FULL PAPER

Adenine and Thymine Effect on Quartz Dissolution at Different Artificial Seawaters

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Abstract:

According to Bernal (1951) minerals may have played important roles in the origin of life such as: protect biomolecules against degradation by UV radiation or hydrolysis, pre-concentrate biomolecules from prebiotic seas and formation of polymers. Today quartz is widely distributed on Earth as well as was widely distributed on the prebiotic Earth. There are several works showing the quartz dissolution, this work shows for the first time, quartz dissolution under prebiotic chemistry conditions. The experiments were carried out with and without adenine and thymine dissolved in several artificial seawaters, distilled water and alkaline distilled water (pH = 11.0). It should be noted that seawater 4.0 Ga resembles the major cations and anions of the sea of the prebiotic Earth. The quantification of dissolved quartz in different seawater, the measurement of pH and of conductivity were performed daily for a 35 day period, at a controlled temperature (30 °C). The dissolution was dependent of water salinity and especially of pH. Depending on the artificial seawater, adenine and thymine can either accelerate the quartz dissolution or protect it.

Keywords: quartz; prebiotic chemistry; adenine; thymine
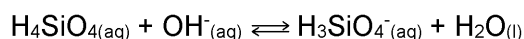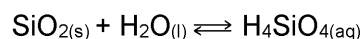
1. Introduction

Prebiotic chemistry studies chemical reactions or processes that could have contributed to the emergence of life on Earth [1]. Bernal (1951) suggested that minerals played important roles in the origin of life on Earth including concentrate biomolecules or precursors of biomolecules from the prebiotic seas, polymerization of biomolecules, protection of biomolecules against hydrolysis or strong irradiation (UV, gamma). Several works show how this could have occurred [2-5]. Quartz was an abundant mineral in prebiotic Earth [6, 7] and could have played important roles in the origin of life on Earth including a preference for L-amino acids over D-amino acids and a potential stereoselectivity catalyst mineral [8, 9]. Since quartz is a primary magmatic rock its weathering by magnesium rich prebiotic oceans could result in clay minerals [10, 11]. These minerals are important pre concentrating agents for prebiotic molecules [12-14]. Human blood contains silicon at nanograms per milliliter concentration but biochemical function was difficult to understand [15, 16]. In plants, association of silica and cell wall molecules makes them less accessible to enzyme degradations and makes plant more resistant to fungi and insect [17]. Many works evaluate quartz solubility considering pH, temperature, ionic strength and pressure. However, few works studied quartz solubility under conditions that could have existed on Earth before life arose on it [18-20]. Quartz solubility in distilled water is higher than seawater and the rate of quartz dissolution controlled the process, not solubility. Decrease of dissolution rate follow decreasing pH to 3.00, lower than rate increases [18]. At basic pH, quartz dissolution occurs according to the reaction shown in Scheme 1 [20].

In the literature there are several studies demonstrating the adsorption of nucleic acid

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bases on minerals. However, there are relatively few studies that have investigated the effect of nucleic acid bases on minerals dissolution under prebiotic chemistry conditions [21, 22]. Nucleic acid bases are easily synthesized under prebiotic chemistry conditions and they have fundamental importance in DNA and RNA composition [3, 23, 24]. Therefore, the effect of adenine and thymine on quartz dissolution is important to understand the origin of life on Earth. In vacuum and high temperature monolayer formation of adenine onto silicon dioxide showed an oriented interaction, about 45°, between amino nitrogen and silicon (111) wafers [25]. However, monolayers were not stable, because thymine evaporation was too quick. Thus, this experiment was not possible. On the other hand, monolayer thymine shaped onto Cu (110) surface at 463 K showed a perpendicular interaction between deprotonated nitrogen and one neighbor oxygen [26]. Both experiments demonstrate that there is an interaction between prebiotic molecules and mineral surface.

$$SiO_{2(s)} + H_2O_{(l)} \rightleftharpoons H_4SiO_{4(aq)}$$

$$H_4SiO_{4(aq)} + OH^-_{(aq)} \rightleftharpoons H_3SiO_4^-_{(aq)} + H_2O_{(l)}$$

