Study of Carbon Dioxide Hydrolysis and Diffusion in Four Different Aqueous Environments

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Abstract

This paper examines the diffusion of CO_2 into water in four different environments: still/stirred freshwater and still/stirred seawater. The drawdown and invasion rates determined for stirred seawater facilitate the most rapid diffusion, with an average of 0.03950 moles/ m^{2*}yrs*µatms. Experimental errors due to leaks within the pressure cell yield incorrect equilibrium concentrations and partial pressures.

1. Introduction

Carbon dioxide in the atmosphere was a widely unrecognized danger for most of human history. The majority of anthropogenic atmospheric CO_2 has been released beginning with the industrial revolution, though some speculate that it began earlier with beavers and marshes in the middle ages. Since 1958 atmospheric CO_2 concentrations have been measured at Mauna Loa, HI, and there has been a relatively steady increase since that time of about 1.4 ppm/yr (Keeling 2005). However, this rate of increase is half as slow as is expected based on our rate of input. If this is the case, where is the CO_2 going?

The answer we are interested in is the oceans. Earths oceans are a major sink for CO_2 and have been absorbing carbon dioxide almost 25% as fast as we are putting it into the atmosphere (Broecker 1998). The sink for the rest of the CO_2 is debatable, but likely the terrestrial biosphere. However, that is a topic for a different paper.

The chemical reaction of CO_2 and water acidifies the water and could cause a myriad of effects within the marine biosphere and other inorganic chemical processes of the ocean. If we consider our dependence on the ocean for primary production of oxygen, not to mention sustenance and recreation, it behooves us to understand this process and its effects as best we can in order to prepare ourselves for what might come in the future. Our experiment is a step in that direction, to understand the drawdown of carbon dioxide into water. We will look at mechanisms, rates, influencing factors and finally modeling.

2. Background

2.1 Chemical and Physical Principles

2.1.1 Fick's Law of Diffusion

Chemical diffusion through water is determined as a stepwise function by Fick's law.

$$F = k(\Delta c)/\Delta d \qquad (1)$$

In this case F is the flux measured in particles per time per area. We used (moles/cm^2*s) for our calculations. "k" is the diffusivity measured in (cm^2/s), and is dependant on temperature. "c" is the concentration of CO_2 measured in (moles/liter) and "d" is the distance between the middle of the two layers being compared. This is usually in relation to some time interval, but that part is not expressed in this calculation. For CO_2 at 25°C, $k = 1.91*10^{-5}$ cm^2/s.

2.1.2 Mass-Transport

The degree of mass-transport into an aqueous layer caused by chemical processes can be quantified by a gas's unique chemical enhancement factor α:

$$1/K_l = 1/\alpha k_l + RT/Hk_g \qquad (2)$$

Where K_l is the gas-transfer coefficient for CO_2, and k1, k2 refer to the molecular diffusion constants of the given liquid and gas films. H is the inverse of Henry's law constant (K_h) for CO_2 (Brezonick 1994). As α becomes larger, k_1, the term that defines the amount of resistance caused by the liquid film becomes smaller. Therefore if a gas is too reactive (large α), diffusion through the liquid film is so fast that virtually no dissociation can occur. If a gas is very slow to react, it will have a small α and thus a larger concentration of gas is needed for effective diffusion to occur (Brezonik 1994). CO_2 has an α value just large enough for effective diffusion to occur and small enough that it dissociates readily in the liquid film of the water.

This characteristic in conjunction with CO_2's high solubility in water and the necessity of dissociated ions in many inorganic processes stress the importance of studying how CO_2 dissociates as a part of kinetic diffusive transport.

2.1.3 Solubility

The solubility of a gas in a liquid is most heavily influenced by the temperature and pressure of the system, and the possible polarities of the respective solute/solvents. Gases are most soluble under conditions of high pressure and low temperature. Our consideration will involve all substances interacting at room temperature and atmospheric pressure.

2.2 Carbon Dioxide

2.2.1 Molecular Structure and Natural Occurrences

Carbon dioxide is a non-polar, covalently bonded molecule that exists in the gas phase within Earths atmosphere. It accounts for roughly 0.0335% of atmospheric constituents and its absorption spectrum is heavily populated by wavelengths in the infrared spectrum. Its relative abundance and susceptibility to "heat dependent" wavelengths cast it in heavy spotlight in the consideration and analysis of greenhouse gases.

2.2.2 Reaction/Disassociation with H_2O

The reaction of CO_2 with water can be defined by the following equilibrium expression:

$$H_2O + CO_{2\,(aq)} \rightleftarrows H_2CO_{3\,(aq)} \tag{3}$$

In this expression, the equilibrium lies far to the left (Stumm et. al 1981, 179). However, H_2CO_3 is rarely reflected as its true concentration and is usually shown as a composite of aqueous CO_2 and true H_2CO_3:

$$[H_2CO_3{}^*] = [CO_{2\,(aq)}] + [H_2CO_3] \tag{4}$$

We can also assume under ideal laws that

$$[CO_{2\,(aq)}] = [H_2CO_3{}^*] \tag{5}$$

For this experiment, we need to obtain a value of virtual P_{CO2} (water) in order to make necessary calculations. This is defined as the P_{CO2} (air) of an imaginary bubble within the water column which is at equilibrium with its surroundings. It can be derived from the distribution mass law constant:

$$K_D = [CO_{2(aq)}]/[CO_{2(g)}] \tag{6}$$

Where

$$[CO_{2(g)}] = P_{CO2} / RT \tag{7}$$

Combining these equations and using eq.5, we get:

$$[CO_{2(aq)}] = (K_D/RT)\, P_{CO2} = K_H P_{CO2} \tag{8}$$

This equilibrium equation is needed to determine the equilibrium concentrations, $[CO_{2(aq)}]$, in the water that are a part of diffusion rate calculations.

