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37 - 48

REVIEW

CLAYS AND THEIR POSSIBLE ROLE IN PREBIOTIC PEPTIDE SYNTHESIS

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Abstract: Numerous reports on various synthetic and catalytic properties of clay minerals from the past few decades are summarized, focussing on the often claimed relevance of these reactions for chemical evolution of life on the primitive Earth. Many of the data available suggest reinvestigation by more significant and more accurate methods, and indeed several of the more recent results really suggest such reinvestigation would be of great importance and worthwhile the effort.

Introduction

According to the "Bible Clay Hypothesis" man was molded from clay. Perhaps it was inspiration for the modern clay hypothesis of life. In 1944, before the role of DNA was known, Schrödinger (1944) speculated that modern genetic material was probably aperiodic crystal. Such a crystal may be the crystal of clays - full of unequivalent substitutions, irregularities and imperfections. A more complex view of the origin of life became clear, after the role of DNA as a genetic code was understood. Two important questions are: What was the primitive genetic material? Did it exist? Many scientists have thought also about the questions: What brought about selectivity in building bio-compounds? Why did only a fraction of many organic compounds survive chemical and bio-chemical development to form the first bio-macromolecules?

Lahav & White (1980) pointed out that heterogeneous environments may provide greater selectivity in template reactions than aqueous conditions. Much earlier, Cairn-Smith (1971), and also later Lawless (1988), hypothesized that clay surfaces, and specific sites therein, may have acted as direct templates in selecting repeatedly-related sequences of amino acids.

There are many possibilities concerning the specific clay surface sites which could have controlled peptide design. One possibility is the adsorption selectivity of clay minerals; this sometimes produces percentages of amino acids incorporated in peptides that differ from the starting monomer percentages (Lahav & White 1980). It is difficult to conclude that the chemical evolution of bio-compounds was self-controlled; this would mean that evolution depended only on the properties and reactivity of certain compounds, and that life is fundamentally a product of catalytic laws. It is also difficult to conclude that primitive genetic material had a significant role. Such primitive genetic material may have been a crystal of some sort, and possibly a layer-lattice silicate (Cairn-Smith 1971).

Clays are considered to be primitive genetic material as well as catalysts in the formation of bio-molecules and bio-polymers. Bernal (1951) was probably the first to point out the difficulty in synthesizing biopolymers from monomers, because the reaction components most likely occurred in primeval oceans in extremely diluted forms. The highest, assumed concentration of amino acids in the primeval ocean could be about 10^{-7} mol.dm^{-3} (Dose 1974); according to Bernal (1951) there was even only as much as about 10^{-15} mol.dm^{-3}. Bernal (1951) suggested that peptide formed in a solution hydrolyzes back to the amino acids. Because of this, he claimed that the aqueous polymerization of small molecules would have been facilitated by adsorption, and possibly heterogeneous catalysis, on the surfaces of clay crystallites. Heterogeneous polymerization does not give rise to the release of amino acids, because one effect of a clay surface is to protect peptides against hydrolysis. The protection of both monomers and polymers may have been highly important in chemical evolution. Clays and other aluminosilicates are likely to have been among the most important minerals in the origin of life, because of their relatively large surface area, catalytic activity (Theng 1974a), and widespread geological occurrence.

Clays were probably common on Earth before prebiotic evolution and have been found to be a major phase in 4.5 milliard year old carbonaceous meteorites (Nagy 1975). The oldest known metasediments (3.8 milliard years) are not very different from those we know now (Schopf 1983); however, the exact sites of occurrence and the distribution of types were probably different from those of today. Under low oxygen conditions, iron-rich clays would have played a large role (Hartman 1975).

The properties of clays and their ability to adsorb certain organic compounds and catalyze reactions are known. There is even a kind of synergy, and self-help between clay minerals and organic molecules during their formation and metamorphosis. Small organic molecules can assist the process of clay synthesis, while organic polymers can affect flocculation behavior (Cairn-Smith 1988).

Generally, the possible roles of clays in the formation of bio-polymers are (Lawless & Levi 1979):

1 – Catalysing the formation of monomers, or other simple compounds promoting the polymerization of monomers.

2 – Selecting bio-monomers from other organic compounds.

3 – Concentrating monomers on the mineral surface.

4 – Catalysing the formation of bio-polymers.

5 – Protecting bio-polymers against hydrolysis and other reactions.

