


Interaction between adenine and Cu^{2+} and Fe^{3+} -montmorillonites: a prebiotic chemistry experiment

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Research Article

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Abstract

The modification of minerals with metals can promote changes in their surface and, consequently, in their physicochemical properties. Minerals could have played an important role in the origin of life as they can protect molecules against degradation by radiation and hydrolysis, pre-concentrate molecules from dilute solutions and catalyse the formation of polymers. Thus, the current work studied the modification of montmorillonite with Cu^{2+} and Fe^{3+} ions. These modified montmorillonites were used to study the interaction with adenine dissolved in distilled water and artificial seawater 4.0 Gy (Gy = billion years ago). The most important result of this work is that the adsorption of adenine onto modified montmorillonites is a complex interaction among adenine, salts in seawater and $\text{Cu}^{2+}/\text{Fe}^{3+}$ -montmorillonite ($\text{Cu}^{2+}/\text{Fe}^{3+}$ -Mont). The adsorption of Cu^{2+} and Fe^{3+} onto montmorillonite decreased its surface area and pore volume. The Sips isotherm model showed the best fit of the data and n values indicate that the adenine adsorption process was homogeneous. The highest adenine adsorption was obtained in artificial seawater 4.0 Gy onto Fe^{3+} -Mont at 60°C and the lowest in distilled water or artificial seawater 4.0 Gy onto montmorillonite [montmorillonite washed with distilled water (Mont-STD)] at 60°C. Adenine adsorption onto Mont-STD/montmorillonite modified with 500 ml of 0.1 mol l⁻¹ of CuCl_2 and Fe^{3+} -Mont was an exothermic process and an endothermic process, respectively. For all adsorptions ΔG was negative. The adsorption of adenine onto Fe^{3+} -Mont was ruled out by entropy and the other samples by enthalpy and entropy, being a major contribution for Gibbs free energy from enthalpy. The Fourier transform-infrared data indicate that the interaction of adenine with minerals may occur through the NH_2 functional group.

Introduction

According to the hypothesis proposed in 1951 by the Irish scientist John Desmond Bernal on primitive Earth minerals was important in the pre-concentration and polymerization of organic molecules, in the protection of these molecules against hydrolysis and ultraviolet (UV) radiation and even as a primitive genetic code (Bernal, 1951). Several studies show that at least the first four roles could have occurred (Lahav and Chang, 1976; Mosqueira *et al.*, 1996; Zaia, 2004; Lambert, 2008; Marshall-Bowman *et al.*, 2010; Baú *et al.*, 2020).

Nowadays on the Earth, there are more than 5000 minerals. However, 3.5–3.8 Gy (Gy = billion years ago), before the appearance of the first living beings, ~500 types of minerals existed on Earth (Westall, 2004; Hazen *et al.*, 2008; Hazen, 2013; Morrison *et al.*, 2018). According to Hazen *et al.* (2008), the main minerals found in this period were Mg-olivines, pyroxene, Fe–Ni metal, FeS, phyllosilicates, carbonates, sulphates and hydroxides. Among the clay minerals, montmorillonite existed on the primitive Earth (Hazen *et al.*, 2008) and since montmorillonite has a high surface area and adsorbs organic molecules, it is one of the most widely studied minerals in prebiotic chemistry (Zaia, 2012; Theng, 2018). Montmorillonite was identified in 1896, and is a phyllosilicate from the smectite group ($(\text{Si}_{7.74}\text{Al}_{0.26})(\text{Al}_{3.06}\text{Fe}_{0.03}^{3+}\text{Fe}_{0.03}^{2+}\text{Mg}_{0.48})\text{O}_{20}(\text{OH})_4\text{Na}_{0.77}$), with a crystalline arrangement of tetrahedral/octahedral sheets type 2:1 (Paineau *et al.*, 2011; Savic, 2014; Uddin, 2018). Montmorillonite is negatively charged, due to the substitution of cations in the tetrahedral and mainly in the octahedral sheets of the clay, providing a negative charge between 0.2 and 0.5 eV. The charge of the layer is compensated by the introduction of interchangeable intercalary cations, usually in its hydrated form (Krupskaya *et al.*, 2017).

Montmorillonite adsorbs several metals, which could modify its properties (Savic *et al.*, 2014; Theng, 2018; Uddin, 2018). Among these, Cu^{2+} and Fe^{3+} ions should be highlighted, because they have great affinity to form complexes with biomolecules (Briner, 1958;

Perrin, 1959, 1960; Hallman *et al.*, 1971; Bryantsev *et al.*, 2009; Masoud *et al.*, 2012), this has great implications in prebiotic chemistry (Lailach *et al.*, 1968*b*; Schwendinger and Rode, 1989; Rode and Schwendinger, 1990; Rode and Suwannachot, 1999; Rode *et al.*, 1999; Remko and Rode, 2001; Fitz *et al.*, 2007; Rimola *et al.*, 2007; Feuillie *et al.*, 2013; Kim and Switzer, 2014; Pedreira-Segade *et al.*, 2016, 2018; Zaia and Zaia, 2021).

Iron is the fourth most abundant element in the Earth's crust (Cornell and Schwertmann, 2003; Hazen *et al.*, 2008). Most of the iron on the prebiotic Earth was in the form of Fe⁰, Fe in alloys and Fe²⁺ in several different minerals such as olivine, pyroxene, iron-oxide, iron-sulfides, iron-carbonates, iron-phosphates and Fe²⁺ in the prebiotic Earth oceans (Hazen *et al.*, 2008; Cleaves *et al.*, 2012; Hazen, 2013; Morrison *et al.*, 2018). Although the prebiotic atmosphere was considerably anoxic (Catling and Claire, 2005), Fe³⁺ ions could be derived from the oxidation of Fe²⁺ by UV radiation or hydrogen peroxide formed in ice (Braterman *et al.*, 1983; Liang *et al.*, 2006). In addition, temperature conditions, ranging from 300 to 350°C; pressures (from 10 to 25 MPa), with alkaline pH (from 9.5 to 14), could also have oxidized Fe²⁺ to Fe³⁺ (Bassez, 2018). Thus, we cannot rule out the existence of minerals containing Fe³⁺ such as clay minerals (berthierine, chamosite, cronstedtite, greenalite, nontronite and vermiculite), oxides and hydroxides (akageneite, ferrihydrite, goethite, hematite, lepidocrocite and magnesioferrite), garnets (andradite and schorlomite), pyroxenes (aegirine and aegirine-augite), amphiboles (arfvedsonite, hastingsite, katophorite, magnesio-arfvedsonite and magnesiohornblende), carbonates (pyroaurite) and micas (celadonite) (Cleaves *et al.*, 2012; Hazen, 2013; Morrison *et al.*, 2018). In addition, we cannot rule out the existence of Fe³⁺ in the prebiotic Earth oceans.