For the diffusion into seawater, this dissociation is important in calculating virtual P_{CO2} (water):

$$H_2CO_3^* \rightleftarrows H^+ + HCO_3^- \qquad (9)$$

This equilibrium lies far to the right in seawater, therefore concentrations of HCO_3^- are important in diffusion calculations (Pytkowitz 1983, 8). The equilibrium equation for this reaction is:

$$K_1 = [H^+][HCO_3^-] / [H_2CO_3] \qquad (10)$$

2.2.3 Driving Force & Invasion Coefficient

Ultimately, the calculations of P_{CO2} will lead to what is known as the "driving force" of CO_2 diffusion. This driving force is defined by the difference of P_{CO2} in air and the virtual P_{CO2} in water, multiplied by the total area of the diffusive interface. CO_2 will diffuse in water when the P_{CO2} of the air is greater than that of the water. As the reaction continues, the driving force will eventually reach zero as ΔPCO_2 reaches zero, corresponding to equilibrium values for both the concentration and partial pressures of CO_2 in air and water.

The determination of the driving force can then lead to a calculation of the invasion rate at a given point in time for the reaction:

$$I = [\Delta mol] / [\Delta t][surface\ area][\Delta PCO_2] \qquad (11)$$

The Δmol is the total amount of moles exchanged between the water and air. This can be calculated from a simple conversion of the recorded loss of ppm of CO_2 in a certain time step. The invasion rate quantifies diffusion and is an indicator of how fast CO_2 molecules cross the gas-liquid interface. It should be constant as diffusion occurs, and will fluctuate greatly when equilibrium occurs and the ΔPCO_2 nears zero.

In order to further characterize CO_2 diffusion and to isolate determining factors, we will compare diffusive processes in four environments, varying particular chemical and kinetic properties of the liquid solution. Temperature, pressure, alkalinity, pH, and the thickness of the film of the water all affect the rate of diffusion. Alkalinity and the thickness of the film will be our variable parameters, since pH is usually controlled by alkalinity in natural bodies of water, and the effects of temperature and pressure are well understood.

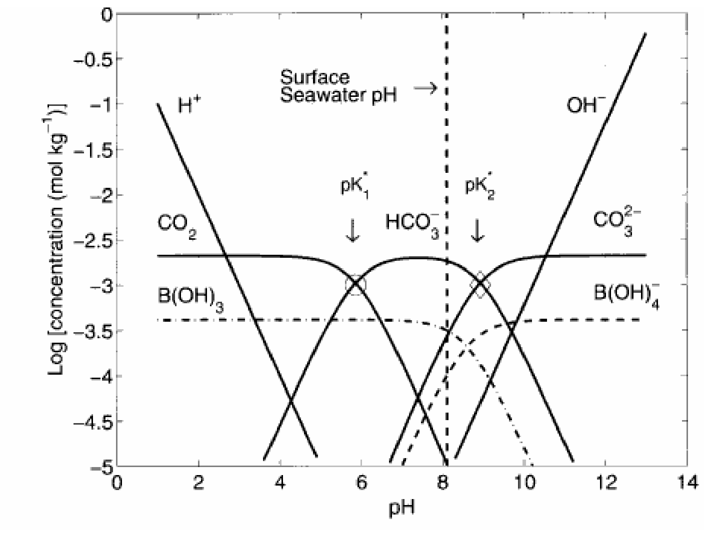
2.2.4 Alkalinity and pH

The rate of diffusion changes in differently alkaline solutions. Alkalinity is defined as a characteristic of aqueous CO_2 that "keeps track of all the charges." Practical alkalinity is defined as:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)^{4-}] + [OH^-] - [H^+] \qquad (12)$$

The total contribution of charges from each ion defines the pH of the solution as seen by the following figure.

Figure 1. Concentration vs. pH (Zeebe 2001)



This figure portrays a logarithmic scale of the concentrations of each ion versus the corresponding pH. Equilibrium rates will differ based on which ions CO_2 dissociates into. Freshwater has a pH of around 6-7 and the principle reaction is the reaction of CO_2 with water to create $CO_{2\,(aq)}$ or $H_2CO_3^*$ (K_h) and its diffusion into the water. Seawater has a pH of about 8.2 and reflects both K_h and the dissociation of $H_2CO_3^*$ into H^+ and HCO_3^-, as well as their respective diffusions into water.

2.2.5 Effects of Film Thickness

The thickness of the surface film also has a significant effect on CO_2 diffusion. Diffusion into the deeper layer is slower than the saturation of the aqueous layer, therefore the rate of diffusion restricts the infiltration of CO_2 into the saturated layer. It is also highly dependent on the thickness of that aqueous layer and the time step involved with that diffusion. A thinner film associated with a smaller time step implies a steeper concentration gradient of P_{CO2} and thus promotes more rapid diffusion. A thicker film with a longer time step establishes a more modest gradient, therefore promoting slower diffusion. Diffusion related to surface layer thickness can be expressed by:

$$K_{tr} = \beta^{-1} S_c^{-n} \tag{13}$$

Where β is a dimensionless constant and S_c is the Schmidt number which denotes the ratio of the viscosity of the liquid and the gas tracer diffusivity of CO_2. "n" is directly related to shape of turbulence decreased toward the interface and ranges from 0.5 for classical surface renewal models (stirring) and 1 for still models (Jahne et al. 1987).

The reduction of film thickness can be produced in several ways. Increasing the temperature, decreasing the pressure, and agitating the solution are all effective techniques in obtaining a thinner surface film. This can be determined by a brief consideration of entropy and the laws of thermodynamics. Our experiment will hold temperature and pressure constant, and for two scenarios will reduce the surface thickness by constantly agitating the liquid solution. This mixing will cause a perpetual replenishment of the deeper layer along with a larger volume of the second layer, the mixed layer, which minimizes the CO_2 concentration, effectively creating a gradient of $CO_{2\,(aq)}$ which is based solely on the solution's depth.

2.3 Historical Models

2.3.1 Oeschger and Siegenthaler Model

While we are attempting to create our own picture of CO_2 infiltration of the oceans it is important to acknowledge the similar precedents. In the mid to late 1970's Hans Oeschger and Uli Siegenthaler were responsible for creating a one dimensional model for CO_2 infiltration of the ocean (Broecker 1998). It was a simple box model with a one box atmosphere and a two box ocean. The two ocean layers were the upper wind mixed layer and the deep, still layer. The deep layer transports CO_2 by eddy diffusion, a macroscopic process used to represent the more complex mechanisms involved with macroscopic diffusion. This is similar to Fick diffusion, except that Fick diffusion is on a more molecular scale.

This is a very simple use for the data we intend to collect in this experiment. Using the invasion and diffusion rates of our experiment it would be possible to attempt a recreation of this model. However, no papers by Oeshger and Siegenthaler regarding CO_2 and the oceans are available to Wesleyan University students and we weren't able to find more specifics of their work.