Clays, their structure and properties

Several reviews and books concerning the structure, chemical, and physical properties of clays have been published (Grim 1968; Bailey 1988; Čiček et al. 1981; Newman 1987). Clays are phyllosilicates composed mainly of layered fine particles, sized from a few µm to several hundred µm. Layers consist of sheets of octahedrally coordinated magnesium or aluminium and tetrahedrally coordinated silicon. When an octahedral sheet is linked to a tetrahedral sheet, a 1 : 1 layer type is formed (e.g. kaolinite); when an octahedral sheet is between two tetrahedral sheets, a 2 : 1 layer type is formed (e.g. montmorillonite). The unequivalent substitution of Al(III) for Si(IV) (in tetrahedral sheets) or of Mg(II) for Al(III) (in octahedral sheets) brings about a net negative charge of layers. The negative charge is balanced by hydrated cations (Ca^{2+}, Na^+, K^+ and others) located in interlayer spaces. These cations can be exchanged for others; clay minerals are natural ion exchangers. Polyvalent inorganic cations are able to occupy exchange positions in general with higher affinity than monovalent cations; some large organic cations even cannot be reexchanged by any hydrated inorganic cations. Large organic cations are held by electrostatic forces as well as by Van der Waals forces. The layers of low charged kaolinite are held together by hydrogen bonds, while montmorillonite particles are joined less firmly by electrostatic forces. Because of this, montmorillonite swells in water and other solvents, and various reactions take place in the interlayer spaces. Montmorillonite swelling in water is affected by the amount and type of interlayer cations (size and charge), the layer charge locality (tetrahedral and octahedral sheets), and the presence of other compounds in the interlayer spaces (organic cations convert clays to hydrophobic material). Interlayer spaces, between kaolinite layers (held together by hydrogen bonds), are not accessible to water. The external surfaces of particles and edges of layers are the main sites for chemical interaction, and the specific surface area of kaolinite is much lower than that of montmorillonite. With the exception of a negative charge due to isomorphic substitution, the layers are charged at their edges and at the sites of broken bonds and lattice imperfections. At these sites the layers of clays can even be positively charged (Hower 1970) and the charge density differs from the density of the charge located on the basal surfaces (Peigneur et al. 1975; Maes at al. 1985). On the other hand, also unequivalent substitution in octahedral and tetrahedral sheets and negative charge distribution on basals are not homogeneous (Lagaly 1979). Besides layer charge, another special property of many clay minerals is their large surface area. The highest values of specific surface areas reach several hundred $m^2.g^{-1}$.

Clay surfaces exhibit the ability to convert an adsorbed base to its conjugate acid, the surface has Brönsted and Lewis acid sites. This is a significant factor in the catalytic activity of clays. Surface acidity is affected by the clay composition and structure, the type of exchangeable cations, the origin of the layer charge, and the amount of water. A decrease in the amount of water converts Brönsted acid sites to Lewis ones (Solomon & Roser 1965). Acid sites on edges and basals are different not only in pK_A values (Frenkel 1974) but also in the softness and hardness of their acidity (Maes et al. 1985). Except for their ability to catalyze protolytic reactions, clays play a part in redox processes (convertion of structural iron $Fe^{2+} <=> Fe^{3+}$ and catalytic activity of other transitional metals present in clay layer lattices) (Solomon 1968). Clays are cation exchangers and can have various exchangeable cations in the interlayer spaces. These cations exhibit different chemical reactivity and significantly affect catalytic and other properties of the mineral (Lawless & Levi 1979). Some transitional metal cations affect protolytic and redox reactions, and the formation of a complex with sorbed compounds, and thus influence the ion-exchange, the sorption, and the reaction between sorbent and sorbate.

Amino acid formation

A large number of papers have been published concerning amino acid synthesis from various simple compounds or elements such as carbon, hydrogen, water, carbon monoxide, carbon dioxide, ammonia, ammonium salts, methane, hydrogen cyanide, formaldehyde, etc. The catalytic effect of clays in these reactions was demonstrated. Clays often enhanced the reaction yield or stabilized the reaction product.

Using kaolinite as a catalyst, Akabori (1959) synthesized not only glycine but also polyglycine from a mixture of formaldehyde, ammonia and hydrogen cyanide at about 130 °C. Some amino acids were prepared through the hydrolysis of KCN under very mild conditions (only 70 °C) in the presence of montmorillonite (Aragon dela Cruz & Viton Barbolla 1979). In this case, the mineral acted as a receptor to the amino acids and stabilized them . Some amino acids were formed by means of UV irradiation of formaldehyde and ammonium salt solutions, when clays were present (Pavlovskaya et al. 1960). Several amino acids (mainly glycine, aspartic acid, threonine and valine) and many other organic compounds were formed using a gaseous mixture of carbon monoxide, ammonia, and hydrogen in the presence of montmorillonite and zeolite after two days of heating at 250–325 °C (Fripiat et al. 1972). Yoshino et al. (1971) synthesized several amino acids like glycine, alanine, sarcosine, aspartic acid, glutamic acid, arginine, lysine, hystidine, ornithine and also other bio-molecules like purines and pyrimidines via the reaction of CO, H_2, NH_3 at 200–500 °C in the presence of montmorillonite. Five proteinaceous and six nonproteinaceous amino acids were synthesized from methane and N_2 in the presence of montmorillonite in water (Shimoyama et al. 1977). Glycine, DL-alanine, DL-aminobutyric acid and sarcosine were the major amino acids produced. The effect of clay was that larger amino acid molecules were produced. The formation of polypeptides and amino acids is achieved by mixing formaldehyde and hydroxylamine in water with small amounts of the compounds of Cu, Co, Mn, Mo, Fe, Zn, potassium phosphate and clay minerals - kaolinite or montmorillonite (Ventila & Egami 1976). The reaction mixture was shaken for 120 h at 80 °C. The yield of the reaction (mainly polymerization) was lower when the clays were not present in the reaction medium. Glycine was the main component both in the low and the high molecular fraction. Besides glycine, the low molecular fraction contained serine and alanine. A lot of amino acids were found in the high molecular fraction but only in small amounts. Kaolinite gave the highest yield among various clays.

