

Review of experimental evidence for effects of CO₂ on calcification of reef builders

C. Langdon¹

ABSTRACT

This paper reviews the experimental evidence that a rise in atmospheric CO₂ will have an effect on the calcification rate of reef building organisms. There have been five studies where the carbonate chemistry of seawater has been varied between present day and what is projected if atmospheric CO₂ doubles or triples. These studies found that calcification declined by an average of 25% (range 11-40%). Three older studies also varied carbonate chemistry but the treatments were extreme relative to projected changes in the next 50-100 years. These studies reported larger decreases in calcification, 36±9%, that probably should be used with caution. Based on current estimates of dissolution rates on reefs, banks and tropical shelves dissolution will not be able to buffer the drop in [CO₃²⁻] over the next 50-100 years.

Keywords CO₂, Carbonate ion, Saturation state, Coral, Coralline algae, Calcification, Dissolution

Introduction

Coral bleaching represents an immediate and acute threat to coral reefs worldwide (Wilkinson 2000). Global warming, caused in part by the rapid rise in atmospheric CO₂, quite likely increases the severity and/or frequency of the warm water episodes that are thought to be responsible for the bleaching. Rising levels of atmospheric CO₂ can also affect coral reefs directly (Gattuso et al. 1998, Kleypas et al. 1999a). Seawater chemistry of the surface ocean will change in direct response to increased atmospheric CO₂. A doubling of the preindustrial level of atmospheric CO₂ is conservatively expected by the middle of this century even if fossil fuel emissions are stabilized today (Wigley 1999). This will result in a 200% increase in aqueous CO₂ (H₂CO₃+CO₂), 35% reduction in [CO₃²⁻] and a 0.24 unit drop in pH (Kleypas et al. 1999a, Kleypas, Langdon, -this volume- for a discussion of the chemical equilibria responsible for the inverse relationship between CO₂ and CO₃²⁻ and the oceanographic evidence that the rise in CO₂ and drop in pH is already measurable).

What effect will these changes in the chemical environment have on the calcification of reef builders? The carbonate chemistry of seawater has usually not been considered to be an important regional physio-chemical or kinetic factor influencing the biogenic precipitation of aragonite or calcite because surface seawater is supersaturated with respect to these minerals. However, it is well known that inorganic precipitation of calcium carbonate is related to [CO₃²⁻] through an empirical rate law that has the form $R=k(\Omega-1)^n$ (Inskeep and Bloom 1985, Zhong and Mucci, 1989). R is the calcification rate, k is the rate constant and $\Omega_{c(or a)}$ is the saturation state defined as $[Ca^{2+}][CO_3^{2-}]/K'$ where $K'_{c(or a)}$ is the stoichiometric solubility product for a particular mineral phase of CaCO₃ (calcite or aragonite). If n=1 then there is a linear or first order relationship between [CO₃²⁻] and the rate of calcification. Buddemeier and Fautin (1996) have explained how this mechanism might control calcification

at the organismal or ecosystem level. They point out that organisms may be able to concentrate or transport limiting constituents (Ca²⁺ or CO₃²⁻) by biochemical processes, but they are ultimately subject to fundamental physio-chemical controls imposed by the external environment, i.e. the amount of CaCO₃ that can be precipitated from a volume of water, and the rate at which the water (or dissolved salts) can be renewed at a location where it is accessible to the calcification process. If the physio-chemically controlled diffusive or advective transport of Ca²⁺ and CO₃²⁻ to the exterior of the coral is slow relative to the active or passive transport by the organism to the internal site of calcification the overall process will exhibit kinetics described by the rate law given above.

There is evidence that regional and temporal changes in Ω exert control over biogenic calcification (Broecker and Takahashi 1966, Smith and Presret 1974, Suzuki et al. 1995, Broecker et al. 2001). Kleypas et al. (1999b) pointed out that the current geographic distribution of reefs correlates well with regional changes in Ω . Opdyke and Wilkinson (1993) showed that latitudinal trends in Phanerozoic carbonate accretion rates correlate well with Ω . There has been a general trend over the last 600 m.y. for calcite secreting metazoans (rugose and tabulate corals, trepostome and cryostome bryozoans and trilobites) to be replaced by aragonite and Mg-calcite secreting metazoans (scleractinian corals, cyclostome and cheilostome bryozoans) (Wilkinson 1979). The only notable exceptions are calcite secreting coccolithophorids and planktonic foraminifera, both protists. Mackenzie and Agegian (1989) argue that these evolutionary changes in the biota may have been caused by a long-term trend in ocean-atmosphere chemistry favoring the secretion of metastable aragonite and high Mg calcite; that is, overall decrease in atmospheric CO₂ and temperature, and increase in the carbonate saturation state and Mg/Ca ratio of ocean water.

