January 2013

Modeling Potential Chemical Environments: Implications for Astrobiology

Brian Craig Szenay
University of South Florida, bszenay@mail.usf.edu

Follow this and additional works at: http://scholarcommons.usf.edu/etd

Part of the Geochemistry Commons

Scholar Commons Citation
Szenay, Brian Craig, "Modeling Potential Chemical Environments: Implications for Astrobiology" (2013). Graduate Theses and Dissertations.
http://scholarcommons.usf.edu/etd/4847

This Thesis is brought to you for free and open access by the Graduate School at Scholar Commons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact scholarcommons@usf.edu.
Modeling Potential Chemical Environments: Implications for Astrobiology

by

Brian Szenay

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
Department of Geosciences
College of Arts and Sciences
University of South Florida

Major Professor: Matthew Pasek, Ph.D.
Len Vacher, Ph.D.
Zachary Atlas, Ph.D.

Date of Approval:
November 15, 2013

Keywords: origin of life, early geochemistry, prebiotic evolution, iron, phosphorus

Copyright © 2013, Brian Szenay
# TABLE OF CONTENTS

LIST OF TABLES .................................................................................................................. ii

LIST OF FIGURES ............................................................................................................... iii

Abstract ................................................................................................................................. iv

1. Introduction ...................................................................................................................... 1

2. Background ..................................................................................................................... 3
   2.1 Earth’s early atmosphere ......................................................................................... 3
   2.2 Early Earth Ocean ................................................................................................. 4
   2.3 Crust Composition ................................................................................................. 5
   2.4 Acidity pH ............................................................................................................. 5
   2.5 Requirements for Life ........................................................................................... 6

3. Methods ......................................................................................................................... 10
   3.1 Normalization ....................................................................................................... 10
   3.2 Modeling ............................................................................................................... 11
   3.3 Modern-day ocean run ......................................................................................... 12
   3.4 Altering the atmosphere ...................................................................................... 12

4. Results ............................................................................................................................ 16

5. Discussion ....................................................................................................................... 27
   5.1 Implications of a CH₄-dominated atmosphere ..................................................... 27
   5.2 Implications of a CO₂-dominated atmosphere .................................................... 28
   5.3 Implications of an atmospheric mixture of gases ............................................... 29
   5.4 Implications of phosphate concentrations ......................................................... 30
   5.5 Future Work .......................................................................................................... 30

6. References ...................................................................................................................... 32
LIST OF TABLES

Table 3.1: List of Compounds ........................................................................................................ 14
Table 3.2: Atmospheric Compositions ....................................................................................... 15
LIST OF FIGURES

Figure 4.1: Modern-day ocean data. ................................................................. 17
Figure 4.2: CH$_4$-dominated atmosphere pH data. ........................................ 18
Figure 4.3: CH$_4$-dominated atmosphere Fe$^{(2+)}$ data................................. 19
Figure 4.4: CO$_2$/CH$_4$ atmosphere mixture pH data.................................... 20
Figure 4.5: CO$_2$/CH$_2$ atmosphere mixture Fe$^{(2+)}$ data............................ 21
Figure 4.6: CO$_2$-dominated atmosphere pH data. ........................................ 22
Figure 4.7: CO$_2$-dominated atmosphere Fe$^{(2+)}$ data................................. 23
Figure 4.8: CO$_2$/H$_2$ atmosphere mixture pH data. ..................................... 24
Figure 4.9: CO$_2$/H$_2$ atmosphere mixture Fe$^{(2+)}$ data............................... 25
Figure 4.10: Summed PO$_4^{3-}$, HPO$_4^{2-}$, H$_2$PO$_4^{-}$ data........................... 26
Abstract

Modeling chemical environments is an important step to understanding the diversity of prebiotic systems that may have formed on the early earth or potentially can occur on other worlds. By using the modern Earth as a test case, these models predict scenarios with systems more conducive to the formation of the organic molecules that are important to life. Here we use the equilibrium thermodynamic modeling program HSC Chem to investigate prebiotic environments. This program uses the raw material that the user inputs into the system in order to calculate the change in amounts of chemical species forming as a function of temperature and pressure using equilibrium (batch reactor) chemistry. Our results show that ferrous ion (Fe$^{2+}$), which may be important in the early formation of organic molecules on Earth, is most abundant in the aqueous phase where the atmosphere contains carbon dioxide as a major constituent. A pure methane atmosphere exhibits the lowest concentrations of this ion, and mixtures tend to end up in between the two extremes. Additionally, we have determined the pH of early oceans, which has implications for biomineralization, chemical reactions, and mineral chemistry. We see that the CO$_2$ atmosphere, and to some extent, the mixtures and CH$_4$ atmospheres, exhibit near neutral pHs. These results allow prediction of processes that might have taken place and could have impacted the development of life on the early earth.
1. Introduction

