

Interaction, at Ambient Temperature and 80 °C, between Minerals and Artificial Seawaters Resembling the Present Ocean Composition and that of 4.0 Billion Years Ago

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Abstract Probably one of the most important roles played by minerals in the origin of life on Earth was to pre-concentrate biomolecules from the prebiotic seas. There are other ways to pre concentrate biomolecules such as wetting/drying cycles and freezing/sublimation. However, adsorption is most important. If the pre-concentration did not occur—because of degradation of the minerals—other roles played by them such as protection against degradation, formation of polymers, or even as primitive cell walls would be seriously compromised. We studied the interaction of two artificial seawaters with kaolinite, bentonite, montmorillonite, goethite, ferrihydrite and quartz. One seawater has a major cation and anion composition similar to that of the oceans of the Earth 4.0 billion years ago (ASW 4.0 Ga). In the other, the major cations and anions are an average of the compositions of the seawaters of today (ASWT). When ASWT, which is rich in Na⁺ and Cl⁻, interacted with bentonite and montmorillonite structural collapse occurred on the 001 plane. However, ASW 4.0 Ga, which is rich in Mg²⁺ and SO₄²⁻, did not induce this behavior. When ASW 4.0 Ga was reacted with the minerals for 24 h at room temperature and 80 °C, the release of Si and Al to the fluid was below 1 % of the amount in the minerals—meaning that dissolution of the minerals did not occur. In general, minerals adsorbed Mg²⁺ and K⁺ from the ASW 4.0 Ga and these cations could be used for the

Dedicated to the memory of Jim Ferris.

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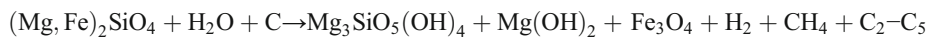
formation of polymers. Also, when the minerals were mixed with ASW 4.0 Ga at 80 °C and ASWT at room temperature or 80 °C it caused the precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and halite, respectively. Finally, further experiments (adsorption, formation of polymers, protection of molecules against degradation, primitive cell wall formation) performed under the conditions described in this paper will probably be more representative of what happened on the prebiotic Earth.

Keywords Seawater · Clay minerals · Iron oxide-hydroxides · Origin of life

Introduction

Minerals probably played important roles in the origin of life. As first suggested by Bernal (1951), they could concentrate biomolecules from the primitive oceans, catalyze the formation of polymers, and protect biomolecules against degradation by hydrolysis or UV radiation. There are several articles in the literature describing tests of these hypotheses (see reviews by Lahav and Chang 1976; Lambert 2008; Zaia 2004, 2012).

Prebiotic chemistry experiments should be performed in the laboratory using conditions that existed on Earth before life arose. Some living organism could probably be found on our planet 3.46 billion years ago (Schopf 1993) or even as far back as 3.8 billion years ago as suggested by Feng et al. (1997). Thus, we should use only minerals that existed on the Earth before 3.8 billion years ago. According to Hazen et al. (2008) our planet has about 4300 different minerals today. However before life arose on our planet there probably existed only 350 to 500 different minerals. The bentonite, kaolinite, montmorillonite, and quartz used in this work could be found on Earth before life arose on it (Hazen et al. 2008). As shown below iron oxides could be produced in hydrothermal environments by reduction of water and oxidation of Fe^{2+} to Fe^{3+} (Martin et al. 2008).



Ferrihydrite was synthesized by bubbling CO_2 into a Fe^{2+} solution with silica at pH 7.0 (Karim 1984). Cornell and Schwertmann (2003) described several methods of the synthesis of goethite from Fe^{2+} solution. Also, Fe^{2+} from (magnetite, pyrite) could be oxidized by peroxide hydrogen formed in ices by UV radiation from the Sun (Liang et al. 2006). As pointed out by Kobayashi et al. (2001) UV radiation from the sun was one the highest energy sources on the prebiotic Earth.

As pointed out by Zaia (2012), most of the experiments related to prebiotic processes were carried using distilled water or sodium chloride solutions, which are not representative of the primitive oceans. Our group has been using an artificial seawater that could better reassemble the seawater of the primitive ocean of 4.0 billion years ago (Anizelli et al. 2015; Canhisares-Filho et al. 2015). This seawater suggested by us (Zaia 2012) was based on the work of Izawa et al. (2010). After performing sequential leaching experiments on meteorites from Tagish Lake, they found the following order for the concentration of cations: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ \approx \text{K}^+$ and for the anions $\text{SO}_4^{2-} > \text{Cl}^-$ (Izawa et al. 2010). Thus, unlike today where the major ions in the oceans are Na^+ and Cl^- (Brown et al. 2004), in the prebiotic oceans the major ions probably were Mg^{2+} and SO_4^{2-} . Tagish lake meteorite is one the most primitive material from solar system and it provide useful information about the soluble substances in oceans of the primitive Earth (Brown et al. 2000).

Many articles appear in the literature that detail the interaction of acidic or basic solutions (often containing a number of cations or anions) with minerals (Gíslason and Arnósson 1993; Langmuir 1997; Alpers et al. 2000; Tombácz and Szekeres 2004; Tomić et al. 2011). However, these experiments are not performed under conditions that could have existed on Earth 4.0 billion years ago. Because minerals could be involved in several aqueous processes that are important in the origin of life, it is important to know how the conditions extant at that time affected them. One reason for that is, if the minerals are severely degraded by the conditions of the prebiotic Earth, they could not be useful for adsorption or protection of biomolecules. We note again that the minerals, artificial seawater, and temperatures used in our experiments could be found on Earth 4.0 billion year ago (Hazen et al. 2008; Martin et al. 2008).

The specific aim of this work was to study the effect of artificial seawaters and distilled water, at two different temperatures, (room temperature and 80 °C) on bentonite, kaolinite, montmorillonite, goethite, ferrihydrite and quartz. Two different artificial seawaters were used—one resembling the chemical composition of seawater of today's oceans (ASWT) and another the oceans of 4.0 billion years ago (ASW 4.0 Ga). Although, ASWT is not representative of seawater of the prebiotic Earth, it is important to use it for purposes of comparison. Because most of the experiments of prebiotic chemistry were performed in distilled water or sodium chloride solutions, usually the effect of these solutions on minerals were not investigated (Zaia 2004, 2012). The changes in the minerals as well as the formation of new minerals were studied using FT-IR spectroscopy and X-ray diffractometry. The adsorption of cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) from seawaters onto minerals and the release of Al and Si from the minerals to the fluids were also measured.

Material and Methods

Materials

All Reagents Were of Analytical Grade (P.A.)

Minerals

Montmorillonite KSF, kaolinite, bentonite, and quartz were purchased from Acros Organics (NJ, USA) and were used as received. The chemical composition (mass fraction) of the montmorillonite is $\text{SiO}_2 = 54 \%$, $\text{Al}_2\text{O}_3 = 17 \%$, $\text{Fe}_2\text{O}_3 = 5.2 \%$, $\text{CaO} = 1.5 \%$, $\text{MgO} = 2.5 \%$, $\text{Na}_2\text{O} = 0.4 \%$, and $\text{K}_2\text{O} = 1.5 \%$ with a specific surface area of $10 \text{ m}^2 \text{ g}^{-1}$. Montmorillonite 53 μm was obtained by passing the original material through a 53-mesh sieve and saturating it with sodium chloride (1.0 mol L^{-1}). Goethite and ferrihydrite were synthesized according to Schwertmann and Cornell (1991). In few words goethite was synthesized as follow: a volume of 400 mL of 2.5 mol L^{-1} of KOH was mixed slowly with 1650 mL of 0.15 mol L^{-1} of $\text{Fe}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ solution in plastic box (450 mL) and mixture was stirred vigorously. The box was closed with a lid was and the dispersions were aged for 60 h at 70 °C. Precipitate were then collected by centrifugation and redispersed in distilled water, this procedure was repeated five times. The precipitate harvested from each synthesis procedure was then lyophilized. Ferrihydrite was synthesized using 8.0 g of $\text{Fe}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ that it was added to a plastic container (450 mL capacity) containing

100 mL of distilled water preheated to 75 °C. Approximately 66 mL of potassium hydroxide (1.0 mol L⁻¹) was added slowly (1 h), the temperature and stirring were kept. The pH of the solution was kept 7.5 during the synthesis. After the material was filtered on a vacuum system with Kitassato flask and Buchener funnel and low porosity filter (8 µm). Then, the material was washed five times with distilled to remove nitrate and was lyophilized and stored in dark flask.

Synthetic Seawater

Table 1 shows the composition of artificial seawaters used in this work. They were prepared as described by Zaia (2012).

