Impacts of Ocean Acidification on Coral Reefs and Other Marine Calcifiers

A Guide for Future Research

Report of a workshop sponsored by

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A report from a workshop sponsored by the National Science Foundation, the National Oceanic and Atmospheric Administration, and the U.S. Geological Survey

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Executive Summary

Research findings of the past decade have led to mounting concern that rising atmospheric carbon dioxide (CO_2) concentrations will cause changes in the ocean's carbonate chemistry system, and that those changes will affect some of the most fundamental biological and geochemical processes of the sea. Thanks to the efforts of large-scale physical and biogeochemical ocean programs such as WOCE, JGOFS, and OACES, ocean-wide changes in the carbonate system are now well documented. Since 1980 ocean uptake of the excess CO_2 released by anthropogenic activities is significant; about a third has been stored in the oceans. The rate of atmospheric CO_2 increase, however, far exceeds the rate at which natural feedbacks can restore the system to normal conditions. Oceanic uptake of CO_2 drives the carbonate system to lower pH and lower saturation states of the carbonate minerals calcite, aragonite, and high-magnesium calcite, the materials used to form supporting skeletal structures in many major groups of marine organisms.

A variety of evidence indicates that calcification rates will decrease, and carbonate dissolution rates increase, as $CaCO_3$ saturation state decreases. This evidence comes from principles of thermodynamics, the geologic record, and the evolutionary pathways of $CaCO_3$ secreting organisms. Further evidence, from controlled experiments of biocalcification under increased CO_2 conditions, confirms that calcification rates of many organisms decrease with decreasing $CaCO_3$ saturation state. Extrapolation of these results to the real world suggests that calcification rates will decrease up to 60% within the 21st century. We know that such extrapolations are oversimplified and do not fully consider other environmental and biological effects (e.g., rising water temperature, biological adaptation); nor do they address effects on organism fitness, community structure, and ecosystem functioning. Any of these factors could increase or decrease the laboratory-based estimates, but it is certain that net production of $CaCO_3$ will decrease in the future.

The St. Petersburg Workshop, sponsored by NSF, NOAA, and the USGS, and held at the USGS Center for Coastal and Watershed Studies on 18–20 April 2005, was designed to take the next step toward understanding the response of marine calcification to increasing atmospheric CO_2 concentration. The aims of the workshop were to summarize existing knowledge on the topic, reach a consensus on what the most pressing scientific issues are, and identify future research strategies for addressing these issues. Although workshop participants were drawn from a wide range of scientific disciplines, there was a clear convergence on the major scientific issues that should be pursued over the next 5–10 years. These include:

- Determine the calcification response to elevated CO_2 in benthic calcifiers such as corals (including cold-water corals), coralline algae, foraminifera, molluscs, and echinoderms; and in planktonic calcifiers such as coccolithophores, foraminifera, and shelled pteropods;
- Discriminate the various mechanisms of calcification within calcifying groups, through physiological experiments, to better understand the cross-taxa range of responses to changing seawater chemistry;
- Determine the interactive effects of multiple variables that affect calcification and dissolution in organisms (saturation state, light, temperature, nutrients) through continued experimental studies on an expanded suite of calcifying groups;
- Establish clear links between laboratory experiments and the natural environment, by combining laboratory experiments with field studies;
- Characterize the diurnal and seasonal cycles of the carbonate system on coral reefs, including commitment to long-term monitoring of the system response to continued increases in CO_2;
- In concert with above, monitor in situ calcification and dissolution in planktonic and benthic organisms, with better characterization of the key environmental controls on calcification;
- Incorporate ecological questions into observations and experiments; e.g., How does a change in calcification rate affect the ecology and survivorship of an organism? How will ecosystem functions differ between communities with and without calcifying species?

- Improve the accounting of coral reef and open ocean carbonate budgets through combined measurements of seawater chemistry, $CaCO_3$ production, dissolution and accumulation, and, in near-shore environments, bioerosion and off-shelf export of $CaCO_3$;
- Quantify and parameterize the mechanisms that contribute to the carbonate system, through biogeochemical and ecological modeling, and apply such modeling to guide future sampling and experimental efforts;
- Develop protocols for the various methodologies used in seawater chemistry and calcification measurements.

Some of these research objectives require technological development, but others can be addressed immediately. While much work remains toward answering the fundamental question: "How will marine calcification rates respond to increasing atmospheric CO_2 concentrations," we need to begin investigations that look forward to answering the question: "What are the consequences of reduced calcification in both planktonic and benthic calcifying communities and ecosystems?" We should not wait until we answer the former question before tackling the latter.

This report is intended as a guide to program managers and researchers toward designing research projects that address these important questions. It is written with the detail and references needed to serve as a resource for researchers, including graduate students, who wish to tackle projects within the sometimes confusing topic of marine carbonate chemistry and calcification.

