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Coral Reefs and Changing Seawater Carbonate Chemistry

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Seawater carbonate chemistry of the mixed layer of the oceans is changing rapidly in response to increases in atmospheric CO₂. The formation and dissolution of calcium carbonate is now known to be strongly affected by these changes, but many questions remain about other controls on biocalcification and inorganic cementation that confound our attempts to make accurate predictions about the effects on both coral reef organisms and reefs themselves. This chapter overviews the current knowledge of the relationship between seawater carbonate chemistry and coral reef calcification, identifies the hurdles in our understanding of the two, and presents a strategy for overcoming those hurdles.

1. Introduction

1.1. History and Background

In the most simplistic context, Earth's carbon cycle can be configured as four different reservoirs: atmosphere, biosphere, hydrosphere and geosphere (Figure 1). Over geologic time, the fluxes of carbon between these reservoirs tend to maintain relative stability in the sizes of the reservoirs. Occasionally, however, a sudden flux of carbon from one reservoir to another upsets the balance, with consequences for Earth's climate and biosphere. The carbon cycle responds with a series of negative feedbacks that cause increased rates of CO₂ uptake in other reservoirs. For example, an increase in atmospheric CO₂ can increase biospheric uptake of carbon, most of which is stored only temporarily, but some of which may be stored for much longer periods (e.g., plant growth which is buried by sediments and eventually becomes converted to fossilized carbon). Over time, these feedbacks bring the cycle back into balance, although not necessarily to the same stasis as before the perturbation.

Fossil fuels were formed through biological processes, but became stored as part of the geologic reservoir over millions of years (most of the oil and coal reserves are more than 50 million years old). Burning the fossilized carbon accelerates the rate of carbon flux from the geosphere to the atmosphere, which greatly outpaces the rates at which other fluxes draw the CO₂ back out of the atmosphere. Thus, the atmospheric reservoir grows, and in turn drives increased fluxes to the biosphere and the ocean (Figure 1). In the biosphere, the increased CO₂ can increase carbon uptake by "fertilizing" plant growth, at least

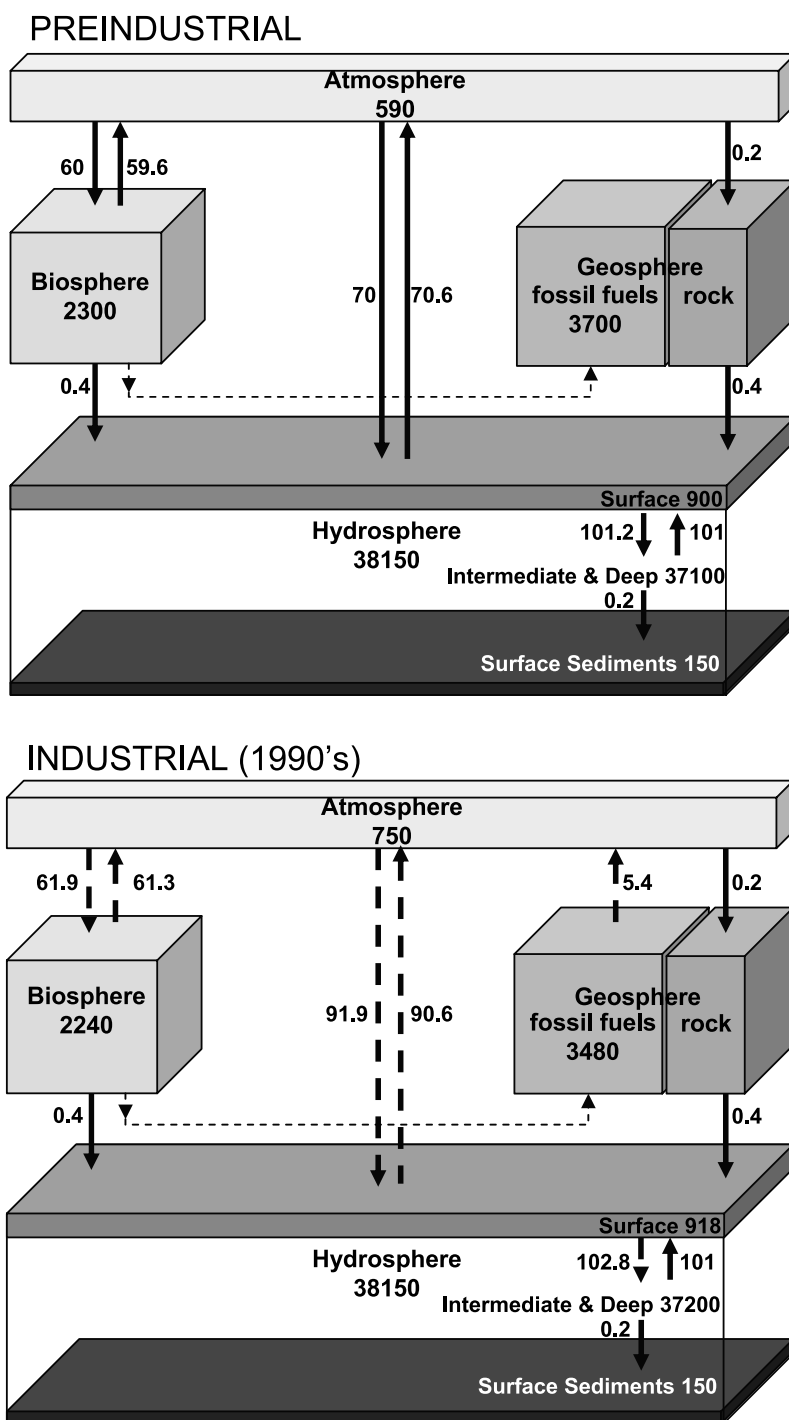


Figure 1. Simplified version of the major reservoirs and fluxes of carbon within the Earth System. Top panel illustrates the preindustrial, quasi-steady state prior to human activities. Lower panel shows present-day state. New and changed fluxes are indicated with dashed arrows.

under conditions where other nutrients are not co-limiting; and by increasing temperature, which under certain conditions can extend the growing season. The bulk of the fluxes from the atmospheric reservoir, however, are to the ocean. Oceanic uptake sequesters more than a third of all fossil fuel emissions, and most of this uptake is geochemical rather than biological. Without oceanic uptake, current day atmospheric CO_2 levels would be about 435 ppmv (parts per million volume), rather than 380 ppmv [Sabine et al., 2004].

The oceans thus have an enormous capacity to buffer changes in atmospheric CO_2 . Oceanic uptake of atmospheric CO_2 , however, alters the carbonate chemistry of seawater. Fluctuations in atmospheric CO_2 in the past have been accompanied by changes in both seawater carbonate chemistry and in production and preservation of calcium carbonate secreting organisms (hereafter called “calcifiers”). This chapter addresses this process with an emphasis on how future changes in carbonate chemistry will affect calcification rates of coral reef organisms as well as reef-building itself.

1.2. Definitions

Different terms are often used to describe the changing carbonate system in seawater, and some of these are used interchangeably. This is because when one component of the system changes, the other components change proportionally. For example, increasing atmospheric CO_2 concentration drives more CO_2 into seawater, and this causes the carbonate system to adjust so that both pH and carbonate ion concentration decrease. So while *ocean acidification* refers to the lowering of pH, it also infers a reduction in carbonate ion concentration. Another term, *calcium carbonate saturation state* (Ω), is a measure of the ion activity product (IAP) of Ca^{2+} and CO_3^{2-} relative to the apparent solubility product (K') for a particular calcium carbonate mineral phase (calcite, Mg-calcite, or aragonite):

$$\Omega = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K' \quad (1)$$

Because Ca^{2+} concentrations are typically 20-30 times that of CO_3^{2-} and do not vary considerably, reduction in $[\text{CO}_3^{2-}]$ is essentially synonymous with a reduction in saturation state. The term *carbonate ion concentration* is probably the best for describing atmospheric-induced changes in carbonate chemistry, because experimental evidence shows that under increased atmospheric CO_2 this appears to be the component of the carbonate system that controls coral calcification [Langdon, 2002]. However, the term *saturation state* provides a useful measure of the level of saturation of a particular carbonate mineral (where values <1 indicate undersaturated conditions, and >1 indicate supersaturated). We use both of these terms to describe the carbonate system in seawater.

1.3. Overall Importance of CaCO_3 in Marine Carbon Cycle

Most CaCO_3 production in the oceans is biogenic, or at least associated with biological activity. Biogenic calcification rates are greatest in the photic zone, while dissolution rates are greatest in the deep ocean where increasing pressure, decreasing temperature, and increased organic matter respiration shifts the saturation state to less than 1. In the open ocean, the marine carbon cycle is affected by the ratio of the “rain rates” of inorganic carbon (CaCO_3) and organic carbon (reviewed by Archer [2003]). Shell formation draws down the total alkalinity in the surface ocean (leaving it more acidic), and subsequent sinking and dissolution of the shells increases the total alkalinity at depth. This “calcium carbonate pump” decreases the capacity for the surface ocean to absorb CO_2 from the

atmosphere. However, marine organic matter production is also largely restricted to shallow waters, and sinking of organic matter to the deep ocean – the “organic carbon pump” – increases the capacity of the ocean to take up atmospheric CO₂, by removing CO₂ from the surface ocean and transporting it to the deep ocean as organic matter. These two processes may not act independently, however; recent evidence suggests that most of the organic carbon that sinks to the deep ocean is “ballasted” by CaCO₃ particles (CaCO₃ provides the higher-density weighting to increase sinking rates [Armstrong et al., 2002]).

The rise and fall of calcification on continental shelves, in concert with glacial-interglacial sea level fluctuations, is also considered an important process in the global carbon cycle. The “coral reef hypothesis” [Berger, 1982; Opdyke and Walker, 1992] states that episodic flooding of continental shelves during postglacial sea level rise led to dramatic increases in CaCO₃ production, which released significant amounts of CO₂ to the atmosphere (by a process explained in section 2.1). Recent modeling efforts attest to the importance of this mechanism [Ridgwell et al., 2003].

2. Seawater Carbonate Chemistry Changes

Ocean sequestration of fossil-fuel CO₂ emissions is already progressing at a very large scale [Sabine et al., 2004], and carbonate chemistry of the surface mixed layer of the oceans is responding rapidly to this uptake [Feely et al., 2004]. As the debate continues over whether to pump liquefied CO₂ into the deep ocean for temporary storage, the surface ocean has already naturally taken up about 30% of anthropogenic CO₂ from the atmosphere [Sabine et al., 2004]. This has altered the carbonate system in seawater. Evidence for ocean uptake of CO₂ and its effects on seawater carbonate chemistry comes from a variety of methods, including 1) measured changes in CO₂ chemistry in seawater over time; 2) isotopic signals; and 3) modeling studies.

2.1. The Carbonate System in Seawater

Understanding the carbonate system in the ocean requires an understanding of both the equilibrium chemistry of the various inorganic forms of carbon dioxide in seawater, and alkalinity. A complete explanation of the carbonate system in seawater cannot be provided here, and the reader is referred to the thorough descriptions in Zeebe and Wolf-Gladrow [2001]. Instead, this section presents the basics of how increasing carbon dioxide concentrations in the atmosphere are causing changes in the carbonate system that ultimately affect calcification rates on coral reefs.