Scheme 1. Reactions of quartz dissolution on water according Schwartzentruber et al. [20]

According to Zaia [27], composition of primitive seawater is crucial to understand prebiotic reactions and interactions between minerals and biomolecules. The composition of today's seawater resembles the average of the major cations and anions of actual seawater. The hydrothermal water 3.2 Ga, seawater 3.2 Ga and seawater 4.0 Ga were suggested by Zaia [27] based on the work of de Ronde et al. [31] and

Izawa et al. [32], respectively. Distilled water, alkaline distilled water, today's seawater, hydrothermal 3.2 Ga and seawater 3.2 Ga are not representative of seawater of prebiotic Earth. However, it is important to employ them for purposes of comparison. The artificial seawater 4.0 Ga best resembles the sea composition of the prebiotic Earth. Izawa et al. [31] performed sequential leaching experiments on meteorites samples from Tagish Lake, the following order of cations and anions concentrations was found: $Mg^{2+} > Ca^{2+} \gg Na^+ \approx K^+$ and $SO_4^{2-} \gg Cl^-$. Today's seawater has higher concentrations of Na^+ and Cl^-, on the other hand artificial seawater 4.0 Ga has higher concentrations of Mg^{2+} and SO_4^{2-} [21].

In the present work, the dissolution of quartz under prebiotic chemistry conditions was studied. Quartz was added to several artificial seawaters, distilled water and distilled water at pH 11.0, with and without adenine or thymine. During a period of 35 days pH, conductivity, silicon concentration, adsorption of adenine or thymine onto quartz were measured. In addition, FT-IR spectra were obtained to study the interaction between adenine or thymine and quartz.

2. Results and Discussion

Samples were collected during 35 days for quantification of adenine and thymine. The adenine and thymine concentration did not change during whole period, demonstrating no significant adsorption onto quartz surface. In addition, FT-IR spectra of all solid samples did not show any characteristic band of adenine or thymine (Figure 1).
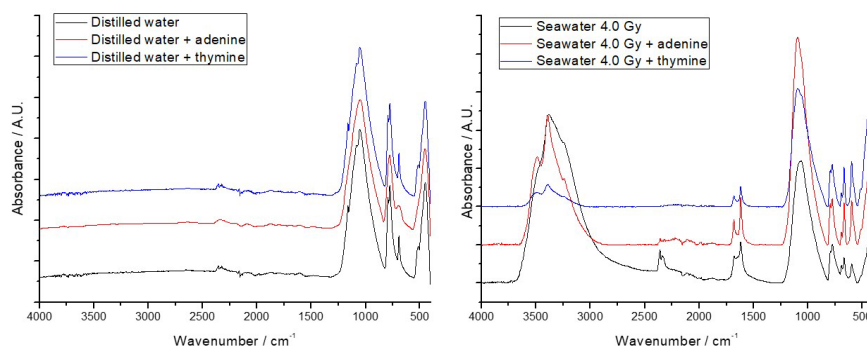

Figure 1. FT-IR spectra for quartz samples at different experiments. Left – Spectra for quartz samples at distilled water experiments. Right – Spectra for quartz samples at Seawater 4.0 Ga experiments.

In general, conductivity values of all samples have no significant increment with and without adenine or thymine. For the range of pH of distilled water samples, adenine and thymine are neutral and dissolved silicon exists as H_4SiO_4. Alkaline distilled water increases conductivity values due to hydroxide anion and high pH values prompt to deprotonated adenine and thymine as well as $H_3SiO_4^-$ [27]. For all other essays, high conductivity values are due to high ionic concentration from dissolved salts of seawater. Thus, the low concentration of adenine and thymine did not have an effect on conductivity values even in high pH values. (Table 1).

Table 1. Average conductivity measured during a period of 35 days.