Life probably arose within the first billion years of the earth’s history (Schopf, 2006). It is likely that this phenomenon occurred as a result of the auspicious coming together of unique geochemical environments, energy gradients, and molecular building blocks. Thus, it is advantageous and important to analyze the geochemistry of this period to better understand the conditions prevalent on the early earth, and to place constraints on certain processes that might have been occurring then.

The chemistry of the early Archean ocean is not very well understood. Specifically, research attempting to elucidate the chemical composition, redox state, and pH of this ocean is limited. On top of this, there has been some debate about the temperature ranges of the early earth. The research outlined in this paper is meant to constrain the early earth’s oceanic and atmospheric chemistry, as well as analyze certain chemical abundances and parameters that are important to the emergence of life that occurred around this time.

One tool that can be used to approach all of these issues is computer modeling. In this study, research was conducted with the HSC Chemistry computer program with various user input, and potential environmental data as output. Using this method, many different possible chemical environments were modeled in the Archean ocean and atmosphere.
It is possible to test these hypotheses regarding the temperature, pH, and chemical species of the early Archean ocean with this program. Specifically, this research investigated 1) the ferrous iron (Fe$^{2+}$) content of these oceans. Ferrous iron may have been very important for the earliest life, taking the place of, or assisting Mg$^{2+}$ in the folding of RNA (Athavale et al., 2012). It was also thought to facilitate single-electron transfer in RNA (Hsiao et al., 2013). Additionally 2) modeling the pH of this ocean can be beneficial in understanding how well early life might thrive at that time. Processes such as biomineralization are highly dependent on neutral pH systems as opposed to acidic ones, which can dissolve minerals, rather than allow them to precipitate. Many chemical reactions also proceed readily at low pH, but are inhibited at higher pH (Kee et al., 2013). Finally, 3) an important element for life in general is phosphorus. Phosphorus is found in DNA, as well as a major component in phospholipids, which make up cell membranes. Here, we investigated the concentration of phosphate in the ocean during the Archean.

It is hoped that through this research, it will be possible to implement models of chemical environments for other worlds as well to strengthen our understanding of planetary habitability. With these methods, it might be possible to model the chemistry of the Jovian moon Europa’s ocean, or the putative Martian ocean, just as it is possible with the early earth. With this information, we can better understand how life evolved here on Earth, as well as elucidating the other environments that may be able to host life.
2. Background

2.1 Earth’s early atmosphere

The atmosphere of the Earth in the early Archean eon, up to the time of 2.4 Ga, most likely had very little free, molecular oxygen. Krull-Davatzes et al. (2010) studied the composition of spinels to determine the partial pressure of oxygen in the Archean, while Pavlov and Kasting (2002) analyzed sulfur isotopes to do the same. Both methods point to a low concentration of oxygen in contrast to present-day levels. From 2.4 Ga to the present, oxygen partial pressure began to rise as a result of photosynthesis mainly by cyanobacteria (Kasting, 1993). Prior to this, the composition of the Archean atmosphere likely consisted of N$_2$, and, CO$_2$, H$_2$, or CH$_4$, or a mixture of these (Walker, 1982). It is likely that carbon dioxide was a predominant gas during the Archean (Rubey, 1955). The higher carbon dioxide partial pressure during this time could explain how the Earth was able to stay relatively warm, even during a time when the solar luminosity was significantly lower than it is today (Owen et al., 1979). It was concluded by Walker (1985) that carbon dioxide partial pressure could have been as high as 10 bars; however, more recent studies conclude that the partial pressure of this gas was more likely as low as three times the present pressure (Kasting, 2010). This also agrees with another study that concluded that the total air density during the Archean could not be more than two times the density of modern levels based on raindrop imprint fossils (Som et al., 2012).
According to Catling et al. (2001), methane could have been another greenhouse gas that kept the planet warm during a time of lower solar luminosity. However, methane is lost by photolysis of C-H bonds, and H₂ would hence have escaped into space, depleting the atmosphere of methane (Catling et al., 2001). A more recent model of H₂ escape to space suggests that it was much slower than originally expected, and that H₂ could have been up to 30% of the Archean atmosphere (Tian et al., 2005).

