

Mineral Catalysis and Prebiotic Synthesis: Montmorillonite-Catalyzed Formation of RNA

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Montmorillonite, a clay mineral formed by the weathering of volcanic ash, may have played a central role in the evolution of life. Because of its structure, montmorillonite tends to adsorb organic compounds and this contributes to its ability to catalyze a variety of organic reactions critical to scenarios of life's origins. We have shown experimentally that RNA molecules bind efficiently to clays and that montmorillonite can catalyze the formation of longer molecules (oligomers), thus lending support to the RNA world hypothesis. This theory proposes that life based on RNA preceded current life, which is based on DNA and protein.

KEYWORDS: prebiotic synthesis, RNA world, montmorillonite, RNA, catalysis

INTRODUCTION

More than half a century ago, Irish physicist John Desmond Bernal and Swiss geochemist Victor M. Goldschmidt independently proposed that clay minerals may have played an important role in prebiotic synthesis (Bernal 1949; Goldschmidt 1952). I concur that mineral catalysis must have had a central role in prebiotic synthesis because most uncatalyzed reactions start from simple precursors like hydrogen cyanide (HCN), formaldehyde (HCHO), carbon monoxide (CO), hydrogen sulfide (H₂S), possibly ammonia (NH₃), and other simple organics. These small molecules lack the three-dimensional conformations that can restrict reaction pathways of surface-bound molecules. Consequently, an indiscriminate array of reaction products is synthesized, as was found in the classic Miller-Urey experiment, where diverse groups of organic compounds formed. In that experiment, the smallest molecules, such as the simple amino acid glycine, were produced in the greatest amounts (Miller 1957). Similarly, the Murchison meteorite contains seventeen classes of organics compounds that seem to have been formed by random processes (Cronin 1998).

Given this chemical diversity, a process like catalysis is required to select just those compounds that can react and combine to form the complex biomolecules and biopolymers that initiated the first life. If, as most scientists believe, these reactions took place in the presence of water, then catalysts will also be needed that selectively bind compounds of similar structures present in solution, such as amino acids or nucleotides, so they have an enhanced concentration on a mineral surface. The catalyst will then

enhance the reaction of the selected species to form biopolymers. Catalysis also accelerates the reactions of the bound molecules so that the formation of the biomolecules proceeds more rapidly than their rates of destruction by water hydrolysis.

In this review I discuss the role of clay minerals in catalyzing reactions of organic compounds, especially those reactions associated with prebiotic processes. In particular, I describe our findings on the role of montmorillonite clay on the assembly of nucleotides to form short RNA polymers.

CLAY MINERALS AND CATALYSIS

Volcanic ash, which covers areas over hundreds of kilometers wide around the volcanic source, weathers to give rise to a wide variety of clay minerals. In the western United States, for example, long periods of volcanic activity deposited ash into ancient seas, where it weathered into vast deposits of montmorillonite clays up to 16 m thick.

The simple crystal structure of clays consists of layers of corner-linked SiO₄ tetrahedra bound to layers of edge-linked AlO₆ octahedra (FIG. 1). These sheets bind to each other like "a deck of cards" by van der Waals forces and interlayer cations. The idealized chemical formula for montmorillonite clay is Al₄Si₈O₂₀(OH)₄, though the actual formula varies as a consequence of elemental substitution. Clays often incorporate Mg²⁺, Fe²⁺, and Fe³⁺ in place of Al³⁺ in the octahedral layers and Al³⁺ for Si⁴⁺ in the tetrahedral layers. Thus, for example, the formula for a montmorillonite from Wyoming with substitution of Fe³⁺ and Mg²⁺ in its octahedral layer, Al³⁺ in its tetrahedral layer, and 0.67 monovalent exchangeable cations (X) is (Al_{2.88}Fe³⁺_{0.68}Mg_{0.47})(Si_{7.71}Al_{0.29})O₂₀(OH)₄X_{0.67}. Note that these substitutions replace a higher valent element with a lower valent one. Since the number of negative oxygen atoms in the lattice is constant, these substitutions result in the generation of negatively charged sites where substitution occurs. The association of cations with the clay lattice neutralizes these negative charges, as the metal ions bind electrostatically in the interlayer between the sheets in the "deck of cards" clay structure.