The carbonate equilibrium in seawater is a complicated system that influences the exchange of CO₂ across the air-sea interface, the interconversion of various inorganic phases of dissolved CO₂, and the formation and dissolution of calcium carbonate (Figure 2). The basic equations describing the carbonate system are:



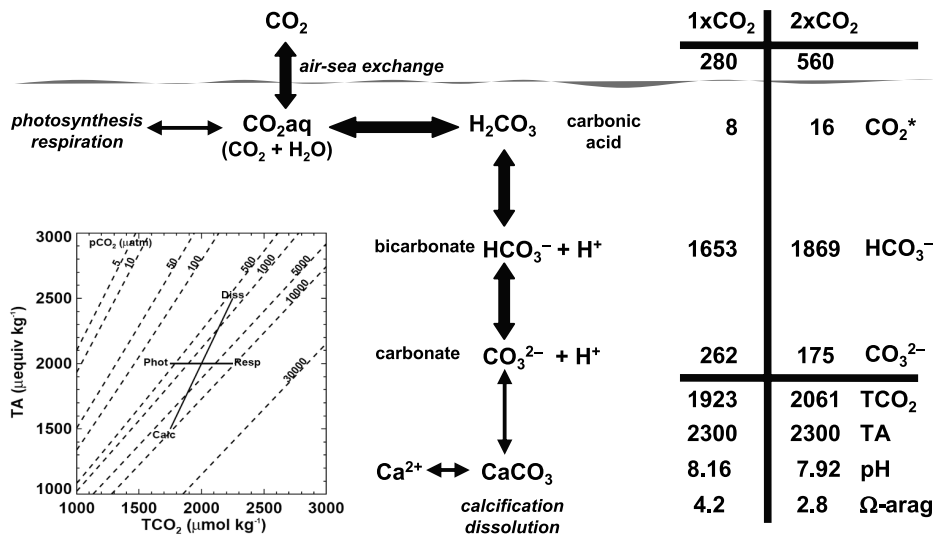


Figure 2. Diagram of the equilibrium carbonate system in seawater, and changes due to forcing by atmospheric CO_2 . Table at right shows calculated changes in carbonate chemistry parameters under preindustrial concentrations of atmospheric CO_2 (280 ppmv) and a doubling (560 ppmv), assuming temperatures of 25°C and 26°C, respectively, salinity = 35, and TA = 2300 $\mu\text{equiv kg}^{-1}$. CO_2^* is the total concentration of $\text{CO}_2(\text{aq})$ and H_2CO_3 . TCO_2 is the sum of CO_2^* , HCO_3^- and CO_3^{2-} . Note that a change in atmospheric CO_2 does not affect TA. Inset illustrates the effects of photosynthesis/respiration versus calcification/dissolution on total alkalinity (TA) and total dissolved inorganic carbon (TCO_2). Dashed lines indicate the associated partial pressure of CO_2 in seawater ($p\text{CO}_2$) in μatm .

where:

CO_2 = carbon dioxide, as gas (g) or aqueous (aq)
 H_2CO_3 = carbonic acid
 HCO_3^- = bicarbonate ion
 CO_3^{2-} = carbonate ion

Note that the total concentration of all the dissolved inorganic carbon species is termed “dissolved inorganic carbon” (DIC), or “total CO_2 ” (TCO_2).

A common inference from Equations (2-5) is that the addition of CO_2 to the water column will ultimately lead to an increase in the carbonate ion content, and given the following equation, one intuitively would consider that this would also lead to an increase in the formation of calcium carbonate (CaCO_3).



This inference is incorrect, however, because carbonic acid is a weak acid, and all of the various carbon species exist simultaneously (note that all of the above reactions are reversible). The relative proportion of each species, particularly the proportion of

HCO_3^- to CO_3^{2-} , is governed by the pH and the need to maintain the ionic charge balance in seawater. This in turn is closely related to the concept of total alkalinity (TA). TA is defined as “the number of moles of hydrogen ion equivalent to the excess of proton acceptors over proton donors in a kilogram of seawater” [DOE, 1994]; but essentially TA equals the charge difference between conservative cations of strong bases and conservative anions of strong acids:

$$\begin{aligned}\text{TA} &= [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] \\ &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] - [\text{H}^+]\end{aligned}\quad (7)$$

Most of the alkalinity (95%) of the right side of Equation (7) is contributed by the first two terms which are also called carbonate alkalinity (CA):

$$\text{CA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]\quad (8)$$

while the 3rd term in the right side of Equation (7) is called borate alkalinity. Since

$$\text{CA} \approx \text{TA}\quad (9)$$

then

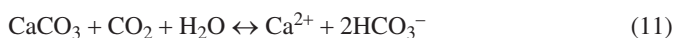
$$[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \approx [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}]\quad (10)$$

As TA decreases, say by the removal of conservative positive ions (e.g., removal of Ca^{2+} by CaCO_3 precipitation), then CA decreases as well, through the conversion of some of the carbonate to bicarbonate. The higher the TA, the more the system moves toward the right in Equation (5), and vice-versa.

TA of seawater changes conservatively with salinity and values are typically around $2300 \mu\text{moles kg}^{-1}$ (note that TA is often presented as $\mu\text{equiv kg}^{-1}$ because it is actually the number of moles of H^+ equivalents needed for its titration). High alkalinity values provide seawater with its strong buffering capacity (the resistance to changes in pH as acids or bases are added). By comparison, freshwater systems have low alkalinity values and experience much more dramatic swings in pH.

A direct consequence of the increasing partial pressure of CO_2 in the atmosphere is an increase in seawater TCO_2 . Adding CO_2 to seawater does not affect the TA, but will lower the pH because CO_2 reacts with water to produce carbonic acid (Equation 3). The carbonic acid will release protons to produce HCO_3^- (Equation 4); however, in order to maintain charge balance some carbonate ions will be converted to bicarbonate, and this will lower the CO_3^{2-} concentration (Table in Figure 2). As a first-order approximation, the carbonate ion concentration can be estimated as the difference $\text{TA} - \text{TCO}_2$. This is because CO_2 and H_2CO_3 are very small compared to HCO_3^- and CO_3^{2-} and $\text{CA} \approx \text{TA}$. An increase in CO_2 thus leads to a decrease in carbonate ion concentration. Figure 2 illustrates how changes in either TA or TCO_2 affect the carbonate ion concentration.

Equation (11) captures the relationship between CaCO_3 and CO_2 . Addition of CO_2 to the system leads to the dissolution of CaCO_3 . The reverse reaction, the formation of calcium carbonate, produces CO_2 .



The carbonate system in seawater is influenced by both physical and biological processes – mainly those that affect concentrations of TCO_2 and/or TA. For example, temperature strongly affects Equation (2), as CO_2 solubility increases with decreasing temperature. Biological processes of primary production and respiration affect the system by removing and adding CO_2 , respectively; while calcium carbonate formation and dissolution alter both TA (Ca^{2+} removal) and TCO_2 concentration (Figure 2 inset).

2.2. Mechanisms and Time-scales of Future Seawater Carbonate Chemistry Changes

Oceanic uptake of atmospheric CO_2 is restricted to the ocean-atmosphere interface; about 50% of the anthropogenic CO_2 in the oceans is still confined to waters shallower than 400 m and generally to waters above the thermocline [Sabine et al., 2004]. Transport of CO_2 to the deep ocean increases the capacity of the surface ocean to take up more CO_2 from the atmosphere, at least over the time scale of ocean turnover (~ 1000 years). Transport of CO_2 to the deeper ocean occurs via physical oceanographic (advection, diffusion) or biological processes. For example, the North Atlantic takes up CO_2 disproportionately to its surface area because downward transport removes CO_2 -rich surface waters to the ocean interior more rapidly than in other ocean regions [Sabine et al., 2004]. Downward transport is generally higher in mid-latitude regions of bottom and intermediate water formation. The formation of organic matter through photosynthesis ($6\text{H}_2\text{O} + 6\text{CO}_2 \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$) also removes CO_2 from shallow ocean waters, and downward flux of this material can effectively store CO_2 in the deep ocean for hundreds of years.

The carbonate chemistry of the oceans has constantly evolved over geologic time in response to changes in other carbon reservoirs. Because the surface ocean is in near thermodynamic equilibrium with the atmosphere, the chemical response of the surface ocean to increased atmospheric CO_2 can be estimated from thermodynamic principles (Figure 2). This is the main driver of surface ocean carbonate chemistry, but the added effects of biological activity and ocean mixing complicate these estimates. Biological activity includes both organic matter production and oxidation, which takes up and releases CO_2 , respectively, and calcium carbonate production and dissolution, which releases and takes up CO_2 , respectively. Predictions in areas of ocean advection, particularly of upwelling and subduction, require estimates of mixing using physical oceanographic techniques.

The time scales of ocean response to increased atmospheric CO_2 vary depending on the processes that transport CO_2 across the air-sea interface, physical processes that transport that CO_2 into the ocean interior, the formation and remineralization of organic matter, and the formation and dissolution of CaCO_3 . CO_2 equilibration between the atmosphere and surface ocean is generally achieved within about a year, while the deep ocean concentrations reflect the atmospheric concentration when they were last in contact with the atmosphere plus the additional CO_2 released via oxidation of organic matter. Even though the oceans have a high capacity to store CO_2 , that capacity is limited by the rate of ocean overturning and the rate of CaCO_3 dissolution, so that thousands of years will be required for oceanic processes to restore atmospheric concentrations to near preindustrial levels [Archer et al., 1998].

In the meantime, the carbonate chemistry of shallow oceanic waters will reflect atmospheric CO_2 concentrations. Because coral reef ecosystems are confined to the upper mixed layer of the ocean, they will be readily exposed to these shifts in the ocean carbonate equilibrium.

2.3. Evidence for Seawater Carbonate Chemistry Changes

2.3.1. Direct measurements

Changes in seawater carbonate chemistry over time have been best observed at the oceanographic stations in Hawaii and Bermuda, where monthly measurements have been taken for over ten years. Data from both stations illustrate that changes in seawater carbonate chemistry coincide with changes in atmospheric CO₂ (Figure 3) [Bates, 2001; Keeling et al., 2004].

A large number of observations of open seawater carbonate chemistry have been obtained in the last decade or so. During the 1990's, inorganic carbon measurements from some 10,000 stations were obtained from nearly 100 oceanographic cruises as part of the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Survey (JGOFS). These measurements were used to map the distribution of carbon in the oceans, to determine what proportion of the carbon was anthropogenic [Sabine et al., 2004], and to determine temporal changes in the ocean CaCO₃ system [Feely et al., 2004] (Plate 1). These changes agree well with predictions. The increased oceanic burden of CO₂ is causing a shift in the CaCO₃ system in the oceans, and a shallowing of the CaCO₃ saturation horizons [Feely et al., 2004].

2.3.2. Isotopic data

Carbon derived from fossil fuel burning is isotopically lighter than that of the atmosphere, and consequently the ¹³C/¹²C ratio (δ¹³C) of the atmosphere is decreasing as more fossil fuel is added to the system. This leads to a parallel decrease in δ¹³C of carbon in the ocean. Quantitative estimates of oceanic uptake of carbon from the atmosphere obtained by measuring the decrease in δ¹³C of oceanic carbon over time have independently verified rates of oceanic carbon uptake [Quay et al., 1992] estimated by direct measurements and modeling.

2.3.3. Modeled data

Ocean circulation models that include carbon system chemistry have increasingly been used to predict changes in oceanic carbon chemistry over time. The Ocean Carbon Model Intercomparison Project (OCMIP) involved some 14 models that included not only carbonate chemistry, but also a simple biological component [Orr et al., 2001]. Among those models deemed to produce the most realistic simulations (based on comparisons with radiocarbon and CFC-11 ocean tracers), modeled oceanic carbon uptake during the 1980s and 1990s agree well with observations [Matsumoto et al., 2004].

The only model to take mineralogical differences into account was that by Anderssen et al. [2003]. This model was designed to examine the capacity of high-Mg calcite dissolution in shelf sediments to buffer the aragonite and calcite saturation states of the oceans, and illustrated that the extent of buffering was small.

