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Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef

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Abstract. The concentration of CO_2 in the atmosphere is projected to reach twice the preindustrial level by the middle of the 21st century. This increase will reduce the concentration of CO_3^{2-} of the surface ocean by 30% relative to the preindustrial level and will reduce the calcium carbonate saturation state of the surface ocean by an equal percentage. Using the large 2650 m^3 coral reef mesocosm at the BIOSPHERE-2 facility near Tucson, Arizona, we investigated the effect of the projected changes in seawater carbonate chemistry on the calcification of coral reef organisms at the community scale. Our experimental design was to obtain a long (3.8 years) time series of the net calcification of the complete system and all relevant physical and chemical variables (temperature, salinity, light, nutrients, Ca^{2+}, pCO_2, TCO_2, and total alkalinity). Periodic additions of $NaHCO_3$, Na_2CO_3, and/or $CaCl_2$ were made to change the calcium carbonate saturation state of the water. We found that there were consistent and reproducible changes in the rate of calcification in response to our manipulations of the saturation state. We show that the net community calcification rate responds to manipulations in the concentrations of both Ca^{2+} and CO_3^{2-} and that the rate is well described as a linear function of the ion concentration product, $[Ca^{2+}]^{0.69}[CO_3^{2-}]$. This suggests that saturation state or a closely related quantity is a primary environmental factor that influences calcification on coral reefs at the ecosystem level. We compare the sensitivity of calcification to short-term (days) and long-term (months to years) changes in saturation state and found that the response was not significantly different. This indicates that coral reef organisms do not seem to be able to acclimate to changing saturation state. The predicted decrease in coral reef calcification between the years 1880 and 2065 A.D. based on our long-term results is 40%. Previous small-scale, short-term organismal studies predicted a calcification reduction of 14-30%. This much longer, community-scale study suggests that the impact on coral reefs may be greater than previously suspected. In the next century coral reefs will be less able to cope with rising sea level and other anthropogenic stresses.

1. Introduction

Levels of carbon dioxide, a greenhouse gas found in Earth's atmosphere, have increased since preindustrialized times, primarily due to the combustion of fossil fuels. On the basis of realistic scenarios of future emissions this trend will continue, resulting in a projected doubling of atmospheric carbon dioxide levels relative to preindustrial levels by the year 2065 [*Houghton et al.*, 1996]. This projected atmospheric change brings with it other potential and uncertain changes to Earth's atmosphere, biosphere, and hydrosphere. As an example, the rise in atmospheric carbon dioxide will via gas exchange increase the partial pressure of CO_2 in the surface ocean, thus causing surface seawater to become more acidic [*Broecker et al.* 1979]. The net chemical reaction is

$$H_2O + (CO_2)_{aq} + CO_3^{2-} \rightarrow 2HCO_3^-.$$

The result of this reaction is that as $(CO_2)_{aq}$ in the surface ocean rises, the CO_3^{2-} concentration falls. The impact of a doubling of $(CO_2)_{aq}$ will be a drop in pH of 0.2-0.3 units and a decline in CO_3^{2-} concentration of 25-35% relative to the preindustrial concentration. The decrease in CO_3^{2-} concentration will reduce the calcium carbonate saturation state of the surface ocean. It is defined as

$$\Omega = \frac{ICP}{K'_{sp}}, \quad (1)$$

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where ICP is the ion concentration product $[Ca^{2+}][CO_3^{2-}]$ and K'_{sp} is the solubility product for a particular mineral phase of $CaCO_3$ (calcite, aragonite). *Broecker et al.* [1979] and more recently *Kleypas et al.* (1999a) have estimated changes in $CaCO_3$ saturation state in global surface ocean waters as the CO_2 concentration in the atmosphere increases through the next century. *Kleypas et al.* (1999a) calculated that 100 years ago, Ω_{arag} in the tropics was 4.6±0.2 (1σ). Presently, it is 4.0±0.2, and it is projected to drop to 3.1±0.2 by the year 2065 and to 2.8±0.2 by 2100.

This reduction in saturation state raises concern because, as noted by *Smith and Buddemeier* [1992], there is evidence in the literature of a positive correlation between saturation state and the rate of production of $CaCO_3$ or calcification. *Broecker and Takahashi* [1966] found that the rate of calcification on the Grand Bahama Banks was proportional to the degree of calcium carbonate supersaturation in the overlying water. *Smith and Pesret* [1974], in a study of calcification in the Fanning Island lagoon, noted that the rate of calcification in one region of the lagoon was one third that expected based on the biomass of corals and suggested that the low Ω_{arag} of this region was responsible. However, they noted that the existence of some other limiting factor could not be ruled out. Studies of calcification by coralline algae, important calcifiers on coral reefs, have shown that elevated CO_2 inhibits calcification and that calcification rates are related to the carbonate ion concentration of the water [*Borowitka*, 1981; *Agegian*, 1985; *Gao et al.*, 1993]. Little comparable work on the effect of elevated CO_2 on corals has been done. There is circumstantial evidence that corals are sensitive to CO_2. Corals can survive outside the tropics, and they can survive in the tropics without symbiotic algae. However, in order to produce massive reefs, they require tropical temperatures and symbiotic algae, both of which tend to decrease the concentration of CO_2 and hence elevate the concentration of CO_3^{2-} in seawater. There is also evidence for a strong dependence of calcification on CO_3^{2-} concentration in a study by *Marubini and Atkinson* [1999]. They found that nubbins of the hermatypic coral *Porites compressa* grown in seawater adjusted to a pH of 7.2 (CO_3^{2-} = 18 μmol kg^{-1}) calcified at one half the rate of identical nubbins grown at pH 8.0 (CO_3^{2-} = 109 μmol kg^{-1}).

Recently, *Gattuso et al.* [1998] demonstrated that the calcification of the hermatypic coral *Stylophora pistillata*, under conditions of constant pH and CO_3^{2-}, was positively (although nonlinearly) dependent on the Ca^{2+} concentration over the range 3.6-10.9 mmol kg^{-1}. Taken together, these organismal level studies support the hypothesis that saturation state controls calcification in corals and marine calcareous algae. However, it should be recalled that the mechanisms of calcification are very different in calcareous algae and corals. Caution should be exercised in extrapolating from Ca^{2+} control in corals and CO_3^{2-} control in coralline algae to the assumption that corals and coralline alga respond in the same way to the ion concentration product. There is a need for organismal and community level studies where both Ca^{2+} and CO_3^{2-} concentrations are varied under controlled conditions and the effect on calcification rate is observed. The issue of saturation state control of calcification in these organisms should not be considered proven until studies are conducted in which both the CO_3^{2-} and Ca^{2+} concentrations are varied, and it is demonstrated that the ion concentration product (ICP) uniquely explains the kinetics.

This paper describes an attempt to test experimentally if elevated atmospheric CO_2, through its effect on the calcium carbonate saturation state of the water, has a significant impact on coral reef calcification rates. We utilized the coral reef mesocosm in the 2650 cubic meter aquarium (artificial seawater) of the BIOSPHERE-2 Center (hereafter BIOSPHERE) located near Tucson, Arizona. This is an assembled community of coral reef organisms consisting of corals, calcifying algae, and other typical reef biota that mimics some of the key aspects of coral reef ecosystems. Although the experimental environment is artificial, it is the best available approximation of a natural community where it is possible to control its chemical environment. We manipulated the saturation state of the water by chemical additions of $NaHCO_3$, Na_2CO_3, and $CaCl_2$. In 1995-1998 the additions of $NaHCO_3$ and Na_2CO_3 were made so as to keep the pH in a narrow range of 8.1±0.1 and isolate the effect of changing CO_3^{2-} concentration. In 1999 the chemical additions were made so as to fully reproduce the carbonate chemistry of tropical seawater 18,000 years ago, i.e., pCO_2 and pH of 192±27 μatm and 8.30±0.06, respectively.

2. Experimental Methods

2.1. Experimental Design

A 3.8 year long time series of net community calcification rate and relevant physical and chemical variables (T, S, light, total dissolved inorganic carbon, total alkalinity, Ca^{2+}, NO_3+NO_2, NH_4, PO_4, and SiO_2) was obtained. Temperature was held constant at 26.5±0.5°C. Natural light, filtered through the glass and steel roof of the BIOSPHERE structure, measured at the water surface varied seasonally from 8 mol photons m^{-2} d^{-1} during the winter to 25 during the summer. Light outside the structure varied from 19 mol photons m^{-2} d^{-1} during the winter to 57 during the summer. While the time series data were being acquired, we manipulated the saturation state of the water and observed the effect on net community calcification rate. This approach is known as time series intervention analysis [*Scheiner and Gurevitch*, 1993]. This is a statistical technique employed in ecological research in situations where the large or unique scale of the system under study defies replication and randomization [*Schindler*, 1987; *Frost et al.*, 1988; *Carpenter*, 1990]. At BIOSPHERE it is not feasible to manipulate the saturation state of the water overlying several complete coral reef ecosystems while observing several other reefs as controls. However, it is possible to obtain a time series of observations at a single coral reef ecosystem on the scale of the BIOSPHERE coral reef and manipulate the saturation state of the complete system. By observing a consistent, reproducible response to our perturbations of the saturation state and the longer term shifts in the mean level of saturation state, we were able to observe reproducibly that the changes in net community calcification rate were related to our manipulations of the saturation state.

Specifically, we took advantage of the fact that the metabolism of the community draws down the saturation state

of the water by the consumption of Ca^{2+} and CO_3^{2-}. By controlling the frequency of chemical additions of carbonate and calcium we were able to maintain the saturation state at a desired level or cause it to alternate between two desired levels. Following a chemical addition, we would observe the relationship between the rate of calcification and concentration of the dissolved species. The decrease in saturation state following a chemical addition was gradual (days to months) and caused by the consumption of the reactants by the corals and coralline algae. Similar rates of change in saturation state occur naturally in atoll lagoons on tidal and longer timescales [*Smith amd Pesret*, 1974; *Smith and Jokiel*, 1978; *Suzuki*, 1995].