Particles of montmorillonite consist of irregular platelets that stack on top of each other when dry. When water is added the metal ions in the interlayer become hydrated, which expands the distance between the platelets. If there

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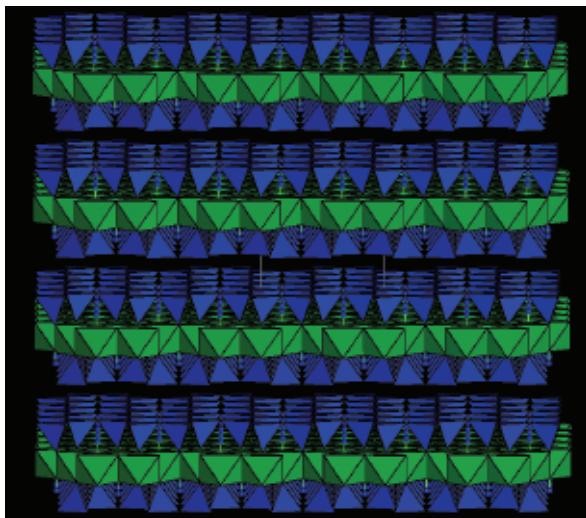


FIGURE 1 In a montmorillonite-type clay, Mg–Fe–Al octahedral layers (green) are linked to two Al–Si tetrahedral layers (blue). Monovalent (Na) and divalent (Ca) cations can occupy the interlayer regions.

is little isomorphous substitution and correspondingly few interlayer cations, then the clay mineral will not expand when water is added.

In a similar fashion, most clay minerals that absorb organic compounds bind them in the interlayers, and the clay expands to accommodate them. In some instances, the organics form complexes with the interlayer cation. Since the clay sheets are held together by van der Waals forces, the energy of the binding of the organics must be greater than that of these forces holding the clay sheets together, so that the sheets can separate to accommodate the bound organics.

Binding also occurs at the broken edges of the clay mineral sheets. The Al^{3+} groups at the edges coordinate with water molecules—a process that enhances the acidity of the water molecules and provides an acidic binding site. Consequently, negatively charged substances tend to bind at these edges. For example, pyrophosphate ions bind at the edges, as do the sodium salts of dicarboxylic acids, polyphenols, and other polyanionic polymers.

This tendency of clays to adsorb organic compounds contributes to their ability to catalyze a variety of organic reactions that are critical to scenarios of life's origins. For example, clay minerals are well known to mediate redox reactions—the donation and acceptance of electrons, especially from iron in the clay lattice or interlayer (FIG. 2). In addition, some clays promote acid-catalyzed reactions, because hydrogen ions readily exchange with other cations in montmorillonite (Nikalje et al. 2000). This ion exchange generates strongly acidic clay that catalyzes a wide variety of reactions initiated by the donation of a proton to the

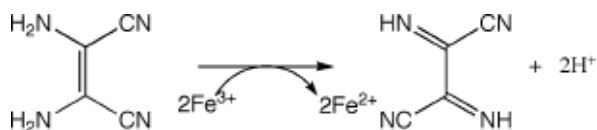


FIGURE 2 Clay minerals can mediate redox reactions. For example, diaminomaleonitrile (DAMN) is oxidized to diiminosuccinonitrile (DISN), when it is bound to montmorillonite containing Fe^{3+} . This reaction is typical of metabolic processes in many cells.

organic substrate. The positively charged organic molecule then undergoes elimination, addition, or rearrangement reactions. One of the earliest commercial uses of acidic clays was in the synthesis of high-octane gasoline by the acid-catalyzed rearrangement and cracking of high molecular weight hydrocarbons.

Clays also have the ability to accelerate organic reactions through the action of bound metal cations (Nikalje et al. 2000). Metal-ion complexes immobilized on clay surfaces make it possible to perform reactions in the solution phase that are comparable to solid-state reactions. The restricted movement and orientations of the metal complexes and the reacting substrates in the interlayer have led to greater reactivity of the bound organic molecule. In commercial applications these complexes usually contain transition metal elements (e.g., rhodium and ruthenium), though these cations are unlikely to have been present in significant amounts in the primitive Earth. Nevertheless, the exceptional ability of clay minerals to adsorb organic molecules and catalyze their reactions suggests an attractive strategy for investigating key steps in life's origins.