Some of the reactions mentioned above proceed also without the presence of clays. However, the presence of clay significantly influences the yield of the reactions and/or the composition of the product.

General consideration on amino acid sorption, concentration and polymerization

Many conclusions about amino acid sorption on clay minerals are presented in the chapter "Complexes with amino acids and peptides" of the book of Theng (1974b). Sorption depends on the type of amino acid (its basicity) and is extremely sensitive to the pH value of the reaction solution. The pH value of the liquid phase and the acidity of the solid phase influence the form of the amino acid. Cations are sorbed readily and much lower amount of amino acid is sorbed when the amino acid forms zwitterions, and anionic amino acid can be adsorbed weakly in very small amounts at the clay particle edges. In the case of cations, the ion-exchange reaction proceeds and zwitterions are held by dipole-dipole interactions. On the other hand, it has been speculated that strongly adsorbed amino acids (ion exchange) are not as active in polymerization as less strongly adsorbed molecules at the edges of the layers (Lahav & Chang 1976).

Besides amino acid basicity and the pH value of the solution, sorption is affected by molecular shape, and more importantly, molecular mass. Both larger peptide and amino acid molecules are more strongly sorbed due to Van der Waals forces. On the other hand, the sorption on different clay minerals depends on the type of mineral, its cation exchange capacity and the surface area, as well as on the presence of the cations able to form complexes with amino acids (Cu, Zn, Co, etc.), which enhances the sorption.

Under neutral pH conditions, assumed for the primeval ocean, amino acids are not readily adsorbed on clay minerals. In spite of this, it was suggested that clay surface is the most likely surface for the concentration of small bio-molecules, the first step leading to polymerization (Bernal 1951; Lahav & Chang 1976; Paecht-Horowitz & Katchalski 1973; Lahav et al. 1978). There is one possibility for the sorption of amino acids in primordial conditions. Certain metal ions, located at cation-exchange positions, change clay minerals into good adsorbers of bio-monomers as amino acids or nucleotides in the pH range of the primitive oceans (Lawless 1988), and even catalyze their polymerization as well (Lawless & Levi 1979). Some of these metal cations are sorbed from extremely low concentrations, e.g. copper from a water solution that contains only 2 ppm of cation (Heydemann 1959). Moreover, the drying of clay - amino acid mixture would increase the clay surface acidity and could convert amino acids into their cationic form (Lahav & Chang 1976).

Lahav & Chang (1976) collected all available data on the sorption of amino acids on the natural exchange forms of clay minerals, and considered the possibility of amino acid polycondensation. Based on the concentration of amino acids assumed for the primordial ocean, the surface area of clay minerals, and the sorption ability of amino acids, the distance between two neighboring molecules would be at least 1000 nm, thus making peptide formation unlikely. Lahav & Chang (1976) pointed out that all published experiments concerning amino acid condensation in a solid-liquid equilibria clay-amino acid solution deal with systems which are too concentrated. In most of these studies, the conditions were chosen to enable maximum yield using organic solvents, unstable compounds, highly concentrated solutions or mineral ion exchange forms of Cu, Ni, Zn or other metal ions. Finally, they concluded that amino acid polymerization could have been more successful if there had been specific sites on clay minerals with better local concentration ability and if sites with temporarily higher concentrations of organic molecules had been taken into consideration. These sites may not only have had different adsorbtion properties, but also different catalytic properties. The main types of sites on clay minerals are (Lahav & Chang 1976):

1 – Edges and planar surfaces.

2 – Surfaces of tetrahedral (SiO_4 tetrahedrals) and octahedral (AlO_6 and MgO_6 octahedrals) sheets.

3 – Crystal lattice imperfections, cracks and distortions.

4 – Exchange sites occupied by different cations.

5 – Brönsted and Lewis acid sites.

6 – Hydrophylic and hydrophobic zones.

7 – Sites with different layer charge densities.

8 – Sites containing different elements in solid phases.

The future investigation of prebiotic reactions on clay minerals requires studying the effect of these different sites on the sorption, yield and mechanism of polymerization reactions (Lahav & Chang 1976).

