THE EFFECTS OF CARBON DIOXIDE ON CORAL REEFS

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ABSTRACT
Corals are important because they are the primary builders of large calcium carbonate structures that make up the reef ecosystem. Recent coral reef degradation is quite possibly caused by climate change. Emission of fossil fuels into the atmosphere increases carbon dioxide (CO₂) concentrations, which can affect coral reefs in two ways. One way is by the greenhouse effect. As temperature increases in the atmosphere, some of the heat is transferred to the surface of the ocean. When sea-surface temperatures become too warm, corals experience bleaching. The second effect is seawater chemistry changes due to absorption of CO₂ in the oceans. As more CO₂ is driven into the oceans, seawater chemistry changes so that less carbonate ion (CO₃²⁻) is available to the coral for calcification (i.e., precipitation of calcium carbonate, (CaCO₃)). As calcification decreases, the coral’s skeleton weakens. In order to examine this effect, we produced an aquarium model to simulate how coral calcification is affected by the increase in atmospheric CO₂, as well as by increases in sea-surface temperature. This model has helped us determine how corals may be affected in the future if CO₂ levels and temperature continue to rise.

INTRODUCTION
Coral is important because it is the primary builder of large calcium carbonate (CaCO₃) structures that make up the reef ecosystem. Coral are found in shallow waters where they can receive sunlight. Coral reefs resemble rainforests in terms of their high biodiversity. Reefs support rich communities through efficient recycling processes [Bryant et al., 1998]. They are also noted for their high level of productivity and are thought to be the most productive of all marine ecosystems, providing seafood, medicine, products, and recreational values.

Economic Value: Seafood from coral reefs contributes about one-fourth of the world’s total fish catch [Colfelt, 1988]. Munro estimated that coral reef ecosystems generate 6 million tons of fish caught worldwide [Hoegh-Guldberg, 1999]. Coral reef fish provide the essential source of protein for millions of people in underdeveloped societies [Hoegh-Guldberg, 1999]. They also provide employment for millions of fishers [Roberts et al., 1998]. Corals can be made into jewelry, and its sand and limestone skeletons are used by the construction industry [Bryant, 1998].

Medicine: New drugs from coral reefs are being produced to provide bone grafts and treat viruses from chemicals found within corals. In the future, drugs from coral reefs may be developed for the treatment of leukemia, skin cancer, and harmful tumors.

Tourism: Coral reefs are popular tourist attractions where people go snorkeling, scuba diving, recreational fishing, and for vacations in the sun. There is a lot of money made from reef attractions: about $1.5 billion is made annually from the Great Barrier Reef in Australia [Done et
et al., 1996], $2.5 billion from the Florida reefs [Birkeland, 1997], and $140 billion from the Caribbean reefs [Jameson et al., 1995].

Protection: Many coral reefs provide protection for adjacent coastlines from waves and from the impact of storms, erosion, and flooding. The protection allows the formation of ecosystems like seagrass beds and mangrove swamps [Hoegh-Guldberg, 1999]. Coral reefs provide shelter for local economies built around ports and harbors [Bryant, et al., 1998]. Fifteen percent of the people around the world live within 100 km of coral reef ecosystems [Pomerance, 1999]. Reefs also supply homes for many kinds of reef-bearing animals [Colfelt, 1988].

Current Threats to Coral Reefs: Many coral reef habitats are being destroyed by bad fishing practices, such as cyanide fishing, dynamite fishing, and overfishing. Pollution is also harming the reefs by sewage and sedimentation. For example, construction work causes pollution in the seawater. The sewage clouds the water and not enough sunlight penetrates the water for the coral to calcify properly. This causes a decrease in coral growth. Natural predators like the crown of thorn starfish which undergo population explosions approximately every 5 years damage the reefs by eating the coral tissue, leaving nothing but their skeleton. Increased tourist pressure that is unregulated causes harm by direct breakage, anchor damage, trampling, and illegal collecting has harmed the reefs [Bryant et al., 1998].