2.2 Early Earth Ocean

The chemistry of the Archean ocean is not well constrained. More specifically, research is limited regarding certain parameters, such as pH and temperature. The Archean ocean is thought to characterize anoxic conditions (Kranendonk et al., 2003).

There is no consensus on the temperature of the ocean at this time. Two different theories have formed regarding the temperature, with Knauth (2005) arguing for a high (55-85°C) temperature of the surface ocean water based on oxygen isotope data of cherts. However, Hren et al. (2009) used hydrogen and oxygen isotope data to conclude that the temperate of the ocean at this time could not be more than 40°C. Indeed, another study by Blake et al. (2010), this time using oxygen isotope data on phosphate, confirms a more moderate ocean temperature during this time. This study examines a very large temperature range, and its effect on different oceanic chemical characteristics.

pH is another parameter that has been studied during this time period, and is thought to not be much different than the pH of the ocean water today (Grotzinger and Kasting, 1992). However, with the increase of the partial pressure of CO₂ in the
atmosphere, which this study does test, the pH will be generally lower than modern-day levels as a result of carbonic acid formation (Walker, 1983).

While it is not the specific intent here to better define the temperature and pH ranges of the ocean at this time, it is hoped that analyzing over a large temperature range, and seeing the effect of different atmospheres on the pH of the ocean, a more well-defined picture of these parameters will emerge.

2.3 Crust Composition

The modern oceanic crust is mafic in composition. That is, it is richer in magnesium and iron than other types of rock, specifically in the continental crust. The oceanic crust during the time of the Archean would have been similar in chemical makeup. Hazen et al. (2008) explains that the earliest rocks would have been mafic to ultramafic, and would be mostly composed of basalts. At this time, continental crust was also forming (Hawkesworth et al., 2010). However, in order to simplify this model, the more prevalent mafic oceanic crust was used.

In order to simulate this mafic rock complex, this study uses elemental percent values from Faure (1991) for an average basaltic rock. These values are an average of two other studies done by Turekian and Wedepohl (1961) and Vinogradov (1962).

2.4 Acidity pH

The pH of a system is the negative logarithm of the activity of the hydrogen ion. The measurement of this activity is valid only at 298 K (Covington, Bates, and Durst, 1985), and at temperatures other than 298 K, the acidity of a system is proportional to
the excess of the hydrogen ion relative to the hydroxide ion. In this study, temperatures range from 0°C to 250°C; therefore, a new term must be defined in order to correctly represent the acidity of the system at any temperature that is being modeled. The term,

$$7 - \left( \frac{1}{2} \right) \log \left( \frac{H^+}{OH^-} \right)$$

is able to correct for the drawbacks of the normal pH equation.

### 2.5 Requirements for Life

Life as we know it on Earth requires certain basic things to survive and thrive. These things include temperature range allowing for organic stability, a specific pH range, and elemental building blocks. These building blocks include things such as: phosphorus and an organic carbon source. These fundamental items were also key for the emergence of life billions of years ago (Orgel, 1998).

Life can thrive under a variety of temperatures, with hyperthermophiles surviving to temperatures up to 121°C (Stetter, 1999; Kashefi and Lovley, 2003). Other extreme organisms (cryophiles) are able to thrive in temperatures that are usually too cold for most life. Junge, Eicken, and Deming (2003) isolated organisms from Arctic ice cores that actively respired at temperatures from -2°C to -20°C. These temperature extremophiles may place upper and lower bounds for the development of life, though most life prefers a much more constrained and mild temperature range.

Organisms usually prefer a more neutral pH environment, but there are also extreme lifeforms that can survive in extremely basic or acidic conditions. The lowest pHs are recorded in acid mine drainage where organisms can survive at a pH of 1 or less (Robbins et al., 2000; Edwards et al., 2000). Life has also been found in waters
with a pH ranging from 9.5 to 9.7, with growth still occurring at pHs slightly above 10 (Zhilina et al., 1997). As with temperature, life does not usually prefer these extreme environments, and it’s unlikely life might have originated under these conditions.

A very important element used by life in many aspects is phosphorus. Phosphorus is used for phospholipids in cell membranes, the energy-giving molecule ATP, and is the backbone element in the extremely important DNA molecule. The process of getting phosphorus within these molecules through a process that is not a biological one is difficult, though, mainly because the primary inorganic phosphate compound, apatite (Ca$_5$(PO$_4$)$_3$(Cl,F,OH)), is not very soluble in water (Pasek, 2008). Pasek (2008) shows that a likely source of reduced phosphite, which is much more reactive and soluble than apatite, on the early earth may have been derived from extraterrestrial origins. The compound schreibersite, an iron-nickel meteoritic phosphide mineral may have been the mechanism by which this phosphorus made it to the early earth. Pasek et al. (2013) showed that schreibersite reacts in water to form the reduced form of phosphorus, and also reacts with glycerol to form a compound for cell membranes.