This paper presents an overview of the direct experimental evidence bearing on the effects of elevated pCO₂ and reduced [CO₃²⁻], pH and saturation state on the rate of calcification or skeletal growth of corals and coralline algae.

¹ Lamont-Doherty Earth Observatory, Palisades, NY 10983, USA. langdon@ldeo.columbia.edu

Methods

Manipulating the CO₂ concentration in seawater

In the studies discussed in this paper, three methods have been employed to vary the CO₂ concentration of the sea water.

- 1) Total alkalinity (TA) held constant and dissolved inorganic carbon (DIC) varied by bubbling with gases of differing CO₂ concentration.
- 2) Dissolved inorganic carbon held constant and total alkalinity varied by addition of strong acid or base.
- 3) pH held constant by adjustment of total alkalinity and dissolved inorganic carbon.

Table 1 shows the values of DIC and TA that one could use in an experiment to vary pCO₂ over the range that coral reefs have experienced in the past and may experience in the next 50-100 years. The real world case closely approximates a type 1 manipulation. The reason is that the response time of the alkalinity of the ocean to a step change in atmospheric CO₂ is 4,000-14,000 years (Sunquist 1990) while the DIC content of the surface ocean has a response time of approximately 624 GtC/2 GtC y⁻¹ or 300 years. Of course the alkalinity of shallow coastal environments will vary from the oceanic value on hourly, daily and seasonal time scales but on average they will track the oceanic value.

Table 1. Relationships between carbonate parameters for three types of CO₂ manipulations. pCO₂ is varied between last glacial maximum, preindustrial, present day, 2-times and 2.5-times preindustrial levels while TA, DIC or pH is held constant. CO₂ parameters were computed with the program CO2SYS (Lewis, Wallace 1998) using Mehrbach et al. (1973) values for K1 and K2. The temperature, salinity and [Ca²⁺] were 26°C, 36 ppt and 10.6 mmol kg⁻¹, respectively.

	TA	DIC	PCO2	HCO3	CO3 ²⁻	pH	Ωarag
	μEqv kg ⁻¹	μmol kg ⁻¹	μatm	μmol kg ⁻¹	μmol kg ⁻¹	sw scale	
TA cnst (Type 1)	2300	1829	200	1501	323	8.26	5.11
	2300	1909	280	1629	272	8.15	4.30
	2300	1959	350	1710	239	8.08	3.79
	2300	2056	560	1863	178	7.91	2.81
	2300	2098	700	1927	152	7.83	2.40
DIC cnst (Type 2)	2532	2000	200	1619	375	8.30	5.94
	2419	2000	280	1698	295	8.17	4.67
	2352	2000	350	1742	248	8.08	3.93
	2234	2000	560	1816	169	7.90	2.67
	2187	2000	700	1842	139	7.81	2.20
PH cnst (Type 3)	1457	1192	200	1034	153	8.10	2.42
	1993	1669	280	1447	214	8.10	3.39
	2462	2087	350	1809	268	8.10	4.24
	3868	3339	560	2895	428	8.10	6.78
	4806	4173	700	3618	536	8.10	8.48

If atmospheric CO₂ reaches 560 μatm by the middle of this century, as projected, the DIC of the tropical surface ocean will increase by 147 μmol kg⁻¹ relative to the preindustrial level in 1880. Table 1 shows that this increase in DIC will cause a 35% decrease in the CO₃²⁻ concentration of tropical surface waters if there is no change in tropical temperatures. If the doubling in CO₂ is also associated with a 2-4°C warming the increase in DIC will be 132 and 117 μmol kg⁻¹, respectively, and the change in CO₃²⁻ will be reduced by 11-22%, respectively. Therefore a rise in temperature will offset the effect of rising atmospheric CO₂ but only by a small amount.

A number of studies have used the type 2 manipulation (constant DIC). It can be seen in Fig. 1 that by careful adjustment of the TA by addition of HCl or NaOH the pCO₂ and [CO₃²⁻] can be made to closely replicate the real world changes. Unless the corals and coralline algae are sensitive to an 8% change in TA or DIC, type 1 and type 2 manipulations should have similar impacts on the organisms. Type 3 manipulations are an

interesting case where both the DIC and TA are varied to achieve the desired change in pCO₂ while holding the pH constant. The changes in TA and DIC needed to effect a doubled pCO₂ and a 35% decrease in CO₃²⁻ are 8-times that required for the type 1 and 2 manipulations (Table 1). This is obviously very unnatural. The advantage of a type 3 manipulation is that the normally inverse relationship between pCO₂ and CO₃²⁻ can be reversed.