	Conductivity / mS.cm^{-1}					
Nucleic acid base	**Distilled Water**	**Alkaline distilled Water**	**Today's Seawater**	**Hydrothermal Water 3.2 Ga****	**Seawater 3.2 Ga****	**Seawater 4.0 Ga****
-	5.6±2 E-3 (7.0±0.4)	9.1±1 E-1 (11.3±0.6)	41±1 (7.0±0.4)	50±1 (11.7±0.2)	54±1 (6.9±0.3)	9.8±1 (6.8±0.2)
*Adenine	5.5±2 E-3 (7.8±0.9)	9.9±1 E-1 (11.4±0.6)	40±1 (7.7±0.4)	49±1 (11.6±0.4)	52±1 (6.9±0.2)	9.4±1 (7.6±0.8)
*Thymine	3.8±1 E-3 (5.9±0.2)	8.7±1 E-1 (11.4±0.1)	41±1 (7.1±0.4)	49±1 (11.5±0.1)	54±1 (6.5±0.2)	9.3±1 (6.2±0.2)

Results are shown as mean ± standard error. One set with four samples. ( ) pH values For each experiment was used 100 mg of quartz and the total volume of each solution was 100 mL. *The concentration of adenine or thymine was 720 µg mL^{-1}. **Ga billion the years ago. The artificial seawaters were prepared as suggested by Zaia (2012) [27].

For artificial seawater 4.0 Ga sample, adenine caused the highest increase in pH values. On the other hand, for distilled water sample, thymine caused the highest decrease in pH values (Table 2). These results could be explained by pKa values of nucleic acid bases (pKa values: adenine 4.2 and 9.9; thymine 9.8) [29]. Adenine and thymine did not have an effect on the pH of alkaline distilled water and hydrothermal water 3.2 Ga samples because hydroxide ion concentration was about six times higher than nucleic acid bases (Table 2).

Table 2. Amount of dissolved silicon after 35 days under incubation at 30 °C.

	Amount of dissolved silicon / µg of Si					
Nucleic acid base	**Distilled Water**	**Alkaline Distilled Water**	**Today's Seawater**	**Hydrothermal Water 3.2 Ga****	**Seawater 3.2 Ga****	**Seawater 4.0 Ga****
-	8.97±0.7^{aA} (7.0±0.4) [9.1]	617±77^{aD} (11.3±0.6)	21.4±0.7^{aA} (7.0±0.4) [18.9]	325±74^{cC} (11.7±0.2)	93.2±6.0^{aB} (6.9±0.3)	18.9±5.5^{bA} (6.8±0.2)
*Adenine	6.34±8.8^{aC} (7.8±0.9)	606±59^{aB} (11.4±0.6)	21.0±8.4^{aC} (7.7±0.4)	556±15^{bB} (11.6±0.4)	106±14^{aA} (6.9±0.2)	127±16^{aA} (7.6±0.8)
*Thymine	8.12±0.6^{aB} (5.9±0.2)	640±26^{aA} (11.4±0.1)	32.8±4.0^{aB} (7.1±0.4)	651±3.0^{aA} (11.5±0.1)	46.1±4.2^{bB} (6.5±0.2)	17.4±2.1^{bB} (6.2±0.2)

Results are shown as mean ± standard error. One set with four samples. ( ) pH values. [ ] Literature values for quartz dissolution after 500 days. [16] For the rows, averages with distinct capital letters are statistically different from each other by Turkey test ($p < 0.05$). For the columns, averages with distinct lowercase letters are statistically different from each other by Turkey test ($p < 0.05$). For each experiment was used 100 mg of quartz and the total volume of each solution was 100 mL. *The concentration of adenine or thymine was 720 µg mL^{-1}. **Ga billion the years ago. The artificial seawaters were prepared as suggested by Zaia (2012) [27].