2.4. Mineralogy, Taxonomy, and Biocalcification Mechanisms

The effects of changing seawater carbonate chemistry on calcifying organisms are likely to vary across taxa. This is due to differences in the physiological mechanisms of shell formation, the site of calcification, as well as mineralogical composition and crystal structure.

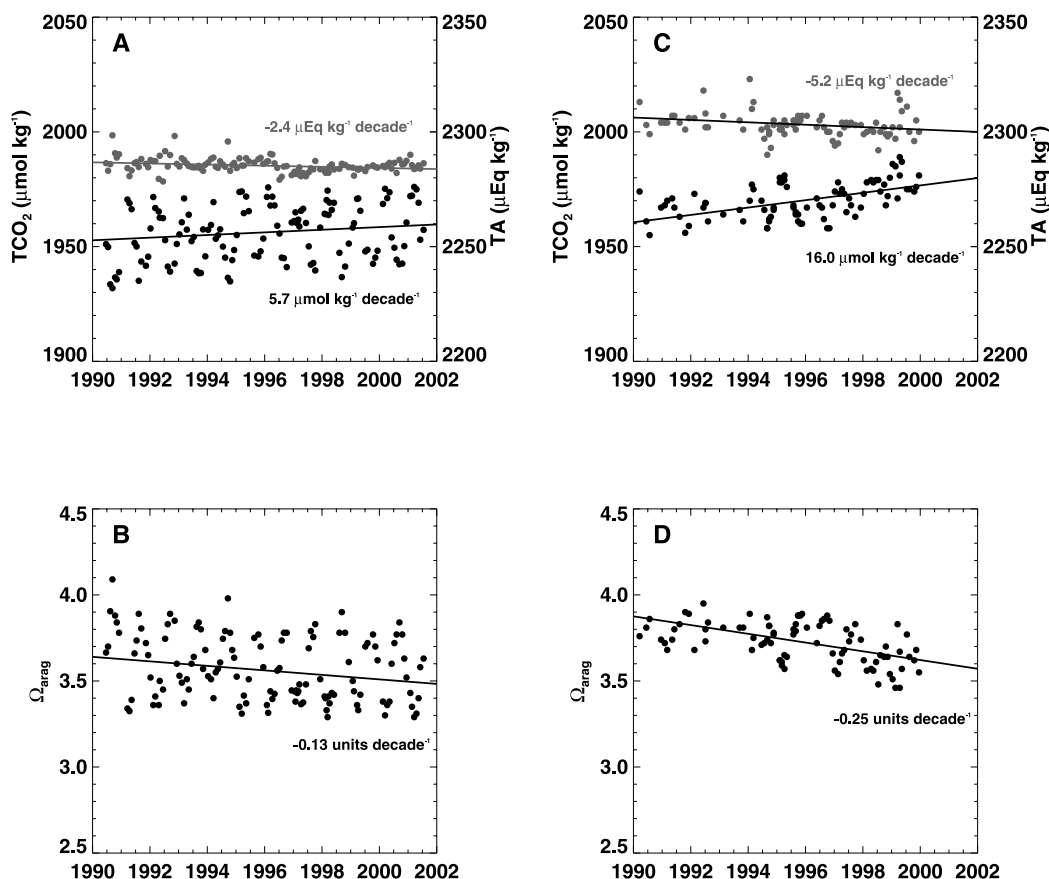


Figure 3. Changes in carbonate chemistry at the Bermuda Atlantic Time Series (BATS) Station and the Hawaiian Ocean Time-series (HOT) Station, for the period 1990 through 2002. A. TCO₂ (black) and TA (gray) at BATS (both normalized to salinity). B. Aragonite saturation state at BATS. C. TCO₂ (black) and TA (gray) at HOT (both normalized to salinity). D. Aragonite saturation state at HOT.

2.4.1. Mineralogy and taxonomy

Marine carbonates on coral reefs exist almost entirely as calcite (also called low-Mg calcite), high-Mg calcite (calcite with $\geq 5\%$ MgCO₃), aragonite, or a combination of calcite and aragonite. Of these, calcite is the most stable in the oceans, while high-Mg calcite with greater than about 12% MgCO₃ is the least stable. The two main reef-builders secrete the more soluble forms of CaCO₃. Corals secrete aragonite, while calcifying algae secrete either aragonite (green algae such as *Halimeda*) or high-Mg calcite (coralline red algae). Tropical benthic foraminifera, also a major contributor to reef sediments, predominantly secrete high-Mg calcite.

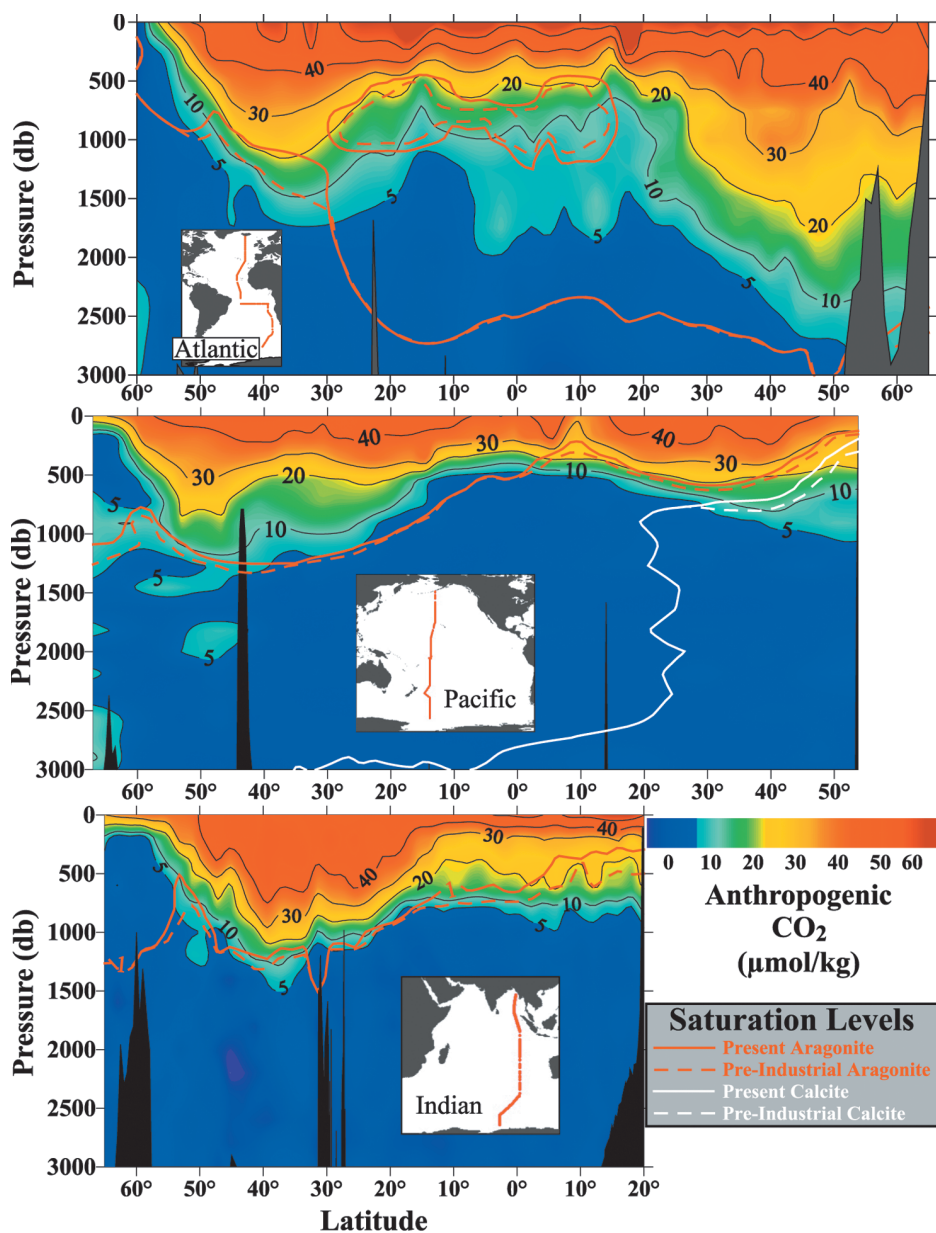


Plate 1. Present-day distribution of anthropogenic CO_2 in the open ocean, showing changes in the depth of the aragonite and calcite saturation horizons (reprinted with permission from Feely et al. [2004], copyright AAAS).

Organisms within major taxonomic groups tend to have the same mineralogy, and this appears to reflect the ocean chemistry conditions, particularly the Mg/Ca ratio, at the time the group evolved [Stanley and Hardie, 1998]. In some groups, skeletal mineralogy reflects changes in ambient conditions; the mineralogy of several species of coralline algae shifted from high-Mg calcite to low-Mg calcite when grown in seawater with a low Mg/Ca ratio [Stanley et al., 2002]. The skeletal bulk of some groups also seems to wax and wane with shifting environmental conditions. Termed “hypercalcifiers” by Stanley and Hardie [1998], these groups include those that tend to secrete massive skeletons and that have “poor control” over calcification (e.g., corals, coralline algae, coccolithophores, and bryozoans; see below).

2.4.2. Biocalcification mechanisms

Mechanisms for biomineralization are sometimes categorized as either biologically-induced or biologically-controlled [Weiner and Dove, 2003]. Biologically-induced calcification occurs as a consequence of biological activities with no direct control by the organism on the calcification process, and the CaCO_3 is usually precipitated external to the living cells. Calcification associated with biofilms is a common biologically-induced process. Calcification in the green alga *Halimeda discoidea* has also been described as biologically-induced by pH changes during photosynthesis [De Beer and Larkum, 2001], although the consistent morphology of *Halimeda* segments indicates that there is at least some biological control [Jonathan Erez, pers. comm.].

Biologically-controlled calcification implies that the organism has some control on the calcification process, and is further categorized according to where calcification occurs: extracellular, intercellular, or intracellular [Weiner and Dove, 2003]. Most calcifiers on coral reefs exert some level of control on calcification. Many coralline algae secrete CaCO_3 intercellularly (outside or within their cell walls), while corals secrete CaCO_3 extracellularly, at the base of the polyps beneath the calciblastic layer. It seems logical to assume that organisms with less biological control over the calcification process are likely to be more sensitive to environmental change than those in which it is more strongly regulated, but this assumption has not been rigorously tested.

Once formed, skeletal carbonates experience differential rates of dissolution. Dissolution rates are not only affected by mineralogy, but also by thickness, texture, and morphology of the skeletal material, whether it is protected by organic matter, by the crystal structure itself, and by the trace element composition and presence of adhered small particles (see, for example, Bischoff et al. [1993]).

2.5. Natural Variability of the Carbonate System on Coral Reefs

Metabolic processes on coral reefs (photosynthesis, respiration and calcification) impose a powerful control on seawater carbonate chemistry in many reef environments. The greater the surface to volume ratio of the system (reef surface to overlying water volume) – that is, the shallower the water depth – the greater the impact these processes have on the carbonate chemistry (Table 1). The diurnal fluctuations in carbonate system parameters can be dramatic (Figure 4). The greatest reported range in aragonite saturation state (1.83–6.36) was from a shallow (<1m depth) reef flat in Okinawa [Ohde and van Woesik, 1999]. Most of this variation was due to high rates of photosynthetic drawdown of CO_2 .

TABLE 1. Reported changes in seawater carbonate chemistry in coral reef waters. TA = total alkalinity.

