A Prebiotic Chemistry Experiment on the Adsorption of Nucleic Acids Bases onto a Natural Zeolite

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Abstract There are currently few mechanisms that can explain how nucleic acid bases were synthesized, concentrated from dilute solutions, and/or protected against degradation by UV radiation or hydrolysis on the prebiotic Earth. A natural zeolite exhibited the potential to adsorb adenine, cytosine, thymine, and uracil over a range of pH, with greater adsorption of adenine and cytosine at acidic pH. Adsorption of all nucleic acid bases was decreased in artificial seawater compared to water, likely due to cation complexation. Furthermore, adsorption of adenine appeared to protect natural zeolite from thermal degradation. The C=O groups from thymine, cytosine and uracil appeared to assist the dissolution of the mineral while the NH_2 group from adenine had no effect. As shown by FT-IR spectroscopy, adenine interacted with a natural zeolite through the NH_2 group, and cytosine through the C=O group. A pseudo-second-order model best described the kinetics of adenine adsorption, which occurred faster in artificial seawaters.

Keywords Prebiotic Earth · Mineral adsorption · Chemisorption · Mineral protection

Introduction

Bernal (1951) was the first to suggest that minerals could have played important roles in prebiotic chemical reactions such as: protecting biomolecules against degradation by UV

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radiation and hydrolysis, concentrating biomolecules from dilute solutions, and catalyzing polymer formation. There are several reviews showing that minerals could have performed all these roles (Lahav and Chang 1976; Ferris et al. 1996; Ferris 2002; Zaia 2004, 2012; Lambert 2008).

Zeolites are crystalline microporous alumino silicates, with periodic arrangements of cages and channels. They are synthesized in hydrothermal environments and may represent one the oldest minerals on our planet (Hazen et al. 2008; Cleaves et al. 2012). These minerals are widely distributed on Earth and were also found in Martian soils (Bishop et al. 2008; Ehlmann et al. 2008; Virta 2008). In addition to the many technological applications of zeolites, including uses as catalysts (Abelló and Montané 2011), and for purification of water (Misaelides 2011), separation of organic substances (Burton and Zones 2007; Piera et al. 1998), and animal health (Papaioannou et al. 2005), some studies have considered their role in prebiotic chemistry (e.g., Smith 1998; Parsons et al. 1998; Carneiro et al. 2011b; Baú et al. 2012). According to these authors, zeolites could have concentrated biomolecules, synthesized biopolymers and served as primitive cells on the prebiotic Earth. As reviewed by Zaia (2004, 2012), minerals generally adsorb ionically charged biomolecules, such as amino acids with positively or negatively charged R-groups, or nucleic acids, such as adenine and cytosine, which are positively charged over a wide range of pH. Thus, on the prebiotic Earth, biomolecules without charged groups would not have been protected against UV radiation or hydrolysis, concentrated from dilute solutions, and consequently, would not have been available for molecular evolution. However, amino acids with uncharged R-groups compose ca. 75 % of modern proteins, and adenine/thymine and cytosine/guanine ratios are close to 1.00 in living beings (Klapper 1977; Lehninger 1984). Because, zeolites with high Si/Al ratios are organophilic minerals, it has been suggested that they may have played important roles in the origin of life by protecting neutral biomolecules from hydrolysis or concentrating them from dilute solutions (Zaia 2004, 2012). In support to this hypothesis, Burton and Zones (2007) reported that neutral organic molecules could interact with organophilic zeolites via van der Waals forces or hydrophobic bonding.

According to Wilde et al. (2001), there is evidence for the existence of liquid water on Earth 4.4 billion years ago; however, due to heavy bombardment, oceans were likely formed and destroyed several times. The first permanent ocean was probably formed 3.9 billion year ago, after a decrease in heavy bombardment (Strom et al. 2005). Recent studies have suggested that the primitive oceans were 1.5 to 2 times more saline than today and that Na^+ and Cl^- were not the major ions (Knauth 1998). Therefore, investigations of prebiotic chemical reactions, including the adsorption of biomolecules onto minerals, should be performed in artificial seawater solutions that resemble the ancient oceans, rather than in solutions of distilled water or NaCl (Zaia 2012).

Also, nucleic acid bases were either synthesized on the prebiotic Earth or delivered by exogenous sources, such as meteorites, comets or interplanetary dust particles. All the nucleic acid bases (adenine, thymine, cytosine, uracil; Fig. 1) used in this work were found in meteorites or were able to be synthesized under conditions found on the prebiotic Earth (Ferris and Hagan 1984; Hua et al. 1986; Saladino et al. 2001; LaRowe and Regnier 2008; Martins et al. 2008).

In the present work, the adsorption of nucleic acid bases onto a natural zeolite was studied at two different pH (2.00, 8.00) in distilled water or in artificial seawater solutions, which were designed to resemble today's ocean (0.0 Ga) or the ocean that may have existed on Earth 4.0 billion years ago (4.0 Ga). The amount of nucleic acid bases adsorbed onto the zeolite and the kinetic mechanism of adenine adsorption were measured and the samples were characterized using FTIR spectroscopy, thermal analysis, Scanning Electron Microscopy (SEM) and X-ray diffractometry.
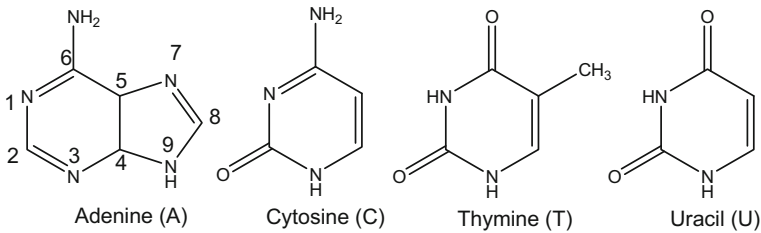
Fig. 1 Molecular structures of nucleic acid bases studied in this work

Materials and Methods

All reagents were of analytical grade.

Materials

Natural Zeolite

A natural zeolite, from Blue Pacific Minerals, was collected in Rotorua/Taupo área, Ngakuru, New Zeland.

Nucleic Acids Bases

Adenine, cytosine, thymine and uracil (Fig. 1) were purchased from Acros Organics (USA), Sigma Aldrich or Fluka, and were used as received.

Seawater 0.0 Ga

The following substances were weighed and dissolved in distilled water: 0.488 mol L^{-1} sodium chloride, 19.0×10^{-3} mol L^{-1} magnesium chloride hexahydrate, 7.2×10^{-3} mol L^{-1} magnesium sulfate, 7.6×10^{-3} mol L^{-1} calcium sulfate, 4.8×10^{-3} mol L^{-1} potassium sulfate, 8.6×10^{-4} mol L^{-1} potassium bromide, and 4.5×10^{-4} mol L^{-1} boric acid (Zaia 2012).