After 35 days, the dissolution of quartz reached an equilibrium (Figure 2), thus this period was used to compare the dissolution of quartz in the samples with and without adenine or thymine (Table 2).
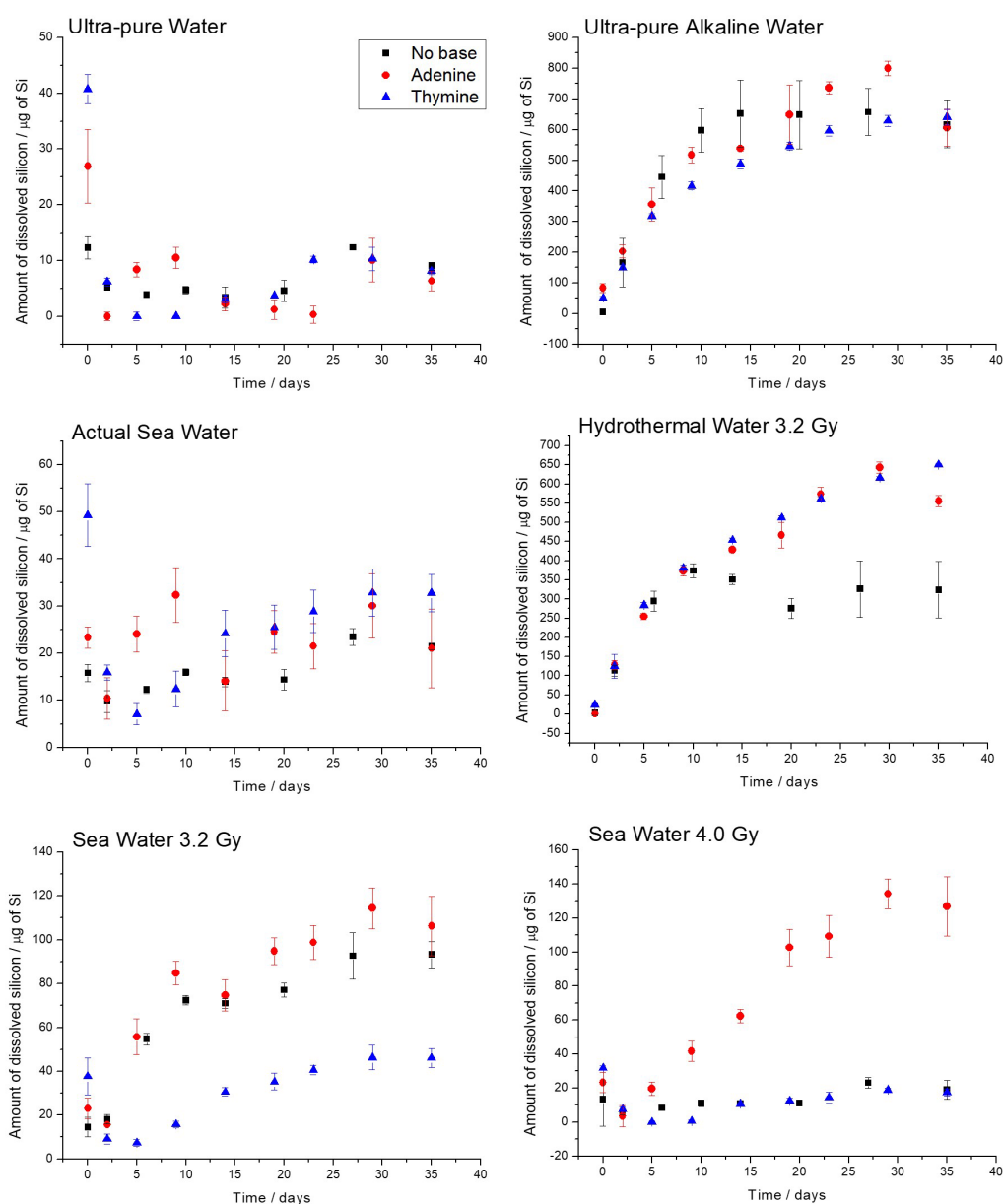

Figure 2. Amount of dissolved silicon from quartz samples for a 35 day period (incubation at 30 °C) at different water environments. (Black square: No base addiction; Red rhomb: Adenine presence; Blue triangle: Thymine presence). One set with four samples. Each experiment used 100 mg of quartz and the total volume of each solution was 100 mL. The concentration of adenine or thymine was 720 µg mL^{-1}. The artificial seawaters were prepared as suggested by Zaia [27].