Study	Location	$p\text{CO}_2$ or $f'\text{CO}_2$ μatm	TA reef $\mu\text{eq kg}^{-1}$	TA offshore $\mu\text{eq kg}^{-1}$	Comments
Frankignoulle et al., 1996; Gattuso et al., 1996	Moorea lagoon	240-400	–	2378 ^a	maximum range of hourly measurements taken over 3 days
”	Yonge Reef	250-700	–	2334 ^a	”
Suzuki and Kawahata, 1999	Palau barrier reef	366-414	–	–	difference between lagoon and offshore values
”	Majuro Atoll	345-370	2264-2266 ^b	2287 ^b	”
”	South Male Atoll	362-368	2291-2317 ^b	2317 ^b	”
Ohde and Van Woesik, 1999	Rukan sho reef flat	37-813	1714-2348 ^a	2294-2336 ^a	max range of hourly measurements taken over 5 separate days
”	Rukan sho lagoon	119-378	1974-2319 ^a	2294-2336 ^a	”
Kawahata et al., 2000	Great Barrier Reef Lagoon				transects of measurements inside and outside GBR
Bates et al., 2001	Bermuda reef flat	340-470	2329-2357 ^c	2378 ^c	$p\text{CO}_2$; max range of hourly measurements taken over 24 days;
					TA: range between 0800 and 1600 h of one day of sampling
Kayanne et al., 2003	Shiraho Reef (Ryukyu Is.)	200-600	2100-2270 ^a	–	range of nearly continuous measurements taken over 3 days;
					note that TA remained nearly constant at 2270 at night.

^a TA normalized to salinity not reported
^b normalized to S = 35
^c normalized to S = 36.41

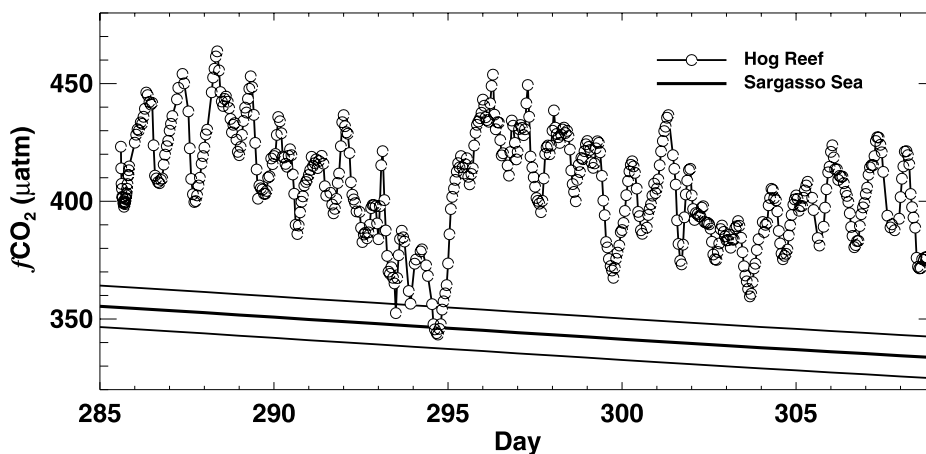


Figure 4. Diurnal fluctuations in $f\text{CO}_2$ on Hog Reef Flat, Bermuda (circles) for a 24-day period in 1998 ($f\text{CO}_2$, the fugacity of CO_2 , is approximately equal to $p\text{CO}_2$). The mean seawater $f\text{CO}_2$ for the Sargasso Sea for a 4-year period (1994-1998) is indicated by the straight line (from Bates et al. [2001]; copyright by the American Society of Limnology and Oceanography, Inc.).

2.6. Misperceptions

2.6.1. The role of mineral buffers

Various biogeochemical feedbacks within the Earth system act to stabilize atmospheric CO_2 and the carbonate system in seawater. The most effective of these is dissolution of marine carbonates. Increasing ocean acidity leads to increased rates of dissolution of carbonate sediments (Equation 5) that nudge the system back toward equilibrium (this is practically applied in marine aquaria, by circulating waters through a calcium carbonate substrate). Under normal conditions, calcite is the most stable of the carbonate minerals, and high-Mg calcite with $\geq 15\%$ MgCO_3 is the least stable (high-Mg calcite solubility increases with Mg content). That is, as saturation state decreases, the first mineral to dissolve is high-Mg calcite, and it is thus the “first responder” to decreasing saturation state (but as already noted, other factors also affect CaCO_3 solubility).

High-Mg calcite is an abundant mineral on coral reefs, mainly due to the predominance of coralline algae, which commonly comprise about 10-45% of reef sediments [Milliman, 1974], and higher percentages on reefs where they are the dominant reef builder. In general, the warmer the water, the greater the Mg content in this mineral, and the higher the Mg content, the greater its solubility [Morse and Mackenzie, 1990]. Measurements of the stoichiometric ion activity product of natural high-Mg calcites ($-\log \text{IAP}_{\text{Mg-calcite}}$) vary between -8.50 and -7.95 depending on the source and the mole % MgCO_3 [Mucci and Morse, 1984; Walter and Morse, 1984; Bischoff et al., 1987]. These measurements indicate that the most soluble high-Mg calcite, produced by the coralline algae *Amphiroa rigida* (22 mole % MgCO_3) is about 1.7-times more soluble than aragonite. Two recent studies support this observation. Morse et al. [2003] determined the solubility of carbonate produced during whittings (the sudden appearance of suspended CaCO_3 particles in the

water column; see section 3.3.2) on the Great Bahamas Bank to be 1.9-times more soluble than aragonite; and Langdon et al. [2000] found that calcification in the Biosphere 2 coral reef mesocosm, a community dominated by *Amphiroa fragillisma*, dropped to zero when $\Omega_{\text{arag}} = 1.7 \pm 0.2$ (Figure 5). Based on these estimates high-Mg calcite begins to dissolve once the partial pressure of CO_2 ($p\text{CO}_2$, that is, the partial pressure of $\text{CO}_2(\text{g})$ that is in equilibrium with the seawater) exceeds $1000 \mu\text{atm}$.

While the $p\text{CO}_2$ of open ocean seawater should remain below $1000 \mu\text{atm}$ for the remainder of this century, respiration of organic matter and other processes in sediments elevates pore water $p\text{CO}_2$ to high levels that cause high-Mg calcites in the sediments dissolve. Measurements of pore waters of reef sediments indicate that the carbonate chemistry is generally maintained near equilibrium with high-Mg calcite. High rates of dissolution of high-Mg calcite have also been measured on natural reefs (Great Barrier Reef algal ridges, Chisholm [2000]; Hawaiian reef sediments, Halley and Yates [2000]), and in reef flat sediments [Boucher et al., 1998]. Leclercq et al. [2002] found that sediment dissolution in their mesocosm experiments did not vary with $p\text{CO}_2$ variations between 411 and $918 \mu\text{atm}$, although it is not clear whether the mesocosm sediments included high-Mg calcite.

While dissolution thus plays an important role in marine carbonate systems, one misperception is that buffering by carbonate dissolution will prevent a decrease in saturation state. Under normal circumstances, dissolution of a particular carbonate mineral proceeds as long as the seawater remains undersaturated with that mineral; dissolution ceases once saturation ($\Omega = 1$) is achieved. A simple example is a sediment mixture of *Amphiroa* (high-Mg calcite with 22% MgCO_3) and coral (aragonite) fragments that is exposed to increasing $p\text{CO}_2$ levels, and maintained at 25°C . Based on the Biosphere 2 experiments described above [Langdon et al., 2000], the high-Mg calcite would begin to dissolve once $\Omega_{\text{hmc}} = 1$, which would occur when $p\text{CO}_2 \approx 1000 \mu\text{atm}$. At that point, $\Omega_{\text{arag}} = 1.7$, so the aragonite

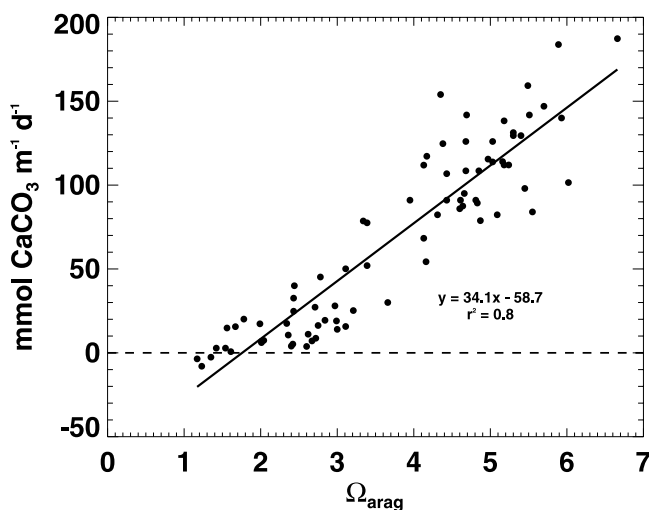
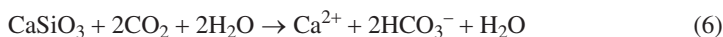


Figure 5. Calcification data from the Biosphere 2 mesocosm. Community was dominated by *Amphiroa fragillisma*, a coralline algae that secretes high-Mg calcite (22% MgCO_3). Calcification goes to 0.0 at $\Omega_{\text{arag}} = 1.7 \pm 0.2$ (data from Langdon et al. [2000] and other Biosphere 2 results).

sediments would not readily dissolve. As long as the high-Mg calcite dissolved rapidly enough, the saturation states would be maintained at $\Omega_{\text{hmc}} = 1$ and $\Omega_{\text{arag}} = 1.7$. Once all of the high-Mg calcite was dissolved, the saturation state would decline until $\Omega_{\text{arag}} = 1.0$, at which point aragonite sediments would readily dissolve. At no point in this process does dissolution bring the saturation state to levels consistent with preindustrial levels of 280 ppmv ($\Omega_{\text{arag}} \sim 4.2$ at 25°C). One can imagine cases where processes of dissolution are separated from the water column, so that the concentration of solutes delivered to the water column are high enough to raise alkalinity to above that of normal seawater (e.g., delivery of high-alkalinity groundwater), but such regions have not been identified.

The effectiveness of dissolution in maintaining the saturation state of a body of water ultimately depends on the residence time of the water. Coral reefs are restricted to full salinity seawater, and depend on regular flushing with open ocean waters. This needed exchange with open ocean waters dilutes the solutes released by dissolution. Some restricted lagoons, for example, may experience significant dissolution between tidal flushings. Observations within the Great Barrier Reef lagoon revealed that lagoon waters reflected a strong calcification signal relative to the open ocean waters adjacent to the lagoon; that is, higher levels of $p\text{CO}_2$, lower alkalinity, and thus a lower saturation state [Kawahata et al., 2000]. However, any dissolution acting to balance the carbonate system was not enough to maintain alkalinity above that of the open ocean waters. Similarly, alkalinity measurements on reef flats and in atoll lagoons are consistently lower than those of adjacent open ocean waters (Table 1). As mentioned earlier, a numerical simulation to investigate the effectiveness of high-Mg calcite dissolution in buffering future ocean pH [Anderssen et al., 2003] found that, although high-Mg calcite dissolution will increase in shelf sediments, the accumulation of alkalinity in surface waters would be small.

Silicate minerals also buffer the carbon system. As atmospheric CO_2 concentrations increase, so does the acidity of rainfall, which increases the rate of chemical weathering of both carbonate and silicate rocks on land, and thus increases the delivery of positive ions (alkalinity) to the ocean. Weathering of silicate rocks consumes atmospheric CO_2 . The chemical reaction is:



Geochemists estimate the rate of silicate weathering at 0.06 gigatons of C y^{-1} [Kump et al., 1999]. This process has immense capacity for taking up atmospheric CO_2 but the flux is too small to have any impact on the present build up of atmospheric CO_2 . Continental weathering is thought to have drawn down the 100 ppmv increase in $p\text{CO}_2$ since the last glacial maximum (18,000 years ago) by about 6–12 ppmv [Munhoven, 2002].

