Orig Life Evol Biosph (2018) 48:181–200
https://doi.org/10.1007/s11084-018-9554-9

PREBIOTIC CHEMISTRY

Salinity Effects on the Adsorption of Nucleic Acid Compounds on Na-Montmorillonite: a Prebiotic Chemistry Experiment

Saúl A. Villafañe-Barajas[1,2] · **João Paulo T. Baú**[3] · **María Colín-García**[2] · **Alicia Negrón-Mendoza**[4] · **Alejandro Heredia-Barbero**[4] · **Teresa Pi-Puig**[2] · **Dimas A. M. Zaia**[3]

Received: 3 August 2017 / Accepted: 8 January 2018 /

Abstract Any proposed model of Earth's primitive environments requires a combination of geochemical variables. Many experiments are prepared in aqueous solutions and in the presence of minerals. However, most sorption experiments are performed in distilled water, and just a few in seawater analogues, mostly inconsistent with a representative primitive ocean model. Therefore, it is necessary to perform experiments that consider the composition and concentration of dissolved salts in the early ocean to understand how these variables could have affected the absorption of organic molecules into minerals. In this work, the adsorption of adenine, adenosine, and 5'AMP onto Na^+montmorillonite was studied using a primitive ocean analog (4.0 Ga) from experimental and computational approaches. The order of sorption of the molecules was: 5'AMP > adenine > adenosine. Infrared spectra showed that the interaction between these molecules and montmorillonite occurs through the NH_2 group. In addition, electrostatic interaction between negatively charged montmorillonite and positively charge N1 of these molecules could occur. Results indicate that dissolved salts affect the sorption in all cases; the size and structure of each organic molecule influence the amount sorbed. Specifically,

---

✉ María Colín-García
mcolin@geologia.unam.mx

✉ Dimas A. M. Zaia
damzaia@uel.br; dimaszaia.quimicaprebiotica@gmail.com

[1] Posgrado en Ciencias de la Tierra, Universidad Nacional Autónoma de México, Ciudad Universitaria, C.P. 04510, Cd. Mx., México

[2] Instituto de Geología, Universidad Nacional Autónoma de México, Ciudad Universitaria, C.P. 04510, Cd. Mx., México

[3] Laboratório de Química Prebiótica, Departamento de Química-CCE, Universidade Estadual de Londrina, Londrina, PR 86051-990, Brazil

[4] Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Ciudad Universitaria, C.P. 04510, Cd. Mx., México

the X-ray diffraction patterns show that dissolved salts occupy the interlayer space in Na-montmorillonite and compete with organic molecules for available sites. The adsorption capacity is clearly affected by dissolved salts in thermodynamic terms as deduced by isotherm models. Indeed, molecular dynamic models suggest that salts are absorbed in the interlamellar space and can interact with oxygen atoms exposed in the edges of clay or in its surface, reducing the sorption of the organic molecules. This research shows that the sorption process could be affected by high concentration of salts, since ions and organic molecules may compete for available sites on inorganic surfaces. Salt concentration in primitive oceans may have strongly affected the sorption, and hence the concentration processes of organic molecules on minerals.

Keywords Nucleobases · Adsorption · Primitive ocean model · Montmorillonite · Prebiotic chemistry

Introduction

Since the work of Miller (1953), experiments on prebiotic chemistry have become more complex because a multidisciplinary approach is necessary in laboratory models. The hypotheses of Bernal (1949) and Cairns-Smith (1966) on the role of clay minerals in the origin of life led to the consideration that minerals were an essential component in prebiotic chemistry studies.

Several studies have shown the synthesis of adenine and related compounds under primitive conditions (Oró and Kimball 1961; Vergne et al. 2000; Orgel 2004; Saladino et al. 2005; Roy et al. 2007; Gull 2014). Numerous experiments have been focused on the sorption of the nucleic acid components and nucleotides onto clay minerals. The high sorption capacity of these minerals and their possible role in the "RNA world hypothesis" has been demonstrated (Lailach et al. 1968; Lailach and Brindley 1969; Graf and Lagaly 1980; Ferris et al. 1989, Ferris 1993, 2004; Winter and Zubay 1995; Ertem 2004; Perezgasga et al. 2005; Benetoli et al. 2008; Hashizume et al. 2010; Feuillie et al. 2013; Pedreira-Segade et al. 2016).

Although Lahav and co-workers pointed out the possible interactions among biomolecules and soluble salts in the context of chemical evolution (Lahav and Sherwood 1982; Orenberg et al. 1985; Chan et al. 1987), this parameter has received limited attention in prebiotic chemistry studies. In fact, sorption experiments are often performed in distilled water solutions, in buffers, and eventually in seawater analogues, which may be inconsistent with a representative primitive ocean model (Zaia 2012). For this reason, to consider interactions between ions and organic molecules on sorption processes is a matter of utmost importance in a prebiotic chemistry context.

There is not total agreement about the composition and concentration of salts in the primitive ocean; however, both conditions must have been very different from the present. Likewise, the alteration of basaltic lavas during the Hadean (rich in Si, Al, Mg, Fe, and Ca) could have increased the concentration of ions in seawater (Wright et al. 1995; Albaréde 2007). Additionaly, hydrous carbonaceous chondrites have been considered an important source of the total ocean water inventory during the last stage of accretion of Earth (Pinti 2005; Jewitt and Young 2015) and they could have also changed the concentration of salts. Using leaching experiments performed in a carbonaceous chondrite, the Tagish Lake meteorite (Izawa et al. 2010), Zaia (2012) proposed a model of seawater analogue. This seawater model (named 4.0 Ga seawater) contains higher concentration of SO_4^{2-},Ca^{2+}, Mg^{2+} than ions like Cl^-, Na^+ or K^+. Therefore, a seawater model where Mg^{2+} and SO_4^{2-}ions dominate the composition could better represent some characteristics of the first permanent ocean (≈4.2 to 3.7 Ga) (Izawa et al. 2010).

Recently, several works have shown that a high concentration of salts could affect the sorption of organic molecules on different minerals (Benetoli et al. 2007, 2008; Zaia 2012; Anizelli et al. 2015, 2016). Additionally, it is well know that inorganic ions affect the membrane's self-assembly and RNA polymerization phenomena (Monnard et al. 2002). Ions could also act as a protective agent against degradation by heat (Tehei et al. 2002), or affect the catalytic properties of clays in RNA synthesis (Joshi and Aldersley 2013).

Testing the role of dissolved salts in the sorption process of organics onto minerals should be a crucial matter in determining the fate of organic molecules in primitive oceans. In this way, this study is devoted to understand the effect of dissolved salts (by modeling an analogue of the primitive ocean of 4.0 Ga) on the sorption of adenine and related compounds onto Na-montmorillonite.

Materials and Methods

Materials

All reagents used were of the highest analytical grade. Montmorillonite, purchased from Acros Organics (NJ, USA), has the following chemical composition (mass fraction): $SiO_2 = 54\%$, $Al_2O_3 = 17\%$, $Fe_2O_3 = 5.2\%$, $CaO = 1.5\%$, $MgO = 2.5\%$, $Na_2O = 0.4\%$, and $K_2O = 1.5\%$. Sodium montmorillonite 53 μm was prepared by passing the clay through a 53 μm sieve and saturating it with sodium chloride solution (1.0 mol L^{-1}) to assure all cations were displaced by sodium (Carneiro et al. 2016).

Seawater 4.0 Ga Preparation

To prepare seawater 4.0 Ga the following substances were dissolved in 1 L of distilled water: Na_2SO_4 (0.271 g), $MgCl_2.6H_2O$ (0.500 g), $CaCl_2.2H_2O$ (2.50 g), KBr (0.050 g), K_2SO_4 (0.400 g), $MgSO_4$ (15.00 g) (according to Zaia 2012).

Methods

Adsorptions

Adsorption experiments were carried out as follows. Solutions of each analyte (adenine, adenosine and adenosine 5'monophosphate) were prepared with seawater 4.0 Ga or distilled water at a concentration of 720 μg/mL. In order to test the effect of salinity, dilutions (volume percent) of seawater 4.0 Ga were made at 100%, 50%, and 10% of the original seawater solution. About 100 mg of clay and 5 mL of each solution were placed into tubes (the experiments were performed in quintuple). Tubes were shaken for 24 h, then centrifuged at 3000 rpm for 10 min. The aqueous phase was used for quantitative analysis. The solid was lyophilized and analyzed by X-ray diffractometry.

Isotherms

To determine the sorption isotherms, different amounts of adenine, adenosine, and adenosine 5′-monophosphate (AMP) were dissolved in distilled water, or in seawater 4.0 Ga. The concentration ranges were 240, 360, 480, 600, 720, 840, and 960 μg/mL. The experiments were made in duplicate, adding 25 mg of mineral and 5 mL of the corresponding solution of each analyte in the above-mentioned concentrations. After shaking for 3 h, the samples were centrifuged at 3000 rpm for 10 min. The aqueous phase was used for quantitative analysis.