A type 1 or 2 manipulation can be used to determine if the substrate of calcification is CO₃²⁻ or HCO₃⁻. Note in Table 2 that as pCO₂ is increased from 350 to 700 μatm the HCO₃⁻ increases by 6-13% while CO₃²⁻ decreases by 36-44% for the type 1 or 2 manipulation, respectively. If calcification drops by a significant amount it is likely responding to the CO₃²⁻. If calcification does not change or increases by a small amount it is likely responding to HCO₃⁻. A type 3 manipulation is useful for determining if calcification is responding to changes in pH of the external environment.

By running both a type 1 or 2 and a type 3 manipulation, it is possible to ascertain if calcification is responding to the change in $p\text{CO}_2$ or the change CO_3^{2-} . If calcification decreases with an increase in $p\text{CO}_2$ in the type 1 or 2 manipulation and increases with the increase in $p\text{CO}_2$ in the type 3 manipulation then we can conclude that calcification is responding to the change in CO_3^{2-} and not $p\text{CO}_2$. On the other hand if calcification increased in both cases then it is clearly responding to the change in $p\text{CO}_2$ and not CO_3^{2-} .

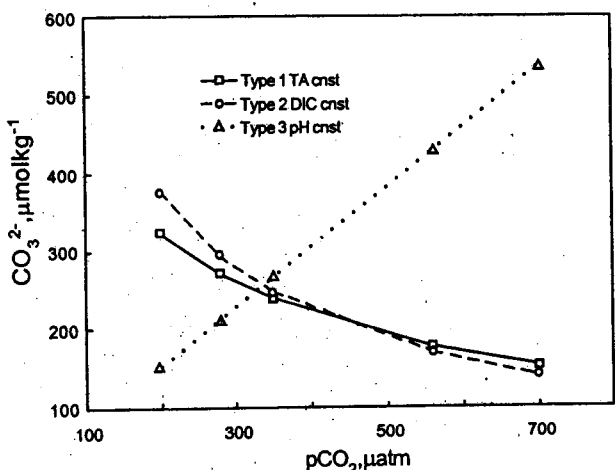


Fig. 1 Relationship between $p\text{CO}_2$ and CO_3^{2-} for type 1, 2 and 3 manipulations. The ocean is following the type 1 trajectory. For simplicity temperature was assumed to be constant.

Results

CO_2 effects on calcification by coral and coralline algae

Six published studies have examined the effect of elevated CO_2 on calcification of corals and coralline algae in isolation and two studies have examined the effects on calcification in more complex assemblages of reef organisms in sea water aquaria that included a sedimentary carbonate phase. The pertinent details of these studies are summarized in Table 2. One needs to be cautious when comparing the results of these studies because the methodologies varied greatly, the time duration of the treatments varied from 3 h to 2 years and the method of measuring calcification ranged from $^{45}\text{Ca}^{2+}$ uptake, ^{14}C uptake, linear growth, weight gain, to TA and Ca^{2+} change. The method of manipulating the carbonate chemistry of the water spanned all the methods discussed in the previous section. In several of the studies (Borowitzka 1981, Gao et al. 1993, Marubini and Atkinson 1999) the changes in $p\text{CO}_2$ and CO_3^{2-} were far outside realistic natural ranges. In the case of the Agegian (1985), Borowitzka (1981), Gao et al. (1993) studies the papers do not provide the CO_3^{2-} concentrations, and I have calculated CO_3^{2-} from Ω_{arag} , DIC and pH or DIC and

$p\text{CO}_2$ depending on what information was provided in the paper.

Despite the differences in methodologies the studies have consistently found a significant linear or curvilinear response between calcification and CO_3^{2-} . The most relevant individual organism studies are Agegian (1985), Schneider and Erez (2000), Marubini et al. (2001). These studies performed type 1 or 2 manipulations and varied the $p\text{CO}_2$ and CO_3^{2-} within the range predicted for the next 100 years.

Agegian (1985) varied the calcite saturation state of seawater between 1 and 8 by adjusting the alkalinity of seawater by the addition of HCl or NaOH and observed the effect on the growth rate of the coralline alga *Porolithon gardineri* measured over a 20-27 day period. CO_3^{2-} concentrations were not given in the paper but are easily calculated since $[\text{Ca}^{2+}]$ would not have changed in the flowing seawater tanks. Growth rate was a linear function of $[\text{CO}_3^{2-}]$, $r^2=0.90$, over the range 40-380 $\mu\text{mol kg}^{-1}$. Photosynthetic rate was not measured but since HCO_3^- and $\text{CO}_{2(\text{aq})}$ were increasing as CO_3^{2-} was decreasing it is unlikely that the decrease in calcification was the indirect result of a decrease in photosynthesis. The reduction in linear growth due to a doubling in CO_2 amounted to 16%.