THE RNA WORLD HYPOTHESIS FOR THE ORIGIN OF LIFE

The discovery that RNA has the ability to catalyze reactions as well as store genetic information suggested that early life was based only on RNA rather than the DNA and protein polymers essential for life today. This hypothesis has the advantage of only requiring prebiotic synthesis of one polymer (RNA) rather than two (DNA and protein).

While the debate between a metabolism-first and genetic-first origin of life continues (see George Cody's article in this issue), I am persuaded that some type of genetic mechanism was essential for life to begin on the long path to cellular evolution. Biochemistry is too complicated to replicate from generation to generation without a reliable mechanism to pass on genetic information. In all known lifeforms, that mechanism depends on the double-stranded molecule DNA and its close relative, the single-stranded RNA, or ribonucleic acid. But there's a catch: You need DNA to make proteins, but you need proteins to make DNA. Which came first?

The proposal that the first life on Earth was based mainly on the familiar genetic molecule RNA was the direct outcome of the discovery that RNA had the ability to play the role of both protein and DNA—to catalyze reactions and to store genetic information. This RNA-first concept had actually been proposed more than a decade earlier (Crick 1968; Orgel 1968), but it was not generally accepted because no viable prebiotic process was known for RNA synthesis. The experimental demonstration of RNA catalysis (Cech et al. 1981; Guerrier-Takeda et al. 1983) suggested the possibility that RNA self-assembly might, in fact, be the key to life's origins.

The building blocks of RNA (TABLE 1; FIG. 3), consist of a sugar molecule (ribose, $\text{C}_5\text{H}_{10}\text{O}_5$), a phosphate group (PO_4), and one of four bases (the one-ring pyrimidines cytosine and uracil, designated C and U, and the two-ring purines adenine and guanine, designated A and G). These three components bond together into a phosphate-sugar-base unit, called a nucleotide. Nucleotides link to each other by forming a sugar-phosphate bond, thus elongating a chain-like RNA polymer. RNA polymers not only carry information in their sequence of bases (A, C, G, and U), but also have the potential to fold into catalytic structures, or ribozymes.

TABLE 1 SOME COMMON TERMS RELATED TO THE RNA WORLD HYPOTHESIS.

RNA	Ribonucleic acid, a polymer that carries genetic information and can act as an enzyme
Ribose	A 5-carbon sugar that forms part of the sugar–phosphate backbone of RNA. The five carbon atoms are numbered 1' through 5' in a nucleotide
Bases	One of four different ring-shaped molecules that serve as letters in the RNA code
Purines	Two-ring bases, including adenine and guanine (A and G)
Pyrimidines	One-ring bases, including cytosine and uracil (C and U)
Phosphate	PO ₄ molecules that form part of the RNA polymer backbone
Nucleoside	A ribose molecule linked to a base at the 1' carbon
Nucleotide	A ribose molecule linked to a base at the 1' carbon and a phosphate at the 2', 3', or 5' hydroxyl groups; also known as an RNA monomer
Activated nucleotide	A nucleotide that has been made chemically reactive (i.e., more likely to form a polymer) by the addition of a reactive molecule to the phosphate (see Fig. 3)
Monomer	A single nucleotide; one unit of an RNA polymer
Oligomer	A chain of several RNA nucleotides; a short RNA polymer. The chain forms when the phosphate of one nucleotide bonds to the ribose 3' carbon of another nucleotide—a so-called 3', 5' phosphodiester bond.
Phosphodiester bond	The bond that forms between two nucleotides in an RNA oligomer

In spite of this remarkable, multi-faceted structure, many scientists do not accept the RNA world hypothesis for the origins of life because no plausible mechanism for the prebiotic synthesis of RNA has been found. Those who reject the proposal that the RNA world was initiated from RNA monomers take the view that the first life used much simpler monomer units that were formed more readily by prebiotic processes. This unknown precursor to the RNA world supposedly evolved into the more versatile, but chemically less stable, RNA. However, no data at the present time describe a plausible prebiotic synthesis of the monomers or polymers of a potential pre-RNA.

