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A Possible Role of Fluctuating Clay-Water Systems in the Production of Ordered Prebiotic Oligomers

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Summary. A model is proposed for the intermediate stages of prebiotic evolution, based on the characteristics of the adsorption and condensation of amino acids and nucleotides on the surface area of clay minerals in a fluctuating environment. Template replication and translation of adsorbed oligonucleotides and catalytic effects by peptide products on further condensation are proposed, due to specific properties of hypohydrous clay surfaces as well as the biomolecules themselves. Experimental evidence supports some of the proposed interactions, and all of them can be tested experimentally.

Key words: Prebiotic – Clays – Peptide formation – Nucleotide – Oligomerization – Polynucleotide template – Chemical evolution

Introduction

The possible role of solid surfaces in peptide condensation reactions during chemical evolution was reexamined by Lahav and Chang (1976). It was concluded that oligomerization reactions in ocean-sediment systems were less likely than in dehydrated systems, and that condensation reactions in prebiotic times would have been favored by fluctuating systems. In such systems, a redistribution mechanism was proposed, according to which adsorbed oligomers and monomers were desorbed and redistributed on the solid surface during the next hydration-dehydration cycle. The importance of a dynamic fluctuating environment has also been discussed by Kuhn (1972, 1976), Usher (1977), Eigen (1971) and Cairns-Smith (1971).

In the following discussion, certain properties of fluctuating clay-water systems are considered for their possible role in more advanced stages of chemical evolution. The clay-water systems under discussion are special cases of the general class of solid-liquid interfaces, but they are the systems in which most of the experimental data on the role of mineral surfaces in condensation reactions have been obtained. Clays are likely to have been among the most important minerals due to their relatively large surface to volume ratio and well-known catalytic properties, as well as a widespread geological occurrence (Anderson and Banin 1975). They must have been abundant in the first

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sediments of the primitive earth, since kaolinite and other clays are the major products of weathering of igneous rocks (Garrels and MacKenzie 1971). It is also worth noting that clays occur as major phases in 4.5 billion year old carbonaceous meterorites (Nagy 1975). The predominant cation associated with clays in equilibrium with seawater is sodium (Sayles and Mangelsdorf 1977), although magnesium, calcium, potassium, and protons are also geologically important.

A fluctuating clay-water system is chemically simple, yet capable of a dynamic interaction with simple precursors to produce prebiotically relevant oligomers. No activated monomers or condensing agents need be provided, yet oligomerization of amino acids occurs in significant yield even at moderate temperature (see below). The following discussion reviews adsorption and condensation of biomonomers in fluctuating clay-water systems, and then speculates on more complex interactions which might operate during condensation reactions.

Adsorptive Properties of Clays

The adsorption characteristics of amino acids and peptides on clay in fluctuating systems have been reviewed (Lahav and Chang 1976). These organic molecules become increasingly strongly attached to the mineral surface during the dehydration process, both because decreasing liquid volume causes increasing concentrations of solute, and because of increasing surface acidity of the clay (Lahav 1975; Mortland 1970; Fripiat and Cruz-Cumplido 1974). This phenomenon is caused by increased ionization of water, and results in protonation of basic functional groups such as carboxylate anion and amino groups, thus causing increasing cationic character of the molecule and increased attraction to anionic sites on the clay. Conversely, upon rehydration both amino acids and peptides tend to be desorbed and redistributed into the bulk aqueous phase by the reverse of the above processes. In general, both increasing peptide chain length and increasing cationic charge cause stronger adsorption (Theng 1974) but all amino acids and peptides will be at least partly desorbed on return to the hydrated state.

The adsorption characteristics of purine and pyrimidine bases and nucleosides on montmorillonite and illite clay minerals are similar to those of the most common amino acids (Lailach et al. 1968, Theng 1974), showing an increase in adsorption as water content decreases and desorption on return to a wet state. Coadsorption effects also influence the adsorption; thymine is not adsorbed from neutral aqueous solution onto montmorillonite, but it is taken up in the presence of adenine (Lailach and Brindley 1969). Adenine becomes protonated and the bases are paired by hydrogen bonding, though not of the Watson-Crick type, and are intercalated in planar arrangements between layers of clay. This is remarkable in comparison with the lack of hydrogen bonding between the free bases in aqueous solution (Theng 1974, p 195).