Marubini et al. (2001) looked at the skeletal growth of the Pacific hermatypic coral *Porites compressa* at three $[\text{CO}_3^{2-}]$'s picked to mimic conditions during the last glacial maximum, $p\text{CO}_2=200$ μatm , present day, $p\text{CO}_2=350$ μatm and the year 2100, $p\text{CO}_2=700$ μatm , and at three light intensities 80, 150 and 700 $\mu\text{E m}^{-2} \text{s}^{-1}$. Skeletal growth measured as the increase in buoyant weight decreased by 30% between the last glacial maximum and the year 2100 treatment, and 11% between the present day and year 2100 treatment. Another important finding of the Marubini et al. (2001) study was that the amount of light received did not have a significant effect on the sensitivity of skeletal growth to CO_3^{2-} concentration.

Schneider and Erez (2000) measured the calcification of the coral *Acropora* sp. collected in the Red Sea. Seawater was treated with HCl and NaOH to change pH (range: 7.9-8.5) without changing DIC (type 2 manipulation). The rates of calcification (in the light and the dark) displayed a positive linear dependence with pH, with a slope of 25% increase per 0.1 pH unit. Rates of calcification in the light were positive at all pH's tested but dark calcification was negative (dissolution) below a pH of 8.06. While Schneider and Erez (2000) stressed the dependence on pH the rates of light and dark calcification were also linearly dependent on the $[\text{CO}_3^{2-}]$ (Erez, pers. Comm.). Photosynthesis did not show any trend with pH calling into question the direct coupling between photosynthesis and calcification in corals.

Table 2. Summary of experimental studies looking at effect of CO₂ on calcification of reef organisms.

Organism	Manipulation n	Time scale of response	System	Light $\mu\text{E m}^{-2} \text{s}^{-1}$	Method	1880-2065 Response %	Source
Algae							
<i>Corallina pilulifera</i>	1,3	12 h	single organism	300	Calcif. by Ca ²⁺	-44	1
<i>Amphiroa foliacea</i>	2,3	3h	single organism	600	Calcif. by ¹⁴ C	-36	2
<i>Porolithon gardineri</i>	2	20-27 d	single organism	full sunlight	Linear growth	-16	3
Corals							
<i>Porites compressa</i>	2	35 d	single organism	80% sunlight	Weight gain	-27	4
<i>Porites compressa</i>	1	21 d	single organism	80-700	Weight gain	-11	5
<i>Acropora sp.</i>	2,3	hours	single organism	350	Calcif. by TA	-37	6
<i>Stylophora pistillata</i>	Ca ²⁺	2.5 h	single organism	450	Calcif. by TA	-1	7
Communities							
Biosphere 2 coral reef mesocosm	2,3	week to years	assembled reef community	sunlight	Calcif. by TA and Ca ²⁺	-40	8
Monaco mesocosm	1	1 d	algal dominated assembled reef community coral dominated	160-600	Calcif. by TA	-21	9

Manipulation key	Source
1 TA cnst. DIC adjusted.	¹ Gao et al. (1993) ² Borowitzka (1981)
2 DIC cnst. TA adjusted with acid or base.	⁶ Schneider and Erez (2000)
3 pH cnst. TA and DIC adjusted.	⁷ Gattuso et al. (1998)
	³ Aegian (1985)
	⁸ Langdon et al. (2000)
	⁴ Marubini and Atkinson (1999)
	⁹ LeClercq et al. (2000)
	⁵ Marubini et al. (2001)