2.3.2 Radiocarbon

Radiocarbon was also very important to the understanding of CO_2 diffusion into water. The hydrogen bomb tests of the 1950's and 60's released massive amounts of ^{14}C into the atmosphere which combined with oxygen to form $^{14}CO_2$ (Broecker 1998). This is an easily traceable isotope and molecule which is not currently present in vast quantities in our atmosphere.

Any $^{14}CO_2$ released at that time is unique within the time range of anthropogenic CO_2 contribution, and is therefore identifiable as from that specific time period.

We were able to track this molecule through the atmosphere and ocean. We measured its rate of diffusion into both calm and turbulent waters. We even measured its infiltration into waters of the southern hemisphere which showed a delay of about one year, expressing an approximate year-long mixing time between the hemispheres (Broecker 1998). It was also used to determine that depth of mixing increases with the square root of time and to test the accuracy of climate models of the day. Finally, it gave us our first concrete invasion rate of 0.064 moles $CO_2/m^2 * yr * \mu atm$ and 2.4 cm^2/sec for the coefficient in eddy diffusion. There were some drawbacks, however, which included a shorter half life than ^{12}C or ^{13}C which reduces residency or traceability from 30 to 10 years. This means that the models and theories tested with radiocarbon could possibly have mechanisms which change over time, but cannot be recorded by ^{14}C.

3. Hypotheses

3.1 Examine Drawdown Rates

Based on past experiments and an analysis of equilibrium factors, predictions can be made regarding each experimental setup. According to Noyes et al., there should be a linear trend in the graph of $\ln(\Delta PCO_2)$ vs. time in the mixed freshwater experiment according to:

$$\ln(\Delta P_{CO2}) = -k_{exp}t + \text{constant} \qquad (14)$$

This equation represents the log of the change in driving force over time (Noyes et. al 1995). Bowers et al. also used a similar method to check the trend of the data. A mixed freshwater curve of the driving force versus time should show a logarithmic curve (and a linear line in the ln(ΔP_{CO2}) plot) since the rate of transfer will depend on the difference in concentration of CO_2 between air and water. If there is not a linear fit in the logarithmic graph, there is error in the experiment. Therefore in our experiment the first thing we will look for is the linear fit as a means of detecting error.

We also predict that the drawdown rates should be faster in the stirred experiments since the deeper layer is being constantly replenished and because of the thinner surface layer. Although it will be hard to predict the effects of seawater on the drawdown rate, we expect that it will differ from the freshwater drawdown due to its initial carbonate concentrations and more complicated equilibrium processes. The complications of an uneven concentration of the deeper layer in the still water experiments may also contribute to a different drawdown rate. We hope to discover these differences in drawdown rates for the still water and seawater experiments.

3.2 Examine Invasion Rates

According to a 2002 experiment done by Wesleyan students, the invasion rate for the mixed freshwater experiment should approach a constant during the diffusion process until the reaction reaches equilibrium when the invasion rate will become unreliable. The magnitude of the number may have a positive correlation with the rate of the reaction. These experiments also purport to investigate these trends.

3.3 Freshwater Diffusion Modeling

We hope to create a working model of the diffusion of CO_2 with depth for the still and mixed freshwater experiments. This will help to determine the parameters and factors which effect the mechanism of diffusion. These principles could also be used to eventually for a model of seawater as well, but the calculations and set up for that model are not within the scope of this project.

4. Methods

- Our pressure cell is comprised of a cylindrical Plexiglas container with a multivariable intake lid. The seal is created by fastening a rubber ring between two heavy lids by nut and bolt. On the top of the cell, we have a pressure gauge, a thermometer, and valves for circulating air. The CO_2 analyzer is sensitive to water vapor and relies on a constant flux of particles. For this reason, we were forced to include an air pump and a desiccant filter in our circulation pathway from the cell to the detector. The volume of the system therefore consists of both the cell and the volume of the tubes.
- For freshwater experiments, we purified and deionized tap water and ran Argon gas through the solution once sealed in the pressure cell. To ensure minimal initial CO_2 concentrations, we allowed the Argon to bubble for 30 minutes.
- For the seawater experiments, we added aquarium salt[1] until the solution reached a salinity level of 35ppt, then sealed the pressure cell and added additional CO_2. All volumes of solution ranged between 3.5-4.0L.
- CO_2 was inserted into the system through an air valve until a value of 1500-1800ppm was obtained.
- Stirred experiments included a 3” magnetic stir bar, controlled to maintain a visible drawdown cone.

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[1] Aquarium Systems Inc., Instant Ocean®

- Once connected and sealed, we adjusted the recording interval of the CO_2 analyzer and allowed the experiment to progress until the CO_2 drawdown rate diminished significantly.
- Coulometer and alkalinity tests were conducted following the seawater experiments to determine the initial concentrations of ions in solution, and to detect possible complexities arising from boron concentrations.