Seawater 3.2 Ga, without adenine and thymine, has the highest quartz dissolution at pH lower than 8.5 (Table 2), confirming the effect of ionic strength on quartz dissolution (the highest conductivity value – Table 1). For distilled water and today's seawater samples, without adenine and thymine, the dissolution of silicon had same results from literature (Table 2). In addition, for these samples, adenine and thymine did not have an effect on quartz dissolution (Table 2, $p > 0.05$) [19]. FTIR spectra did not show an interaction between adenine or thymine and quartz (Figure 1). The recovery of adenine and thymine from the solutions was 100% meaning

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that quartz did not adsorb them.

As expected for alkaline distilled water, a large dissolution of quartz was observed. It is well known that solutions with pH higher than 8.5 have a large increase of quartz dissolution. The high dissolution of quartz is due the influence of OH^- ions (Scheme 1) [20, 28]. When adenine or thymine were added to the samples of alkaline distilled water the amount of dissolved quartz did not change (Table 2, $p > 0.05$).

Hydrothermal seawater 3.2 Ga and alkaline distilled water samples have almost the same pH, thus it was expected similar quartz dissolution (Table 2). However, for the hydrothermal seawater 3.2 Ga sample quartz dissolution was half of alkaline distilled water sample (Table 2). Similar results as alkaline distilled water were found when nucleic acid bases were added to hydrothermal seawater 3.2 Ga samples (Table 2). This seawater has high calcium and magnesium concentration and at pH 11.5, hydroxide of calcium or magnesium were formed, thus these hydroxides could create a protective layer on quartz surface. When adenine and thymine were added to hydrothermal seawater 3.2 Ga sample, the interaction between calcium/magnesium and negative charged nucleic acid bases would disrupt this layer formation [34].

Conductivity and pH values for seawater 3.2 Ga are close to today's seawater (Table1). However, the quartz dissolution was close only for the sample with thymine (Table 2, $p > 0.05$). Seawater 3.2 Ga and seawater 3.2 Ga with adenine showed higher values for dissolved silicon when compared to seawater 3.2 Ga with thymine and today's seawater samples (Table 2, $p < 0.05$). Thus, the seawater composition was crucial for silicon dissolution. It should be noted that there is a high calcium concentration in seawater 3.2 Ga, indicating that calcium can act as equilibrium shifter. The complex between thymine and calcium is more stable than the complex between adenine and calcium, explaining why only adenine altered quartz dissolution [34]. An opposite trend was observed for seawater 4.0 Ga, since only seawater 4.0 Ga with adenine considerably increased quartz dissolution (Table 2, $p < 0.05$).

For silicon dissolution, comparing seawater 4.0 Ga and today's seawater, same values were found except when adenine was added to seawater 4.0 Ga (Table 2, $p < 0.05$). Since today's seawater and 4.0 Ga seawater have low calcium concentration, the same silicon dissolution was expected. However, at this moment, we cannot explain why adenine increased the silicon dissolution. Baú et al. found an opposite trend for zeolite-A where thymine increased mineral dissolution and adenine protected it [3]. It should be noted that mineral structure and pH range worked were different.

In general, it should be noted that the dissolution of quartz was in the range from 0.006 % (distilled water with adenine) to 0.65 % (hydrothermal water 3.2 Ga with thymine). Carneiro et al. also obtained similar results [33]. They studied the dissolution of quartz as well as several other minerals using the same artificial seawaters of this work. However, they performed the experiments under different conditions of this work. They mixed the minerals with artificial seawaters for 24 h at two different temperatures ambient and 80 °C. Analysis of silicon and aluminum showed that dissolution of minerals were under 1%

3. Material and Methods

3.1. Materials

All reagents are analytical grade. Adenine and thymine were purchased from Acros Organics (USA) and were used as received. Quartz (particles ≤ 230 mech) was purchased from Fluka Chemika AG (Switzerland) and was used as received. Distilled water was obtained from Merck with 18.0 MΩ.cm at 25 °C. Alkaline distilled water was prepared by adding NaOH until pH reach 11. Today's seawater, hydrothermal water 3.2 Ga, seawater 3.2 Ga and seawater 4.0 Ga (Ga = billion years ago) were prepared as described by Zaia et al [27].