Very little is known about the adsorption of nucleotides and nucleic acids on mineral surfaces. The spermidine-N-(5'-phosphoadensine) studied by Burton and coworkers (1974) is probably irrelevant to primordial chemical evolution (Lahav and Chang 1976). Alanine adenylate is readily adsorbed on sodium-montmorillonite at pH 8 (Paecht-Horowitz 1976) but the protonated amino group may be important to this interaction, so the significance of the nucleotide is not clear. Burton and Neuman (1971) measured the adsorption of AMP, ADP, and ATP on apatite at pH 5.4 and showed that the ex-

tent of adsorption increases with the number of phosphate groups. Apparently the adsorption of these nucleotides is governed by the attraction between the negatively charged phosphate groups of the nucleotide and positively charged sites on the apatite surface, the isoelectric point of which is above 8.0 (Chander and Fuerstenau 1979). We have found that 5'-AMP is not appreciably adsorbed on sodium kaolinite at pH 5-7 in aqueous solution (Lahav, unpublished). Edelson and Lawless (1980) found the same result for 5'-AMP on sodium bentonite, although it was appreciably adsorbed on certain metal-substituted bentonites. Polyribonucleotides are significantly adsorbed onto sodium bentonite with the exception of polycytidylic acid (Seidl et al. 1978), with increasing adsorption with divalent or transition metal-exchanged clays. Although much more data are required, it is reasonable at this point to presume that nucleotides and oligonucleotides resemble amino acids and peptides in being more strongly adsorbed at low pH and dehydrated conditions, partially or totally desorbed upon rehydration, and more strongly adsorbed as chain length increases.

Oligopeptide Formation on Clay Surfaces

Since Bernal first suggested the possible role of clay surfaces as catalysts for prebiotic oligomerization (1951), the promotion of oligopeptide formation has been demonstrated in several non-fluctuating systems. Fripiat and coworkers (1966) obtained oligopeptides by heating amino acids on montmorillonite at temperatures which are too high to have prebiotic significance. A non-clay mineral, hydroxyapatite, was found to promote oligopeptide formation in hypohydrous conditions (Burton and Neuman 1971), and a similar reaction was promoted by added cyanate at 95°C (Flores and Leckie 1973). Degens and Matheja (1971) claimed that montmorillonite and kaolinite promoted polymerization of aspartic acid at 80°C in aqueous solution, but Flores and Bonner (1974) disputed that claim. Degens and Matheja (1971) also reported synthesis of peptides on these clays in the dry state at 140°C. Paecht-Horowitz (1976 and references therein) used activated amino acid adenylates adsorbed on montmorillonite in aqueous solution to obtain higher degreees of polymerization than in the absence of clay. Condensation has also been observed in a dehydrated system in the absence of mineral surfaces at temperatures below 100°C (Rohlfing 1976).

We have shown (Lahav et al. 1978) that the clay minerals montmorillonite and kaolinite significantly enhance glycine condensation in dehydrated systems at 94°C compared to controls without clay and that yields are greatly enhanced by repeated fluctuations in water content and temperature. Typical yields were 1—3%, which is low by normal experimental standards but reasonable for a prebiotic reaction which can continue on a geological time scale. In fact, high yields may be a disadvantage when more highly ordered processes begin to compete (White 1980).

The fluctuating clay-water system provides a simple and geologically relevant model for peptide bond formation from amino acids during the dehydrated stage. Upon rehydration, most of the oligopeptides formed, as well as the monomers, are desorbed and redistributed into the aqueous phase (to a greater or lesser extent, depending on their adsorptive characteristics which were described earlier). Many if not most of the surface sites on which peptide bonds formed are thereby freed to accumulate monomers and repeat the condensation reaction during the next cycle. It has been noted by Lahav and Chang (1976) that the increased adsorption with increasing peptide chain

length would produce a higher oligomer to monomer ratio on the clay surface than in solution. This would favor the growth of the pre-formed oligomers and fusion of short chains into long chains in preference to continued formation of additional amounts of short-chain oligomers as the reaction preceeds. Thus it might be expected that the recycling process would produce increasing amounts of longer oligomers with continued reaction. This has indeed been observed to be the case in the reaction of glycine on kaolinite (Lahav et al. 1978).

When mixtures of amino acids are allowed to react, the following processes may act to produce selectivity or partial ordering of amino acids in the peptides produced.

1. Selectivity of adsorption by the clay surface and variations in rates of condensation and decomposition (Dose 1976) may produce ratios of amino acids incorporated in peptides that differ from starting monomer ratios.
2. Nearest-neighbor interactions may partially constrain sequences (Steinman 1967; Paecht-Horowitz 1976; Dose 1976).
3. The clay surface may contain sites that act as direct templates (although probably not highly specific) to repeatedly select related sequences of amino acids (Cairns-Smith 1971).