5.Results

5.1 Drawdown Curves

Figure 2. Drawdown Into Still Freshwater

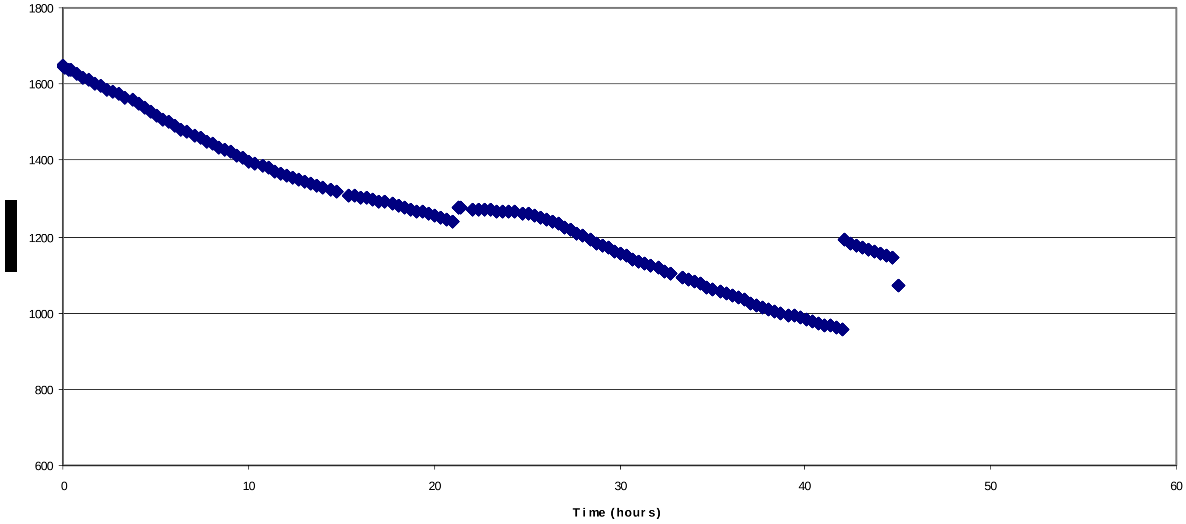


Figure 3. Drawdown Into Stirred Freshwater

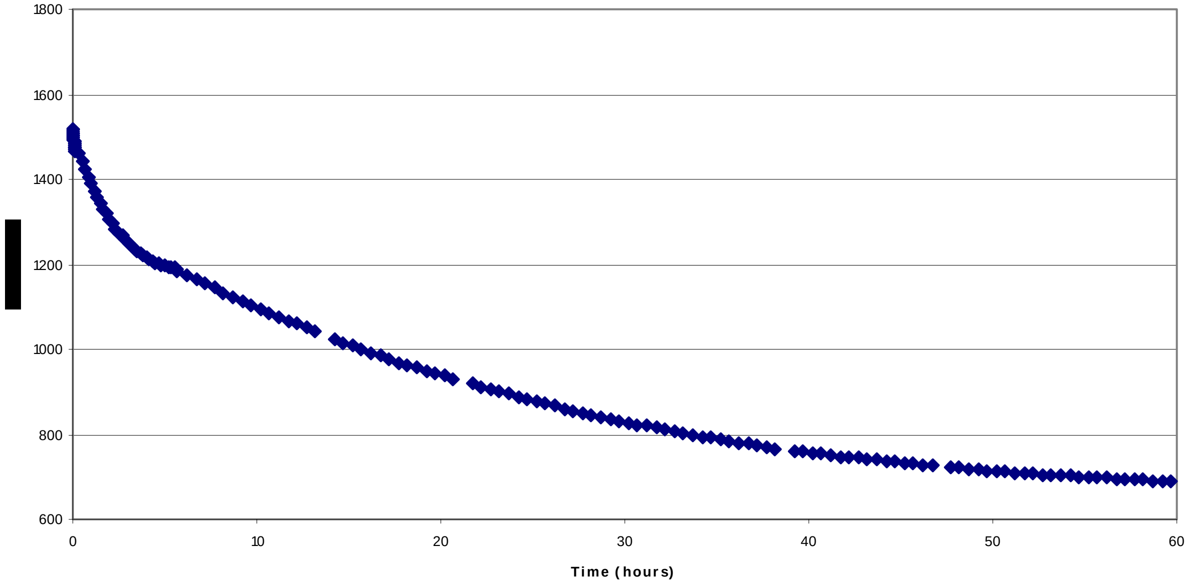


Figure 4. Drawdown Into Still Seawater

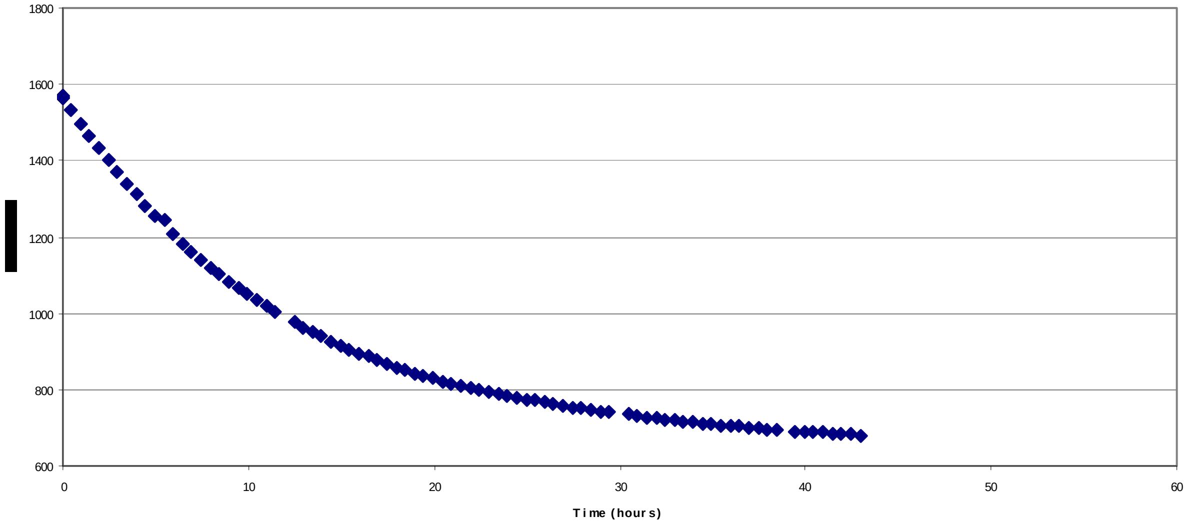