When clay minerals are able to collect amino acid molecules, there is a chance for peptide synthesis catalysis. However, amino acid molecules are relatively stable. The main problem of peptide synthesis is to overcome the thermodynamic barrier to form peptide bonds. This can be approached by heating and activating monomers, and by using condensing agents which, in many cases, are not formed under the assumed prebiotic conditions (Lawless & Levi 1979). In the case of clay minerals, one plausible mechanism for condensing amino acids is a catalyst which binds the simpler stable molecules and activates them for polymerization reaction (Collins et al. 1988). The yields of the polymerization of unactivated amino acids are low when natural forms of clay minerals are used, but are sufficient for the long term development of bio-compounds. On the other hand, it is suggested that high-yield condensation reactions do not create a secondary structure of peptides. These reactions may have been harmful for development, and more highly ordered condensations may have been inhibited by the lack of monomers (Lahav & White 1980).

A crucial factor in peptide synthesis on clays is the increase of the adsorption of oligomers with the increase of oligomer sites; given this, desorption becomes less likely as oligomer size increases (Theng 1974b). Thus the growth of long chain oligomers is preferred to the higher yield of shorter chains, and so controls the reaction.

On the basis of summarized, published data on sorption and condensation of amino acids on clays and clay minerals, Lahav & Chang (1976) studied the possibility of this reaction in these different environmental systems:

1 – an ocean-sediment system;

2 – a lagoon bed dehydrated by evaporation;

3 – the surface of frozen sediment;

4 – a fluctuating system where hydration and dehydration take place in a cyclic manner.

They concluded that if pH was approximately neutral in the prebiotic ocean, low adsorption of amino acids is expected and thus condensation is unlikely. Sorption is higher and polymerization is more probable in frozen and dehydrated systems. The best conditions for condensation are in fluctuating systems.

Peptide formation from amino acid–clay system; reactivity of optical isomers

Glycine was polymerized on both bentonite and kaolinite while wetting-drying and heating cycles with temperature fluctuation were applied. The result was a better yield of oligopeptides and diketopiperazine than when performed without clay minerals (Lahav et al. 1978; White & Erickson 1980). The cycles imitated drying and wetting in small lagoons or lakes and thus reflected possible primordial conditions. The amount of diglycine formed increased with higher temperature and was easily detected after one week at 94 °C. The rate of diglycine formation was two and a half to four times slower at 80 °C. At 60 °C, only traces of diglycine were detected after 35 days (Lahav et al. 1978). Oligopeptides prepared using kaolinite contained up to five segments of glycine. With bentonite, no oligomers higher then triglycine were detected. The total yields of oligopeptides formed, using wetting-drying and temperature fluctuation cycles are better than the yields when only temperature fluctuation cycles are used. Cyclic wetting of samples can bring about the redistribution of monomers and oligomers which affect the yield; however, the hydrolysis of oligomers can also occur. Over a large number of cycles the balance of oligopeptide bond formation and destruction can provide a generation of oligomers with non-random sequences of monomers.

Highly promising results were obtained in experiments which used diglycine solution as a starting medium for polymerization (Bujdák et al. 1994; Bujdák et al. 1995a, b). Only 10 % of diglycine hydrolyzed to glycine at 80 °C, confirming the ability of montmorillonite to protect oligomers against hydrolysis. The yields of triglycine and tetraglycine obtained from diglycine were much higher than those of diglycine and triglycine when glycine was used. Clays' possible role in peptide synthesis, to lengthen small peptides, was thus experimentally proven. Higher reactivity of dimer than monomer results from the assumed reaction mechanisms of clay-catalyzed peptide bond formation (Bujdák et al. 1995b). Activation of amino acids at the edges of clay particles (see below) does not lead to the high yield oligomerization because the reaction centers are probably too distant for small amino acid molecules. In cases of longer oligopeptide molecules, amino group of first activated molecule is able to reach and thus to react with activated carbonyl of the second oligopeptide. Besides that, the formation of cyclic anhydrides (formed directly only from dimer by intramolecular condensation reaction) is at least just as important for peptide chain elongation on clays, as is the activation of oligomers at clay particle edges (Bujdák et al. 1995b).

Spectroscopic observation of the intermediate was proposed and confirmed the mechanism of the formation of acyl aluminate or silicate at the edges of clay layers (esters of carboxylic acids) (White & Erickson 1980). An acyl-Si bond appears to be a high-energy intermediate that is important in some bio-polymerization processes (White et al. 1984; Jewett & Lawless 1981). Collins et al. (1988) studied a theoretical model (ab initio quantum mechanical calculation) of amino acid activation by anhydride formation with tetrahedral silicate and aluminate in clays and phosphates. They calculated:

1 – The thermodynamics of activated complex formation and its susceptibility to hydrolysis.

2 – The properties of the activated complex, and its ability to form peptide bonds.

The extent of anhydride formation and the stability against hydrolysis were in the growing order: P, Si, Al. The relative ability of the anhydrides to promote peptide bond formation was evaluated using thermodynamic (heats of reactions) and chemical reactivity (electrophilicity of carbonyl carbon and nucleophilicity of the oxygen) criteria. According to the heats of the reactions, this ability is predicted in the growing order: Al, Si, P and the phosphate activated complex is the only one which gives an exothermic reaction. The value of the heat of the Si intermediate formation was positive but very small. According to chemical reactivity criteria, there are two possibilities: if the reaction has a dominantly nucleophilic character, Al sites should be more active than Si sites and if the electrophilic character is dominant, the order would be reversed.