Model 4.0 Ga Seawater

The following substances were weighed and dissolved in distilled water:1.909×10^{-3} mol L^{-1} sodium sulfate, 2.457×10^{-3} mol L^{-1} magnesium chloride hexahydrate, 1.701×10^{-2} mol L^{-1} calcium chloride dihydrate, 4.730×10^{-4} mol L^{-1} magnesium bromide, 2.296×10^{-2} mol L^{-1} potassium sulfate, and 0.1242 mol L^{-1} magnesium sulfate (Zaia 2012). The model 4.0 Ga seawater (cf. Zaia 2012) was based on dissolution of rocks from the Tagish Lake as described by Izawa et al. (2010).

Methods

Adsorption of Nucleic Acids Bases

Adenine, thymine, uraciland cytosine were dissolved in seawater (0.0 or 4.0 Ga) at a concentration of 720 µg mL^{-1}. A natural zeolite, 100 mg, was placed in conical tube (15 mL) containing either: (a) 5.0 mL of artificial seawater 0.0 Ga; (b) 5.0 mL of artificial

seawater 0.0 Ga with 720 µg mL^{-1} of nucleic acid base (adenine, thymine, uracil, cytosine); (c) 5.0 mL of artificial seawater 4.0 Ga; (d) 5.0 mL of artificial seawater 4.0 Ga with 720 µg mL^{-1} of nucleic acid base (adenine, thymine, uracil, cytosine); (e) distilled water; or (f) distilled water with 720 µg mL^{-1} of nucleic acid base (adenine, thymine, uracil, cytosine). The pH of the solutions was adjusted to 2.00 with HCl (1.0 mol L^{-1}) or to 8.00 with NaOH (0.1 mol L^{-1}). The tubes were stirred for 24 h, then centrifuged ("HT"-HB-003-84019-0, rotor 2.0 cm) for 5 min at 6000 rpm. The supernatant was decanted and the solid was lyophilized and analyzed using FT-IR, thermal analyses, scanning electron microscopy (SEM) and ray-X diffractometry.

The experiments of adsorption kinetics were performed with adenine dissolved in distilled water, artificial seawater 0.0 or 4.0 Ga at pH 2.00. A natural zeolite (ca. 100 mg) was added to a series of 15 mL conical flasks then 5.0 mL of an adenine solution (720 µg mL^{-1}) was added. The tubes were stirred and sampled at different time intervals at 298 K.

The pseudo-first-order model is described by the equation (Ho et al. 2000):

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2,303}t \tag{1}$$

Where k_1 (min^{-1}) is the pseudo-first-order constant, q_e is the amount of adenine adsorbed (mg g^{-1}) at the equilibrium concentration and q_t is the amount adsorbed (mg g^{-1}) at time t.

The pseudo-second-order model is given by the following equation (Ho et al. 2000):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{2}$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order constant, q_e is the amount of adenine adsorbed (mg g^{-1}) at the equilibrium concentration and q_t is the amount adsorbed (mg g^{-1}) at time t.

The intra-particle diffusion model is given by the following equation (Ho et al. 2000):

$$q_t = k_d t^{1/2}$$

where q_t is the amount adsorbed (mg g^{-1}) at time t and k_d is the intra-particle diffusion rate constant (m g^{-1} min$^{-1/2}$).

UV/VIS Spectrophotometric Method

Absorbance of nucleic acid bases was measured with a Shimadzu UV–Vis spectrophotometer in the UV region, using the wavelengths of 260 nm for adenine, 265 nm for thymine, 258 nm for uracil and 267 nm for cytosine. The following equation was used to calculate the amount of base adsorbed onto zeolite.

$$C_{adsorbed/mg} = (C_{initial} - C_{solution}),$$

where $C_{solution} = [(C_{initial}) (Abs_{sample}/Abs_{initial})]$.

FT-IR Spectroscopy

The IR spectra were recorded with a Shimadzu 8300 FT-IR spectrophotometer. KBr disc pellets were prepared and spectra were recorded from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} after 98 scans. FT-IR spectra were analyzed using the Origin program (8.0, 2007).

X-Ray Diffractometry

Zeolite samples were analyzed by powder X-ray diffraction using a Shimadzu D 6000 diffractometer using Co Kα radiation (40 kV, 30 mA) and an iron filter in a step-scanning mode (0.02°2θ/0.6 s). All peak positions were analyzed using Grams 8.0 software.

Thermal Analyses (TG)

The TG curve of lyophilized samples (20 mg) were obtained from Perkin-Elmer TGA 4000, scanning from 50 to 900 °C, with a heating ratio of 10 °C min^{-1} and nitrogen flow rate of 20 mL min^{-1}.

Scanning Electron Microscopy (SEM)

SEM images were acquired using a Philips model Quanta 200 (FEI) SEM, in the Scanning Electron Microscope and Microanalysis laboratory of the UEL (Universidade Estadual de Londrina), equipped with an energy dispersive X-ray (EDX) model INCA 200 at 30 keV. The samples were fixed on 'stubs' using carbon silver adhesive tape and then coated with a 30 nm thick layer of gold.

Results and Discussion

Characterization of Material

Figure 2 shows that the zeolite sample which we studied, without any previous treatment, is composed of five phases, including mordenite, sanidine, muscovite, labradorite and albite (Piera et al. 1998; Anbalagan et al. 2003; Santos et al. 2011). Because mordenite is one of the most abundant natural zeolites (Tschernich 1992), it was expected to be found in our sample. At pH 2.00, mixing of a natural zeolite in distilled water (Fig. 2a) or artificial seawaters (not shown) did not result in mineral dissolution. These results were also confirmed by SEM images (Fig. 3). Diffraction patterns of all lyophilized samples showed halite and gypsum after mixing with artificial seawaters 0.0 and 4.0 Ga, respectively. These results were expected because artificial seawater 0.0 Ga is rich in sodium and chloride and artificial seawater 4.0 Ga is rich in calcium and sulfate. Baú et al. (2012) obtained similar results when synthetic zeolites were mixed with artificial seawater.