While I recognize that the absence of a prebiotic route to RNA monomers remains an important problem to be solved, my group has continued to study the formation of RNA oligomers from RNA monomers. This research illuminates the central role of catalysis in prebiotic synthesis. In addition, we feel that continued research on the formation of RNA monomers is warranted, as there has been significant progress in the prebiotic formation of ribose (Müller et al. 1990; Zubay 1998; Ricardo et al. 2004; Springsteen and Joyce 2004) as well as in the synthesis of RNA by the reaction of monomers on an RNA template (e.g., Orgel 2004).

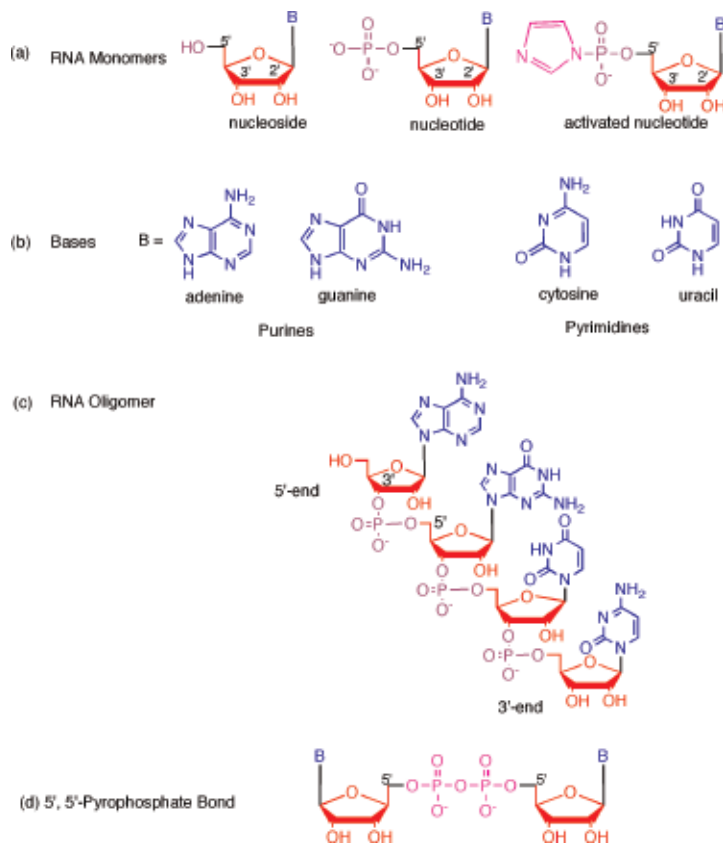


FIGURE 3 Structures of RNA nucleosides, monomers, oligomers, and pyrophosphates.

At present, the key elements lacking in our understanding of prebiotic RNA synthesis are the efficient reaction of the purine and pyrimidine bases with ribose to generate nucleosides and the synthesis of the activated mononucleotides required for RNA polymerization.

CLAYS AND THE PREBIOTIC SYNTHESIS OF RNA OLIGOMERS

Montmorillonite was first recognized as a potential prebiotic catalyst for the formation of the phosphodiester bond of RNA when it was observed that the yield of the 2', 3'-cyclic phosphate was enhanced in the presence of montmorillonite clay (Ferris and Hagan 1986; Ferris et al. 1988), as illustrated in Figure 4. While this clay-catalyzed reaction did not initiate the bonding of the ribose 5' carbon to phosphate, as required for RNA (Fig. 3), it did foster the search for conditions that might catalyze oligonucleotide formation.

A key to our eventual success was the discovery that montmorillonite-catalyzed reactions of nucleotides work best when we convert clays to forms with a single kind of interlayer cation—a procedure that avoids reactions or inhibition due to the metal ions bound in the interlayers of the naturally occurring montmorillonite (Banin 1973). We accomplished this conversion either by treatment of the montmorillonite with excess salts of the cation (saturation procedure) or by conversion to the acid form by acid treatment and then back titration of the hydrogen form of the clay with the desired cation. We observed that when the alkali and alkaline earth metal ions (with the exception of Mg) are the exchangeable cations, catalytically active clays are obtained. Montmorillonites with Fe and other transition metals as exchangeable cations, on the other hand, are not catalytically active.