Even though average crustal abundance of copper (50 ppm) is much lower than the iron (41 000 ppm) (Hazen, 2013), its importance for the molecular evolution and formation of polymers, makes it an important element to use in prebiotic chemistry experiments (Schwendinger and Rode, 1989; Rode and Schwendinger, 1990; Rode and Suwannachot, 1999; Rode *et al.*, 1999; Remko and Rode, 2001; Fitz *et al.*, 2007; Rimola *et al.*, 2007; Kim and Switzer, 2014; Zaia and Zaia, 2021). As reported above for the iron, copper could also be found on the prebiotic Earth as Cu⁰ metal, Cu in (Cu, Ni, Zn) alloys and Cu⁺ in several minerals such as copper-sulfides, copper-oxides and copper-sulfosalts, as well as Cu⁺ in the seas of the prebiotic Earth (Hazen *et al.*, 2008; Hazen, 2013; Morrison *et al.*, 2018). Although the oxygen concentration in Earth's atmosphere was very low (Catling and Claire, 2005), it was sufficient to oxidize Cu⁺ to Cu²⁺ (Ochiai, 1978). Thus, we could expect to have minerals containing Cu²⁺ on the prebiotic Earth, such as copper-carbonates (azurite and malachite) and copper-sulphates (brochantite and chalcantite) and Cu²⁺ in the prebiotic Earth oceans (Morrison *et al.*, 2018).

It should be noted that the minerals described above that contain Cu²⁺ and Fe³⁺ are volumetrically significant enough to be considered important in prebiotic chemistry experiments (Hazen, 2013; Morrison *et al.*, 2018).

Nowadays, iron and copper play important roles in the physiological processes of living beings (Murad and Fischer, 1988; Williams, 2007; Curi and Procopio, 2017). Probably due to high affinity for amino acids, several metalloenzymes contain iron and copper (Ochiai, 1978, 1983; Williams, 1985; Andreini *et al.*, 2008). Thus, it could be expected that iron and copper were important for the origin of life.

According to Knauth (1998), the primitive oceans were approximately twice as saline as those of today, which present high concentrations of Na⁺ and Cl⁻ ions. With this in mind, Zaia (2012) suggested a seawater composition, using the information from the work of Izawa *et al.* (2010), in which the main ions are Mg²⁺, Ca²⁺ and SO₄²⁻. The high concentrations of these ions were determined based on the concentration of ions present in the Tagish Lake meteorite, found in Tagish Lake (Yucon, Canada). The meteorite is a carbonaceous chondrite that provides important information on the composition and evolution of primitive oceans (Brown *et al.*, 2000). This seawater better represents the saline composition of the prebiotic Earth compared with current seawater and is denominated seawater 4.0 Ga.

There are several studies describing the synthesis of adenine under prebiotic chemical conditions (Basile *et al.*, 1984; Orgel, 2004; Borquez *et al.*, 2005; Larowe and Regnier, 2008; Cleaves *et al.*, 2012; Iqbal *et al.*, 2019; Yadav *et al.*, 2020), as well as its detection in meteorites (Hua *et al.*, 1986). Therefore, adenine and montmorillonite were most likely present in the primitive Earth and it is probable that they could have interacted.

There are several works showing that the adsorption of adenine and adenine nucleotides onto clays depends on the pH and the exchangeable cations (Lailach *et al.*, 1968*a*, 1968*b*; Lailach and Brindley, 1969; Winter and Zubay, 1995; Benetoli *et al.*, 2008; Carneiro *et al.*, 2011; Cleaves *et al.*, 2012; Feuillie *et al.*, 2013, 2015; Pedreira-Segade *et al.*, 2016; Villafañe-Barajas *et al.*, 2018; Baú *et al.*, 2020). The interaction of biomolecules with mineral surfaces could have contributed to chemical evolution. In addition, the adsorption of adenine and adenine nucleotides has been studied in several other minerals such as silica (Basiuk *et al.*, 1995; Cohn *et al.*, 2001; Cleaves *et al.*, 2012), iron-sulfides (Cohn *et al.*, 2001), forsterite (Cohn *et al.*, 2001), graphite (Sowerby *et al.*, 2001), rutile (Cleaves *et al.*, 2010), apatite (Winter and Zubay, 1995; Hammami *et al.*, 2015), iron oxides (Cohn *et al.*, 2001; Canhisares-Filho *et al.*, 2015) and zeolites (Baú *et al.*, 2012; Anizelli *et al.*, 2016). Depending on the environment in which a given mineral is found, its surface and physical-chemical properties may be different due to modifications by elements or molecules that could have interacted with it. For clay minerals, the main properties that can be modified are the increase in the interlamellar space and the capacity of ionic exchange capacity. Thus, a biomolecule that would be poorly adsorbed in a mineral under certain conditions may have an increased adsorption if the mineral has been modified (Mortland *et al.*, 1986).

Thus, the main goal of this work was to modify the montmorillonite mineral with Cu²⁺ and Fe³⁺ ions, in order to determine the adsorption capacity of adenine under prebiotic chemistry conditions on the modified material, and to investigate the interaction of the adenine with the montmorillonite [montmorillonite washed with distilled water (Mont-STD)], Cu²⁺-montmorillonite [montmorillonite modified with 500 ml of 0.1 mol l⁻¹ of CuCl₂ (Cu²⁺-Mont)] and Fe³⁺-montmorillonite [montmorillonite modified with 500 ml of 0.1 mol l⁻¹ FeCl₃ solution (Fe³⁺-Mont)] using different adsorption isotherm models, infrared (IR) spectroscopy-Fourier transform-IR (FT-IR) and X-ray diffractometry. Adsorption isotherms were obtained at the temperatures of 30, 45 and 60°C, because they are easily controlled using a water bath. Furthermore, these temperatures are in the range of the primitive oceans of the Earth (Krissansen-Totton *et al.*, 2018). To better represent the primitive Earth, the prebiotic chemistry experiments were performed in saline solution.