X-ray diffraction measurements revealed that the mineral was not dissolved in distilled water (pH 8.00); this result was also confirmed by SEM (Fig. 3b). However, the addition of thymine, cytosine or uracil resulted in the partial dissolution of the mordenite as well as other minerals (Fig. 2b). Indeed, several diffraction peaks of mordenite, albite, muscovite, sanidine vanished (Fig. 2b). Thus, after addition of a nucleic acid base, the remaining unlabeled peak in the X-ray diffractogram (Fig. 2b) likely belongs to a mordenite d_{202} diffraction plane. Quartz is a minor component that was only observable in some XRDs, but with a very small d_{011} diffraction plane. The diffraction d_{001} is usually on the left shoulder of the d_{-202} of labradorite or d_{-201} of albite (Fig. 2b). Moreover, at pH 8.00, mordenite was not dissolved in the presence of adenine, probably because the NH_2 group of adenine had no effect on the mordenite phase (Burton and Zones 2007). As shown by FT-IR, the interaction between adenine with natural zeolites was via the NH_2 group, whereas cytosine interacts via the C=O group (see below). Thymine and uracil are also likely to interact with natural zeolite via the C=O group. Thus, it

Fig. 2 **a** X-Ray diffraction patterns of natural zeolite and after treatment with solution of nucleic acid bases in water at pH 2.00 and **b** X-Ray diffraction patterns of natural zeolite and after treatment with solution of nucleic acid bases in water at pH 8.00. All samples were stirred for 24 h before being centrifuged for 5 min. at 6000 rpm. The solid was separated from supernatant and lyophilized. *Alb* albite, *Lab* labradorite, *Mor* mordenite, *Mus* muscovite, *San* sanidine

appears that the amino groups have no effect on the dissolution of a natural zeolite, whereas interaction with carbonyl groups results in dissolution. Baú et al. (2012) observed a similar effect on the dissolution of synthetic zeolites. When natural zeolite was mixed with artificial seawaters (0.0 or 4.0 Ga), at pH 8.00, mineral dissolution did not occur (Fig. 2b). These results were also confirmed by SEM (Fig. 3d, f). It thus appears that the ions in artificial seawater had no effect on the dissolution of the natural zeolite. As pointed out by Zaia (2012), it is important for the prebiotic chemistry to know the effect that minerals have on biomolecules (protection against degradation, formation of polymers, etc.), but it is also important the effect that biomolecules have on minerals.

Scanning electron microscopy (SEM) images revealed that, when mixed with distilled water at pH 2.00, the rods of a natural zeolite were dissolved and granules with a diameter 0.1–0.5 μm were formed (Fig. 3a). However, at pH 8.00, most structures were rods or large groups of rods (Fig. 3b). When a natural zeolite was mixed with artificial seawater 0.0 Ga at pH 2.00, no change in morphology was observed (Fig. 3c); however, at pH 8.00, rods were dissolved and granules with a diameter of 0.1–0.5 μm were formed (Fig. 3d). In artificial seawater 4.0 Ga at pH 2.00 and pH 8.00, most of the natural zeolite was shaped as rods, ranging 0.1 to 0.5 μm in diameter (Fig. 3e, f).

Consistent with the findings of Castaldi et al. (2005), untreated, a natural zeolite exhibited a characteristic loss of hydration water, as indicated by the peak in the DTG curve at 115 °C (Fig. 4; Table 1). Another peak in the DTG curve at 447 °C was assigned to the loss of more strongly associated water (Alver et al. 2010). X-ray diffractograms of a natural zeolite heated at 200, 500 and 800 °C did not show decomposition (data not shown).

The percentage of weight lost after the first event ranged from 5.35 to 8.01 % and from 1.13 to 2.87 % after the second event (Table 1). In general, the shift of the second event was larger in the treatments with adenine compared to cytosine (Fig. 4c, f; Table 1). Specifically, displacement of the peak of the second event was directly related to the adsorption of adenine, such that, at acidic pH, greater adsorption of adenine resulted in larger peak displacement of the peak of the second event (Table 1, 2; $p < 0.05$). In contrast, the amount of cytosine adsorbed by natural zeolite did not affect the shifting the peak (Fig. 4a, b; Tables 1 and 2). Therefore, it appears that adenine protects a natural zeolite against thermal degradation.

Degradation of the biomolecules adsorbed onto the mineral was not observable in the DTG curves (data not shown). Because, thermal degradation of adenine and cytosine could occur along with the second event of weight loss of a natural zeolite, the decomposition of these biomolecules may be difficult to observe using this technique. In the fact, degradation was not also observable when TG experiments were performed in the presence of oxygen (data not show); however, the second weight loss event was more drastic in the treatments containing adenine and cytosine (Table 1). These observations suggest that both biomolecules were adsorbed onto the mineral.