1. Introduction

1.1 Background

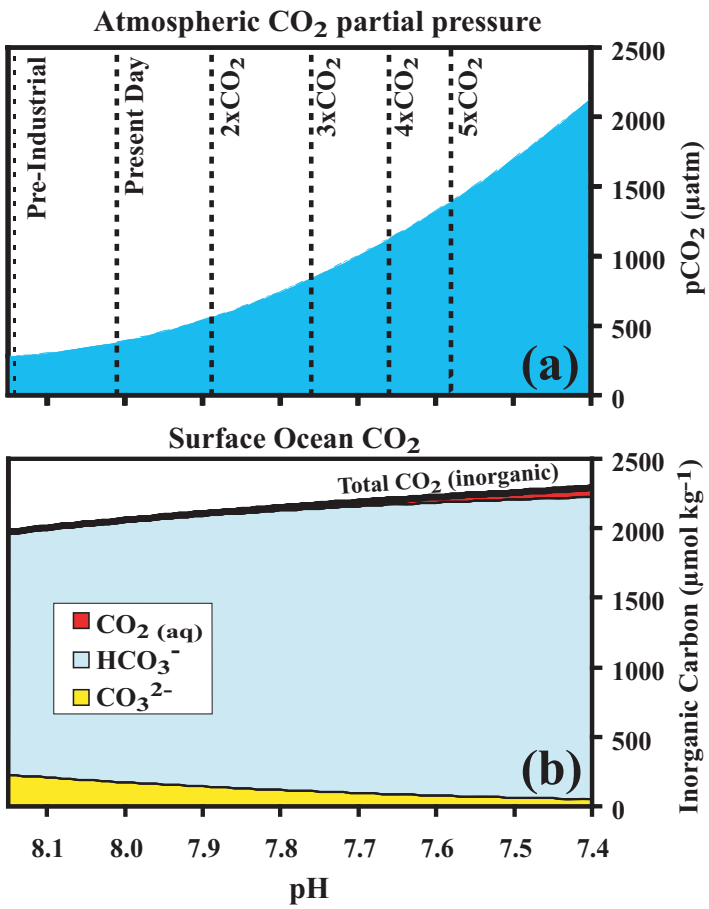
Carbon dioxide (CO_2) is one of the most important gases in the atmosphere, affecting the radiative heat balance of the earth as well as the calcium carbonate ($CaCO_3$) equilibrium of the oceans. For 650,000 y (650 ky) prior to the Industrial Revolution, atmospheric CO_2 concentrations remained between 180 to 300 parts per million by volume (ppmv) (Petit *et al.*, 1999; Augustin *et al.*, 2004; Siegenthaler *et al.*, 2005). Increased fossil fuel burning associated with industrialization, cement production, and land use changes associated with agricultural activities are causing atmospheric CO_2 concentrations to rise, and at increasing rates (rates of increase have risen from 0.25% y^{-1} in the 1960s to 0.75% y^{-1} in the last five years). The current atmospheric CO_2 concentration is about 380 ppmv and is expected to continue to rise by about 1% y^{-1} over the next few decades (Houghton, 2001) (**Figure 1–1**). The rate of current and projected CO_2 increase is about 100x faster than has occurred over the past 650,000 years and the rising atmospheric CO_2 levels are irreversible on human timescales (Royal Society, 2005).

Over the two decades of the 1980s and 1990s only about half of the CO_2 released by human activity has remained in the atmosphere, with the oceans having taken up about 30% and the terrestrial biosphere 20% (Sabine *et al.*, 2004). Similar partitioning of anthropogenic CO_2 is expected to continue with the result that the partial pressure of CO_2 (pCO_2) dissolved in the surface ocean is likely to double its pre-industrial value within the next 50 years. Over the next millennium, the ocean will absorb about 90% of the anthropogenic CO_2 released to the atmosphere (Archer *et al.*, 1998).

Increasing the amount of CO_2 dissolved in the ocean lowers the pH, and decreases the availability of carbonate (CO_3^{2-}) ions and lowers the saturation state of the major shell-forming carbonate minerals (**Box 1**). Tripling the pre-industrial atmospheric CO_2 concentration will cause a reduction in surface ocean pH that is almost three times greater than that experienced during transitions from glacial to interglacial periods. This is often termed "ocean acidification" because it describes the process of decreasing pH. Current projections of ocean acidification suggest that the pH of surface ocean waters will continue to decline. However, the term can also lead to confusion when it is wrongly assumed that the oceans will become acidic, when in reality, ocean pH is never expected to fall below 7.0; i.e., the oceans are becoming less basic, but not acidic. Such a phenomenon could only occur in the unlikely event that CO_2 emissions reach more than 10,000 Pg C (Caldeira and Wickett, 2005). In this report, we use the term "ocean acidification" to conform with current terminology, with the recognition that it refers to the process rather than an end state.

There is clear evidence that the carbonate equilibrium of the oceans is shifting in response to increasing atmospheric CO_2 concentrations. Carbonate chemistry measurements at the Hawaiian Ocean Time-series (HOT), the Bermuda-Atlantic Time-series (BATS), and the European Station for Times Series in the Ocean at the Canary Islands (ESTOC) show a shift in carbonate equilibrium consistent with increases in atmospheric CO_2 (**Figure 1–2**) (Bates, 2001; Gruber *et al.*, 2002, González-Dávila *et al.*, 2003; Brix *et al.*, 2004). Over the last two decades, several large-scale programs (Joint Global Ocean Survey, World Ocean Circulation Experiment, Ocean-Atmosphere Carbon Exchange Study) have measured the carbonate chemistry (mainly the total dissolved inorganic carbon, DIC, and the total alkalinity, A_T) along multiple ocean transects. These measurements allowed quantification of the anthropogenic carbon in the oceans, regionally and with depth (Sabine *et al.*, 2004) (**Box 2**), and have been used to estimate changes in the calcite and aragonite saturation states (Feely *et al.*, 2004).

