Adsorption of Nucleic Acid Bases, Ribose, and Phosphate by Some Clay Minerals

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Abstract: Besides having a large capacity for taking up organic molecules, clay minerals can catalyze a variety of organic reactions. Derived from rock weathering, clay minerals would have been abundant in the early Earth. As such, they might be expected to play a role in chemical evolution. The interactions of clay minerals with biopolymers, including RNA, have been the subject of many investigations. The behavior of RNA components at clay mineral surfaces needs to be assessed if we are to appreciate how clays might catalyze the formation of nucleosides, nucleotides and polynucleotides in the “RNA world”. The adsorption of purines, pyrimidines and nucleosides from aqueous solution to clay minerals is affected by suspension pH. With montmorillonite, adsorption is also influenced by the nature of the exchangeable cations. Here, we review the interactions of some clay minerals with RNA components.

Keywords: adsorption; clay minerals; adenine; adenosine; 5-AMP; cytosine; uracil; ribose; phosphate

1. Introduction

Because of their fine particle size, large surface area, and peculiar charge characteristics, clay minerals are capable of adsorbing and catalyzing the polymerization of various organic molecules [1]. Clay minerals have also been implicated in chemical evolution and associated with the origin of life on Earth [2,3]. Clay minerals would be easily dispersed in the ocean of the early Earth in the form of very fine particles that would adsorb organic molecules dissolved in the ocean. Thus, organic molecules
would be deposited and concentrated on the ocean floor. Organic molecules might be able react with each other via the catalytic activity of clay minerals. Organic molecules might be formed as bioorganic molecules or biopolymers. It is therefore hypothesized that clay minerals could have played an important role in the origin of life.

Clay minerals are defined as very fine particles (less than 2 μm in diameter) [4]. Clay minerals are generally formed by weathering of rock-forming minerals. Fragmented minerals are also classified as clay minerals. The chemical compositions of clay minerals are mainly hydroxilicate and metal hydroxide. Configurations of clay minerals are mainly as a sheet, tube, or spherule. Clay minerals used for studies of the origin of life are generally a form of sheet silicate, such as smectite and kaoline minerals.

Indeed, clay minerals could function as a primitive form of genetic material, capable of replicating information stored in the form of structural, layer charge, and layer stacking faults [2,5,6]. Bioorganic molecules, polymerized into biopolymers in the interlayers of clay minerals, might replicate with the aid of the mineral host over time. This hypothesis is unique, but its validity is difficult to demonstrate experimentally [6].

Polynucleotides formed in such a manner could transform into a proto-RNA, and function as both a storehouse of genetic information and an enzyme (catalyst) in the primitive “RNA world” [7,8]. Here again, no experimental evidence exists to indicate that clay minerals can catalyze the formation of nucleotides from nucleic acid bases, ribose, and phosphate, let alone that of polynucleotides. However, oligomers of RNA monomers, “activated” by an imidazole or a methyl group attached to the phosphate group, can form in the presence of montmorillonite. Under certain conditions, RNA with up to 50 monomers can be obtained by these means [9–11].

The interaction of clay minerals with biomolecules has attracted a great deal of attention. In early studies, Lailach et al. [12,13] determined the adsorption of purine and pyrimidine bases by montmorillonite as a function of solution pH. Adsorption of adenine and cytosine decreased with increasing pH, becoming negligibly small at pH ≈ 8. More recently, Benetoli et al. [14] reported that more adenine, cytosine, uracil, and thymine were adsorbed by montmorillonite more at pH 2 than at pH 7.2.

Here, we summarize adsorption of RNA components with some clay minerals, including smectite, kaoline minerals, allophane, and layered double hydroxide.

2. Smectite

Smectite is a group including montmorillonite, beidellite, nontronite, saponite, hectorite, sauconite, and stevensite. The general structure of smectite is shown in Figure 1. Montmorillonite, beidellite, and nontronite are called dioctahedral smectite. The octahedral site is normally occupied by trivalent cations (e.g., Al³⁺, Fe³⁺, Mn³⁺). Saponite, hectorite, sauconite, and stevensite are called trioctahedral smectite. The octahedral site usually has divalent cations (e.g., Mg²⁺, Fe²⁺, Mn²⁺, Ni²⁺). Si⁴⁺ and Al³⁺ are mainly present in the tetrahedral site. One of the typical characteristics of the smectite group is the presence of an exchangeable cation (e.g., Na⁺, K⁺, Ca²⁺) between layers and smectite swells by intercalating water molecules between layers. Smectite can easily disperse in water and the interlayer cations can exchange with ionic organic molecules. Montmorillonite is frequently used in studies of the origin of life. The planar surface usually has a negative charge. The edge surface of montmorillonite has an
isoelectric point (pH approximately 7). At pH < 7, the edge surface shows a positive charge and at pH > 7, it has a negative charge [15].

Figure 1. The layer structure of smectite group.

Lailach et al. [12,13] showed adsorption of adenine, cytosine, and other related organic materials at various pH values by cation-exchanged montmorillonites, of which interlayer cations were Li⁺, Na⁺, Mg²⁺, and Ca²⁺. Almost all adsorbates were adsorbed by montmorillonite at a low pH. Adsorption suddenly decreased around pH 5 and at pH 8, montmorillonite did not adsorb these organic molecules. No major difference in adsorption by the interlayer cations was observed.