In general, Al sites can serve as stable sites (against hydrolysis) where peptides may be formed, and Si sites are more effective in amino acid activation for reaction. Neighboring Al impurities can play an important role in polypeptide synthesis. Al protection against hydrolysis seems to be very important in peptide formation catalysis. Pure alumina was found to be better than pure silica for polypeptide formation, probably due to anti-hydrolysis stability (White et al. 1984).

The thermodynamic feasibility of a hypothetical lysine/dilysine condensation reaction at 90 °C was evaluated over a range of experimental conditions by combining the measured Gibbs energies of a lysine/dilysine cation exchange on kaolinite and on montmorillonite, and the Gibbs energies for condensation in a homogeneous solution. The results indicate that the thermodynamic barrier to surface condensation of unsubstituted amino acids on clay minerals is not lower than it is in a homogeneous solution (Flegman & Scholefield 1978).

There are several works concerning the preferential synthesis of peptides from L-isomers of amino acids to D-isomers. Degens & Mathéja (1968, 1970) reported synthesis of peptides of a high relative molecular mass (>10 000) by the condensation of L-amino acids on montmorillonite and kaolinite in dried state at 140 °C. The reaction proceeds on a kaolinite surface also under milder conditions below 100 °C.

It was claimed that kaolinites preferentially polymerized the L-optical isomers of amino acids over those of the D-isomers (Degens et al. 1970; Jackson 1971). This would be a very important fact, because proteins in a living system are composed of L-amino acids. Jackson (1971) measured the yield of polymerization of L- and D-isomers and of the racemic mixture of aspartic acid on kaolinite at 363 K after 32 days. The reported yield of polymerization of aspartic acid on kaolinite was up to 25 %, and the amount of peptide reportedly formed from L-isomer was about 10 times higher than that from D-isomer. The racemic mixture polymerized at an intermediate rate. The reaction also proceeded without clays but did not favour L-isomer (Jackson 1971). The preferential catalysis of one of two optical isomers could be explained by the amino and carboxyl group interaction with the surface of a mineral. Amino and carboxyl groups of amino acids are connected to aluminium at the edges, but dipole-dipole and H-bonding interaction also play parts in the sorption of monomer and in the reaction as well (Jackson 1971). L-isomers could preferentially bond at the edges of kaolinite particles, perhaps because of the possible enantiomorphy of crystals (Bailey 1963). The other, simplier explanation is the presence of impurity of optically active mineral in clay used. However, the effect of kaolinite on aspartic acid polymerization was not confirmed by other laboratories (Flegman & Scholefield 1978; Flores & Boner 1974). No polymer was detected in L- and D-aspartic acid incubated with Na- or Al-kaolinite. Compounds found in the reaction mixture of Jackson's work (1971) were probably cyclic dimers (for aspartic acid) and lactam pyrrolidone carboxylic acid (for glutamic acid) (Flegman & Scholefield 1978). These discrepancies still have not been resolved.

Several years later Bondy & Harrington (1979) investigated the adsorption of D- and L-isomers of leucine and asparagine and claimed that L-isomers bound to bentonite a much greater extent than the D-isomer. Moreover, the bentonite surface was reported to prefer adsorbing the D-isomer of glucose, common in plants, to adsorbing the L-isomer. Stereospecific sorption and preferential deamination of glutamic and aspartic acids catalyzed by montmorillonite were recently published (Naidja & Siffert 1992). L-isomers were sorbed and deaminated better than D-isomers. The origin of clay chirality is still unknown and the authors' hypothesis is that L- and D-isomers have different abilities to be sorbed because of the different orientation of their functional groups. The difficulty of the sorption measurements are caused by very low amounts of amino acids sorbed on clay which was determined from slight change of amino acid concentration in solution over suspensions. Unfortunately, neither experimental details about amino acid determination, nor standard deviations of sorbed amounts were presented in this work.

If the preference to sorb and catalyze L-amino acids is confirmed, it might turn out to be of great significance in explaining why chemical evolution preferred peptide formation from L-isomers to that from D-isomers. Probably both L- and D-isomers were present in peptides on primitive Earth, but only L-configuration, preferentially formed, survived the evolutionary process (Wald 1957). When peptides are atactic they have no potential for life because of their inability to form secondary structures due to steric hindrance and intramolecular repulsion (Wald 1957; Miller et al. 1967; Gratzer & Cowburn 1969).

Formation of hippuric acid from glycine in the presence of clays

The smectite catalytic ability to promote amino acids' polymerization was demonstrated by the synthesis of hippuric acid from glycine and benzoic acid in ether. In the presence of ethylphosphate, long-chain peptides were obtained (Kassaissia & Siffert 1980). The formation of hippuric acid from glycine and benzoic acid in water is not as easy as in ether and gives much lower yields. The reaction in water is possible at about 60 °C and depends on the type of exchangeable cations. The best results have been achieved with montmorillonites containing transition metal ions such as Cu^{2+}, Ni^{2+} and Zn^{2+} that form the complex between these metal cations and glycine. This complex is probably an intermediate state of this reaction.