Clearly the products would not be totally random, nor would they be highly ordered as in modern biological proteins. The products would best be described as statistical peptides with some degree of internal order, and some degree of relatedness between copies. The mineral serves both as a crude template and a catalyst, and the fluctuating environment supplies the monomers, the energy for condensation through temperature fluctuations, and the liquid phase needed for redistribution.

Peptide Catalysis

The peptide products from cycling reactions may themselves be catalytic toward the formation of more peptide bonds. Kenyon and Steinman (1969) discuss the potential autocatalytic properties of oligopeptides. We have found that histidyl-histidine is a catalyst for glycine oligomerization during cycling on kaolinite (White and Erickson 1980a). Thus it is likely that mixtures of amino acids would produce peptides which were autocatalytic, and that the composition of peptides produced would be open to further evolution as catalysis proceeds.

The enhanced synthesis of oligopeptides from amino acids in bulk observed by Rohlfing (1976) compared to our control reactions of glycine on glass (Lahav et al. 1978) may in fact be due to catalysis by oligopeptide product formed during the reaction. Alternatively, the amino acid starting materials in bulk phase may themselves be mildly catalytic due to acidic and basic functional groups. If product catalysis indeed occurred, Rohlfing would have observed a mild autocatalytic effect, but his results are not sufficiently detailed to determine whether that was the case.

Oligonucleotide Formation on Clays

It may also be possible to form single-stranded oligonucleotides from mononucleotides, preferably without the help of condensing agents, on clay surfaces during an anhydrous stage. The reaction would be expected to resemble the oligopeptide condensation, with enhanced synthesis as a result of multiple cycles of dehydration-rehydra-

tion due to the redistribution effect. However, experimental evidence of oligonucleotide synthesis on clay is scanty and not very encouraging.

Ibanez et al. (1971a) obtained low yields of oligothymidylic acid through the trimer by using cyanamide in aqueous solution. When montmorillonite was added, the total yield was lower but the higher oligomers up to at least the pentamer were enhanced. Orgel and Lohrmann (1974) reported no oligonucleotide formation with montmorillonite and activated nucleotides in solution. In order to investigate the effect of dehydration and cycling, Odom et al. (1979) studied the oligomerization of thymidine 5'-phosphate on sodium kaolinite with cycling at 60°C in the presence of cyanamide and ammonium chloride. The presence of kaolinite had a marginal effect when cyanamide was used as a condensing agent. No oligomers were detected when kaolinite was used in the absence of cyanamide at 60°C. In the absence of clay, it has been shown that hypohydrous conditions enhance oligonucleotide formation (Orgel and Lohrmann 1974), and that multiple cycles enhance yields considerably, allowing reaction at 37°C with cyanamide (Odom et al. 1976).

Schramm (1962) has reported that the phosphoester bonds of RNA are hydrolyzed at pH 2.4. (Under the same conditions N-glycosidic linkages of DNA are broken to give apurinic acids, while RNA undergoes that reaction very slowly.) This suggests that the surface acidity of clays may be adequate to reversibly make and break phosphoester bonds of ribonucleotides, and that under hypohydrous conditions synthesis may be favored, whereas aqueous conditions favor hydrolysis.

Although there is no experimental evidence at present to support the proposed role of dehydrated clays in oligonucleotide formation, much work remains to be done. It may be possible to find small amounts of oligomerization at 60°C or higher temperatures with more sensitive analytical techniques. The reaction would most preferably occur without a condensing agent in order to present the simplest and most widespread prebiotic environmental conditions. The expected low yields, as in the formation of oligopeptides, are no detriment and perhaps an advantage for further evolution (White 1980). Furthermore, specific peptide catalysts might enhance nucleotide condensation in a manner similar to that previously discussed for peptide condensation.

There are experimental examples which support the idea that specific peptides may be able to catalyze oligonucleotide formation. Ibanez, et al. (1971b) found that polyornithine enhanced the oligomerization yield of deoxy-5'-adenylic acid and caused the appearance of about 4% of high molecular weight material in reaction in aqueous solution activated by cyanamide. Imidazole enhanced oligomer yields but histidine did not. Polyarginine enhanced condensation of nucleotides in the presence of polyphosphates (Schramm et al. 1962).