Perezgasga et al. [16] investigated the blocking effect of hexadecyltrimethyl ammonium cation (HDTMA) on adsorption of adenine and uracil by Na⁺-montmorillonite at pH 2, 6, and 10. Without HDTMA, 98% of adenine was adsorbed at pH 2, but at pH 6 and 10, adenine was not adsorbed. Conversely, 37% of the adenine was adsorbed at pH 2 with HDTMA. HDTMA blocked the intercalation of adenine. For uracil, 30% was adsorbed by montmorillonite. The effect on HDTMA decreased uracil adsorption from 30% to 6%. The extent of adenine adsorption decreased from 98% to 48% due to the addition of either HDTMA or phosphate. At pH 2, the adsorption achieved an equilibrium concentration for only 15 min.

Winter and Zubay [17] studied adsorption of adenine or uracil in a buffered solution and a model seawater. The buffer consisted of disodium salt, piperazine-N, N-bis-2-ethanesulfonic acid, NaCl, and MgCl₂ at pH 6.7. The seawater model comprised sodium, magnesium and potassium colloid, and either sulfate or carbonate at pH 8.6. Adenine was well adsorbed in the buffer and seawater model at either a neutral or basic pH. The maximum adsorption of adenine was approximately 0.18 mmol·g⁻¹ of about 0.2 mmol·dm⁻³ of the equilibrium concentration of solute, in buffering condition, and 0.08 mmol·g⁻¹ of approximately 1.8 mmol·dm⁻³ in the seawater model. Approximately 0.27 mmol·g⁻¹ of uracil was adsorbed at about 13 mmol·dm⁻³ by montmorillonite. Adenine adsorption was increased compared with uracil in the seawater model.

Hashizume et al. [18] previously determined the isotherms for the adsorption of adenine, cytosine, uracil, ribose, and phosphate by Mg²⁺-exchanged montmorillonite at pH 7–8. In their experimental
Life 2015, 5 640

condition, all isotherms were approximately linear lines. Under standard conditions, adsorption decreases in the following order: adenine > cytosine > uracil. The extent of adenine adsorption was 0.08 mmol·g⁻¹ at 4 mmol·dm⁻³; cytosine adsorption was 0.15 mmol·g⁻¹ at 15 mmol·dm⁻³ and uracil adsorption was 0.03 mmol·g⁻¹ at 18 mmol·dm⁻³. Winter and Zubay [17] observed that adsorption of adenine and uracil was higher than values reported by Hashizume et al. [18]; however, their respective experimental conditions were different.

Mechanisms of nucleic acid base adsorption were described by Hashizme et al. [18] and Perezgasga et al. [16]. Their observations may be explained in terms of differences in acid dissociation constant (pKa), solubility, and molecular weight (size) of the various compounds (Table 1). Nucleic acid bases are apparently intercalated by H-bonding with water molecules. As such, adsorption would decrease with an increase in basicity (pKa value), in line with experimental observations. Generally, adsorption of a solute decreases as its solubility (in water) increases, and increases with molecular weight. Cytosine is more soluble in water than uracil, while the molecular weight of cytosine is nearly equivalent to uracil. Nevertheless, more cytosine than uracil is adsorbed, suggesting that basicity is the determining factor. In the case of adenine, however, both molecular weight and basicity contribute to its relatively high adsorption.

| Dissociation constant | Adenine | Cytosine | Uracil | Adenosine | Ribose | 5′-AMP |
|-----------------------|---------|----------|--------|-----------|--------|--------|
| pKa₁                  | 4.15 *  | 4.58 †   | 9.48 † | 3.5 *     | 3.80 ‡ |        |
| pKa₂                  | 9.8 *   | 12.15 †  | 12.5 * | 6.19 ‡    |        |        |
| pKa₃                  |         |          | 13.06 ‡|           |        |        |

Table 1. Dissociation constant, solubility, and molecular weight of adenine, cytosine, uracil, adenosine, ribose, and 5′-AMP. (T) in solubility is temperature of measurement.

| Solubility (g/100g) | Adenine | Cytosine | Uracil | Adenosine | Ribose | 5′-AMP |
|---------------------|---------|----------|--------|-----------|--------|--------|
| (T)                 | 0.12 (25 °C) † | 0.743 (?) † | 0.36 (25 °C) † | 0.7 (?) ‡ | 10 (?) ‡ | 97 (25 °C) ^ |
| Molecular weight    | 135     | 111      | 112    | 267       | 150    | 347    |

Dissociation constant: * [17]. † [19]. ‡ [20]. Solubility; † [21,22]. ‡ [23]. ‡ [24]. ^ [25]. ? is not shown.