Potential long-term impacts of anthropogenic CO_2 on the calcite and aragonite saturation state of the oceans have been discussed in detail (Broecker *et al.*, 1979; Feely and Chen, 1982; Feely *et al.*, 1984; Feely *et al.*, 1988; Kleypas *et al.*, 1999; Broecker, 2003; Caldeira and Wickett, 2003; Feely *et al.*, 2004; Caldeira and Wickett, 2005; Orr *et al.*, 2005). Past, present, and future aragonite saturation horizons have been modeled based on historical data and IPCC "business-as-usual" CO_2 emission scenarios (Orr *et al.*, 2005) (**Figure 1–3**). These results indicate that in the cold high-latitude surface waters typical of the subarctic North



Parameter	Symbol	Unit	Glacial	Preindust.	Present	$2 \times CO_2$	$3 \times CO_2$
Temperature	T	°C	15.7	19	19.7	20.7	22.7
Salinity	S	ppt	35.5	34.5	34.5	34.5	34.5
Total alkalinity	A_T	µequiv kg^{-1}	2356	2287	2287	2287	2287
pCO_2 in seawater	pCO_2	µatm	180	280	380	560	840
			–56	0	35.7	100	200
Carbonic acid	H_2CO_3	µmol kg^{-1}	7	9	13	18	25
			–29	0	44	100	178
Bicarbonate ion	HCO_3^-	µmol kg^{-1}	1666	1739	1827	1925	2004
			–4	0	5	11	15
Carbonate ion	CO_3^{2-}	µmol kg^{-1}	279	222	186	146	115
			20	0	–16	–34	–48
Hydrogen ion	H^+	µmol kg^{-1}	4.79×10^{-03}	6.92×10^{-03}	8.92×10^{-03}	1.23×10^{-02}	1.74×10^{-02}
			–45	0	29	78	151
Calcite saturation	Ω_{calc}		6.63	5.32	4.46	3.52	2.77
			20	0	–16	–34	–48
Aragonite saturation	Ω_{arag}		4.26	3.44	2.9	2.29	1.81
			19	0	–16	–33	–47
Dissolved inorganic carbon	DIC	µmol kg^{-1}	1952	1970	2026	2090	2144
			–1	0	2.8	6.1	8.8
Total pH	pH_T		8.32	8.16	8.05	7.91	7.76

Figure 1–1: (a) Increasing atmospheric CO_2 partial pressure and (b) associated changes in the surface ocean carbonate chemistry. Table shows carbon system parameter and temperature changes in surface seawater based on IPCC IS92a CO_2 emission scenario (Houghton *et al.*, 2001), assuming PO_4 = 0.5 μmol L^{-1}, Si = 4.8 μmol L^{-1}; and using the carbonic acid dissociation constants of Mehrbach *et al.* (1973) as refit by Dickson and Millero (1987). pH_T is based on seawater scale. Percent change from pre-industrial values are in magenta.

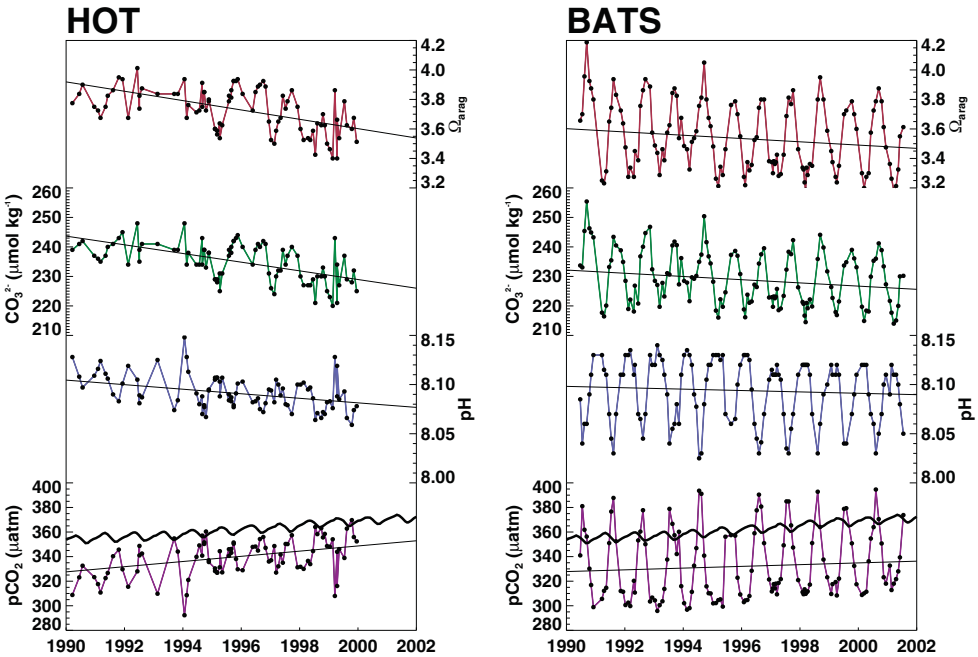


Figure 1–2: Monthly carbon-system parameters at two time-series stations in subtropical gyres: HOT (Hawaii Ocean Time-series station) and BATS (Bermuda-Atlantic Time-series Station). The lowest plot in each graph includes both the surface water pCO_2 (line with dots), and the Mauna Loa atmospheric CO_2 record (line without dots).