UV Spectroscopy

The absorbance at 260 nm was measured in all cases by UV spectrophotometry (Spectronic Genesys®). To calculate the amount of analyte absorbed in the clay, the following equation was used:

$$\frac{C_{adsorbed}}{\mu g} = C_{initial} - C_{solution} \text{ where, } \qquad C_{solution} = (C_{initial})\left(\frac{Abs_{sample}}{Abs_{initial}}\right)$$

FT-IR-Spectroscopy

FT-IR spectra were recorded with an FT-IR spectrophotometer (Bruker® model Vertex 70) with reflectance accessory Platinum ATR. Spectra were recorded from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and a total of 10 scans. Spectra were analyzed with the Origin (Pro 8.0) program.

X-Ray Diffractometry

Samples were analyzed by powder X-ray diffraction as random powder and oriented aggregates both air dried and treated with ethylene glycol. Air-dried oriented preparations were obtained by pipetting the sample's suspension (particle size <2 μm) onto a glass slide, which was then dried at 30 °C. Ethylene glycol solvation of the samples was achieved by exposing them to ethylene glycol vapor at 70 °C for a minimum of 12 h (Moore and Reynolds 1997). Measurements were made with an Empyrean diffractometer, with an accelerating voltage of 45 kV and a filament current of 30 mA, using CuK_{α} radiation, nickel filter, and PixCELL 3D detector. All the random-powder samples were measured over a 2θ angle range of 4–70° with a step size of 0.04° and 40 s of scan step time. Oriented samples were examined by XRD in the air-dried form and saturated with ethylene glycol. The preparations were measured over a 2θ angle range of 4–30° with the same step size and scan step time as the random powder samples.

Statistic Analysis

A Tukey test, with a significance level of $p < 0.05$, was performed to analyze the sorption differences in the experimental series, both for salt concentration and for the organic compound tested.

Computational Methods

Molecular models were carried out by molecular mechanic and semi-empiric methods, as implemented in the HyperChem® program, version 8.0. In order to find the coordinates of molecular structures, geometry optimizations were used. Likewise, molecular dynamics relaxation of the optimized structures was performed to obtain local minima (step size of 0.0001, at 298.15 K). The full geometry optimization was performed by using the settings in the MM^+ force field, the Polak-Ribiere conjugate gradient algorithm, and a root mean square (RMS) gradient of 1×10^{-5} kcal $Å^{-1}$ mol^{-1}. In the same way, the geometries obtained by the MM^+ molecular mechanics were optimized with PM3 semi-empirical methods to corroborate the most stable configuration.

Results and Discussion

Adsorption Experiments

In all cases the sorption of the organic molecules on montmorillonite was observed (Table 1). The order of sorption of the molecules was: 5'AMP > adenine >adenosine ($p < 0.05$). It is possible that these differences of sorption could be attributed firstly to the structure and charge of organic molecules, and by the capacity of binding to the clay. In all cases, the measured pH in the sorption experiments was close to the pK_a of protonation of the molecules (Lailach and Brindley 1969). Therefore, adenine (pK_a 4.2), adenosine (pK_a 3.6) and 5'AMP (pK_a 3.8) are all positively charged on N_1 at these conditions.

Three different mechanisms of adsorption can be proposed. First, the adsorption process may occur by electrostatic interactions; the surface of the clay is negatively charged (with permanent negative charges) and the adsorbed molecules are positively charged at the experimental pH (Table 1).So, electrostatic forces act between the protonated organic molecules and the negatively charged clay. Lailach et al. (1968) proposed different mechanisms that could explain the greater adsorption of nucleic bases. The size and planar structure on the one hand, and the sharing of π-electrons of the aromatic ring with an oxygen atom in the surface of silicates, trough van der Waal forces on the other. In a similar way, nucleosides may have lower adsorption because their perpendicular structure makes it difficult to interact with the minerals. Hashizume et al. (2010) proposed that adenine forms hydrogen bonds with water molecules that are coordinated with the interlayer ions of clays.

The second possible adsorption mechanism is via cationic interchange between the protonated organic molecules and ions, in this case Na^+, of the interlamellar space. Perezgasga et al. (2005) and Carneiro et al. (2011) showed that in acidic solutions the adsorption of nucleobases and related compounds occurs mainly in the interlayer space by ionic exchange. In the case of adenine absorption, both authors observed a strong affinity of the molecule to the negatively charged internal space of the clay. Furthermore, the edges of crystals are negatively

Table 1 Amount of adenine and related compounds adsorbed on Na^+-Montmorillonite (μg/mg)

Molecule	Seawater (100%)	Seawater (50%)	Seawater (10%)	Distilled water	*pH** range
Adenine	$27.37 \pm 0.42^{b,D}$	$28.48 \pm 0.26^{b,C}$	$29.64 \pm 0.31^{b,B}$	$31.40 \pm 0.16^{b,A}$	3.9–4.6
Adenosine	$18.50 \pm 0.32^{c,D}$	$23.46 \pm 0.39^{c,C}$	$26.61 \pm 0.19^{c,B}$	$29.22 \pm 0.19^{c,A}$	3.4–4.0
5'AMP	$32.32 \pm 0.52^{a,C}$	$34.04 \pm 0.15^{a,B}$	$34.77 \pm 0.06^{a,A}$	$34.87 \pm 0.09^{a,A}$	2.7–3.4

In rows, mean values for each seawater concentration quoted by different capital letters indicate a statistically significant difference by Tukey's test ($P < 0.05$). In columns, molecules with distinct lowercase letters are statistically different from each other by Tukey's test ($P < 0.05$)

Results are presented as mean ± standard error of mean. Each result is the mean of five experiments

* pH values were measured after mixing the samples for 24 h

Different treatments in salt concentration are shown charged (these charges are pH dependent) at the pH value in measured isoelectric points (pH_{iep}~2), a similar value found by Carneiro et al. (2013). Accordingly, if the organic molecules are predominantly positively charged, they can interact by electrostatic forces with the edges of the mineral. Figure 1 shows the schematic structure of the clay mineral, its charges, and interlamellar cations. Likewise, the highest sorption of 5’AMP would be the result of cation exchange between the protonated N_1 site of 5-AMP molecule and the cations in the interlayer space (Banin et al. 1985) and by the capability of the phosphate group to ligand exchange with the OH-groups on the edges of mineral (Graf and Lagaly 1980).

Finally, the third mechanism would involve the adsorption of ribonucleotides by the phosphate group through a monodentate inner-sphere complex formation (Feuillie et al. 2013, 2014; Pedreira-Segade et al. 2016). The formation of inner sphere complex is predicted to occur at low pH’s values (Arora and Kamaluddin 2009) and this mechanism could explain the highest sorption of 5’AMP when compared to adenine and adenosine. Nonetheless, it was not possible to detect it by IR spectroscopy, because montmorillonite has several bands in the same region that phosphate group of 5’AMP (Nakamoto 1978). The pH of the samples of the present work were in the range from 2.7 to 3.4 (Table 1); thus, probably in this case, the protonated N1 is also playing a role in the adsorption.

Another factor related to the differences of sorption between 5’AMP, adenine, and adenosine is the pH of samples. It is important to mention that the pH s of the samples were not modified, and the reported values are those measured after shaking (24 h). However, all samples, after shaking, tend to have a relatively acid pH (Table 1). The low pH values could be the result of mineral dissolution; for instance, by the release of protons from trivalent aluminum monomers, hidroxi-Al polymers or H_3O^+ groups on the edges of minerals

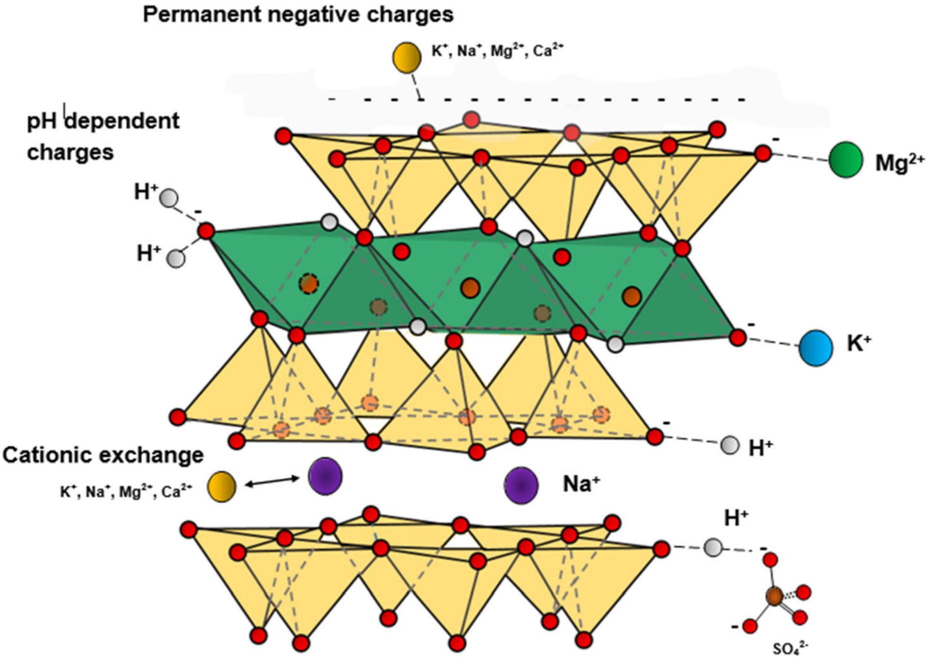


Fig. 1 Possible mechanism of interaction among dissolved ions and mineral. The ionic exchange and electrostatic forces are shown, both on surfaces and onedges; pH dependent charges and permanent charge sites are also shown

(Besoain 1985), or by the acidity of the solvated exchangeable cations with the release of protons (Sposito 2008).