The isotherm for the adsorption of ribose by Mg²⁺-montmorillonite is shown in Figure 2a. The points are scattered and very little is adsorbed because ribose is highly basic (pKa = 12.2). Furthermore, ribose would be negatively charged at the experimental pH (≈ 8), and hence be repelled from the (basal) silicate surface. The isotherm for the adsorption of phosphate (Figure 2b) is of the L-type [26], reaching a plateau when the solute concentration exceeds 1.2 mmol·dm⁻³. At an acidic pH, phosphate can adsorb by electrostatic attraction to the edge surface of montmorillonite particles, which is then positively charged because the isoelectric point of the edge surface of montmorillonite is around pH 6.5 [27]. However, at pH ≈ 8, both the basal and edge surfaces of montmorillonite are negatively charged. Under these conditions, phosphate can still adsorb by ligand exchange with hydroxyl groups attached to “under-coordinated” aluminum ions at particle edges (Figure 1).
For pH dependence on nucleoside adsorption by montmorillonite, Li⁺, Na⁺, Mg²⁺, and Ca²⁺-montmorillonite adsorbed adenosine well at less than pH 4. Over pH 4, adsorption by Li⁺- and Na⁺-montmorillonite decreased gradually until pH 8, but adsorption by Mg²⁺- and Ca²⁺-montmorillonite decreased very quickly and at pH around 6, adenosine was not adsorbed at all. Adsorption of guanidine decreases from pH 3. Adsorption by Li⁺- and Na⁺-montmorillonite decreased gradually and around pH 7, adsorption did not occur. Mg²⁺- and Ca²⁺-montmorillonite did not gradually adsorb guanidine around pH 4. Cytidine adsorption by Li⁺- and Na⁺-montmorillonite was similar to adenosine but adsorption by Mg²⁺- and Ca²⁺-montmorillonite was lower compared with adenosine. Montmorillonite with a divalent cation achieved lower adsorption of adenosine, guanidine, and cytidine compared with a monovalent cation [12,13].

Winter and Zubay [17] investigated adenosine adsorption by montmorillonite with use of a buffer. They observed that adenosine adsorption was lower compared with adenine at pH 2 in the buffering condition. Thus, the buffer interfered with adenosine adsorption.

Nucleotide adsorption is also affected by pH. Lawless et al. [28] evaluated adsorption of 5'-, 3'- and 2'-adenosine monophosphate (AMP) by montmorillonite with various divalent cations in interlayers. The extent of adsorption of 5'-AMP by Zn²⁺-montmorillonite displayed two maximal peaks at pH 3 and 7 with increasing pH. Adsorption of 3'- and 2'-AMP also displayed two small peaks with increasing pH, but these were relatively small. Adsorption of 5'-CMP showed a similar tendency as 5'-AMP. 5'-AMP was more adsorbed compared with 5'-CMP. For Cu²⁺ as the exchangeable cation, the adsorptive profile of 5'-AMP was similar as Zn²⁺-montmorillonite. For other interlayer cations (Na⁺, Mn²⁺, Fe³⁺, Co²⁺, and Ni²⁺), adsorption of 5'-AMP decreased with increasing pH; no peaks were observed. The difference between Zn²⁺ or Cu²⁺ montmorillonites and other montmorillonites might be associated with altered coordination. Cu²⁺ and Zn²⁺ display a four-fold coordination, whereas Mn²⁺, Fe²⁺, Co²⁺, and Ni²⁺ have a six- fold coordination. Banin et al. [20] investigated adsorption of 5'-AMP by montmorillonite, in which the interlayer cation changed from 100% Ca²⁺ and 0% Fe²⁺ to 0% Ca²⁺ and 100% Fe²⁺ at different pH values. Fe²⁺-rich montmorillonite adsorbed more 5'-AMP compared with Ca²⁺-rich montmorillonite. Adsorption decreased with increasing pH regardless of the interlayer cations.

Adsorption of AMP, ADP, and ATP by montmorillonite at pH 2 was investigated at different times by Perezgasga et al. [16]. It took approximately 15 min to achieve an adsorptive equilibrium. Adsorption was lower than that of adenine. In addition to HDTMA or phosphate in the solution, adsorption was lower than without addition. Winter and Zubay [17] also investigated adsorption of 5'-AMP, ADP, and ATP in the buffered solution at pH 6.7. Adsorption decreased in the following order: ATP > ADP >
AMP. Feuillie et al. [29] studied the adsorption of AMP, GMP, CMP, UMP, and dGMP by montmorillonite and nontronite at pH 6.5. Compared with isotherms for adsorption by montmorillonite and nontronite, isotherms by nontronite were higher compared with montmorillonite for the five nucleotides. At pH 6.5, nucleotides would be adsorbed on the edge surface because of a positive charge. Conversely, the planar surface always has a negative charge. Thus, the nucleotide could not be adsorbed on the planar surface at pH 6.5. The authors expected the edge surface of nontronite to be different compared with montmorillonite.

Adsorption of polynucleotides by montmorillonite with a different interlayer cation (Na\(^+\), Ca\(^{2+}\), or Mg\(^{2+}\)) was carried out by Franchi et al. [30]. Na\(^+\)-montmorillonite did not adsorb polyadenylic acid (polyA), polyuridylic acid (polyU), polydeoxyadenylic acid (polydA), polydeoxymididylic acid (polydT) and chromosomal DNA (DNAchr). However, Ca\(^{2+}\) or Mg\(^{2+}\)-montmorillonite almost completely adsorbed them from about 1 mmol·dm\(^{-3}\). The authors explained that the divalent cations played a bridging role between the montmorillonite surface and the polynucleotide.