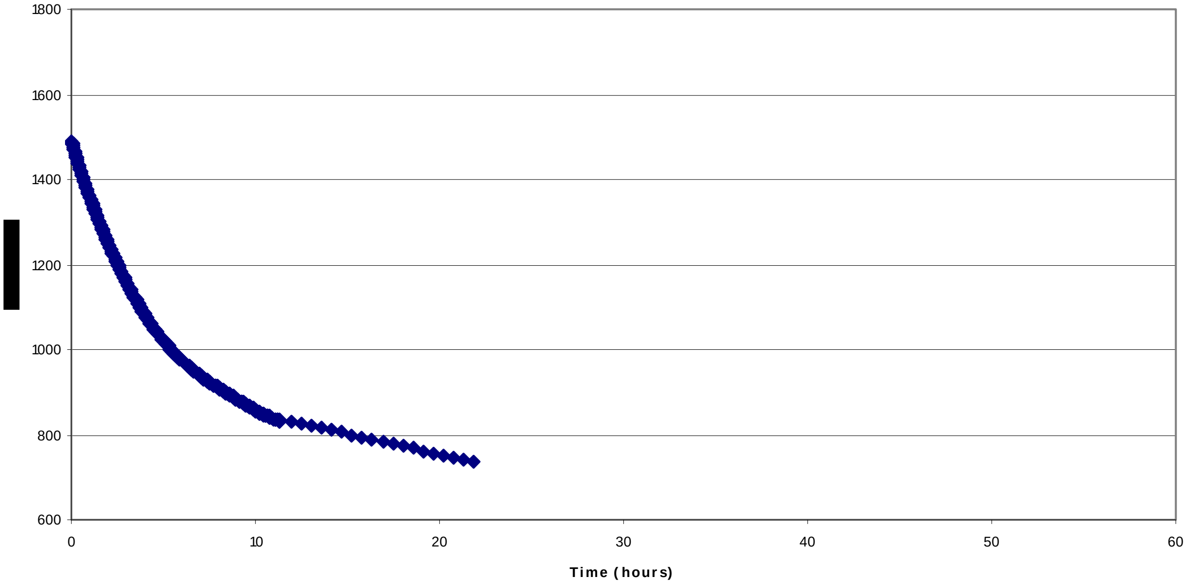
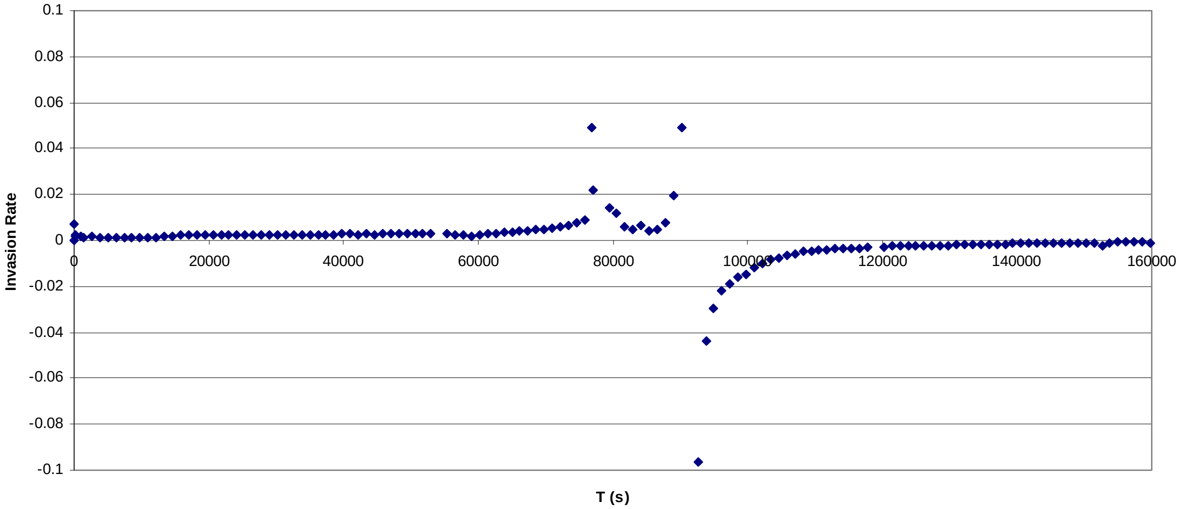


Figure 5. Drawdown Into Stirred Seawater



5.2 Graphs of Invasion Rate v. Time

Figure 6. Invasion Rate for Still Freshwater*



*NOTE: All invasion rates are in the units [mol] / [µatm*yr*m^2]