The experiments also show that the sorption of all tested molecules is strongly affected by the concentration of dissolved salts. Table 1 shows that there is an increase of sorption when salt concentration decreases, from the solutions that contained 100% seawater to those made with pure distilled water. These results have great importance in prebiotic chemistry because when considering a primitive ocean analog, the concentration of salts interferes in the sorption of organic molecules (Zaia 2012).

Recently, several experiments have shown that seawater analogues (Zaia 2012) with high salts concentration modified the sorption of organics as the available sites in the mineral can be occupied by dissolved ions. These experiments have been performed with different organic molecules and several minerals: clays (Benetoli et al. 2007, 2008; de Santana et al. 2010; Carneiro et al. 2011; Farias et al. 2014), silicates (de Souza et al. 2013), zeolites (Baú et al. 2012; Anizelli et al. 2015, 2016), and iron oxides (Vieira et al. 2011; Canhisares-Filho et al. 2015). These results suggested that the presence of ions can be a crucial factor on sorption; for instance, it would be determinant in self-assembly phenomena, governed by thermodynamic and transport properties of the solutions (Spitzer and Poolman 2009).

The organic molecules can be intercalated into the interlayer space of clays, and the dissolved cations are capable of displacing them through different mechanisms. Those mechanisms include ion exchange between the silicate layers, and through the formation of inner-sphere complexes with the silicate layers or with Si–O and Al–O groups on the edges of clay (El-Nahhal and Lagaly 2005; El-Bayaa et al. 2009; Jiang et al. 2010).

Likewise, another important process in the global behavior of sorption is the formation of complexes between organic compounds and salts; this could occur via a direct coordination with the interlayer cations, or bound by water bridges (Lagaly et al. 2006). The ions present in our seawater analogue behave as hard acids (e.g., Mg^{2+}) and bases (e.g., SO_4^{2-}), so they could be bonded with organic molecules by water bridges (Lagaly et al. 2006). This last point was studied theoretically by Anizelli et al. (2014) who proposed that adenine forms complexes with ions (i.e., Mg^{2+}). Additionally, Franchi et al. (2002) showed that some cations would be directly involved in the adsorption onto clay minerals, acting as bridges between the negative charges of mineral and the phosphate group of nucleic acids. However, our results suggest that the ions reduce or limit the sorption, both in the interlayer space and on the external surface. This would imply that although there are several interactions between "ions-organic molecules-mineral," some of them could be favored, such as the affinity of the ions for available sites on minerals, and the capability to associate directly with clay minerals (Sposito et al. 1999; Sposito 2008).

In summary, the presence of cations in solution (e.g., Mg^{2+}, K^+, Na^+) could affect the adsorption of the organics; the surface of the clay is negatively charged as well as the edges (negatively charged at the pH range used), and therefore, reduces the electrostatic interactions of the organic molecules. The interaction of opposite charges would favor the accumulation of these cations on the surface and, therefore, these ions would hinder the interaction between the organic molecule and the mineral (Fig. 1). Also, the increase of ionic strength would lead to the increase of the electrostatic potential (making it more positive) of the adsorption plane (Bolan et al. 1986). The increase in ionic strength may affect the interaction between the organic and the surface by decreasing the electrostatic forces, hydrogen bonds, and/or the electron interaction of the aromatic rings of organic molecules due to the ion screen effect of the solution (Kyriakopoulos et al. 2006; Sposito 2008). Likewise, cations would be involved in ion exchange mechanisms in the interlamellar space of clay. In particular, it is proposed that cationic exchange may be the mechanism that mostly affects the absorption of the tested molecules, since the absorption of the three molecules is reported to occur mainly in the interlamellar channel (Perezgasga et al. 2005).

Isotherms

Isotherm models give information about the adsorption capability of the mineral. The most common isotherm models are sorption models of Langmuir and Freundlich. The Langmuir model assumes that the adsorption process occurs on a homogeneous surface, so the available sites in the mineral are energetically equivalent. The adsorption model is described by the following linearized equation:

$$\frac{C_{eq}}{q} = \frac{1}{K_L b} + \frac{C_{eq}}{b}$$

Where C_{eq} is the equilibrium concentration (μg mL^{-1}), q is the amount of analyte sorbed (μg mg^{-1}), and b (μg mg^{-1}) and K_L (mL μg^{-1}) are Langmuir constants related to maximum sorption capacity and energy of sorption, respectively. Likewise, the adsorption type is related with the equilibrium parameter R_L, which is defined by:

$$R_{L=}\frac{1}{(1 + K_L C_o)}$$

Where K_L is the Langmuir constant (mL μg^{-1}) and Co is the initial concentration (μg mL^{-1}).

On the other hand, the Freundlich model assumes that adsorption occurs on a heterogeneous surface, and it is represented by the equation:

$$\log q = logK_F + \frac{1}{n} * logC_{eq}$$

Where Ceq is the equilibrium concentration (μg mL^{-1}), q is the amount of adsorbed analyte (μg mg^{-1}), and n and K_F (mL μg^{-1}) are Freundlich constants, related to adsorption intensity and adsorption capacity.

Figure 2 shows the isotherms obtained, and Tables 2 and 3 show the results of the isothermal models and their coefficient values for both the Langmuir and Freundlich models. In general, values are consistent with the Langmuir model, since they have a better linear fit ($R^2 \approx 0.99$) compared to the Freundlich model (Tables 2 and 3).

The adsorption process can be expressed in an equation to understand the values of Langmuir s constant. If the equilibrium is shifted to the right side of the equation, the adsorption is favorable, and therefore the equilibrium constant will be greater than 1.

$$\text{Clay (solid phase)} + \text{Analyte (liquid phase)} = \text{Analyte}-\text{Clay Complex}$$

With the exception of adenosine in seawater 4.0 Ga, the results of the isotherm experiments, both for distilled water and seawater, showed that the equilibrium constant (K_L) is greater than 1. This implies that there is a tendency towards the formation of the analyte–clay complex. The values of the equilibrium parameter (R_L) range from 0.036 to 0.148 (Table 2).This suggests that the adsorption of organic compounds on clay is favorable both in distilled water and in seawater 4.0 Ga conditions, and that in the concentrations and pH used the sorption is feasible (Rahman and Islam 2009). These values are consistent with other works that studied the

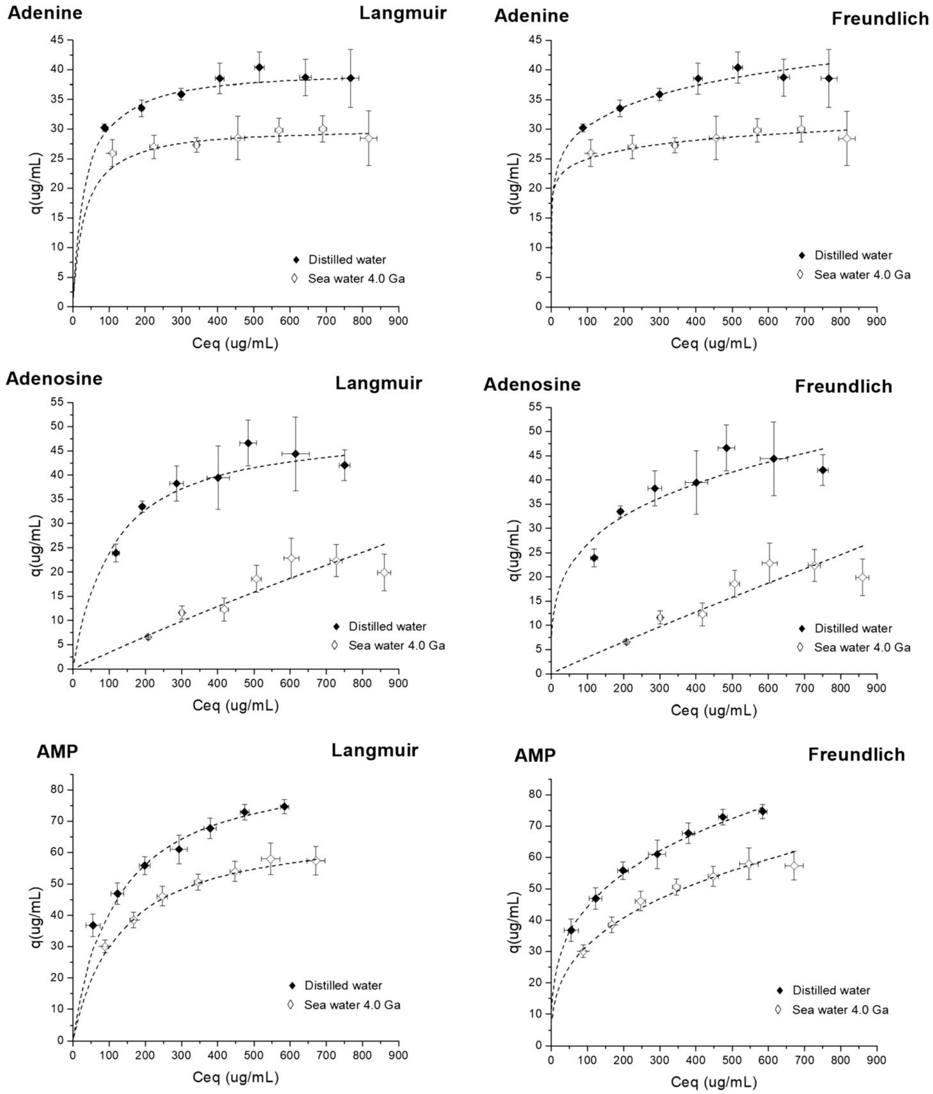


Fig. 2 Adsorption isotherms for adenine, adenosine and AMP. Results are presented for Langmuir and Freundlich models in experiments with salts (sea water 4.0 Ga) and in distilled water

adsorption of different cations onto clays (Bhattacharyya and Gupta 2006; Gupta and Bhattacharyya 2006; Vimonses et al. 2009). It is remarkable that the values of the equilibrium constant (K_L) of adenine are the highest for the organic compounds tested. The high values of Langmuir s constant can be explained if the adsorption mechanism of adenine on montmorillonite occurs by stacking bases on the basal surface and the interlamellar channel of the clay, and that this is done by sharing of π-electrons (Lailach et al. 1968). This planar arrangement would suggest a homogeneous absorption onto clay, and could explain the high values of Langmuir s constant.