Sample Preparation

We added 200 mg of each mineral to three different sets of eight tubes (15 mL). To the first set of 8 tubes was added 10.0 mL of distilled water, to the second set of 8 tubes was added 10.0 mL of artificial seawater of today (ASWT) and to the third set of 8 tubes was added 10.0 mL of artificial seawater 4.0 billion years ago (ASW 4.0 Ga). The contents in four tubes were mixed for 24 h at ambient temperature and the other four at 80 °C. Each treatment was repeated four times. After being spun for 15 min at 2000 rpm, the aqueous phases were withdrawn and used for cation determination and the solid phases of the samples were lyophilized. The lyophilized phases were used for FT-IR spectroscopy and X-ray diffractometry.

Methods

FTIR Spectroscopy

The FT-IR spectra were recorded with a Shimadzu FTIR 8300 spectrophotometer from 400 cm⁻¹ to 4000 cm⁻¹, using pressed KBr disks with a resolution of 4 cm⁻¹ after 95 scans. FTIR spectra were analyzed using the Origin program (8.0, 2007).

Table 1 Composition of artificial seawaters

Period (Ga)*	Composition of seawater (g L ⁻¹ and mmol L ⁻¹)**	Conductivity (µS cm ⁻¹)
ASWT [†]	NaCl (28.57 g; 489 mmol), MgCl ₂ ·6H ₂ O (3.88 g; 19.1 mmol), KBr (0.103 g; 0.866 mmol), CaSO ₄ (1.308 g; 9.61 mmol), K ₂ SO ₄ (0.832 g; 4.77 mmol), H ₃ BO ₃ (0.028 g; 0.453 mmol), MgSO ₄ (1.787 g; 14.8 mmol),	40.56
ASW-4.0-Ga [‡]	Na ₂ SO ₄ (0.271 g; 1.91 mmol), MgCl ₂ ·6H ₂ O (0.500 g; 2.5 mmol), CaCl ₂ ·2H ₂ O (2.50 g; 17.0 mmol), KBr (0.050 g; 0.420 mmol), K ₂ SO ₄ (0.400 g; 2.30 mmol), MgSO ₄ (15.00 g; 125 mmol)	9.48

Initial pH ambient temperature: ASWT =6.65, ASW 4.0 Ga = 5.59 and distilled water =5.18. Initial pH 80°C: ASWT =6.09, ASW 4.0 Ga = 5.75 and distilled water =6.15

*Billion years ago

**Each salt should be added in the order as they are shown (Zaia 2012)

[†] Artificial seawater of today

[‡] Artificial seawater of 4.0 billion years ago

X-Ray Diffraction

Powdered solid materials before and after the experiments were analyzed by powder method by X-rays diffraction using a Shimadzu D 6000 diffractometer, with $\text{CuK}\alpha$ radiation (40 kV, 30 mA), a step-scanning mode (0.02° $2\theta/0.6$ s) from 5° to 70° 2θ amplitude. All peaks positions were analyzed using X'PertHighScore 2.1 and Origin (8.0, 2007) software.

Determination of Na and K (Flame Photometer)

A standard curve was prepared by dilution of a solution of 1000 ppm of K (Merck). The concentration of K was from 2.0 mg L^{-1} to 70 mg L^{-1} . A standard curve was also prepared by dilution of a solution of 1000 ppm of Na (Merck). The concentration of Na was from 2.0 mg L^{-1} to 50 mg L^{-1} . The samples were injected into a Digimed NK-2004 flame photometer.

Determination of Ca and Mg (Atomic Absorption Spectrometer)

An AA-7000-Shimadzu atomic absorption spectrometer was used for Ca and Mg analysis using an air/acetylene flame with a flow rate of 1.8 mL min^{-1} . Standard curves were prepared with solutions of 1000 ppm Ca (0.05 mg L^{-1} to 2.0 mg L^{-1}) and Mg (0.02 mg L^{-1} to 0.5 mg L^{-1}) (Merck). The samples were diluted with distilled water (Milli Q).

Determination of Si and Al (UV-Vis Spectrophotometer)

For Si and Al determinations, ammonium molybdate and aluminon ($\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_9$, tri ammonium salt of aurintricarboxylic acid) were used as described in AWWA-APHA-WPCI (2006). For Si, a standard curve from 0.3 mg L^{-1} to 5.0 mg L^{-1} of Si was prepared with the absorbance set at 660 nm. For Al, a standard curve from 0.2 mg L^{-1} to 20.0 mg L^{-1} of Al was prepared with the absorbance set at 534 nm. For all determinations a UV-Vis Genesis 2 Thermo Spectronic was used.

Statistical Analysis

Comparisons among means were assessed by using ANOVA and Student-Newman-Keuls test at a significance level of $p < 0.05$.

Results

Characterization of the Minerals

Bentonite, kaolinite, montmorillonite and montmorillonite $53 \mu\text{m}$, without any previous treatment (pure), are a mixture of montmorillonite/ilite/muscovite/quartz, kaolinite/muscovite, montmorillonite/ilite and montmorillonite/ilite, respectively (Fig. 1). X-rays diffractograms of bentonite, montmorillonite and montmorillonite $53 \mu\text{m}$ after having been mixed with artificial seawater of today (ASWT) showed a decrease on the d_{001} spacing plane (Fig. 1). In contrast, when bentonite, montmorillonite and montmorillonite $53 \mu\text{m}$ were mixed with seawater similar to that of 4.0 billion years ago (ASW 4.0 Ga) this effect was not observed (Fig. 1).

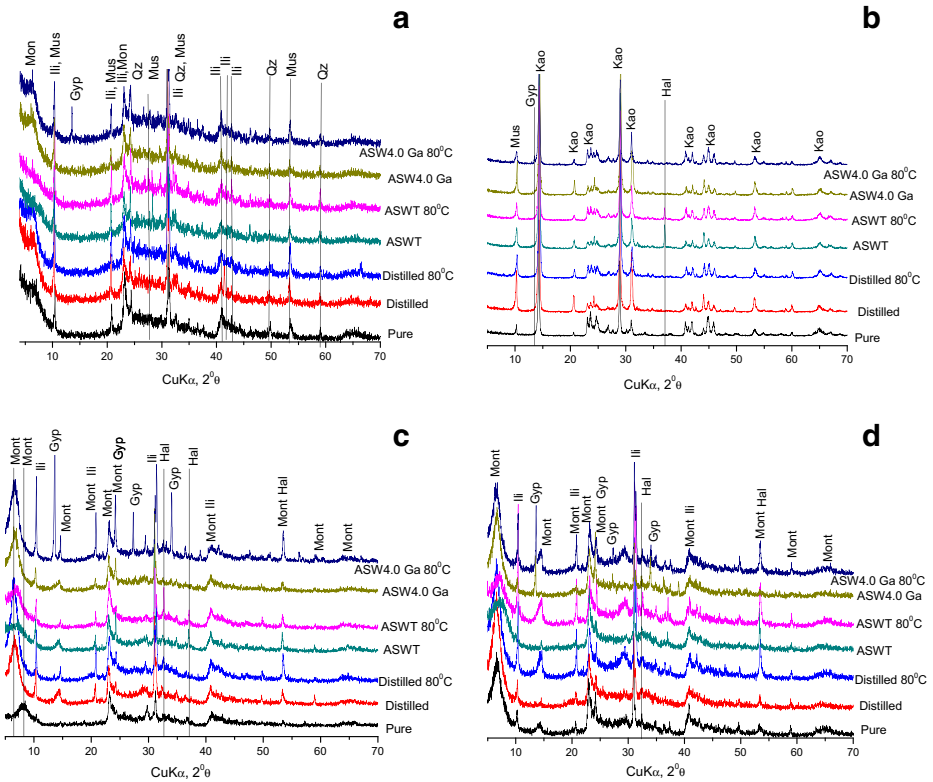


Fig. 1 X-ray diffractogram of the samples: **a** bentonite, **b** kaolinite, **c** montmorillonite **d** montmorillonite 53 μm . pure = no further preparation, distilled = mixed for 24 h with distilled water at room temperature, distilled 80 $^{\circ}\text{C}$ = mixed for 24 h with distilled water at 80 $^{\circ}\text{C}$, ASWT = mixed for 24 h with artificial seawater of today at room temperature, ASWT 80 $^{\circ}\text{C}$ = mixed for 24 h with artificial seawater of today at 80 $^{\circ}\text{C}$, ASW 4.0 Ga = mixed for 24 h with artificial seawater of 4.0 billion years ago at room temperature and ASW 4.0 Ga 80 $^{\circ}\text{C}$ = mixed for 24 h with artificial seawater of 4.0 billion years ago at 80 $^{\circ}\text{C}$. Artificial seawaters were prepared as describe by Zaia (2012). Gyp = gypsum, Hal = halite, Ili = illite, Kao = kaolinite, Mon = montmorillonite, Mus = muscovite, QZ = quartz

After the treatment with ASW 4.0 Ga at 80 $^{\circ}\text{C}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precipitated onto bentonite, kaolinite, montmorillonite and montmorillonite 53 μm (Fig. 1). With exception of the montmorillonite 53 μm sample mixed with ASW 4.0 Ga at room temperature, other treatments did not precipitate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ onto the minerals (Fig. 1). After the treatments with ASWT at room temperature and 80 $^{\circ}\text{C}$, x-rays diffraction patterns showed that halite was formed on kaolinite, montmorillonite and montmorillonite 53 μm (Fig. 1-b, c). Because montmorillonite 53 μm was saturated with NaCl, diffraction patterns appeared in all diffractograms of this mineral; however halite peaks were easily recognizable in the samples treated with artificial seawater ASWT at 80 $^{\circ}\text{C}$ (Fig. 1-d). The formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ using ASW 4.0 Ga and halite using ASWT were expected because they contain high concentrations of $\text{Ca}^{2+}/\text{SO}_4^{2-}$ and Na^+/Cl^- , respectively (Table 1).