Borowitzka (1981) varied the pH of artificial Pacific seawater with a DIC of 2.2 μmol between 7.0 and 9.0 by addition of HCl or NaOH (type 2 manipulation) and observed the effects on the calcification and photosynthesis of the coralline alga *Amphiroa foliacea*. The results of these experiments are difficult to interpret. Calcification at pH 7.2 and 8.3 were almost the same, dropped by 55% at pH 9.0 and reached a maximum at pH 9.7. Photosynthesis also dropped between pH 8.3 and 9.0 but it did not increase when pH was raised to 9.7. No other explanation was offered for the strange behavior of calcification. The results of the constant pH experiments were more interpretable. DIC was adjusted between 0.5 and 7.0 μmol (type 3 manipulation) while the pH was held at 8.5 or 8.8. Calcification increased steadily with increasing DIC and at any given concentration the rate of calcification was lower at pH 8.5 than at pH 8.8. The ratio of calcification at pH 8.5 to that at pH 8.8 was very close to the ratio of [CO₃²⁻] concentrations at the respective pH's. Calcification of dead *A. foliacea* in the light and living plants in the dark followed the same patterns but the rates were 10% of living plants in the

light. Photosynthetic rate increased up to a DIC of 3 μmol at pH 8.5 and then leveled off. Calcification increased in an exponential fashion up to the highest DIC tested with no change in the shape of the curve at the point that photosynthesis became saturated. Clearly light and photosynthesis have a significant effect on calcification of this alga but there is also evidence that calcification is responding directly to changes in the CO₃²⁻ concentration in the external medium and not just indirectly through effects of carbon availability on photosynthesis.

Gao et al. (1993) used a different coralline alga, *Corallina pilulifera*, and manipulated the carbonate system differently but arrived at essentially the same conclusions. They adjusted the pCO₂ of natural seawater to 350 or 1600 μatm by bubbling with air or an air-CO₂ mix (type 1 manipulation). At 350 μatm they observed strong calcification in the light and a much slower rate in the dark. At 1600 μatm they observed no detectable calcification in the light and a slow rate of dissolution in the dark. Unfortunately they did not report photosynthetic rates for this experiment but based on the data of Borowitzka (1981) the conditions should have been near

optimal for photosynthesis at the 1600 μatm treatment. The pH of this treatment was 7.6 and Borowitzka (1981) observed maximal rates of photosynthesis at pH 6.5 to 7.5 for a closely related red alga.

In another series of experiments they varied DIC between 1 and 10 μmol while holding pH constant at 8.22 (type 3 manipulation). Both photosynthesis and calcification increased up to the highest concentration tested, 10 μmol . The saturation of photosynthesis at a DIC of 3 μmol reported by Borowitzka (1981) was not observed. Two explanations are possible, 1) calcification is responding directly to the increase in CO_3^{2-} or HCO_3^- or, 2) photosynthesis is carbon limited and calcification changes because photosynthesis supplies something needed by the calcification process. The type 1 experiment helps us decide between these two possibilities. The increase in pCO_2 from 350 to 1600 μatm caused DIC and HCO_3^- to increase by only 9% while CO_3^{2-} dropped by 71% (Gao et al. 1993 Table 2). In response the calcification rate dropped from 0.06 $\mu\text{mol Ca}^{2+} \text{ h}^{-1}$ to zero. The most reasonable conclusion is that calcification is responding to the carbonate concentration in the external medium.

Gattuso et al. (1998) varied the $[\text{Ca}^{2+}]$ of artificial seawater and observed the short-term calcification response of the Mediterranean coral *Stylophora pistillata*. DIC and TA were adjusted to be close to values typical of Mediterranean surface seawater with a salinity of 38.5 ppt. Carbonate parameters were not manipulated during these experiments. A strong saturating response of calcification to aragonite saturation state (Ω_a) was observed. A doubling in calcification rate was observed between Ω_a 's of 1 and 2 and above an Ω_a of 2.5 calcification rate was constant. The results of this experiment are quite different from the other studies mentioned which observed a 1st (5 cases) or 2nd order (1 case) response to Ω and significant decrease in calcification for drops in Ω_a between 4.3 and 2.8. One explanation is that some difference in the physiology of *Stylophora* or in the conditions of the experiment caused the transition from physio-chemical to biological control to occur at a lower Ω than in the other studies. Another explanation is that

the shape of the response curves to Ca^{2+} and CO_3^{2-} are different. If this is the case then the hypothesis of saturation state control in corals must be rejected and an alternative explanation for the effects of a rise in pCO_2 and drop in pH and CO_3^{2-} on calcification must be found.

