

Overview of CO₂-induced Changes in Seawater Chemistry

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Abstract The most direct and predictable consequence of increased atmospheric CO₂ on coral reef environments is the shift in the carbonate equilibrium of seawater which results in lower pH and lower concentration of the carbonate ion (CO₃²⁻). Many experiments have produced the remarkably consistent result that coral and algal calcification rates decrease in response to lowered [CO₃²⁻]. This paper reviews information which both supports and refutes this hypothesis. The most pressing questions outlining this issue are highlighted.

Keywords CO₂, CaCO₃, calcium carbonate, calcification

Introduction

Future changes in atmospheric CO₂ can affect coral reefs in a number of ways (Fig. 1): by

altering seawater chemistry; by greenhouse warming; or by other climatic changes. Recent coral bleaching events point convincingly to global warming as an immediate and acute threat to coral reefs (Wilkinson 2000). However, increasing evidence also supports the hypothesis that future increases in atmospheric CO₂ will affect calcification in several major groups of marine organisms. This is a more direct, albeit chronic, effect of fossil fuel emissions and is based on two relationships: 1) an increase in total CO₂ in seawater results in a reduction in carbonate ion concentration (Fig. 2); and 2) many independent experiments show a strong positive relationship between carbonate ion concentration and calcification rate in numerous species of calcifying algae, scleractinian corals, and coccolithophores.

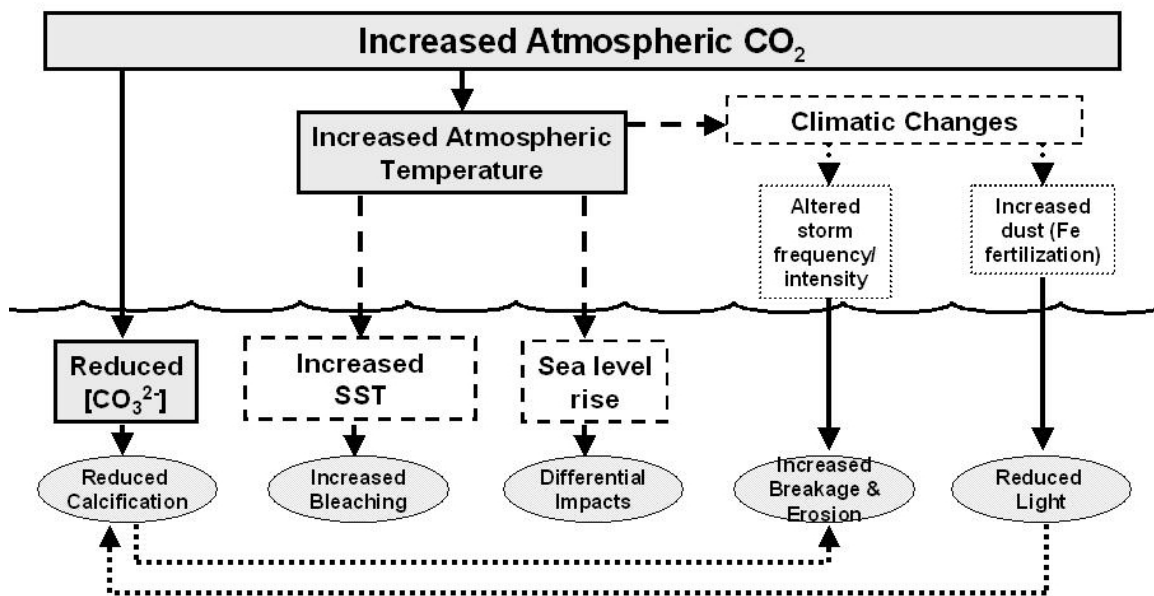


Fig. 1 Direct versus indirect impacts of increased atmospheric CO₂ on coral reefs. Most direct effects are shown as solid lines; least direct as dotted. Direct impacts are not necessarily worse than indirect impacts, but are more predictable.

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Changes in surface ocean chemistry in response to increasing atmospheric CO₂ concentration are predictable and supported by field evidence; while biological responses of calcifying organisms and the mechanisms of these responses, are less understood and difficult to detect in the field. This paper summarizes what is known about both of these relationships, and attempts to clarify certain misconceptions about this potentially confusing topic.