2.2. Study Site

The BIOSPHERE-2 Center is located 50 km north of Tucson, Arizona (32.57°N, 110.85°W) at an altitude of 1200 m. The facility contains five biomes: a tropical rain forest, a savanna, a desert, a mangrove, and a coral reef all completely isolated from the ambient environment by a glass and steel structure. The coral reef biome is constructed from a stainless steel lined tank coated with epoxy resin. The tank measures 45.2 m long, 19.1 m wide, and has two depths 6.8 m and 4.3 m. The BIOSPHERE reef biome attempts to mimic the physical features of reefs typically found in the Caribbean. Details on the construction of the biome, the water circulation, temperature control, water chemistry, stocking with reef organisms and complete species lists are given by *Atkinson et al.* [1999]. The water in the tank was initially comprised of 10% natural seawater from the southern California coast and 90% local well water mixed with Instant Ocean salts. Concentrations of the major ions compare favorably with natural seawater [*Atkinson et al.*, 1999]. The concentration of total boron was similar to that of seawater. The pH buffering of the water is the same as natural seawater, i.e., bicarbonate, carbonate, and borate. Depending on the experimental protocol described below, the pH was maintained at 8.1 or 8.3 by manipulation of the TCO_2 and total alkalinity (TA) of the water.

The present community of organisms is largely composed of macroalgae, including 11 genera of green algae, 8 general of red algae, 2 genera of brown algae, and some blue-green algae. Fishes comprise 16 genera and echinoids comprise 7 genera. There are 25 genera of coral and 2 genera of sponges, but they do not dominate the benthos. Several coral species have successfully reproduced sexually including *Porites astreoides*, *Favia fragum*, *Agaricia* sp., *Siderastrea* sp. and *Acropora cervicornis*. Measurement of the extension rate of a *Siderastrea* colony indicated that it had been growing at the average rate of 4 mm yr^{-1} over the 4 year period between 1992 and 1995 (M. Raymo, personal communication, 1997). This is about 1/2 to 1/3 of the maximum rate for this species but is consistent with the low saturation state of the water at the time as the findings of this study will show. The dominant calcifier in the system is the geniculate coralline alga *Amphiroa*. Two species, *A. fragillissima* and *A. rigida*, are present in roughly equal amounts (Ed Glenn personal communication, 1999). The BIOSPHERE coral reef biome is best characterized as an algal dominated reef similar to fringing reefs close to populated areas in many parts of the world.

The strengths of the facility as a research tool are the large size (2650 m^3 of seawater and 750 m^2 of live benthos) and the ability to control the temperature and chemistry of the water. The weaknesses of the facility are chiefly related to light. The latitude of the facility means that there will be greater seasonal changes in light than at most natural reefs. A cliff along the west wall casts a shadow across the tank in the afternoon. Also, the glass and steel structure of the building attenuates the sunlight reaching the water surface by ~50% and completely blocks UV radiation. Finally, the water contains a high concentration of dissolved organic matter (DOM) which discolors the water giving a yellowish tint and increases the attenuation of light with depth. Despite the unnatural light field it is clear that the coral reef biome is behaving like a natural reef in many important regards. The nutrient concentrations in the water are low (except for SiO_2) and similar to those on natural reefs: NO_3+NO_2, 0.05-0.5 μmol L^{-1}; NH_4, 0.05 μmol L^{-1}; PO_4, 0.03 μmol L^{-1}; SiO_2 2-25 μmol L^{-1} [*Atkinson et al.*, 1999]. These low concentrations are maintained by the biota. Nutrient uptake rates are similar to those on natural reefs [*M. Atkinson*, manuscript in preparation, 2000] and allow the biota to achieve a high rate of gross production (0.7-2.8 g OrgC m^{-2} d^{-1}) despite low-nutrient concentrations. The photosynthesis to respiration ratio (P/R) of the BIOSPHERE coral reef biome averages 1.0±0.2. This is consistent with that of natural coral reefs. A third characteristic of a natural coral reef is a high rate of calcification. Calcification rates in the BIOSPHERE coral reef range from ~8 to 125 mmol $CaCO_3$ m^{-2} d^{-1} depending on the chemistry of the water. When the $[Ca^{2+}]$ and $[CO_3^{2-}]$ are similar to that of natural tropical surface water, the rate of calcification is 75 mmol $CaCO_3$ m^{-2} d^{-1} equivalent to 2.9 kg $CaCO_3$ m^{-2} y^{-1}. The rates of community metabolism at BIOSPHERE are comparable to estimates of complete reef metabolism at One Tree (23°S, 152°E) and Lizard Islands (15°S, 145°E) and fall intermediate between Kinsey's modal values for lagoon and reef-flat environments (Table 1).

2.3. Measurements

Temperature and salinity were measured using a Sea Bird Electronics SeaCat mini-Conductivity Temperature Depth recorder (CTD) located at 1.5 m below the surface in the deep end of the tank. Photosynthetically available quantum irradiance reaching the water surface was measured with a LiCOR 192 cosine collector sensor from a location just above the wave wall on the north end of the tank. Temperature, salinity, and light were recorded every 15 min. The pCO_2 of the water and overlying atmosphere were measured every 8 min with an equilibrator-infrared gas analyzer system described in section 2.4 which automatically went through a self-calibration cycle every 2 hours. Water samples for total dissolved CO_2 (TCO_2) and total alkalinity (TA) were collected using tubing and a pump from the same location as the CTD. The frequency of water sampling varied. Immediately before and after a change in the saturation state water samples were collected daily at 0800-0900 LT (often also at 1600-1700 LT) for a period of 1-2 weeks, and then the frequency of sampling

Table 1. Published Values for Community Metabolism in Coral Reef Systems

Description	Gross photosynthesis, mmol C m^{-2} d^{-1}	Calcification, mmol $CaCO_3$ m^{-2} d^{-1}	Reference
"Complete" reef systems			
Fanning Island		26	*Smith and Pesret* [1974]
Canton Island	500	13	*Smith & Jokiel* [1978]
One Tree Island	192	39	*Kinsey* [1977]
Lizard Island	267	47	*Kinsey and Davies* [1979]
Christmas Island		3	*Smith et al.* [1985]
"Kinsey's modal values"			
Lagoons	83	13-21	*Kinsey* [1983]
Reef-flats	417	104	*Kinsey* [1983]
Complete coral cover	1667	261	*Kinsey* [1983]
BIOSPHERE-2	108-292	75	this study

Values have been converted from the original units of gC m^{-2} d^{-1} and kg $CaCO_3$ m^{-2} yr^{-1} given in the references.

was reduced to once per week as the rate of carbonate chemistry changes slowed. Water samples for Ca^{2+} were collected weekly, but only monthly samples have been analyzed to date. Ca^{2+} concentrations at intervening times where interpolated based on the change in TA.

Chemical additions of commercial grade $NaHCO_3$ and Na_2CO_3 and $CaCl_2$ were made to increase the saturation state of the water. The dates and amounts added are given in Table 2. The chemicals were added separately in the order $NaHCO_3$, Na_2CO_3, and $CaCl_2$. Each chemical was added in

Table 2. Dates and Amounts of Chemicals Added to Control the Saturation State of the Water

Date	Na_2CO_3, mmol L^{-1}	$NaHCO_3$, mmol L^{-1}	$CaCl_2$, mmol L^{-1}
March 17, 1995	nd	nd	nd
July 24, 1995	0.116	0	0
Aug.18, 1995	0.027	0	0.173
March 19, 1996	0.265	0.090	0.245
July 8, 1996	0.304	0.225	0.262
Oct. 29, 1996	0.277	0.081	0.299
March 4, 1997	nd	nd	nd
June 6, 1997	0.073	0.485	0.320
June 30, 1997	0.180	1.222	0
Sep. 18, 1997	0.051	0.315	0
Oct. 8, 1997	0.216	0.382	0
Nov. 18, 1997	0.231	0.409	0
Jan. 13, 1998	0.238	0.407	0
March 11, 1998	0.242	0.587	0
July 9, 1998	0	0	2.468
Sep. 8, 1998	0.265	1.020	0
Jan. 22, 1999	0	0	1.710
Feb. 18, 1999	0.087	0.030	0
Feb. 22, 1999	0.180	0	0
March 1, 1999	0.264	0	0
March 4, 1999	0	0	1.061
March 8, 1999	0.266	0	0
March 15, 1999	0.210	0.071	0
March 22, 1999	0.264	0	0

Volume of seawater is 2.65 x 10^3 m^3. nd denotes dates when the data have been misplaced.

aliquots to a large tub, mixed until dissolved, and then discharged into the tank. The $NaHCO_3$ and Na_2CO_3 were mixed into seawater. The $CaCl_2$ was dissolved in freshwater (reverse osmosis treated to remove nutrients). Care was taken to avoid raising the saturation state to the point that spontaneous precipitation of $CaCO_3$ would occur in the mixing tub or when the solution first came in contact with the water in the tank.

2.4. CO_2 Measurements

Water samples for chemical analyses were drawn from a depth of ~1 m at the deep end of the tank. Contemporaneous sampling at multiple locations around the tank indicated that the chosen sampling location was representative of the entire tank. Water samples for TCO_2 and TA were drawn into 250 ml glass stoppered bottles, and 100 μL of saturated $HgCl_2$ was added to prevent biological alteration of samples during storage. The TCO_2 was determined coulometrically [*Chipman et al.*, 1993]. Analyses were run in triplicate, and the precision (1σ) and accuracy were estimated to be ± 1 μmol kg^{-1}. The TA was determined in triplicate using an automated Gran titration. We used commercially prepared 0.2 N HCl certified to be within 0.5% of the stated concentration. We also checked the accuracy by comparison against seawater reference material prepared by Andrew Dickson (Scripps Institution of Oceanography) with a certified TA. The precision (1σ) was typically ±2-3 μeq kg^{-1}. The accuracy was estimated to be ± 10 μeq kg^{-1}, consistent with the accuracy to which the concentration of the HCl was known. The pCO_2 of the water was measured continuously. Water from 1.5 m below the surface was pumped into a 20 L equilibration chamber through a shower head (~5 L min^{-1}) which facilitated rapid exchange of CO_2 between the water and the gas phase [*Bates et al.*, 1998]. The equilibrated air was then passed through a PermaPure drying column to remove water from the equilibrated gas and then through an infrared gas analyzer (LICOR Model LI-6251) at a rate of 30 mL min^{-1} alternatively with the atmospheric gas samples. Each sample was measured over a 3-min time interval. Calibration of the instrument was performed automatically every 2 hours using four CO_2-air gas mixtures consistent with the World Meteorological Organization standards. The precision and accuracy of the pCO_2 measurements is estimated to be ±1% or ± 2-4 μatm. As a check on the internal consistency of the dissociation constants for carbonic and boric acid in seawater used to compute the components of the carbonate system, TA was computed using measured values of temperature, salinity, TCO_2, pCO_2 as described by *Peng et al.* [1987] using the apparent dissociation constants of carbonic acid determined by *Mehrbach et al.* [1973], the boric acid apparent dissociation constant of *Dickson* [1990], and the solubility of CO_2 gas in seawater (*Weiss*, 1974). Nutrient concentrations were assumed to be zero. The total boron concentration of the BIOSPHERE water was determined to be 382.7 μmol kg^{-1} by A. Sanyal (personal communication, 1998) using an isotope-dilution mass spectrometric method (*Hemming and Hansen*, 1994). Computed TA was consistently less than the measured TA by ~10 μeq kg^{-1}. We believe that this is most likely explained by the presence of organic acid in the water. The aragonite solubility product was computed using the equations given by *Mucci* [1983].