Table 2 Langmuir parameters calculated for tested molecules adsorbed on sodium montmorillonite

Molecule	R^2	b (μg/mg)	K_L(L/g)	R_L	pH
Distilled water					
Adenine	0.997	40.161 ± 0.88	34 ± 4	0.039	≈5.8
Adenosine	0.973	49.975 ± 3.40	10 ± 2	0.122	≈4.43
5'AMP	0.995	88.574 ± 2.44	9 ± 0.9	0.134	≈3
Seawater 4.0 Ga					
Adenine	0.995	30.303 ± 0.84	37 ± 0.12	0.036	≈4.34
Adenosine	0.346	62.111 ± 30.59	0.6 ± 0.09	0.698	≈4.01
5'AMP	0.997	68.260 ± 1.39	8 ± 0.4	0.148	≈2.87

Results are presented as mean ± standard error. Each result is the mean of three experiments, measurements were made in duplicate

Two different series with distilled water and seawater analog (100%) are shown

* pH values were measured after the samples were mixed 3 h

The parameter *b* (maximum amount of adsorption) in the Langmuir model describes certain features of the adsorption behavior. In general, the values for the experiments in seawater are smaller than those of distilled water, with the exception of adenosine (Table 2). The Langmuir model assumes a monolayer adsorption containing a finite number of available sites. A lower *b* value for seawater experiments implies that adsorption of the organic molecules is smaller since the dissolved salts are occupying available sites, which supports the proposed adsorption mechanism. In other words, it is possible that protonated organic molecules and cations compete for the negative charges on the surface and edges of the clay.

Nonetheless, the adsorption of adenosine in seawater is better explained by the Freundlich model (Table 3). In general, this model predicts a multilayer adsorption on heterogeneous sites on the mineral surface. The low adsorption capacity value obtained (K_F) suggests that salts are interfering in the adsorption of adenosine. The adsorption intensity (*n*), is ≈1, which suggests non-specific adsorption in a heterogeneous surface, energetically non-uniform, and related to physical adsorption processes through van der Waals forces (Bhattacharyya and Sharma 2004; Vimonses et al. 2009).

IR Analysis

Infrared spectra were realized in order to understand in detail how the sorption occurs. IR spectra of adenine, adenosine and 5'-AMP in the region between 1400 cm^{-1} and 2000 cm^{-1}

Table 3 Freundlich parameters calculated for tested molecules adsorbed on sodium montmorillonite

Molecule	R^2	n	K_F	pH
Distilled water				
Adenine	0.974	7.125 ± 0.48	16.146 ± 0.282	≈4.34
Adenosine	0.721	3.773 ± 0.93	8.031 ± 1.391	≈4.01
5'AMP	0.988	3.370 ± 0.15	11.472 ± 0.37	≈2.87
Seawater 4.0 Ga				
Adenine	0.77	12.288 ± 2.66	17.302 ± 0.632	≈4.34
Adenosine	0.93	1.059 ± 0.12	0.044 ± 0.008	≈4.01
5'AMP	0.96	2.954 ± 0.21	6.822 ± 0.49	≈2.87

Results are presented as mean ± standard error. Each result is a mean of three experiments, measurements were made in duplicate

Two different series, with distilled water and seawater analog (100%), are shown

* pH values were measured after the samples were mixed 3 h

are shown in Fig. 3. The 1600 cm^{-1} and 1668 cm^{-1} bands in adenine (Fig. 3a) can be attributed to the weakness interaction of the C=N bond and the NH_2 bond of the purine ring, respectively. In the same way, the bands of adenosine at 1604 cm^{-1} and 1664 cm^{-1} (Fig. 3b), and 1592 cm^{-1} and 1642 cm^{-1} in 5'AMP (Fig. 3c) could be attributed to the same bonds (Colthup et al. 1964; Mathlouthi et al. 1984; Jankovics et al. 2002; Benetoli et al. 2008; Carneiro et al. 2011; Anizelli et al. 2014). The infrared spectrum of montmorillonite shows a band at 1630 cm^{-1} that is related to water, coordinated with interchangeable clay cations (Theng 1974).

The infrared spectra of adenine and derivates sorbed, both in distilled water and seawater 4.0 Ga, show similar behaviors. In all cases, the band attributed to the NH_2 shifts to ≈1700 cm^{-1}. This suggests that the interaction between adenine and its derivatives occurs through the NH_2 group, as suggested by other authors (Colthup et al. 1964; Benetoli et al. 2008; Carneiro et al. 2011).This shifting would be the result of a neighboring positive charge (N_1) with respect the NH_2 (Angell 1961), and it suggests that molecules are aligned with C-NH_2 group along the surface (Kundu et al. 2009). Because the organic molecules are positively charged, they can interact with the negatively charged surface of clay by electrostatic attraction (Perezgasga et al. 2005). Similarly, in samples where organic the compound is sorbed, there is a shift in the band at 1600 cm^{-1} to 1630 cm^{-1}. This band is possibly related to the bond C=N in the purine ring (i.e., the interaction occurs with all the structure (R_1-C=N-R_2) (Colthup 1975). However, this shift could be overestimated since this band coincides with the characteristic asorption band of the water coordinated with the cations in the interlaminar space (Porubcan et al. 1978). On the other hand, the role of pH seems to be a very important parameter that affects the sorption process. Particularly, the protonation of N1 in the imidazol ring in adenine (and related compounds) would be associated with the asorption in the interlayer space, by ionic exchange (Graf and Lagaly 1980; Banin et al. 1985; Perezgasga et al. 2005; Carneiro et al. 2011).

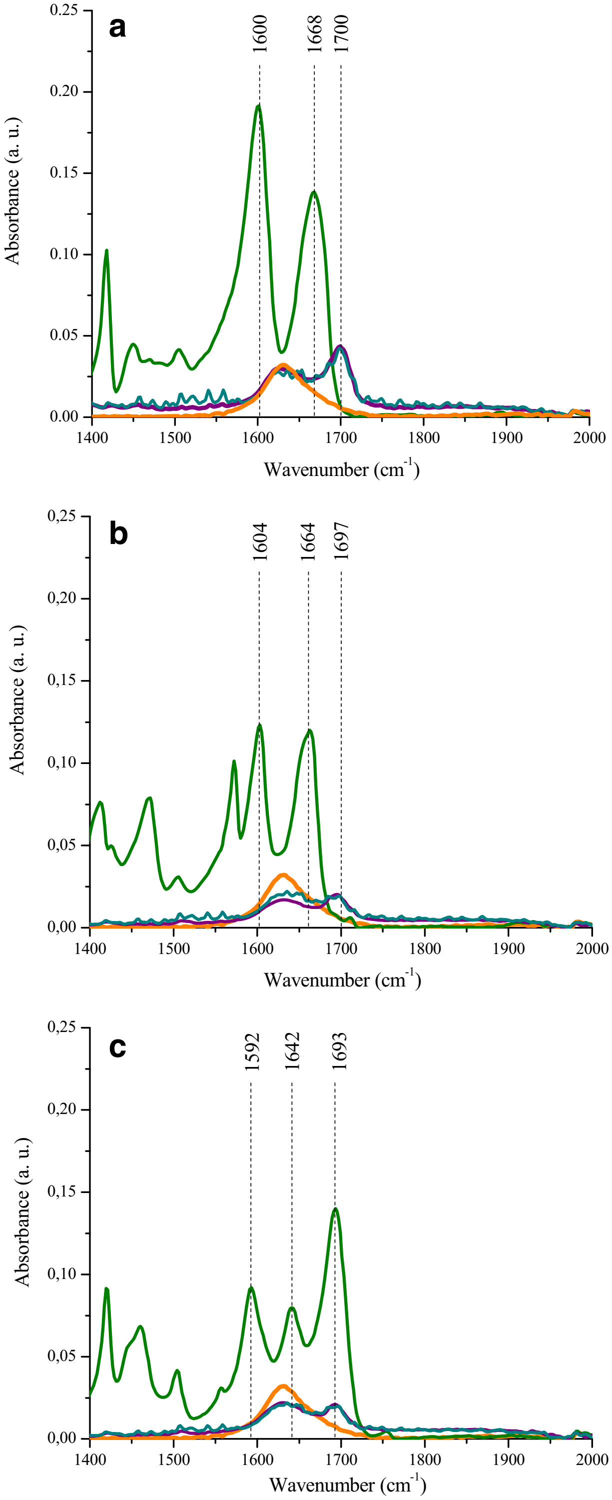
Through IR spectra it was possibly to corroborate that molecules are really sorbed on clay. Nonetheless, the IR spectra of molecules sorbed in presence of salt do not show appreciable differences from the ones prepared in distilled water dissolutions. Consequently, it is not possible to determine if there is an effect of salts on the sorption by IR spectroscopy.