CO_2 effects on calcification of mesocosms

Mesocosm studies (Langdon et al. 2000 in the Biosphere 2; Leclercq et al. 2000 in the Monaco mesocosm) have the potential to capture some of the subtleties of interactions between different reef organisms and between the chemistry of the water and the sediments that would be missed in the experiments discussed above. The Monaco mesocosm included seven coral species, two red calcareous alga species, and microfauna including small crustaceans, polychaetes and gastropods. The substratum of the aquaria (0.34 m^2) consisted of a carbonate sand layer 0.05 m thick. The Biosphere 2 mesocosm had an even greater species diversity with 25 coral species, two sponge species, 30+ species of macroalgae, 16 species of fish, sea urchins, sea cucumbers, decapods, brittle stars, tunicates, polychaetes and amphipods (Atkinson et al. 1999). The substratum of the Biosphere 2 aquaria consists of a foundation of limestone boulders overlain with crushed limestone, crushed oyster shells and in some areas 30-45 cm of aragonitic beach sand from the Caribbean. After ten years during which the pCO_2 was in excess of 1000 μatm for extended periods these oyster shells are still readily recognizable. Wide areas of the bottom are now covered by red coralline algae, principally *Amphiroa fragillissima* and *Haliptilon cubense* both of which secrete skeletons of high magnesium carbonate.

The Biosphere 2 mesocosm study is the longest and largest experiment performed to date and the only experiment where both Ca^{2+} and CO_3^{2-} were manipulated.

During the first 3.5 years of the study pH was held constant at 8.0 ± 0.1 and DIC and TA were adjusted to hold $[\text{CO}_3^{2-}]$ at $122 \pm 30 \mu\text{mol kg}^{-1}$ for 2.3 years and $262 \pm 60 \mu\text{mol kg}^{-1}$ for 1.4 years (type 3 manipulation).

Table 3. Summary of CO_2 treatments in the Biosphere 2 mesocosm and the response of the community in terms of calcification.

Dates	TA $\mu\text{Equiv kg}^{-1}$	DIC $\mu\text{mol kg}^{-1}$	pCO_2 μatm	HCO_3^- $\mu\text{mol kg}^{-1}$	CO_3^{2-} $\mu\text{mol kg}^{-1}$	pH	Ca^{2+} mmol kg^{-1}	Ω_{arag}	Calcification $\text{mmol CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$	SE	n
3/16/95- 6/30/97	2022	1854	700	1714	122	7.97	8.97	1.6	8	3	12
7/3/97- 11/12/98	2906	2576	586	2293	262	8.09	7.89	3.1	40	7	29
2/2/99-3/30/99	2463	1929	192	1549	375	8.30	9.15	5.2	114	7	9
4/1/99-6/14/99	2283	1955	366	1712	232	8.06	9.72	3.5	61	4	8
7/7/99-9/21/99	2321	2121	727	1950	151	7.82	9.33	2.1	31	6	10
10/29/99-2/11/00	2288	1960	371	1719	231	8.06	8.66	3.2	42	3	15
2/25/00-6/12/00	2290	2090	710	1920	151	7.83	8.55	2.0	32	5	12

Beginning in 1999 we switched to a type 2 manipulation where the DIC was held constant and TA was adjusted by addition of HCl or NaOH to obtain a $p\text{CO}_2$ of 200, 350 and 700 μatm . Table 3 summarizes the chemical conditions during the different phases of the study and rates of calcification observed.

Several important observations can be made by looking at the data in Table 3 plotted against CO_3^{2-} , HCO_3^- and Ω_{arag} (Fig. 2). First, there is an obvious positive effect of $[\text{CO}_3^{2-}]$ and Ω_{arag} on calcification (Fig. 2A and 2C). Second, the variations in calcification rate can not be explained by the changes in $[\text{HCO}_3^-]$ (Fig. 2B). This is illustrated by the alternations between intermediate and high $p\text{CO}_2$ that occurred between 4/1/99 and 7/7/99 and between 10/29/99 and 2/25/00 (Table 3). In each case the HCO_3^- increases by 14% and the CO_3^{2-} decreases by 35%. In the first instance calcification rate declines by 49% and in the latter by 24%. On average the decline is 37%. It is quite evident from these data that calcification is responding to the change in $[\text{CO}_3^{2-}]$ and not $[\text{HCO}_3^-]$. It is clear that Ω_{arag} gives the best fit to the data by taking into account variations in $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ (see Langdon et al. 2000) for more detailed discussion of the evidence that saturation state controls calcification in this system). Another important result is that data points for the long term treatments (open squares) fall very close to the line defined by the short term treatments (solid squares) in Fig. 2C. This indicates that the community is unable to acclimate or adapt to changes in saturation state, at least on the time scale of a few years. The results of the most recent data from the Biosphere 2 mesocosm experiment indicate that a drop in $[\text{CO}_3^{2-}]$ from 272 (preindustrial) to 177 $\mu\text{mol kg}^{-1}$ ($2\times \text{CO}_2$) will produce a 49% decrease in calcification rate.