2.5. Calcium Measurements

Water samples for Ca analysis were placed in HCl-washed, sample-rinsed 125 mL polyethylene bottles, acidified with 3 mL of CP grade HNO_3, and shipped to the University of Hawaii for analysis. The calcium ion concentration was determined by EGTA complexometric titration using a Ca^{2+} specific electrode as the detector [Kanamori and Ikegami, 1980]. Three replicate analyses were performed on each seawater sample, and the arithmatic mean was used.

2.6. Calcification Rate Measurements

The net community calcification rate was determined by the alkalinity anomaly method. This method is based on the assumption that precipitation of one mole of $CaCO_3$ reduces the total alkalinity by two equivalents. Deviations from this simple stoichiometry can occur in response to production and degradation of organic carbon through assimilation and remineralization of nitrate [*Brewer and Goldman*, 1976]. However, these fluxes are minor in the biogeochemical budgets of calcifying systems [*Smith and Atkinson*, 1983]. *Chisholm and Gattuso* [1991] made a comparison of calcification rates measured by complexometric titration of Ca with EGTA and the alkalinity anomaly method with and without correction for changes in nutrient concentrations. Their results confirmed that the assumptions of the alkalinity anomaly technique are fundamentally correct. Calcification rates were determined by linear regression through a week or more of TA data except when the rates were very high and changing rapidly with time in which case fewer days where used in the linear regression. This approach yields the average net calcification rate and an estimate of the variability over the specified period. For all cases expect one (Table 4, June 23, 1995), three or more data points were used for the regression analysis.

$$G = (-0.5)(2650/750)\Delta TA / \Delta t,$$

where G is the net calcification rate in mmol $CaCO_3$ m^{-2} d^{-1}, 2650/750 is the ratio of the volume of water to the area of live benthos, and $\Delta TA/\Delta t$ is the change in total alkalinity in meq m^{-3} per unit time.

2.7. Production and Respiration Rate Measurements

The net community production was computed by the method of oxygen mass balance. Using oxygen sensor data which had been calibrated against Winkler determined oxygen, the finite difference form of the differential equation describing the oxygen mass balance in the BIOSPHERE coral reef biome was summed over a 24-hour period:

$$NP = \sum_{i=1}^{96} (2650/750)(O_i - O_{i-1}) + \frac{2.1}{96}(O_i - C_i^*),$$

where 2650/750 is the ratio of the volume water to surface area of live benthos in meters, O_i is the oxygen concentration at time i in mmol m^{-3}, 2.1 is the gas exchange coefficient in m d^{-1} estimated by injecting O_2 gas into the water and observing

the rate of re-equilibration with the atmosphere, 96 is the number of 15-min time steps in a day, and C_i^* is the solubility of oxygen in the water at time i. The equations of *Benson and Krause* [1984] were used to compute C^* as a function of temperature and salinity at sea level and then a factor of ($_bP$/1013.25) was applied to correct C^* to the barometeric pressure ($_bP$ in millibars) measured at BIOSPHERE. Daily respiration (R) was computed by averaging hourly net production (NP) over the 0000-0500 LT and 1800-2400 LT periods and expressing the rate on a 24-h basis. The gross production (GP) was computed as the sum of NP and R.

3. Results and Discussion

Before presenting the results of the saturation state manipulation experiments, we briefly present some of the chemical data we collected that show that the BIOSPHERE coral reef mesocosm is behaving like the natural systems we are trying to understand. A representative portion of the TA and TCO_2 time series is given at full temporal resolution in Table 3. The impact of biological processes on the carbonate chemistry of the water is readily apparent. TCO_2 and TA decrease during the day due to the combined effects of photosynthesis and calcification. During the night, TCO_2 increases due to respiration, while TA decreases at a reduced rate indicating that calcification continues in the dark but at a reduced rate. The ratios of light:dark calcification (1.3-2.6), calcification:gross production (0.2-0.3), and production:respiration ratio (0.8-1.1) all look reasonable for a coral reef [*Gattuso et al.*, 1999].

The complete 3.8-year time series of Ca^{2+} and CO_3^{2-} are shown in Figure 1. Also shown are the dates when chemical additions were made. Table 2 gives the amounts of $NaHCO_3$, Na_2CO_3, and $CaCl_2$ which were added. Throughout most of the study saturation state was varied by varying CO_3^{2-} while holding Ca^{2+} at an average value of 9.1 mmol kg^{-1} (range 8.0-9.5). However, between July 1997 and July 1998, we allowed both Ca^{2+} and CO_3^{2-} to vary, and at the end of that period we produced a large sudden increase in Ca^{2+} so that we could observe the effect of an increase in saturation state produced purely by a change in Ca^{2+}. In a relative sense the maximum change in Ca^{2+} (36%) was small compared to the 270% change in CO_3^{2-} concentration. As a result, saturation state strongly tracks CO_3^{2-} in this study.

The time series can be separated into three periods based on the average CO_3^{2-} concentration. We controlled the CO_3^{2-} concentration in a time average sense by adjusting the frequency of additions and the amounts of chemicals added. Note how the period between chemical additions, indicated by the vertical bars along the time axis, varied from an average of 105 days during the first period to 62 days during the second and 7 days during the third. During the "low" period between March 17, 1995, and June 30, 1997, the average CO_3^{2-} concentration was 138±29 (1σ) μmol kg^{-1}. During the "intermediate" period between July 3, 1997, and Nov. 12, 1998, the the average CO_3^{2-} concentration was 245±63 μmol kg^{-1}. During the "high" period between February 2 and March 30, 1999, the average CO_3^{2-} concentration was 369±46 μmol kg^{-1}. The corresponding average aragonite saturation states for the three periods were 1.6±0.3, 3.1±0.7, and 5.2±0.7.

Figure 2 shows the TA time series. These are the data used to compute the community calification rates. The low, intermediate, and high CO_3^{2-}/saturation state phases of the study are indicated by the horizontal reference lines. The calcification rate is simply proportional to the time rate of change of TA. It is visually apparent that the rate of change increased as the CO_3^{2-}/saturation state increased from low to intermediate to high. It is also seen from the nonlinearity of the time trend that the rate of change decreased with time following individual chemical additions. Table 4 summarizes how the net community calcification rate varied over the course of the study. The time series was broken up into 42 time periods. The time periods average 20 days but are quite variable in length. When the CO_3^{2-}/saturation state was low, the TA changes tended to occur slowly, so we averaged the chemical variables and calcification rates over a longer time period. When the CO_3^{2-}/saturation state was high the chemical conditions tended to change rapidly, and we shortened the averaging period so that we could capture the

Table 3. Rates of Production and Calcification on the BIOSPHERE-2 Coral Reef

Date, Time	TCO_2, μmol kg^{-1}	TA, μeq kg^{-1}	NP, μmol C L^{-1} h^{-1}	GP, μmol C L^{-1} h^{-1}	Calcif., μmol $CaCO_3$ L^{-1} h^{-1}	NP, μmol C L^{-1} d^{-1}	Calcif/GP	L:D	P:R
Feb. 19, 1999, 0817 LT	1969	2503							
Feb. 19, 1999, 1702 LT	1918	2468	5.6	6.7	2.0		0.30	1.4	
Feb. 20, 1999, 0842 LT	1935	2424	-1.2		1.4	-6			0.8
Feb. 20, 1999, 1656 LT	1881	2395	6.4	7.5	1.8		0.23	1.3	
Feb. 21, 1999, 0848 LT	1897	2352	-1.1		1.4	2			1.1
Feb. 21, 1999, 1722 LT	1846	2324	5.8	7.5	1.6		0.22	2.6	
Feb. 22, 1999, 0829 LT	1871	2305	-1.7		0.6	2			1.1
Daily average						-1	0.25	1.8	1.0

NP and GP are net and gross organic carbon production. Calcif./GP is the ratio of calcification to gross production during the light period. L:D is the light to dark calcification ratio. P:R is the ratio of gross production to respiration on a daily basis.