Finally, life as we know it does not function or exist without organic carbon. Organic carbon, with methane as the simplest molecule, was likely required for the origin of life. However, before the emergence of life, organic carbon had to be produced by nonbiotic processes, and subsequently, it had to be incorporated in the biomolecules we see today. Because of the reducing environment on the early earth, methane was most likely the source of organic carbon at the time that life emerged.
Today, abiogenic methane is formed mainly by two different processes: serpentinization of mid-ocean ridges, and volcanic activity. Kasting and Catling (2003) estimated the global methane production from mid-ocean ridges by multiplying methane production at the Lost City hydrothermal field by the total water flow off ridges, and determined it would create a methane concentration of 0.5 ppm in a reducing, early earth ocean. Emmanuel and Ague (2007) confirmed this amount by calculating the total amount of ocean ridge exposed for this process to take place, and warned that the Kasting and Catling method might be a slight overestimate due to methanogenic organisms near the vents.

Methane from the outgassing of volcanoes is also a significant source of methane today. Estimates of global methane production from this process vary from 0.78 to 6.23 Mt/yr (Cadle, 1980; Lacroix, 1993). Emmanuel and Ague (2007) applied a mathematical method to estimate the total production of methane, in which, they multiply the methane outgassing rate by the CO$_2$/CH$_4$ ratio for volcanoes. This produces a total of 0.093 Mt/yr by volcanic outgassing. An estimated total for abiogenic methane production yields a value of 4 ppmv in a reducing atmosphere (Emmanuel and Ague, 2007). This value seems relatively small, especially to the amount of methane produced by biological means today. However, methane could still have been an important source of organic carbon during this period, and for the emergence of life on the earth.

Life certainly requires more than what has just been listed in this section. Specifically, organic molecules are made up of more than just carbon and phosphorus.
Nitrogen, oxygen, sulfur, and hydrogen are also important to life in many different ways, but these elements fall out of the purview of this thesis.
3. Methods

This section will discuss the input parameters of the model, and how they were used by the software. These input parameters determine the compositional changes of the system once equilibrium is reached, which then predicts the final chemical makeup of an environment.

3.1 Normalization

The earth’s atmosphere and oceans hold an immense amount of material. The mass of the atmosphere is about $5 \times 10^{18}$ kg of total gas, and the oceans have a combined mass of about $1 \times 10^{21}$ kg (Trenberth and Guillemot, 1994). The modeling software used has a difficult time with these huge numbers, and they usually can affect the calculation stability. Because of this, a normalization method was used in order to reduce the size of the numbers, while still keeping the proportions of all the gases, oxides, and water content the same.

The first step was to normalize the composition of the model being investigated. A value of $10^6$ moles of water was chosen to represent the $10^{21}$ kg of ocean water. After the normalization factor was found for the ocean, the basalt rock values (in weight percent) of each element were made into oxides, so that they could be included into the modeling software. The total atmospheric mass was also normalized using this value. The modeling software does not take into account the units being used. As long as the
user has the units in mind, and stays consistent throughout the modeling process, the software will output values in the chosen units.

### 3.2 Modeling

The program HSC Chemistry (v. 7.0, Outotec Oy) was used for all modeling analyses. Specifically, the equilibrium compositions module was used to compute the concentrations of the given chemical species. This module uses the GIBBS energy solver (White et al., 1958) in order to calculate the most thermodynamically stable states at the temperatures, pressures, and allowed species involved in the model.

The user inputs a variety of information (temperature range, pressure of the gases, raw ingredients (moles of elements), and important chemical species) into the program interface before it begins its simulation. For these simulations, the temperature was set to range from 0°C to 250 °C. Pressure was kept constant (isobaric) for each simulation, and was changed during subsequent runs by adding more moles of gases to the system. Raw, elemental ingredients were added to the system as atmospheric gases or oxides contained in the simulated rock layer (e.g. MgO). The rock layer is able to interact with the water in the simulated environment to produce dissolved constituents in solution and new minerals. Specific aqueous species and minerals can then be investigated to determine their concentration and abundance as a function of temperature. A list of all the gases and oxides used, as well as species included in the model, is presented as Table 3.1. This method was previously used successfully to find vaporization temperatures of materials in fulgurites (Pasek et al., 2012), model the
acidification of the moon Europa’s ocean (Pasek and Greenberg, 2012), as well as model the precipitation chemistry of phosphate minerals (Gull and Pasek, 2013).