Materials and methods

All the reagents were of analytical grade P.A.

Materials

Montmorillonite

Montmorillonite KSF (CAS 1318-93-0) was purchased from Acros Organics, NJ, USA and was used as received.

Artificial Seawater

Artificial seawater 4.0 Gy was prepared as described by Zaia (2012). The following salts were dissolved in 1.0 l of ultrapure water: Na₂SO₄ (0.271 g), MgCl₂·6H₂O (0.500 g), CaCl₂·2H₂O (2.50 g), KBr (0.050 g), K₂SO₄ (0.400 g) and MgSO₄ (15.00 g).

Modification of montmorillonite

Mont-STD was prepared by making a suspension of 5 g of montmorillonite KSF in 500 ml of distilled water under constant stirring for 24 h. The suspension was filtered and washed with 3.0 l of distilled water and then it was lyophilized.

To prepare the montmorillonite modified with Cu²⁺ (Cu²⁺-Mont) and Fe³⁺ (Fe³⁺-Mont), the clay was saturated with Cu²⁺ or Fe³⁺ by stirring 5 g of montmorillonite with 500 ml of 0.1 mol l⁻¹ of CuCl₂ or FeCl₃ solution for 24 h. The suspension was filtered and washed with distilled water until it was free of Cl⁻ ions and then lyophilized.

Methods

Adsorption isotherms

To obtain the adsorption isotherms, 10 mg adenine dissolved in distilled water or in artificial seawater 4.0 Gy with concentrations ranging from 0 to 800 mg l⁻¹ were mixed with 50 mg of Mont-STD, Cu²⁺-Mont, or Fe³⁺-Mont (all experiments were performed by triplicate) in 15 mL Falcon tubes. The samples were stirred for 1 h at three different temperatures (30, 45 and 60°C), at a pH range of 5.00–6.00. The temperatures were controlled (±0.2°C) using a thermostatic water bath. Next, the samples were centrifuged at 6000 rpm, the supernatant was collected and the adenine was quantified using a spectrophotometer UV-Vis Spectrum SP-2000UV at 260 nm.

The results of adenine adsorption on different montmorillonites were fitted to non-linear isotherm models: Langmuir, Freundlich and Sips models (Limousin *et al.*, 2007; Foo and Hameed, 2010).

Non-linear Langmuir isotherm model

$$q_e = \frac{k_{eq} Q_{max} C}{(1 + C)} \quad (1)$$

where C (mg l⁻¹) is the concentration of adenine in the solution after the equilibrium; q_e (mg g⁻¹) is the concentration of adenine adsorbed onto montmorillonite (difference between initial adenine concentration and the concentration after the equilibrium) by mass unity; Q_{max} (mg g⁻¹) is the theoretical limit of adsorbed adenine onto montmorillonite; and k_{eq} (L mg⁻¹) is the equilibrium constant (adsorbate-adsorbent).

Non-linear Freundlich isotherm model

$$q_e = K_f C^n \quad (2)$$

where K_f is the adsorption capacity of Freundlich and n is the index of heterogeneity.

Table 1. Parameters obtained from N₂ adsorption/desorption isotherm

Parameters	Methods	Mont-STD	Cu ²⁺ -Mont	Fe ³⁺ -Mont
Superficial area (m ² g ⁻¹)	BET	200.6	170.0	158.7
Pore volume (cm ³ g ⁻¹)	BJH	0.19	0.11	0.14
	DH	0.19	0.11	0.14
Pore size (Å)	BJH	19.1	19.1	18.8
	DH	19.1	19.1	18.8

BET, Brunauer, Emmett and Teller method used for superficial area determination; BJH: Barret-Joyner-Halenda; DH: Dollimore and Heal methods used for pore volume and pore size determinations. Mont-STD is montmorillonite washed with distilled water. Cu²⁺-Mont is montmorillonite modified with CuCl₂ solution (0.1 mol l⁻¹). Fe³⁺-Mont is montmorillonite modified with FeCl₃ solution (0.1 mol l⁻¹). Each result is the mean of two experiments.

Non-linear Sips isotherm model

$$q_e = \frac{Q_{max}(KC)^n}{1 + (KC)^n} \quad (3)$$

where K (L mg⁻¹) is the affinity constant for adsorption and n is the index of heterogeneity.

N₂ isotherm

Determination of surface area, volume and pore size was performed on a High Speed Gas Sorption Analyzer, Version 11.02. The samples were previously treated at 120°C under vacuum for 3 h. Measurements were performed at liquid N₂ temperature (77.3 K). Data were analysed with NovaWin 11.0 software. The Brunauer, Emmett and Teller (BET) method was used to calculate the surface area by plotting $P/v(P_0 - P)$ versus P/P_0 (equation (4)).

$$\frac{P}{v(P_0 - P)} = \frac{1}{v_m C} + \frac{(C - 1)P}{C v_m P_0}$$

where P_0 is the equilibrium pressure, P is the saturation pressure, v is the adsorbed gas volume, v_m is the adsorbed gas monolayer volume and C is the BET constant. The Barret-Joyner-Halenda (BJH) and Dollimore and Heal (DH) methods were used to calculate pore size and volume.

FT-IR spectroscopy

FT-IR spectra were obtained using a Bruker FT-IR spectrophotometer, model Vertex 70, with Platinum ATR reflectance accessory. The spectra from 400 to 4000 cm⁻¹ were obtained from 16 scans at a resolution of 4 cm⁻¹.

Results and discussion

Specific surface area

The surface area and pore volume of montmorillonites modified with Fe³⁺ and Cu²⁺ decreased compared with Mont-STD (Table 1). The decrease in surface area and pore volume could be attributed to the sorption of metals onto montmorillonite. The pore size was not changed after modification with the ions.