Effects of Carbon Dioxide

Burning of fossil fuels causes an increase in the atmosphere of the greenhouse gas carbon dioxide (CO₂). Increased atmospheric CO₂ affects coral reefs in two ways. An increase of CO₂ through the greenhouse effect results in an increase in the sea surface temperature, which can cause coral to bleach. With the resulting warmer temperatures, coral are more susceptible to the pathogens and competitors that weaken the coral. Bleaching usually occurs in the temperature range of 32°C to 35°C [Bruce, 1999]. In the bleaching process, the symbiotic algae, known as zooxanthellae, are expelled from the coral tissue [Bryant et al., 1998]. The algae are expelled when they become damaged by light at higher temperatures than they are exposed to regularly. Zooxanthellae transmit up to 95% of their photosynthetic production, made up of amino acids, sugars, carbohydrates, and small peptides, to the coral for energy and the essential compounds needed for healthy survival [Hoegh-Guldberg, 1999]. Photosynthesis by the symbiotic algae is thought to enhance calcification by removing CO₂ from the surrounding water: This in turn increases the CaCO₃ saturation state (see below) [Kawahata et al., submitted].

\[ 6\text{H}_2\text{O} + 6\text{CO}_2 \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \] [Baggs, 1995] (1)

Another way in which increased atmospheric CO₂ affects coral reefs is by altering the ocean's chemistry. As the atmospheric carbon dioxide level increases, much of it is absorbed into the oceans since the oceans make up about 70% of the area of the earth. The increase in atmospheric CO₂ increases the partial pressure of CO₂ in the sea-surface water by diffusion, causing it to become more acidic. The pH decreases by 0.2 to 0.3 units if the CO₂ concentration is doubled, causing the carbonate ion (CO₃²⁻) concentration to decrease by 25% to 35% as the seawater chemistry finds its new equilibrium. Since the CO₃²⁻ decreases, the CaCO₃ saturation state of the sea-surface water also decreases [Langdon et al., submitted]. Several researchers have shown that coral calcification is reduced as CO₃²⁻ is reduced [Gattuso et al., 1998, Langdon, submitted]. Coral rely on warm tropical temperatures, just as long as they are not too high and their symbiotic algae decrease the concentration of carbon dioxide and increase the concentration of the carbonate ion in seawater. CO₂ can dissolve more readily in cooler waters. Precipitation of CaCO₃
is favorable in warmer waters [Langdon et al., submitted]. The reactions of carbon dioxide with water are as follows:

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \quad \text{(carbonic acid)} \]  
(2)

\[ \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad \text{(bicarbonate ion)} \]  
(3)

\[ \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad \text{(carbonate ion)} \]  
(4)

When gaseous carbon dioxide reacts with water, it forms carbonic acid. Then the carbonic acid dissociates into hydrogen ions and bicarbonate ions in the water. By dissociation a second time the bicarbonate ions separate into carbonate ions and more hydrogen ions, which increases the acidity of the ocean water [Boggs, 1995]. The relative concentration of carbonic acid (\(\text{H}_2\text{CO}_3\)), bicarbonate ion (\(\text{HCO}_3^-\)), and \(\text{CO}_3^{2-}\) depend on pH, as shown in Figure 1. As pH decreases the \(\text{CO}_3^{2-}\) also decreases.

The remainder of this paper is concerned with modeling the seawater chemistry associated with sea-surface temperature rise and increased atmospheric carbon dioxide. The experiments that follow explore the sensitivity of modeled coral growth to these changes.

**METHODS**

**Part I:** A mathematical model was developed previously to determine the effects of different parameters of the \(\text{CO}_2\) system on corals in an artificial aquarium. The model determines how seawater chemistry affects coral calcification and how calcification affects seawater chemistry. The aquarium model is a computer simulation of the real world experiment done by H. Kawahata and his team on the coast of the Great Barrier Reef lagoons. They determined that calcification is the main reason for the increase in \(\text{CO}_2\) fugacity of the reef because there is a low level of total alkalinity and total carbon present [Kawahata et al., submitted]. Since the aquarium model and the lagoon represent isolated environments, we can expect the model results to apply the lagoon.