X-Ray Diffraction

The X-ray diffraction patterns of samples sorbed in the presence of dissolved salts (Fig. 4) show peaks that correspond to hexahydrite ($MgSO_4.6H_2O$). This salt was formed in all the experiments. Vieira et al. (2011) and Carneiro et al. (2016) also detected the presence of salts on X-ray diffractograms using seawater analogue models with several minerals.

For both clay samples (random powder and oriented aggregates), two parameters were determined: the d-spacing of the basal layer (d_{001}), which represents the thickness of the silicate layer, and the "crystallinity." This last parameter was measured as the full width at half maximum (FWHM), and is related with variations of the crystal size and crystal imperfections, both of which contribute to the broadening of diffraction peaks. These values (d_{001} and FWHM) are clearly affected by the presence of seawater and present specific ranges for each organic molecule (adenine, adenosine, 5'AMP).

For oriented aggregates, the d-spacing value of the basal peak d_{001} of the montmorillonite is always greater for samples saturated with salts than for samples treated with distilled water. This suggests that salts penetrate into the interlayer space. The oriented samples (Moore and Reynolds 1997), air dried and treated with ethylene glycol, provide essential information to verify that salts


a
1600
1668
1700
Absorbance (a. u.)
0.25
0.20
0.15
0.10
0.05
0.00
1400
1500
1600
1700
1800
1900
2000
Wavenumber (cm^{-1})
b
1604
1664
1697
Absorbance (a. u.)
0,25
0,20
0,15
0,10
0,05
0,00
1400
1500
1600
1700
1800
1900
2000
Wavenumber (cm^{-1})
c
1592
1642
1693
Absorbance (a. u.)
0,25
0,20
0,15
0,10
0,05
0,00
1400
1500
1600
1700
1800
1900
2000
Wavenumber (cm^{-1})

◀ **Fig. 3** FTIR spectra of the molecules, blanks, and treated samples. **(a)** Adenine, **(b)** Adenosine, **(c)** 5’AMP; (---) solid montmorillonite (---) organic compound solid (---) adsorbed onto montmorillonite-distilled water (---) adsorbed onto montmorillonite-seawater 4.0 Ga

were actually inside the interlayer channel. The variations are showed in Fig. 5, where the FWHM is plotted against 2θ. The air-dried sample of montmorillonite plus adenine, with or without salts, shows similar d_{001} and FWHM values. This demonstrates that adenine is intercalated in the clay, and limits salt interaction. In the case of montmorillonite treated with adenine and distilled water, the values of d_{001} and FWHM are lower than for the same sample in presence of seawater. This suggests that the intercalation of ethylene glycol is more difficult as the adenine is occupying much of the available sites in the interlayer space (due to its planar structure), and it cannot be easily displaced. However, in the presence of dissolved salts, the ethylene glycol can partially penetrate the interlayer space and consequently the interlayer distance increases, and the “crystallinity” decreases (Zipkin et al. 1962). This confirms that dissolved salts are in the interlayer channel and therefore compete with organic molecules for available sites.

In the case of adenosine, the samples with salts both the air dried and those treated with ethylene glycol show higher value of interplanar distance than samples treated only with distilled water. The sample with seawater treated with ethylene glycol shows a complete expansion, comparable with the one obtained for the standard montmorillonite sample. This result suggests that the ethylene glycol can displace the previously absorbed adenosine molecules, because this molecule is weakly bound in the interlayer space of montmorillonite and easily extractable.

The values of d_{001} and FWHM for the 5’AMP in the samples that were air dried and treated with ethylene glycol show comparable values to the ones obtained for the standards indicating that the channel is not affected by the presence of 5’AMP. Particularly, 5’AMP is a relatively large molecule and probably not directly intercalated in the channel, but only absorbed on the external surfaces or edges of the clay.

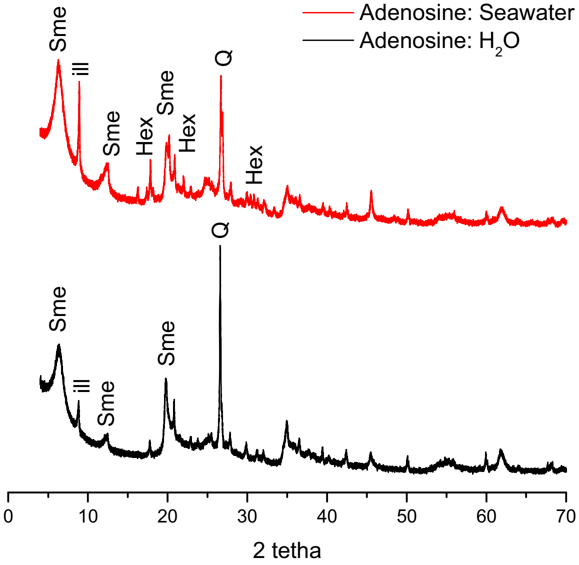
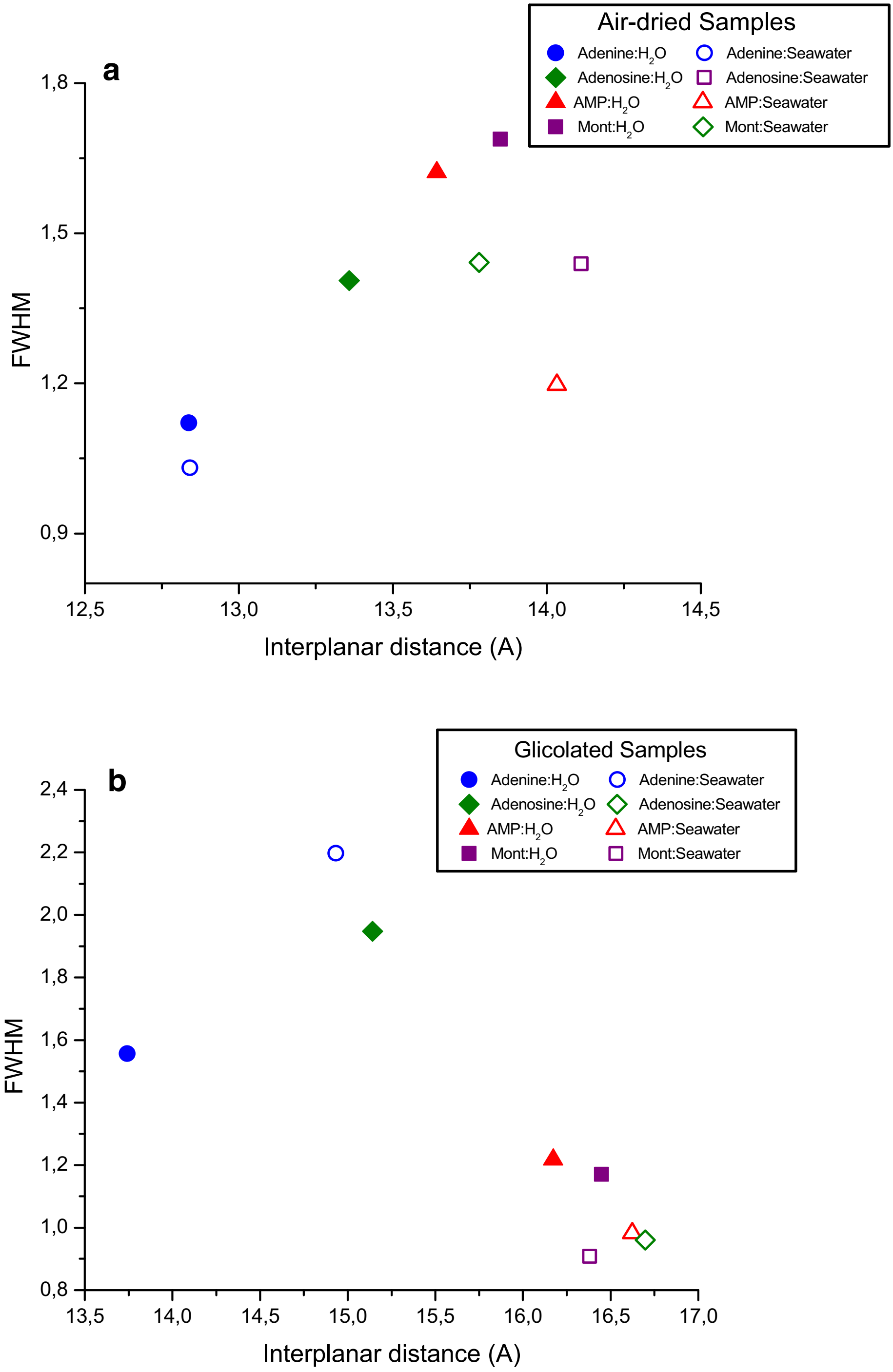