Adsorption isotherms

The adsorbed adenine, dissolved in distilled water or artificial seawater 4.0 Gy, onto Mont-STD and Cu²⁺-Mont decreased as

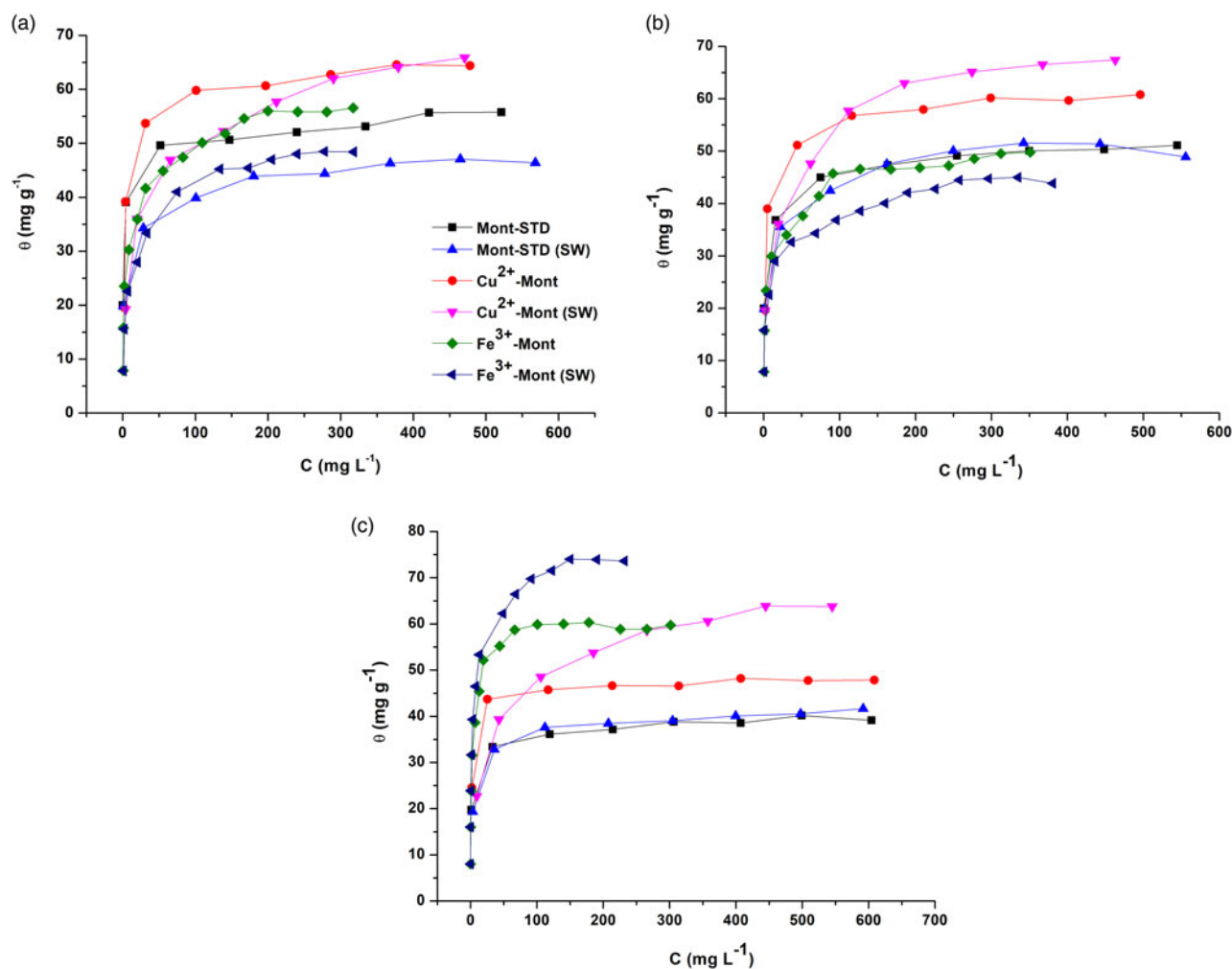


Fig. 1. Adsorption isotherms of adenine onto different montmorillonites in distilled water and artificial seawater 4.0 Gy at (a) 30°C; (b) 45°C and (c) 60°C. C (mg L⁻¹) is the concentration of adenine in solution after the equilibrium, θ (mg g⁻¹) is the amount of adenine adsorbed onto montmorillonites. **Mont-STD:** adenine dissolved in distilled water adsorbed onto Mont-STD; **Mont-STD (SW):** adenine dissolved in artificial seawater 4.0 Gy adsorbed onto Mont-STD; **Cu²⁺-Mont:** adenine dissolved in distilled water adsorbed onto Cu²⁺-Mont; **Cu²⁺-Mont (SW):** adenine dissolved in artificial seawater 4.0 Gy adsorbed onto Cu²⁺-Mont; **Fe³⁺-Mont:** adenine dissolved in distilled water adsorbed onto Fe³⁺-Mont; **Fe³⁺-Mont (SW):** adenine dissolved in artificial seawater 4.0 Gy adsorbed onto Fe³⁺-Mont. Mont-STD is montmorillonite washed with distilled water. Cu²⁺-Mont is montmorillonite modified with CuCl₂ solution (0.1 mol L⁻¹). Fe³⁺-Mont is montmorillonite modified with FeCl₃ solution (0.1 mol L⁻¹). Each result was a mean of three experiments. The solutions were stirred for 1 h at 30, 45 and 60°C, with 50 mg of montmorillonite, at pH range 5.0–6.0. Artificial seawater 4.0 Gy was prepared as described by Zaia (2012).

temperature increased (Fig. 1). However, we observed an opposite trend for adenine adsorbed onto Fe³⁺-Mont (Fig. 1). Thus, an exothermic process occurred for adenine adsorbed onto Mont-STD or Cu²⁺-Mont, while an endothermic process occurred for adenine adsorbed onto Fe³⁺-Mont. The highest adenine adsorption occurred when adenine was dissolved in artificial seawater 4.0 Gy onto Fe³⁺-Mont at 60°C (Fig. 1). The lowest adenine adsorption occurred when adenine was dissolved in distilled water or artificial seawater 4.0 Gy onto Mont-STD (Fig. 1). Adenine dissolved in artificial seawater 4.0 Gy adsorbed little less on montmorillonite than adenine dissolved in distilled water (Fig. 1, Table 2), however, depending on the pH (3.9–4.6) this effect was higher (Villafañe-Barajas *et al.*, 2018) and at very acidic pH (2.20–2.74) there was no difference between them (Baú *et al.*, 2020). The adenine adsorption, at several pH ranges, onto ferrihydrite decreased in all seawaters (seawater 4.0 Gy, today's seawater) when compared with distilled water (Canhisares-Filho *et al.*, 2015). Furthermore, the adsorption of uridine-5'-monophosphate onto brucite decreased in NaCl solution when compared with distilled water (Fornaro

