & Khan, 1972). Marine humic substances which have been suggested to be melanoidin-like have been shown to contain characteristic assemblages of trace metals (Nissenbaum & Swaine, 1975). Hoering (1973) has shown that preparation of melanoidins in the presence of iron can result in incorporation of 3.5% Fe (by weight) into the polymer. The flavine coenzymes contain metals which take part in the oxidation-reduction chain. These metals are Zn, Mo, Cu, and Fe. It is interesting to note that exactly the same suite of metals is highly concentrated in marine humic substances (Nissenbaum & Swaine, 1975).

We endeavored to show that melanoidins and some of the coenzymes which take part in what is considered a primitive type of electron transport (i.e., glycolysis) have many properties in common. We therefore suggest that melanoidins may have acted as primeval, external electron acceptors in prebiotic times. We would also speculate that diagenetic cleavage of part of the melanoidin polymer, as occurs during the transformation of humic acid to kerogen, may have liberated moieties with limited enzyme-like activity into the aqueous environment. Further interaction of these moieties with coacervate-like microscopic particles characteristic of the melanoidin polymer itself (Kenyon & Nissenbaum, in preparation) may have simulated the behavior of endoenzymes. A possible confirmation of this model can be cited from the studies of Schindler et al. (1975). They have shown that humic materials can act as catalytic electron carriers in the reduction of tetrazolium to formazan by ascorbic acid and in other oxidation-reduction reactions. This electron-transforming activity of humic substances simulates in a general way the kinds of reactions occurring in the biochemical respiratory assemblage.

MELANOIDIN ROLE IN CONCENTRATING ORGANIC MATTER

So far, we have discussed the formation of melanoidin polymers from simple monomers. However, melanoidin may have also played a role as a concentrating medium for low and high molecular weight compounds which do not build the backbone of the polymer. For example, Abelson & Hare (1970) have shown that melanoidin polymers can remove amino acids from solution. That melanoidins interact with proteins, and may thus remove them from solution under natural conditions, is suggested by the following observations: 1. proteins can react with carbohydrates to form protein-bound brown pigments (Clark & Tannenbaum, 1970); and 2. recently, Rowell et al. (1973) prepared complexes of proteases with humic acid aromatic analogs, which retain their enzymatic activities. The ability to scavenge material from solution is not limited to organic compounds since humic substances can also remove considerable amounts of heavy metals from solution (Rashid, 1974).

Therefore, it is possible that melanoidin may have acted as an adsorptive matrix for both micromolecules and macromolecules, which would 1. concentrate them 2. provide a suitable environment for keeping molecules in close contact, and 3. enhance the stability of adsorbed species toward environmental changes. The exact nature of the adsorption mechanism is not known. However, it is appealing to assume that preferential adsorption of certain classes of molecules, such as amino acids, on which would be superimposed a selection for particular molecules of those classes, would constitute some limited molecular "directing ability". Any other process of reaction in a random milieu would make the production of macromolecules more of a hit-or-miss affair with far fewer opportunities for producing the correct combinations typical of living systems.

MELANOIDIN AND NUCLEOTIDES

The possible formation of nitrogenous bases in the melanoidin reaction has been discussed above. The prebiotic formation of melanoidin may explain why nitrogenous bases and ribose would have been "selected" for so many different roles in the living world. This is especially true for ribose. So far, no theory of chemical evolution has explained why this particular sugar, which is not formed in any high yield by any technique used for prebiotic carbohydrate formation, is selected over other sugars. However, Traitteur (1951) has

shown that ribose has the tendency to react with glycine at a far higher rate than any other sugar. This is probably because ribose exists mostly in the more reactive furanose ring structure which is also the form in which ribose exists in nucleotides. The high reactivity of ribose in the melanoidin reaction could, therefore, cause a selective enrichment of this sugar into prebiological melanoidin.

The role of phosphorous in the melanoidin reaction is not clearly known. It has been shown that phosphates promote the sugar-amino acid condensation (see references in Ellis, 1959). Glucose phosphates and fructose phosphate have been shown to react faster with amino acids than glucose or fructose (Ellis, 1959).

It is therefore possible that melanoidin may simulate not only some of the structure of the nitrogenous bases, but part of the structures of nucleosides and nucleotides as well. This is at present extremely speculative. But the implication of this hypothesis is obviously of extreme importance.

THE LOCUS OF PROTOBIOTIC REACTIONS

Several scenarios have been suggested for the reconstruction of the environment or environments in which life arose. The hypothetical environments range from the intermediate-depth oceanic environment (Weyl, 1963) to the surfaces of hot rocks (Fox & Dose, 1972). One of the more appealing scenarios is that of Bernal (1967) who suggested that life originated where the aqueous systems were in contact with clays. It has been frequently suggested that silicates played an important role in prebiotic chemical evolution by acting as concentrators and by providing the hypohydrous environment necessary for condensation and polymerization.

We suggest that the use of the melanoidin model provides an alternative, realistic model for protobiotic reactions, which does not conflict with basic geological or chemical assumptions, and which, moreover, can be tested at least partly in the laboratory.