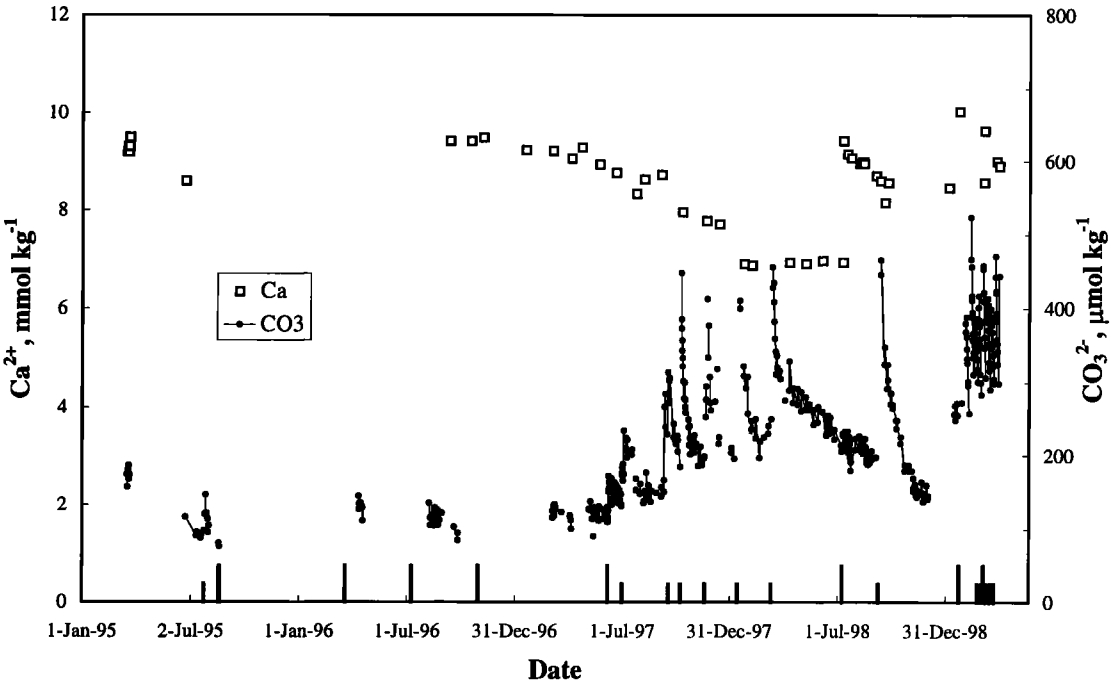

Figure 1. Time series of Ca^{2+} and CO_3^{2-} concentrations. The short vertical bars along the ordinate indicate when HCO_3^- and CO_3^{2-} were added, and the long bars indicate when Ca^{2+} was added.

performance of the system at several levels as the saturation state fell.

The calcification time series is shown in Figure 3. Several features are readily apparent. First, there is a clear positive response to the long-term changes in mean saturation state. Second, a tight coupling to relatively small changes in saturation state on a monthly to bimonthly timescale is readily apparent (Figure 3 inset). The long-term calcification rates are 5.3±6 (N=10), 40±14 (N=28), and 115±10 (N=36) mmol $CaCO_3$ m^{-2} d^{-1} for the low, intermediate, and high saturation

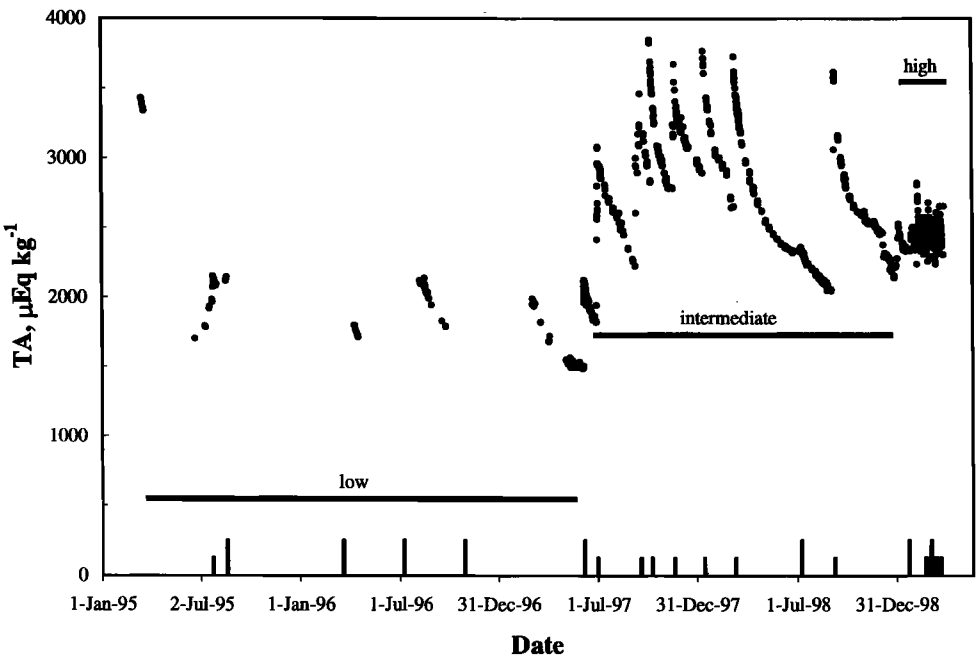

Figure 2. Time series of total alkalinity (TA). The horizontal reference lines indicate the step changes in saturation state. The vertical bars along the ordinate denote when and what type of chemical addition occurred as explained in the legend for Figure 1.

Table. 4 Summary of Measurements of Net Community Calcification Rate and Average Light and Chemical Conditions Over the Period of Measurement

Dates		Light, mol m^{-2}	TA, $\mu eq\ kg^{-1}$	TCO_2, $\mu mol\ kg^{-1}$	pCO_2, μatm	pH	Ca^{2+}, $mmol\ kg^{-1}$	CO_3^{2-}, $\mu mol\ kg^{-1}$	HCO_3^-, $\mu mol\ kg^{-1}$	Ω_{arag}	ICP, $(mol/kg)^2$	G, mmol $CaCO_3$ $m^{-2}\ d^{-1}$
Mar. 16,1995	Mar. 21, 1995	11.9	3384	3200	1394	7.88	9.27	174.5	2981.3	2.43	1.62E-06	32.7
Mar. 21,1995	June 23, 1995	16.7	2517	2331	890	7.97	9.14	146.0	2160.3	2.01	1.33E-06	8.7
June 23,1995	July 11, 1995	20.3	1743	1591	571	7.97	8.66	104.1	1471.0	1.35	9.01E-07	-2.6
July 11, 1995	July 24, 1995	23.2	1877	1753	777	7.88	8.77	93.3	1638.1	1.23	8.18E-07	-8.0
July 25, 1995	Aug. 1, 1995	20.4	2101	1929	713	7.94	8.78	118.4	1797.0	1.56	1.04E-06	14.8
Aug. 1, 1995	Aug. 19, 1995	14.8	2120	2019	1160	7.78	8.83	87.9	1920.5	1.17	7.76E-07	-3.6
Apr. 9, 1996	Apr. 17, 1996	23.2	1748	1548	416	8.09	8.98	131.7	1404.6	1.78	1.18E-06	20.1
Aug. 7, 1996	Sep. 25, 1996	20.1	1834	1694	688	7.92	9.34	101.0	1573.9	1.42	9.43E-07	2.9
Mar. 4, 1997	Apr. 5, 1997	16.3	1861	1686	555	8.01	9.15	121.2	1549.1	1.67	1.11E-06	16.1
Apr. 5, 1997	May 5, 1997	22.4	1633	1456	443	8.05	9.01	113.7	1329.8	1.54	1.02E-06	2.8
May 5, 1997	June 6, 1997	23.2	1510	1314	337	8.11	8.89	120.2	1184.1	1.61	1.07E-06	0.8
June 7, 1997	June 30, 1997	22.3	1941	1724	458	8.09	8.80	151.6	1554.2	2.01	1.33E-06	6.1
July 3, 1997	July 17, 1997	23.2	2906	2643	739	8.04	8.62	209.1	2412.0	2.71	1.80E-06	27.3
July 17, 1997	Sep. 9, 1997	18.8	2523	2303	842	7.96	8.55	154.8	2136.6	1.99	1.32E-06	17.9
Sep. 19, 1997	Sep. 26, 1997	14.2	3249	2905	773	8.10	8.60	258.5	2655.5	3.34	2.22E-06	78.6
Sep. 26, 1997	Oct. 8, 1997	15.8	3004	2726	811	8.05	8.47	218.4	2496.8	2.78	1.85E-06	45.2
Oct. 9, 1997	Oct. 12, 1997	15.1	3548	3143	623	8.20	8.03	345.1	2772.3	4.17	2.77E-06	117.2
Oct. 12, 1997	Oct. 16, 1997	14.7	3347	2984	710	8.14	7.82	288.2	2684.9	3.39	2.25E-06	77.6
Oct. 23, 1997	Nov. 13, 1997	22.7	2913	2619	790	8.05	7.61	212.4	2421.5	2.43	1.62E-06	24.8
Nov. 21, 1997	Nov. 26, 1997	8.1	3468	2982	566	8.23	7.69	357.5	2651.1	4.13	2.75E-06	111.9
Nov. 26, 1997	Dec. 1, 1997	7.2	3287	2982	717	8.13	7.60	280.8	2670.5	3.21	2.13E-06	25.2
Dec. 1, 1997	Dec. 18, 1997	6.6	3154	2895	729	8.10	7.62	258.4	2596.6	2.84	1.97E-06	19.4
Jan. 2, 1998	Jan. 12, 1998	6.8	2942	2693	832	8.03	7.64	203.8	2473.4	2.34	1.56E-06	17.5
Jan. 14, 1998	Jan. 20, 1998	6.8	3644	3191	526	8.28	7.55	405.3	2770.8	4.60	3.06E-06	85.9
Jan. 20, 1998	Jan. 29, 1998	7.8	3310	2910	611	8.17	6.96	297.5	2594.6	3.11	2.07E-06	50.1
Feb. 5, 1998	Feb. 19, 1998	8.2	2983	2709	733	8.08	6.86	229.1	2449.4	2.36	1.57E-06	10.6
Feb. 26, 1998	Mar. 10, 1998	15.1	2728	2415	548	8.16	6.84	236.7	2162.9	2.44	1.62E-06	40.0
Mar. 11, 1998	Mar. 15, 1998	12.9	3565	3040	414	8.32	6.89	422.1	2615.4	4.38	2.91E-06	124.7
Mar. 15, 1998	Mar. 26, 1998	15.0	3278	2880	548	8.22	6.90	326.1	2548.1	3.39	2.25E-06	52.0
Mar. 26, 1998	Apr. 16, 1998	18.7	2919	2566	471	8.08	6.93	285.7	2269.1	2.97	1.98E-06	28.0
Apr. 16, 1998	May 7, 1998	24.4	2650	2299	401	8.09	6.86	266.6	2016.7	2.75	1.83E-06	16.3
May 7, 1998	May 28, 1998	25.2	2479	2142	366	8.08	6.87	253.4	1867.2	2.62	1.74E-06	11.1
May 28, 1998	June 25, 1998	26.4	2364	2050	364	8.05	6.95	231.8	1572.5	2.42	1.61E-06	5.2
July 10, 1998	July 22, 1998	23.8	2284	1986	383	8.02	9.27	223.3	1737.6	3.11	2.07E-06	15.7
July 22, 1998	Aug. 11, 1998	22.8	2194	1916	397	8.03	9.49	190.8	1708.1	2.72	1.81E-06	8.7
Aug. 11, 1998	Aug. 26, 1998	23.5	2110	1831	368	8.03	9.45	187.4	1634.7	2.67	1.77E-06	7.1
Aug. 26, 1998	Sep. 3, 1998	21.9	2065	1797	366	8.11	8.87	195.0	1597.8	2.60	1.73E-06	3.8
Sep. 10, 1998	Sep. 22, 1998	20.9	3227	2784	457	8.05	9.03	366.6	2405.3	4.66	3.31E-06	95.0
Sep. 22, 1998	Oct. 1, 1998	21.1	2893	2544	495	7.96	8.44	287.8	2242.8	3.66	2.43E-06	30.0
Oct. 1, 1998	Oct. 22, 1998	16.0	2694	2405	580	7.96	8.01	236.1	2157.3	2.99	1.89E-06	19.0
Oct. 22, 1998	Nov. 12, 1998	10.9	2561	2364	821	7.81	8.29	163.4	2179.5	2.04	1.35E-06	7.4
Feb. 2, 1999	Mar. 30, 1999	14.8	2463	1929	192	8.30	9.15	375.0	1549.0	5.16	3.43E-06	114.0