et al., 2018). However, artificial seawater 4.0 Gy did not decrease the adsorption of adenine onto several Fe-ZSM-5 zeolites (Anizelli *et al.*, 2016). Although the modification of montmorillonite with Fe³⁺ and Cu²⁺ decreased its surface area (Table 1), the adsorption of adenine onto these clays, in general, was higher than on Mont-STD (Fig. 1). It should be noted that, in general, transition metals enhanced the adsorption of nucleic acid bases and nucleotides onto clay minerals (Lailach *et al.*, 1968a; Pedreira-Segade *et al.*, 2016, 2018; Hao *et al.*, 2019). In addition, the effect of an increase in adsorption of adenine onto modified montmorillonites was higher at higher temperatures (Fig. 1(c)). The adsorption of adenine onto montmorillonites was not due to electrostatic interaction, since in the pH range used (5.0–6.0), adenine is uncharged (Christensen *et al.*, 1970). Cu²⁺-Mont or Fe³⁺-Mont adsorbed the same amount of positively or uncharged adenine (Lailach *et al.*, 1968b). Thus, it is probable that adenine interacts with the adsorbed metals on montmorillonite.

Among the isotherm models studied, for all samples with one exception, the Sips model showed the best coefficient of

Table 2. Sips parameters obtained for non-linear model adjustment of adenine adsorption onto different montmorillonites in distilled water or artificial seawater 4.0 Gy

Sample	Parameters	Distilled water		
		30°C	45°C	60°C
Mont-STD	Q_{\max}	65.24	68.27	43.15
	K	0.984	0.143	0.529
	n	0.270	0.256	0.412
Cu ²⁺ -Mont	Q_{\max}	64.47	63.30	47.81
	K	0.191	0.164	0.546
	n	0.897	0.723	0.860
Fe ³⁺ -Mont	Q_{\max}	69.33	57.65	66.91
	K	0.066	0.095	0.390
	n	0.500	0.514	0.506
Sample	Parameters	Seawater 4.0 Gy		
		30°C	45°C	60°C
Mont-STD	Q_{\max}	64.43	67.65	43.90
	K	0.059	0.073	0.199
	n	0.293	0.320	0.547
Cu ²⁺ -Mont	Q_{\max}	91.43	91.75	82.45
	K	0.016	0.023	0.019
	n	0.457	0.467	0.548
Fe ³⁺ -Mont	Q_{\max}	60.75	60.81	96.65
	K	0.046	0.037	0.109
	n	0.541	0.395	0.393

Each result is a mean of three experiments. The solutions were stirred for 1 h at 30, 45 and 60°C, with 50 mg of montmorillonite, at pH range 5.00–6.00. Q_{\max} : maximum adsorption capacity (mg g^{-1}); K : adsorbate–adsorbent affinities (L mg^{-1}); n : empiric constant. Artificial seawater 4.0 Gy was prepared as described by Zaia (2012). Mont-STD is montmorillonite washed with distilled water. Cu²⁺-Mont is montmorillonite modified with CuCl₂ solution (0.1 mol L⁻¹). Fe³⁺-Mont is montmorillonite modified with FeCl₃ solution (0.1 mol L⁻¹).

determination- R^2 (Table 3). Thus, this model was used to obtain maximum adsorption capacity (Q_{\max}), adsorbate–adsorbent affinities (k) and empiric constant (n) (Table 2).

For experiments carried out in distilled water, the maximum adsorption capacity (Q_{\max}) values of adenine adsorbed onto Mont-STD and Cu²⁺-Mont did not demonstrate large differences at 30 and 45°C; however, there was a considerable decrease at 60°C (Table 2). In addition, Mont-STD and Cu²⁺-Mont presented almost the same Q_{\max} values (Table 2), meaning that Cu²⁺ did not have an effect on adenine adsorption when it was dissolved in distilled water (Table 2). In addition, artificial seawater 4.0 Gy did not have an effect on the adsorption of adenine onto Mont-STD. However, at 30 and 45°C, artificial seawater 4.0 Gy had a large effect on the adsorption of adenine onto Cu²⁺-Mont (Table 2). For all these experiments, the adsorption of adenine decreased at 60°C (Fig. 1, Table 2). This decrease in adsorption with increasing temperature indicates that adenine adsorption on these montmorillonites is an exothermic process. In addition, the adsorption of adenine onto graphite is an exothermic process (Sowerby *et al.*, 2001). The Q_{\max} values for the adsorption of adenine onto Fe³⁺-Mont at 30 and 45°C did not show a large variation in

Table 3. R^2 parameters for isothermal modelling of adenine adsorption onto different montmorillonites in distilled water or artificial seawater 4.0 Gy

Sample	Model	Distilled water		
		30°C	45°C	60°C
Mont-STD	Langmuir	0.921	0.936	0.962
	Freundlich	0.961	0.976	0.938
	Sips	0.994	0.998	0.994
Cu ²⁺ -Mont	Langmuir	0.983	0.972	0.993
	Freundlich	0.951	0.944	0.938
	Sips	0.982	0.985	0.995
Fe ³⁺ -Mont	Langmuir	0.929	0.931	0.932
	Freundlich	0.954	0.940	0.909
	Sips	0.987	0.982	0.987
Sample	Model	Seawater 4.0 Gy		
		30°C	45°C	60°C
Mont-STD	Langmuir	0.932	0.913	0.976
	Freundlich	0.976	0.953	0.924
	Sips	0.995	0.980	0.996
Cu ²⁺ -Mont	Langmuir	0.935	0.972	0.957
	Freundlich	0.979	0.965	0.972
	Sips	0.995	0.992	0.998
Fe ³⁺ -Mont	Langmuir	0.952	0.888	0.927
	Freundlich	0.965	0.962	0.969
	Sips	0.994	0.981	0.993

Each result is a mean of three experiments. Artificial seawater 4.0 Gy was prepared as described by Zaia (2012). Mont-STD is montmorillonite washed with distilled water. Cu²⁺-Mont is montmorillonite modified with CuCl₂ solution (0.1 mol L⁻¹). Fe³⁺-Mont is montmorillonite modified with FeCl₃ solution (0.1 mol L⁻¹).

distilled water or artificial seawater (Table 2). Furthermore, these Q_{\max} values were almost the same as those obtained when adenine was dissolved in distilled water and artificial seawater 4.0 Gy and adsorbed onto Mont-STD or Cu²⁺-Mont and Mont-STD, respectively (Table 2). However, when adenine was dissolved in artificial seawater 4.0 Gy and adsorbed onto Fe³⁺-Mont at 60°C, the highest Q_{\max} value was obtained (Table 2). Thus, in this case, the adsorption is an endothermic process. These results suggest that the adsorption of adenine onto Cu²⁺-Mont or Fe³⁺-Mont involves a complex interaction among adenine, salts in seawater and Cu²⁺/Fe³⁺. A possible explanation for these data would be that the salts of the artificial seawater decreased the activity of the water, thereby reducing the hydration sphere of adenine, as well as of the metals, facilitating its interaction with Cu²⁺/Fe³⁺-Mont (Do Nascimento Vieira *et al.*, 2020).

