

Primordial Ocean Chemistry and its Compatibility with the RNA World

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Abstract We examine the stability of three key components needed to establish an RNA World under a range of potential conditions present on the early earth. The stability of ribose, cytosine, and the phosphodiester bond are estimated at different pH values and temperatures by extrapolating available experimental data. The conditions we have chosen range from highly acidic or alkaline hydrothermal vents, to the milder conditions in a primordial ocean at a range of atmospheric CO₂ partial pressures.

Keywords Early ocean chemistry · RNA stability

Introduction

The RNA World hypothesis assumes that both RNA and its ribose and nucleobase components are sufficiently stable under primordial conditions to allow for both stored genetic information and catalytic functions to be transferred to the next generation by self-replication. The chemical conditions in the environment such as pH and ionic composition would play a critical role in determining the stability of RNA and its components. In typical “RNA evolution in a test tube” experiments, pH is in the range 7.0–8.5, Mg²⁺ concentrations are typically 5–100 mM, and temperatures are 25–40°C (Gesteland et al 1999).

Unlike the present day ocean of pH ~ 8, the pH of the primitive oceans could have been significantly lower because of elevated levels of CO₂ (0.1–10 atm) supposedly needed to compensate for the faint-young sun and keep surface temperatures above freezing (Kasting 1993). Highly acidic or highly alkaline conditions such as found in hydrothermal vents

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have also been proposed as plausible sites for prebiotic chemistry and the origin of the RNA World (Shock 1992; Martin and Russell 2009).

The goal of our study is to calculate the stability of RNA and its components across a range of pH and temperature values in order to determine which of these putative conditions for the origin of life contributes to the maximal stability of RNA World precursors. We calculated half-lives from extrapolations of experimental data available for the rates of ribose decomposition, cytosine deamination and phosphodiester bond hydrolysis.

Results and Discussion

Early Ocean pH and Other Conditions

The partial pressure of CO₂ (pCO₂) is proportional to ocean pH according to the relationship:

$$P_{CO_2} = \frac{[H^+]^3/2}{K_1 K_H} \left(\frac{2K_{sp}}{K_2} \right)^{1/2}$$

where $K_H = \frac{[H_2CO_3]}{P_{CO_2}}$; $K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$; $K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$; $K_{sp} = [Ca^{2+}][CO_3^{2-}]$.

Values of these four equilibrium constants were calculated as a function of temperature and salinity using the equations derived by Weiss and Price (1980) for K_H , Cai and Wang (1998) for K_1 and K_2 , and Mucci (1983), Plummer and Busenberg (1982) for K_{sp} . These four expressions are:

$$\ln K_H = \left(a_0 + \frac{a_1}{T} + a_2 T^2 + a_3 \ln T \right) + S(b_0 + b_1 T + b_2 T^2)$$

where $a_0 = -5.75 \times 10^2$, $a_1 = 2.15 \times 10^4$, $a_2 = -1.48 \times 10^{-4}$, $a_3 = 8.99 \times 10^1$, $b_0 = 2.99 \times 10^{-2}$, $b_1 = -2.75 \times 10^{-4}$, $b_2 = 5.34 \times 10^{-7}$

$$pK_1 = \left(a_0 + \frac{a_1}{T} + a_2 T \right) + S^{0.5} \left(b_0 + \frac{b_1}{T} \right) + S \left(c_0 + \frac{c_1}{T} \right)$$

where $a_0 = -1.48 \times 10^1$, $a_1 = 3.40 \times 10^3$, $a_2 = 3.28 \times 10^{-2}$, $b_0 = -2.31 \times 10^{-2}$, $b_1 = -1.43 \times 10^1$, $c_0 = 6.29 \times 10^{-4}$, $c_1 = 4.3 \times 10^{-1}$