Adsorption

In general, in the acidic media, the adsorption order of nucleic acid bases onto natural zeolite was: adenine > cytosine > thymine ≈ uracil (Table 2; $p < 0.05$). A similar adsorption order was observed
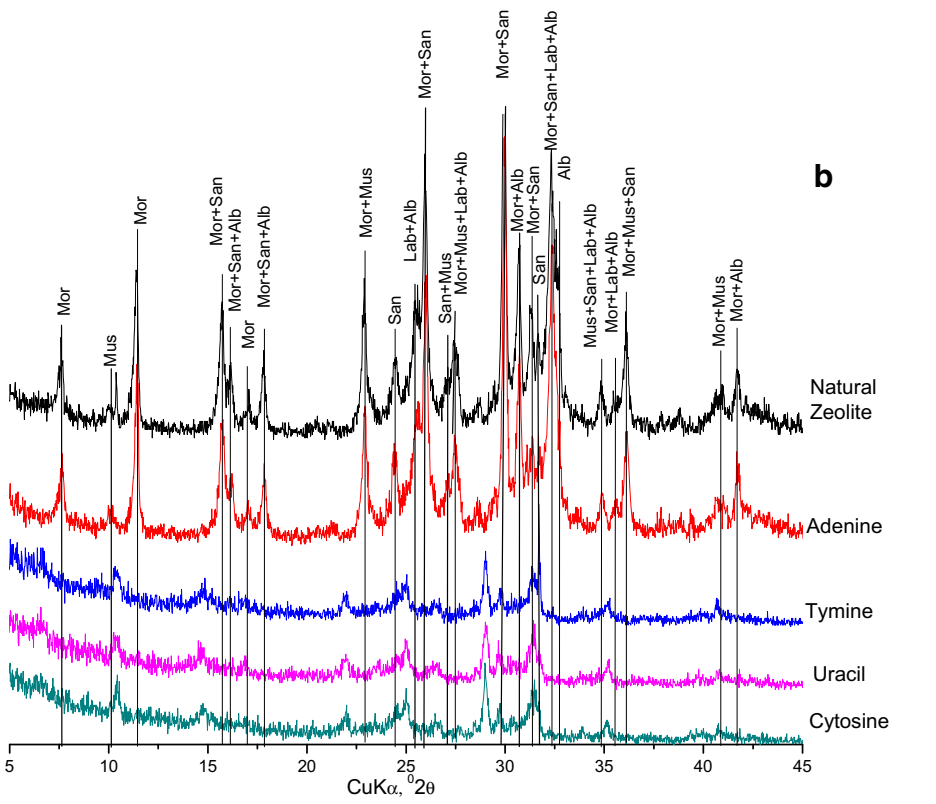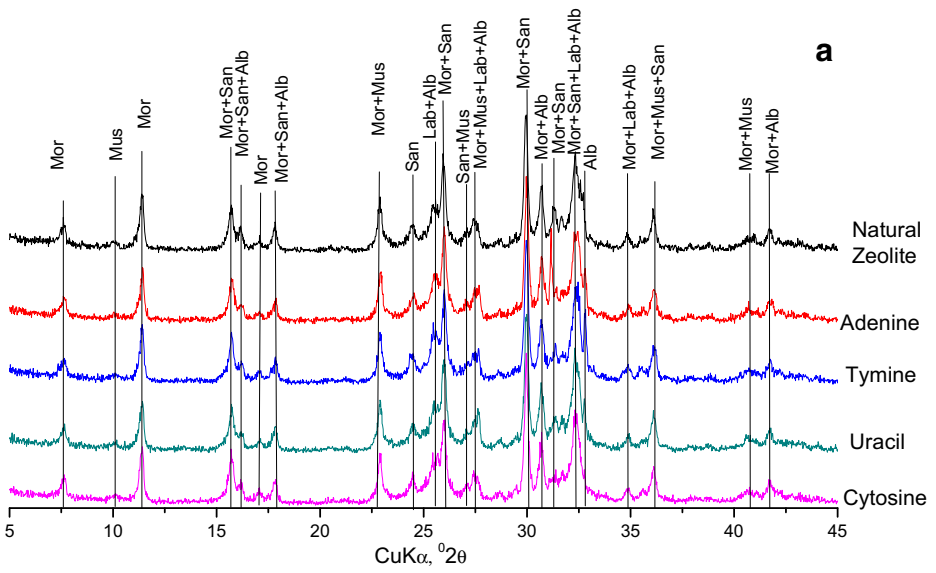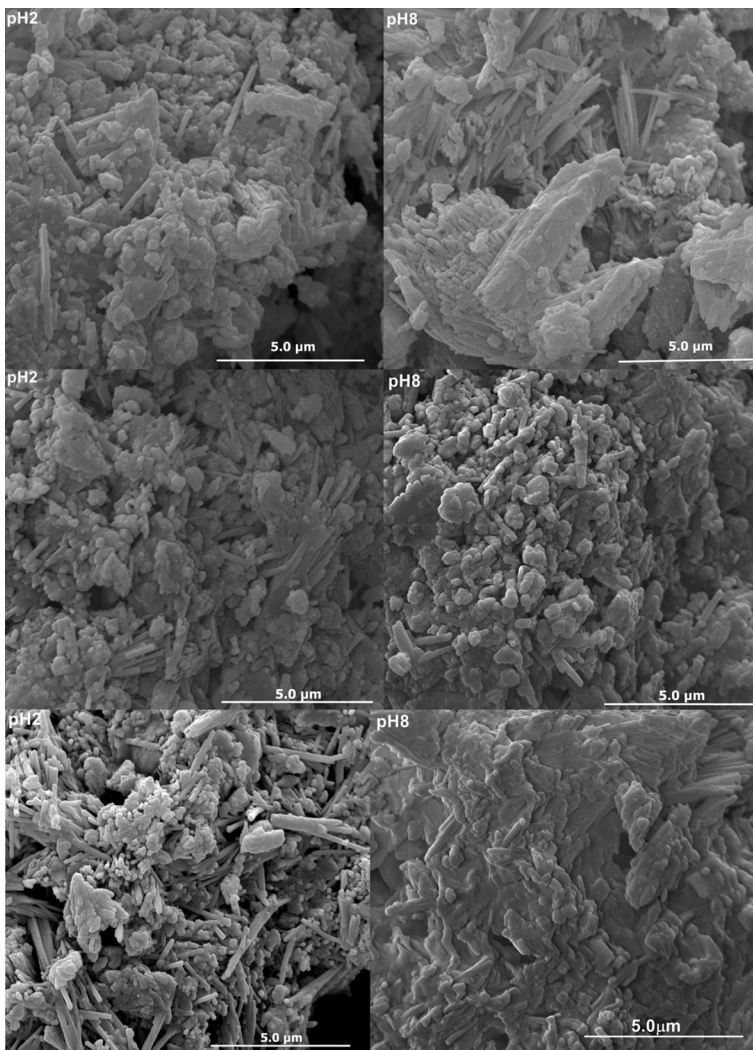
Fig. 3 SEM images from **a** natural zeolite mixed with water at pH=2.00, **b** natural zeolite mixed with water at pH=8.00, **c** natural zeolite mixed with artificial seawater 0.0 Ga at pH=2.00 and **d** natural zeolite mixed with artificial seawater 0.0 Ga at pH 8.00, **e** natural zeolite mixed with artificial seawater 4.0 Ga at pH=2.00 and **f** natural zeolite mixed with artificial seawater 4.0 Ga at pH 8.00. All samples were mixed for 24 h before being centrifuged for 5 min. at 6000 rpm. The solid was separated from supernatant and lyophilized. Artificial seawaters 0.0 and 4.0 Ga were prepared as described by Zaia (2012)

onto clays (Lailach et al. 1968a, b; Lailach and Brindley 1969; Winter and Zubay 1995; Perezgasga et al. 2005; Benetoli et al. 2007; Hashizume et al. 2010; Carneiro et al. 2011a), rutile (Cleaves et al. 2010) and synthetic zeolites (Baú et al. 2012), but graphite (Sowerby et al. 2001) and magnesium oxide (Fornaro et al. 2013) exhibited a different adsorption order.