Goethite samples without any previous treatment (pure) showed only its own diffraction patterns (Fig. 2-b). The pure ferrihydrite sample, however, showed its own large diffraction reflexes (two) and others associated with potassium nitrate (Fig. 2-a). The last mineral is

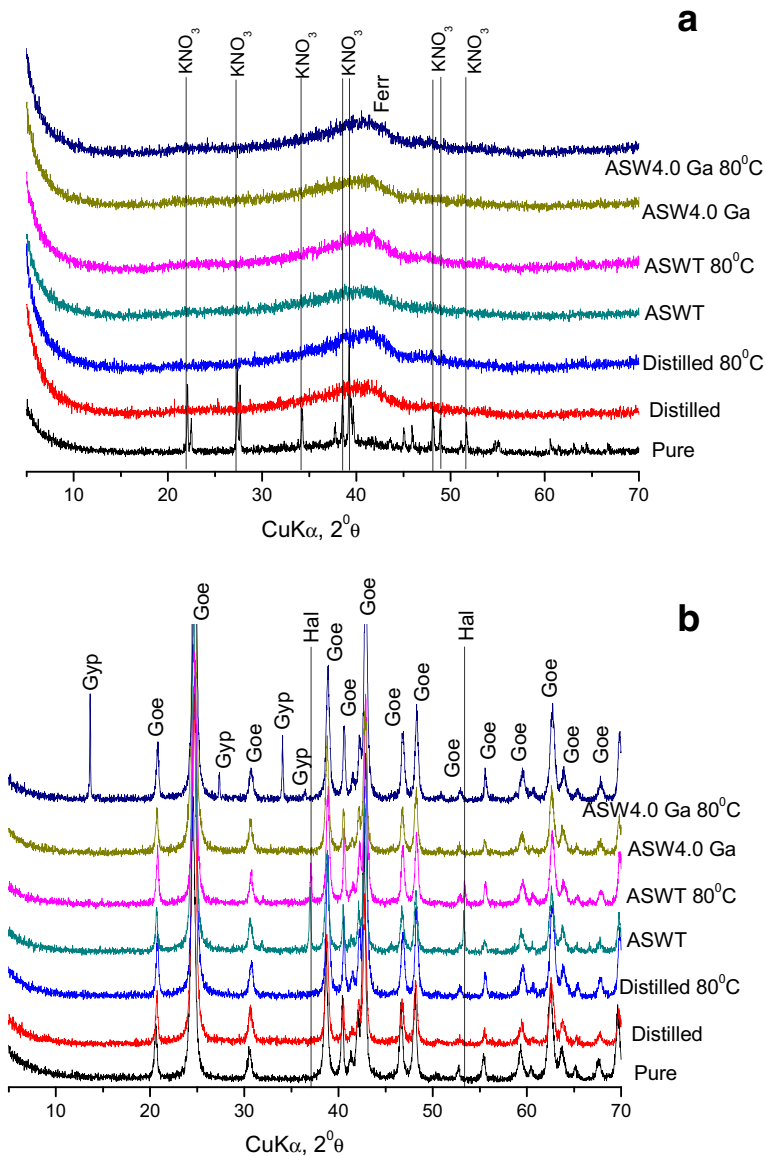


Fig. 2 X-ray diffractogram of the samples: **a** Ferrihydrate, **b** Goethite pure = no further preparation, distilled = mixed for 24 h with distilled water at room temperature, distilled 80 °C = mixed for 24 h with distilled water at 80 °C, ASWT = mixed for 24 h with artificial seawater of today at room temperature, ASWT 80 °C = mixed for 24 h with artificial seawater of today at 80 °C, ASW 4.0 Ga = mixed for 24 h with artificial seawater of 4.0 billion years ago at room temperature and ASW 4.0 Ga 80 °C = mixed for 24 h with artificial seawater of 3.8 billion years ago at 80 °C. Artificial seawaters were prepared as describe by Zaia (2012). Ferr = ferrihydrate, Gyp = gypsum, Hal = halite, Goe = Goethite

actually a residue of the synthesis (starting reagents: iron (III) nitrate and potassium hydroxide). It should be noted that ferrihydrate is a poorly crystalline iron oxide mineral (Schwertmann and Cornell 1991). Thus, any other mineral, with higher crystallinity, formed

during the synthesis experiment will have a much more stronger XRD pattern. After treatments with distilled water and artificial seawaters at room temperature and 80 °C, the two diffraction lines from ferrihydrite were still observed (Fig. 2-A). X-rays diffractograms showed the formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the goethite sample treated with ASW 4.0 Ga at 80 °C, and halite (NaCl) in the goethite samples treated with ASWT at room temperature and 80 °C (Fig. 2-b).

X-ray diffractograms show that the quartz pure sample was actually composed of solely quartz (Fig. 3). Diffraction patterns of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was observed in the quartz after treatment with ASW 4.0 Ga at 80 °C (Fig. 3). Halite was observed in quartz samples after treatment with ASWT at room temperature and 80 °C (Fig. 3-a).

FT-IR spectra of bentonite, montmorillonite and montmorillonite 53 μm did not change with the treatments and they are very similar to each other (Fig. 4). In general, the following bands were observed: 466 cm^{-1} (Si-O-Si bending), 525 cm^{-1} (Si-O-Al bending), 800 cm^{-1} (Si-O stretching of quartz), 915 cm^{-1} (AlAlOH bending), 1042 cm^{-1} (Si-O stretching in plane) and 1111 cm^{-1} (Si-O stretching out of plane) (Nakamoto 1978; Madejová 2003; Tyagi et al. 2006).

The treatments did not change the FT-IR spectra of kaolinite samples and the following bands were observed: 425 cm^{-1} , 470 cm^{-1} (Si-O-Si bending), 540 cm^{-1} (Si-O-Al bending), 696 cm^{-1} , 754 cm^{-1} (Al-OH bending), 796 cm^{-1} (Si-O stretching of quartz), 910 cm^{-1} (AlAlOH bending), 1006 cm^{-1} , 1035 cm^{-1} (Si-O stretching in plane) and 1111 cm^{-1} (Si-O stretching out of plane) (Fig. 4) (Nakamoto 1978; Madejová 2003; Tyagi et al. 2006).

All quartz samples showed the following bands: 462 cm^{-1} (Si-O asymmetric bending), 512 cm^{-1} (shoulder), 690 cm^{-1} (Si-O symmetric bending), 788 cm^{-1} , 1081 cm^{-1} and 1173 cm^{-1} (shoulder) (Nakamoto 1978).

Ferrihydrite samples showed the following bands: 454 cm^{-1} (bulk OH deformation), 593 cm^{-1} , 709 cm^{-1} (shoulder) and 1628 cm^{-1} (Fig. 4). The band at 1385 cm^{-1} (N-O

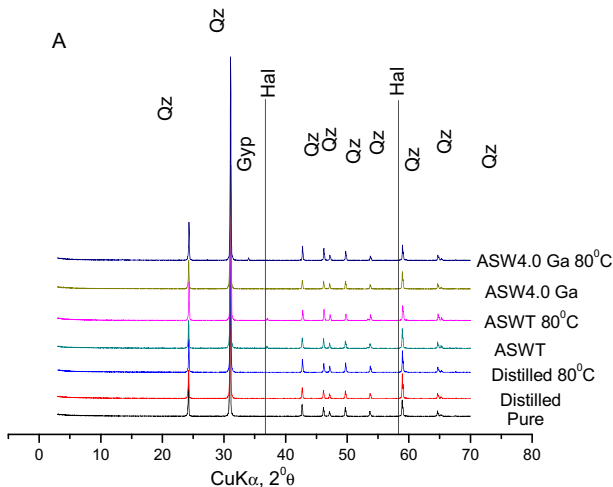


Fig. 3 X-ray diffractogram of Quartz, pure = no further preparation, distilled = mixed for 24 h with distilled water at room temperature, distilled 80 °C = mixed for 24 h with distilled water at 80 °C, ASWT = mixed for 24 h with artificial seawater of today at room temperature, ASWT 80 °C = mixed for 24 h with artificial seawater of today at 80 °C, ASW 4.0 Ga = mixed for 24 h with artificial seawater of 4.0 billion years ago at room temperature and ASW 4.0 Ga 80 °C = mixed for 24 h with artificial seawater of 4.0 billion years ago at 80 °C. Artificial seawaters were prepared as describe by Zaia (2012). Hal = halite, QZ = quartz