Initial studies revealed that, under acidic conditions, basic purine and pyrimidine rings are protonated and bind strongly to the negatively charged clay lattice (Lailach et al. 1968). This binding decreases sharply as the pH is increased to values greater than 4. In our studies of the binding of nucleotides to montmorillonite (Ferris et al. 1989a), we find that activated monomers bind more strongly than the unactivated nucleotides because they have one less negative charge. Furthermore, activated purine nucleotides with their larger aromatic ring structures bind more strongly than pyrimidine nucleotides—a result that shows the importance of the van der Waals forces in the adsorption of these molecules onto clays.

In studies designed to confirm the binding sites of these activated nucleotide monomers, we exposed the clays to various organic compounds that are known to bind strongly to positively charged interlayer sites or the negatively charged edge sites. We found that substances binding to the montmorillonite interlayer sites inhibited RNA oligomer formation (Ertem and Ferris 1998), whereas organic substances bound to the edge sites on the montmorillonite had little effect on the inhibition of catalytic activity.

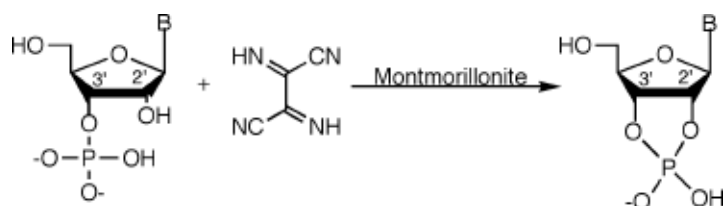


FIGURE 4 Montmorillonite enhances the yield in the DISN-driven cyclization of the 3'-phosphate to the 2', 3'-cyclic phosphate.

RNA Oligomer Formation

Our studies had demonstrated that RNA monomers can bind efficiently to clays, but would the clays catalyze the formation of RNA oligomers? Initial success came with experiments that exposed Na-montmorillonite to a solution containing nucleotides and carbodiimide (RN=C=R; a so-called “condensing agent” that induces polymerization reactions). We found a significant yield of both non-biological 2', 5'-linked RNA dimers (see Fig. 3) and biologically relevant 3', 5'-linked RNA dimers (Ferris et al. 1989b).

The use of an imidazole activating group bound to the phosphate group (Fig. 3) provided a major improvement, with oligomers up to 10-mers formed in the montmorillonite-catalyzed reaction (Ferris and Ertem 1992). Structure analysis revealed the presence of both 2', 5'- and 3', 5'-phosphodiester bonds between the monomer units, with biological 3', 5'-links present about 70% of the time.

An important aspect of this RNA oligomer formation is sequence selectivity—the preferential linkage of different nucleotides with bases A, C, G, or U. In experiments where we began with equal amounts of these four bases, clay catalysis resulted in the formation of a non-uniform distribution of the 16 possible pair sequences (Ertem and Ferris 2000; Miyakawa and Ferris 2003). In fact, eight of the sixteen dimers accounted for 84% of the reaction products, and all eight of these dimers have a purine nucleotide at their 5'-end.