Polylysine and derivatives of imidazole catalyzed oligomerization from nucleoside triphosphates (Sawai et al. 1975; Weber et al. 1977). Polyamines such as ethylenediamine also catalyze condensations in aqueous solution (Renz et al. 1971; Usher and McHale 1976) and in the dry state (Orgel and Lohrmann 1974), suggesting that specific basic peptide sequences may be able to do similar catalysis. The active site of the modern enzyme DNA polymerase contains arginine and histidine residues (Stephen-Sherwood and Oró 1973), and ribonuclease also contains arginine and histidine residues at the active site (Mathias et al. 1964). Thus basic residues such as lysine, ornithine, histidine, and arginine are likely candidates for constituents of an oligopeptide cataly-

tic for phosphodiester bond formation. Similar suggestions have been made by Oró and Stephen-Sherwood (1974) and by Renz et al. (1971). However, none of these examples or others (reviewed by White and Erickson, 1980a) demonstrated catalytic turnover numbers greater than one, which would demonstrate regeneration.

A clay surface might further enhance the catalysis of oligonucleotide condensation by basic oligopeptides. Since both the clay surface and the nucleotides are anionic, the cationic peptides may serve to collect monomers on the clay surface. Either the clay surface or the peptide or both might then participate in catalyzing the bond-formation reactions of the nucleotides.

Another possibility which has not been explored is whether clays can catalyze the production of activated nucleotides. For instance, nucleosides, inorganic phosphate, and urea produce nucleoside 2', 3'-cyclic phosphates on prolonged heating in the solid state (Orgel and Lohrmann 1974), and this reaction might be enhanced by the presence of a clay surface.

If oligonucleotides are indeed produced in a fluctuating clay environment, the products would remain partly adsorbed on the clay surface during rehydration. Thus, the same kind of redistribution mechanism can be expected to occur as with peptides, in which monomers and part of the oligomers are desorbed during rehydration and longer-chain oligomers form during dehydration. Also, little is expected from this model in terms of specific ordering of monomers during oligonucleotide formation, though the mechanisms discussed for partial ordering of peptides may operate here also. There may be some advantages to using hypohydrous conditions in order to obtain the biologically-relevant 3'→5'phosphodiester bonding in oligonucleotides. Orgel and Lohrmann (1974) note that when they use dry (non-cycling) conditions in the absence of a template, the product is primarily 3'→5', while in aqueous solution the major product in presence or absence of a template is primarily 2'→5' or 5'→5'.

Template Replication

The attempt to demonstrate replication of oligonucleotides in aqueous solution, on the assumption that prebiotic processes should resemble those in modern cells, has revealed some difficulties (Orgel and Lohrmann 1974; Oró and Stephen-Sherwood 1974). Pyrimidines fail to bind to a polypurine template, due to insufficient stacking interaction compared to the more hydrophobic purines, which are able to bind to polypyrimidines. Furthermore, when template interactions do occur in aqueous solution, they tend to produce "nonbiological" products, such as predominantly 2' → 5' phosphodiester bonds rather than 3' → 5'. Although neither of the above shortcomings is adequate to rule out aqueous templating (for example, see Usher 1977 and Orgel 1974), it may be worthwhile to consider dehydrated systems as an alternative, and to begin to develop experimental methods to evaluate these alternatives.

If the formation of single-stranded oligonucleotides on clay surfaces (not yet demonstrated experimentally) can indeed occur, perhaps with the aid of peptide catalysts, then adsorbed oligonucleotides might act as templates for the formation of complementary oligonucleotides by base-pairing, as a crude precursor to the process of DNA replication in the modern cell. The interactions may be considerably enhanced or greatly altered by reacting in hypohydrous rather than aqueous condition.

An interesting situation exists when an oligonucleotide molecule is adsorbed on a mineral. The phosphate groups are strongly attached to the solid surface, whereas the heterocyclic rings are less strongly attached, allowing them to interact with other molecules. In this position the adsorbed oligonucleotide could serve as a template. This type of oriented adsorption could take place on positively charged sites such as crystal edges of kaolinite, or the hydroxy interlayer of interstratified clays of the chlorite type. Alternatively, the phosphate group might bind to exchangeable cations such as Mg^{++} or Ca^{++}, which are in turn bound to the clay surface.