Fig. 4 Diffractograms of samples of adenosine adsorbed onto Na-montmorillonite. The samples were absorbed in presence of seawater 4.0 Ga and distilled water. Besides the expected peaks of clay, hexahydrite ($MgSO_4.6H_2O$) features are detected. This salt is precipitated in all cases where seawater is present. Key: Sme: smectite, Illite: Illite, Hex: hexahydrite, Q: quartz


a
Air-dried Samples
Adenine:H_2O
Adenine:Seawater
Adenosine:H_2O
Adenosine:Seawater
AMP:H_2O
AMP:Seawater
Mont:H_2O
Mont:Seawater
FWHM
1,8
1,5
1,2
0,9
12,5
13,0
13,5
14,0
14,5
Interplanar distance (A)
b
Glicolated Samples
Adenine:H_2O
Adenine:Seawater
Adenosine:H_2O
Adenosine:Seawater
AMP:H_2O
AMP:Seawater
Mont:H_2O
Mont:Seawater
FWHM
2,4
2,2
2,0
1,8
1,6
1,4
1,2
1,0
0,8
13,5
14,0
14,5
15,0
15,5
16,0
16,5
17,0
Interplanar distance (A)

◀ **Fig. 5** Correlation between interplanar distance and FWHM in treated samples, obtained by DRX. Two treatments are showed: **(a)** air dried and **(b)** treated with ethylene glycol. Plots of air-dried and treated with ethylene glycol samples shows that the values of d001 of smectite are greater for the samples with salts than for the samples treated with distilled water. This suggests that salts are in the interlayer space and affect the intercalation of the organic molecules

In general, these results support the idea that in the presence of salts, the organic molecules compete with them for available sites in the clay, either on the surface, at the edges, or in interlayer channels. In general, this suggests that salts could have played an important role in prebiotic oceans when interacting with organics and minerals.

Computational Methods

Simulations of molecular mechanics were obtained in order to get insight about the interactions between organic molecules, inorganic ions, and the montmorillonite mineral. As a first approximation, models were performed minimizing the interaction between organic molecules and the montmorillonite surface, inserting the organic molecule at a distance of ≈4.5 Å in vacuum (Fig. 6a). Particularly, the presence of SO_4^{-2} and Mg^{2+} ions enrich our analogue of seawater 4.0 Ga. After geometry optimization and molecular dynamics cycles in MM+ force field we obtained several local energy minima and the most stable configuration of the system. In the same way, the optimized geometries that were obtained by the MM+ molecular mechanics were further optimized with PM3 semi-empirical method.

The simulations resulted in a planar configuration of the molecules on the montmorillonite surface. As shown in Fig. 6b, the adsorption mechanism of adenine onto montmorillonite might be through a "base-stacking" mechanism by π-electron interaction (electron cloud sharing between the nitrogen base and the unpaired electrons of the oxygen in the tetrahedral sheet of the clay). These results agree with previous computational studies. Some authors (Mignon et al. 2009) show that a "face-to-face orientation" has the minimum energy interaction between nucleic acids and montmorillonite surface. Swadling et al. (2010) obtained the same behavior with RNA oligomers. Furthermore, this planar-arranged conformation has been suggested in other minerals (Cohn et al. 2001; Sowerby et al. 2004). For adenine, the mechanism involved may be via weak bond formations. In adenosine, the ring of the

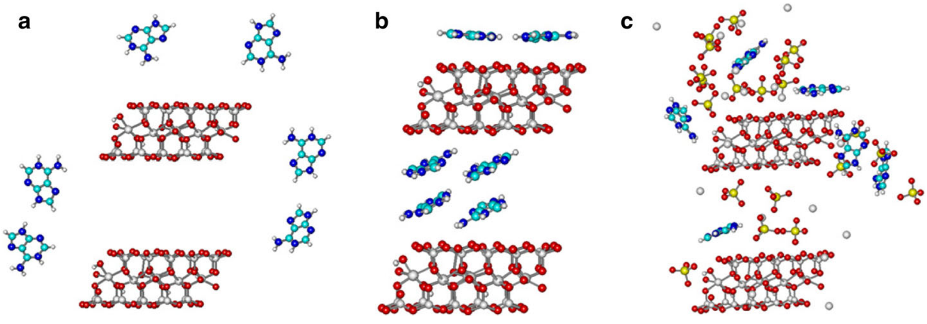


Fig. 6 Molecular mechanics (MM$^+$) simulations performed in the software HyperChemVersion 8.0.**(a)** The distances used to minimize the interaction between organic molecules and inorganic surfacesare shown (≈4.5 Å). **(b)** The more stable configuration between adenine and the surface of mineralsis reached; as it is observed, a planar-arranged fashion is the result. **(c)** The action of ions in the interaction of adenine and montmorillonite is shown; ions clearly interfere with adenine molecules in the computational model

nucleobase dominates the interactions with the mineral; the other possible configuration, the perpendicular orientation of the molecule on the mineral surface, would make the adsorption in the interlayer space difficult. In the case of the simulated monophosphate, the adsorption energy in the interlayer space was considerably lower than for the other organic compounds, possibly because the 5’AMP is a high molecular weight compound. However, the simulations suggest that the interactions between the edges of the montmorillonite and the phosphate group are responsible for the adsorption, and therefore might be the mechanism that dominates the organic-inorganic interaction (Graf and Lagaly 1980).

In the presence of the inorganic ions SO_4^{-2} and Mg^2, the simulations showed that the dissolved metals screen the adsorption process in a possible double layer mechanism. Fig. 6c shows that sulphates are directly screening the adsorption of adenine. We suggest a competitive behavior for the interlayer channel, where the sulfate ions displace adenine. Although it is possible that the base-stacking mechanism occurs on the clay surface, the adenine molecules might experience interference from the anions. In the case of adenosine, the screening effect is more noticeable. Particularly, the adsorption of 5’AMP in presence of inorganic ions seems to be not screened and even might be favored. Franchi et al. (2002) suggested that the divalent cations form bridges between the phosphate groups and minerals, thus improving the adsorption mechanism. It is necessary to continue to gain more realistic simulations concerning ionic exchange, hydrogen bridges, ligand exchange, and electrostatic forces. These results support that the dissolved inorganic ions in general decrease the interaction forces between organic compounds and clay.

Conclusions

The adsorption of organic compounds may be one of the first steps in chemical evolution toward molecular complexity. Although there are several experiments about the adsorption of organic molecules, many are not representative of the primitive environments.

The sorption of adenine, adenosine, and 5’AMP onto Na^+montmorillonite showed following order: 5’AMP > adenine > adenosine. In the range of pH used in this study, montmorillonite was negatively charged and adenine, adenosine, and 5’AMP had positive charge on N1, thus electrostatic interaction between them could occur. In addition, infrared spectra showed that the interaction between these molecules and montmorillonite occurs through the NH_2 group.

The results of this study, using an analogue of seawater 4.0 Ga in the adsorption of nucleic acids components, demonstrate that high concentration of dissolved salts affect the adsorption process. In all cases, the ions reduce the amount of organic compound adsorbed. However, the structure and size of each organic molecule influence the process. In thermodynamic terms, the adsorption capability is lower in the presence of dissolved salts. Furthermore, the X-ray diffraction patterns show corresponding peaks of hexahydrite and greater d-spacing values of the basal peak d_{001} in samples (air dried and treated with ethylene-glycol) that were absorbed in presence of dissolved salts. Indeed, the models of molecular dynamics support dissolved metals generally diminishing the interaction between organic compounds with clay. This research shows that the adsorption process could be affected when using solutions with high concentrations of salts as the ions and organic molecules may compete for available sites on inorganic surfaces. Although there is not total agreement about the conditions that existed in the early oceans, the possible role that the composition would have played in the sorption process seems to be a crucial parameter in the availability of organic molecules.

Acknowledgements SVB thanks CONACyT (697442) for the support to the internship at State University of Londrina and for the grant given during his master studies. JPTB acknowledge the PhD fellowship from Capes. The authors thank the support of DGAPA-PAPIIT (IA203217) and CNPq/FundaçãoAraucária (Programa de apoio a núcleos de excelência-PRONEX, protocol 24732) to this research.