Pacific and North Atlantic, and the sub-Antarctic and polar regions of the Southern Ocean, aragonite and calcite undersaturation will occur when pCO_2 reaches 600 and 900 μatm, respectively. In the warm tropical and subtropical waters undersaturation will occur when pCO_2 values reach about 1700 and 2800 μatm, respectively. If CO_2 emissions continue as projected, aragonite undersaturated regions will develop in the sub-Arctic, sub-Antarctic, and polar surface waters by the end of the 21st century. This would occur first in the wintertime when surface water temperatures are coldest and pCO_2 values are highest due to wind-driven mixing of subsurface waters into the mixed layer. Undersaturated regions would then expand toward the equator, although it is unlikely that the tropical and warmest subtropical surface waters will ever become undersaturated with respect to calcite, as model projections of CO_2 emissions predict an upper limit of atmospheric CO_2 concentration of about 2000 ppmv (Caldeira and Wickett, 2003).

Calcifying organisms of both neritic and pelagic environments are sensitive to changes in saturation state; calcification rates of several major groups of marine calcifiers decrease as the carbonate ion concentration decreases (**Figure 1–4**; **Table 1.1**). There is also evidence that dissolution rates of carbonates will increase in response to CO_2 forcing. Even small changes in CO_2 concentrations in surface waters may have large negative impacts on marine calcifiers and natural biogeochemical cycles of the ocean (Gattuso *et al.*, 1998; Wolf-Gladrow *et al.*, 1999; Langdon *et al.*, 2000; Riebesell *et al.*, 2000; Marubini *et al.*, 2001; Zondervan *et al.*, 2001; Reynaud *et al.*, 2003). For example, decreased carbonate ion concentration significantly reduces the ability of corals to produce their calcium carbonate skeletons. This affects individual corals and the ability of the reef to maintain a positive balance between reef building and reef erosion (Kleypas *et al.*, 2001). New research is necessary to gain a better understanding of how ocean biology and chemistry respond to higher CO_2 and lower pH conditions, so that predictive models can include appropriate mathematical representations of these processes.

1.2 Geologic Context

Anthropogenic changes in atmospheric composition are forcing Earth's climate and ocean chemistry toward conditions that have not occurred over geologic timescales of millions of years (My) (**Figure 1–5**) (Caldeira and Wickett, 2003). When viewed against the Pleistocene record of atmospheric CO_2 variability, the increase in atmospheric CO_2 over the past century constitutes an unprecedented spike in greenhouse gas concentration which is certain to increase with continued fossil fuel burning. The best records of

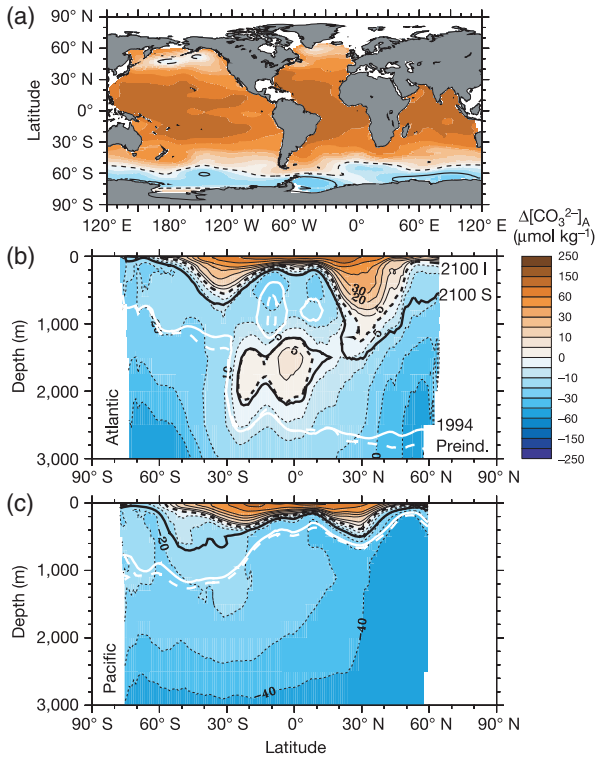


Figure 1–3: Median concentrations of $\Delta[CO_3^{2-}]$ (in situ $[CO_3^{2-}]$ minus $[CO_3^{2-}]$ for aragonite-equilibrated sea water) for the year 2100 under scenario IS92a, based on model results from the Ocean Carbon Model Intercomparison Project (OCMIP-2). (a) Surface map, and zonal averages for (b) Atlantic, and (c) Pacific. Thick lines indicate the aragonite saturation horizons for the pre-industrial, 1994, and 2100 (using scenarios S650 and IS92a). Reprinted from Orr *et al.* (2005) with permission from *Nature*, copyright 2006.

past atmospheric concentrations are from direct sampling of air bubbles trapped within ice cores. The Vostok and EPICA Dome Concordia ice core records, of which the past 650 ky have been analyzed, indicate that atmospheric CO_2 concentrations remained between 180 and 300 ppmv over eight major glaciations (Petit *et al.*, 1999; Siegenthaler *et al.*, 2005). These values are supported by leaf stomatal index data for the last interglacial (115–130 ka), which indicate more variable but similarly low atmospheric concentrations (Rundgren and Bennike, 2002).

CO_2 data extending back millions of years are scarce. Leaf stomatal index data from fossil trees dating from about 50–60 millions of years ago (Ma) indicate that atmospheric CO_2 concentrations in the early Tertiary remained between 300 and 450 ppmv, only slightly higher than that of recent interglacials (Royer *et al.*, 2001). Data from the marine environment, however (e.g., calcium isotopes (De la Rocha and DePaolo, 2000), boron isotopes (Pearson and Palmer, 2000; Pearson *et al.*, 2001), and alkenones (Pagani, 2002)) all indicate that atmospheric CO_2 concentrations were probably much higher in the early Tertiary and by the Early Miocene (24 Ma) had likely decreased to below 300 ppmv. The GEOCARB model, which hindcasts atmospheric CO_2 levels over the past 600 My by combining geological, geochemical, biological, and climatological data, suggests that early Tertiary CO_2 levels were up to five times that of pre-industrial levels (Berner, 1994, 1997; Berner and Kothavala, 2001).