Figure 7. Invasion Rate for Stirred Freshwater*

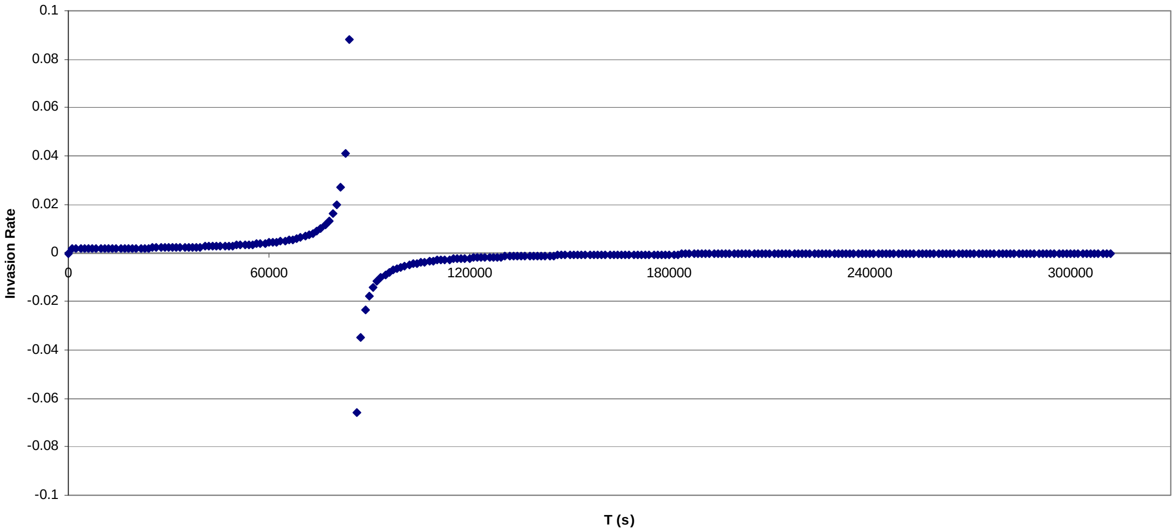
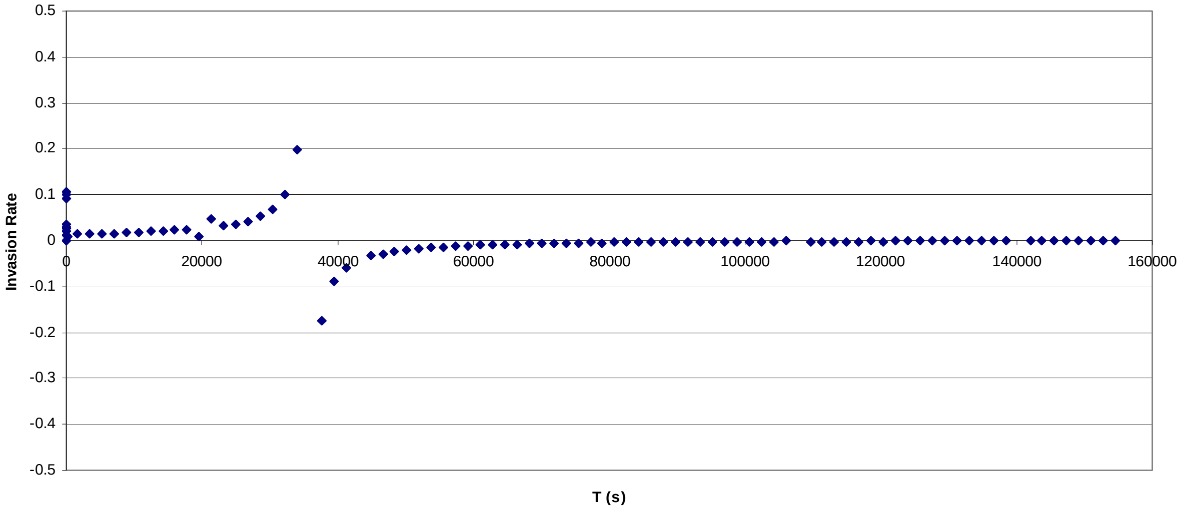
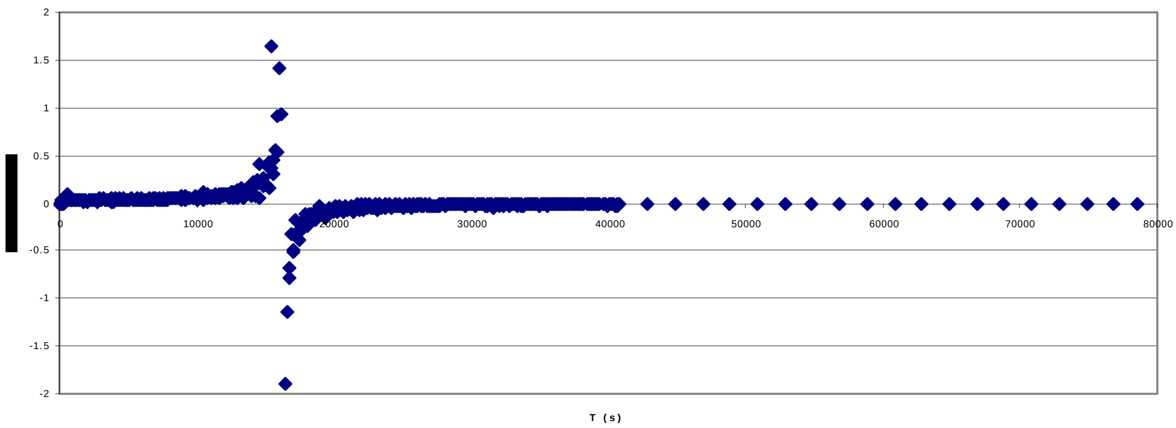


Figure 8. Invasion Rate for Still Seawater*



*NOTE: All invasion rates are in the units [mol] / [μatm*yr*m^2]

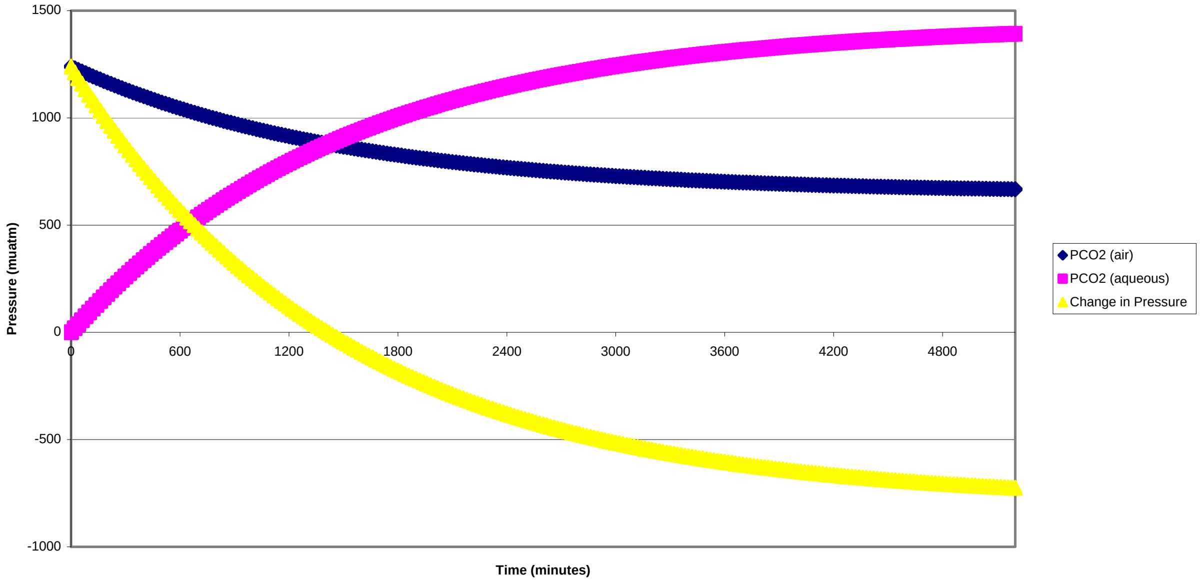
Figure 9. Invasion Rate for Stirred Seawater*



*NOTE: All invasion rates are in the units [mol] / [μatm*yr*m^2]