Montmorillonite can adsorb nucleic acid bases, nucleosides, nucleotides, and polynucleotides. In the early Earth, high-energy radiation and UV light would come from space. Biomolecules might be destroyed by such radiations. Biondi et al. [31] and Agnilar-Orando and Negron-Mendoza [32] studied the decomposition of adenosine and RNA by irradiation of \(^{60}\)Co \(\gamma\)-ray or 254 nm UV ray when they were adsorbed by montmorillonite or they were by themselves. When both adenosine and RNA was adsorbed by montmorillonite, they remained at a high concentration compared with the biomolecule by themselves, indicated a protective effect of the montmorillonite.

Theoretical or computer simulation studies on adsorption of nucleic acid bases, nucleotides, and polynucleotides were also reported. For example, Mignon et al. [33] simulated the adsorptive energies and distance between nucleic acid bases and a Na\(^+\)-montmorillonite surface. The morphology of adsorption between nucleic acid bases and montmorillonite affected the adsorptive energy. The energies of face-to-face nucleic acid bases and montmorillonite were generally higher than those of cations-\(\pi\) bonding. Mathew and Luthey-Schulten [34] computed the relation of a nucleotide to di-nucleotide within and without an interlayer of Ca\(^{2+}\)-montmorillonite. They indicated that the reaction from monomer to dimer was made better in the interlayer than out of the interlayer. In addition, a 3′–5′ reaction of ribose was superior to 2′–5′ reaction within the interlayer. Swadling et al. [35] studied the interaction between montmorillonite and RNA. When RNA was adsorbed on a montmorillonite surface, the RNA conformation changed and shrunk because of the surface charge. Montmorillonite might affect the formation of polynucleotides or RNA synthesis.

Joshi et al. [36] investigated the catalytic activity of montmorillonites in three regions (Wyoming, Otay, and Chambers). These montmorillonites are different from the adsorptive activity of adenine-5′-phophorimidazolide (impA), impC, and impU. Three montmorillonites were different for preservation of impA, which has negatively charged nucleotide derivatives. There are many published articles that describe polymerization catalyzed by montmorillonite, especially the work of Ferris and colleagues [37,38].

3. Kaoline Minerals

Kaoline minerals are kaolinite, dickite, and nacrite. Kaoline minerals are composed of Al, Si, O, and OH. The chemical formula is Al\(_2\)Si\(_2\)O\(_5\)(OH)\(_4\). The structure overlaps with an octahedral (O) and a
Life 2015, 5

463
tetrahedral sheet (T), alternatively. One layer is T-O and there are not any exchangeable ions. However, cations can intercalate into interlayers of kaoline minerals following treatment with alcohols or surfactants. The point of zero charge (PZC) of kaolinite is pH 4 [39]. Kaolinite has a positive charge under pH 4. Conversely, at a pH over 4, kaolinite has a negative charge.

Benetoli et al. [14] studied the adsorption of adenine by kaolinite and montmorillonite. They showed Langmuir and Freundlich parameters of isotherm for adsorption. Kaolinite adsorbed adenine at pH 2. The maximum extent of adsorption by kaolinite was much lower compared with montmorillonite. The maximum adsorption by kaolinite was 0.407 μg·mg⁻¹, while that of montmorillonite was 21.7 μg·mg⁻¹. Evaluation of adsorption of 5'-AMP, ADP, and ATP by kaolinite at neutral pH was performed by Graf and Lagaly [40]. Adsorption increased in the following order: ATP < ADP << AMP. Adsorption of AMP by kaolinite was nearly equivalent to that of Ca²⁺-montmorillonite and higher than that of beidellite. However, beidellite adsorbed ADP and ATP better than kaolinite.

Franchi et al. [30] investigated adsorption of polyA, polyU, polydA, polydT and DNAchr by kaolinite, and modified kaolinite at pH 5 to 5.5, which Ca²⁺ and Mg²⁺ were intercalated in the interlayers. Kaolinite itself hardly adsorbed those polymers at a low concentration. At high concentrations, kaolinite adsorbed about 80% of the polymers except DNAchr. Conversely, kaolinite with a divalent cation adsorbed almost all of the polymers over 1 mmol·dm⁻³. Thus, Mg²⁺ and Ca²⁺ cations could help connect kaolinite and polymers, similar to the interaction between montmorillonite and polymers.

Computer simulations of adsorption of thymine and uracil by kaolinite and dickite were carried out by Robinson et al. [41] and Michalkova et al. [42], respectively. The interaction energy between uracil or thymine and kaolinite in sodium solution was calculated by Robinson et al. [41]. The energy of uracil was lower compared with thymine. The difference between the energies of uracil and thymine was very small. The interaction energy between dickite and uracil was also smaller than that of thymine. In kaolinite minerals, the interaction energy can be investigated between nucleic acid bases and a tetrahedral surface or an octahedral surface. The interaction energy between the octahedral surface and uracil or thymine was lower compared with a tetrahedral surface. The octahedral site has a vacancy for the charge valance. The vacancy might affect the different interaction energy between the octahedral and tetrahedral surfaces.