2.6.2. CO_2 fertilization of zooxanthellae

A common misperception is that, similar to CO_2 -fertilization of land plants, increases in CO_2 will enhance growth of the algal symbionts in corals, which in turn will lead to higher calcification rates. This misperception is based on two assumptions about the coral/algal symbiotic relationship: a) that increased photosynthesis increases calcification rates, and b) that zooxanthellar photosynthesis will increase with rising CO_2 . The first assumption is based on the fact that zooxanthellate corals calcify faster in the light than in the dark (estimated three times as fast by Gattuso et al. [1999]), and also that calcification in bleached corals slows or stops [Leder et al., 1991]. The inference is that photosynthesis enhances calcification. It should be noted, however, that the mechanisms for light-enhanced

calcification have not been adequately resolved, and that the opposite – that calcification enhances photosynthesis – has also been suggested [McConnaughey and Whelan, 1997; Cohen and McConnaughey, 2003] (see Section 4.1).

The importance of the second assumption is somewhat tempered by the fact that zooxanthellae primarily use HCO_3^- as a substrate for photosynthesis, and secondarily use CO_2 (some of which is respired CO_2). While aqueous CO_2 concentrations will increase about 100% in concert with a doubling of atmospheric CO_2 , HCO_3^- concentrations will increase only about 14% (Figure 2). This increase in CO_2 and HCO_3^- may in fact stimulate photosynthesis by zooxanthellae, but it is accompanied by a decrease rather than an increase in calcification [Langdon and Atkinson, 2005]. This may be due to competition between zooxanthellae and the host for the same internal pool of dissolved inorganic carbon [Marubini and Davies, 1996; Cruz-Pinon et al., 2003].

2.6.3. Seawater carbonate chemistry is the only variable that affects calcification

Although carbonate saturation state is a likely control on marine biocalcification, at least in some taxa, it is not the only variable that affects calcification rates in corals and other reef builders. In particular, two other variables that are known to affect calcification rates are temperature [Coles and Jokiel, 1978; Houck et al., 1987; Reynaud et al., 2003; Marshall and Clode, 2004], and light [Barnes, 1982; Chalker and Taylor, 1978; Marubini et al., 2001]. These variables help define the “optimum niche” for coral calcification, and their combined effects are addressed in Section 3.3.

3. Calcification Response

3.1. Field Evidence

The first field study showing a correlation between calcification and seawater carbonate chemistry was based on precise observations of the carbonate chemistry of seawater (TA, TCO_2 , and $p\text{CO}_2$) in waters overlying the Great Bahamas Bank [Broecker and Takahashi, 1966]. This study illustrated a relationship between the age of a parcel of water based on its salinity or ^{14}C concentration and the draw-down in total alkalinity relative to the oceanic end member (alkalinity drawdown is almost entirely caused by calcification). When Broecker and Takahashi [1966] plotted calcification rate ($\Delta\text{TA}/\text{age}$ of the water parcel) against the IAP of Ca^{2+} and CO_3^{2-} (essentially the numerator of Equation (1)), they were surprised to find a strong linear relationship. At the time they thought such a clear chemical control on the calcification rate could only mean that the calcification was abiotic. We now know that many calcifying organisms also respond linearly to changing IAP or saturation state [Langdon et al., 2000].

Coral “growth rates” have been measured in the field using several methods, but only some of these can be used as a measure of calcification rate. Calcification rates are a measure of the total CaCO_3 precipitated per unit area per unit time. Most early works tracked changes in coral growth by measuring extension rate (length per unit time), but this value neglects variation in skeletal density. Other methods that are used to track growth rates are weighing the specimen at regular intervals (e.g., buoyant weight; Jokiel et al. [1978]), or keeping track of the chemistry changes in seawater to account for the CO_3^{2-} uptake by the organism (e.g., alkalinity anomaly; [Smith and Kinsey, 1978; Chisholm and Gattuso, 1991]). Unfortunately, these methods have rarely been applied to corals in the field.

Retrospective records of calcification have, however, been documented from corals in the field. These are obtained from massive corals, by combining skeletal density and skeletal extension rate along the growth axis of a specimen. This technique has been used by Lough and Barnes [1997, 2000] to document historical changes in *Porites* calcification rates along the Great Barrier Reef; and similar techniques have been used by others (Table 2). All of these studies found that calcification rates in these massive corals correlated well with temperature records, and somewhat with irradiance. The original analysis of Lough and Barnes [1997] was from 35 coral cores spanning latitudes 9.4°–23.3°S, and which shared a common period of 1934–1982. Across this latitudinal range, average annual calcification in these corals increased by about $0.16 \text{ g cm}^{-2} \text{ y}^{-1}$ per 1°C . This correlation was reinforced by an additional analysis of an eight-year period on some 245 *Porites* coral heads from 29 Great Barrier Reef sites and extended to 44 sites in the Indo-Pacific [Lough and Barnes, 2000]. The spatial analysis illustrated a strong correlation between calcification rate and temperature ($0.33 \text{ g cm}^{-2} \text{ y}^{-1}$ per 1°C ; Figure 6; Table 2).

These same studies provided no clear evidence that calcification rates had declined over time. Average calcification rates did decrease over the last few decades, but given that 1) the 1930–1979 average calcification rate was 4% higher than that of 1880–1929, and 2) longer records extending over more than two centuries illustrate considerable variability in calcification, the authors considered the decrease as natural variability rather than an indication of changing seawater carbonate chemistry [Lough and Barnes, 1997, 2000]. The single *Porites* core analyzed by Bessat and Buigues [2003] showed an increase in calcification over time in concert with increasing air temperature records, rather than a decrease as predicted by Kleypas et al. [1999].

These temperature-calcification correlations, particularly the spatial correlations, also include the effects of other variables that co-vary with latitude and temperature, such as aragonite saturation state and light. However, records for these are few, and can only be estimated for most reef locations. What these records highlight is that coral calcification responds to a combination of variables acting both on the seawater carbonate chemistry and on the biological processes of the organisms. Some investigators have predicted that coral calcification will increase rather than decrease as a consequence of fossil fuel burning, because the effects of a temperature increase will outweigh the effects of a saturation state decrease [McNeil et al., 2004]. However, if one considers the complete picture of coral response to increasing temperature – that coral growth and calcification increase to a coral's 'optimum' temperature (close to average summertime maximum) and then decreases rapidly after (Section 3.3.1) – it is likely that the positive response to increased temperature will be short-lived [Kleypas et al., 2005]. In addition, the ability of coral adaptation to keep pace with rising temperature has not been demonstrated, particularly in light of increases in the frequency of coral bleaching over the last few decades [Hoegh-Guldberg, 1999].

3.2. Experimental Evidence

Most experimental work on coral and coral reef ecosystem responses to rising CO_2 has occurred under controlled laboratory conditions, in which seawater carbonate chemistry was manipulated while holding other variables constant (reviewed by Langdon [2002]). Although seawater carbonate chemistry can be manipulated in multiple ways (e.g., adding acid or base; bubbling CO_2 through the system; allowing community metabolism to alter the chemistry) experimental results have consistently shown that coral and coral mesocosm calcification rates are positively correlated with carbonate ion content (Table 3). The calcification response of a coral or a mesocosm to doubled CO_2 varies from about –15%

TABLE 2. Studies of measured calcification rates from massive coral skeletons. G = calcification rate.

Location/ Latitude Range	Species	Time Period	Findings	Reference
Great Barrier Reef 9.4°S-23.3°S	<i>Porites</i> spp. cores from 35 large colonies	common period: 1934-1982 total range: 1746-1982	Strong correlation with SST $G = 0.16 \text{ g cm}^{-2} \text{ y}^{-1}$ per 1°C weaker correlation with irradiance avg $G = 1.72 \text{ g cm}^{-2} \text{ y}^{-1}$ G most strongly correlated with extension	Lough and Barnes, 1997
Great Barrier Reef 29 reefs between 12.4°S-21.7°S	<i>Porites lobata</i> <i>P. lutea</i> <i>P. australiensis</i> <i>P. solida</i> 245 colonies	common period: 1979-1986	$G = 0.39 \text{ g cm}^{-2} \text{ y}^{-1}$ per 1°C ($G = 0.33 \text{ g cm}^{-2} \text{ y}^{-1}$ per 1°C when combined with data from Hawaii and Thailand) avg $G = 1.63 \text{ g cm}^{-2} \text{ y}^{-1}$ G most strongly correlated with extension	Lough and Barnes, 2000
Moorea 17.5°S	<i>Porites lutea</i> 1 colony	1800-1990	strong correlation with local air temperature records: $G = 0.45 \text{ g cm}^{-2}$ y^{-1} per 1°C avg $G = 1.25 \text{ g cm}^{-2} \text{ y}^{-1}$ G most strongly correlated with extension	Bessat and Buigues, 2001
Caribbean and Gulf of Mexico (12 locations)	<i>Montastraea annularis</i>	total range: 1968-1997 (not all specimens share common growth period)	Gulf specimen growth: 0.55 g $\text{cm}^{-2} \text{ y}^{-1}$ per 1°C Caribbean growth: 0.58 g $\text{cm}^{-2} \text{ y}^{-1}$ per 1°C G most strongly correlated with density	Carricart-Ganivet, 2004

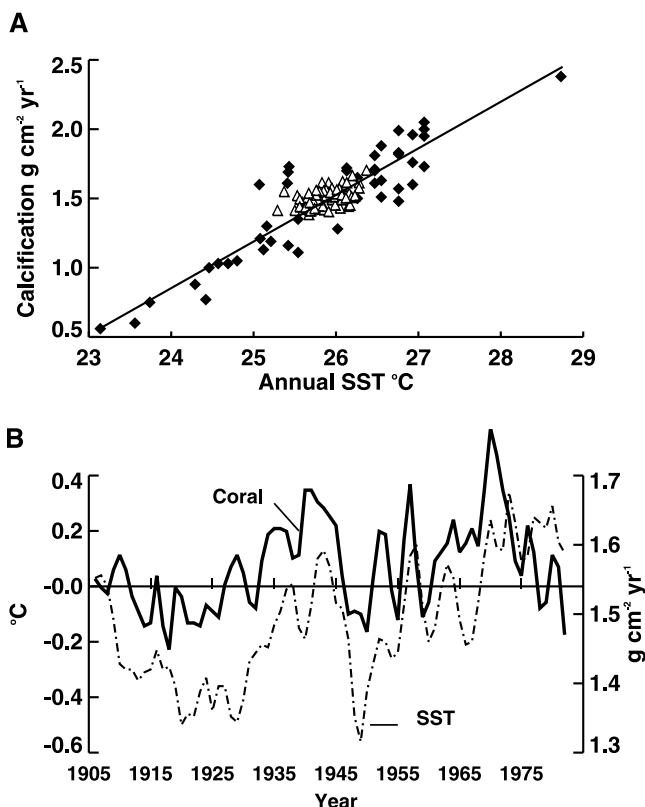


Figure 6. A. Average calcification rate from *Porites* cores versus average sea surface temperature; solid diamonds are the 1979-1986 averages from 44 *Porites* colonies; open triangles are the 1903-1982 averages from ten large *Porites* cores from the Great Barrier Reef (from Lough and Barnes [2000]). B. time-series of the 1906-1982 average calcification rates from ten large *Porites* cores from the Great Barrier Reef, shown with average Great Barrier Reef sea surface temperature for the same period (from Lough and Barnes [1997]). Both figures reprinted with permission from Elsevier.

to -54%. This range almost certainly reflects variation between species (calcification mechanisms, mineralogy, etc.) and environmental conditions (temperature, light, nutrients, etc.). Adaptation to changing seawater carbonate chemistry conditions has not been observed. Although most of these experiments have been conducted over hours to weeks, the Biosphere 2 experiments were conducted over many months, without any indication of adaptation [Langdon, 2000].