3.3 Modern-day ocean run

The modern ocean composition was analyzed and put into the program as a test case to make sure the allowable species, thermodynamic data, and atmospheric reactivity were valid. This was to test the accuracy of the method to known parameters, such as the dissolved major ions in the ocean today, and the ocean’s pH. This run, along with every other run, used a normalized one million liters of water to simulate the ocean. Along with the water, raw ingredients, including atmospheric gases and oxides, were also normalized to this value. A list of all the species, oxides, and gases used in this run can be found on Table 3.1.

3.4 Altering the atmosphere

After the validity of the input parameters to the program were established, atmospheric gases and partial pressures were altered in order to simulate different conditions that could have been on the early Archean earth. Four different atmospheres were tested using the program. The early earth may have had a reducing atmosphere (Pavlov and Kasting, 2002), so in these simulations, molecular oxygen gas (O₂) was removed, and replaced with a CO₂, a CO₂ and H₂ mixture, CH₄, or a CH₄ and CO₂ mixture atmosphere. Each of these mixtures was input at a 1:1 mole ratio to the oxygen that was removed, and tested at what the partial pressures of these gases would be at one, two, three, and ten bars of atmosphere. The decision on the upward bound of the
pressure was made based on the study proposed by Walker (1985). However, it is more likely that the density was no more than twice the levels that it is today (Som et al., 2012). Therefore, a range of pressures was analyzed to elucidate all scenarios.

As previously mentioned, this study was specifically looking for the activity of certain ions dissolved in the water at each pressure of the different gases. The Fe$^{2+}$ ion, as well as H$_2$PO$_4^-$, HPO$_4^{2-}$, and PO$_4^{3-}$ ions, were investigated as a function of temperature and atmospheric composition to see changes in concentrations. The phosphate ions were summed to determine the overall phosphorus abundance. In addition to the ions, the pH was also analyzed at the 0°C to 250 °C temperature range. A list of the gases, oxides, dissolved ions, minerals, and salts used in all of these analyses can be found on Table 3.1. Table 3.2 shows the percentages of all the atmospheric gases used in the models for each type of atmosphere, and each pressure analyzed.
Table 3.1: List of Compounds

<table>
<thead>
<tr>
<th>Gases</th>
<th>CO₂, N₂, Cl₂, CH₄, NH₃, O₂, H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides</td>
<td>FeO, Fe₂O₃, SiO₂, Al₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅</td>
</tr>
<tr>
<td>Aqueous Species</td>
<td>H₂O, CH₄, CO, CO₂, CO₃²⁻, Fe³⁺, Fe²⁺, FeCO₃, Fe₂(CO₃)₃, FeO, FeO⁺, FeO⁻, Fe(OH)₂, Fe(OH)₃, Fe(OH)²⁺, FeOH⁺, Fe(OH)₂⁺, Fe(OH)⁻, Fe(OH)₃⁻, Fe(OH)₄⁻, FeSO₄⁺, H₂, H⁺, Al³⁺, H₂CO₃, HCO₃⁻, HFeO₂, HFeO₂⁻, H₂O₂, HO₂, H₂S, HS⁻, HS₂⁻, H₂SO₃, H₄SiO₄, HSO₃⁻, HSO₄⁻, HSO₅⁻, O₂, O₃, Mg²⁺, Na⁺, Cl⁻, K⁺, Ca²⁺, O⁻, O₂⁻, O₂²⁻, OH, OH⁻, S²⁻, S₂⁻, SO₂⁻, SO₃⁻, SO₄²⁻, SO₄³⁻</td>
</tr>
<tr>
<td>Minerals</td>
<td>Fe₀.₉₄₅O, Fe₀.₉₄₇O, Fe₃O₄, Fe(OH)₂, Fe(OH)₃, Fe₂O₃·H₂O, Fe₂O₃·3H₂O, FeSO₄, Fe₂SO₄·H₂O, FeSO₄·4H₂O, FeSO₄·7H₂O, H₂SO₄, Fe₀.₈₇₇S, FeS, FeS₂, Fe, S, MgSiO₃, FeSiO₃, CaMgSi₂O₆, MgCO₃, FeCO₃, CaCO₃, NaAlSi₃O₈, KAlSi₃O₈, CaAl₂Si₂O₆, Al₂Si₂O₅(OH)₄, Al₂SiO₅, CaSO₄·2H₂O, MgSO₄·7H₂O, MgSO₄·6H₂O, MgSO₄·5H₂O, MgSO₄·4H₂O, MgSO₄·2H₂O, MgSO₄·H₂O, MgSO₄, Mg₃Si₄O₁₀(OH)₂, Mg₇H₂Si₆O₁₈, Mg₃H₄SiO₉, Na₉₉Al₉₉Si₂₀₄O₁₂·H₂O, Mg₃Al₂Si₂O₁₀(OH)₈, Mg₄Si₇O₂₁H₁₂, Mg₃Si₂O₅(OH)₄, NaAl₂(AlSi₃O₁₀)(OH)₂, Ca₂FeAl₂Si₃O₁₂·OH, Ca₂Mg₃Si₅O₁₉H, CaAl₂Si₃O₁₀(OH)₂, Mg(OH)₂, Mg₃Al₂Si₃O₁₂, Fe₃Al₂Si₃O₁₂, Ca₃Al₂Si₃O₁₂</td>
</tr>
<tr>
<td>Salts</td>
<td>MgCl₂, KCl, NaCl, CaCl₂, FeCl₂</td>
</tr>
</tbody>
</table>
### Table 3.2: Atmospheric Compositions*