$$pK_2 = \left(a_0 + \frac{a_1}{T} + a_2 T \right) + S^{0.5} \left(b_0 + \frac{b_1}{T} \right) + S \left(c_0 + \frac{c_1}{T} \right)$$

where $a_0 = -6.50$, $a_1 = 2.90 \times 10^3$, $a_2 = 2.38 \times 10^{-2}$, $b_0 = -4.59 \times 10^{-1}$, $b_1 = 4.12 \times 10^1$, $c_0 = 2.85 \times 10^{-2}$, $c_1 = -2.56$

$$-pK_{sp} = a_0 + a_1 T + \frac{a_2}{T} + a_3 \log T + \left(b_0 + b_1 T + \frac{b_2}{T} \right) S^{0.5} + c_0 S + d_0 S^{1.5}$$

where $a_0 = -1.72 \times 10^2$, $a_1 = -7.80 \times 10^{-2}$, $a_2 = -2.84 \times 10^3$, $a_3 = 7.16 \times 10^1$, $b_0 = -7.77 \times 10^{-1}$, $b_1 = 2.84 \times 10^{-3}$, $b_2 = 1.78 \times 10^2$, $c_0 = -7.71 \times 10^{-2}$, $d_0 = 4.12 \times 10^{-3}$

Assuming a salinity similar to the present ocean of 35‰, the calculated pH vs $p\text{CO}_2$ profile is shown in Fig. 1. Following the limits proposed by Kasting (1993), if $p\text{CO}_2$ is 10 atm, the lowest ocean pH will be ~ 5.4 , and if $p\text{CO}_2=0.1$ atm, ocean pH will be ~ 6.7 , assuming the ocean temperatures are 50°C or lower. Our simple model treats $p\text{CO}_2$ and temperature independently. If the salinity of the early ocean was double the present value as suggested by Knauth (1998), pH only increases by ~ 0.1 from our calculations. For a more comprehensive review covering constraints on the composition of the early ocean including the relationship between pH and $p\text{CO}_2$, the reader is referred to Grotzinger and Kasting (1993).

For our analyses of ribose, cytosine and phosphodiester bond stability, we chose five representative pH values. In addition to pH 5.4 and 6.7 for the $p\text{CO}_2$ values discussed above, we chose pH 8 to represent low $p\text{CO}_2$ values closer to present day, pH 3.5 for an average acidic hydrothermal vent, and pH 10 for an average alkaline hydrothermal vent (e.g., Lost City).

Ribose Stability

Larralde et al (1995) measured the rate of ribose decomposition by monitoring the signal decrease of the C1-hydrogen of ribose via ^1H NMR spectroscopy. Measurements were made in the pH 4–8 range at four temperatures: 60, 80, 100, 118°C . They found that the rate of ribose decomposition increased with increasing pH but then reached a plateau at pH 7–8.

Our $\log k$ versus $1/T$ Arrhenius plots of the data yielded linear fits with R^2 values of 0.96–0.99 as shown in Fig. 2. For pH 3.5, we extrapolated the curves and assumed an Arrhenius plot with the same slope as pH 4. Since the rate is constant for $\text{pH} > 7$, we assumed that the rate at pH 10 was the same as pH 8. At 25°C , the calculated half-lives at pH 3.5, 5.4, 6.7, 8 (and 10) are 1,960 years, 15 years, 1 year and 238 days respectively, i.e., ribose becomes more stable as the acidity of the solution increases. Data at different