Surprisingly few realistic experiments testing calcification rates versus carbonate chemistry have been conducted on calcifying red algae and green algae (e.g., *Halimeda*) of coral reefs. Some of the studies originally cited as illustrating an effect of saturation state on algal calcification [Borowitzka, 1981; Gao, 1993] were conducted over unrealistic chemistry ranges. Borowitzka and Larkum [1976] measured both photosynthesis and calcification

TABLE 3. Measured calcification response in coral reef organisms and mesocosms (based on an earlier version by Langdon, 2002). Percent change in calcification rate (ΔG) was calculated by normalizing calcification rate to percent of the preindustrial value (assuming a preindustrial $\Omega_{\text{arag}} = 4.6$). Manipulations of carbonate chemistry are indicated by methods (1) TA held constant, TCO_2 adjusted by bubbling CO_2 gas; (2) TCO_2 held constant, TA adjusted with acid or base; (3) pH held constant, TA and TCO_2 adjusted; (4) CO_2 (aq) held constant, pH, TCO_2 , TA allowed to vary; (5) natural community alters seawater carbonate chemistry; and (6) Ca^{2+} concentration adjusted. For reference, in 26°C seawater with $p\text{CO}_2 = 280$ ppmv, average Ω_{arag} is about 4.6; a shift to $\Omega_{\text{arag}} = 3.6$ (one unit) is equivalent to an increase in $p\text{CO}_2$ of about 140 ppmv (when $p\text{CO}_2 = 420$ ppmv). HMC = high-Mg calcite.

Organism/ System	Mineralogy	Manip.	Temp $^\circ\text{C}$	Duration	% ΔG per unit decrease in Ω_{arag}	Reference
Calcifying Algae						
<i>Porolithon gardineri</i>	HMC	2	19.5-30.0	20-27 d	-10.0 ^a	Agegian, 1985
Corals						
<i>Stylophora pistillata</i>	aragonite	6	27	2.5 h	-9.0 ^b	Gattuso et al., 1998
<i>S. pistillata</i>	aragonite	1	25.2	5 weeks	-4.5	Reynaud et al., 2003
<i>S. pistillata</i>	aragonite	1	28.2	5 weeks	-38.1	Reynaud et al., 2003
<i>Madracis mirabilis</i>	aragonite	2	26-30	12 d	-22.0	Horst and Edmunds, 2006
<i>Acropora cervicornis</i>	aragonite	1	25	2 months	-27.0	Renegar and Riegl, 2005
<i>Acropora eurystoma</i>	aragonite	2,3,4	24	1-2h	-24.0 ^c	Schneider and Erez, 2006
<i>Acropora verweyi</i>	aragonite	2	26.5	8 d	-8.3	Marubini et al., 2003
<i>Porites compressa</i>	aragonite	1	26.5	10 weeks	-10.6	Marubini et al., 2001
<i>P. compressa</i> + <i>Montipora capitata</i>	aragonite	2	23.4	1.5 h	-29.0	Langdon and Atkinson, 2005
<i>P. compressa</i> + <i>M. capitata</i>	aragonite	2	27.3	1.5 h	-24.2	Langdon and Atkinson, 2005
<i>Porites lutea</i>	aragonite	2	25.0	3-6 d	-25.0	Ohde and Hossain, 2004
<i>Porites lutea</i>	aragonite	2	25.0	2-3 d	-22.0	Hossain and Ohde, 2006
<i>Porites rus</i>	aragonite	2	25-28	8 d	-40.0	Horst and Edmunds, 2006
<i>Pavona cactus</i>	aragonite	2	26.5	8 d	-9.0	Marubini et al., 2003

TABLE 3. (Continued)

<i>Fungia</i> sp.	aragonite	2	25	2-3 d	-31.0	Hossain and Ohde, 2006
<i>Galaxea fascicularis</i>	aragonite	2	26.5	8 d	-7.6	Marubini et al., 2003
<i>G. fascicularis</i>	aragonite	6	23.0	2-4 h	-39.0	Marshall and Clode, 2002
<i>G. fascicularis</i>	aragonite	6	19.0	2-4 h	-35.0	Marshall and Clode, 2002
<i>Turbinaria reniformis</i>	aragonite	2	26.5	8 d	-5.9	Marubini et al., 2003
Carbonate systems						
Gr. Bahamas Banks*	mixed	5	27.0-28.9	n/a	-37.9	Broecker and Takahashi, 1966
Okinawa reef flat	mixed	5	n/a	8 h	-30.1	Broecker et al., 2001 Ohde and van Woesik, 1999
B2 mesocosm*	mixed, mainly HMC	1,3,5	26.5	days-months	-37.2	Langdon et al., 2000
Monaco mesocosm	mixed	1	26.0	24 h	-7.8	Leclercq et al., 2000
Monaco mesocosm	mixed	1	26.0	9-30 d	-6.5	Leclercq et al., 2002

^a Based on linear extension^b Based on Ω_{arag} in the range 1.9-4.0^c Based on light-calcification only; dark calcification value was -27%

in *Halimeda tuna* over various manipulations of seawater carbonate chemistry. Their results indicate that while photosynthesis responds to changes in CO_2 and HCO_3^- concentrations, calcification responds to changes in CO_3^{2-} concentration. Probably the best experimental data on coralline algae are those of Agegian [1985] on *Porolithon gardineri*; her results, which examined both temperature and saturation state, indicate that extension rate (used as a proxy for calcification rate, which may or may not be an appropriate measure in this species) will decline by 40% under doubled CO_2 conditions. This agrees well with the results obtained in Biosphere 2, which was dominated by coralline red algae.

3.3. Biological versus Inorganic Components of Calcification

On coral reefs, nearly all of the calcium carbonate precipitated is biogenic. Corals, coralline algae, and benthic foraminifera secrete the bulk of the biogenic CaCO_3 , with echinoderms, mollusks and a few other groups secreting the remainder. Inorganic precipitation of marine cements occurs at much slower rates, but can become a significant component over time.

3.3.1. Biological calcification

As described earlier, biological calcification implies that the organism exerts some level of control on its calcification. Environmental factors that affect the physiology of calcifying organisms should, therefore, also be considered as factors affecting calcification; three of these being light, temperature, and nutrients.

Relatively little is known about the combined effects of carbonate ion concentration and light levels. Only one study to date has looked at the interaction, in a two-factor experiment where *Porites compressa* was grown at four light levels and three saturation states [Marubini et al., 2001]. The results indicated no significant change in the slope of the calcification- Ω_{arag} relationship across the range of light levels tested (Figure 7); i.e., no evidence for interaction between light and saturation state.

Temperature is also known to affect calcification rates in corals. Most species calcify faster with increasing temperature until an optimal temperature is reached; beyond which calcification rates decline [Clausen, 1971; Clausen and Roth, 1975; Jokiel and Coles, 1977]. The field data from *Porites* corals [Lough and Barnes, 2000; Bessat and Buigues, 2001] and from *Montastrea* [Carricart-Ganivet, 2004] illustrate a strong correlation between temperature and calcification that has essentially overridden the predicted decrease in calcification over the Industrial Period. However, only two experimental studies have looked at the interaction between temperature and saturation state, and these produced different results. Reynaud et al. [2003] varied temperature between 25°C and 28°C and varied $p\text{CO}_2$ between 460 and 760 μatm . At 25°C, calcification of *Stylophora pistillata* increased slightly with increased $p\text{CO}_2$, while at 28°C calcification decreased by 50%. Langdon and Atkinson [2005] measured the calcification of an assemblage of *Porites compressa* and *Montipora capitata* under summer (27.3°C) and winter (23.4°C) conditions. They found no significant change in the slope or intercept of the calcification- Ω_{arag}

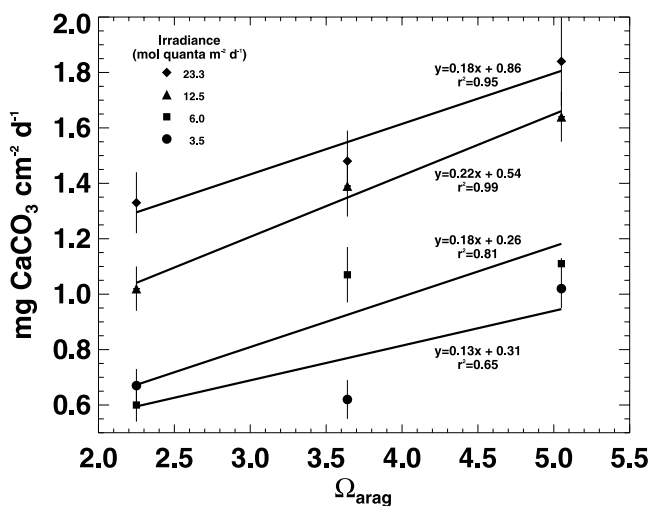


Figure 7. Interaction between altered carbonate chemistry and irradiance on the calcification of *Porites compressa* (data from Marubini et al. [2001]).

relationship between summer and winter temperatures. At present it is not known whether the CO_2 -temperature interaction of typical corals is minimal or strong.

Only two studies have considered the interacting effects of nutrients and saturation state on coral calcification. Marubini and Thake [1999] measured the skeletal weight increase of *Porites porites* at three nutrient levels (ambient, +20 μM NO_3 and +20 μM NH_4) and two saturation states (2.6 and 7.4) (Figure 8A). The change in saturation state was achieved by doubling the dissolved inorganic carbon concentration with the addition of bicarbonate. Calcification decreased with nutrient enrichment in the low saturation state treatments (–25% with NH_4 enrichment, and –52% with NO_3 enrichment), but increased in the high saturation state treatments (+12% with NH_4 enrichment, and +33% with NO_3 enrichment). In essence, calcification in *P. porites* was more sensitive to changes in Ω_{arag} under increased nutrient

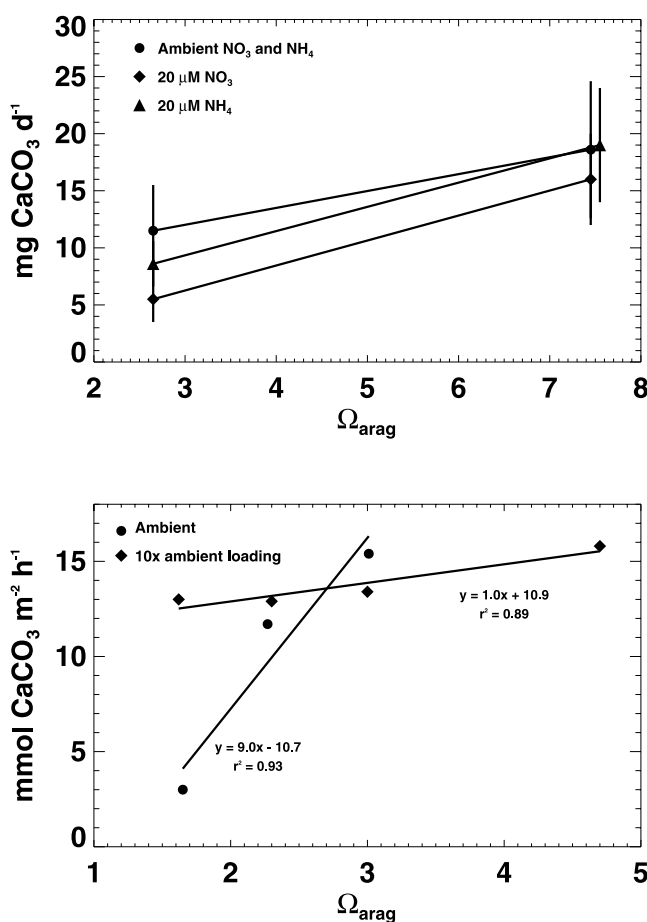


Figure 8. Interactions between altered carbonate chemistry and nutrient enrichment. A. *Porites porites* (data from Marubini and Thake [1999]). B. Mixed assemblages of *Porites compressa* and *Montipora capitata* (data from Langdon and Atkinson [2005]).

conditions. Langdon and Atkinson [2005] observed the opposite interaction (Figure 8B). They added PO_4 and NH_4 in daily pulses and observed the effect on calcification at ambient saturation state and a reduced saturation state produced by doubling the $p\text{CO}_2$ after only four days of nutrient enrichment. They found that nutrient enrichment made the corals *P. compressa* and *M. capitata* much less sensitive to a change in Ω_{arag} .