<table>
<thead>
<tr>
<th></th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 bar</td>
<td>2 bars</td>
<td>3 bars</td>
<td>10 bars</td>
<td>1 bar</td>
</tr>
<tr>
<td><strong>O_2</strong></td>
<td>22.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>CO_2</strong></td>
<td>0.06</td>
<td>0.06</td>
<td>0.03</td>
<td>0.02</td>
<td>negl</td>
</tr>
<tr>
<td><strong>N_2</strong></td>
<td>77.3</td>
<td>77.3</td>
<td>36.3</td>
<td>22.2</td>
<td>6.40</td>
</tr>
<tr>
<td><strong>H_2</strong></td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>CH_4</strong></td>
<td>negl</td>
<td>22.6</td>
<td>63.7</td>
<td>77.8</td>
<td>93.6</td>
</tr>
<tr>
<td><strong>NH_3</strong></td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>Cl_2</strong></td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

* : all values in percent of total mixture  
negl: a negligible amount of gas in the mixture  
R1: modern-day model  
R2: CH_4-dominated model  
R3: CO_2/CH_4 mixture model  
R4: CO_2-dominated model  
R5: CO_2/H_2 mixture model
4. Results

The figures shown in this section are representations of ferrous iron concentrations, pH, and phosphate species concentrations for each category of atmosphere modeled. The phosphate figures show a combined concentration of PO$_4^{3-}$, HPO$_4^{2-}$, and H$_2$PO$_4^-$ species.