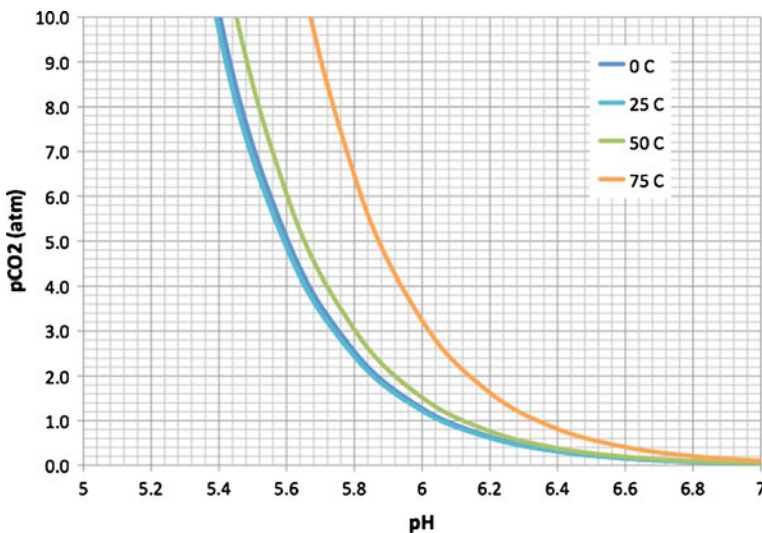


Fig. 1 Plot of pH vs $p\text{CO}_2$ at salinity 35‰ at different temperatures

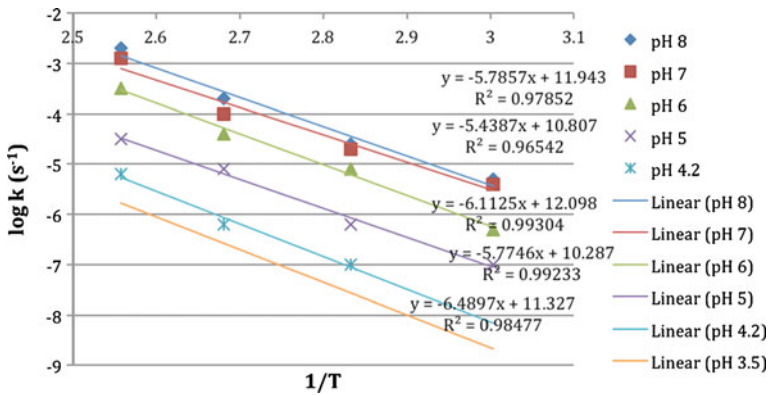


Fig. 2 Arrhenius plots for ribose decomposition

temperatures are shown in Fig. 3 along with the half-lives for cytosine and phosphodiester bond stability.

Cytosine Stability

We focused our analysis on cytosine since it is the least stable of the four nucleobases (Levy and Miller 1998). Garrett and Tsau (1972) measured the rate of cytosine deamination via UV spectroscopy, monitoring the shift of λ_{max} from 274 nm for cytosine to 259 nm for uracil. Measurements were made in the pH 1–12 range at four temperatures: 70, 80, 85, 90°C. They found that cytosine was maximally stable with a constant decomposition rate in the pH 4.5–9 range; the rate increased below pH 4.5 and above pH 9.

Our Arrhenius plots shown in Fig. 4 yielded linear fits with R² values of 0.98 or higher. At 25°C, the calculated half-lives at pH 3.5 and 10 were 132 and 143 years respectively.