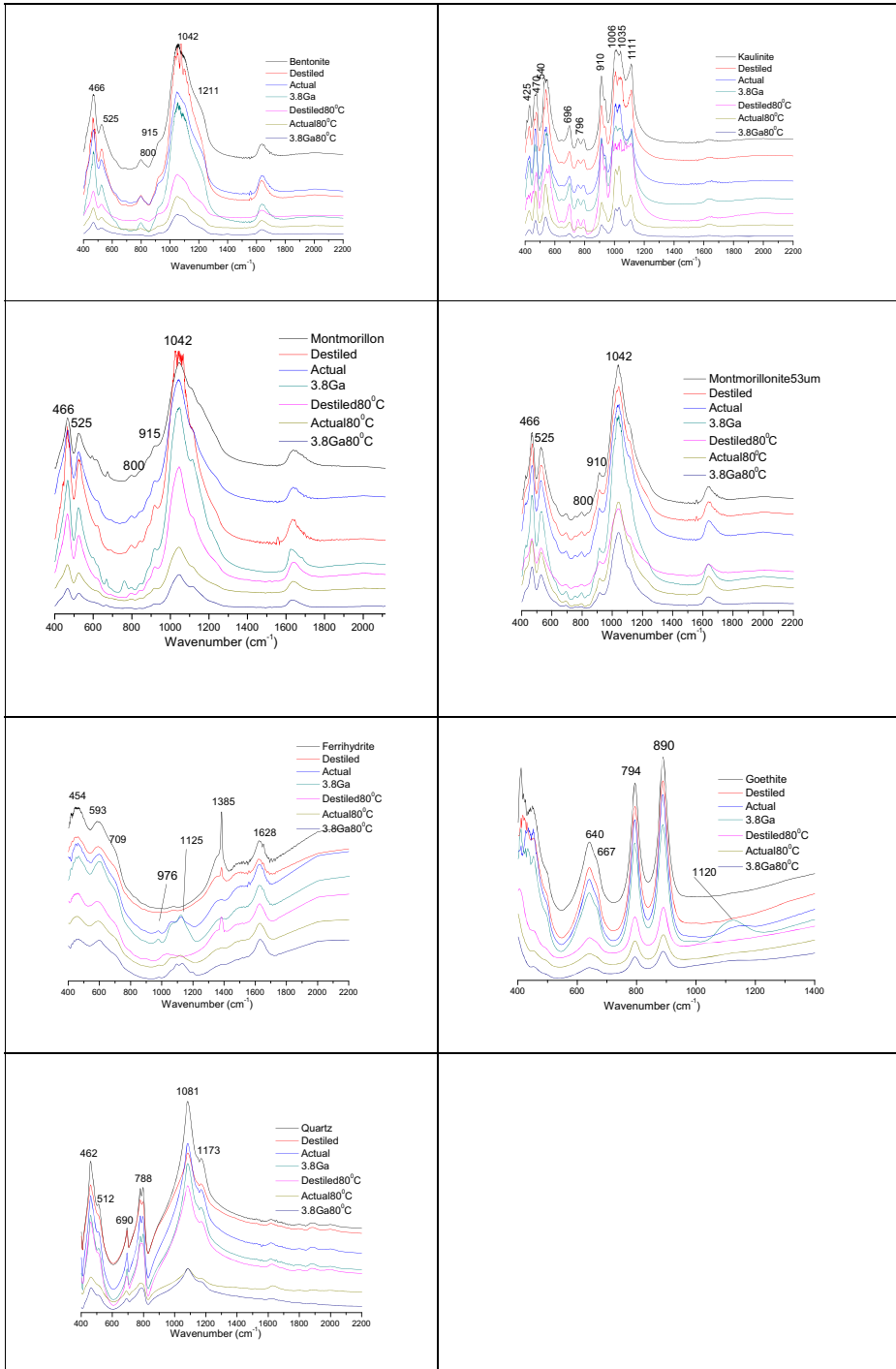
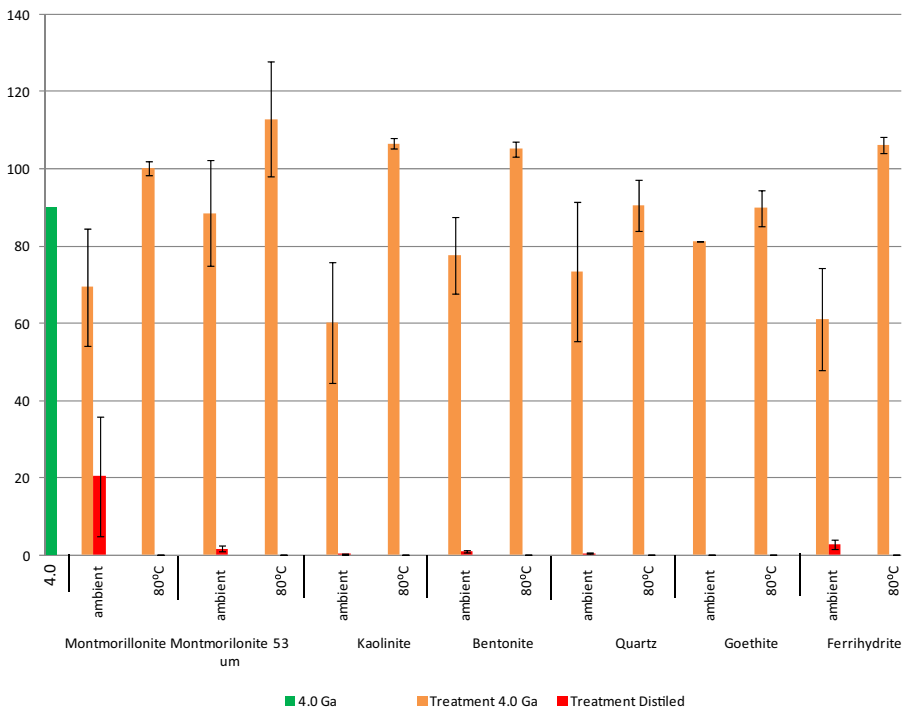
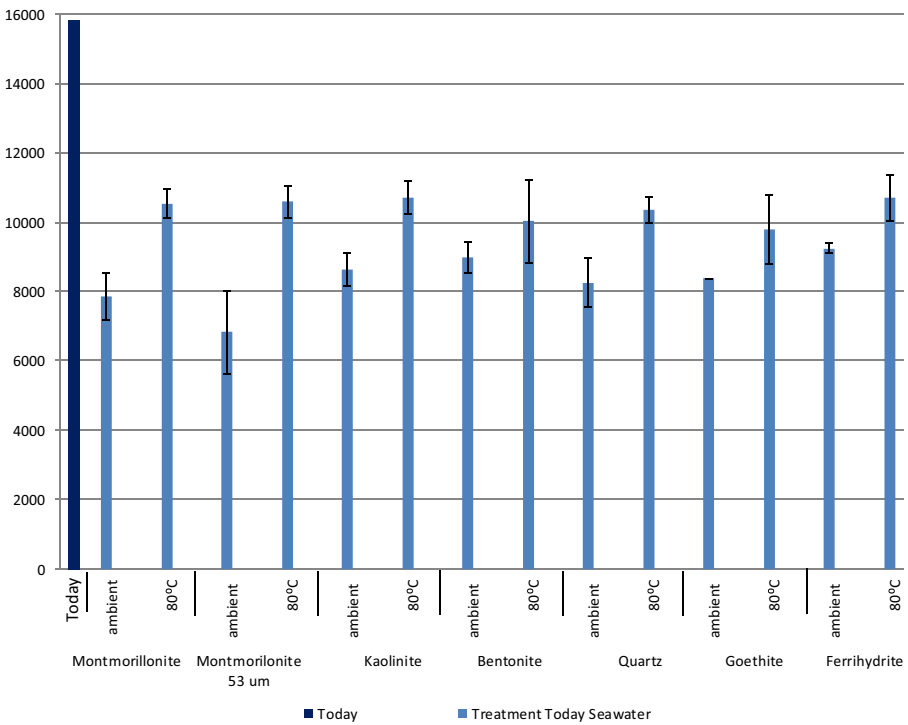


Fig. 4 FT-IR spectra of minerals after they were mixed with distilled water and artificial seawaters in two different temperatures. Artificial seawaters were prepared as describe by Zaia (2012). The samples in the tubes were mixed for 24 h and spun for 15 min at 2000 rpm. The solid phase of the samples was lyophilized and was used for FT-IR spectroscopy



◀ **Fig. 5** Concentration of sodium (mg L^{-1}) in distilled water and artificial seawaters, after the solutions were mixed with 200 mg of each mineral for 24 h in two different temperatures. The number of experiments was four. Artificial seawaters were prepared as describe by Zaia (2012). For the same mineral: means with different lowercase letters were statistically different from each other by Student-Newman-Keuls test ($p < 0.05$)

stretching) was observed only for the samples of ferrihydrite without previous treatment and mixed with distilled water, at both temperatures. However, X-ray diffraction patterns of potassium nitrate appear only for the sample of ferrihydrite without previous treatment (Fig. 2a). Also, for the samples of ferrihydrite mixed with both artificial seawaters (ASWT, ASW 4.0 Ga) at both temperatures (Fig. 4), in the region from 976 cm^{-1} to 1125 cm^{-1} (S-O stretching) three bands were observed (Nakamoto 1978; Cornell and Schwertmann 2003). It should be noted that X-ray diffraction patterns did not show sulfate species precipitated on the mineral (Fig. 2a).