CO_2 levels are only one parameter controlling ocean carbonate chemistry, however; alkalinity also determines the carbonate ion concentration. Ocean alkalinities could have been higher during periods with high CO_2 levels, since higher CO_2 levels accelerate rock weathering and $CaCO_3$ dissolution, which raises alkalinity. Over long timescales, this feedback tends to maintain a balance between atmospheric CO_2 and oceanic alkalinity. At the current rate of atmospheric CO_2 increase, however, this feedback operates too slowly to raise alkalinity significantly.

The suite of marine calcifiers has evolved considerably since the Cretaceous. For example, most of today's important reef-building coral families appeared sometime in the Eocene, and acroporids (fast-growing, branching corals common on reefs today) were not dominant on coral reefs until the late Oligocene (23–28 Ma, Schuster, 2002). Coccoliths first appear in the fossil record in the Late Triassic (Bown *et al.*, 2004), although their abundance is most evident in the large, Cretaceous chalk deposits of northern Europe and other regions. Only about 20% of extant coccolithophore species are known from Quaternary records (Young, 1994), and today's most common coccolithophore, *Emiliania huxleyi*, evolved less than 300,000 years ago (Thierstein *et al.*, 1977). Similar to corals, modern thecosomatous pteropod families appeared in the Eocene and Miocene (cf., Lalli and Gilmer, 1989). Geologic deposits produced by calcifying ecosystems of the early Tertiary (Paleocene and Eocene, ca. 65–35 Ma), when atmospheric CO_2 levels were probably at least 500 ppmv, may provide important clues regarding calcification/dissolution patterns, distribution patterns, etc., but they are less useful for providing information about ecological response because the community composition and ecological relationships were probably quite different from those of present-day ecosystems.

The most recent time period when oceanic carbonate chemistry could have approached those of today is the Paleocene/Eocene Thermal Maximum (PETM) about 55 Ma (Kennett and Stott, 1991; Zachos *et al.*, 1993; Zachos *et al.*, 2003; Zachos *et al.*, 2005). This boundary is characterized by an anomalous depletion in ^{13}C indicative of a rapid release of ^{13}C-

Table 1.1: Measured biogenic calcification responses to increased pCO_2.

Organism/System	Mineralogy	Approx. % change in calcification when pCO_2 is 2x preind.	3x preind.	References	Notes
Coccolithophores					
Emiliania huxleyi	Calcite	−25		Sciandra *et al.*, 2003	
E. huxleyi	"	−9	−18	Riebesell *et al.*, 2000; Zondervan *et al.*, 2001	Decrease in $CaCO_3$/cell
Gephyrocapsa oceanica	"	−29	−66	"	"
Foraminifera					
Orbicula universa	Calcite	−8	−14	Spero *et al.*, 1997; Bijma *et al.*, 1999; Bijma *et al.*, 2002	Decrease in shell weight
Globigerinoides sacculifer	"	−4 to −6	−6 to −8	Bijma *et al.*, 1999; Bijma *et al.*, 2002	Decrease in shell weight
Scleractinian corals					
Stylophora pistillata	"	−14	−20	Gattuso *et al.*, 1998b	Curve was nonlinear, linear fit was made for Ω_{arag} from 2.0−3.9
S. pistillata	"	0 to −50		Reynaud *et al.*, 2003	Level of response is temperature-dependent
Acropora cervicornis	Aragonite	−40	−59	Renegar and Riegl, 2005	
Acropora eurystoma	"	−38	−56	Schneider and Erez, 2006	
Acropora verweyi	"	−12	−18	Marubini *et al.*, 2003	
P. compressa + *Montipora capitata*	"	−40	−59	Langdon and Atkinson, 2005	
Porites compressa	"	−17	−25	Marubini *et al.*, 2001	
P. lutea	"	−38	−56	Ohde and Hossain, 2004	
P. lutea	"	−33	−49	Hossain and Ohde, in press	
P. porites	"	−16		Marubini and Thake, 1999	
Pavona cactus	"	−14	−20	Marubini *et al.*, 2003	
Fungia sp.	"	−47	−69	Hossain and Ohde, in press	
Galaxea fascicularis	"	−12	−18	Marubini *et al.*, 2003	
G. fascicularis	"	−56	−83	Marshall and Clode, 2002	
Turbinaria reniformis	"	−9	−13	Marubini *et al.*, 2003	
Coralline red algae					
Porolithon gardineri	High-Mg calcite	−25		Agegian, 1985	
Mesocosms and field studies					
Biosphere 2	Mixed	−56	−83	Langdon *et al.*, 2000	Dominated by coralline red algae
Monaco mesocosm	"	−21		Leclercq *et al.*, 2000	
Monaco mesocosm	"	−15		Leclercq *et al.*, 2002	
Bahamas Bank	"	−57	−85	Broecker and Takahashi, 1966	
Rukan-sho, Okinawa	"	−45	−67	Ohde and van Woesik, 1999	