E-06 denotes 10^{-6}.

state treatments, respectively, where N is the number of measurements and the uncertainties are the 95% confidence intervals. Each treatment is significantly different from the other at P=0.0001 according to a Student's t test.

Clearly, our manipulations of water chemistry are having a large impact on community calcification, and the response is exceeding the normal seasonal and interannual variability of the system. In order to better understand the data in Figure 3, we examine the results of a short piece of the time series in detail. By looking at a short period of time, we minimize the potential effects of seasonal changes in light and biomass and get the clearest picture of the impact of the chemical changes. In Figure 4 we show the response of calcification to a calcium addition on July 9, 1998, and a carbonate/bicarbonate addition

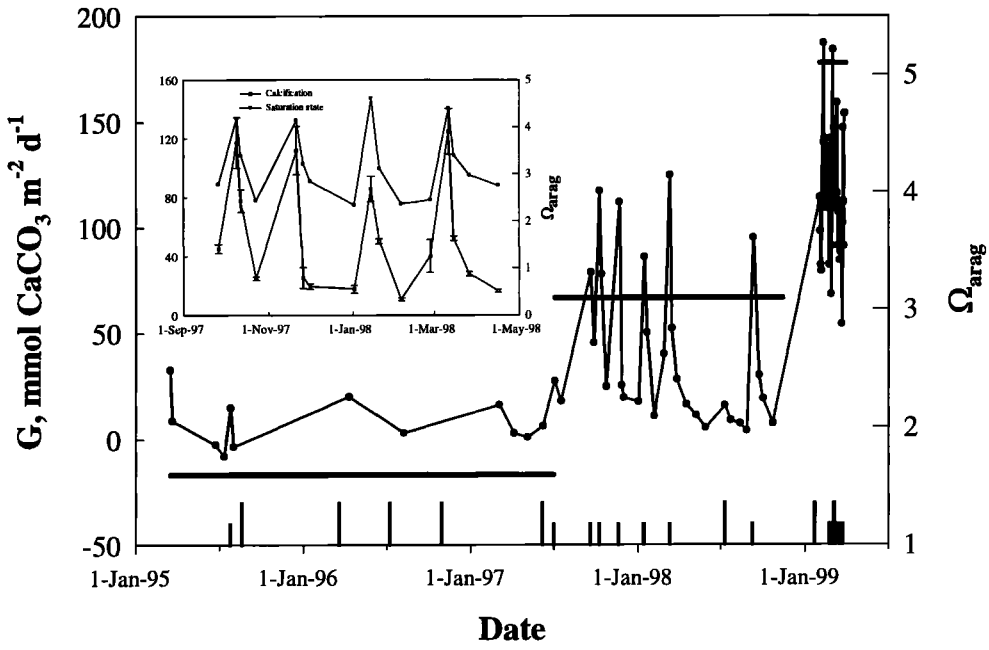

Figure 3. Time series of net community calcification rate (G) in mmol $CaCO_3$ m^{-2} d^{-1} where m^{-2} is the area of live benthos. The step level changes in the calcium carbonate saturation state of aragonite (Ω_{arag}) are indicated by the horizontal reference lines. For reference, Ω_{arag} is 3.5-4.1 in the present day ocean where well-developed coral reefs are found [*Kleypas et al.*, 1999b]. During the last glacial maximum 18,000 years ago the Ω_{arag} is thought to have been ~5.7 and by the year 2065 the Ω_{arag} is predicted to decline to 3.1. The inset shows the variations in saturation state and calcification rate in detail for the period September 1997 through April 1998. Note the tight coupling that exists between changes in saturation state and calcification rate even for relatively small changes in saturation state.

on September 8, 1998. In order to test the effect of a change in Ca^{2+} we first let the Ca^{2+} concentration decline to ~7 mmol kg^{-1} by not adding $CaCl_2$ to the system for almost 1 year. Then on July 9, 1998, we added 726 kg of $CaCl_2 2H_2O$ to the tank. The observed increase in Ca^{2+} concentration of 2.48 mmol kg^{-1} was in excellent agreement with the expected increase of 2.41. Figure 4 shows the response of the system. In response to the 36% increase in Ca^{2+} concentration from 6.9 to 9.4 mmol kg^{-1}, there was an almost immediate increase in the rate of calcification. The rate of net community calcification increased 2.9-fold from 5.2±0.4 mmol $CaCO_3$ m^{-2} d^{-1} just before the addition to 15.7±0.8 mmol $CaCO_3$ m^{-2} d^{-1} just after the addition. The CO_3^{2-} concentration over the same period dropped from 242 to 221 μmol kg^{-1}.

Two months later the CO_3^{2-} concentration was increased by addition of $NaHCO_3$ and Na_2CO_3. A total of 87 kg of $Na_2CO_3 H_2O$ and 222 kg of $NaHCO_3$ were added. The predicted increase in TA was 1527 μeq kg^{-1} compared to the observed increase of 1565. The predicted increase in TCO_2 was 1262 μmol kg^{-1}, compared to the observed increase of 1293. The agreement is well within the uncertainties of the amounts added and the volume of the tank. The addition increased the CO_3^{2-} concentration from 198 to 446 μmol kg^{-1}. There was an abrupt increase in the calcification rate from 7.5 to 92 mmol $CaCO_3$ m^{-2} d^{-1} coincident with the increase in CO_3^{2-} concentration. Was the response due to the change in CO_3^{2-} or some other aspect of the carbonate system that was changed by the chemical addition? There were also increases in HCO_3^- from 1597 to 2405 μmol kg^{-1} and in $(CO_2)_{aq}$ from 10.2 to 12.7 μmol kg^{-1}. It is conceivable that photosynthesis of the corals and coralline algae was carbon limited and that the increased availability of $(CO_2)_{aq}$ or HCO_3^- spurred higher rates of photosynthesis as has been suggested by *Marubini and Thake* [1999]. This could have resulted in a higher rate of calcification because photosynthesis and calcification are often observed to be coupled. However, the slight, statistically insignificant, increase we observed in the rate of gross production could not possibly account for the 12-fold increase in the rate of calcification. The average gross production during the period August 26-Sep. 3, 1998, was 281±47 mmol O_2 m^{-2} d^{-1} compared to 304±97 during the period September 10-22, 1998, just after the HCO_3^-/CO_3^{2-} addition.

The previous results indicate that we are seeing a direct response of calcification to the altered Ca^{2+} and CO_3^{2-} concentrations. It is of interest to explore the functional form of the Ca^{2+} and CO_3^{2-} dependence of community calcification. Again we focus on the data from the July 9 and September 8, 1998, experiments which occurred close together and in which large changes in Ca^{2+} and CO_3^{2-} concentration were observed. Figure 5 shows the relationship between calcification rate and CO_3^{2-} concentration for the same period shown in Figure 4. The decline in calcification rate between April 2 and June 25, 1998, is explained by the decrease in CO_3^{2-} concentration as evidenced by the tight linear relationship between calcification and CO_3^{2-} (r^2=0.98). Following the increase in Ca^{2+} concentration on July 9, 1998, the relationship shifts so that comparable rates are achieved at CO_3^{2-} concentrations which are ~20-25% lower than at the lower Ca^{2+} concentration. Two months after the Ca addition,

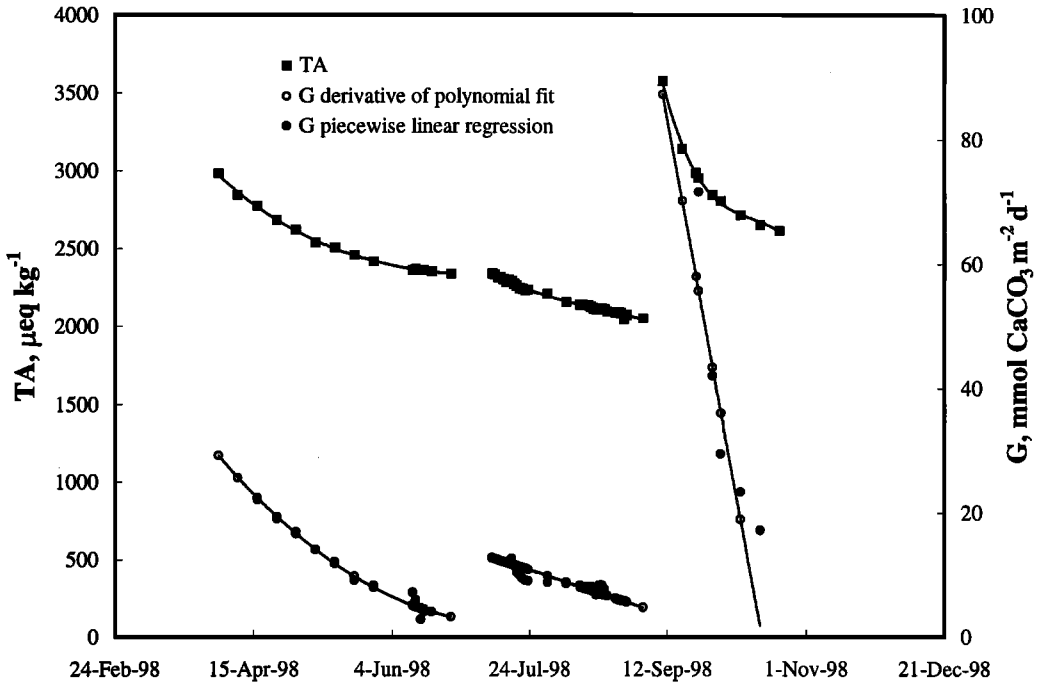

Figure 4. TA time series for the period April 2 to October 22, 1998, showing the response to a 2.4 mmol kg^{-1} Ca^{2+} increase on July 9, 1998 and a 248 μmol kg^{-1} increase in CO_3^{2-} on September 8, 1998. Calcification rates were computed in two ways. The solid circles were computed from the slopes of linear regressions through 5-15 successive TA values. The open circles were computed by fitting a 2nd or 3rd order polynomial to all the TA data between additions and differentiating with respect to time.