Goethite without and with treatments showed the following bands: 640 cm^{-1} (Fe-O symmetric stretching), 667 cm^{-1} (shoulder), 794 cm^{-1} (O-H bending out plane) and 890 cm^{-1} (O-H bending in plane) cm^{-1} (Fig. 4) (Nakamoto 1978; Cornell and Schwertmann 2003). The FT-IR spectrum of the goethite sample after treatment with ASW 4.0 Ga at $80 \text{ }^\circ\text{C}$ showed a characteristic band at 1120 cm^{-1} that could be attributed to S-O stretching (Nakamoto 1978).

Adsorption of Na^+ , K^+ , Ca^{2+} and Mg^{2+} onto the Minerals

For the mineral samples mixed with ASWT, a large decrease in the Na^+ concentration in the fluid was observed when compared to the sample without the mineral. This effect was not observed for the mineral samples mixed with ASW 4.0 Ga (Fig. 5). Montmorillonite showed the highest Na^+ release when mixed with distilled water at room temperature (Fig. 5). The temperature had no effect on the amount of adsorbed Na^+ on each mineral ($p > 0.05$, Fig. 5).

For the ASWT with and without mineral, with the exception of ferrihydrite at $80 \text{ }^\circ\text{C}$, all other samples showed a decrease in the concentration of K^+ in the fluid (Fig. 6). Montmorillonite, montmorillonite $53 \text{ }\mu\text{m}$, kaolinite, quartz, and goethite samples with ASWT showed a dependence of K^+ concentration on temperature (Fig. 6, $p < 0.05$). With the exception of ferrihydrite mixed with ASW 4.0 Ga at $80 \text{ }^\circ\text{C}$ (that showed an increase in K^+ concentration), the following samples showed a small decrease in the K^+ concentration: bentonite, kaolinite, montmorillonite and montmorillonite $53 \text{ }\mu\text{m}$ (room temperature) and quartz (room temperature) (Fig. 6). It should be noted that when ASW 4.0 Ga was mixed with minerals, temperature did not affect K^+ concentration (Fig. 6, $p > 0.05$).

Minerals mixed with artificial seawaters (ASWT, ASW 4.0 Ga) a decrease in Mg^{2+} concentration was observed only at room temperature (Fig. 7). Thus, in general, temperature has an effect on Mg^{2+} concentration (Fig. 7, $p < 0.05$). In addition, montmorillonite $53 \text{ }\mu\text{m}$ mixed with distilled water released Mg^{2+} at both temperatures (Fig. 7).

In general, the presence of the minerals decreased the Ca^{2+} concentration of the artificial seawater ASWT when compared to the sample without minerals (Fig. 8). For the montmorillonite sample mixed with artificial seawater ASWT, temperature had an effect on the Ca^{2+} concentration adsorbed (Fig. 8, $p < 0.05$). In contrast, all mineral samples when mixed with ASW 4.0 Ga showed a decrease of Ca^{2+} concentration in the fluid when compared to samples without minerals (Fig. 8). However, temperature did not have an effect on the Ca^{2+}

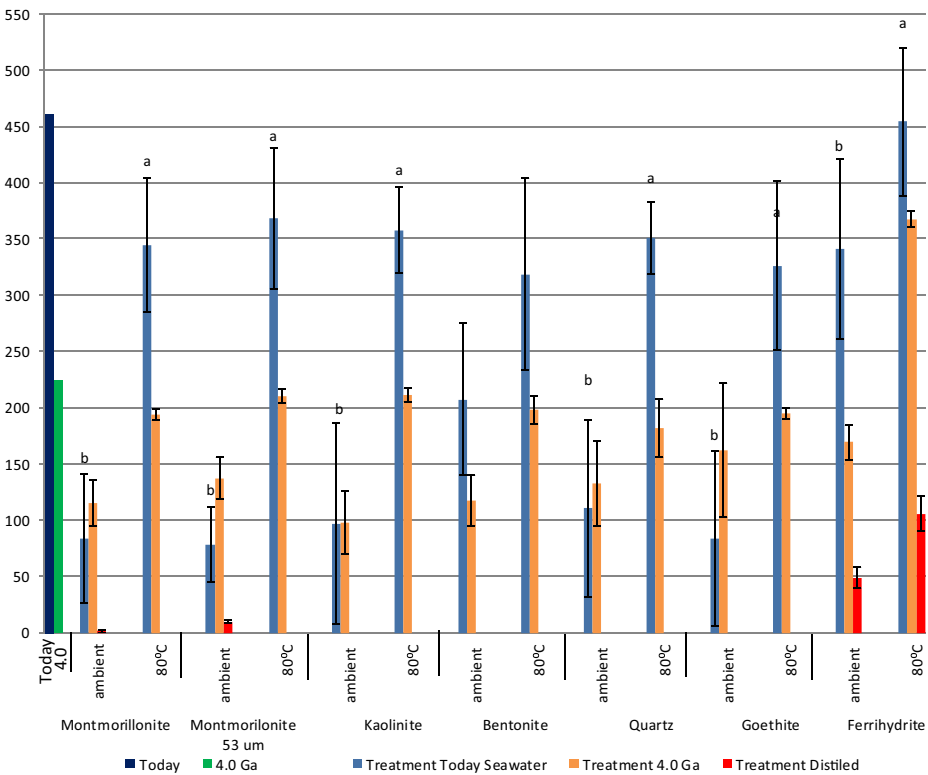


Fig. 6 Concentration of potassium (mg L^{-1}) in distilled water and artificial seawaters, after the solutions were mixed with 200 mg of each mineral for 24 h in two different temperatures. The number of experiments was four. Artificial seawaters were prepared as describe by Zaia (2012). For the same mineral: means with different lowercase letters were statistically different from each other by Student-Newman-Keuls test ($p < 0.05$)

concentration adsorbed by the minerals (Fig. 8, $p > 0.05$).). In addition, montmorillonite $53 \mu\text{m}$ mixed with distilled water released Ca^{2+} at both temperatures (Fig. 8).

Si and Al Release from Minerals

For the bentonite, kaolinite, montmorillonite, montmorillonite $53 \mu\text{m}$ and quartz samples, at 80°C , the amount of Si released from the minerals distilled water and artificial seawaters followed the order: ASW 4.0 Ga > ASWT >> distilled water (Table 2, $p < 0.05$). In contrast, at room temperature, the amount of Si released from the minerals by distilled water and artificial seawaters were: ASWT > ASW 4.0 Ga \approx distilled water (bentonite) and ASWT > distilled water (montmorillonite $53 \mu\text{m}$) (Table 2, $p < 0.05$). For all samples, higher temperature increased the release of Si from the minerals (Table 2, $p < 0.05$). The [Si released at 80°C] / [Si released at room temperature] ratios were: for distilled water 40.9 (bentonite) > 24.8 (montmorillonite $53 \mu\text{m}$) > 15.4 (montmorillonite) > 7.9 (quartz) > 3.0 (kaolinite); for ASWT 15.0 (quartz) > 10.8 (montmorillonite) > 5.6 (montmorillonite $53 \mu\text{m}$) > 4.8 (bentonite) > 4.6 (kaolinite); and for ASW 4.0 Ga 32.6 (montmorillonite) > 27.3 (bentonite, quartz) > 24.6 (montmorillonite $53 \mu\text{m}$) > 4.6 (kaolinite).