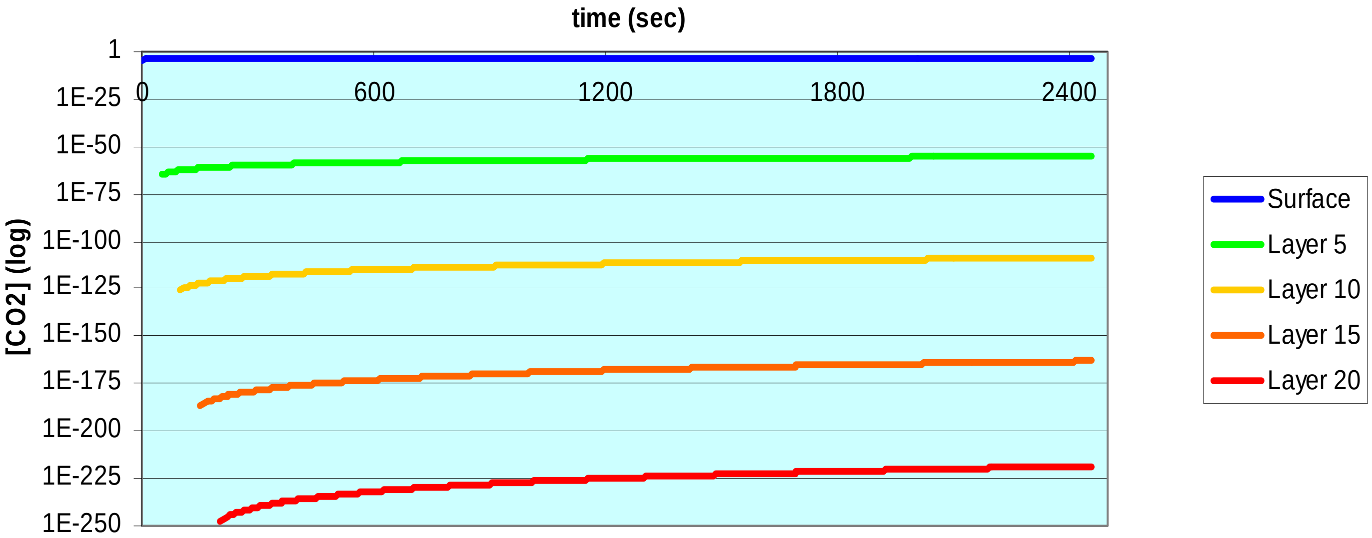
5.3 Graph of Sample Pressures v. Time

Figure 10. Sample Pressure Changes



5.4 Modeling [CO_2] with Depth over Time

Figure 11. Time variance of [CO_2] with Depth for Still Freshwater



5.5 Initial/Final Conditions

Table 1. Initial and Final Conditions

	Initial (ppm)	**Final (ppm)**	**Time Elapsed (hrs)**	**Volume of Liq (L)**	**Volume of Air (L)**
Still Freshwater	1647	956	42	3.71	7.97
Stirred Freshwater	1517	647	87	3.87	7.81
Still Seawater	1567	680	43	3.29	8.39
Stirred Seawater	1490	738	22	3.50	8.18

6. Discussion

6.1 Results/Implications of pH/Coulometer Tests

The results of the coulometer and alkalinity tests found that boron's contribution was negligible. The amount of carbon found in solution by the coulometer was similar to the total concentration of ions found by the alkalinity test. The coulometer found that 3.505 mmol/kg were in solution for about 35 ppt salinity. A pH test also found that the pH was around 8.16.

6.2 Discussion of Drawdown Trends

Empirical results suggest that no experiment produced a pure logarithmic graph of ln(PCO_2), which would be shown by a linear fit to the adjusted data. This is due to the presence of several negative values in P(air)-P(w). The graphs also show that most experiments did not even reach equilibrium in the allotted time they were run.

The stirred freshwater experiment is the most unreliable dataset due to missing data in the first 100 minutes caused by a mechanical failure (See Figure 3). To compensate for this loss, we extrapolated the data in that region in order to fit an exponential curve. This data also reports a total duration of over 60 hours, which we know from observation to be false. Despite these mishaps, we can still conclude that the stirred freshwater had a faster drawdown rate than the still freshwater. The mixed seawater experiment proved to be the fastest to reach a semi-equilibrium state at about 24 hours. It also has the steepest initial drawdown rate of the four situations.

Both still water experiments reached a semi-equilibrium in about 45 hours, though the still seawater was much closer to equilibrium. This may suggest that the still seawater experiment had a faster rate of diffusion than the still freshwater. The different alkalinity and equilibrium concentrations of seawater likely contributed to this difference in reaction rate.

Specifically, the freshwater experiments only dealt with the diffusion rate of [H_2CO3*] in to the deeper layer, while the seawater experiment dealt with both the diffusion rate of [H_2CO_3*] and the diffusion of the dissociated ion [HCO_3^-], which pulled the equilibrium equation to the right, increasing CO_2 drawdown in the surface layer. This could be a reason for the difference between freshwater and seawater reaction rates.

6.2 Discussion of Invasion Rate Trends

According to the invasion rate graphs, the invasion rate for all four experiments is constant for at least the first third of the experiment and then exhibits asymptotic behavior reflecting the changeover of a +ΔPCO_2(air-w) to a –ΔPCO_2(air-w). The shift to a negative change in PCO_2 should have occurred around equilibrium, if at all, because the exchange of CO_2 would have ceased, but because of some experimental error the ΔPCO_2(air-w) changeover was premature (Figure 10). Despite this error, the average value for the invasion rate for the mixed freshwater (before ΔPCO_2(air-w) became negative) was around 0.006038 mols/m^{2*}yrs*µatms and the still freshwater was around 0.0024 mols/m^{2*}yrs*µatms. The 0.006038 value is fairly close to the value found by the 2002 experiment, though off by a factor of 10 from the value found by radio carbon analysis (Keeling 2005). The still freshwater value is also within an order of magnitude of the experimental mixed freshwater value, though somewhat smaller. This confirms our prediction that the magnitude of the invasion rate is proportional to reaction rates.

The invasion rate average values found (before ΔPCO_2(air-w) became negative) for the seawater experiments were 0.03089 mols/m^{2*}yrs*µatms for the still seawater experiment and 0.03950 /m^{2*}yrs*µatms for the mixed seawater experiment. These invasion rates also suggest a relationship to reaction rates since the still seawater seemed to reach equilibrium faster than the still freshwater, and the mixed seawater seemed to diffuse faster than the mixed freshwater from human observation. Both average still water invasion rates are an order of magnitude larger than the average invasion rates for the stirred experiments.

The empirical data and invasion rate graphs, though not completely reliable, seems to suggest that the seawater experiments have faster drawdown rates than the still water experiments, and that the mixed water experiments have faster drawdown rates than the still water experiments. If we extrapolate this trend to a macroscopic model, than we could infer that actual ocean water (resembling the mixed seawater model) sucks in CO_2 at a faster rate than a still fresh water body does, although it is difficult to represent such a large scale scenario from our experimental data. We did not have access to any past experiments that dealt with CO_2 diffusion in seawater, but these results seem to indicate that CO_2 diffusion in the ocean may be faster than previously thought if CO_2 diffusion rates in the ocean were previously assumed to be close to that of mixed freshwater diffusion rates.