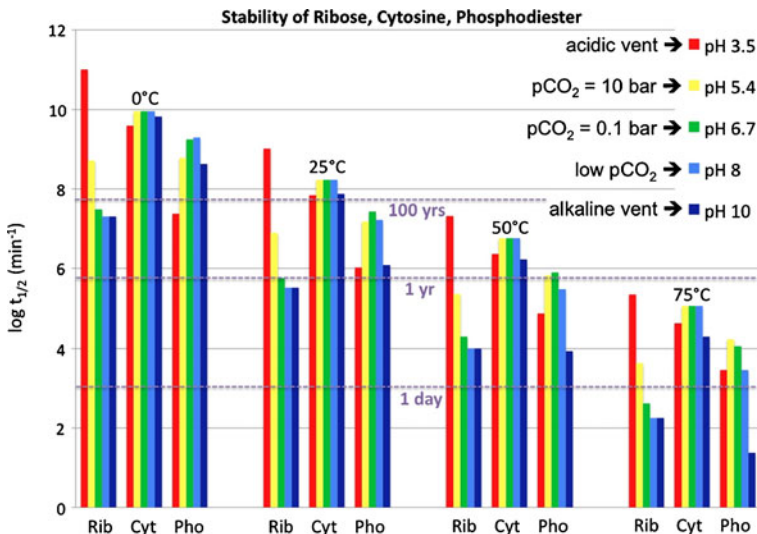
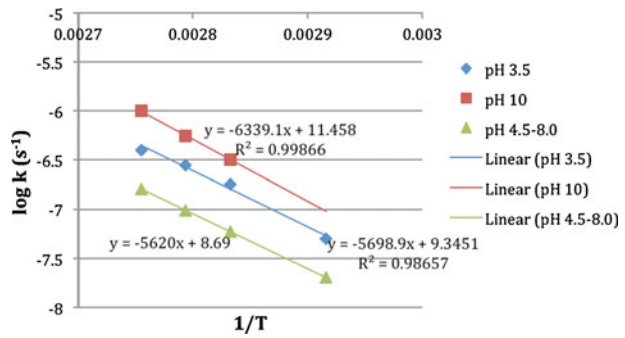


Fig. 3 Half-lives of ribose, cytosine and the phosphodiester bond

Fig. 4 Arrhenius plots for cytosine decomposition

For pH 5.4, 6.7 and 8, the half-life is 324 years. Similar trends were observed for adenine and guanine (Levy and Miller 1998), but with longer half-lives. Except for pH 3.5, cytosine is more stable than ribose (see Fig. 3).

Phosphodiester Bond Stability

Linjalahti and Mikkola (2007) measured the rate of phosphodiester hydrolysis in a 13-mer oligo-U designed to have only one scissile phosphodiester bond (by methylating the 2'-O position all nucleotides except one in the middle). Hydrolysis rates were measured by observing migration times via capillary zone electrophoresis. Measurements were made in the pH 2–12 range at just two temperatures: 35 and 90°C. At 90°C, the hydrolysis rate was at a minimum at pH 5–6 and increased at both lower and higher pHs. At 35°C, data points were only obtained for pH 2–3.5 and 8.5–12 due to very slow rates in the pH 4–8 range; however the trend looks similar to that at 90°C.

The log k versus pH data at 90°C was fit to a quadratic curve ($y=0.1489x^2 - 1.6752x - 1.2786$; $R^2=0.978$). Although missing the “middle” the 35°C data also fits a quadratic curve ($y=0.1343x^2 - 1.7589x - 2.9683$; $R^2=0.997$). We then generated two-point Arrhenius curves for the desired pH values. At 25°C, the calculated half-lives at pH 3.5, 5.4, 6.7, 8 and 10 are 2, 29, 51, 32 and 2 years respectively. From Fig. 3, the phosphodiester bond is slightly more stable than ribose in the pH 5.4–8 range, and significantly less stable at lower pH. At high pH, ribose is less stable at low temperatures but more stable at high temperatures.

Conclusion

For the three processes studied, overall maximal stability is found at pH ~ 5 suggesting that an early ocean with high $p\text{CO}_2$ could reduce the degradation of components needed for primitive RNA World entities to survive, replicate and evolve. Although acidic conditions favor stability, the high temperatures (250–350°C) of submarine hydrothermal vents result in rapid degradation. Even the lower temperature alkaline hydrothermal vents would show half-lives of less than a day at 75°C. Minerals and dissolved ions may alter the decomposition rates. Li and Breaker (1999) have measured the accelerated kinetics of phosphodiester bond cleavage in the presence of Mg^{2+} . In addition, the pK_a values of the canonical nucleobases results in compromised informational pairing ability for pH < 5.5 and pH > 8.5 (Zhang and Krishnamurthy 2009).

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