The Monaco mesocosm study was a type 1 manipulation. The DIC of the water was changed by bubbling the water with gas mixtures of $p\text{CO}_2$ ranging from 150 to 1000 μatm . The calcification of the system was determined from the change in TA. The results were reported in terms of the aragonite saturation state. However, because the Ca^{2+} concentration was not changing, the system was really responding to the change in CO_3^{2-} . Leclercq et al. (2000) found that calcification was a linear function of Ω_{arag} (also CO_3^{2-}) and that there was a 21% decrease in calcification in response to the projected decrease in CO_3^{2-} between 1880 and 2065.

Can dissolution limit the drop in $[\text{CO}_3^{2-}]$?

Dissolution of CaCO_3 in the sediments releases CO_3^{2-} that can react with CO_2 via the reaction $\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^-$. By neutralizing some of the CO_2 , dissolution can buffer the drop in $[\text{CO}_3^{2-}]$ that would otherwise result from the invasion of CO_2 . Calcium carbonate in modern coral reef framework (Tribble 1990) and tropical platform carbonate deposits (Morse et al. 1985) may be dissolving despite highly supersaturated seawater flowing over them, but the rate of dissolution in these structures is poorly documented.

Smith (1973) found no evidence of dissolution on the windward interisland reef flat at Eniwetok Atoll. Likewise, Gattuso et al. (1996) found no dissolution on reef flats at Moorea (French Polynesia) or Yonge Reef (Great Barrier Reef). An extensive survey of surface water chemical properties within and around the Great Barrier Reef (GBR) found that waters in the lagoon of the GBR (along a ship track of more than 2000 km) exhibited a $p\text{CO}_2$ that was about 15 μatm higher than the surrounding oceanic water (Kawahata et al. 2000).

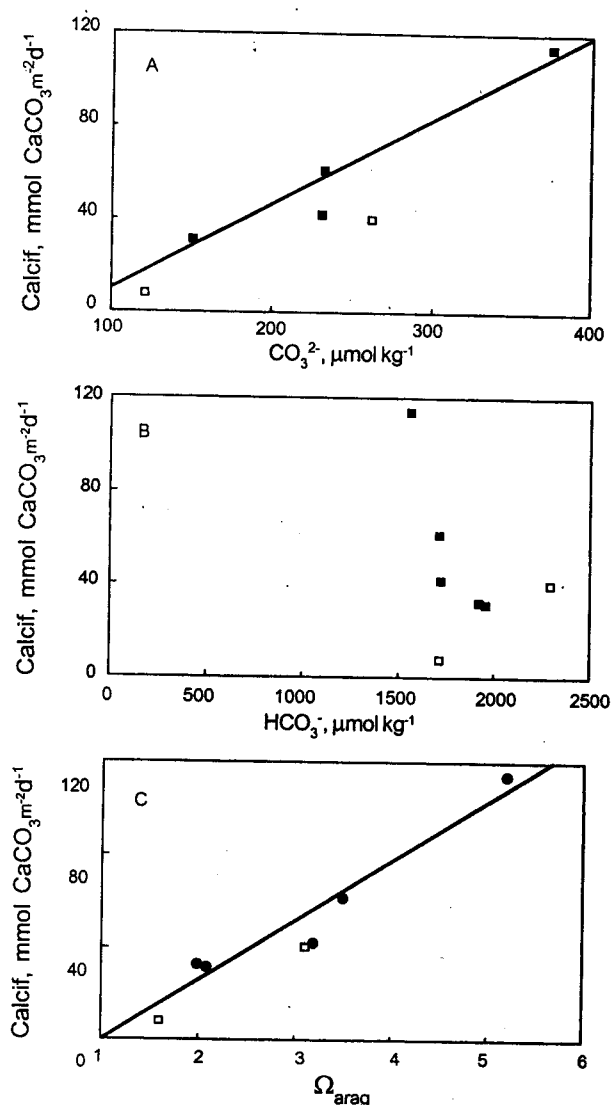


Fig. 2 Relationship between the calcification rate of the Biosphere 2 coral reef mesocosm and A) CO_3^{2-} concentration, B) HCO_3^- concentration and C) Ω_{arag} . Based on the data in Table 2. The long-term, constant pH data are shown as open squares and the 2-4 month long type 2 manipulations are shown as the solid squares. The equation for the best fit line through the data in panel A is $\text{Calcif} = 0.358 \cdot \text{CO}_3^{2-} - 31.09$, $r^2=0.86$. The equation for the best fit line through the data in panel C is $\text{Calcif} = 25.60 \cdot \Omega_{\text{arag}} - 31.8$, $r^2=0.93$.