We envisage that the prebiotic production of simple molecules, such as aldehydes, amines, aldoses and amino acids and their dissolution in the ocean was followed by rapid condensation and polymerization into melanoidin-type polymers. The melanoidins were concentrated mostly in near-shore, shallow shelf seas due to trapping by detrital minerals, and particularly so by clays, which are known to interact strongly with humic substances (Schnitzer & Khan,

1972). In order to utilize UV radiation, which was presumably the primary energy source necessary for protobiotic reactions, we assume that the major loci for such reactions were at the sediment-water interface at relatively shallow water depth (around a few meters). This particular environment is favored, because it will also act as a trap for all the organic molecules which are deposited on land, but are removed to the oceans by erosion processes. Part of those allochthonous organics would be trapped by the melanoidin or by melanoidin-clay complexes which would cause the sediments to be relatively enriched in organic matter. Some of the elements necessary for life activity would be introduced into the melanoidin from the environment. For example, sulfur is known to have been introduced into humic substances from the sulfide occurring in reducing sediments (Nissenbaum & Kaplan, 1972). Phosphorous could be supplied from upward diffusion of interstitial phosphate as suggested by Halmann (1975). Heavy metals would be supplied by the dissolution of detrital minerals by melanoidins in the same manner as has been suggested for the accumulation of heavy metals in marine humic substances (Nissenbaum & Swaine, 1975).

An interesting side effect of the accumulation of melanoidin would be the absorption of radiation and the resulting small increase in temperature of the bottom sediment. Such heating would facilitate many chemical reactions which could occur even if the prebiotic oceans were as cold as suggested by Miller & Orgel (1974).

The melanoidin model does not require any extraordinary environment. The way we see it, this model is an inevitable result of reactions which occurred in an environment very similar to the recent aquatic environment. Moreover, this model is not restricted to the earth's prebiotic environment. It could have occurred on other planetary bodies as well, if only a very modest amount of water was available. In this context it is interesting to cite a very recent study by Hayatsu et al. (1975) who reported the presence of nitrogenous bases in the Murchison meteorite. According to this report, the nitrogenous bases (which include adenine) are present mainly in macromolecular organic matter.

It would have been satisfying to present direct evidence for the occurrence of melanoidin in prebiotic sediments. This is not to be expected, as melanoidin is a geologically unstable intermediate in the formation of kerogen (Fig.1). Kerogen is indeed known from sediments which may antedate the origin of life, but, of course, it is the dominant reservoir of organic carbon in younger sediments as well.

Fig.1 shows that kerogen would be the end product of melanoidin formation whether through the biotic mode or the abiotic mode, and therefore, it should be present in post-biotic as well as in prebiotic sediments. However, we would expect some subtle differences in the finer structure of the kerogen, which could be indicative of whether it was biotically or abiotically derived. One such difference would be in the distribution of stable carbon isotopes which is strongly dependent on vital activity. It is interesting to note that, indeed, kerogen from the lowermost Onverwacht series (>3.3 billion years old) which may antedate the origin of life, has C^{13}/C^{12} ratios which are markedly different from those of most younger kerogens (Oehler et al., 1972).

In previous paragraphs we have discussed the possible role of melanoidin-type polymers in prebiotic evolution. We realize that other types of polymers probably have been present on the primitive earth. For example, it is well known that insoluble organic polymers are formed in prebiotic experiments, as in the Miller-Urey electrical discharge synthesis (Miller & Orgel, 1974), by the direct condensation of hydrogen cyanide (Oro & Kamat, 1961), or by reaction of ammonium cyanide with ammonium (Lowe et al., 1963). The nature of these polymers has not been well studied but they are assumed to be similar to the hydrogen cyanide polymers studied by Volker (1951), Ferris et al. (1975), and others. Some of the putative structural characteristics of these polymers, such as the formation of heterocyclic nitrogen rings, may have analogs in the melanoidin structure, and it is possible that some of the properties which we have attributed to melanoidin may apply to these polymers as well.

CONCLUDING REMARKS

In this article we have speculated on the possible role of organic polymers of the melanoidin type, as alternatives to inorganic surfaces, as the loci for some protobiotic reactions. The suggestion that insoluble organic matter played a role in prebiotic evolution has been forwarded by Blois (1965) who proposed that melanins may have been involved in concentrating small organic molecules by providing stereospecific adsorption sites due to the heterogeneity of this polymer. However, melanins are formed from aromatic amino acids and require oxygen for polymerization (Kenyon, 1964). These requirements are difficult to reconcile with the gen-

erally accepted prebiotic scenario. We have attempted to show that many of the attractive points of a melanin matrix (Kenyon & Steinman, 1969) can be found in melanoidins, which have other chemically relevant properties as well. It is appealing to assume that life, which is organic, arose on organic matrices with inorganic materials providing a stabilizing environment. Our model has the advantage that it postulates a kind of biogeochemical unity - the transformation of simple molecules likely to have been abundant in the primitive hydrosphere into ever increasing arrays of melanoidin and kerogen polymers of the kind which constitute the bulk of organic matter in sediments. The polymers act as the final sink of organic matter in the sedimentary environment. The polymers are stable relative to its simple precursors, unless energy is introduced into it from external sources such as geothermal heat during burial, and thus would have been preserved for a relatively long time in the sediment-water interface. It can be formed from products of either biotic or nonbiotic reactants. The interaction of these polymers with external organic matter may then exhibit primitive analogs to some of the biochemical attributes of living matter. We do not suggest that the melanoidin itself is a precursor of living material. It does provide, however, an environment which can mimic some of the reactions typical of the biosphere, especially in regard to electron transport. It would primarily act as a template, and when much more highly specific systems were developed, the role of melanoidin as a prebiotic matrix would be diminished. At present, the melanoidins exert only a small influence on the biosphere; this may not necessarily have been so in the past.

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