4. Allophane and Other Silicates

Allophane is a nanosized hydrated aluminosilicate with short-range order and an Al/Si ratio of 1 ~ 2 found in many soils derived from volcanic ash and weathered pumice. The unit particle of allophane consists of a hollow spherule with an outer diameter of 4–5.5 nm. The 0.7–1.0 nm thick spherule wall is composed of an outer gibbsitic sheet, to which O₃SiOH groups are attached on the inside. Defects in the wall structure give rise to ~0.3 nm wide perforations (Figure 3). Unlike montmorillonite, allophane has neither a permanent negative charge nor exchangeable cations. Rather, the charge characteristics of allophane vary with pH, since the (OH)Al(OH₃) groups exposed at wall perforations can either acquire or lose protons, depending on suspension pH. The point of zero charge of the allophane sample, used in this instance, is close to 6 [43].
Figure 3. Diagram showing the hollow spherule structure of an allophane particle ("nanoball"), and composition of the (perforated) spherule wall. See Figure 1 in [44].

Hashizume and Theng [44] have determined the isotherms for the adsorption of adenine, adenosine, ribose, and 5'-AMP by allophane at pH 4, 6, and 8 (Figures 4–7). Little adenine is adsorbed at all three pH values. As for adenine, adsorption of adenosine increases in the following order: pH 4 < pH 6 < pH 8 (Figure 5). A similar trend was observed with ribose (Figure 6). The adsorption of adenosine would be affected by the adenine component of adenosine. The ribose component of adenosine did not affect adenosine adsorption.

Figure 4. Isotherms for the adsorption of adenine by allophane at pH 4, 6, and 8.

Figure 5. Isotherms for adsorption of adenosine by allophane at pH 4, 6, and 8.
The isotherms for the adsorption of a 5'-AMP at pH 4, 6, and 8 are shown in Figure 7. At pH 4 and 6, the amount adsorbed at low solute concentrations (<0.05 mmol·dm⁻³) was at least two orders of magnitude greater than that for adenosine. Even at pH 8, when the allophane surface is negatively charged, appreciable adsorption of 5'-AMP was observed (Table 2). According to Theng et al. [45] and Rajan [46], the dramatic increase in adsorption may be ascribed to ligand exchange between the phosphate group of 5'-AMP and the hydroxyl of (OH)Al(OH₂) groups on the surface of allophane spherules (Figure 3), forming monodentate and bidentate surface complexes [44]. Allophane was a superior clay mineral of nucleotide adsorption compared with montmorillonite. In a recent study of the interaction of DNA with allophane, Matsuura et al. [47] showed that allophane was adsorbed on single-stranded DNA (ss-DNA). The authors also mentioned that the phosphate group of ss-DNA strongly associated with Al-OH group of allophane.

Table 2. Charge characteristics of adenine, adenosine, 5'-AMP, and allophane at pH 4, 6 and 8 [20,44].

|          | pH 4 | pH 6 | pH 8 |
|----------|------|------|------|
| adenine  | ++   | (+) N| N (+)|
| adenosine| ++   | (+) N| N    |
| 5'-AMP   | +    | –    | –    |
| allophane| ++   | N    | –    |

+: positive; -: negative; N: neutral; N(+): weakly positive; ++: strongly positive; −−: strongly negative
Graf and Lagaly [40] investigated adsorption of AMP, ADP, and ATP by illite, quartz and silt-quartz. Illite is included in a mica group. The crystal structure is similar to smectite (Figure 1). The ideal chemical composition is $K_{0.75}(Al_{1.75}(Mg,Fe^{2+})_{0.25})(Si_{2.5}Al_{0.5})O_{10}(OH)_2$. The interlayer cation does not basically exchange to other cations. The intercalation into interlayers does not occur. Quartz is composed of $SiO_2$. Silt of quartz-silt means a particles size. The silt is 2–20 μm in diameter, according to The International Soild Method of the International Society of Soil Science [4]. The authors mentioned that illite hardly adsorbed AMP, ADP, or ATP. In the case of quartz, they compared adsorption by quartz to that by quartz-silt. Quartz-silt did not contain AMP, ADP and ATP after a removing treatment.

5. Layered Double Hydroxide (LDH)

LDH is a clay mineral that can exchange anions. The crystal structure is shown in Figure 8. Natural LDHs have divalent and trivalent cations and the interlayer is occupied by anions (Table 3).

![Figure 8. Schematic figure of Layered Double Hydroxide (LDH) structure.](image)