The model determines how calcification affects the aquarium’s seawater chemistry. A prescribed amount of \(\text{CaCO}_3\) is allowed to precipitate and the resulting changes in seawater chemistry are calculated. The model allows examination of two different extremes in \(\text{CO}_2\) diffusion across the air-sea interface. One ("closed system") determines seawater chemistry when no diffusion is allowed so that no \(\text{CO}_2\) is allowed to escape from the ocean surface, causing a build-up of \(\text{CO}_2\) in the aquarium’s seawater. The other ("open system") assumes that \(\text{CO}_2\) transfer across the air-sea interface is instantaneous. In reality, open ocean systems are somewhere between these two extremes, but this model allows examination of the range of chemistry changes due to calcification that could occur under natural conditions. The program input values which were used include pH of 8.1, initial atmospheric \(\text{CO}_2\) concentration of 350 \(\mu\text{atm}\), temperature of 25C in the seawater, salinity of 35 ppt, \(\text{PO}_4\) concentration of 0.0, \(\text{SiO}_4\) concentration of 0.0, and the initial \(\text{CaCO}_3\) precipitation rate of -0.5 \(\text{mM/L/d}\). The program output includes the changes of calcification, partial pressure of carbon dioxide, dissolved \(\text{CO}_2\), \(\text{HCO}_3^-\), \(\text{CO}_3^{2-}\), pH, total carbon, total alkalinity, calcium ion \(\text{Ca}^{2+}\) concentration, and saturation state over a 14-day time scale in the open and closed systems. Plots were made of the data from output files versus model run time.

In the aquarium model, calculations focus on the carbon chemistry. The carbonate chemistry depends on four different parameters that corals are sensitive to total alkalinity, total carbon (which is the sum of dissolved \(\text{CO}_2\), \(\text{HCO}_3^-\), and \(\text{CO}_3^{2-}\)), partial pressure of \(\text{CO}_2\) in the air
that is in equilibrium with the water, and the pH of the water. These concentrations can be simultaneously determined. The resulting CO$_3^{2-}$ concentration can be determined, which can be used to calculate calcification rates of the corals. In the model the initial atmospheric carbon dioxide concentration and pH are known numbers. The model assumes that the pCO$_2$ of the seawater is in equilibrium with the initial CO$_2$ in the atmosphere. The pCO$_2$ level is calculated using the solubility constant $K_0$ of CO$_2$ gas in seawater that depends on temperature and salinity [Weiss, 1974]. The solubility constant determines the reaction of CO$_2$ gas into aqueous CO$_2$ and carbonic acid.

There are two other equilibrium constants that determine the concentrations of the ions produced that also depend on temperature and salinity of the seawater. $K_1$ is the constant for the dissociation of carbonic acid into bicarbonate ion

$$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^{-}.$$  \hspace{1cm} (3)

and $K_2$ is the constant for the dissociation of bicarbonate ion into carbonate

$$\text{HCO}_3^{-} \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}.$$  \hspace{1cm} (4)

The constants $K_1$ and $K_2$ have many different ways of being determined, but the model uses the most widely accepted formulas of Dickson and Millero [1987].

CaCO$_3$ saturation state is a measure of how much calcium carbonate is dissolved in the seawater. It forms when the surface ocean becomes supersaturated with CaCO$_3$ and precipitates the undissolved compound by the reaction

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3.$$  \hspace{1cm} (5)

Supersaturation occurs when Mg$^{2+}$ reacts with crystallized CaCO$_3$ in the water. The precipitate, CaCO$_3$, is aragonite. Aragonite saturation state is determined as

$$\Omega = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K_{sp}.$$  \hspace{1cm} (6)

Where $K_{sp}$ is the solubility constant of aragonite determined by Mucci [1993]. Saturation state decreases as the CO$_3^{2-}$ decreases.