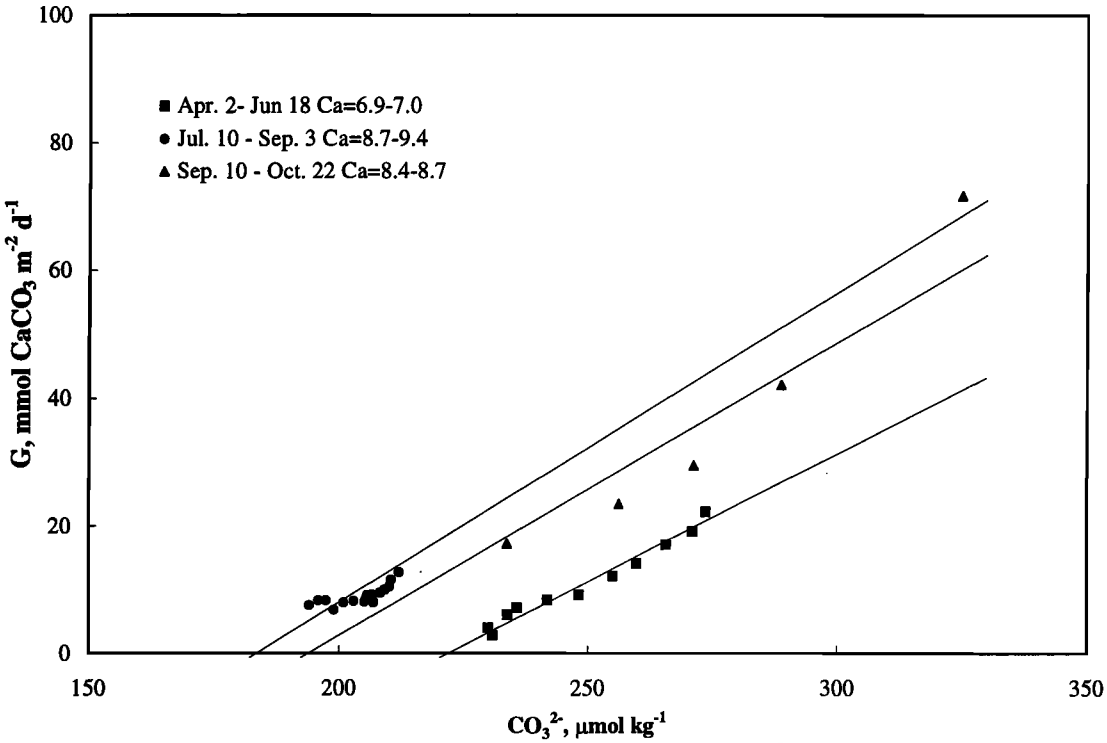

Figure 5. Relationship between net community calcification rate (G) and CO_3^{2-} concentration for the period of time covered by Figure 4. The data are segregated into three periods of time corresponding to different concentrations of Ca^{2+}. The solid squares correspond to the period between April 2 and June 25 when $[Ca^{2+}]$ was 7.0-6.9 mmol kg^{-1}, the solid circles correspond to the period between July 10 and September 3 when $[Ca^{2+}]$ was 9.4-8.7, and the solid triangles correspond to the period September 10 to October 22 when the $[Ca^{2+}]$ had declined to 8.7-8.4. The three lines show the expected G-CO_3^{2-} relationship as a function of $[Ca^{2+}]$ based on the rate expression obtained in Figure 6.

the Ca^{2+} concentration was 8.7 mmol kg^{-1}, and by October 22 it had fallen to 8.4 mmol kg^{-1}. Note how the data points in Figure 5 for the period September 10 – October 22, when Ca^{2+} was 8.4-8.7 mmol kg^{-1}, tend to fall between the data points when Ca^{2+} was 6.9-7.0 (April 2- June 25) and 8.7-9.4 (July 10- September 3). Clearly, the calcification rate-carbonate ion concentration relationship is affected by the Ca^{2+} concentration.

The three-fold calcification increase in response to the Ca^{2+} addition and the shifts in the calcification-carbonate relationship tend to support the hypothesis that coral reef calcification is dependent on $[Ca^{2+}][CO_3^{2-}]$ or some closely related quantity. We explored rate expressions of several different forms starting with one of the form

$$G = k[Ca^{2+}][CO_3^{2-}] + C, \quad (2)$$

where G is the calcification rate in mmol $CaCO_3$ m^{-2} d^{-1} and k is a factor that would depend on the areal biomass of calcifying organisms and physical environmental conditions such as temperature, light, and flow rate. C does not have any biological significance, but the quantity $-C/k$ corresponds to the ion concentration product at which net calcification is equal to zero. Rate expressions of this form have been used to describe the kinetics of chemical precipitation of $CaCO_3$ in seawater. A fit of this expression to the data shown in Figure 5 yielded k=4.45 x 10^7 and C= -70.2. The r^2 was 0.88 indicating that the expression explained most of the combined effects of Ca^{2+} and CO_3^{2-} on calcification. However, it was clear that the expression was over correcting for the dependence of Ca^{2+} as indicated by the fact that the residuals plotted versus Ca^{2+} were not randomly distributed. It is well known that the response of calcification to Ca^{2+} tends to saturate at a concentration of around 10 mmol kg^{-1} [*Ip and Krishnaveni*, 1991; *Tambutte et al.*, 1996; *Gattuso et al.*, 1998]. We therefore experimented with ways to build more biological realism into the rate expression. The form the expression that worked best was

$$G = k[Ca^{2+}]^n[CO_3^{2-}] + C. \quad (3)$$

When n<1, the change in G for given change in Ca^{2+} decreases as Ca^{2+} increases. This is a simple way of representing a saturating response. A nonlinear regression fitting program (SigmaPlot) was used to fit the April 2 – October 22, 1998, data set to (3). The r^2 was 0.93, and the best fit parameter values were k=1.2±0.3 x 10^7, n=0.69±0.04, and C= -89±4. A zero net calcification rate will occur when $[Ca^{2+}]^{0.69}[CO_3^{2-}] = -C/k$ or 7.23 x 10^{-6}. At a $[Ca^{2+}]$ of 10.12 mmol kg^{-1}, typical of seawater, zero net calcification would occur at a $[CO_3^{2-}]$ of 172 µmol kg^{-1}. For comparison, the concentration of CO_3^{2-} at equilibrium with aragonite at 25°C, 35 ppt, 1 atm, and $[Ca^{2+}]$ of 10.12 mmol kg^{-1} is 73 µmol kg^{-1}. It is interesting that such a large super saturation is required for net calcification in our system. More experimentation is required to see if this is representative of other communities.

It can be seen in Figure 6 that the quantity $[Ca^{2+}]^{0.69}[CO_3^{2-}]$ explains well the variability in community calcification rate over the range of Ca^{2+} and CO_3^{2-} concentrations tested. An F test confirmed that (3) explained significantly more of the observed variability in calcification than (2) at P=0.05. However, the difference between the two models is small, and it will be necessary to collect data over a wider range of Ca^{2+} concentrations to be able to decide conclusively if the extra

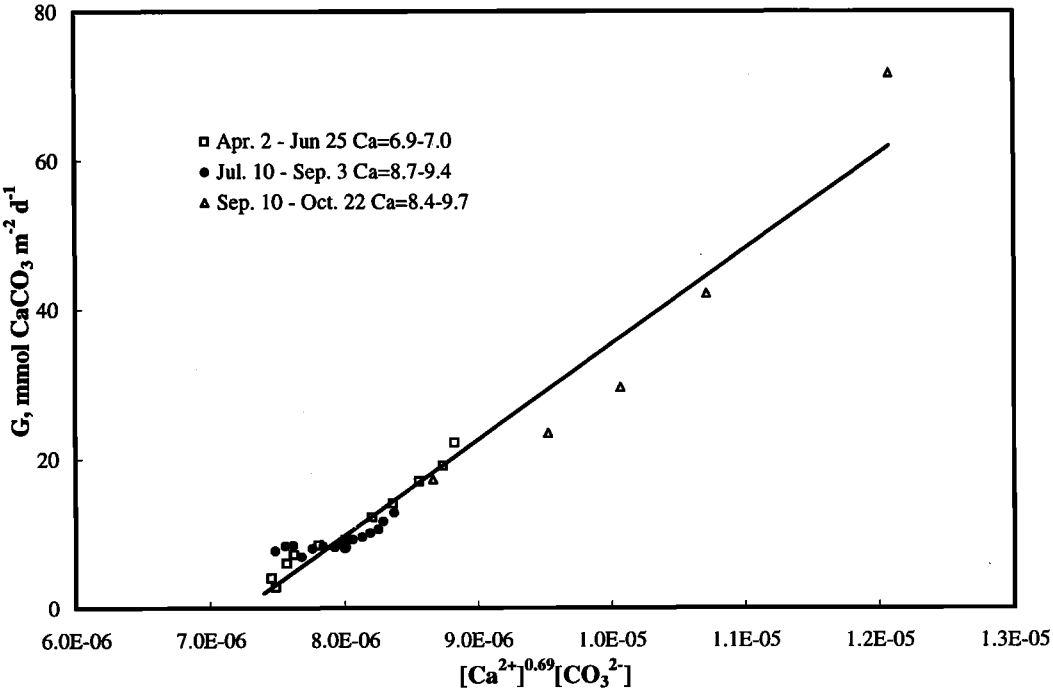

Figure 6. The relationship between net community calcificate rate (G) and ion concentration product $[Ca^{2+}]^{0.69}[CO_3^{2-}]$ for the same data shown in Figure 4. The solid line represents the best fit of equation (3) to the data where k=1.2±0.3 x 10^7, n=0.69±0.04, and C= -89±4. The uncertainities are standard errors.

parameter is justified. Regardless of the correct form of the rate expression, it is clear from the observed interactions of Ca^{2+} and CO_3^{2-} that saturation state or some closely related quantity has a controlling effect on community calcification. The form of the rate expression is not of importance from a practical standpoint because the Ca^{2+} concentration is nearly constant in most natural environments; however, it is of interest from a theoretical standpoint because it provides a mechanism for the strong CO_3^{2-} dependence of calcification, which is of great practical importance. To be consistent with earlier literature, we will continue to talk about saturation state in terms of the quantity, Ω_{arag}; however, it should be borne in mind that in systems where Ca^{2+} varies by more than 30%, the quantity $[Ca^{2+}]^{0.69}[CO_3^{2-}]$ may describe the kinetics more reliably.