Total alkalinity-total inorganic carbon property plots indicated that calcification was mainly responsible for the raised $p\text{CO}_2$. Similar surveys around oceanic islands in the Indo-Pacific region, including Majuro Atoll, South Male Atoll and Palau Barrier Reef also found that lagoonal surface waters were 6-46 μatm higher than the adjacent oceanic waters and that TA-DIC plots indicated that calcification was the process mainly responsible for the elevated $p\text{CO}_2$ (Suzuki and Kawahata 1999). Suzuki et al. (1995) observed net dissolution at night but net precipitation averaged over 24-h at Shiraho Reef, a fringing reef located on Ishigaki Island in southwest Japan. A fringing reef that has shifted to a macroalgal-dominated benthic community due to anthropogenic stresses was found to have a slight net dissolution of 0.8 $\text{mmol m}^{-2} \text{d}^{-1}$ (Gattuso et al. 1997). Walter and Burton (1990) implanted carbonate substrates (red algae; 18 mol percent Mg-calcite; echinoid, 12 mol percent Mg-calcite; and coral, aragonite) in the upper meter of carbonate bank sediments at Rodriguez Key, Florida Reef tract and determined an *in situ* mass loss rate of 13.7 $\text{mmol CaCO}_3 \text{m}^{-2} \text{d}^{-1}$. It would appear that little dissolution is occurring on coral reefs except in a few unique or modified environments. However, appreciable dissolution may be occurring on carbonate banks.

Milliman (1993) assembled data on carbonate production and accumulation of the present day global ocean. He concluded that approximately 2.5×10^{13} moles of CaCO_3 per year was produced on reefs, banks and tropical shelves of which about 1.5×10^{13} moles accumulates; the other 1×10^{13} moles y^{-1} is dissolved or exported. Using Milliman's (1993) estimate for the area of the ocean floor covered by reefs, banks and tropical shelves ($2.7 \times 10^{13} \text{m}^2$) and assuming that all the missing CaCO_3 is dissolved I arrive an areal dissolution rate of 1.0 $\text{mmol CaCO}_3 \text{m}^{-2} \text{d}^{-1}$. This is at the lower end of the range of direct measurements, i.e. 0-13.7 $\text{mmol CaCO}_3 \text{m}^{-2} \text{d}^{-1}$. It can also be observed that a dissolution of 1×10^{13} moles $\text{CaCO}_3 \text{y}^{-1}$ on reefs, banks and tropical shelves would neutralize just 6% of the 1.7×10^{14} moles of CO_2 that enter the ocean each year. Clearly, at the present rate dissolution won't be much of a factor in buffering the ocean in the short term. However, as CO_2 levels rise rates of calcification will fall and rates of dissolution will increase. Experiments have shown that when $p\text{CO}_2$ exceeds 560 μatm sandy and coral rubble substrates will become areas of net dissolution and when $p\text{CO}_2$ exceeds 1600 μatm macroalgal-dominated fringing reef environments similar to that modeled by the Biosphere 2 coral reef mesocosm will become areas of net dissolution (Langdon et al. 2000). The average rate of dissolution for reefs, banks and tropical shelves combined would have to reach 17 $\text{mmol m}^{-2} \text{d}^{-1}$ in order to stabilize the $[\text{CO}_3^{2-}]$. Based on the Langdon et al. (2000) studies the CO_2 level will have to rise to 600-2200 μatm before this rate of dissolution is reached.

Conclusions

The studies to date, while still few in number and diverse in methodology, uniformly find that calcification

is sensitive to the CO_3^{2-} concentration of the water. The consensus from the studies discussed in this paper is that calcification rates on coral reefs could decline by 11 to 44% by the middle of this century. The consequences of a long term reduction in skeletal growth are not known, but it is likely that corals will be less competitive for space and light and more susceptible to bioerosion, storm damage and possibly disease.

There is good experimental evidence that saturation state controls the calcification of algae, however, the evidence for corals is contradictory. Changes in CO_3^{2-} clearly effect the calcification of corals but changes in Ca^{2+} within the range of natural seawater may not. An experiment is needed where both Ca^{2+} and CO_3^{2-} are varied in order to definitively test whether or not Ω controls coral calcification.

Acknowledgements I would like to thank Joan Kleypas, Jonathan Erez, Marlin Atkinson, Franscesca Marubini, Robert Halley and Richard Grigg for helpful discussions. Financial support for portions of this work was provided by the Columbia University Earth Institute Biosphere 2 Center and a grant from the David and Lucile Packard Foundation #99-8306. Lamont-Doherty Earth Observatory contribution no. 6222. Biosphere 2 contribution no. 2001-1.

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