Both adenine and cytosine were likely protonated and positively charged at pH 2.0 (e.g., Christensen et al. 1970). This could explain their high adsorption onto a natural zeolite, which maintains a permanent negative charge (Lambert 2008). Electrostatic interactions were also invoked to explain the high adsorption of adenine and cytosine onto clay minerals at acidic pH
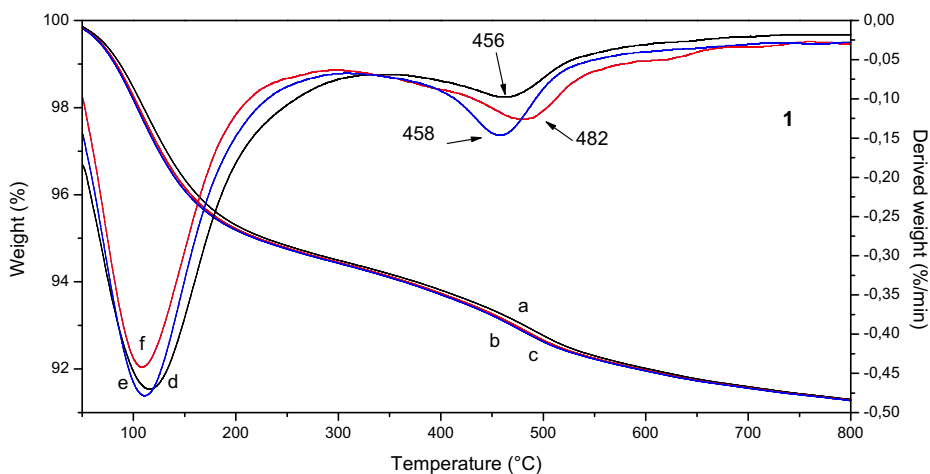
Fig. 4 TG curves (*a*) natural zeolite with treatment in water at pH 2.00; (*b*) natural zeolite with cytosine adsorbed from water solution at pH 2.00; (*c*) natural zeolite with adenine adsorbed from water solution at pH 2.00; DTG curves (*d*) natural zeolite with treatment in water at pH 2.00; (*e*) natural zeolite with cytosine adsorbed from water solution at pH 2.00; (*f*) natural zeolite with adenine adsorbed from water solution at pH 2.00

(Lailach et al. 1968a; Winter and Zubay 1995; Perezgasga et al. 2005; Benetoli et al. 2008; Negrón-Mendoza et al. 2010; Carneiro et al. 2011a). Thymine and uracil are not protonated at pH 2.0 (Christensen et al. 1970), thus explaining their lower adsorption onto the mineral in acidic media (Table 2). In basic media, all nucleic acid bases adsorbed similarly onto natural zeolite (Table 2, $p > 0.05$). However, in water, the adsorptions of cytosine, thymine and uracil were not measured because a natural zeolite was partially dissolved by these nucleic acid bases (Fig. 2b). It should be noted that Lailach et al. (1968a) reported no adsorption of thymine or uracil onto montmorillonite over a wide range of pH (1.70–11.0).

The adsorption of adenine and thymine onto a natural zeolite in artificial seawater 0.0 Ga at pH 2.00 observed in this study (669.5 and 190.9 μg, respectively), was lower than that observed for synthetic zeolites (i.e., up to 2742.8 and 906.4 μg, respectively; Baú et al. 2012). This may be a result of differences in pore size, Si/Al ratio or even surface area of the synthetic zeolites.

The adsorption of nucleic acid bases onto a natural zeolite was similar in both artificial seawaters (Table 2; $p > 0.05$). In acidic and basic artificial seawater media, the adsorption of adenine and cytosine onto a natural zeolite was decreased relative to that in distilled water (Table 2; $p < 0.05$). However, for thymine and uracil, this effect was observed only in acidic artificial seawater media (Table 2; $p < 0.05$). Previous studies have also observed that increases in salt concentration resulted in a decrease in the adsorption of amino acids onto clays and rutile (Hedges 1977; Naidja and Huang 1994; Jonsson et al. 2010) and MDA and EDDA onto Goethite (Norén et al. 2008). Such decreases in adsorption could be due to the occupation of adsorption sites by cations in artificial seawater. Cations may also form complexes with nucleic acid bases (e.g., Anizelli et al. 2014), which would also compete with free cations in artificial seawater for the adsorption sites of a natural zeolite.

The adsorption of nucleic acid bases onto a natural zeolite showed an effect on pH (Table 2). Although this effect was greater in the experiments with artificial seawater, it was also observed when nucleic acid bases were dissolved in water. Thus, nucleic acid bases and salts appear to have released protons (H^+) from zeolite, decreasing the pH.

Table 1 Loss of weight events from thermal analyses of natural zeolite and natural zeolite obtained from lyophilization after adsorption test of adenine and cytosine

Sample	1° event (50–300 °C)	Loss (%)	2° event (320–650 °C)	Loss (%)
Natural zeolite	115	6.46	447	1.70
Zeolite (water)	118	6.29	455	1.13
Zeolite (water in pH 2.00)	113	6.27	452	1.92
Zeolite (water in pH 8.00)	112	6.77	446	1.72
Zeolite-adenine (water in pH 2.00)	109	5.35	480	2.52
Zeolite-adenine (water in pH 8.00)	122	6.50	470	1.77
Zeolite-cytosine (water in pH 2.00)	112	6.22	459	2.35
Zeolite-cytosine (water in pH 8.00)	122	7.86	469	1.61
Zeolite (0.0 Ga)	119	6.58	462	1.45
Zeolite (0.0 Ga in pH 2.00)	113	6.96	461	2.19
Zeolite (0.0 Ga in pH 8.00)	115	6.34	460	1.51
Zeolite-adenine (0.0 Ga in pH 2.00)	118	6.42	476	2.87
Zeolite-adenine (0.0 Ga in pH 8.00)	122	7.18	478	1.91
Zeolite-cytosine (0.0 Ga in pH 2.00)	116	6.09	456	2.85
Zeolite-cytosine (0.0 Ga in pH 8.00)	122	6.65	472	2.18
Zeolite (4.0 Ga)	124	6.617	454	2.00
Zeolite (4.0 Ga in pH 2.00)	121	7.110	451	1.75
Zeolite (4.0 Ga in pH 8.00)	125	6.849	449	1.58
Zeolite-adenine (4.0 Ga in pH 2.00)	119	7.08	480	2.76
Zeolite-adenine (4.0 Ga in pH 8.00)	127	6.83	470	1.49
Zeolite-cytosine (4.0 Ga in pH 2.00)	120	6.77	454	1.92
Zeolite-cytosine (4.0 Ga in pH 8.00)	132	8.01	475	1.40

Artificial seawaters 0.0 and 4.0 Ga were prepared as described by Zaia (2012)