In order to get a sense of whether the response of community calcification rate to a change in saturation state is dependent of the timescale of the change, we compared the response to a series of short-term changes in saturation state over the period September 26, 1997 to April 16, 1998, with the response to the long-term changes in saturation state. Starting in September 1997, there was a series of experiments where the saturation state was allowed to drop to 2.6±0.2, and then an addition of HCO_3^-/CO_3^{2-} was made sufficient to raise the saturation state to an average of 4.3±0.2 (inset Figure 3). This sequence was repeated 4 times. These data points are indicated by the open squares in Figure 7 and represent the response of the community to short-term changes saturation state. The r^2 for the regression through these data is 0.82. The data points indicated by the solid circles were determined by averaging the calcification rates given in Table 4 over the low (Ω_{arag} 1.6±0.3 for 2.3 years), intermediate (Ω_{arag} 3.1±0.7 for 1.3 years), and high saturation state (Ω_{arag} 5.2±0.7 for 1.9 months) phases of the study. The data points represent the mean response of the community to long-term exposure to different saturation states. The r^2 of the regression through the long-term data points is 0.98. The agreement between the short-term and long-term responses to saturation state is critical. If the community experienced stress or if the organisms possessed the capacity to acclimate to lower or higher saturation states, we would expect the slope of the long-term relationship to be significantly flatter than the short-term relationship. Also, it might have been argued that the long-term changes in community calcification were unrelated to our manipulations of saturation state and merely reflected a long-term increase in the biomass or activity of the calcifying organisms. However, by showing that we can manipulate the saturation state repetitively between two levels over a 200-day period and reproduce essentially the same response rules out coincidence beyond all reasonable doubt.

The regression through the short-term points in Figure 7 predicts a 48% decline in calcification if Ω_{arag} drops from 4.0 to 3.1, i.e., the predicted drop between 1880 and 2065. The regression through the long-term points predicts a 37% decrease for the same change in Ω_{arag}. The difference in the slopes of the two lines suggests that some acclimation to a suboptimal saturation state may occur. However, the difference is not statistically significant at P=0.05, and we are

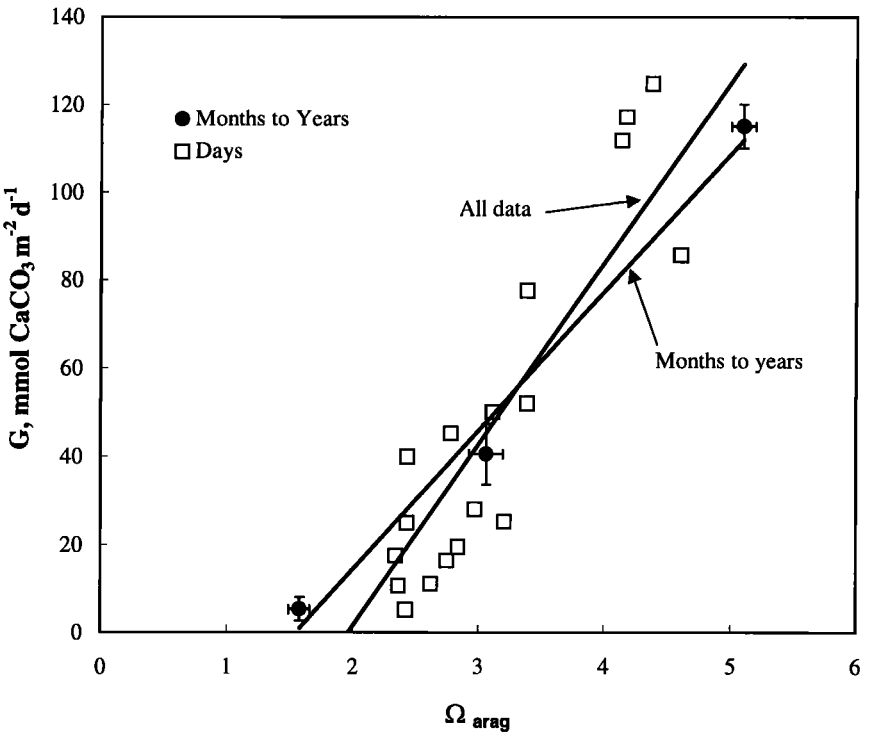

Figure 7. Comparison of the response of calcification to changes in saturation state on timescale of days and months to years. The equation for the best fit line through combined short- and long-term data is $G = 41.56 \cdot \Omega_{arag} - 81.9$, r^2=0.82. The equation for just the long-term data is $G = 32.04 \cdot \Omega_{arag} - 49.7$, r^2=0.98. Not shown is the best fit line for the short-term data $G = 47.72 \cdot \Omega_{arag} - 101.4$, r^2=0.82. Error bars on the long term points are ±1 SE.

forced to conclude there is no evidence of significant acclimation occurring in the BIOSPHERE coral reef.

Efforts to explain the residual variability in terms of the other measured variables, i.e., light, pH, and HCO_3^-, has so far proven unsuccessful. The lack of a strong effect of light is particularly surprising because it is well known that light is an important factor in regulating calcification. If we compare day and night time calcification rates, we see that rates are higher in the light by a factor of up to 3 (Table 3). Also, over short periods of time, we do see depressed calcification rates on very overcast days. So we do see evidence of a light effect in our data at the hourly and daily timescales. We think that the importance of light at the seasonal timescale is obscured by changes in the biomass of the dominant calcifier, *Amphiroa*, which qualitatively is more abundant during the winter when light is lowest and least abundant in the summer when light is highest.

Before discussing the results of our experiments, we briefly discuss the basis for our assumption that the alkalinity changes we observe in the BIOSPHERE coral reef biome are due to calcification by the corals and calcareous algae and not due to inorganic chemical processes. There are two concerns: first that some of the observed decrease in alkalinity is due to inorganic precipitation of $CaCO_3$ and second that there is an input of alkalinity from the sediment. We address the first concern by noting that we have evidence that on average the rate of decline of TA during the daylight period is 1.3- to 2.6-fold greater than the decline during the night (Table 3). This is evidence that the $CaCO_3$ precipitation is biologically mediated because it is well known that calcification of corals and coralline algae are enhanced in the light by a factor of 1-5 [*Gattuso et al.*, 1999]. Conversely, nonbiological precipitation would not be expected to be light dependent. We also have the evidence that community calcification varies as the 0.69 power of the $[Ca^{2+}]$. This is consistent with work which has shown that biological calcification exhibits a saturation response to Ca^{2+} [*Ip and Krishnaveni*, 1991; *Tambutte et al.*, 1996; *Gattuso et al.*, 1998]. Inorganic precipitation would not exhibit a saturating response to Ca^{2+}.

The second concern was that there might be a significant flux of alkalinity out of the sediments due to dissolution of carbonate sediments. Dissolution occurs only when the bottom water or pore water in the case of sediments becomes undersaturated with respect to the carbonate minerals present. *Broecker et al.* [1979] showed that pCO_2 must increase to 1760 and 2860 μatm, respectively, before the surface seawater becomes undersaturated with respect to aragonite and calcite. In addition to calcite and aragonite, high magnesium calcite produced by the red coralline alga Amphiroa is an important form of carbonate in the BIOSPHERE tank. The solubility of *Amphiroa rigida* (22% mol % $MgCO_3$) in seawater at 25°C was determined by *Bischoff et al.* [1987]. They defined the ion activity product (IAP) as

$$IAP_{Mg-Calcite} = (a_{Ca^{2+}})^{(1-x)}(a_{Mg^{2+}})^{x}(a_{CO_3^{2-}}),$$

where a is the activity of the ion in solution and x is the mole fraction of $MgCO_3$ in the solid phase. Using the value of $IAP_{Mg\text{-}Calcite}$ ($10^{-8.08}$) determined by *Bischoff et al.* [1987] and the activities of Mg^{2+} and Ca^{2+} in seawater estimated using the modified Garrels-Thompson complex ion model of seawater [*Garrels and Thompson*, 1962; *Simpson and Takahashi*, 1973], we computed the concentration of CO_3^{2-} at saturation with 22 mol % $MgCO_3$ to be 84 μmol kg^{-1}. This means that the high magnesium calcite produced by *Amphiroa* is only 12% more soluble than aragonite. The pCO_2 of the water in the BIOSPHERE tank has ranged from 200 to 1100 μatm during our study, except for a brief period in March 1995 when it reached 1400 μatm. The average pCO_2 during our study was 560 μatm. We conclude that pCO_2 has never risen high enough or CO_3^{2-} has dropped low enough to cause dissolution of high magnesium calcite or aragonite. The lack of dissolution on the bottom is further evidenced by the accumulation of Amphiroa that collects on the bottom and is periodically removed by divers. It is possible that some metabolically induced $CaCO_3$ dissolution is occurring in the top few centimeters of sediment. We do not have any direct measurements of this flux in BIOSPHERE, and there do not seem to be any data in the literature for similar shallow coral reef environments in nature. It seems to be the general consensus that little dissolution is occurring in shallow coral reef sediment. This could be explained by the very low net production rate of coral reefs and hence the low organic matter content of coral reef sediment. There is also evidence based on foraminiferal dissolution indices and shell fragmentation that little $CaCO_3$ dissolution occurs above the saturation horizon [*Berger et al.*, 1982; *Peterson and Prell*, 1985]. *Milliman* [1993] assumed that 10% of $CaCO_3$ produced on coral reefs is lost to dissolution. If in fact there is some dissolution occuring in the BIOSPHERE coral reef sediments, the flux would be expected to vary inversely with the saturation state of the overlying water. The result would be that calcification rates at the lowest saturation states would be underestimated somewhat and the rates at high saturation states would be unaffected. This would tend to reduce our estimates of the carbonate ion effect slightly but would not change the conclusions of this study.