Box 1—Controls on Marine Carbonate Chemistry

Marine carbonate chemistry is a complex but predictable series of chemical equilibria, governed mainly by the total concentration of dissolved inorganic carbon species (DIC or TCO_2; the molar sum of the carbonate species: dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}), and total alkalinity (A_T; the concentration of all the bases that can accept H^+, when a titration is made with HCl to the carbonic acid endpoint). Processes that increase DIC (e.g., adding CO_2 to the water column) shift the equilibrium toward lower pH and lower CO_3^{2-} concentration; while processes that increase A_T (e.g., the dissolution of calcium carbonates) shift the equilibrium toward higher pH and higher CO_3^{2-} concentration. Photosynthesis and respiration primarily affect DIC, while calcification and dissolution affect both DIC and A_T (see right-hand figure). Marine calcification draws down A_T twice as fast as it draws down DIC, and thus leads to a decrease in pH, which decreases the capacity of the upper ocean to take up atmospheric CO_2. Dissolution of marine carbonates has the opposite effect, and neutralizes CO_2 via the reaction:

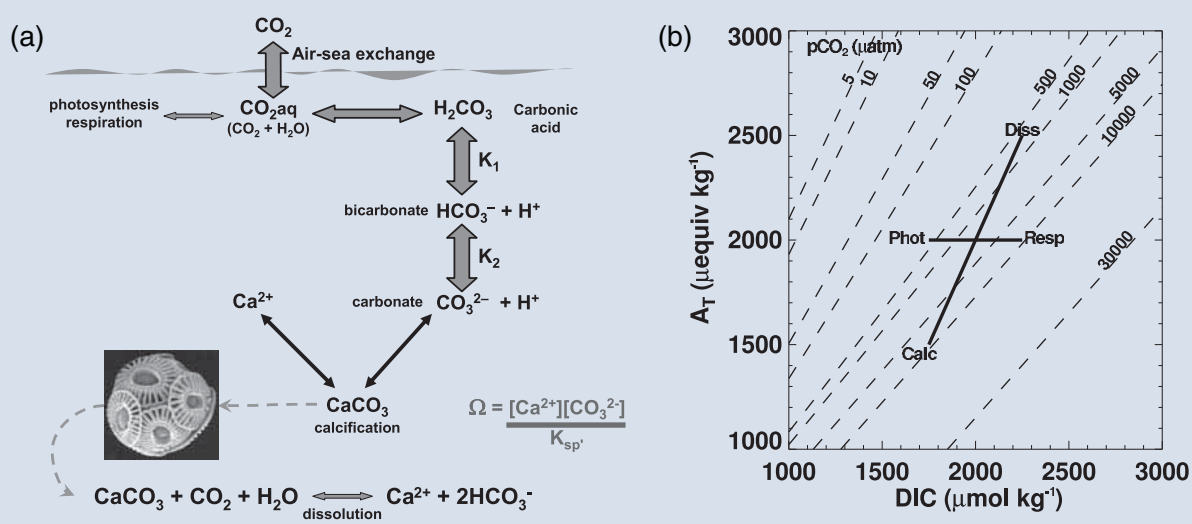
$$CaCO_3 + CO_2 + H_2O \leftrightarrow 2HCO_3^- + Ca^{2+} \quad (1)$$

The degree of saturation of seawater with respect to calcite and aragonite is the ion product of the concentrations of calcium and carbonate ions, at the in situ temperature, salinity, and pressure, divided by the stoichiometric solubility product (K^*_{sp}) for those conditions:

$$\Omega_{arag} = [Ca^{2+}][CO_3^{2-}]/K^*_{sp_{arag}} \quad (2)$$

$$\Omega_{calc} = [Ca^{2+}][CO_3^{2-}]/K^*_{sp_{calc}} \quad (3)$$

where the calcium concentration is either measured or estimated from the salinity and the carbonate ion concentration is calculated using known relationships between two carbonate system parameters (pCO_2, DIC, A_T, pH). Since the calcium to salinity ratio in seawater does not vary by more than 1.5%, variations in the ratio of $[CO_3^{2-}]$ to the stoichiometric solubility product primarily govern the degree of saturation of seawater with respect to magnesian calcite, aragonite, and calcite.



(a) A simplified diagram of the carbonate system in seawater. K_1 and K_2 are the dissociation constants for H_2CO_3 and HCO_3^-, respectively. (b) pCO_2 concentration (dashed lines) as a function of A_T and DIC. Photosynthesis and respiration affect only DIC, while calcification and dissolution affect both DIC and A_T.

depleted carbon (e.g., release of bacterially produced methane stored as gas hydrates (Dickens *et al.*, 1995), or thermogenic methane associated with volcanism (Svensen *et al.*, 2004)), and is accompanied by a sharp rise in sea surface temperatures (5–9°C) over a short time period (~100–1000 y). There is also evidence that the oceans experienced a simultaneous decrease in ocean pH during this event; the deep ocean's calcite saturation horizon shallowed at least 2 km, suggesting >2000 Pg of carbon dissolved into the ocean over a relatively short period of time (1,000–2,000 y) (Zachos *et al.*, 2005). Sedimentary data and model results suggest the ocean required 10–15 ky to again accumulate $CaCO_3$ at 1500 m depth and as much as 60 ky for the deep ocean to attain saturation levels. The increase in atmospheric CO_2 associated with this event is esti-