The experimental details were quite different in these two studies, which likely contributed to the different responses. The different results in these combined Ω_{arag} -nutrient studies, as well as in the combined Ω_{arag} -temperature studies, illustrate the complexity of these interactions, and the need for more controlled studies.

3.3.2. Inorganic calcification

Inorganic calcification within coral reef habitats or carbonate banks includes the formation of marine ooids, the precipitation of marine CaCO_3 cements within reef sediments and skeletal framework, and possibly the spontaneous precipitation of crystals within the water column (whittings). Although the origin of whittings remains equivocal [Morse et al., 2003], all three of these inorganic forms of CaCO_3 are suspected to be mediated by biological activity, or at least by the presence of organic matter [Folk and Lynch, 2001; Robbins and Blackwelder, 1992]. However, one might assume that precipitation of these “inorganic” forms of calcium carbonate should more closely reflect environmental controls. Indeed, ooids and whittings do seem to be restricted to regions where carbonate saturation state is high; e.g., the Bahamas Bank and the Persian Gulf.

The presence of marine cements within the coral reef environment exhibits spatial variation across reef systems, within individual reefs, and within corals themselves. This is partly controlled by sediment chemistry, and partly by exchange with overlying waters. Pore-water chemistry of reefs tends to be maintained close to equilibrium with aragonite and high-Mg calcite, by processes such as microbially-mediated respiration and sulfate reduction (reviewed by Morse and Mackenzie [1990]; and Morse [2003]). Cementation tends to be greatest where abundant flushing with overlying seawater supplies an adequate supply of ions. Within coral reef systems cementation is thus greatest near the continental shelf edge and lowest within inner reefs (e.g., Belize Barrier Reef: James et al., [1976]; Great Barrier Reef: Marshall, [1985]; Kleypas [1991]). On individual reefs, it tends to be greater on windward margins [Marshall, 1985]. Within individual coral heads, cementation can occur nearly contemporaneously with coral growth, with greater accumulation of inorganic cements at the base of a coral than near the living surface which, incidentally, can contaminate the geochemical records (e.g., isotopes, Ca/Sr ratios, etc. [Müller et al., 2001]). The mineralogy of submarine reef cements is overwhelmingly aragonite and high-Mg calcite.

Patterns of reef cementation across oceanic regions have been noted but have not been explicitly studied. High cementation rates have been reported in regions such as the Red Sea [Friedman et al., 1974], while reefs in the eastern Pacific have low cementation rates [Cortés, 1997]. Whether these regional differences in cementation are related to differences in seawater carbonate chemistry has not been investigated.

The important role of cementation in reef building has often been suggested, but quantitative studies have been few. Submarine cementation rates within reefs are low compared to biological rates [Oberdorfer and Buddemeier, 1986], yet cementation continues long after the biocalcifiers have died, and increases a reef's resistance to erosive hydrologic forces [Lighty, 1985]. It is not clear if cementation protects a reef from bioerosion. Highly exposed and highly indurated coralline algal reefs attract a different suite

of borers and bioeroders than poorly cemented reefs in lower-energy environments [Bosence, 1985]. Bioerosion in the high-energy reefs was more extensive than in lower energy environments, but did not destroy the overall reef framework. It is unclear whether these bioeroders were more attracted by the high-indurated reef surface, or by the high-energy environment, but is clear that bioerosion can have a profound effect on reef-building. Following the 1982-83 mortality on many Eastern Pacific reef communities, bioerosion removed thousands of years of coral reef accumulation in a matter of a few years [Glynn, 1994; Eakin, 1996]. Here, bioeroders preferred softer substrates as well as the coralline algae pavements [Reaka-Kudla et al., 1996]. Did lack of cementation play a role in this high rate of erosion, or was this simply a biological process?

Whitings are not considered a major contributor to carbonate production on the Bahamas Bank [Morse et al., 2003]; but carbonate production rates by whitings and oöid formation are poorly quantified.

4. Consequences For Reef Organisms And Communities

4.1. Calcification in Various Reef-Builders

How decreased calcification rates affect biological functioning or organism survival on coral reefs remains essentially unstudied. Predictions about how corals or other calcifying organisms will be affected by decreased calcification rates are conjectural based on the fact that secretion of calcium carbonate by organisms serves some function (or multiple functions) that arguably benefits the organism. Biogenic calcification (shell formation) evolved sometime during the Cambrian period, coincident with a sudden rise in Ca^{2+} , which because high Ca^{2+} is toxic to cellular processes, suggests that it arose as a detoxification mechanism [Brennan et al., 2004]. Organisms have since evolved to put these CaCO_3 secretions to good use as skeletal support, protection, and many other functions.

These functions vary from species to species, and indeed within some species over the course of their life cycle. In corals and coralline algae, for example, calcification first appears when the planulae or larvae secrete calcium carbonate to cement the organism to a hard substrate. In experiments with *Porolithon*, recruitment declined under elevated $p\text{CO}_2$ conditions [Agegian, 1985].

Once an organism is established, continued calcification is partitioned into skeletal extension and skeletal strengthening (density). Extension provides support for colony expansion through both individual polyp growth, and colonial expansion of the organism. Skeletal extension elevates the coral above the substrate and into the hydrodynamic regime, and thus increases access to food, nutrients and well-oxygenated waters. Calcification in branching forms also brings them closer to the surface and higher light intensities. Faster growth is one strategy by which corals compete for space on a reef (reviewed by Lang and Chornesky [1990]); with some growing upward and “overtopping” lower-growing species [Glynn and Wellington, 1983]. There is also evidence that in some species, the reflectance by the aragonitic skeleton increases light gathering [Enriquez et al., 2005].

Growth rates may also influence reproduction by affecting either extension rate or density (which increases skeletal resistance to breakage). Some corals do not reproduce until they reach a certain size [Sakai, 1998; Fautin, 2002], while some take advantage of skeletal fragmentation to propagate. Skeletal fragmentation in *Acropora palmata* can actually increase asexual propagation of the species, but it has also been correlated with a lowered potential for sexual reproduction [Lirman, 2000].

Finally, calcification may enhance photosynthesis in some species by providing protons for conversion of HCO_3^- to $\text{CO}_2(\text{aq})$ [McConnaughey and Whelan, 1997]. This model was not supported in experiments with *Stylophora pistillata*, where suppression of calcification did not affect its photosynthetic rate [Gattuso et al., 2000], but Cohen and McConnaughey [2003] argue that the photosynthetic need for CO_2 and calcification supply of CO_2 increases the likelihood of a coupling between the two processes. Schneider and Erez [2006] support this argument with experimental data from *Acropora eurystoma*. They propose that calcification enhances photosynthesis by elevating $\text{CO}_2(\text{aq})$ in the coral coelenteron, which prevents CO_2 limitation of the zooxanthellae; and that the relatively constant offset between light and dark calcification can be explained by increases in coelenteron pH associated with photosynthesis (that is, photosynthesis enhances calcification).

Several studies indicate that coral skeletal growth rates are more poorly correlated with environmental conditions than are tissue growth rates [Edinger et al., 2000], perhaps because energy allocation is prioritized for skeletal rather than tissue growth, at least in larger colonies [Anthony et al., 2002]. Nonetheless, some species show dramatic ranges in coral calcification rates, accommodated by changes in either skeletal extension or density. Calcification rates in massive *Porites* decrease five-fold from low to high latitudes, a change that is reflected in extension rather than skeletal density [Lough and Barnes, 2000]. In *Montastrea annularis*, extension rates appear to be conserved regardless of the calcification rate [Carricart-Ganivet, 2004]. In the branching species *Acropora formosa* from the high latitude Houtman Abrolhos reefs, extension rate and density varied considerably between environments, but overall skeletal mass did not [Harriott, 1998].

Such variability in skeletal growth strategies under natural environmental conditions makes it difficult to predict just how reef calcifiers will cope with any future reduction in calcification rates. It is reasonable to assume that some species will be affected more than others if their calcification rates decrease due to lowered saturation state. These effects could affect a reef calcifier at multiple stages of its life cycle, from larval settlement, to its ability to compete for space and light, to its ability to reproduce. These changes are likely to affect the composition of coral reef communities, and their cumulative calcification rates.

4.2. Calcification in Reef Communities and Reefs

Reef-building requires a net positive balance of calcium carbonate production. Even in areas where CaCO_3 production is high, if CaCO_3 removal is also high, reef-building will be low, and vice-versa. The direct removal of calcifiers, such as during a severe bleaching episode, affects reef-building by removing the main source of carbonate production. The net response of coral community calcification to changing seawater carbonate chemistry, for example a decrease in average pH from 8.2 to 7.8, will be the sum of many interrelated processes such as 1) the response of calcifying organisms, 2) changes in inorganic processes of carbonate precipitation and dissolution, and 3) the response of bioeroders to changes in community structure and perhaps in cementation patterns.

Reef building requires reef-builders. Once the calcifying community is removed, reef building ceases or reverses. The opposite notion – that reef-builders require reefs – is less certain [Kleypas et al., 2001]. Although a minimum amount of net carbonate production is required to build a reef, is there also a minimum amount necessary to support a coral reef community, regardless of whether it builds a reef or not? Many coral communities do not appear to be building a reef, yet they seem to function similarly to those that are building reefs. Some aspects of reef-building are obviously important to the reef community: 1) the ability to keep up with sea level rise, 2) the creation of spatial complexity that supports

diversity, 3) the depth gradient that also supports biodiversity, and 4) the structural influence on the local hydrodynamic regime.

5. Knowledge Gaps and Future Research Directions

Finally, it is necessary to stress that the researches here described are but tentative early advances in a largely new field – so new that the greatest obstacle to progress is simply a lack of data. Faced with new problems we must go back to the beginning and patiently start again the task of describing and measuring before we can hope to make secure generalizations. – Bathurst, 1974.

Following the original warning that changing seawater carbonate chemistry might impact coral reefs of the future [Smith and Buddemeier, 1992], multiple studies have verified these concerns, both with respect to observations that the carbonate chemistry of the surface ocean is changing, and that calcification rates of major groups of organisms decline under increasing acidification. But many questions remain before we can make accurate predictions of how coral reef ecosystems will respond to calcium carbonate saturation states that are probably lower than have occurred for at least several hundred thousand years. We close this chapter by identifying major gaps in our scientific understanding of this problem, and a discussion of what approaches might best fill these gaps.

Most of the work that remains is an echo of that stated by Bathurst [1974] above, in his consideration of research needs within another aspect of carbonate chemistry, that of marine diagenesis. Even though the effects of changing seawater carbonate chemistry on coral reefs are potentially extremely important, there is resistance to understanding the problem, in part because *the greatest obstacle to progress is simply a lack of data.*

5.1. Gaps and the Need for a Comprehensive, Integrated Research Plan

5.1.1. Field measurements of seawater carbonate chemistry and calcification rates

One of the largest gaps in our understanding of coral reef calcification in relation to carbonate chemistry is our lack of observations of seawater carbonate chemistry in reef environments. There are very few measurements of seawater carbonate chemistry changes on coral reefs, and many of these are limited both spatially and temporally. If we are to understand the effects of changing ocean chemistry on coral reef ecosystems, many more measurements are needed in coral reef environments; perhaps not as routinely as temperature measurements, but at least as routine as measurements of light. The recent, large-scale observations of ocean chemistry associated with WOCE and JGOFS have provided invaluable data about oceanic responses to increasing atmospheric CO₂, but these observations were taken from open ocean waters, almost entirely away from carbonate platforms.