A proportional relationship between $CaCO_3$ precipitation rate of a natural body of water and the ion activity product was first observed by *Broecker and Takahashi* [1966] in the Bahama Banks. Eight years later, *Smith and Pesret* [1974] invoked a calcification-ion activity product proportionality as one possible mechanism to explain why calcification in the Fanning Island lagoon was much lower than might be expected based on the standing crop and expected growth rate of corals there. They suggested that certain calcifying organisms (such as corals) might be able to calcify only when the water surrounding them exceeded some minimum $CaCO_3$ ion activity product. They argued that limitation of calcification by the IAP of the bulk water was consistent with models of coral calcification [e.g., *Goreau*, 1959; *Simkiss*, 1964; *Pearse and Muscatine* 1971]. They suggested that some process related to the IAP of the bulk water affected the supply of ions from seawater to the calcification sites of corals and some other calcifiers before any of the internal controls could exert themselves. Since these papers it has become more common to speak about the saturation state (Ω) [*Smith and Buddemeier*, 1992; *Gattuso et al.*, 1998; *Kleypas et al.*, 1999a]. The two terms can be used interchangeably since they are related by a constant, i.e., (1). The results of this study show that for very precise work or to better

understand the underlying mechanism controlling calcification on reefs, it is necessary to move beyond the IAP or Ω to a rate law expression such as (3) which has the $[Ca^{2+}]$ raised to a fractional power to allow for the saturation response of living organisms. However, in most cases in a natural system, the Ca^{2+} will be essentially constant, and in that case ICP, Ω_{arag} or simply $[CO_3^{2-}]$ will suffice to explain the variability.

The results of this ecosystem study are consistent with what is known about the response of individual species. The work of *Borowitzka* [1981], *Agegian* [1985], and *Gao et al.* [1993] has shown that the calcification of coralline algae respond to changes in CO_3^{2-} in a linear fashion and show a sensitivity comparable to that of the BIOSPHERE coral reef, i.e., a –24 to –42% decrease in calcification for the predicted change in CO_3^{2-} between the year 1880 and 2065. Little is known about the response of scleractinian corals to changes in CO_3^{2-}. *Leclercq et al.* (2000) measured the response of calcification of a mixed assemblage of corals in a 150 L aquarium to variations in pCO_2 ranging from 200-1500 µatm. The response was highly variable but suggest a decline in coral calcification of 20% between 1880 and 2065. *Marubini and Atkinson* [1999] measured the growth rate of nubbins of *Porites compressa* based on weight gain in normal seawater and seawater adjusted with HCl to a pH of 7.2. The corals were placed in outdoor aquaria covered with a neutral density screen and received ~80% of natural sunlight. They observed an immediate reduction in growth rate from 18.9 to 9.5 mg d^{-1}. The carbonate ion concentration dropped from 112 to 18 µmol kg^{-1}. When the corals were returned to normal seawater the growth rate rapidly recovered to 16.0 mg d^{-1}. Two points do not tell us about the shape of the response, but if we assume that the response to CO_3^{2-} was linear, the inferred response to the predicted drop in CO_3^{2-} between the year 1880 and 2065 was –28%. *Marubini and Thake* [1999] measured the growth rate of nubbins of *Porites porites* based on weight gain in normal seawater and in seawater to which $NaHCO_3$ had been added sufficient to double the TCO_2 and TA. The addition had the effect increasing the $(CO_2)_{aq}$ by 1/3, the HCO_3^- by a factor of 2, and the CO_3^{2-} by a factor of 3. The growth rate of *Porites porites* in the experimental treatment was observed to be double that in the control. The authors interpreted this experiment as evidence that HCO_3^- is limiting coral calcification at the present day concentration in seawater. However, it is equally pausible that the corals were responding to the change in CO_3^{2-}. If we assume that CO_3^{2-} was limiting the calcification of the coral, the inferred sensitivity to a change in CO_3^{2-} is similar but weaker than that of coralline algae, i.e., a –16% decrease in calcification for the predicted change in CO_3^{2-} between the year 1880 and 2065. The coral nubbins in this experiment were illuminated with metal halide lamps at an irradiance of 200 µmol photons m^{-2} s^{-1}. This is far less than the 1000-2000 µmol photons m^{-2} s^{-1} that would reach corals growing near the surface in a natural reef. We have recently collected data that indicate that the CO_3^{2-} sensitivity of freshly collected Hawaiian corals illuminated with full natural sunlight is comparable to that of coralline algae and of the BIOSPHERE coral reef, i.e., –50% reduction calcification for the predicted change in CO_3^{2-} between the year 1880 and 2065 (C. Langdon and M. Atkinson, in preparation, 2000). Finally, for the past year we have been following the growth response of coral nubbins of the species *Porites compressa* to the same chemical changes we imposed on the BIOSPHERE coral reef as a whole. These experiments are not yet completed, but the data to date indicate that the corals are responding to the changes in CO_3^{2-} similarly to the coralline algae (F. Marubini, personal communication, 2000).

Recognizing that the BIOSPHERE coral reef is algal dominated, can the results of this study be applied to predicting what will happen to real coral reef ecosystems? We believe the answer is yes? Algae are far more important producers of carbonate on reefs than generally thought. *Adey* [1998] has written an excellent review on the subject. He points out that a boring from a back reef at Funa-Futi Atoll showed for the Pleistocene and Holocene that the biotic source of reef carbonate was in order of volume; (1) coralline algae, (2) foraminifera, (3) *Halimeda*, and (4) scleractinian coral. Even in a modern, coral-dominated reef, average coral coverage ranges from 10%-30% [*Dullo et al.*, 1990]. Reef bore holes rarely pass through many meters of solid coral but more characteristically show 50-80% carbonate sand-filled cavities. Corals provide the framework of reefs, but algae provide the sedimentary infill within the reef framework or in the lagoon. This infill is just as important as the coral framework in creating and sustaining the reef environment.

4. Conclusions

Our experiments demonstrate that changes in the concentration of Ca^{2+} and CO_3^{2-} of the bulk water have a large impact on the rate of calcification of the BIOSPHERE-2 coral reef biome. An increase in Ca^{2+} concentration from 6.9 to 9.4 mmol kg^{-1} on July 9, 1998, increased the calcification rate 3-fold, and an increase in CO_3^{2-} concentration from 198 to 446 µmol kg^{-1} on September 8, 1998, increased the calcification rate 12-fold (Figure 4). We were also able to show that the relationship between calcification and CO_3^{2-} concentration varied with the Ca^{2+} concentration and that the interaction of the effects of Ca^{2+} and CO_3^{2-} on calcification could be explained by a rate expression of the form $G=k[Ca^{2+}]^{0.69}[CO_3^{2-}]+C$. This is the strongest "experimental" evidence to date that saturation state (and not pH, pCO_2, HCO_3^-) affects coral reef calcification. Previous organismal level studies have shown that calcification rates of tropical marine calcareous algae were controlled by CO_3^{2-} concentration [*Borowitzka*, 1981; *Agegian*, 1985; *Gao et al.*, 1993] and *Gattuso et al.* [1998] showed that changes in Ca^{2+} affected the calcification of the scleractinian coral *Stylophora pistillata*. However, to our knowledge, there have been no prior studies where both CO_3^{2-} and Ca^{2+} were manipulated and the effect on calcification rate of the organism or community was observed.

We examined the possibility that the unnatural rapid increases in saturation state caused by our chemical additions were shocking or stressing the calcifying organisms into showing a response to saturation state that would not occur if the change was more gradual. We raised the saturation state 25% higher than the present day ocean and observed that the community calcification rate promptly rose to the expected

rate based on our "transient" experiments and sustained that rate for the 2-month period of observation. We conclude that there is no evidence of a stress response. This experiment is the first of a proposed 2 year series where we will alternate the pCO_2 of the water between 200, 350, and 700 µatm at 4 month intervals in an attempt to conduct a more natural simulation of the changes in CO_2 and saturation state. These longer experiments will also allow us to observe changes in growth rates of individual corals and alga in addition to community metabolism.

Our results predict that coral reef calcification will decrease between 1880 and 2065 due to the effect of rising CO_2 and temperature on saturation state. Our data indicate that significant acclimation to a reduced saturation state will not occur. The best guess based on our long-term data is a 40% decline in calcification rates by 2065. We caution that these results are biased toward reef environments characterized by a high percentage of calcareous algal cover. Reefs characterized by a high percentage of hard coral cover may be more or less sensitive to elevated CO_2. We are currently conducting experiments at BIOSPHERE-2 to look at the effect of elevated CO_2 specifically on corals and possible interactions with light.

In summary, our results show that calcium carbonate saturation state is an important environmental variable that affects calcium carbonate deposition on the timescale of days to years. There is evidence that it also may control accumulation rates of shallow water carbonate deposits on geological timescales [*Opdyke and Wilkinson*, 1993] and in fact may have had a controlling effect on the evolution of corals and their close noncalcifying cousins, sea anemones [Buddemeier amd Fautin, 1996a,b]. Unlike many terrestrial ecosystems, globally increasing atmospheric CO_2 has a negative impact on coral reef ecosystems. This finding does not alter the assessment that the primary stress to reefs at the present time is local (pollution, overfishing, and coastal development). However, it does substantially alter the previously common view that the effects of global climate change are negligible, or indeed potentially positive, compared to local impacts. Instead, global-scale changes are expected to significantly and progressively increase the vulnerability of many reefs to both acute and chronic local stresses.

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