The n parameter of the Sips isotherm model could be related to the heterogeneity of the system (Do, 1998). The adsorption is heterogeneous when montmorillonites have several different adsorption sites and adenine interacts differently with them. For the Sips isotherm model, if the n values are >1, this means that the system is more heterogeneous (Do, 1998). For all experiments, the n values were <1, which means that the adenine adsorption process on the montmorillonites is homogeneous (Table 2).

Table 4. Thermodynamic parameters found for adenine adsorption onto different montmorillonites at distilled water or seawater 4.0 Gy

Sample	Temperature (°C)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹)
Mont-STD/distilled water	30	-10.09	-6.92	+10.58
	45	-10.36		
	60	-10.41		
Cu ²⁺ -Mont/distilled water	30	-10.50	-7.85	+8.88
	45	-10.75		
	60	-10.77		
Fe ³⁺ -Mont/distilled water	30	-10.08	+3.53	+44.83
	45	-10.20		
	60	-10.40		
Mont-STD/artificial seawater 4.0 Gy	30	-9.81	-5.34	+14.92
	45	-10.20		
	60	-10.26		
Cu ²⁺ -Mont/artificial seawater 4.0 Gy	30	-10.85	-1.98	+29.30
	45	-11.33		
	60	-11.73		
Fe ³⁺ -Mont/artificial seawater 4.0 Gy	30	-9.90	+12.56	+73.32
	45	-10.29		
	60	-12.10		

Each result is a mean of three experiments. Gibbs free energy (ΔG), enthalpy (ΔH), entropy (ΔS). Artificial seawater 4.0 Gy was prepared as described by Zaia (2012). Mont-STD is montmorillonite washed with distilled water. Cu²⁺-Mont is montmorillonite modified with CuCl₂ solution (0.1 mol l⁻¹). Fe³⁺-Mont is montmorillonite modified with FeCl₃ solution (0.1 mol l⁻¹).

Thermodynamic functions (ΔG , ΔH , ΔS)

For better understanding of the adsorption process, the thermodynamic parameters, namely Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), were determined from equations (5) and (6):

$$\Delta G = -RT \ln(K_d) \quad (5)$$

$$\ln K_d = \Delta S/R - \Delta H/RT \quad (6)$$

where R is the thermodynamic gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature (K) and K_d is the distribution coefficient (Lg⁻¹) that can be obtained by plotting q_e/C versus q_e and extrapolating q_e to zero.

For all experiments, ΔG presented negative values, indicating that adenine adsorption on different montmorillonites is a spontaneous and favourable process (Table 4). Furthermore, the adsorption of adenine, adenosine-5'-monophosphate and nucleosides (adenosine, inosine)/nucleotides (adenosine triphosphate and uridine-5'-triphosphate) onto graphite, apatite and silica presented negative values for ΔG , respectively (Basiuk *et al.*, 1995; Sowerby *et al.*, 2001; Hammami *et al.*, 2015). The adsorption of adenine dissolved in distilled water or artificial seawater 4.0 Gy onto Fe³⁺-Mont was ruled by entropy (Table 4). However, from the point of view of enthalpy, the process is endothermic (Table 4). The adsorption of adenine, dissolved in distilled water or artificial seawater 4.0 Gy onto Mont-STD, is thermodynamically favourable from the point of view of enthalpy ($\Delta H < 0$) and entropy ($\Delta S > 0$) (Table 4). The same can be said for

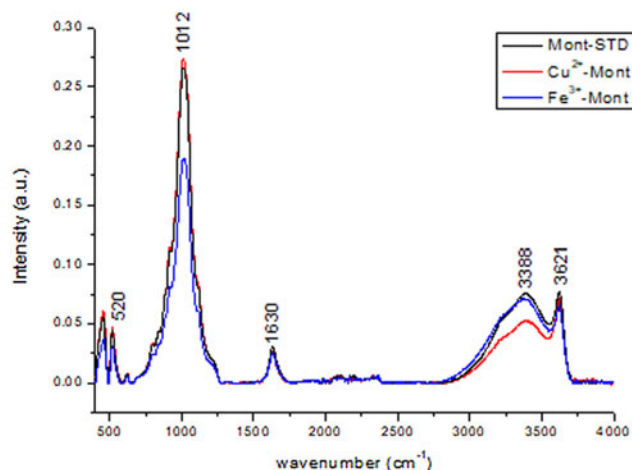


Fig. 2. FT-IR spectra of different montmorillonites. Mont-STD is montmorillonite washed with distilled water. Cu²⁺-Mont is montmorillonite modified with CuCl₂ solution (0.1 mol l⁻¹). Fe³⁺-Mont is montmorillonite modified with FeCl₃ solution (0.1 mol l⁻¹).

the system of adenine adsorbed on Cu²⁺-Mont. However, the major contribution for ΔG comes from enthalpy (Table 4). For all experiments, ΔS values were positive (Table 4), indicating that adenine adsorption onto montmorillonites increased the system disorder. It should be noted that for the samples with artificial seawater the variation in entropy was larger than the values calculated for the samples without artificial seawater (Table 4). In addition, the highest ΔS values were obtained for the samples of adenine dissolved in distilled water or artificial seawater adsorbed onto Fe³⁺-Mont (Table 4). Usually in the adsorption