The amounts of adenine or thymine adsorbed onto a natural zeolite at basic pH were not statistically different (Table 2, $p > 0.05$). The observed adenine/thymine ratios (0.30 and 0.87; Table 3) were not similar to the ratio found in several organisms (Table 3). For the treatments of nucleic acid bases in water at basic pH, the adenine/thymine ratio (Table 3) was not shown because a natural zeolite was partially dissolved by thymine (Fig. 2b). However, it should be pointed out that the amounts of adenine or thymine adsorbed onto natural zeolite were not statistically different (Table 2, $p > 0.05$). Thus, the ratios could be closer to 1.0 as found in living organisms (Table 3). For synthetic zeolite-A and zeolite-Y (Baú et al. 2012), and for montmorillonite modified with sodium sulfide at pH 7.00 (Carneiro et al. 2011a, 2013), adenine/thymine ratios were closer to 1.00. This ratio was much higher for clays and graphite (Lailach and Brindley 1969; Sowerby et al. 2001; Benetoli et al. 2008; Carneiro et al. 2011a). As reviewed by Zaia (2004), minerals adsorb much more amino acids with charged-R groups than uncharged R-groups. Similarly, several minerals also appear to preferentially adsorb charged adenine over uncharged thymine (Table 3). Zeolite appears to be an exception, as it exhibited almost the same adsorption of amino acids with charged and uncharged R groups (Carneiro et al. 2011b). Therefore, both charged and uncharged amino acids and nucleic acid bases could have been protected from hydrolysis or UV degradation by zeolites, and thus available for molecular evolution. Given that uncharged amino acids compose ca. 75 % of

Table 2 Amounts of nucleic acid bases (µg) adsorbed on 100 mg of natural zeolite

Solvent		Adenine		Thymine		Uracil		Cytosine	
		Ads	Range pH	Ads	pH	Ads	pH	Ads	pH
Ácid*	$^\Delta$water	754.2±26.3aA	1.90–2.15	263.1±49.2aC	1.95–2.18	197.6±23.2aC	2.02–2.26	522.8±52.5aB	1.98–2.27
	$^{\Delta\Delta}$O Ga	669.5±23.5abA	1.78–2.60	190.9±11.5abC	1.80–2.30	96.7±23.2bC	2.02–2.26	367.3±22.7bB	1.92–2.30
	$^{\Delta\Delta\Delta}$4.0 Ga	610.9±20.7bA	2.00–2.32	120.8±26.7bC	2.01–2.34	24.5±12.7bC	1.87–2.33	358.9±20.4bB	2.11–2.33
Basic*	$^\Delta$water	248.8±37.2α	6.22–8.28	ND	6.12–8.14	ND	6.81–7.40	ND	6.69–8.19
	$^{\Delta\Delta}$O Ga	44.1±8.5β	6.31–7.93	149.1±26.4	6.54–8.45	93.6±22.0	7.40–7.99	115.6±21.6	5.73–7.60
	$^{\Delta\Delta\Delta}$4.0 Ga	118.0±33.0β	5.72–7.15	135.5±21.3	6.27–6.95	100.2±17.1	6.93–744	178.1±23.7	6.29–7.37

The results are presented as mean±standard error of mean. The number of sets was five with two samples each set. It was added 3600 µg of nucleic acid bases. *ND* not determinate because natural zeolite was partially dissolved by these nucleic acid bases. For the rows, averages with distinct capital letters are statistically different from each other by Tukey test ($p<0.05$). For the columns, acidic pH, averages with distinct lowercase letters are statistically different from each other by Tukey test ($p<0.05$). For the columns, basic pH, averages with distinct Greek letters are statistically different from each other by Tukey test ($p<0.05$). The values of pHs were measured after 24 h of stirring. $^\Delta$In water, $^{\Delta\Delta}$in simulated 0 Ga artificial seawater and $^{\Delta\Delta\Delta}$in simulated 4.0 Ga artificial seawater. The artificial seawaters were prepared as described by Zaia (2012)

Table 3 Adenine/thymine ratios obtained in the present study, other authors and living beings

*Adenine/thymine	**Adenine/thymine	***Adenine/thymine
2.87 Acidic pH $^{\triangle}$water	From 3.26 to 114.5, montmorillonite (Lailach and Brindley 1969)	1.05-homo sapiens
3.51 Acidic pH $^{\triangle\triangle}$0 Ga	3.1 graphite (Sowerby et al. 2001)	1.03-sheep
5.06 Acidic pH $^{\triangle\triangle\triangle}$4.0 Ga	From 4.68 to 25.1, clays (Benetoli et al. 2008)	1.02-chicken
ND	From 0.79 to 3.87, clays (Carneiro et al. 2011a, b)	1.05-turtle
0.30 Basic pH $^{\triangle\triangle}$0 Ga	From 1.04 to 3.03 (Baú et al. 2012)	1.02-salmon
0.87 Basic pH $^{\triangle\triangle\triangle}$4.0 Ga		1.02-sea urchin
		1.00-grasshopper
		0.95-yeast
		1.04-E. coli
		1.05-Staphylococcus aureus

*Adenine/thymine ratios of the present work, **Adenine/thymine ratios obtained by several authors, ***Adenine/thymine ratios of several organisms (Lehninger 1984). *ND* not determinate because natural zeolite was partially dissolved by thymine. $^{\triangle}$ In water, $^{\triangle\triangle}$ in simulated 0 Ga artificial seawater and $^{\triangle\triangle\triangle}$ in simulated 4.0 Ga artificial seawater. The artificial seawaters were prepared as described by Zaia (2012)

most proteins (Klapper 1977), and, in living beings, adenine/thymine ratios are close to 1.0 (Lehninger 1984), zeolites may have played an important role in the concentration of uncharged biomolecules on the prebiotic Earth.