Some data points were removed from the graphed curves because they were determined to be artifacts of the modeling process. These artifacts occur when the equilibrium module, which is dependent on energy flow, determines that a new phase is stable for a particular temperature. This creates a change in composition. If the module does not make this same calculation for the subsequent temperatures, there can be large fluctuations and step features shown on the curve (Pasek et al., 2005).
Figure 4.1: Modern-day ocean data. A) Cl⁻, Na⁺, Mg²⁺, Ca²⁺, and K⁺ ion concentrations molarity vs. temperature (°C). B) pH vs. Temperature (°C).
Figure 4.2: CH$_4$-dominated atmosphere pH data. A) pH vs. Temperature (°C) at 1 bar CH$_4$ B) pH vs. Temperature (°C) at 2 bars CH$_4$ C) pH vs. Temperature (°C) at 3 bars CH$_4$ D) pH vs. Temperature (°C) at 10 bars CH$_4$
Figure 4.3: CH$_4$-dominated atmosphere Fe$^{2+}$ data. A) Molarity vs. Temperature at 1 bar CH$_4$ B) Molarity vs. Temperature (°C) at 2 bars CH$_4$ C) Molarity vs. Temperature (°C) at 3 bars CH$_4$ D) Molarity vs. Temperature (°C) at 10 bars CH$_4$
Figure 4.4: CO$_2$/CH$_4$ atmosphere mixture pH data. A) pH vs. Temperature (°C) at 1 bar mixture B) pH vs. Temperature (°C) at 2 bars mixture C) pH vs. Temperature (°C) at 3 bars mixture D) pH vs. Temperature (°C) at 10 bars mixture
Figure 4.5: CO$_2$/CH$_4$ atmosphere mixture Fe$^{(2+)}$ data. A) Molarity vs. Temperature (°C) at 1 bar mixture B) Molarity vs. Temperature (°C) at 2 bars mixture C) Molarity vs. Temperature (°C) at 3 bars mixture D) Molarity vs. Temperature (°C) at 10 bars mixture
Figure 4.6: CO₂-dominated atmosphere pH data. A) pH vs. Temperature (°C) at 1 bar CO₂ B) pH vs. Temperature (°C) at 2 bars CO₂ C) pH vs. Temperature (°C) at 3 bars CO₂ D) pH vs. Temperature (°C) at 10 bars CO₂
Figure 4.7: CO$_2$-dominated atmosphere Fe$^{(2+)}$ data. A) Molarity vs. Temperature (°C) at 1 bar CO$_2$ B) Molarity vs. Temperature (°C) at 2 bars CO$_2$ C) Molarity vs. Temperature (°C) at 3 bars CO$_2$ D) Molarity vs. Temperature (°C) at 10 bars CO$_2$
Figure 4.8: CO$_2$/H$_2$ atmosphere mixture pH data. A) pH vs. Temperature (°C) at 1 bar mixture B) pH vs. Temperature (°C) at 2 bars mixture C) pH vs. Temperature (°C) at 3 bars mixture D) pH vs. Temperature (°C) at 10 bars mixture
Figure 4.9: CO$_2$/H$_2$ atmosphere mixture Fe$^{(2+)}$ data. A) Molarity vs. Temperature (°C) at 1 bar mixture B) Molarity vs. Temperature (°C) at 2 bars mixture C) Molarity vs. Temperature (°C) at 3 bars mixture D) Molarity vs. Temperature (°C) at 10 bars mixture
Figure 4.10: Summed $\text{PO}_4^{3-}$, $\text{HPO}_4^{2-}$, $\text{H}_2\text{PO}_4^{-}$ data. A) Molarity vs. Temperature ($^\circ$C) in CH$_4$ atmosphere B) Molarity vs. Temperature ($^\circ$C) in CO$_2$/CH$_4$ mixture C) Molarity vs. Temperature ($^\circ$C) in CO$_2$ atmosphere D) Molarity vs. Temperature ($^\circ$C) in CO$_2$/H$_2$ mixture
5. Discussion

5.1 Implications of a CH$_4$-dominated atmosphere

A CH$_4$-dominated atmosphere exhibits a more basic pH than its CO$_2$ atmosphere counterpart, and allows for a much lower total molarity of the ferrous iron ion. Part of this may be due to methane’s low solubility and reactivity in water. At all modeled methane pressures, pH remains relatively unchanged. At ambient temperatures, pH is around 9.5, and goes to 6.0 at a high temperature. Similarly, the ferrous iron ion changes very little under a methane atmosphere at varying pressures.

Although methane is not a likely significant gas in the early earth atmosphere based on the pH and Fe$^{2+}$ ion data presented here, it could still be an extremely important gas for the production of early biomolecules during this time period. Tian et al. (2011) found that hydrogen cyanide (HCN), an important prebiotic molecule for the early earth, is more readily formed in a methane-rich atmosphere. However, the methane concentration modeled in that study is much lower than what was used in this study. Glycoaldehyde, another important precursor molecule for sugars, is also produced more readily under atmospheric methane concentrations lower than what was used in this study (Harman et al., 2013). Based on the results of this study, methane does not seem a viable gas for the production of the Fe$^{2+}$ ion, but could alternatively have been an important molecule for early carbon-based biomolecules.
5.2 Implications of a CO$_2$-dominated atmosphere

The important results shown from the CO$_2$-dominated atmosphere are two-fold. First, this atmosphere generates the largest amount of ferrous iron ion leached from the rock of all the atmospheric conditions modeled. At one bar, the molarity of Fe$^{2+}$ is an order of magnitude higher at more ambient temperatures than it is in a CH$_4$-dominated atmosphere. However, at two bars of pressure and above, the Fe$^{2+}$ concentration is not much different than the concentrations from the other atmospheric mixtures. This might suggest some limiting reagent mechanism, such as the amount of iron supplied by the reacting rock, is taking place here, independent of atmospheric pressure.