**Table 3.** Natural LDHs with various divalent and trivalent cations and interlayer anions [53].

| Mineral name | Cation      | Anion          |
|--------------|-------------|----------------|
| Rhombohedral | Hexagonal   | $M^{2+}$ $M^{3+}$ | $\text{CO}_3^{2-}$ $\text{SO}_4^{2-}$ $\text{Cl}^-$ $\text{OH}^-$ |
| Hydrotalcite | Maasseite   | Mg Al           | $\text{CO}_3^{2-}$ |
| Motukoreaite |             | Mg Al           | $\text{SO}_4^{2-}$ $\text{CO}_3^{2-}$ |
| Stichtite    | Barbertonite| Mg Cr           | $\text{CO}_3^{2-}$ |
| Pyroaurite   | Sjögrenite  | Mg Fe           | $\text{CO}_3^{2-}$ |
| Iowaite      |             | Mg Fe           | $\text{Cl}^-$ $\text{CO}_3^{2-}$ |
| Chlormagaluminite | Hydrocalmite | Mg Fe | $\text{Cl}^-$ $\text{CO}_3^{2-}$ |
| Green Rust 1 |             | Ca Al           | $\text{OH}^-$ |
| Berthierine  |             | Fe Fe           | $\text{CO}_3^{2-}$ $\text{SiO}_4^{4-}$ |
| Takovite     |             | Ni Al           | $\text{CO}_3^{2-}$ |
| Reevesite    |             | Ni Fe           | $\text{CO}_3^{2-}$ |
| Honessite    |             | Ni Fe           | $\text{SO}_4^{2-}$ |
| Eardlyite    |             | Zn, Ni Al       | $\text{CO}_3^{2-}$ |
| Meixnerite   |             | Mg Al           | $\text{OH}^-$ |
LDH has often been investigated in association with sugars, polynucleotides, RNA. Aizawa et al. [48] studied the synthesis of LDH in a ribose solution. LDH was composed of Mg$^{2+}$ and Al$^{3+}$ cations containing ribose between layers, while Zn$^{2+}$ and Al$^{3+}$-LDH could not be formed in ribose solution. Swadling et al. [49] and Swadling et al. [50] calculated the stability of RNA, DNA, and PNA in the interlayer of LDH and showed that DNA was the most stable. The authors also simulated the bonding between RNA and the surface of LDH composed of Mg$^{2+}$ and Al$^{3+}$. They showed that the phosphate of RNA connected with the LDH surface. The interlayer of LDH was used to synthesize sugar-phosphate in other reactions [51,52].

6. Conclusions

We have shown that some clay minerals can adsorb RNA components. Although the extent of their adsorption is rather limited, the results provide valuable information about the mechanisms underlying the interaction between clay minerals and simple bioorganic compounds. Organic molecules, synthesized abiotically in the ocean [54–57], could be immobilized and concentrated on clay mineral surfaces. The resultant organic-rich mineral particles would sink and accumulate on the ocean floor. The ability of clay minerals to take up and concentrate key components of RNA has been experimentally demonstrated. A more pertinent point is the large capacity of allophane for binding and retaining phosphate, as phosphorus is not major element making up the chemical composition of the Earth’s crust. Organic molecules, including polymer adsorbed on clay minerals, might be protected from radiation from UV rays and cosmic rays [31,32].