The water content will have a great effect on the forces acting between the oligonucleotide molecule and the solid surface, and as a result, on the orientation of the adsorbed molecule and its ability to function as a template. In the hydrated state adsorption is less and the predominant interaction would probably occur between the phosphate group of the adsorbed oligonucleotide and the positively charged sites on the mineral surface. When most of the water is lost in the dehydration process, the adsorbed molecule will be attached much more strongly to the surface. In the partially dehydrated system considerable surface acidity will develop (Mortland 1970) and the heterocyclic moieties of the oligonucleotide might become protonated, which would greatly increase their attraction to the negatively charged sites of the crystal lattice (see Lailach et al. 1968). As was discussed in the section on adsorption (above) hydrogen-bonding between bases adsorbed on clays appears to be stronger than in solution, although not always following the Watson-Crick pattern.

In addition, there is the possibility that increased acidity will affect the templating abilities of nucleic acids by inducing conformational changes (Parthasarathy et al. 1976) or self-pairing (Eigen and Porschke 1970). Thus the ability of the oligonucleotide to be adsorbed and to act as a template depends on several factors such as the water content, mineral surface properties and exchangeable cations; and may be considerably different from reactions in pure aqueous solution.

Assuming that some of the adsorbed oligonucleotides are attached to the mineral surface by their phosphate groups, we can visualize the extended bases to be capable of base-pairing with mononucleotides or small oligonucleotides. The adsorbed oligonucleotides can then conceivably act as templates for their own replication. It can be assumed that a great excess of mononucleotides over oligonucleotides was present in the prebiotic environment. Since oligomers are probably adsorbed more strongly than monomers, the oligonucleotides will be relatively fixed on the solid phase whereas the mononucleotides will move more freely in the system. Given enough time, some of the monomers will diffuse and reach the templates and pair with them, either in the Watson-Crick manner or possibly with variations due to protonation, etc., and condense to form the new strand. The next step will be the separation of the template from its complementary oligonucleotide. Presumably this process will depend on changes of either the temperature (see Oró and Stephen-Sherwood 1974) or water content or both. Eigen (1971) proposed that strong temperature fluctuations were necessary to separate oligonucleotide strands in order for repeated template reaction to occur. Usher (1977) also proposed temperature and moisture fluctuations as the mechanism for strand separation.

There is a physical basis for suggesting that base-pairing of nucleotides on an oligonucleotide template could occur in dehydrated conditions rather than in aqueous solu-

tion. Complementary pairs of purine and pyrimidine derivatives cocrystallize due to both base stacking and hydrogen bonding, but while the GC pair has Watson-Crick hydrogen bonds, the AU pair has a different orientation involving the N-7 of adenine (Ts'o 1970). This is the same pattern observed by Lailach and Brindley (1969) in the coadsorption of adenine and thymine on montmorillonite. The bases or their derivatives give stable hydrogen-bonded complexes in solution with chloroform or CCl_4, with enthalpies of formation of 2–3 kcal/mole per hydrogen-bond. The stacking interaction was considerably less important in non-polar solution than in water, while the hydrogen bonding was more important (Ts'o 1970; Leng et al. 1973).

Thus it is clear that hydrogen-bonding between bases becomes *more* important in non-aqueous conditions than in aqueous solution, where water can replace the hydrogen bonds of the base pair. For example, Schramm et al. (1962) observed that polyadenylic acid enhanced the oligomerization of uridylic acid tenfold under anhydrous conditions at 55°C. Thus it is possible that highly specific and moderately stable complexes could form between oligonucleotides and mononucleotides (or short oligonucleotides) on dehydrated clay surfaces, and that condensation would result in replication of the oligonucleotide sequence. Experimental evidence on these possibilities is needed.

Since it is unlikely that complexes of sufficient stability for template-directed condensation would occur between nucleotides and oligomers at the high temperatures (94°C) used for amino acid oligomerization, the environmental scheme may have to be altered if clays are to play a role in replication. Possible alternatives include:

1. Reaction on dehydrated clays at cooler temperatures, using catalysts to promote the reaction or using activated nucleotide monomers (possibly produced on hot, dehydrated clays).
2. Reaction in the vicinity of clays in aqueous solution during the hydration/redistribution step, requiring activated monomers. (See Ibanez et al. 1971a, for a non-templated condensation of activated nucleotides on hydrated clays.) In this model the hot, dry stage separates double helices into single strands and also promotes peptide synthesis. The cool, wet stage then allows the separated oligonucleotides to replicate using activated monomers to form a new double helix, perhaps with the help of peptide catalysts. (See Usher 1977, for a similar model of hydration/dehydration in the absence of clays.)
3. Reaction on clay surfaces in a frozen environment, since the surface of a clay in frozen water contains only a few molecular layers of semi-liquid water and resembles a dehydrated clay in many ways (Anderson 1967). The template-directed condensation of adenosine 2', 3' cyclic phosphate on Poly-U was most efficient when the solution was frozen to -15°C (Renz et al. 1971) which can be interpreted as a "dehydration" but without clay surfaces present.