Peptide formation from an amino acid – clay – transitional metal ion system

Recently, the ability of some transitional metals to catalyze amino acid polymerization was discovered. Salt induced peptide formation (Cu(II) in NaCl solution) gives high yields of oligomerized amino acids up to several per cent of the initial amino acid amount (Rode & Schwendinger 1989; Schwendinger & Rode 1989, 1991; Rode et al. 1993a, b).

Several reports have been published claiming good yields of peptide formation in the presence of clay containing certain metal ions in the exchangeable positions. Some of these works suggested peptide bond formation during sorption on clay. Siffert & Kessaissia (1978) claimed that sorption of cysteine and proline on Na-montmorillonite and of lysine on Cu-, and Ni-montmorillonite is followed by polymerization. The oligomerization of histidine seemed to occur under ambient conditions and mainly after in vacuo heating with Al montmorillonite, but not with Cu-, Ca- or Na-clays (Heller-Kallai et al. 1973). Peptide formation was determined by insufficient infrared spectra data and has not yet been confirmed or denied by other scientists using modern methods of analysis.

Using Cu-, Ni-, Zn-, and Na-bentonites, the effect of cations was observed on the condensation of glycine and alanine (Lawless & Levi 1979). The clay-amino acid mixture was dried at 45 °C for two days, heated at 94 °C for five days, and a small amount of water was added. These steps were repeated eight times. Copper was the most effective metal, Cu-bentonite produced 6.2 % glycine oligomerized to di-, tri-, tetra-, and pentaglycine while the degree of alanine polymerization was at 2.0 % and only dialanine was produced. Sodium was the least effective, only 0.9 % of glycine and 0.7 % of alanine was oligomerized. The preferential oligomerization of glycine over alanine is most and least pronounced in Cu- and Zn-bentonite, respectively. These observations suggest that amino acids could have been selected from the mixture, and this selection would have been affected by the concentration of exchangeable cations present. The simultaneous interaction of clays and metal ions with organic molecules could have played a role in the processes leading to the formation of biologically important compounds (Lawless & Levi 1979). Higher yields of oligomers, after glycine polymerization using Cu-montmorillonite at 80 °C, were not observed, compared to those using Ca-montmorillonite (Bujdák et al. 1994, 1995a). After short reaction time Ca-montmorillonites exhibited at least the same ability to catalyze this reaction as Cu-montmorillonite. After longer reaction only a very small amount of glycine oligomers were detected in reaction medium obtaining Cu-montmorillonite. This is mainly due to the oxidation of glycine (decreased to 10 per cent of the initial concentration) and the reaction products by copper cations.

Peptide synthesis from an amino acid – adenosine triphosphate (ATP) – clay system

Cells in organisms produce peptides by using energy from ATP. But ATP prebiotic synthesis is not known and moreover ATP is unstable and rapidly decomposes under assumed prebiotic conditions when oligopeptides are synthesized from amino acids. Rishop et al. (1982) see the role of clay minerals as stabilizors and protectors of this supply of energy. They studied the sorption of ATP and ADP on montmorillonite, kaolinite and $Al(OH)_3$ and their influence on the polymerization of glycine. The sorption of ATP and ADP was higher on Zn and Mg montmorillonite than that on Na montmorillonite, the effect of cations in kaolinite was very small. Peptization in reaction system without clay proceeded at 70 °C with yields of 0.25 %, but the presence of clay prolonged the life of ATP, leading to a higher condensation rate of glycine molecules, and diglycine could be formed even at temperatures lower than 50 °C (Rishop et al. 1982).

Peptide synthesis from amino acid adenylates

Many studies have been carried out using activated adenylate derivates, especially alanine adenylate. These are produced by cellular systems before protein synthesis and can produce short chain oligopeptides in aqueous solutions in the absence of clay.

Paecht-Horowitz et al. (1970) observed that montmorillonite could catalyze the formation of long chain polypeptides from amino acid adenylates. Kaolinite exhibits very little activity, suggesting that adenylate derivates must be intercalated before reaction. However, Brack (1976) found that montmorillonite-mediated polymerization of amino acid adenylates does not lead to long chain polypeptides and that montmorillonite showed only weak catalytic properties. But the catalytic effect of montmorillonite was confirmed later by several experiments. The crucial problem of the hypothesis of prebiotic peptide synthesis from amino acid adenylates is the preparation of amino acid adenylates (substrate for peptide condensation) under prebiotic conditions. This was claimed (Paecht-Horowitz & Katchalski 1973), but reproduction of these results was unsuccessful (Warden et al. 1974).

Montmorillonite catalyzed polycondensation of amino acid adenylates is shown in the scheme (Paecht-Horowitz et al. 1970):

$$A{-}P + A{-}P \Rightarrow A_2{-}P + P'$$

$$A_2{-}P + A{-}P \Rightarrow A_3{-}P + P'$$

$$A_3{-}P + A_2{-}P \Rightarrow A_5{-}P + P'$$

A-P is activated amino acid adenylate, A and P denote amino acid and adenylate segments respectively, A_2, A_3 and A_5 are oligopeptide chains. Formed free adenylic acid is marked as "P′".