CO₂ effects on carbonate equilibria in seawater

Seawater chemistry of the surface ocean (ocean mixed layer) will change in direct

thermodynamic response to increased atmospheric pCO₂ (Fig. 2), and the magnitude of this response can be predicted with a high degree of confidence. Carbon dioxide exists as several different species in the ocean. The proportions of these species to each other are governed by the need to balance the alkalinity (sum of positive charge in the ocean). As illustrated by Broecker (1974), to a first approximation, the carbonate ion concentration is equal to the difference between total alkalinity and total CO₂. Therefore, as alkalinity decreases (such as through removal of Ca²⁺ during calcification) or as total CO₂ increases (such as through increased CO₂ from the atmosphere, and/or respiration), CO₃²⁻ decreases.

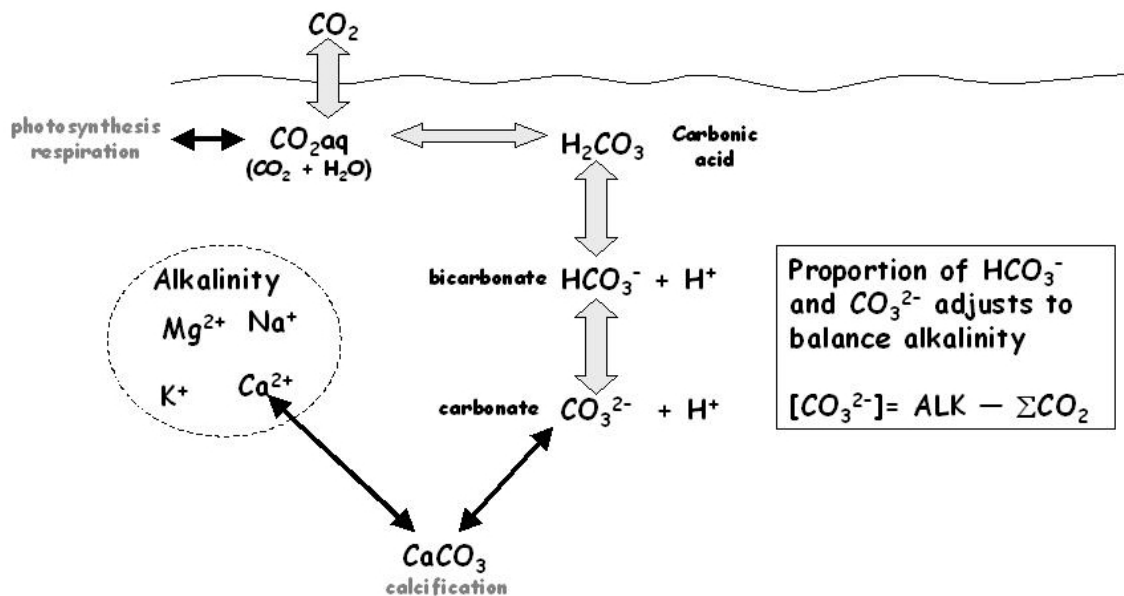


Fig. 2 The carbonate system in seawater and its response to increased atmospheric CO₂. Seawater alkalinity changes on time-scales of millenia, while atmospheric CO₂ changes on time-scales of decades to centuries. The carbonate ion concentration can be approximated as total alkalinity - total CO₂; hence an increase in total CO₂ lowers the concentration of CO₃²⁻.

Reef-builders require both Ca²⁺ and CO₃²⁻ ions for calcification. [Ca²⁺] in seawater is much higher than [CO₃²⁻] and is not considered limiting to calcification except under unusual circumstances, but [CO₃²⁻] is considered limiting to calcification. Even if fossil fuel emissions were stabilized today, atmospheric CO₂ would still reach double preindustrial levels by the end of this century, and best estimates indicate that it will double by the year 2065 (Wigley 1999).

This doubling of CO₂ will invoke an approximately 30% decrease in [CO₃²⁻] (Table 1).