3.2. Sample preparation

Quartz (100 mg) was added to 100 mL of different solutions, distilled water, alkaline distilled water and artificial seawaters, with (adenine or thymine 720 µg.mL^{-1}) or without. The temperature was kept at 30 ± 0.2 °C and samples were kept standing for quartz particles did not suspend. Aliquots were collected on

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different days for determination of pH, conductivity, silicon and adenine/thymine concentrations. After the period of 35 days, the solid was separated from the solution by centrifugation, lyophilized and used for FT-IR spectroscopy.

3.3. Methods

Silicon was measured as described by Pereira et al. [28]. An aliquot of 100 μL was added to 0.1 mL of sulpho-molybidic reagent (7.5 g ammonium molybdate + 10 mL of concentrated H_2SO_4). After 10 min, 0.2 mL of 200 g L^{-1} tartaric acid solution was added. After 5 min, 1.0 mL of 3.0 g L^{-1} ascorbic acid was added. One hour later, using a Thermo Spectronic Genesys 2 spectrophotometer the absorbance at 660 nm was read against the blank.

Conductivity was measured with a DL-150 DEL Lab condutivymeter using glass electrode. pH measurements was made with ION pHB 500 pH-mether.

For adenine and thymine determinations, aliquots of 50 μL were 100 times diluted and using a Thermo Spectronic Genesys 2 spectrophotometer the absorbance at UV region (260-265 nm) was read against the blank. The following equation was used for the calculation of the amount of adenine or thymine adsorbed on quartz.

$$C_{adsorbed/\mu g} = (C_{initial} - C_{solution}), \text{ where } C_{solution} = [(C_{initial})(Abs_{sample}/Abs_{initial})]$$

Equation 1. Equation for calculation of adenine and thymine amount adsorbed onto quartz.

The total volume used for all silicon determinations was 5.4 mL and the total solution volume was 100 mL. After each withdrawn for analysis, the volume was corrected.

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

The Tukey test was used to compare means at a significant level of $p < 0.05$.

4. Relevance these Experiments for Prebiotic Chemistry

Bernal was the first to suggest that minerals could have played important roles in the origin of life [2]. According to Bernal, minerals could concentrate biomolecules from prebiotic oceans, catalyze the formation of polymers, protect biomolecules against degradation by UV, gamma radiation or hydrolysis and act as primitive genetic code. Because quartz and thymine/adenine existed on the prebiotic Earth, it is important to study the interaction between them. Quartz dissolution has been studied before; however, these studies were generally not carried out under conditions which life on Earth was still inexistent. In the present study, the dissolution of quartz using several artificial seawaters, alkaline distilled water and distilled water was studied. In addition, the effect of adenine and thymine on the dissolution of quartz was also measured. Artificial seawater 4.0 Ga is one that could better resemble the composition of the major cations and anions of seawater of the prebiotic Earth. The other seawaters were used for purposes of comparison.

It should be noted that most of the work in the field of prebiotic chemistry was carried out in distilled water or sodium chloride solution and a few experiments using some sort of artificial seawater are also described [18]. Naturally, distilled water or sodium chloride solution or even some sort of seawater did not resemble what could have existed on prebiotic Earth. Artificial seawater 4.0 Ga did not have an effect on dissolution of quartz when compared to distilled water. As observed before for quartz and other minerals, under different conditions of this work, artificial seawater 4.0 Ga did not interact with minerals [33]. Since quartz did not suffer dissolution when in contact with artificial seawater 4.0, quartz could be used for prebiotic experiments under this condition. Therefore, this result is important for prebiotic chemistry. However, artificial seawater 4.0 Ga plus adenine increased the dissolution of quartz for about 6.7 times when compared to the sample without adenine (Table 2). On the other hand, thymine did not show an effect on the dissolution of quartz. The increase of dissolution of quartz by

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adenine, even at low concentrations, shows that Bernal's hypothesis could be not valid for all systems. Finally, origin of life on prebiotic Earth can be studied in many other ways. Namely, how these changes could result in new minerals or new biomolecules and how this is part of the process of molecular evolution that may have occurred on the prebiotic Earth.

Acknowledgments

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