The number of monomers in the polymer chains formed was between 30 and 56; all formed peptides carried adenilic acid residues and little or no monomer was observed. Formed adenylic acid inhibits reaction due to the reactive amino group but it is able to diffuse out from the interlayer spaces.

The reaction of amino acid adenylates in the presence of montmorillonite is a little different from the one in the absence of montmorillonite (Paecht-Horowitz et al. 1970). Amino acid adenylates are sorbed on montmorillonite faces and edges by ion exchange and ion-pair mediated polar sorption. Peptides are arranged in well-defined layers (Eirich 1971). Only the edges of the layers have to be free for polymerization of amino acid adenylates, but the accessibility of the interlayer spaces increases the reaction yields. In the interlayers, all the repulsion forces of molecules are neutralized and the probability of polymerization increases (Paecht-Horowitz 1977a). This mechanism was verified by the adsorption and polymerization of DL-alanine adenylate on montmorillonite which was studied after blocking the edges and faces of layers with Na hexametaphosphate and histidine, respectively. Polymerization occurred only when the phosphate part of the monomer was sorbed on the edges, and it took place in the interlayers, but only in spaces neighboring the edges (Paecht-Horowitz 1978a). Aminoacyladenylate conformation related to polypeptide formation was studied. The effect of montmorillonite was to compensate for the anionic and cationic charges and to prevent the formation of a ring. When the amino groups remained neutral, and the ring was not stable, steric and electrostatic conditions were good for polypeptide synthesis (Broch et al. 1981).

A different reaction yield was found when different exchanged forms were used. The polymerization rate of alanine adenylate on montmorillonite saturated with different cations increases in the growing order: Mg, Ca, Fe, Al, Na (Paecht-Horowitz 1978b). The yield of polymerization of amino acid adenylates was much lower on non-swelling Al-montmorillonite than that obtained in the presence of swelling Na-montmorillonite. The changes of interlayer spacing enhance the polymerization yield (Paecht-Horowitz & Lahav 1977). The rate of polymerization of alanine adenylate depends on the composition and type of smectite, and increases in the growing order: montmorillonite, nontronite, hectorite. Only hectorite was able to catalyze the polymerization of lysine (Paecht-Horowitz 1978b).

Polymerization using other derivates is possible. The polymerization of serine guanylate in water proceeds in the same way as that of serine adenylate. However, the rate of polymerization of serine guanylate in the presence of montmorillonite is lower than that of serine adenylate. Guanylic acid is bound more strongly to the edges of layers of montmorillonite; it blocks the layer edges and inhibits their catalytic activity (Paecht-Horowitz 1981). Copolymerization of amino acid adenylates was studied. Only smaller amino acids were able to polymerize (Paecht-Horowitz 1973).

The spontaneous polymerization of amino acid adenylates proceeds on Na-montmorillonite in dilute, neutral suspension after polypeptides have been pre-adsorbed on the clay (Paecht-Horowitz & Eirich 1988). Preadsorbed polyalanine and polyhydroxyproline on montmorillonite influenced the polymerization of alanine. The ratio between the amount of peptide adsorbed and the amount of clay was important for the yield of polymerization. An excess of peptide disturbed the polymerization, but a certain amount of preadsorbed peptide induced better reaction results (Paecht-Horowitz 1984). This can be explained by the role of the fractional occupation of the individual intercalation layers of the polypeptides. The adsorption of monomer molecules increases towards the 1st complete monolayer, and eventually to the 2nd and 3rd complete interlayers. Spaces which correspond to an intermediate occupation are good for the polymerization of sorbed monomers, but those nearly empty or filled did not give such high yields (Paecht-Horowitz & Eirich 1988).

Other peptide synthesis involving clays

The condensation of glycine in the presence of kaolinite was enhanced by polyribonucleotides as polyadenylic acid (poly-A), polycytidylic acid (poly-C), polyguanylic acid (poly-G) and polyuridylic acid (poly-U) (White & Erickson 1981). Polydeoxyribonucleotides gave no enhancement. Oligopeptide yields were greatly reduced in the absence of clay. A small preference to catalyze the reaction was observed in the growing order: poly-C, poly-A and poly-U, poly-G at high density of polynucleotide on the clay mineral surface; and in growing order: poly-A, poly-C, poly-U, poly-G at low density. The best polymerization yield was 20 % with equal amounts of poly-A and glycine. The reaction mechanism was most likely as follows: glycine activated on the clay surface probably forms some intermediate, then esters are formed between glycine and the 2'-OH groups of polyribonucleotides. A peptide bond is formed between adjacent amino acyl esters.