Part 2: An edited version of the first model was developed to determine calcification with a diurnal light cycle and including a gas exchange coefficient for CO$_2$ from seawater to atmosphere. The initial CO$_2$ level was set at 350 µatm. The wind speed was 5 m/s and the depth was at 10 cm. This model is an improvement over the closed vs. open system as CO$_2$ is allowed to diffuse from seawater to air in a realistic fashion. The amount of calcification in the aquarium was calculated according to the equation derived from experiments in the coral reef mesocosm in Biosphere2, allowing for a dependence calcification rate on calcium carbonate saturation as:

$$G = 0.0698 ([\text{CO}_3^{2-}] - 89.0);$$  \hspace{1cm} (7)

where $G =$ calcification rate of the corals [Langdon, personal communication]. Since calcification in coral has been shown to vary with the degree of CaCO$_3$ saturation state [Gattuso et al., 1998, 1999, Langdon, submitted]. The model allows calcification to vary as the CO$_3^{2-}$ decreases.

The model was made to determine the air/sea flux of carbon dioxide into the ocean. The flux equation is:

$$\text{Flux} = k_w (C_{\text{air}} - C_{\text{ocen}}).$$  \hspace{1cm} (8)
There will be flux into the ocean if the calculated flux is greater than zero. The $C_{\text{atm}}$ is the carbon dioxide concentration in equilibrium with the atmosphere and $C_{\text{croc}}$ is carbon dioxide concentration in the ocean. $K_w$ is the piston velocity measured in length per time. When the piston velocity is large, then the flux is rapid; when it is small, the flux is slow. The piston velocity is divided by the depth of the seawater to produce the time scale for equilibrium with the atmosphere:

$$t = \frac{\text{depth}}{K_w}.$$  \hspace{1cm} (9)

Piston velocity is parameterized as being proportional to the square of the wind speed, following Wanninkhof (1992):

$$K_w = a \times (\text{wind\_speed})^2 \times (\text{Schmidt}/660)^{-1/2}.$$  \hspace{1cm} (10)

The Schmidt number is the temperature-dependence of the gas transfer rate: again following Wanninkhof, it is parameterized as a third order polynomial in temperature:

$$\text{Schmidt} = A_b - B_b \times \text{sst} + C_b \times (\text{sst})^2 - D_b \times (\text{sst})^3.$$  \hspace{1cm} (11)

$sst$ is the temperature of the seawater. The constants in the equation as given by Wanninkhof are:

$A_b = 2073.1$, $B_b = 125.62/\text{C}$, $C_b = 3.6276/\text{C}$, $D_b = 0.043219/\text{C}$.

The constant $a$ relates piston velocity to the square of the wind speed at the temperature of the seawater:

$$a = 0.337 / 3.6e5 \text{ sec/m}.$$  \hspace{1cm} (12)

The value of this constant comes from the Ocean Carbon Model Intercomparison Project (OCMIP).

The rate of change of the carbon dioxide concentration in water is calculated as:

$$R = \frac{\text{Flux}}{\text{depth}}.$$  \hspace{1cm} (13)

The change of carbon dioxide in the ocean over a time $\Delta t$ is thus:

$$\Delta C_{\text{CO}_2} = R (\Delta t)$$  \hspace{1cm} (14)

The initial $\text{CO}_2$ was set at 350 $\mu$atm.

**Part 3:** The same model was used as in Part 2 above. In the first scenario of the experiment the initial $\text{CO}_2$ was changed to 280 $\mu$atm, and pH to 8.15 to reflect pre-industrial values, and temperature was set at 25C. In the second scenario, temperature was increased to 28C, while initial $\text{CO}_2$ was kept at 280 $\mu$atm and pH maintained at 8.15. The third scenario doubled the initial $\text{CO}_2$ to 560 $\mu$atm and kept the temperature at 25C. The pH was decreased to 7.95 to allow the proper alkalinity. The last scenario doubled the initial $\text{CO}_2$ to 560 $\mu$atm and raised the temperature to 28C.