The predicted changes in seawater chemistry have been verified during many recent field campaigns to track the fate of CO₂ once it enters the ocean. Results from the Joint Global Ocean Flux Study (JGOFS) as well as the World Ocean Circulation Experiment (WOCE) and other large scale ocean surveys clearly indicate that pCO₂ of the surface ocean reaches equilibrium with

atmospheric pCO₂ on the time-scale of one year, and that changes in the associated carbonate

parameters have changed as expected (Bates 2001; Brewer et al. 1997; Quay et al. 1992).

Table 1 Comparison of seawater carbonate equilibrium concentrations under the preindustrial atmospheric CO₂ level (1 x CO₂) and its doubling (2 x CO₂). Values were determined assuming a temperature = 25°C, salinity = 35 PSU, and alkalinity=2300 µequiv kg⁻¹.

Parameter	Concentration at 1 x CO ₂	Concentration at 2 x CO ₂
pCO ₂ (µatm)	280	560
H ₂ CO ₃ + CO ₂ (µmol kg ⁻¹)	8	16
HCO ₃ ⁻ (µmol kg ⁻¹)	1635	1867
CO ₃ ²⁻ (µmol kg ⁻¹)	272	177
Total CO ₂ (µmol kg ⁻¹)	1915	2061
pH	8.17	7.93

Past Changes in Atmospheric CO₂ and Seawater Chemistry

One point that is often raised is that coral reefs have survived fluctuations in ocean chemistry for millions of years, including such rapid fluctuations of the last 2–3 million ice-age years. The question here is: What exactly were those fluctuations in ocean chemistry? Reconstruction of seawater chemistry requires at least two measures of several components of the carbonate system (i.e., pH, total CO₂, pCO₂, alkalinity, [HCO₃⁻], [CO₃²⁻]). Estimating atmospheric and/or seawater chemistry during past climates is difficult because there are very few methods for obtaining records of these components. The most reliable estimates come from analysis of air trapped in ice cores, and the longest record shows that CO₂ levels from 420,000 years ago through the preindustrial period (and spanning many glacial oscillations) fluctuated between 180–300 ppmv but never exceeded 300 ppmv (Petit et al. 1999) until after the industrial revolution (currently 380 ppmv). Pearson and Palmer (2000) used boron isotopes in forams to estimate surface ocean pH for most of the Cenozoic. Their records suggest that atmospheric CO₂ concentrations were considerably higher than today prior to the early Miocene (24 million years ago), and have remained below 500 ppmv since then. Berner (1997) has also estimated past CO₂ concentrations using paleosols, and his records also indicate a significant decrease in CO₂ concentration between the early and mid-Cenozoic. Interestingly, although hermatypic corals and other reef-builders were present during the early Cenozoic, global compilations of reef distribution (Kiessling et al. 1999) reveal that reef-building was not widespread until the

late Eocene to early Miocene. The summary relationship here is that coral reefs have not co-existed with atmospheric CO₂ higher than that of today for at least a half-million years, and probably longer. Opdyke and Buddemeier (this session) presented further evidence that such projections of future carbonate chemistry in the surface ocean constitute an ocean chemistry very unlike that seen in the Cenozoic.

Calcification versus [CO₃²⁻]

Many experiments in aquaria and mesocosms illustrate that a wide variety of calcifying organisms exhibit reduced calcification in response to lowered [CO₃²⁻], and are not particularly sensitive to how the [CO₃²⁻] is manipulated (see Langdon, this session). Both Langdon (this session) with the Biosphere 2 algal-dominated coral reef community and Schneider and Erez (this session) with *Acropora* sp. tested calcification rates against several carbonate parameters (alkalinity, total CO₂, pH) while holding the others constant, and verified that CO₃²⁻ is indeed the limiting species. This relationship is approximately linear, and in algae, coral and coccolithophores (see Riebesell et al. 2000) at least, seems to represent a more geochemical rather than biochemical relationship. However, the biological mechanisms of calcification are not well understood (Gattuso et al. 1999; Schneider and Erez, this session; Marubini, this session). The general line of reasoning is that light enhances calcification because photosynthesis by zooxanthellae removes CO₂ and thus raises [CO₃²⁻] (Goreau 1963). However, there is still debate as to whether zooxanthellae utilize CO₂ or [HCO₃⁻] as the substrate for photosynthesis (Gattuso et al. 1999). There is also conflicting

evidence as to whether increased CO₂ enhances net primary production. Schneider and Erez (this session) reported no enhancement in net or gross photosynthesis to elevated pCO₂, although Amat (this session) did see an increase in biomass, regardless of a decrease in calcification, in three coral species.