IR Spectroscopy

The infrared spectrum of adenine shows two characteristic bands at 1603 and 1673 cm^{-1} (Fig. 5a), which can be attributed to C=C stretching and the NH$_2$ group, respectively (Santamaria et al. 1999; Anizelli et al. 2014). The infrared spectrum of zeolite showed a band at 1638 cm^{-1}, which could be attributed to hydration water (O–H bending; Fig. 5e). When adenine was adsorbed onto the mineral, the band at 1603 cm^{-1} was shifted to 1635 cm^{-1}, to with in the same region of O–H bending of hydration water (Fig. 5f). The band at 1673 cm^{-1} was shifted to 1685 cm^{-1} (Fig. 5f). These data suggest that the interaction between adenine and a natural zeolite occurs through the NH$_2$ group of adenine, and C=C group could also be involved. At pH 2.00, protonated adenine exhibited bands at 1573, 1609 and 1699 cm^{-1} (Anizelli et al. 2014); however, the band at 1573 cm^{-1} was not observed in our spectrum (Fig. 5f). Therefore, while the shift of the band at 1673–1685 cm^{-1} may have been due to the interaction of the NH$_2$ group with natural zeolite, another explanation could be the complexation of cations with zeolites and/or adenine (Anizelli et al. 2014). It should be noted that metals of artificial seawater formed a complex with adenine through the NH$_2$ group and nitrogen of the imidazole ring (Anizelli et al. 2014). Several other authors also observed that the interaction of adenine with clays, zeolites and metals could occur through NH$_2$ group
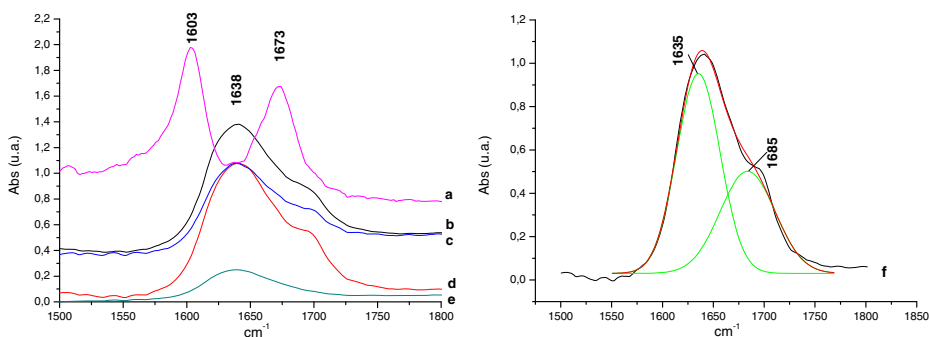
Fig. 5 FTIR spectra: (*a*) solid adenine (*b*) adenine adsorbed onto natural zeolite at pH 2.00-seawater 4.0 Ga; (*c*) adenine adsorbed onto natural zeolite at pH 2.00-seawater 0 Ga; (*d*) adenine adsorbed onto natural zeolite at pH 2.00-water; *e*) solid natural zeolite; *f*) Deconvolution of the spectrum of adenine adsorbed from solution of water at pH 2.00. The deconvolution of band of adenine adsorbed from solution of water was done in the range from 1550 to 1770 cm^{-1}. The best fitting was obtained with two band (r^2=0.997), in the Origin Progam 8.0. All samples were stirred for 24 h before being centrifuged for 5 min. at 6000 rpm. The solid was separated from supernatant and lyophilized. Artificial seawaters 0.0 and 4.0 Ga were prepared as described by Zaia (2012)

(Chen et al. 2002; Yamada et al. 2004; Furukawa et al. 2007; Benetoli et al. 2008; Carneiro et al. 2011a, b; Baú et al. 2012). On the other hand, McNutt et al. (2003) suggested that interaction between adenine and Cu (110) occurred through nitrogen in the pyrimidine ring.

The infrared spectrum of cytosine (Fig. 6a) in the region between 1550 and 1750 cm^{-1} shows one large mode of vibration at 1654 cm^{-1}, which could be attributed to the C=O stretch, with a small contribution from the NH$_2$ group (Colthup et al. 1990; Santamaria et al. 1999; Yamada et al. 2004). Zeolite shows a band at 1638 cm^{-1}, which was attributed to hydration water (Fig. 6e). When cytosine was adsorbed onto a natural zeolite, the band at 1654 cm^{-1} was split into two bands: one at 1681 cm^{-1} and another at 1733 cm^{-1} (Fig. 6f), which suggests that the adsorption occurs via the carbonyl group. Benetoli et al. (2008) and Carneiro et al. (2011a) observed similar results when cytosine was adsorbed onto clays.
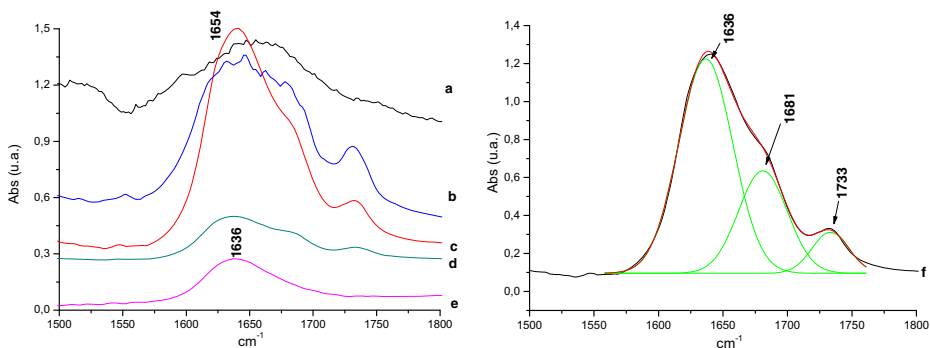

Fig. 6 FTIR spectra: *a*) solid cytosine *b*) cytosine adsorbed on natural zeolite at pH 2.00-seawater 4.0 Ga; *c*) cytosine adsorbed on natural zeolite at pH 2.00-seawater 0 Ga; *d*) cytosine adsorbed on natural zeolite at pH 2.00-water; *e*) solid natural zeolite; *f*) Deconvolution of the spectrum of cytosine adsorbed from solution of water at pH 2.00. The deconvolution of band of adenine adsorbed from solution of water was done in the range from 1500 to 1800 cm^{-1}. The best fitting was obtained with three band (r^2=0.998), in the Origin Program 8.0. All samples were stirred for 24 h before being centrifuged for 5 min. at 6000 rpm. The solid was separated from supernatant and lyophilized. Artificial seawaters 0.0 and 4.0 Ga were prepared as described by Zaia (2012)
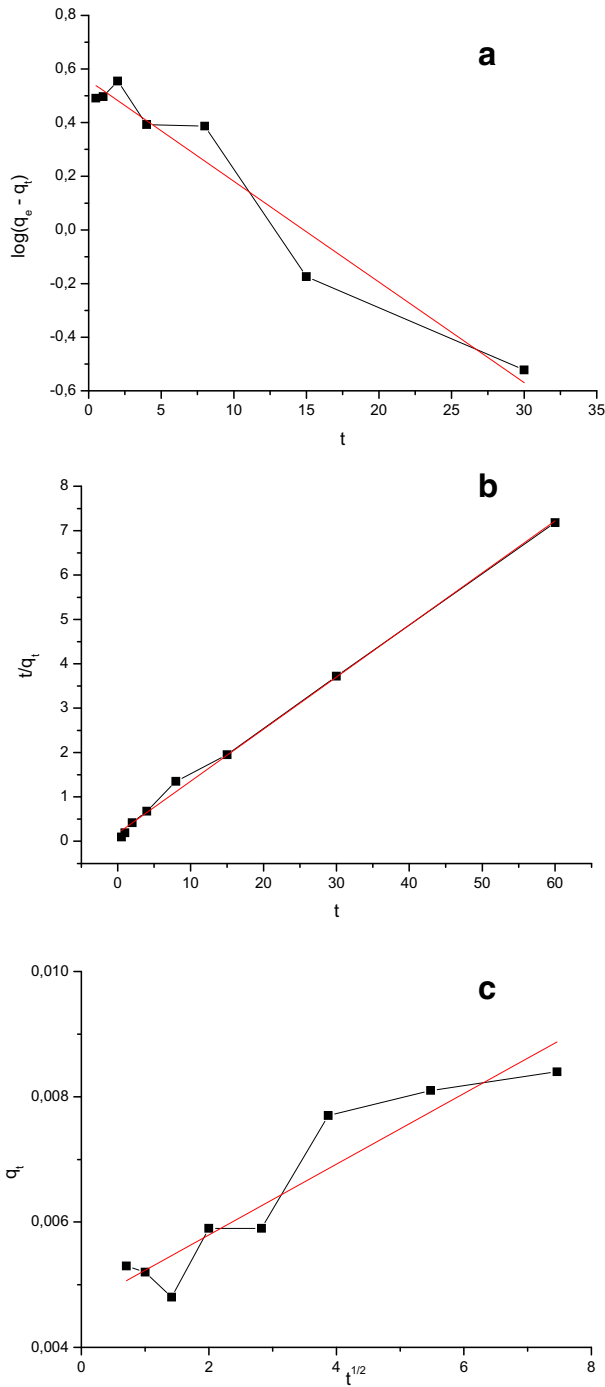
Fig. 7 **a** Pseudo-first-order kinetic plots for adenine adsorption onto natural zeolite in water at pH 2.0; **b** Pseudo-second-order kinetic plots for adenine adsorption onto natural zeolite in water at pH 2.0 and **c** Intra-particle diffusion plots for adenine adsorption onto natural zeolite in water at pH 2 0