This idea came from the observation that the concentration of $\text{CO}_2$ in the atmosphere reported during pre-industrial times will double by the middle of the 21st century. The increase in $\text{CO}_2$ in the atmosphere will reduce the concentration of $\text{CO}_3^{2-}$ in the sea-surface by 30% relative to the pre-industrial level. This increase will also reduce the $\text{CaCO}_3$ saturation state of the surface ocean by about 30% [Langdon et al., submitted].

**Part 4:** The wind speed of the model was decreased to 1 m/s. The initial $\text{CO}_2$ concentration was set at 350 $\mu$atm at 25C at a pH of 8.15. The model was modified so that calcification could be integrated over time. This was done to compare the calcification in the open ocean where the seawater is constantly flushed out, to that in a lagoon where the water is flushed out only about every 14 days.
RESULTS

Part 1: Seawater changes in a closed versus open aquarium

Open: The partial pressure of CO₂ had no change over time (Figure 2: black line). The pH level decreased slowly as time progressed (Figure 3: black) and the CO₃²⁻ level decreased (Figure 4: black). Saturation state decreased as the days passed (Figure 5: black). The calcification rate gradually decreased over time (Figure 6: black). Ca²⁺ concentration slowly decreased over the 14-day time period due to calcification (Figure 7: black). The total alkalinity level decreased (Figure 8: black).

Closed: The partial pressure of CO₂ level increased rapidly (Figure 2: red line). While the pH, CO₃²⁻, and saturation state decreased radially (Figure 3, 4, 5: red). The calcification rate decreased more slowly than in the open system (Figure 6: red). The Ca²⁺ concentration decreased more slowly than the open system due to the reduced calcification rate (Figure 7: red). Likewise, the total alkalinity level decreased more slowly than in the open system (Figure 8: red).

Part 2: Seawater changes in an aquarium with light-controlled realistic calcification and gas exchange (only from open ocean system)

In the open system, partial pressure of CO₂ increased to 352 μatm in daylight and returned to 350 μatm at night (Figure 9). The pH level decreased slowly over time (Figure 10). The CO₃²⁻ (Figure 11), Ca²⁺ (Figure 12), and saturation state (Figure 13) steadily decreased during the day and remained constant at night. Calcification occurred during the day and was absent at night: the maximum daily calcification rate steadily decreased over the period of time (Figure 14).

Part 3: Seawater change comparison between the pre-industrial era to the scenario of doubled CO₂ in the future

In the open system when the initial CO₂ was at 280 μatm and temperature at 25°C, calcification increased during the day and was absent at night: the maximum daily calcification rate steadily decreased over the period of time (Figure 15: black line). Partial pressure of CO₂ concentration increased during the day and diffused out of the water at night. As time progressed pCO₂ slowly increased (Figure 16: black). The CO₃²⁻ (Figure 17: black), Ca²⁺ (Figure 18: black) and saturation state steadily decreased during the day and remained constant at night (Figure 19: black). The pH level decreased slowly over time (Figure 20: black).

Compared to the first scenario, when temperature was increased and CO₂ was held constant, calcification increased by 12% (Figure 15: red line). The partial pressure of CO₂ increased at a slightly slower rate than the original values (Figure 16: red). Although pH was initialized at a lower value than in scenario one, to maintain realistic alkalinity. The rate of decrease in pH was nearly identical to that in scenario one (Figure 20: red). The initial CO₃²⁻ increased by about 30% and then steadily decreasing over time (Figure 17: red). The rate of Ca²⁺ decrease was more rapid than in scenario one (Figure 18: red). The initial saturation state increased by about 13% and then decreasing over time (Figure 19: red).

In the third scenario of the experiment the plots were compared to the first scenario. The carbon dioxide level was doubled, pH was decreased by 2.5%, and the atmospheric temperature remained the same at 25°C. The peak calcification decreased by about 19% (Figure 15: green line) and the saturation decreased by about 21% (Figure 19: green). The CO₃²⁻ concentration decreased
by about 20% (Figure 17: green). The pH level decreased due to alkalinity content (Figure 20: green). The Ca$^{2+}$ concentration decreased at a slower rate (Figure 18: green).