The synthesis of peptides on clay surfaces could be autocatalytic as demonstrated by the catalytic effect of histidyl-histidine on clay surfaces (White & Erickson 1980). Histidyl-histidine is a catalyst for glycine oligomerization during wetting-drying cycles on kaolinite. The formation of oligoglycine was enhanced threefold. Imidazole, histidine and N-acethylhistidine gave only small enhancements. Histidyl-histidine was termed, therefore, as "proto-enzyme", and 1 nmol produced 52 nmol additional oligoglycine. Unfortunately it was not reported, whether also heterooligomers obtaining glycine and histidine segments had been analyzed after the reaction.

High temperature synthesis of peptides

Several papers have been published concerning peptide formation at higher temperatures, in general not accepted as possible prebiotic conditions for peptide formation due to possible occurrence of destructive side reactions. The significance of these works in the investigation of prebiotic peptide synthesis is therefore lower. On the other hand, some authors have suggested that peptides could have been synthesized under these conditions on local high temperatures places (on lava, hydrothermal vents).

Cloos et al. (1966) found from IR spectra that a complex between a carboxyl group and an ammonium group of another molecule is dehydrated at about 430 °C and a secondary amide linkage of glycine or alanine is formed. It is likely that heating the vermiculite-ornithine complex produced peptides. This was also proved, however, only by the identification of peptide bonds in an infrared spectrum (Mifsud et al. 1970). Rak (1989) studied the reaction of amino acids on the surface of montmorillonite and vermiculite. At 180 °C, peptide bond formation occured on montmorillonite. However, Ovcharenko et al. (1969) did not notice any evidence of the formation of a secondary amide band in any of the IR spectra of lysine-montmorillonite complex after applying heat up to 215 °C. Peptide-like polymers and silicates were formed hydrothermally, at 250 °C, from a mixture water solution of glycine, alanine, aspartic acid, and valine in glass tube (Yanagawa & Kojima 1985). Peptides and silicates created microspheres, and an aminosilyl bond was found.

Besides clay catalyzed reactions, also enhanced temperature transformation of amino acids and oligopeptides on silica or alumina has been studied, yielding to higher oligopeptides, cyclic anhydrides (Basiuk et al. 1991a, b; Gromovoy et al. 1991) or bi- and tricyclic amidines (Basiuk 1992).

Other possible prebio-catalytic properties of clays

Modified clays are not only able to catalyze amino acid and peptide formation, but can also selectively catalyze other bio-reactions and the synthesis of other bio-monomers and polymers. Cu-smectite with pyridoxal phosphate exhibits pseudo-enzyme properties such as selectively deaminating DL-glutamic acid and glutamine (Mortland 1984). Highly similar, aspartic acid and asparagine remain unchanged. Pyridoxal phosphate reacts with glutamic acid and pyridoxamine phosphate and α-ketoglutamic acid is formed. The role of Cu-smectite is the catalytic deamination of pyridoxamine phosphate to initial pyridoxal phosphate.

At pH = 7 clays are able to selectively decarboxylate various amino acids with the exception of those used by our present biology (Levi & Lawless 1977). Montmorillonite decarboxylates isocitric acid (Naidja & Siffert 1989) and deaminates glutamic acid (Naidja & Siffert 1990). This implies that the interaction of amino acids with clay minerals could be important in prebiotic chemistry.

Clay minerals can catalyze the reactions of other bio-compounds. Evaporation and mild heating of urea and ß-alanine in the presence of clay minerals led to the formation of 5,6-dihydrouracil, which was converted to uracil. Adding acetic anions to this system resulted in the formation of thymine (Schwartz & Chittenden 1977; Chittenden & Schwartz 1976). Cu-montmorillonite converts adenine and adenosine to hypoxanthine and inosine respectively (Strašák 1991). Melanoidins were formed by treating glucose with glutamic acid, valine and lysine. The formation of N-rich polymers is favored with great affinity for clay minerals (Hedges 1978). Kaolinite can catalyze the synthesis of carbohydrates and lipids (Theng 1974a). Recently much work concerning clay catalysis of nucleotide oligomer formation has been done by Ferris and his coworkers (Ferris et al. 1990; Holm et al. 1993; Prabahar et al. 1994; Ferris & Ertem 1992, 1993a, b). Some aspects of the possibility of the role of clay minerals as prebio-catalysts still are yet to be revealed; thus this topic continues to be of much interest to scientists today.

Conclusions

The rewiew of all the works performed on clay chemistry, with special regards towards a possible prebiotic and evolutionary relevance, certainly reveals that clay minerals could have played a significant role in many aspects on the primordial earth, when precursor molecules of life were created. On the other hand, many of the results reported so far have never been confirmed or challenged by modern analytical chemistry methods and other research groups. In the light of some recent findings that clay minerals can undoubtedly play an important part in peptide synthesis by their chain-elongating ability, it seems most worthwhile to reinvestigate critically also some of the other interesting aspects of a possible prebiotic clay chemistry. With the help of modern analytical instrumentarium and, based on critical considerations of realistic prebiotic scenarios, such a new focus on this topic can certainly shade new light on chemical evolution on the way to the origin of life.

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