Field measurements of calcification on coral reefs are similarly limited, despite the fact that these observations attest to the tremendous impact of calcification on the surrounding seawater carbonate chemistry, and even fewer measurements have been made of dissolution. Can we design ways to monitor calcification and dissolution rates within reef-building organisms and within coral communities as a whole? And if so, can we find ways to effectively manipulate the carbonate chemistry on a coral reef similarly to the efforts in the terrestrial environment (e.g., Free Air CO₂ Enrichment (FACE) [Hendrey et al., [1999]])?

These observational gaps exist for a good reason. There are tremendous difficulties associated with monitoring both the carbonate system in seawater and calcification rates. Characterization of the carbonate system requires measuring at least two of the parameters: pH, total CO_2 , alkalinity, $p\text{CO}_2$. Although automated instrumentation is currently being developed to simultaneously measure these parameters [Kayanne et al., 2002a, 2002b; Watanabe et al., 2004], field measurements by-and-large still require sample collection and laboratory analysis. In addition, most previous studies relied on extension rates (length per unit time) as a measure of “growth” and did not measure true calcification rate (mass per unit time), and there is strong evidence that the two measurements are not interchangeable [Lough and Barnes, 1997].

Coral reefs occur across a range of environments that will affect both organic and inorganic carbon exchange on the reef (Figure 9) [Suzuki and Kawahata, 2003]; as well as the exchange between sediment pore-water and seawater. Even very good measurements in this environment must be coupled with good measurements of hydrodynamic exchanges,

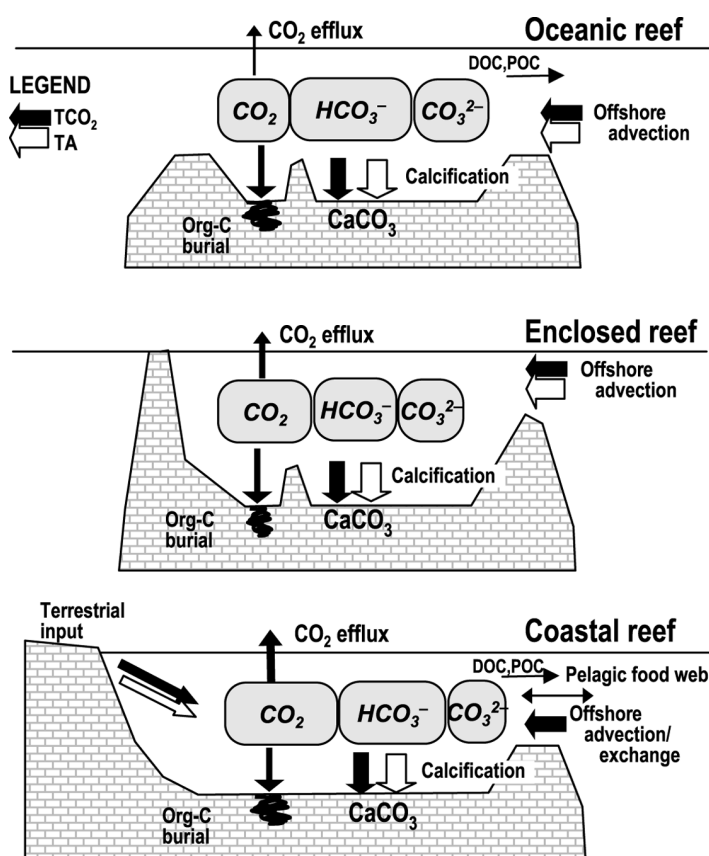


Figure 9. Variation in carbon cycling on coral reefs, as a function of reef morphology and proximity to land. AT = total alkalinity, DIC = dissolved inorganic carbon, DOC = dissolved organic carbon, POC = particulate organic carbon, DIN = dissolved inorganic nitrogen, DIP = dissolved inorganic phosphorus (from Suzuki and Kawahata [2003]; copyright Blackwell Publishing).

because it is likely the system is responding in multiple ways to CO₂ forcing, and in multiple parts of the system. Future collection of seawater carbonate chemistry and calcification data would ideally be complemented with measurements of those environmental variables that affect them. These include the obvious parameters of temperature, salinity and light, but also wind speed, the hydrodynamic regime, and the carbonate chemistry of the adjacent open ocean water mass. Installation of weather/ocean observing stations on reefs has increased in recent years, largely motivated by the need to monitor and research conditions that lead to coral bleaching, and many of these include measurements of temperature, salinity, light, and wind speeds (e.g., Berkelmans et al. [2002]). These stations are logical platforms for future collection of carbonate chemistry data.

5.1.2. Experimental needs

Essentially all published studies on the biocalcification response to increases in $p\text{CO}_2$ have come from laboratory experiments. Most of these have concentrated on measuring the response to saturation state alone, and most have focused on scleractinian corals. The next step in these experiments is to measure the combined effects of multiple variables known to affect coral calcification; e.g., temperature, light, and nutrients. In addition, there are many reef-building and reef-dwelling calcifying organisms that have not been tested in such experiments. One prime candidate for such studies is the calcifying green alga *Halimeda*, which is not only capable of high rates of calcium carbonate production [Hillis, 1997], but also appears to have little biological control on calcification. Other candidates include the main reef-building crustose coralline algae; but beyond the reef-builders many important members of the coral reef community, for example benthic foraminifera and echinoderms (both groups secrete high-Mg calcite), may also be affected by increases in $p\text{CO}_2$.

5.1.3. Standardization of measurements

Finally, there is a need to standardize methodologies. How can the various measurements of calcification – buoyant weight, alkalinity anomaly technique, ⁴⁵Ca uptake, densitometry, and tomography – be related to each other (Table 4)? Some of these techniques work better over short time scales and others over longer time scales; some require destruction of the coral while others do not. Many of these techniques have been qualitatively evaluated against other methods, but systematic comparisons of techniques within the same experiment are few. Understandably, these techniques do not necessarily measure the same aspect of calcification rate. Coral calcification rates taken over hours to weeks may not be comparable to calcification rates integrated over an entire year. In some measurements, dissolution and inorganic cementation must also be taken into account.

5.2. A Recommended Strategy

It is tempting to label as “controversial” the separate facts that 1) experimental results indicate that calcification rates should be decreasing in reef-building calcifiers due to rising CO₂, and 2) such a decrease has not been detected in massive corals. But differences between laboratory and field studies, particularly so few, should not be surprising. Nor is it surprising that coral reef calcification probably responds in complex ways to multiple

TABLE 4. Methods used to measure calcification rates in coral reef environments. G_{skel} = skeletal calcification; D_{skel} = skeletal dissolution; G_{inorg} = inorganic cementation; G_{sys} = system calcification; D_{sys} = system dissolution.

Technique	Parameter Measured	Timescale	Reference
Individual Organisms			
⁴⁵ Ca labeling	G_{skel}	Duration of incubation (hours)	Clausen and Roth, 1975
Buoyant weight	$G_{\text{skel}} + D_{\text{skel}}$	Duration of experiment (weeks to years)	Jokiel et al., 1976 Dodge et al., 1984
Coral band increment (extension \times density); density obtained via x-radiography tomography, densitometry	$G_{\text{skel}} + D_{\text{skel}} + G_{\text{inorg}}$	Integrated over time of band formation + post-depositional cementation	Lough and Barnes, 1997 Bessat and Buigues, 2001 Carricart-Ganivet, 2004
Δ Alk of monoculture	$G_{\text{skel}} + D_{\text{skel}}$	Discrete measurements over duration of experiment	Gattuso et al., 1998 Marubini et al., 2003
Systems			
Δ Alk of closed system	$G_{\text{sys}} + D_{\text{sys}}$	Discrete measurements over duration of experiment	Langdon et al., 2000 Leclercq et al., 2000
Δ Alk in open system	$G_{\text{sys}} + D_{\text{sys}} + \text{mixing}$	Discrete measurements over duration of experiment – requires knowledge of mixing regime	Smith and Key, 1975
Geometric measurements (reef volume \times reef density)	$G_{\text{sys}} + D_{\text{sys}} + \text{imported CaCO}_3 - \text{exported CaCO}_3$	Integrated over geologic timescales; calculates volume of reef structure; CaCO_3 content based on assumptions of porosity of structure; requires radiometric dating to estimate time range of accumulation	Ryan et al., 2001

changes in a highly variable environment (temperature, saturation state, nutrients etc.). A successful research strategy to study the effects of changing seawater carbonate chemistry on calcification in coral reef ecosystems will require a combination of efforts from multiple disciplines and across multiple spatial and temporal scales. The following research needs provide a starting point toward developing such a strategy:

1. Increase measurements of the carbonate system on coral reefs, and commit to monitoring over periods adequate for detecting the response of the system to continued

- increases in CO₂. Focus on collecting information from a variety of ocean settings that cover the important environmental ranges and seawater carbonate chemistry conditions; as well as the range of reef settings (e.g., well-mixed open ocean versus lagoonal) and environments (e.g., forereef, reef flat, lagoonal).
2. In concert with above, monitor *in situ* calcification and dissolution in organisms, with better characterization of the key environmental controls on calcification. Supplement and cross-check present-day measurements with coral skeletal records of calcification.
 3. Continue experimental studies that combine multiple variables that affect calcification in organisms: saturation state, light, temperature, nutrients; and extend the range of calcifying groups tested.
 4. Combine laboratory experiments with those in the natural environment. Develop and deploy technology for continuous field experiments analogous to the CO₂ enrichment experiments performed in terrestrial systems.
 5. Incorporate ecological questions into observations and experiments; e.g., how does a change in calcification rate affect the ecology of an organism; at the ecosystem scale, what are the ecological differences between coral reefs and non-reef building coral communities.
 6. Improve our accounting of coral reef carbonate budgets, through combined measurements of seawater carbonate chemistry, bioerosion, dissolution, and off-reef export of calcium carbonate.
 7. Apply biogeochemical and ecological modeling to help quantify the mechanisms that contribute to the carbonate system, and to guide future sampling and experimental efforts.
 8. Conduct physiological experiments to discriminate the various mechanisms of biocalcification within calcifying groups, and thus better understand the cross-taxa range of responses to changing seawater carbonate chemistry.
 9. Develop protocols for the various methodologies used in seawater carbonate chemistry and calcification measurements. Establish the pros and cons of each procedure, and when possible, how each measurement can be related to the others.

5.3. Closing Comment

We now know that the carbonate chemistry of the surface ocean is changing in response to CO₂ forcing from fossil fuel emissions. We also know that the near-future changes in the CO₂ system in seawater will lie outside the range of conditions experienced by coral reefs for the past hundreds of thousands of years. Based on controlled experiments, calcification rates of reef organisms are expected to decrease under increased *p*CO₂ conditions; but coral records over the past century have not recorded a clear post-industrial signal of decreased calcification. The overarching question: “How will calcification rates of reef-building organisms and reefs themselves change in response to increased *p*CO₂ forcing” remains unanswered. Here, we have attempted to provide the background necessary for understanding the complexity of the question, as a first step toward answering it.

Acknowledgments. This chapter summarizes research from many in the scientific community, and in that sense, all of the names listed in the References are acknowledged for their contributions to this topic. Janice Lough, as usual, offered valuable comments

on an early draft. We also thank Jonathan Erez and an anonymous reviewer for their very constructive inputs.

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