In the fourth scenario, which was compared to the first scenario, the CO$_2$ level was doubled and the temperature increased. The calcification decreased by about 10% (Figure 15: blue line). The CO$_3^{2-}$ concentration decreased by about 13% (Figure 17: blue). The saturation state decreased by 12% (Figure 19: blue). The Ca$^{2+}$ concentration increased slightly (Figures 18: blue)

**Part 4:** The partial pressure CO$_2$ increased more during the day than in previous experiments because the slower the wind speed the slower the rate of CO$_2$ diffusion (Figure 21). The calcification rate in the lagoon was two-thirds that in the lagoon as in the open ocean (Figure 22).

**DISCUSSION**

**Part 1:** Increased CO$_2$ in the closed system caused the saturation state, carbonate level, and pH to decrease. The pH decreased because of the reaction of the CO$_2$ with the seawater to increase the hydrogen ion concentration. The partial pressure CO$_2$ level increased because the gas could not escape from the aquarium. Calcification decreased in the closed system compared to the open system, because the carbon dioxide build up in the aquarium caused a decrease in the carbonate ion concentration.

**Part 2:** Calcification was high during the day since the coral’s algae use light through photosynthesis to provide nutrients for the coral to aid in the production of their calcium carbonate skeleton. At night, there was no calcification because there was no sunlight. The partial pressure of the CO$_2$ level increased during the day because calcification removes CO$_3^{2-}$, leaves the H$^+$ unbalanced, decreases pH, and shifts the reaction toward the production of more CO$_2$. At night, no CO$_2$ is released into seawater because calcification has ceased, and the CO$_2$ level remained the same. The calcium and CO$_3^{2-}$ concentration decreased during the day and remained constant at night because calcification consumed the calcium and CO$_3^{2-}$ to produce calcium carbonate. Because calcification increases during the day, the saturation state also increases due to the increase of CO$_3^{2-}$ ions being produced for calcification. The pH level stayed the same at night when there was no calcification, but it decreased during the day because hydrogen ions were being produced to make the seawater more acidic over time.

**Part 3:** The calcification level increased as the temperature was raised from 25°C in scenario one, to 28°C in scenario two. This was because warmer water holds less CO$_2$. The less CO$_2$, the less carbonic acid (H$_2$CO$_3$) is formed, which results in a higher pH and higher CO$_3^{2-}$ concentration. The saturation state increased because it depends on high concentrations of CO$_3^{2-}$. Calcification rates depend on CO$_3^{2-}$ concentration. Calcium is used to make calcium carbonate in the process of calcification, and so decreased gradually as calcification proceeded.

In scenario three, when atmospheric CO$_2$ was doubled, calcification was reduced. This effect was greatest at lower temperatures because CO$_2$ absorbs well in cooler waters. Because higher CO2 results in lower CO$_3^{2-}$ concentration, calcification decreases. Since calcification decreases the rate of the calcium uptake also decreases.

In scenario four, when the CO$_2$ was doubled and the temperature was increased, the results were similar to the previous experiment, but were reduced in magnitude. Calcification did not decrease as much since it is favored in warmer water temperatures. This is because CO$_2$ is less
soluble in warm water than in colder water. The calcium level, saturation state, and CO\textsubscript{3}\textsuperscript{2} level did increased compared to the scenario three, due to the warmer temperature.

Part 4: The CO\textsubscript{2} level increased more than previous experiments because the slower wind speed resulted in a slower diffusion rate. Calcification was higher in the open ocean since the seawater chemistry was always being renewed with fresh water to keep the calcification rate constant. After two weeks, total calcification in the lagoon was about 70\% of that in the open ocean.

CONCLUSION

The model gave good results on how calcification was affected due to temperature increase and CO\textsubscript{2} change. We determined that calcification is strongly affected by increases in atmospheric CO\textsubscript{2}. This is offset somewhat by increases in sea-surface temperature as long as the temperature remains below bleaching limits. Decreased calcification causes weaker coral skeletons and can cause reefs to grow at a slower rate. This can cause the reefs to be more susceptible to erosion.