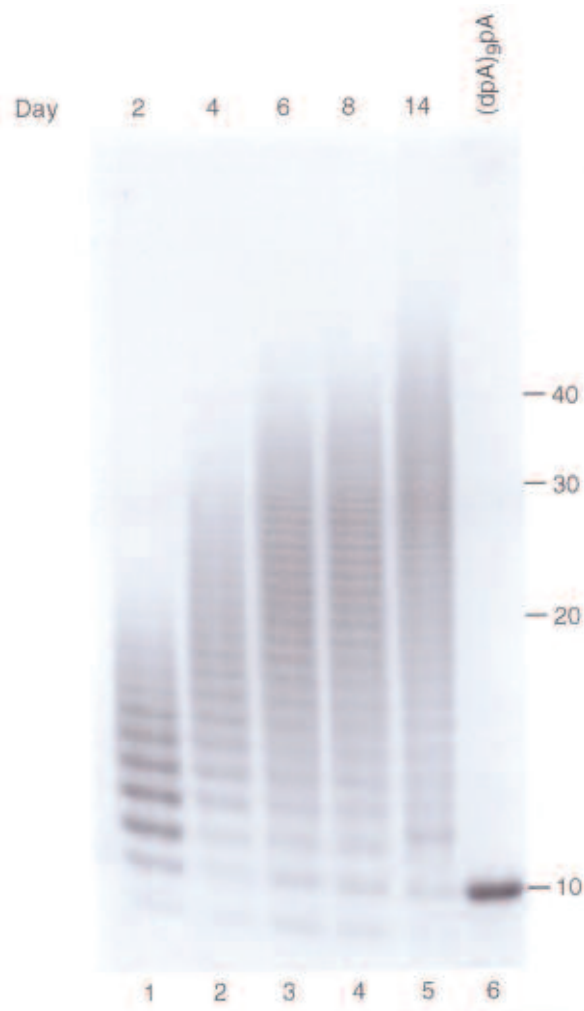


FIGURE 5 Gel electrophoresis separates the products of feeding reactions by their length. Activated monomer was added daily to $^{32}\text{pdA}(\text{pdA})_8\text{pA}$ bound to montmorillonite, and the five reaction mixtures were allowed to stand at 25°C for the times shown at the top of the gel. They were then added to lanes at the top of the gel. A voltage was applied across the gel and the negatively charged RNA oligomers migrated down the gel at rates proportional to their lengths. The migration positions are shown at the right for 10-, 20-, 30- and 40-mers (Ferris et al. 1996).

Additional studies revealed that the rate of clay-catalyzed RNA elongation depends strongly on the specific bases exposed at the 3'-end of the strand. Pyrimidine nucleotides elongate at a significantly slower rate than purine nucleotides. Consequently, the sequence of RNA nucleotides formed by clay catalysis is not the result of a random synthetic process.

Another aspect of nucleotide selectivity arises from the existence of both right-handed (D) and left-handed (L) ribose, leading to both D and L nucleotides. Both D- and L-enantiomers of RNA monomers must have been present on the primitive Earth. However, clay catalysis of a mixture of D and L nucleotides results in the formation of dimers that are predominantly D-D or L-L, as opposed to mixed D-L (Joshi et al. 2000). This important finding, if it holds for longer oligomers as well, points to a prebiotic pathway to form homochiral (same handedness) RNA from a heterochiral prebiotic milieu. Homochiral oligomers will have the same folding and interactions with other chiral molecules that life's exclusively D-RNA does today.

Toward a Synthetic RNA World

RNAs that served early life as a storehouse of genetic information as well as catalysts had to have been longer than 10-mers. In fact, theoretical studies suggest that oligomers greater than 40-mers would be required to serve as catalysts and templates for the formation of the complementary RNAs (Ferris 2002; Joyce and Orgel 1999; Szostak and Ellington 1993). Consequently, we explored the formation of longer oligomers by the daily addition of activated nucleotides to a 10-mer primer that had adsorbed on the montmorillonite (Ferris et al. 1996). After "feeding" this system for 14 days, we observed that the primer elongated by adding as many as 40 monomers units (FIG. 5). Furthermore, by changing the activating group on the nucleotides from imidazole to 1-methyladenine (a plausible prebiotic compound), we found it was possible to form 40-mers in only one or two days (Huang and Ferris 2003; Prabahaar and Ferris 1997). Given these findings, a plausible mineral-catalyzed pathway from prebiotic organic molecules to the RNA world seems within reach.

CONCLUSIONS

Catalysis was essential for the formation of the biopolymers required for the origin of the first life. The catalysts avail-

able on the primitive Earth included minerals and metal ions. In experiments, catalysis results in the generation of oligomers that represent only a limited range of all possible nucleotide sequences, so that they would be quite similar. This result suggests there was a sufficient supply of oligomers available to initiate the first life and to maintain it until an RNA catalyst for template-directed synthesis evolved. Catalysis can also assist in the formation of D- and L-homochiral polymers from random racemic mixtures of starting materials. This scenario raises the possibility of two coexisting worlds of opposite handedness, thus postponing chiral selection to a later date in the evolutionary process.

I may be wrong in assuming the RNA world arose from prebiotic reactions on the primitive Earth, but I am convinced that mineral and metal-ion catalysis was absolutely essential for the formation of the complex organic structures that were necessary for the first life on Earth.

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