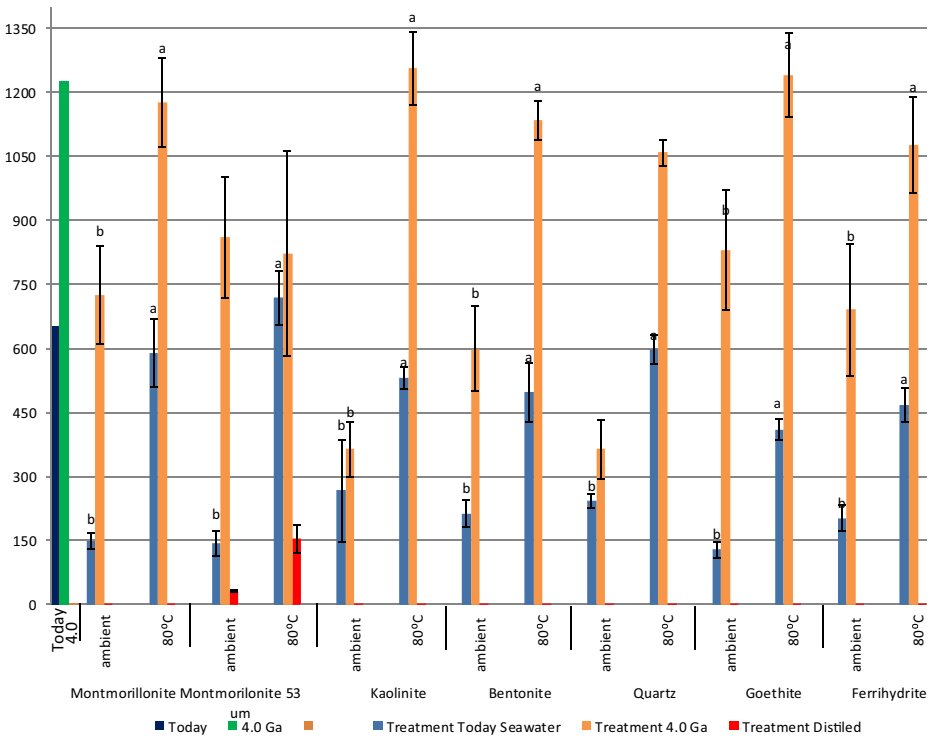


Fig. 7 Concentration of magnesium (mg L^{-1}) in distilled water and artificial seawaters, after the solutions were mixed with 200 mg of each mineral for 24 h in two different temperatures. The number of experiments was four. Artificial seawaters were prepared as describe by Zaia (2012). For the same mineral: means with different lowercase letters were statistically different from each other by Student-Newman-Keuls test ($p < 0.05$)

For bentonite samples at room temperature and 80 °C, the amount of Al released from the mineral in distilled water and artificial seawaters followed the order: ASWT > ASW 4.0 Ga > > distilled water (Table 3, $p < 0.05$). Montmorillonite 53 μm samples after treatments released Al in the following order: ASW 4.0 Ga > ASWT > > distilled water (80 °C) and ASWT \approx ASW 4.0 Ga > > distilled water (room temperature) (Table 3, $p < 0.05$). Also, montmorillonite samples, at 80 °C, released Al after treatments in the following order: ASWT > ASW 4.0 Ga \approx distilled water (Table 3, $p < 0.05$). For kaolinite sample a small amount of Al was released (Table 3). In general, for all treatments, an increase in the temperature decreased the amount of Al released (Table 3, $p < 0.05$).

Discussion

Characterization of the Materials

The decrease of the d_{001} diffraction plane of the bentonite, montmorillonite and montmorillonite 53 μm was due to the high adsorption of Na^+ and K^+ from ASWT (Figs. 5, 6) (Howard 1981; Guizhen et al. 2009). It should be noticed that these cations are in higher concentration in ASWT than in ASW 4.0 Ga (Table 1). The decrease of the d_{001} diffraction plane of the

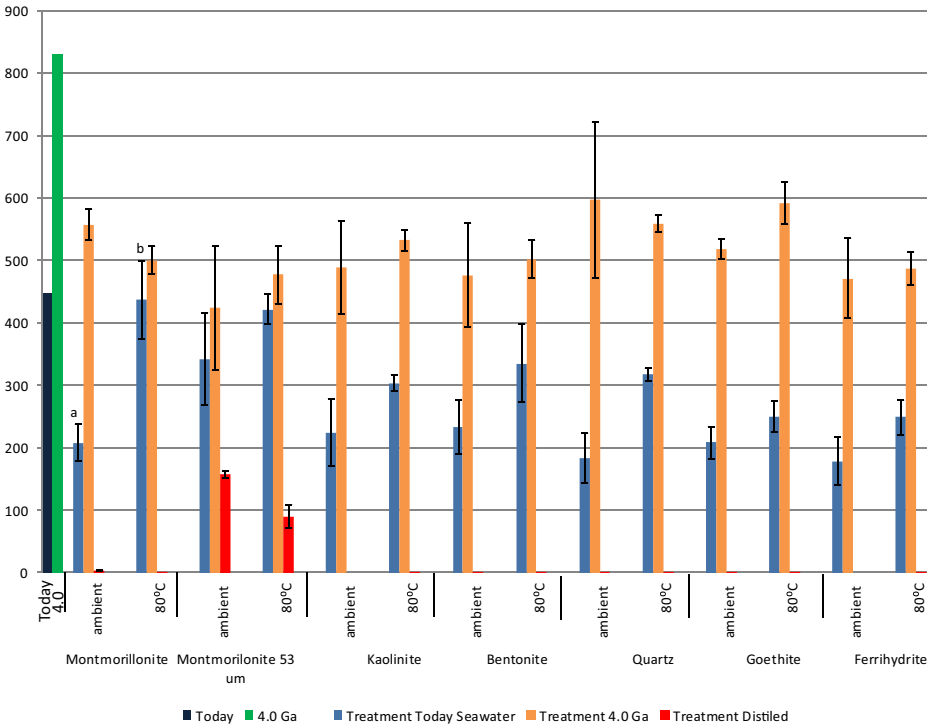


Fig. 8 Concentration of calcium (mg L^{-1}) in distilled water and artificial seawaters, after the solutions were mixed with 200 mg of each mineral for 24 h in two different temperatures. The number of experiments was four. Artificial seawaters were prepared as describe by Zaia (2012). For the same mineral: means with different lowercase letters were statistically different from each other by Student-Newman-Keuls test ($p < 0.05$)

Table 2 Concentration of silicon (mg L^{-1}) in the supernatant after the minerals were mixed with distilled water and artificial seawaters for 24 h in two different temperatures (ambient and 80°C)

Mineral	Temperature	Treatments		
		ASWT	ASW 4.0 Ga	Distilled Water
Bentonite	ambient	$6.78 \pm 0.60^{\text{Ab}}$	$1.70 \pm 0.40^{\text{Bb}}$	$0.33 \pm 0.19^{\text{Bb}}$
	80°C	$32.51 \pm 0.79^{\text{Ba}}$	$46.41 \pm 1.91^{\text{Aa}}$	$13.51 \pm 0.22^{\text{Ca}}$
Kaolinite	ambient	$1.17 \pm 0.14^{\text{b}}$	$1.14 \pm 0.19^{\text{b}}$	$1.12 \pm 0.26^{\text{b}}$
	80°C	$7.97 \pm 0.24^{\text{Ba}}$	$8.15 \pm 0.35^{\text{Aa}}$	$3.34 \pm 0.20^{\text{Ca}}$
Montmorillonite	ambient	$1.73 \pm 0.11^{\text{b}}$	$0.94 \pm 0.10^{\text{b}}$	$0.76 \pm 0.06^{\text{b}}$
	80°C	$18.71 \pm 0.33^{\text{Ba}}$	$29.36 \pm 0.56^{\text{Aa}}$	$11.71 \pm 0.10^{\text{Ca}}$
Montmorillonite 53 μm	ambient	$3.74 \pm 0.48^{\text{Ab}}$	$1.35 \pm 0.35^{\text{ABb}}$	$0.62 \pm 0.23^{\text{Bb}}$
	80°C	$21.04 \pm 1.29^{\text{Ba}}$	$33.15 \pm 1.01^{\text{Aa}}$	$15.38 \pm 0.89^{\text{Ca}}$
Quartz	ambient	$1.45 \pm 0.13^{\text{b}}$	$0.86 \pm 0.08^{\text{b}}$	$0.60 \pm 0.21^{\text{b}}$
	80°C	$21.77 \pm 0.78^{\text{Ba}}$	$23.47 \pm 0.83^{\text{Aa}}$	$4.73 \pm 0.09^{\text{Ca}}$

ASWT = artificial seawater of today, ASW 4.0 Ga = artificial seawater of 4.0 billion years ago. Artificial seawaters were prepared as describe by Zaia (2012). The results are presented as mean \pm standard error of mean. The number of samples was four. For lines, means with different capital letters were statistically different from each other by SNK test ($p < 0.05$). For columns, same mineral and solution, means with different lower case letters were statistically different from each other by Student-Newman-Keuls test ($p < 0.05$)

Table 3 Concentration of aluminum (mg L^{-1}) after the minerals were mixed with distilled water and artificial seawaters for 24 h in two different temperatures (ambient and 80°C)