In the future, we look forward to editing the model to portray real world reefs as the realistic data taken by Frankignoulle et al. [1996] (Figure 23), possibly to include how photosynthesis/respiration affects carbon dioxide in seawater. We also want to determine how mixing with surrounding waters can change the concentrations in the seawater.

ACKNOWLEDGMENTS

I acknowledge Joanie Kleypas for helping me to understand the importance of coral reefs and how they are affected. I thank Matthew Hecht for helping me understand how to run the model and learn a little of programming. I thank Tom Windham, Beverly Johnson, Kathi Elder, and the SOARS (Significant Opportunities in Atmospheric Research and Science) program for allowing me to work at NCAR (National Center for Atmospheric Research) for the summer. I acknowledge Marie Boyko and Rene Munoz for teaching me how to write a good technical paper. Finally, I thank Pat Baker for being there for me when I needed her the most.

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The Carbonate System

\[ \text{CO}_2 + \text{H}_2 \text{O} \leftrightarrow \text{H}_2 \text{CO}_3 \]

\[ \text{CO}_2 \text{ (aq)} \leftrightarrow \text{H}^+ + \text{H}^+ \]

\[ \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \]

\[ \text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3 \]

\[ \text{CO}_2 \text{ (aq)} = \text{diss CO}_2 \& \text{H}_2 \text{CO}_3 \]
Figure 5: Saturation State ion vs Time

Saturation State

Time (days)

open system
closed system
Figure 7.

[Calcium] ion vs Time

- open system
- closed system

**Time (days)**

- 0
- 5
- 10
- 15

**[Ca]**

- $1.030 \times 10^4$
- $1.020 \times 10^4$
- $1.010 \times 10^4$
- $1.000 \times 10^4$
- $0.990 \times 10^3$
- $0.980 \times 10^3$
- $0.970 \times 10^3$
- $0.960 \times 10^3$
Figure 8. Total Alkalinity vs Time

- Open system
- Closed system

Total Alkalinity (meq kg⁻¹) vs time (days)
Figure 10.
Figure 11.
Calcification Rate vs Time

- Initial CO2: 280; Temperature: 25
- Initial CO2: 280; Temperature: 28
- Initial CO2: 560; Temperature: 25
- Initial CO2: 560; Temperature: 28
Figure 14.

[Carbonate] ion vs Time

Initial CO2: 280; temperature: 25
Initial CO2: 280; temperature: 28
Initial CO2: 560; temperature: 25
Initial CO2: 560; temperature: 28
[Calcium] ion vs Time

- initial CO2:280; temperature:25
- initial CO2:280; temperature:28
- initial CO2:560; temperature:25
- initial CO2:560; temperature:28

Time (hours)

[Ca]

1.030 x 10^4
1.020 x 10^4
1.010 x 10^4
1.000 x 10^4
9.900 x 10^3
Saturation State vs Time

initial CO2:280; temperature:25
initial CO2:280; temperature:28
initial CO2:560; temperature:25
initial CO2:560; temperature:28
Figure 20.

pH vs Time

- Initial CO2: 280; Temperature: 25
- Initial CO2: 280; Temperature: 28
- Initial CO2: 560; Temperature: 25
- Initial CO2: 560; Temperature: 28
Fig. 1. Variations in air-sea CO₂ fluxes (positive value for evasion), CO₂ partial pressure, dissolved oxygen saturation level, tide, water temperature and irradiance during three 24 h cycles carried out at the back reef at Moorea. pCO₂ was calculated from pH and total alkalinity, tide was calculated using the SHM package. Irradiance data were obtained using a 10-point moving average, with 1 measurement taken per minute. On flux/pCO₂ graphs, vertical lines indicate when pCO₂ was at atmospheric equilibrium (~355 µatm) and the horizontal line represents the negative flux attributed to the initial oceanic under-saturation (this flux, ~32 mmol m⁻² s⁻¹, was estimated using the measured oceanic pCO₂ and the average exchange coefficient observed in the reef flat).