6.5 Sources of Error

Error in our data includes the absence of equilibration in multiple experiments, the significant duration of mixed fresh water experiment, the erroneous points in the still freshwater experiment, and the reaction reaching a pressure difference between air and water of 0 before observed equilibrium occurred.

Both the lack of equilibration in many experiments and the reaction reaching a $\Delta PCO_{2\,(air\text{-}water)}$ of 0 before actual equilibrium can be explained by a probable malfunction in the cell's vacuum seal. This leak is most likely caused by an unused intake valve in the lid, which were sealed only with parafilm. If a leak existed, our calculations would need to take in to account the concentration of the CO2 in the room as well. This theoretical increase in atmospheric CO_2 concentration would explain why calculative equilibrium took so long to reach and why the $\Delta PCO_{2\ (air\text{-}water)}$ seemed to change to a negative value.

The longer than expected duration of the mixed freshwater was probably due to technical error, because human observation indicates that the experiment took much less time. The error shown in the empirical data of the still freshwater (Figure 2) was likely caused by the room heating up due to afternoon sun. This temporarily reversed the diffusive interaction because of decreased solubility caused by warmer temperatures.

6.9 Still Freshwater Diffusion Modeling

For the purposes of data modeling we needed a data set that had no errors or deviations. In order to create this kind of data we wrote an equation with many variables in order to make a line best fit to the data we already had. We used this baseline:

$$\text{ppm} = b*(f + e\text{^}(t/\tau)) \qquad (15)$$

where b is the endpoint ppm, f is a constant close to 1 and τ is another constant, referred to as the relaxation time. These three values were manipulated until the artificial data set mimicked the real data. For the still freshwater experiment, the following fit our data set:

$$\text{ppm} = 1{,}200*(0.63 + e\text{^}(t/140{,}000)) \qquad (16)$$

Once the data set was created a one dimensional diffusion model was set up. The surface layer of the water, with depth Δd and a known surface area, was set to reach equilibrium with $PCO_{2\ air}$ as the CO_2 concentration in equation (6). This takes place over a specific time step, Δt. Δd and Δt are variables in our model. The surface concentration of carbon dioxide is always determined solely by $PCO_{2\ air}$ from the artificial data set. It is also the only calculation done for time step 1.

Time step 2 brings in Fick's law of diffusion (1). In the layer just below the surface, layer 1, the concentration is initially 0. Using Δd and the time step 1 concentrations of the surface layer and layer 1 for Δc we can calculate the flux from the surface layer to layer 1 for time step 2.

For the first non surface layer step, this is enough. However, in the next step layer 1 gains CO_2 from the surface layer but loses CO_2 to layer 2. In this case we calculate the flux from the surface to layer 1 using time step 2 values, and multiply by the surface area of the layer and the time step, Δt, to calculate moles added to layer 1 from the surface:

$$\text{moles}_{sl\text{->}l1} = F*SA*\Delta d \qquad (17)$$

Next calculate the flux from layer 1 to layer 2, using zero for the time step 2 concentration of layer 2, and by (#3) calculate the number of moles removed from layer 1 to layer 2. Then multiply the time step 2 concentration by the volume (using the known surface area and Δd converted to liters) to find the number of moles present:

$$\text{moles} = [CO_2]*V \qquad (18)$$

Finally add the present moles to the added moles, subtract the lost moles and divide by the volume to find the time step 3 concentration of CO_2:

$$[CO_2]_{l1,t3} = (\text{moles}_{l1,t2} + \text{moles}_{sl\text{->}l1} - \text{moles}_{l1\text{->}l2})/V \qquad (19)$$

This calculation is repeated for each layer for each time step as far as the excel spreadsheet allows. At this point we must verify that this data is valid. In order to do so we must calculate the ppm CO_2 in the air based on the drawdown mechanism described. If it matches the artificial data it should be a good model of CO_2 drawdown in unmixed fresh water. This is done by the following.

If the previous calculations used the atmospheric ppm as the baseline data, for this calculation we use the surface layer CO_2 concentration. First we calculate the total number of moles of CO_2 in the air of the apparatus by using initial ppm and volume of air. Then calculate the number of moles of CO_2 in the surface layer by concentration multiplied by volume (V = surface area*Δd). Then for time step 2 calculate the number of moles transferred from the surface to layer 1 (#3) and the amount of CO_2 in the surface layer at the end of time step 2 (#4). The final number of moles is equal to the initial number minus the amount removed to layer 1 plus the amount received from the air, so final minus initial plus subtracted equals amount added to the surface layer from the air, or the amount removed from the air:

$$\text{moles}_{air\text{->}sl} = \text{moles}_{sl,t2} - \text{moles}_{sl,t1} + \text{moles}_{sl\text{->}l1} \tag{20}$$

Finally take the initial number of moles of CO_2 in the air, subtract the amount added to the surface layer and divide by the volume of air again and convert that concentration to ppm for the atmospheric CO_2 verification of the model. This is calculated for each time step, and compared to the artificial data.

At this point one must adjust depth of diffusion and the time step of that diffusion until the verification ppm matches the artificial data. Our analysis came up with a time step of 10 seconds and a diffusion depth of 0.017mm. This is a very slow diffusion rate, ending with possibly 0.147m of infiltration within one day, if the concentrations are high enough at that depth to pass more CO_2 to the next layer. As this model was very complex, with a lot of room for error, it would not be out of order to say that this data is very likely skewed or even incorrect. However, a graph of concentration over time of selected layers is displayed in Figure 11.

7. Conclusion

Although the data may not have been very reliable due to experimental error in the setup, we found that both seawater and mixed water have faster drawdown rates and invasion rates than fresh and still water.

In future experiments, the model must be vacuum sealed and completely free of CO_2 before a known amount is injected in to the cell. In this kind of experiment, better conclusions may be made about differences in the rates of seawater and still water. It would also be beneficial to explore the effects of argon bubbling, and a possible comparison to other gases and their ability to remove CO_2 from an aqueous solution. This would give us more confidence in our initial ion concentrations which would give us a more accurate representation of the final equilibrium.

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