Cleaves et al. (2008) tested organic compound synthesis in a neutral CO$_2$ atmosphere. Their results indicate that, when adding ferrous iron into the reaction, organic molecule production increased. Based on the results of this study, it seems likely that Fe$^{2+}$ concentrations may have been high enough in a CO$_2$ atmosphere to facilitate the synthesis of biomolecules that were important to the emergence of life on the early earth. In addition, these results bode well for the studies on RNA folding, catalysis, and electron transfer (Athavale et al., 2012; Hsiao et al., 2013).

The other important result from the CO$_2$-dominated atmosphere is the relatively lower pH that is generated. This is likely the result of the reaction of CO$_2$ in the water, which creates carbonic acid, and thus lowers the pH of the system. At higher pressures of CO$_2$, the pH tends to be even more acidic at ambient temperatures. A lower pH might have been an important factor on the early earth. Many studies have shown that organic molecules have been formed more readily under lower pH conditions (Choughuley et al., 1977; Borquez et al., 2005). Based on the results of a CO$_2$
atmosphere in this study, and the suggested importance of low pH, a relatively high molarity of dissolved ferrous iron, and the role CO₂ might have played to keep the early earth warm enough for life to emerge, it is quite possible that CO₂ played a vital role on the Archean earth.

5.3 Implications of an atmospheric mixture of gases

The two mixtures modeled in this study were CO₂/CH₄ and an atmosphere consisting of H₂ at 70% CO₂ to 30% of the accessory gas. Not surprisingly, both mixtures of gases exhibit a very similar pH at all pressures, except for a slightly more basic pH from the CO₂/H₂ mixture at one bar and lower temperatures. This is most likely caused because of the identical partial pressures of methane and H₂ gases, which are both very reducing. Because of the dominance of the CO₂ partial pressures of both mixtures, the Fe²⁺ molarity of both is almost identical to that of the CO₂ atmosphere’s ferrous iron molarity.

Despite these mixtures looking mostly like the results from the CO₂-dominated atmosphere, they do present some interesting scenarios. In particular, the CO₂/CH₄ atmosphere seems to not only allow for a decent molarity of the Fe²⁺ ion, but also allows for a lower pH for prebiotic reactions to take place. On top of this, the concentration of methane would be high enough so that it could be used for the production of carbon-based biomolecules.
5.4 Implications of phosphate concentrations

Phosphate concentrations in all the modeled atmospheres tend to be extremely low, even with all phosphate species being summed together to generate the molarities. The CO$_2$ atmosphere, as well as the mixtures have phosphate molarities that fall between $10^{-9}$M and $10^{-8}$M near ambient temperatures. The CH$_4$-dominated atmosphere exhibits an even lower molarity closer to $10^{-11}$M. These values seem to be far too low for such a widely-used biological element as phosphorus. Powner et al. (2009) showed that phosphate could have been a useful pH buffer and a catalyst in prebiotic reactions. However, the molarity of 1.0M used to test these reactions may be too large, and does not seem likely from a simple water/rock reaction mechanism. Nonetheless, phosphorus was likely prevalent on the early earth in order for it to be used in so many different biomolecules. As a viable terrestrial source of phosphorus does not seem very plausible, it could have its origins in an extraterrestrial source, such as the mineral schreibersite found in meteorites as suggested by Pasek (2008).

5.5 Future Work

Based on the results presented in this thesis, it seems that a carbon dioxide-dominated atmosphere allows for more readily generated Fe$^{2+}$, which may have been an important catalyst for RNA on the early earth. CO$_2$ also allows for a more acidic pH, which most likely facilitated the production of biomolecules at that time. While methane did not allow for good production of Fe$^{2+}$, and also created a more basic system, it still may have been very important as a source of organic carbon at the time.
Future studies could reduce the concentration of the methane gas in the CO₂ mixture to levels shown in Harman et al. (2013) and Tian et al. (2011), in order to see if the ferrous iron ion is still produced at useable levels. Future scenarios could also be modeled where the pressure of the atmospheric gas is on one axis on the graph, and concentrations of important molecules or elements are on the other. In this situation, one would have to choose an average temperature that would stay constant while the pressure changes. This is different than this study, where pressure was kept constant, and temperature changed on the x-axis. The difficulty would be choosing a temperature that would represent the temperature of ocean water during the Archean. However, as was done in this study with pressure, a variety of temperatures can be chosen and modeled separately. This method would be able to look at more subtle changes in concentrations that are sensitive to pressure changes.
6. References


Harman, C.E. et al., 2013, Atmospheric production of glycolaldehyde under hazy prebiotic conditions: Orig Life Evol Biosph, v. 43, p. 77-98.