Mineral	Temperature	Treatments		
		ASWT	ASW 4.0 Ga	Distilled Water
Bentonite	ambient	$20.1 \pm 5.0^{\text{Aa}}$	$16.7 \pm 1.3^{\text{Ba}}$	$0.40 \pm 0.035^{\text{C}}$
	80°C	$9.58 \pm 0.41^{\text{Ab}}$	$5.77 \pm 0.44^{\text{Bb}}$	0.00^{C}
Kaolinite	ambient	$0.23 \pm 0.05^{\text{B}}$	$0.38 \pm 0.19^{\text{Ba}}$	$0.58 \pm 0.08^{\text{Aa}}$
	80°C	0.00	0.00^{b}	0.00^{b}
Montmorillonite	ambient	414.0 ± 33.2	$430.1 \pm 28.4^{\text{a}}$	$395.1 \pm 35.0^{\text{a}}$
	80°C	$435.2 \pm 12.5^{\text{A}}$	$233.6 \pm 25.4^{\text{Bb}}$	$180.3 \pm 9.5^{\text{Bb}}$
Montmorillonite 53 μm	ambient	$77.0 \pm 6.2^{\text{Aa}}$	$78.5 \pm 2.8^{\text{A}}$	$0.76 \pm 0.17^{\text{B}}$
	80°C	$28.5 \pm 2.1^{\text{Bb}}$	$71.4 \pm 7.0^{\text{A}}$	0.00^{C}

ASWT = artificial seawater of today, ASW 4.8 Ga = artificial seawater of 4.0 billion years ago. Artificial seawaters were prepared as describe by Zai (2012). The results are presented as mean \pm standard error of mean. The number of experiments was four. For lines, means with different capital letters were statistically different from each other by Student-Newman-Keuls test ($p < 0.05$). For columns, same mineral and solution, means with different lower case letters were statistically different from each other by Student-Newman-Keuls test ($p < 0.05$)

bentonite, montmorillonite and montmorillonite 53 μm reduces their internal surface area (Macht et al. 2011). Since K^+ causes very low expandability in these minerals, it could hinder the entrance of organic molecules into their interlayers (Howard 1981). Consequently, for the bentonite, montmorillonite and montmorillonite 53 μm , protection of biomolecules and the effect of catalysis could be seriously compromised (Lahav and Chang 1976; Lambert 2008). Thus, this could diminish the role of these minerals or even disable them in experiments on prebiotic chemistry. However, when bentonite, montmorillonite and montmorillonite 53 μm were mixed with ASW 4.0 Ga, whose salts composition is probably more similar to the actual composition of the seas of Earth of 4.0 billion years ago, this did not occur (Fig. 1).

The K_{sp} of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 25°C and 80°C were calculated using the equation $\ln(k_T) = a + c/T + d \log T$ (where $a = 68.2401$, $c = -3221.51$, $d = -25.0627$, Langmuir 1997). K_{sp} values at 25°C and 80°C are $2.69 \cdot 10^{-5}$ and $1.82 \cdot 10^{-5}$, respectively. The experimental value of K_{sp} at 25°C is $2.51 \cdot 10^{-5}$ (Langmuir 1997). Using the equation for saturation index = $\{([\text{Ca}^{2+}][\text{SO}_4^{2-}]/K_{\text{sp}})\}$, at room temperature, for ASWT and ASW 4.0 Ga the saturation indices are 5.86 and 46.76, respectively. Thus, the amount of SO_4^{2-} and Ca^{2+} added to ASWT and ASW 4.0 Ga (Table 1) could be enough to cause the precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ onto the minerals. For ASWT, because of the high concentration of Na^+ and Cl^- , the ionic strength is also high, and the precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ does not occur (Alpers et al. 2000). The low amount of Na^+ and Cl^- in ASW 4.0 Ga is enough to avoid the precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. It should be noted that Ca^{2+} could form an ion pair with SO_4^{2-} or Cl^- , thus the hydration sphere of the ions could remain intact resulting in neutral or charged species (Bearman 2004). The formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was observed only for the samples containing bentonite, kaolinite, montmorillonite, montmorillonite 53 μm , goethite and quartz mixed with ASW 4.0 Ga at 80°C and for montmorillonite 53 μm at room temperature (Figs. 1, 2, 3). In both artificial seawaters and at both temperatures Ca^{2+} was adsorbed by the minerals (Fig. 8). Also, FT-IR spectra showed the presence of SO_4^{2-} adsorbed onto ferrihydrite mixed with both artificial seawaters and at both temperatures (Fig. 4). The adsorption of SO_4^{2-} onto ferrihydrite was expected because its pH_{pzc} is 8.6 and the pHs of the experiments were in

Table 4 Values of pH_{pzc} of minerals and pH of the samples

Minerals	pH_{pzc}	Temperature	ASWT		ASW 4.0 Ga		Distilled Water	
			initial	final	initial	final	initial	final
Bentonite	3.0–8.0	ambient	3.41	3.35	3.59	3.58	4.31	4.29
		80°C	3.37	2.58	2.88	2.88	4.25	3.55
Kaolinite	2.7–4.1	ambient	5.97	5.90	5.41	5.66	6.22	6.40
		80°C	5.48	5.11	5.36	4.94	5.85	5.31
Ferrihydrite	5.3–8.0	ambient	6.64	6.84	6.84	6.87	5.29	5.34
		80°C	6.61	6.25	6.85	6.36	5.31	5.60
Goethite	7.4–9.0	ambient	6.77	6.90	6.81	6.99	6.75	7.64
		80°C	6.66	6.57	6.81	6.26	7.66	7.46
Montmorillonite	4.0–6.5	ambient	2.52	2.51	2.72	2.76	2.63	2.60
		80°C	2.51	2.07	2.80	2.41	2.74	2.35
Montmorillonite 53 μ	4.0–6.5	ambient	3.20	3.16	3.38	3.36	3.64	3.62
		80°C	3.23	2.46	3.50	2.76	3.66	3.27
Quartz	< 4.0	ambient	6.56	6.33	5.99	6.20	6.82	7.18
		80°C	5.91	6.29	5.90	5.52	6.54	6.44

*The values of pH_{pzc} were obtained from: Schwertmann and Fechter 1982; Appel et al. 2003; Kim 2003; Tombácz and Szekeres 2004; Kosmulski 2002, 2006, 2009; ASWT = artificial seawater of today, ASW 4.0 Ga = artificial seawater of 4.0 billion years ago. Initial pH ambient temperature: ASWT =6.65, ASW 4.0 Ga = 5.59 and distilled water =5.18. Initial pH 80°C: ASWT =6.09, ASW 4.0 Ga = 5.75 and distilled water =6.15. Artificial seawaters were prepared as describe by Zaia (2012). The results are means of four samples

the range from 5.34 to 6.87 (Table 4). It should be noted that for the other minerals the characteristic bands of SO_4^{2-} are not observed—probably because minerals have bands in the same region (Fig. 4). Thus, even for those minerals where precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was not observed, the adsorption of Ca^{2+} and SO_4^{2-} occurred (Figs. 4, 8).

The precipitation of halite was observed only for the kaolinite, montmorillonite, montmorillonite 53 μm , goethite, and quartz samples mixed with ASWT at both temperatures (Figs. 1, 2, 3). It should be noted that the solubility of halite is about 6.2 mol L^{-1} at 298 K (Langmuir 1997). Taking into account the amount of Na^+ and Cl^- added to artificial seawaters (Table 2), even using ASWT, the precipitation of halite should not occur. However, it should be pointed out that no washing of the samples was performed between centrifugation and lyophilization, thus some seawater solution remained in the samples. The samples were not washed because as recommended by Lambert (2008) washing could withdraw adsorbed biomolecules or ions from the mineral. Probably the system is closer to the reality when washing is not applied to the samples.

Using FT-IR spectroscopy, Vicente-Rodríguez et al. (1996) and Tomić et al. (2011) studied structural modifications on several silicates (sepiolite, palygorskite, saponites and bentonites) after acid treatments. Vicente-Rodríguez et al. (1996) observed an increase of the bands at 470 cm^{-1} and 795 cm^{-1} as a result of the formation of free silica and a shift of the characteristic bands of Si-O-Si ($1100 \text{ cm}^{-1} - 1000 \text{ cm}^{-1}$) resulting from the formation of amorphous silica. Tomić et al. (2011) observed a decrease of the bands caused by Si-O-Al (region 518 cm^{-1}), Al-Mg-OH (region 840 cm^{-1}), and Al-Al-OH (region 915 cm^{-1}). The treatments carried out in this work did not result in changes in these bands (Fig. 4). Also, it should be noted that, besides

the precipitation of halite and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, X-rays diffractograms did not show other major changes in the bentonite, kaolinite, montmorillonite, montmorillonite 53 μm and quartz.