Some clay minerals are useful for nucleotide polymerization [58]. It is also difficult to form nucleoside and nucleotide in the prebiotic condition. Even if clay minerals such as montmorillonite and kaolinite, exist with nucleic acid bases, ribose and phosphate, nucleosides and nucleotides can not formed, easily. There are several hundred kinds of clay minerals and other minerals in total. Some clay minerals in them might have a function for the formation of nucleosides and nucleotides as a catalyst. As the basic investigation, it is important to study adsorption of RNA components using various clay minerals.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. Theng, B.K.G. The Chemistry of Clay-Organic Reactions; Adam Hilger: London, UK, 1974; p. 343.
2. Bernal, J.D. The Physical Basis of Life; Routledge and Kegan Paul: London, UK, 1951; p. 364.
3. Ponnamperuma, C.; Shimoyama, A.; Friebel, E. Clay and the origin of life. Orig. Life 1982, 12, 9–49.
4. The Clay Mineral Society of Japan, Ed. *Handbook of Clays and Clay Minerals*, 3rd ed.; Gihodoshuppan: Tokyo, Japan, 2009; pp. 11–17. (In Japanese)
5. Cairns-Smith, A.G. *Genetic Takeover and the Mineral Origins of Life*; Cambridge University Press: Cambridge, UK, 1982; p. 133.
6. Brack, A. Clay minerals and the origin of life. In *Handbook of Clay Science*; Bergaya, F., Theng, B.K.G., Lagaly, G., Eds.; Elsevier: Amsterdam, The Netherlands, 2006; pp. 379–391.
7. Cech, T.R. A model for the RNA-catalyzed replication of RNA. *Proc. Nat. Acad. Sci. USA* 1986, 83, 4360–4363.
8. Guerrier-Takada, C.; Altman, S. Catalytic activity of an RNA molecule prepared by transcription in vitro. *Science* 1984, 223, 285–286.
9. Ferris, J.P.; Hill, A.R., Jr.; Liu, R.; Orgel, L.E. Synthesis of long prebiotic oligomers on mineral surfaces. *Nature* 1996, 381, 59–61.
10. Ferris, J.P. Mineral catalysis and prebiotic synthesis: Montmorillonite-Catalyzed formation of RNA. *Elements* 2005, 1, 145–149.
11. Ferris, J.P. Montmorillonite catalysis of 30–50 mer oligonucleotides: Laboratory demonstration of potential steps in the origin of the RNA world. *Orig. Life Evol. Biosph.* 2002, 32, 311–332.
12. Lailach, G.E.; Thompson, T.D.; Brindley, G.W. Adsorption of pyrimidines, purines, and nucleosides by Li-, Na-, Mg-, and Ca-montmorillonite (Clay-organic studies XII). *Clays Clay Miner.* 1968, 16, 285–293.
13. Lailach, G.E.; Thompson, T.D.; Brindley, G.W. Absorption of pyrimidines, purines, and nucleosides by Co-, Ni-, Cu-, and Fe(III)- montmorillonite (Clay-organic studies XIII). *Clays Clay Miner.* 1968, 16, 295–301.
14. Benetoli, L.O.B.; de Santana, H.; Zaia, C.T.B.V.; Zaia, D.A.M. Adsorption of nucleic acid bases on clays: An investigation using Langmuir and Freundlich isotherms and FT-IR spectroscopy. *Monatsh. Chem.* 2008, 139, 753–761.
15. Pecini, E.M.; Avena, M.J. Measureing the isoelectric point of the edges of clay mineral particles: The case of montmorillonite. *Langmuir* 2013, 29, 14926–14934.
16. Perezgasga, L.; Serrato-Díaz, A.; Negron-Mendóza, A.; Galán, L.D.; Mosqueira, F.G. Sites of adsorption of adenine, uracil and their corresponding derivatives on sodium montmorillonite. *Orig. Life Evol. Biosph.* 2005, 35, 91–110.
17. Winter, D.; Zubay, G. Binding of adenine and adenosine-related compounds to the clay montmorillonite and the mineral hydroxyapatite. *Orig. Life Envol. Biosph.* 1995, 25, 61–81.
18. Hashizume, H.; van der Gaast, S.; Theng, B.K.G. Adsorption of adenine, cytosine, uracil, ribose, and phosphate by Mg-exchanged montmorillonite. *Clay Miner.* 2010, 45, 469–475.
19. The chemical Society of Japan, Ed. *Kagakubinran*; Maruzen: Tokyo, Japan, 1993; pp. II317–II321.
20. Banin, A.; Lawless, J.G.; Church, F.M.; Margulies, L.; Orenberg, J.B. pH profile of the adsorption of nucleotides onto montmorillonite. II. Adsorption and desorption of 5'-AMP in iron-calcium montmorillonite systems. *Orig. Life* 1985, 15, 89–101.
21. The chemical Society of Japan, Ed. *Kagakubinran*; Maruzen: Tokyo, Japan, 1993; pp. II176–II178.
22. Pub Chem. Available online: http://our.edu/cccda/sl/solubility/allsolvent (accessed on 17 December 2014).
23. Product Information. Available online: http://www.sigmaaldrich.com/ (accessed on 17 December 2014).
24. Lookchem. Available online: http://www.lookchem.com (accessed on 17 December 2014).

25. Wang, D.; Li, Z.-J.; Ying, H.-J. Solubility of adenosine 5'-monophosphate in different solvents from \((288.15\) to \(330.15\))K. J. Chem. Eng. Data 2010, 55, 992–993.

26. Giles, C.H.; MacEwan, T.H.; Nakhwa, S.N.; Smith, D. Studies in adsorption. XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J. Chem. Soc. 1960, 3973–3993.

27. Durán, J.D.G.; Ramos-Tejada, M.; Arroyo, F.J.; González-Caballero, F. Rheological and Electrokinetic properties of sodium montmorillonite suspensions. J. Colloid Interface Sci. 2000, 229, 107–117.

28. Lawless, L.G.; Church, F.M.; Mazzurco, J.; Huff, R.; Kao, J.; Cook, A.; Lowe, T.; Orenberg, J.B.; Edelason, E. pH profiles of the adsorption of nucleotides onto montmorillonite. I. Selected homoionic clays. Orig. Life 1985, 15, 77–88.

29. Feuillie, C.; Daniel, I.; Michot, L.J.; Pedreira-Segada, U. Adsorption of nucleotides onto Fe-Mg-Al rich swelling clays. Geochim. Cosmochim. Acta 2013, 120, 97–108.

30. Franchi, M.; Ferris, J.P.; Gallori, E. Cations as mediators of the adsorption of nucleic acids on clay surfaces in prebiotic environments. Orig. Life Evol. Biosph. 2003, 33, 1–16.

31. Biondi, E.; Branciamore, S.; Maurel, M.-C.; Gallori, E. Motmrorillonite protection of an UV-irradiated hairpin ribozyme: Evolution of the RNA world in a mineral environment. BMC Evol. Biol. 2007, 7, 1–7.

32. Aguilar-Ovando, E.; Negron-Medoza, A. Radiation chemistry approach to the study of sedimentary microenvironments as models for the protection of bio-organic molecules on the early earth. J. Radiational Nucleic Chem. 2010, 286, 637–642.

33. Mignon, P.; Ugleingo, P.; Sodupe, M. Theoretical study of the adsorption of RNA/DNA bases on the external surfaces of Na⁺-montmorillonite. J. Phys. Chem. C 2009, 113, 13741–13749.

34. Mathew, D.C.; Luthey-Schulten, Z. Influence of montmorillonite on nucleotide oligomerization reactions: A molecular dynamics study. Orig. Life Evol. Biosph. 2010, 40, 303–317.