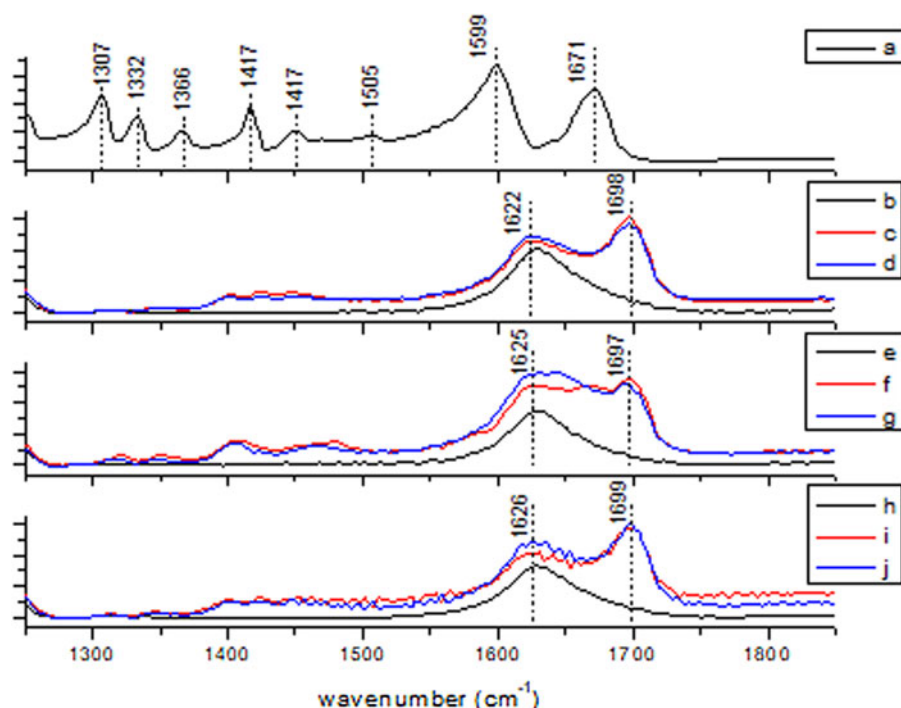


Fig. 3. FT-IR spectra: (a) adenine; (b) Mont-STD; (c) Mont-STD plus adenine in distilled water; (d) Mont-STD plus adenine in artificial seawater 4.0 Gy; (e) Cu²⁺-Mont; (f) Cu²⁺-Mont plus adenine in distilled; (g) Cu²⁺-Mont plus adenine in artificial seawater 4.0 Gy; (h) Fe³⁺-Mont; (i) Fe³⁺-Mont plus adenine in distilled water; (j) Fe³⁺-Mont plus adenine in artificial seawater 4.0 Gy. Adenine (500 mg l⁻¹) was dissolved in distilled water or artificial seawater 4.0 Gy and adsorbed onto Mont-STD, Cu²⁺-Mont or Fe³⁺-Mont. Mont-STD is montmorillonite washed with distilled water. Cu²⁺-Mont is montmorillonite modified with CuCl₂ solution (0.1 mol l⁻¹). Fe³⁺-Mont is montmorillonite modified with FeCl₃ solution (0.1 mol l⁻¹). Artificial seawater 4.0 Gy was prepared as described by Zaia (2012).

process, when the solute in the liquid phase is adsorbed by the solid, there is a reduction in the system disorder at the solid-liquid interface, as the solute loses some degree of freedom (including translation and rotation), so the entropy process is reduced (Mortland, 1970). In these experiments, the increase in entropy could be linked to the release of water from the hydration sphere of adenine or metals, or even by the adsorbed water on the clay (Mortland, 1970). This explanation is reinforced by the fact that the Fe³⁺-Mont samples showed the highest entropy variation. The ionic radius of Fe³⁺ (coordination number 6, 0.55 Å) is lower than that of Cu²⁺ (coordination number 6, 0.73 Å) and the charge of Fe³⁺ is higher than that of Cu²⁺ (Haynes, 2017). Thus, Fe³⁺ has higher charge density. As a consequence, the hydration sphere of Fe³⁺ is larger than that of Cu²⁺. Therefore, the interaction of adenine with Fe³⁺ releases more water than the interaction of adenine with Cu²⁺.

IR spectroscopy (FT-IR)

Figure 2 shows FT-IR spectra of the standard montmorillonite, washed with distilled water (Mont-STD), montmorillonite modified with FeCl₃ solution (0.1 mol l⁻¹) (Fe³⁺-Mont) and montmorillonite modified with CuCl₂ solution (0.1 mol l⁻¹) (Cu²⁺-Mont). The FT-IR spectrum of Mont-STD was very similar to the FT-IR spectrum of Cu²⁺-Mont and Fe³⁺-Mont (Fig. 2, Table 5). The FT-IR spectra showed four regions with bands at 520, 1012, 1630, 3388 and 3621 cm⁻¹ (Fig. 2, Table 5). The band at 520 cm⁻¹ could be attributed to the angular deformation of the Si-O bond of the clay (Tyagi *et al.*, 2006). The broad band at 1012 cm⁻¹ is due to the sum of several frequencies such as: Si-O deformation, O-H deformation of hydroxyl linked to Fe³⁺ and Al³⁺, Si-O-Si stretching and Si-O stretching (Bukka *et al.*, 1992). The band at 1630 cm⁻¹ could be attributed to hydration of clay or H-O-H bending (Bukka *et al.*, 1992; Tyagi *et al.*, 2006). The broad band at 3388 cm⁻¹ and the band at 3621 cm⁻¹ could be attributed to OH stretching, due to the hydration

of clay, with both water and coordinated hydroxyl groups with mineral cations, e.g. Al³⁺, Mg²⁺, Fe³⁺, respectively (Bukka *et al.*, 1992; Madejová, 2003; Tyagi *et al.*, 2006).

Adenine has two characteristic bands at 1599 and 1671 cm⁻¹ (Fig. 3) that can be attributed to the C=C stretch and NH₂ bending, respectively (Colthup *et al.*, 1964). After adenine adsorption on different montmorillonites, in both distilled water and 4.0 Ga seawater, the band at 1599 cm⁻¹ shifted to the region of 1622–1626 cm⁻¹; the band at 1671 cm⁻¹ shifted to the region of 1697–1699 cm⁻¹ (Fig. 3, Table 5). The displacement of the NH₂ deformation band indicates that the interaction of adenine with mineral may occur through this functional group. However, Strašák (1991) attributed the band in the region 1697–1699 cm⁻¹ to the C=O stretching, after the adenine was adsorbed onto Cu²⁺-Mont reacted with Cu²⁺ forming hypoxanthine. Nevertheless, Strašák (1991) assumed that this unique band could be due to hypoxanthine. It should be noted that Baú *et al.* (2012) studied the adsorption of adenine onto several synthetic zeolites, which do not contain Cu²⁺ and observed the same shift of the band 1671 cm⁻¹. Carneiro *et al.* (2011) using FT-IR spectroscopy observed the same shift in the adenine bands when several nucleic acid bases adsorbed onto sulfide modified montmorillonite. However, Mössbauer spectroscopy showed a decrease in the amount of Fe²⁺. Thus, further investigation of the adsorption of nucleic acid bases onto minerals bearing transition metals should be carried out to verify a possible reaction among them. The displacement of the C=C stretch band for the region of 1622–1626 cm⁻¹ could not be attributed to an interaction of C=C with the mineral, since montmorillonite has a band at 1630 cm⁻¹ attributed to clay hydration with water (Fig. 3, Table 5).