FT-IR spectra showed that, for both seawaters and temperatures, sulfate was adsorbed by ferrihydrite (Fig. 4). This was expected since the pH of these samples was in the range from 6.25 to 6.87 (Table 4), and pH_{pzc} of ferrihydrite is about 8.0 (Cornell and Schwertmann 2003). FT-IR spectra of these samples showed three bands in the region 970 cm^{-1} to 1130 cm^{-1} (Fig. 4) that are characteristics of an inner sphere complex (Peak et al. 1999; Cornell and Schwertmann 2003). For goethite, a band in the region of 1120 cm^{-1} , characteristic of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, was observed. Thus, sulfate was adsorbed onto ferrihydrite and precipitated on goethite as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Adsorption of Na^+ , K^+ , Ca^{2+} and Mg^{2+} onto the Minerals

All minerals decreased the Na^+ concentration in ASWT, however, for ASW 4.0 Ga this effect was more pronounced for montmorillonite, kaolinite and ferrihydrite at room temperature (Fig. 5). Probably the high concentration of Mg^{2+} and Ca^{2+} in ASW 4.0 Ga (Table 1) prevents adsorption of Na^+ on the minerals. In contrast, the low Mg^{2+} and Ca^{2+} concentrations in the ASWT (compared to Na^+) did not prevent them from being adsorbed by minerals (Figs. 7, 8). According to Charlet and Tournassat (2005), in solutions with high Cl^- concentration, such as found in seawater, Na^+ and the ion pair (CaCl^+) were adsorbed on montmorillonite. In addition, minerals decreased the Na^+ and Ca^{2+} concentrations in the fluids when mixed with ASWT and ASW 4.0 Ga, respectively—temperature had no effect on their decrease (Figs. 5, 8). However, there are two mechanism for decreasing Ca^{2+} concentration in ASWT and ASW 4.0 Ga. When minerals were mixed with ASW 4.0 Ga at $80\text{ }^\circ\text{C}$, because of the high Ca^{2+} concentration in this seawater and low solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at high temperature (Langmuir 1997), Ca^{2+} precipitated. In the other cases Ca^{2+} was adsorbed onto the minerals. For kaolinite, montmorillonite, montmorillonite 53 μm , goethite and quartz minerals, halite formation was observed at room temperature and $80\text{ }^\circ\text{C}$ (Figs. 1, 2, 3). For the other minerals, the decrease in Na^+ was a result of adsorption.

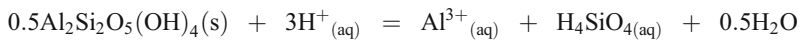
Probably, K^+ and Mg^{2+} were adsorbed by the minerals (Figs. 6, 7), because x-ray diffractograms did not show any mineral containing K^+ and Mg^{2+} (Figs. 1, 2, 3). Also, in general, an increase in the temperature decreased the amount of K^+ and Mg^{2+} adsorbed on minerals ($p < 0.05$, Figs. 6, 7). Because K^+ and Mg^{2+} were not precipitated on minerals, but they were concentrated on them by adsorption, they could be available to participate in prebiotic chemistry reactions. It should be noticed that K^+ and Mg^{2+} could be used to catalyze the formation of peptides in a salt-induced peptide formation reaction (Dubina et al. 2013) and in nucleoside formation, which may have been important for RNA and DNA synthesis (Sheng et al. 2009). On the other hand, Ferris and Ertem (1993) observed that exchange cation Mg^{2+} of montmorillonite did not have any catalytic effect on formation of oligomers of adenylic acid.

The adsorption of cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) forming complexes with the minerals surfaces occurs through two different mechanisms. Firstly, if $\text{pH}_{\text{pzc}} < \text{range of pH of the samples}$ (Table 4), the surfaces of minerals have an excess of negative charge. Thus, adsorption of cations on these minerals occurs because of electrostatic interaction. Secondly, if $\text{pH}_{\text{pzc}} > \text{range of pH of the samples}$ (Table 4), the surfaces of the minerals have an excess of positive charge. Thus, the adsorption should not occur, however cations were adsorbed on

minerals (Figs. 5, 6, 7, and 8). All seawater solutions contained Cl^- and SO_4^{2-} and FT-IR spectra showed the presence of SO_4^{2-} adsorbed onto ferrihydrite. Thus, complexes between the anions adsorbed on minerals and cations could be formed (Swedlund et al. 2009). Another possibility is the formation of ion pairs between the cations and $\text{Cl}^-/\text{SO}_4^{2-}$. These ion pairs could decrease the charge of the cations allowing them to adsorb on minerals (Bearman 2004). Rundberg et al. (1994) did not observe the adsorption of Na^+ onto goethite for $\text{pH} < \text{pH}_{\text{pzc}}$.

Si and Al Release from Minerals

For all samples, an increase in the temperature caused an increase in concentration of aqueous Si (Table 2). This effect was expected, in light of the fact that seawater and rivers/lakes contain approximately 6.0 mg L^{-1} and 14 mg L^{-1} of $\text{SiO}_{2(\text{aq})}$, respectively. However, at higher temperatures ($100 \text{ }^\circ\text{C}$) the concentration of $\text{SiO}_{2(\text{aq})}$ is enhanced from 53 mg L^{-1} to 373 mg L^{-1} (Langmuir 1997). In general, among the clays, the samples containing bentonite showed the highest concentration of Si in solution (Table 2). Those containing kaolinite at 80°C showed the lowest values of dissolved Si (Table 2). This is probably because the pH of the kaolinite sample is in the range from 4.94 to 6.40 (Table 4). Thus, as shown below the release of Si is not favored.



For the montmorillonite and bentonite a high release of Si was observed—probably because of the low pH of these samples (Table 4). This could mean that under hydrothermal conditions such as found in black smokers, where pH is very low and the temperature is much higher than used in this experiment, clays could be dissolved (Martin et al. 2008).

For kaolinite sample a low amount of dissolved Al (Table 3) was found, probably because the high pH (Table 4) of these samples favored the formation of $\text{Al}(\text{OH})_3$ (Table 5). In general, an increase in the temperature caused a decrease in the amount of Al released from the minerals (Table 3). Probably, the increase in the equilibrium constant of the Al species with temperature (Table 5), decreased the amount of Al^{3+} measured by the aluminon method (AWWA-APHA-WPCI 2006).

Table 5 Values of K_{sp} of Al species at 298.15 and 353.15 K

specie	Temperature (K)	Keq	Constants
$\text{Al}(\text{OH})^{2+}$	298.15	$1.0 \cdot 10^{-5}$	$a = -38.253$
	353.15	$2.4 \cdot 10^{-4}$	$c = -656.27$ $d = 14.327$
$\text{Al}(\text{OH})_2^+$	298.15	$7.6 \cdot 10^{-11}$	$a = 88.50$
	353.15	$6.3 \cdot 10^{-8}$	$c = -9,391.6$ $d = -27.121$
$\text{Al}(\text{OH})_3$	298.15	$2.5 \cdot 10^{128}$	$a = 226.374$
	353.15	$6.3 \cdot 10^{136}$	$c = -18,247.8$ $d = -14.865$
$\text{Al}(\text{OH})_4^-$	298.15	$2.1 \cdot 10^{-23}$	$a = 51.578$
	353.15	$1.2 \cdot 10^{-18}$	$c = -11,168.9$ $d = -14.865$

For the calculation of K_{sp} was used the equation $\log K_T = a + c/T + d \log T$ (Langmuir 1997)

Relevance of these Experiments for Prebiotic Chemistry

It should be noted that most of the previous prebiotic chemistry experiments were performed in distilled water or sodium chloride solutions using montmorillonite as the adsorbent mineral (Lahav and Chang 1976; Lambert 2008; Zaia 2004, 2012). In this study we used two different artificial seawaters. One was ASW 4.0 Ga, rich in Mg^{2+} and SO_4^{2-} , that probably resembles the seawater of the oceans before life arose on Earth. The other, ASWT, rich in Na^+ and Cl^- , has a composition that is the average of the major cations and anions of today's oceans. The high concentration of Na^+ and Cl^- in ASWT decreased the d_{001} spacing of the montmorillonite, montmorillonite 53 μm and bentonite. However, this was not observed in the experiments using ASW 4.0 Ga—meaning that in primitive oceans the cations of the seawater did not promote any reduction in d_{001} spacing of the montmorillonite, montmorillonite 53 μm and bentonite. Thus, these minerals would be intact and able to adsorb biomolecules. For all experiments, the amount of Si and Al released from the minerals, even at high temperature (80 °C, heating for 24 h), was less than 1 % of the amount of the mineral, meaning these treatments did not substantially alter the minerals. The role of exchangeable cations as catalysts on the formation of peptides and nucleosides is not totally understood, thus these results are important for further experiments (Ferris and Ertem 1993; Sheng et al. 2009; Dubina et al. 2013). Finally, because bentonite, montmorillonite, kaolinite, goethite and ferrihydrite did not suffer dissolution when interacted with artificial seawater 4.0 Ga, at room temperature or at 80 °C, they could be used for experiments on prebiotic adsorption, polymerization and protection against degradation. Further experiments performed under the conditions described above will probably resemble more closely what might have happened on the prebiotic Earth.

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