References

Albaréde F (2007) The formation of crust and mantle of the rocky planets and the mineral environment of the origin of life. In: Muriel Gargaud et al. (Eds.), Lectures in Astrobiology. Springer, Berlin, pp 75–102. https://doi.org/10.1007/10913314_3

Anizelli PR, Baú JP, Nabeshima HS, da Costa MF, de Santana H, Zaia DM (2014) An experimental and theoretical vibrational study of interaction of adenine and thymine with artificial seawaters: A prebiotic chemistry experiment. Spectrochim Acta A126:184–196. https://doi.org/10.1016/j.saa.2014.02.011

Anizelli PR, Baú JPT, Gomes F, da Costa ACS, Carneiro CEA, Zaia CTBV, Zaia DAM (2015) A prebiotic chemistry experiment on the adsorption of nucleic acid bases onto a natural zeolite. Orig Life Evol Biosph 45:289–306. https://doi.org/10.1007/s11084-015-9401-1

Anizelli PR, Baú JPT, Valezi D, Canton L, Carneiro CEA, Di Mauro E, da Costa ACS, Galante D, Braga A, Rodrigues F, Coronas J, Casado-Coterillo C, Zaia CTBV, Zaia DAM (2016) Adenine interaction with and adsorption on Fe-ZSM-5 zeolites: a prebiotic chemistry study using different techniques. Micropor Mesopor Mater 226:493–504. https://doi.org/10.1016/j.micromeso.2016.02.004

Angell C (1961) 100. An infrared spectroscopic investigation of nucleic acid constituents. J Chem Soc 504–515. https://doi.org/10.1039/JR9610000504

Arora AK, Kamaluddin (2009) Role of metal oxides in chemical evolution: interaction of ribose nucleotides with alumina. Astrobiology 9:165–171. https://doi.org/10.1089/ast.2007.0143

Banin A, Lawless J, Mazzurco J, Church F, Margulies L, Orenberg J (1985) pH profile of the adsorption of nucleotides onto montmorillonite. Orig Life Evol Biosph 15:89–101. https://doi.org/10.1007/BF01809491

Baú JPT, Carneiro CEA, de Souza I, de Souza C, da Costa ACS, de Mauro E, Zaia CTBV, Coronas J, Casado C, de Santana H, Zaia DAM (2012) Adsorption of adenine and thymine on zeolites: FT-IR and EPR spectroscopy and X-ray Diffractometry and SEM studies. Orig Life Evol Biosph 42:19–29. https://doi.org/10.1007/s11084-011-9246-1

Benetoli LOB, de Souza C, da Silva L, de Souza I, de Santana H, Paesano A, da Costa ACS, Zaia CTBV, Zaia DAM (2007) Amino acid interaction with adsorption on clays :FT-IR and Mössbauer spectroscopy and X-ray diffractometry. Orig Life Evol Biosph 37:479–493. https://doi.org/10.1007/s11084-007-9072-7

Benetoli LOB, de Santana H, Zaia CTBV, Zaia D (2008) Adsorption of nucleic acid bases on clays: an investigation using Langmuir and Freundlich isotherms and FT-IR spectroscopy. Monatshftefür Chemie 139:753–761. https://doi.org/10.1007/s00706-008-0862-z

Bernal JD (1949) The physical basis of life. Proc Phys Soc Sect B 62(9):537

Besoain E (1985) Mineralogía de arcillas de suelos Instituto Interamericano de Cooperación para la agricultura. Serie de libros y materiales educativos San José, Costa Rica

Bhattacharyya K, Gupta S (2006) Adsorption of Fe (III) from water by natural and acid activated clays: studies on equilibrium isotherm, kinetics and thermodynamics of interactions. Adsorption 12:185–204. https://doi.org/10.1007/s10450-006-0145-0

Bhattacharyya K, Sharma A (2004) Adsorption of Pb (II) from aqueous solution by *Azadirachta indica* (neem) leaf powder. J Hazard Mater 113:97–109. https://doi.org/10.1016/j.jhazmat.2004.05.034

Bolan N, Syers J, Tillman R (1986) Ionic strength effects on surface charge and adsorption of phosphate and sulphate by soils. Eur J Soil Sci 37:379–388. https://doi.org/10.1111/j.1365-2389.1986.tb00371.x

Cairns-Smith AG (1966) The origin of life and the nature of the primitive gene. J Theor Biol 10(1):53–88. https://doi.org/10.1016/0022-5193(66)90178-0

Canhisares-Filho JE, Carneiro CEA, de Santana H, Urbano A, da Costa ACS, Zaia CTBV, Zaia DAM (2015) Characterization of the adsorption of nucleic acid bases onto Ferrihydrite via Fourier transform infrared and surface-enhanced Raman spectroscopy and X-ray Diffractometry. Astrobiology 15:728–738. https://doi.org/10.1089/ast.2015.1309

Carneiro CEA, Berndt G, de Souza I, de Souza C, Paesano A, da Costa ACS, di Mauro E, de Santana H, Zaia CTBV, Zaia DAM (2011) Adsorption of adenine, cytosine, thymine, and uracil on sulfide-modified montmorillonite:FT-IR, Mössbauer and EPR spectroscopy and X-ray Diffractometry studies. Orig Life Evol Biosph 41:453–468. https://doi.org/10.1007/s11084-011-9244-3

Carneiro CEA, Machado C, De Souza I Jr, Paesano A Jr, Di Mauro E, Da Costa ACS, De Souza C, De Santana H, Zaia DAM (2013) Modification of montmorillonite with sodium sulfide for prebiotic chemistry studies:

characterization using spectroscopy methods and X-ray diffractometry. Appl Clay Sci 86:18–22. https://doi.org/10.1016/j.clay.2013.09.016

Carneiro CEA, Stabile A, Gomes F, da Costa A, Zaia CTBV, Zaia DAM (2016) Interaction, at ambient temperature and 80°C, between minerals and artificial seawaters resembling the present ocean composition and that of 4.0 billion years ago. Orig Life Evol Biosph:1–21. https://doi.org/10.1007/s11084-016-9524-z

Chan S, Orenberg J, Lahav N (1987) Soluble minerals in chemical evolution II. Characterization of the adsorption of 5′-AMP and 5′-CMP on variety of soluble minerals salts. Orig Life Evol Biosph 17:121–134. https://doi.org/10.1007/BF01808240

Cohn C, Hansson T, Larsson H, Sowerby S, Holm N (2001) Fate of prebiotic adenine. Astrobiology 1:447–480. https://doi.org/10.1089/153110701753593874

Colthup NB, Daly LH, Wiberley SE (1964) Introduction to infrared and raman spectroscopy. Academic Press, New York

Colthup N (1975) Introduction to infrared and Raman spectroscopy, 2nd edn. Academic Press, New York

El-Bayaa A, Badawy N, AlKhalik E (2009) Effect of ionic strength on the adsorption of copper and chromium ions by vermiculite pure clay mineral. J Hazard Mater 170:1204–1209. https://doi.org/10.1016/j.jhazmat.2009.05.100

El-Nahhal Y, Lagaly G (2005) Salt effects on the bentonite. Colloid Polym Sci 283:968–974. https://doi.org/10.1007/s00396-004-1244-7

Ertem G (2004) Montmorillonite, oligonucleotides, RNA and the origin of life. Orig Life Evol Biosph 17:69–84. https://doi.org/10.1023/B:ORIG.0000043130.49790.a7

Farias APSF, Tadayozzi YS, Carneiro CEA, Zaia DAM (2014) Salinity and pH affect Na+−montmorillonite dissolution and amino acid adsorption: a prebiotic chemistry study. Int J Astrobiol 13:259–270. https://doi.org/10.1017/S1473550414000044

Ferris J (1993) Catalysis and prebiotic RNA synthesis. Orig Life Evol Biosph 23:307–315. https://doi.org/10.1007/BF01582081

Ferris J (2004) Montmorillonite catalysis of 30-50 Mer oligonucleotides: laboratory demonstration of potential steps in the origin of the RNA world. Orig Life Evol Biosph 4:311–332. https://doi.org/10.1023/A:1020543312109

Ferris J, Ertem G, Agarwal V (1989) The adsorption of nucleotides and polynucleotides on montmorillonita clay. Orig Life Evol Biosph 19:153–164. https://doi.org/10.1007/BF01808149

Feuillie C, Daniel I, Michot LJ, Pedreira-Segade U (2013) Adsorption of nucleotides onto Fe–mg–al rich swelling clays. Geochim Cosmochim Acta 120:97–108. https://doi.org/10.1016/j.gca.2013.06.021

Feuillie C, Sverjensky DA, Hazen RM (2014) Attachment of ribonucleotides on α-alumina as a function of pH, ionic strength, and surface loading. Langmuir 31(1):240–248. https://doi.org/10.1021/la504034k

Franchi M, Ferris J, Gallori E (2002) Cations as mediators of the adsorption of nucleic acids on clay surfaces in prebiotic environments. Orig Life Evol Biosph 33:1–16. https://doi.org/10.1023/A:1023982008714

Graf G, Lagaly G (1980) Interaction of clay minerals with adenosine-5-phosphates. Clay Clay Miner 28:12–18. https://doi.org/10.1346/CCMN.1980.0280102

Gull M (2014) Prebiotic phosphorylation reactions on the early earth. Challenges 5:193–212. https://doi.org/10.3390/challe5020193

Gupta S, Bhattacharyya K (2006) Adsorption of Ni(II) on clays. J Colloid Interface Sci 295:21–32. https://doi.org/10.1016/j.jcis.2005.07.073

Hashizume H, van der Gaast S, Theng B (2010) Adsorption of adenine, cytosine, uracil, ribose and phosphate by mg-exchanged montmorillonita. Clay Miner 45:469–475. https://doi.org/10.1180/claymin.2010.045.4.469

Izawa M, Nesbit H, MacRae N, Hoffman E (2010) Composition and evolution of the early oceans: evidence from the Tagish Lake meteorite. Earth Planet Sci Lett 298:443–449. https://doi.org/10.1016/j.epsl.2010.08.026

Jankovics H, Nagy L, Buzás N, Pellerito L, Barbieri R (2002) Coordination properties of adenosine-5′-monophosphate and related ligands towards Me2Sn(IV)2+ in aqueous solution. J Inorg Biochem 92:55–64

Jewitt D, Young E (2015) Oceans from the skies. Sci Am 312:36–43. https://doi.org/10.1038/scientificamerican0315-36