Regardless of the internal biochemical mechanisms of calcification, these relationships imply that given the 35% increase in atmospheric CO₂ since preindustrial times, coral calcification should have already declined significantly (Gattuso et al. 1998; Kleypas et al., 1999; Langdon et al. 2000), although clearly the response is species-dependent. Although data from some coral cores might show such a decline (Hemley et al., this session), Lough and Barnes (2000a, 2000b) illustrated that natural variability in coral calcification between corals and over time would greatly confound this signal. In fact, average calcification measured from cores of ten long-lived (1746–1982) *Porites* from the Great Barrier Reef, Lough and Barnes (2000a) found a strong calcification to temperature relationship but no net calcification decrease since preindustrial times.

Three papers in this session (Langdon, Barnes and Cuff, Halley and Yates) offered evidence that dissolution of high magnesian calcite in carbonate rock and sediments may help to maintain CaCO₃ saturation states in at least some reef systems. Halley and Yates (this session) presented data obtained from enclosed "tents" placed within various reef environments, which illustrated that dissolution of HMC sediments did help to buffer the carbonate system. They observed dissolution in turbid environments when pCO₂ was elevated to greater than 540 μatm ([CO₃²⁻] ≈ 178 μM). Langdon (this session) also illustrated that dissolution in the Biosphere 2 did buffer the system to maintain [CO₃²⁻] at 110 μmol kg⁻¹. However, these CO₃²⁻ concentrations correspond to atmospheric CO₂ concentrations of 500–1000 μatm, when calcification rates will have already declined by 30–100%. Assessing the role of dissolution in maintaining carbonate saturation state around reefs is further complicated by hydrodynamic mixing, which on many reefs would greatly dilute the dissolution products.

One major observation borne out in this session was that despite reduced calcification rates, coral health does not seem compromised by increased CO₂ (pers.comm: F. Marubini, M. Atkinson, C. Langdon), and that both gross and net photosynthesis rates remain normal or even

slightly enhanced under higher pCO₂ conditions. The long term consequences of reduced skeletal growth rate are not yet clear, but it is likely that corals will be more susceptible to erosion and less competitive for space and light. Because coral reefs are a consequence of carbonate production, any reduction in skeletal building translates into less reef building. Present-day ocean chemistry appears to be headed into a state which has no analog within the Tertiary Period (Opdyke and Buddemeier, this session).

Summary and Remaining Questions

1. Both laboratory and field experiments continue to show that calcification in corals and coralline algae will decrease in response to future increases in atmospheric CO₂. These experiments also verify that CO₃²⁻ is the limiting component of coral and algal calcification.
2. Environmental records of past atmospheric CO₂ levels and ocean pH imply that projections of future atmospheric CO₂ levels are higher than any levels of the past 24 million years. Reef-building corals and coralline algae will therefore be exposed to a very different ocean chemistry than has existed for millenia, and reductions in calcification rates are likely.
3. Long-term trends in calcification, as derived from coral cores of massive species such as *Porites*, do not show the expected decrease in calcification since the preindustrial period. The reasons for this are unclear, but one of the following is certainly possible: a) *Porites* (and perhaps other coral taxa) is not as sensitive to seawater chemistry changes as laboratory experiments indicate; b) seawater chemistry in the GBR lagoon is significantly buffered by dissolution processes; c) effects of other environmental factors important to calcification, such as temperature and light, have masked the effects of seawater chemistry.
4. The biochemical mechanisms for calcification are still poorly understood, particularly with respect to the relationship between photosynthesis and calcification.
5. Dissolution of high magnesian calcite can potentially buffer the carbonate system in coral reef environments, particularly once

seawater becomes undersaturated with respect to that mineral. In coral reef lagoons, and on reefs with relatively high seawater residence times, such dissolution could help maintain saturation states higher than those in the open ocean.

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