Implications for prebiotic chemistry

First, we should remember that due to exogenous and endogenous sources, prebiotic seas probably contain biomolecules (amino acids, nucleic acid bases, etc.), precursors of biomolecules (CN⁻,

Table 5. Assignments of frequencies (cm^{-1}) in FT-IR spectra of Mont-STD, Mont-STD, Cu^{2+} -Mont, Fe^{3+} -Mont, adenine and adenine adsorbed onto Mont-STD, Cu^{2+} -Mont and Fe^{3+} -Mont

Mons (cm^{-1}) ^a	Adenine (cm^{-1})	Adsorbed adenine onto (cm^{-1})			Tentative assignments
		Mont-STD	Cu^{2+} -Mont	Fe^{3+} -Mont	
520					Si-O deformation ^b
1012					O-H (linked to Fe^{3+} , Al^{3+}) deformation, Si-O-Si stretching, Si-O stretching ^{b,c}
	1307				C-N stretching ^d
	1332				C-N stretching ^d
	1366				C-H deformation ^d
	1417				C-H deformation ^d
	1450/1505				C=N stretching ^d
	1599				C=C stretching ^d
		1622	1625	1626	C=C stretching or hydration water ^e
1630					Hydration water ^{b,c}
	1671				NH_2 -bending ^d
		1698	1697	1699	NH_2 -bending ^e
3388/3621					hydroxyl coordinated to Mg^{2+} , Fe^{3+} , Al^{3+} , or O-H stretching (hydration water of clay) ^{b,c,f}

^aMons = Mont-STD, Cu^{2+} -Mont and Fe^{3+} -Mont showed the same bands.

^bTyagi *et al.* (2006).

^cBukka *et al.* (1992).

^dColthup *et al.* (1964).

^eBaú *et al.* (2012).

^fMadejová (2003).

SCN^- , NH_3 , CH_2O , etc.), salts of seawater and metals. It is likely that prebiotic seas were a complex solution and all these substances could be adsorbed onto minerals. Thus, due to a large variety of species, this complex solution could lead to more possibilities for the formation of different and more complex molecules. However, this complex solution could not lead to the formation of any important molecule or biopolymer in high concentrations that could be used for the molecular evolution. If the latter occurs it is a dead end for prebiotic chemistry. This problem has been highlighted by Schwartz (2007), which he discussed in his article 'Intractable mixtures and the origin of life'. In summary, to better understand what could have occurred on the Earth 4.0 Gy, prebiotic chemistry experiments should represent, as closely as possible, what happened on Earth. Iron is the fourth most abundant element in the Earth's crust (Cornell and Schwertmann, 2003; Hazen *et al.*, 2008; Hazen, 2013; Morrison *et al.*, 2018). In addition, although copper is not as abundant as iron, it could be easily found on prebiotic Earth (Hazen *et al.*, 2008; Hazen, 2013; Morrison *et al.*, 2018). Thus, it would be expected that minerals, including montmorillonite, contain iron and copper. Furthermore, these experiments were performed with artificial seawater that probably better resembles the major composition of cations and anions of the seas of prebiotic Earth. The most outstanding result of this work was that the adsorption of adenine onto modified montmorillonites depends on a complex interaction among adenine, salts in the seawater and $\text{Cu}^{2+}/\text{Fe}^{3+}$. The salts of artificial seawater plus Cu^{2+} or Fe^{3+} increased the amount of adenine adsorbed onto modified montmorillonites. For all the experiments ΔG was negative, meaning the adsorption of adenine onto montmorillonites is a spontaneous process. However, there were differences among them,

with the adsorption of adenine onto Fe^{3+} -Mont and Mont-STD or Cu^{2+} -Mont ruled out by entropy and enthalpy/entropy, respectively. This difference comes from the higher charge density of Fe^{3+} compared with Cu^{2+} . Thus, these data better represent what could have happened on the prebiotic Earth.

Conclusions

Montmorillonite modification with Cu^{2+} and Fe^{3+} decreased its surface area and pore volume, but pore size did not change. Among the isotherm models, the Sips model presented the best fit of the data. The n parameter of Sips indicated that the adenine adsorption process on the montmorillonites was homogeneous. Adenine dissolved in artificial seawater 4.0 Gy showed the highest adsorption (96.65 mg g^{-1}) onto Fe^{3+} -Mont at 60°C . The lowest adenine adsorption occurred when adenine was dissolved in distilled water (43.15 mg g^{-1}) or artificial seawater 4.0 Gy (43.90 mg g^{-1}) onto Mont-STD at 60°C . When adenine was dissolved in distilled water or artificial seawater 4.0 Gy, its adsorption onto Mont-STD and Cu^{2+} -Mont was an exothermic process. However, for adenine dissolved in distilled water or artificial seawater 4.0 Gy, its adsorption onto Fe^{3+} -Mont was an endothermic process. For all adsorptions ΔG was negative, meaning that adenine adsorption on different montmorillonites is a spontaneous and favourable process. The adsorption of adenine onto Fe^{3+} -Mont was ruled out by entropy. For the other samples, the adsorption of adenine was ruled by enthalpy and entropy, being a major contribution for Gibbs free energy from enthalpy. Since the adsorption of adenine onto modified montmorillonites changed when carried out in artificial seawater, the adsorption of adenine onto modified montmorillonites involves a complex interaction among adenine, salts in seawater and $\text{Cu}^{2+}/\text{Fe}^{3+}$. The FT-IR

data indicate that the interaction of adenine with mineral may occur through the NH₂ functional group.

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