Jiang M, Jin X, Lu X, Chen Z (2010) Adsoprtion of Pb(II), cd(II), Ni(II) and cu(II) onto natural kaolinita clay. Desalination 252:33–39. https://doi.org/10.1016/j.desal.2009.11.005

Joshi P, Aldersley M (2013) Significance of mineral salts in prebiotic RNA synthesis catalyzed by montmorillonite. J Mol Evol 76:371–379. https://doi.org/10.1007/s00239-013-9568-x

Kundu J, Neumann O, Janesko BG, Zhang D, Lal S, Barhoumi A, Halas NJ (2009) Adenine− and adenosine monophosphate (AMP)− gold binding interactions studied by surface-enhanced Raman and infrared spectroscopies. J Phys Chem C 113(32):14390–14397. https://doi.org/10.1021/jp903126f

Kyriakopoulos G, Doulia D, Hourdakis A (2006) Effect of ionic strength and pH on the adsorption of selected herbicides on Amberlite. Int J Environ Anal Chem 86:207–214. https://doi.org/10.1080/03067310500247678

Lagaly G, Ogawa M, Dékány I (2006) Clay mineral organic interactions in: developments in clay science, Vol 1. Elsevier pp 141-245. https://doi.org/10.1016/S1572-4352(05)01010-X

Lahav N, Sherwood C (1982) The possible role of soluble salts in chemical evolution. J Mol Evol 19:36–46. https://doi.org/10.1007/BF02100222

Lailach G, Brindley G (1969) Specific co-absorption of purines and pyrimidines by montmorillonita (clay-organic studies XV). Clay Clay Miner 17:95–100. https://doi.org/10.1346/CCMN.1969.0170207

Lailach G, Thompson T, Brindley G (1968) Adsorption of pyrimidine, purines, and nucleosides by li-, Na-, mg-, and ca-Motmorillonite (clay-organic studies XII). Clay Clay Miner 16:285–293. https://doi.org/10.1346/CCMN.1968.01600405

Mathlouthi M, Seuvre AM, Koenig JL (1984) FT-IR and laser-Raman spectra of adenine and adenosine. Carbohydr Research 131:1–15. https://doi.org/10.1016/0008-6215(84)85398-7

Mignon P, Ugliengo P, Sodupe M (2009) Theoretical study of the adsorption of RNA/DNA bases on the external surfaces of Na+-montmorillonite. J PhysChem C 113:13741–13749. https://doi.org/10.1021/jp901699q

Miller S (1953) A production of amino acids under possible primitive earth conditions. Science 117:528–529. https://doi.org/10.1126/science.117.3046.528

Monnard P, Apel C, Kanavarioti A, Deamer D (2002) Influence of ionic inorganic solutes on self-assebly and polymerization processes related to early forms of life: implications for a prebiotic aqueous medium. Astrobiology 2:139–152. https://doi.org/10.1089/15311070260192237

Moore D, Reynolds R (1997) X-ray diffraction and the identification and analysis of clay minerals. New York, Oxford

Nakamoto K (1978) Infrared and Raman spectra of inorganic and coordination compounds. Wiley, New York

Orenberg J, Chang S, Calderon J, Lahav N (1985) Soluble minerals in chemical evolution. I. Adsoprtion of 5-AMP on CaSO4—a model system. Orig Life Evol Biosph 15:121–129. https://doi.org/10.1007/BF01809494

Orgel L (2004) Prebiotic chemistry and the origin of the RNA. Crit Rev Biochem Mol Biol 39:99–123. https://doi.org/10.1080/10409230490460765

Mathlouthi M, Seuvre, AM, Koenig JL (1984) FT-IR and laser-Raman spectra of adenine and adenosine. Carbohydr Res 131:1–15. https://doi.org/10.1016/0008-6215(84)85398-7

Pedreira-Segade U, Feuillie C, Pelletier M, Michot LJ, Daniel I (2016) Adsorption of nucleotides onto ferromagnesian phyllosilicates: Significance for the origin of life. Geochimica et Cosmochimica Acta 176: 81–95. https://doi.org/10.1016/j.gca.2015.12.025

Perezgasga L, Serrato-Diaz A, Negrón-Mendoza A, De Pablo-Galán L, Mosqueira F (2005) Sites of adsorption of adenine, uracil, and their corresponding derivates on sodium montmorillonite. Orig Life Evol Biosph 35: 91–110. https://doi.org/10.1007/s11084-005-0199-0

Pinti D (2005) The origin and evolution of the oceans. In: Muriel Gargaud et al. (Eds.), lectures in astrobiology. Springer, Berlin, pp 83–112. https://doi.org/10.1007/10913406_4

Porubcan L, Serna C, White J, Hem S (1978) Mechanism of adsorption of clindamycin and tetracycline by montmorillonite. J Pharm Sci 67:1081–1087. https://doi.org/10.1002/jps.2600670815

Rahman M, Islam M (2009) Effects of pH on isotherms modeling for cu (II) ions adsorption using maple wood sawdust. Chem Eng J 149:273–280. https://doi.org/10.1016/j.cej.2008.11.029

Roy D, Najafian K, Schleyer P (2007) Chemical evolution: the mechanism of the formation of adenine under prebiotic conditions. Proc Natl Acad Sci U S A 104:17272–17277. https://doi.org/10.1073/pnas.0708434104

Saladino R, Crestini C, Costanzo G, Di Mauro E (2005) On the prebiotic synthesis of nucleobases, nucleotides, oligonucleotides, pre-RNA and pre-DNA molecules. Top CurrChem 259:29–68. https://doi.org/10.1007/b136152

de Santana H, Paesano A, da Costa A, di Mauro E, de Souza I, Ivashita F, de Souza C, Zaia T, Zaia D (2010) Cysteine, thiourea and thiocyanate interactions with clays: FT-IR, Mössbauer and EPR spectroscopy and X-ray diffractometry studies. Amino Acids 38:1089–1099. https://doi.org/10.1007/s00726-009-0318-8

de Souza C, Carneiro CEA, Baú JPT, da Costa ACS, Ivashita F, Paesano A, di Mauro E, de Santana H, Holm N, Neubeck A, Zaia CTBV, Zaia DAM (2013) Interaction of forsterite-91 with distilled water and artificial seawater: a prebiotic chemistry experiment. Int J Astrobiol 12:135–143. https://doi.org/10.1017/S147355041200050X

Sowerby S, Mörth C, Holm N (2004) Effect of temperature on the adsorption of adenine. Astrobiology 1:481–487. https://doi.org/10.1089/153110701753593883

Spitzer J, Poolman B (2009) The role of biomacromolecular crowding, ionic strength, and physicochemical gradients in the complexities of life s emergence. Microbiol Mol Biol Rev 73:371–388. https://doi.org/10.1128/MMBR.00010-09

Sposito G (2008) The chemistry of soils. Oxford University Press, Oxford

Sposito G, Skipper N, Sutton R, Park S, Soper K, Greathouse J (1999) Surface geochemistry of the clay minerals. Proc Natl Acad Sci U S A 96:3358–3364. https://doi.org/10.1073/pnas.96.7.3358

Swadling J, Coveney P, Greenwell C (2010) Clay minerals mediate folding and Regioselective interactions of RNA: a large-scale atomistic simulation study. J Am Chem Soc 132:13750–13764. https://doi.org/10.1021/ja104106y

Tehei M, Franzetti B, Maurel M, Vergne J, Hountondji C, Zaceai G (2002) The search for traces of life: the protective effect of salt on biological macromolecules. Extremophiles 6:427–430. https://doi.org/10.1007/s00792-002-0275-6

Theng BKG (1974) The chemistry of clay-organic reactions. John Wiley and Sons, New York

Vergne J, Dumas L, Décout J, Maurel M (2000) Possible prebiotic catalysts formed from adenine and aldehyde. Planet Space Sci 48:1139–1142. https://doi.org/10.1016/S0032-0633(00)00087-8

Vieira AP, Berndt G, de Souza IG, di Mauro E, Paesano A, de Santana H, da Costa ACS, Zaia CTBV, Zaia DAM (2011) Adsorption of cystine on hematite, magnetite and ferrihydrite: FT-IR, Mössbauer, EPR spectrocopy and X-ray diffractometry studies. Amino Acids 40:205–214. https://doi.org/10.1007/s00726-010-0635-y

Vimonses V, Lei S, Jin B, Chow C, Saint C (2009) Kinetic study and equilibrium isotherm analysis of Congo red adsorption by clay materials. Chem Eng J 148:354–364. https://doi.org/10.1016/j.cej.2008.09.009

Winter D, Zubay G (1995) Binding of adenine and adenine-related compounds to the clay montmorillonite and the mineral hydroxylapatite. Orig Life Evol Biosph 25:61–81. https://doi.org/10.1007/BF01581574

Wright J, Colling A, Bearman G (1995) Seawater: its composition, properties and behavior. Elsevier Ltd, Oxford

Zaia DAM (2012) Adsorption of amino acids and nucleic acids bases onto minerals: a few suggestions for prebiotic chemistry experiments. Int J Astrobiol 11:229–234. https://doi.org/10.2307/3171566

Zipkin I, Posner AS, Eanes ED (1962) The effect of fluoride on the X-ray-diffraction pattern of the apatite of human bone. Biochim Biophys Acta 59:255–258. https://doi.org/10.1016/0006-3002(62)90730-8