There is a clear need for experimental verification of the various possibilities, and all of these environments could be simulated in laboratory experiments.

Template Translation and Further Evolution

The concept of an adsorbed template may also be applied to oligonucleotides acting as crude templates for the formation of oligopeptides as a simple precursor to the process of RNA translation in the modern cell. Forces similar to those discussed in the section

on replication could operate here, including binding the oligonucleotide to the clay surface with bases oriented away from the surface; greater interaction and specificity between animo acids and oligonucleotides in a hypohydrous environment than in aqueous solution; and catalysis by specific peptides. We have tested this hypothesis (White and Erickson 1980b) and found that homopolyribonucleotides increased the yield of glycine condensation in a fluctuating clay environment to different extents depending on the base content of the polynucleotide. The results are not sufficient to prove a translation effect, since that would require that other amino acids are selected to different extents and that the selectivities are specific to each position when the base sequence is heterogeneous. However, the results are suggestive in that the different bases are altering the transition state energy in some manner to accelerate the reaction. The acceleration by polyribonucleotides but not by polydeoxyribonucleotides led to a proposed mechanism of direct esterification of amino acids to the 2'-OH of the ribonucleotide, which could provide the basis for a direct template effect.

Futher evolution is possible if the processes of oligopeptide and oligonucleotide syntheses are combined. Oligonucleotides might act as adsorbed templates for oligonucleotide replication and peptide translation, and oligopeptides might then catalyze both of these template processes. The theory of such a combined system is further developed in the autogen theory for the origin of a self-replicating chemical system (White 1980) which is an outgrowth of the ideas contained herein. That theory and the accompanying computer simulation were originally designed on the basis of known and proposed properties of the fluctuating clay environment, then later broadened as the applicability of the theory to other environments became clear. The fluctuating clay environment has the advantage of concentrating monomers and of being hypohydrous during one phase of the cycle, which may promote catalysis and increase selectivity as noted above. The adsorption of oligomers on the clay surface may be an advantage for localization of the components of the autogen, but whether clay can play that role as well as or better than microspheres or membranes, remains to be seen. Some problems with the fluctuating clay environment which may make it inappropriate for the autogen theory are the lack of evidence for nucleotide oligomerization and replication, discussed above, and the problem of how changeover occurred to reduce or eliminate the dependence on clays in later organisms. It is certainly not obvious at this time that clays are uniquely suited as an environment for molecular evolution, but an understanding of their possible role is far from complete.

Conclusion

The potential of fluctuating clay surfaces in catalyzing prebiotic reactions has just begun to be explored. We have suggested a number of areas that need to be investigated before the role of clays in further evolution can be evaluated. The features of clays that are of primary importance are the production of peptides from dilute solutions of amino acids by dehydration, the redistribution mechanism which allows higher oligomers to accumulate despite low overall yields, and the potential of the clay surface to adsorb molecules and to structure reactions in ways that cannot be achieved in aqueous solution. The potential limitations of clays are poorly understood, including competitive adsorption by other organic molecules, the effects of high

salt concentrations or uv irradiation, and the possibility of poisoning of sites on the clay surface. Since clays are chemically complex and heterogeneous, the mechanisms we have postulated are necessarily sketchy.

Several points are worth being considered in prebiotic chemistry, regardless of the involvement of clay surfaces. Hypohydrous or heterogeneous environments may provide greater selectivity in templating reactions than aqueous conditions. Specific peptides (or families of peptides) may catalyze condensation reactions which otherwise give low yields. High-yield reactions may be viewed as deleterious since the development and further evolution of more highly ordered (catalyzed or templated) condensation reactions may be inhibited by the depletion of monomers.

Like all the chemical evolution models, the present one is speculative, and certainly neither entirely new nor the only answer to the problems under study. Other heterogeneous environments, such as microspheres, coacervates, micelles, or other minerals may serve in roles similar to those we propose for clays. In the words of the late A. Katchalsky, (1973): "... any attempt to establish prebiotic chemistry or prebiotic physics is bound to be rather arbitrary. The only thing we can do is to propose a large number of models from which the geologist and the biologist will have to pick out those models which fit into a consistent picture."

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