Table 4 Parameters obtained from the kinetic study of the adsorption of adenine onto natural zeolite

	Pseudo-first-order			Pseudo-second-order			Intra-particle difusion model
	k_1 (min^{-1})	q_e (mg g^{-1})	R	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R	R
$^{\triangle}$water	0.086	3.61	0.934	0.076	8.52	0.997	0.861
$^{\triangle\triangle}$0.0 Ga	0.244	8.02	0.827	0.097	7.46	0.994	0.755
$^{\triangle\triangle\triangle}$4.0 Ga	0.020	2.86	0.118	0.099	8.50	0.995	0.828

Each value is a mean of three results. $^{\triangle}$ In water, $^{\triangle\triangle}$ in simulated 0 Ga artificial seawater and $^{\triangle\triangle\triangle}$ in simulated 4.0 Ga artificial seawater. The artificial seawaters were prepared as described by Zaia (2012)

Due to the low adsorption of thymine and uracil onto natural zeolite (Table 2), FT-IR spectra did not show any bands belonging to these nucleic acid bases (not shown).

Adsorption Kinetics

The experimental results show that the pseudo-second-order model provided the best fit to the adsorption of adenine onto a natural zeolite over time, while the pseudo-first-order and intra-particle diffusion models did not correlate well with the data (Fig. 7, Table 4). For the intra-particle diffusion model, the linear regressions of q_t versus $t^{1/2}$ did not pass through the origin (Fig. 7). Mordenite was found in the natural zeolite (Fig. 2) and contains micropores that are cylindrical (0.65×0.70 nm; Carneiro et al. 2011b) and similar to the diameter of adenine (0.67 nm; Iyoda et al. 2012). Thus, it is expected that adenine could not enter the micropores of a natural zeolite, and intra-particle diffusion was not likely the rate-limiting step of the adsorption of adenine onto natural zeolite. We note that the equilibrium concentration predicted by the pseudo-second-order model (Fig. 7, Table 4), is close to the value observed in batch experiments (Table 2). Table 4 shows that the salt concentration had an effect on the rate constant of adsorption, which was faster in artificial seawaters (0.0, 4.0 Ga) compared to water (Table 4). Presumably, adenine formed complexes with Ca^{2+} and Mg^{2+} in artificial seawater (Anizelli et al. 2014), thereby increasing the positive charge of adenine and facilitating its interaction with the negatively charged surface of natural zeolite (Yang et al. 2012). The protonation of adenine carrying a divalent metal is possible, as shown by Šponer et al. (2001), who found that the protonation of N1 adenine was favorable when this nucleic acid base was chelated with Pt^{2+} on N7. Indeed, Ca^{2+} and Mg^{2+} were shown to interact with the same nitrogen on the nucleic acid base (Anizelli et al. 2014).

Conclusions

The X-Ray diffractograms showed that a natural zeolite was composed of five phases, including mordenite, sanidine, muscovite, labradorite and albite. Mineral dissolution occurred only in distilled water in the presence of thymine, uracil and cytosine at pH 8.00. The C=O groups from thymine, cytosine and uracil appeared to assist the dissolution of a natural zeolite while the NH_2 group from adenine had no effect.

SEM images revealed that the zeolite mostly comprised rod structures in both distilled water and artificial seawater. The dissolution of rods was observed when that the mineral was mixed with distilled water at pH 2.00 and artificial seawater 0.0 Ga at pH 8.00.

DTG curves of the mineral, without any previous treatments, showed a peak at 115 °C, characteristic of the loss of hydration water, and another peak at 447 °C, assigned to the loss of more strongly associated water. The adsorption of adenine by the zeolite appeared to protect it against thermal degradation.

Under acidic conditions, the following order of adsorption of nucleic acid bases onto the mineral was observed: adenine > cytosine > thymine ≈ uracil ($p < 0.05$). In contrast, under basic conditions, the amounts of nucleic acid bases adsorbed onto the samples were not statistically different ($p > 0.05$). At basic pH, thymine/adenine ratios were close to 1.0, meaning both molecules were equally adsorbed onto the mineral, thus they could be protected from degradation by hydrolysis or UV radiation. Artificial seawaters decreased the adsorption of nucleic acid bases onto the samples, probably because the cations in artificial seawaters decreased the number of adsorption sites, or the complexes formed between the cations and nucleic acid bases increased their solubility.

FT-IR spectra showed that the interaction between adenine and the mineral occurs through the NH_2 and $C=C$ groups. In the case of cytosine, interaction was through the $C=O$ group.

The kinetic study showed a good correlation to the experimental data when a pseudo-second-order model was used. The adsorption occurred faster in artificial seawaters compared to water, probably because the increase of the positive charge of adenine by the cations facilitated the interaction with the negatively charged surface of the mineral.

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