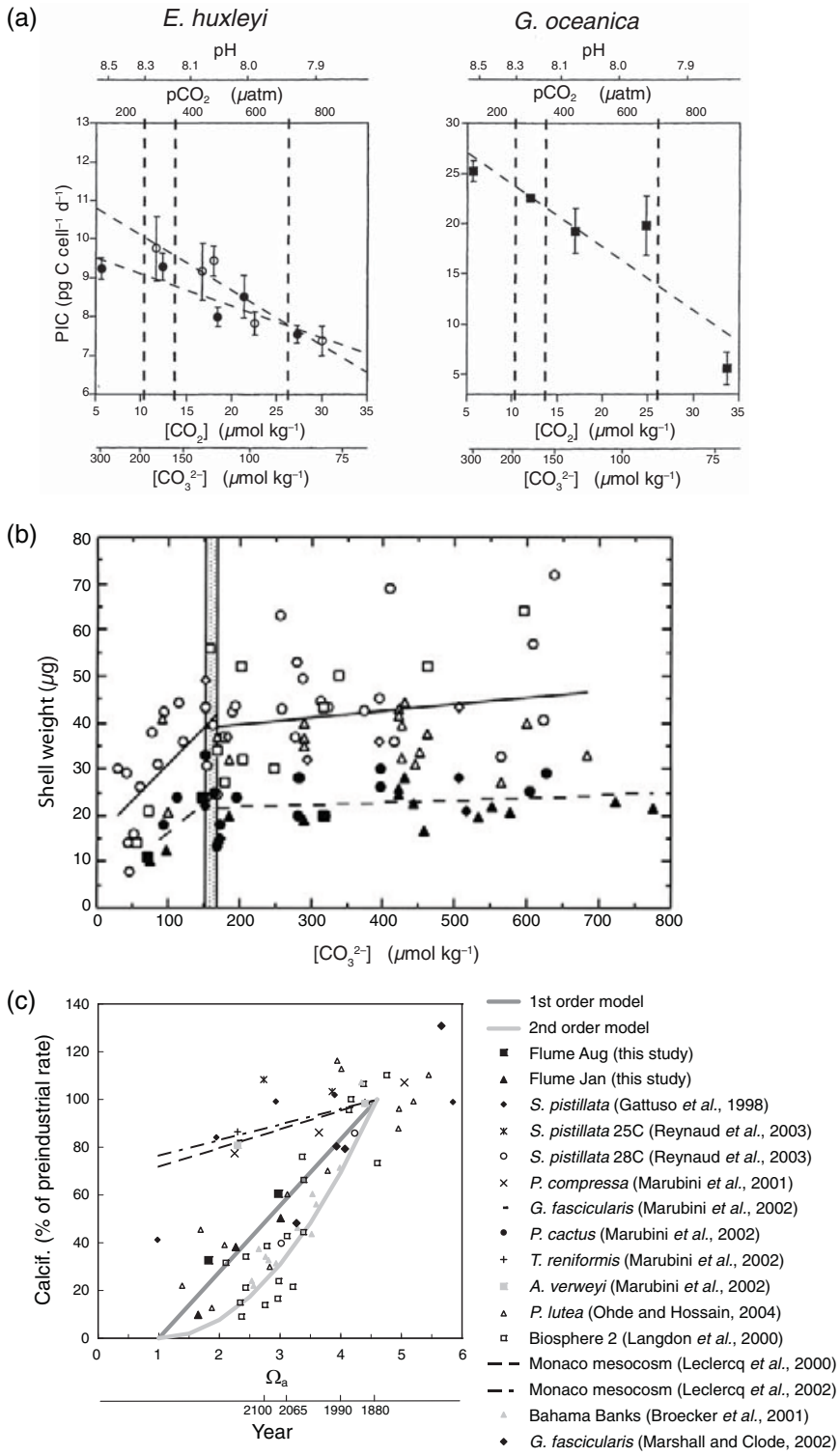
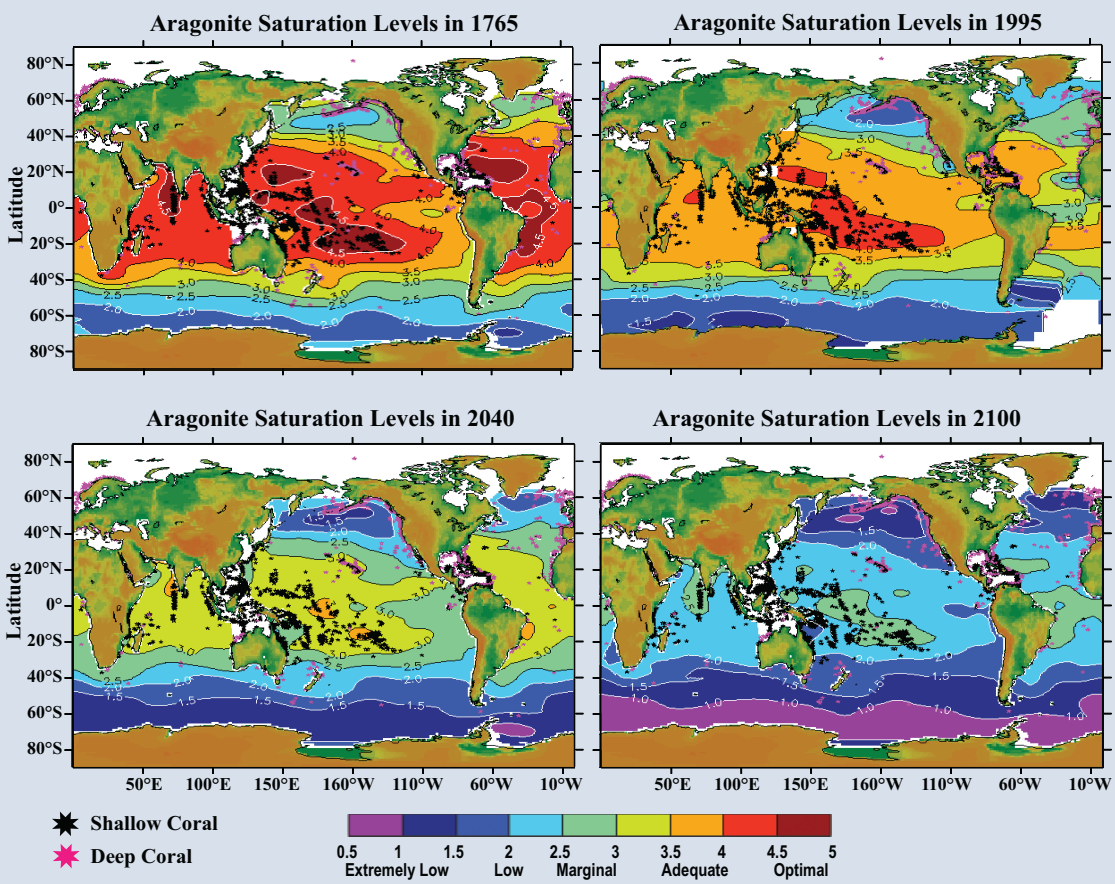