35. Swadling, J.B.; Coveney, P.V.; Greenwell, H.C. Clay minerals mediate folding and regioselective interactions of RNA: A large-scale atmistic simulation study. J. Am. Chem. Soc. 2010, 132, 13750–13764.

36. Joshi, P.C.; Aldersley, M.F.; Delano, J.W.; Ferris, J.P. Mechanism of montmroillonite catalysis in the formation of RNA oligomers. J. Am. Chem. Soc. 2009, 131, 13369–13374.

37. Ertem, G.; Ferris, J.P. Sequence- and regio-selectivity in the montmorillonite-catalyzed systems of RNA. Orig. Life Evol. Biosph. 2000, 30, 411–422.

38. Ertem, G.; Ferris, J.P. Synthesis of RNA ligomers on heterogenous templates. Nature 1996, 379, 238–240.

39. The clay mineral society of Japan. Available online: http://www.cssj2.org/seminar1/section04/ext.html (accessed on 16 January 2015). (In Japanese)

40. Graf, G.; Lagaly, G. Interaction of clay minerals with adenosine-5-phosphates. Clays Clay Miner. 1980, 20, 12–18.

41. Robinson, T.L.; Michalkova, A.; Gorb, L.; Leszczynaski, J. Hydrogen bonding of thymine and uracil with surface of dickite: An ab intio study. J. Mol. Struc. 2007, 844–845, 48–58.
42. Michalkove, A.; Robinson, T.L.; Leszczynski, J. Adsorption of thymine and uracil on 1:1 clay mineral surfaces: Comprehensive ab initio study on influence of sodium cation and water. *Phys. Chem. Chem. Phys.* 2011, 13, 7862–7881.

43. Hashizume, H.; Theng, B.K.G. Adsorption of D,L-alanine by allophane: Effect of pH and unit particle aggregation. *Clay Miner.* 1999, 34, 233–238.

44. Hashizume, H.; Theng, B.K.G. Adenine, adenosine, ribose and 5′-AMP adsorption to allophane. *Clays Clay Miner.* 2007, 55, 599–605.

45. Theng, B.K.G.; Russell, M.; Churchman, G.J.; Parfitt, R.L. Surface properties of allophane, halloysite, and imogolite. *Clays Clay Miner.* 1982, 30, 143–149.

46. Rajan, S.S.S. Mechanism of phosphate adsorption by allophane clays. *N. Zeal. J. Sci.* 1975, 18, 93–101.

47. Matsuura, Y.; yoda, F.; Arakawa, S.; John, B.; Okamoto, M.; Hayashi, H. DNA adsorption characteristics of hollow spherule allophane nano-particles. *Mater. Sci. Eng. C* 2013, 33, 5079–5083.

48. Aisawa, S.; Hirahara, H.; Ishiyama, K.; Ogasawara, W.; Umetsu, Y.; Narita, E. Sugar-anionic clay composite materials: Interaction of pentoses in layered double hydroxide. *J. Solid State Chem.* 2003, 174, 342–348.

49. Swadling, J.B.; Suter, J.L.; Christopher Greenwell, H.; Coveney, P.V. Influence of surface chemistry on mineral-RNA inteactions. *Langmuir* 2013, 29, 1573–1583.

50. Swadling, J.B.; Coveney, P.V.; Christopher Greenwell, H. Stability of free and minerals-protected nucleic acids: Implications for the RNA world. *Geochim. Cosmochim. Acta* 2013, 83, 360–378.

51. Saladino, R.; Neri, V.; Crestini, C. Role of clays in the prebiotic synthesis of sugar derivatives from formamide. *Philos. Mag.* 2010, 90, 2329–2337.

52. Pitsch, S.; Eschenmoser, A.; Gedulin, B.; Hui, S.; Arrhenius, G. Mineral induced formation of sugar phosphates. *Orig. Life Evol. Biosph.* 1995, 25, 297–334.

53. The Clay Mineral Society of Japan, Ed. *Handbook of Clays and Clay Minerals*, 3rd ed.; Gihodoshuppan: Tokyo, Japan, 2009; pp. 99–103. (In Japanese)

54. Miller, S.L. A production of amino acids under possible primitive Earth conditions. *Science* 1953, 117, 528–529.

55. Miller, S.L.; Urey, H.C. Organic compound synthesis on the primitive Earth. *Science* 1959, 130, 245–251.

56. Parker, E.T.; Cleaves, H.J.; Dwoeink, J.P.; Glavin, D.P.; Callahan, M.; Aubrey, A.; Lazcano, A.; Bada, J.L. Primordial synthesis of amines and amino acids in a 1958 Miller H2S-rich spark discharge experiment. *Proc. Natl. Acad. Sci. USA* 2011, 108, 5526–5531.

57. Powner, M.W.; Gerland, B.; Sheraland, J.D. Synthesis of activated pyrimidine ribonucleotides in prebiotically plausible conditions. *Nature* 2009, 459, 239–242.

58. Ferris, J.P.; Erten, G.; Agarwel, V. Mineral catalysis of the formation of dimmers of 5′-AMP in aqueous soltion: The possible role of montmorillonite clays I the prebiotic synthesis of RNA. *Orig. Life Evol. Biosph.* 1989, 19, 165–178.

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