Figure 1–4: Calcification and shell growth rates reported as a function of a variety of carbonate chemistry parameters: (a) Coccolithophore calcification per cell as a function of carbonate ion concentration for *Emiliania huxleyi* and *Gephyrocapsa oceanica* (modified from Zondervan *et al.*, 2001). (b) Shell weight of the foraminifera *Orbulina universa* as a function of carbonate ion concentration, grown in high light (open symbols) and in the dark (closed symbols). Circles = constant alkalinity conditions; triangles = constant DIC conditions; squares = constant pH conditions. Shaded vertical bar indicates range of ambient conditions (reprinted from Bijma *et al.*, 1999, with kind permission of Springer-Verlag and Business Media). (c) Calcification rates (relative to pre-industrial values) of corals, coral mesocosms, and on the Bahama Banks, as a function of aragonite saturation state (reprinted from Langdon and Atkinson, 2005).

Box 2—Anthropogenic Carbon in the Oceans, and Shoaling of Aragonite and Calcite Saturation Horizons

In the 1990s, several agencies supported an international effort to survey inorganic carbon of the oceans (WOCE, JGOFS, OACES). This produced observations from more than 72,000 locations collected on over 95 expeditions. These observations were analyzed with a tracer-based separation technique to estimate the global content of anthropogenic CO_2 in the oceans that had accumulated over the period 1800–1994 (Sabine *et al.*, 2004), and showed that the distribution of anthropogenic CO_2 in the ocean is not uniform. Over half of the 118 ± 19 petagrams of anthropogenic carbon that has accumulated in the ocean is stored in the upper 10% of the ocean water column (upper 400 m). The largest column inventories of anthropogenic CO_2 are observed in areas where surface waters are transporting carbon into the ocean interior (see **Figure 2–1**). The oceanic sink accounts for ~48% of the total fossil fuel and cement manufacturing emissions, implying that the terrestrial biosphere was a net source of CO_2 to the atmosphere of about 39 ± 28 Pg C for this period. Thus, the ocean has been the only long-term sink for CO_2 released to the atmosphere by human activity.

This uptake is affecting the saturation horizons (the depth where saturation state = 1) of both calcite and aragonite (Feely *et al.*, 2004). There is natural shoaling of both the aragonite and calcite saturation horizons from the Atlantic through the Indian to the Pacific, because of the higher DIC/A_T ratios in the intermediate and deep waters of the Indian and Pacific relative to the Atlantic. This is the result of the cumulative large-scale enrichment of DIC relative to A_T due to respiration processes as ocean water circulates along the deep conveyor belt from the Atlantic to Indian and Pacific (Broecker and Peng, 1982; Broecker, 2003; Broecker and Clark, 2003). The intermediate waters of the North Pacific show evidence for undersaturation in the shallow waters between approximately 200 m and 1000 m where they have also been impacted by anthropogenic CO_2 (Feely *et al.*, 2004). Surprisingly, however, portions of the northern Indian Ocean and southeastern Atlantic Ocean are also undersaturated with respect to aragonite at shallow depths and these regions appear to be increasing in areal extent as a consequence of anthropogenic CO_2 accumulations (Feely *et al.*, 2002; Sabine *et al.*, 2002; Chung *et al.*, 2003; Feely *et al.*, 2004).



Estimated aragonite saturation states of the surface ocean for the years 1765, 1995, 2040, and 2100 (Feely *et al.*, submitted), based on the modeling results of Orr *et al.* (2005) and a Business-As-Usual CO_2 emissions scenario. The distributions of deep-sea coral banks are from Guinotte *et al.* (2006).

Box 2—(contined)

For example, **Figure 1–3** shows a comparison of the pre-industrial, 1994, and 2100 saturation horizons for the Atlantic and Pacific based on the modeling results of Orr *et al.* (2005). There are several distinct regions where the undersaturation zone has already expanded or could significantly expand in the future. Similarly, additional modeling efforts (Feely *et al.*, submitted) for surface waters indicate significant reductions in aragonite saturation state of the tropical and subtropical oceans over the 21st century (see figure on the previous page). Superimposed on the maps are locations of present day shallow and deep-water coral ecosystems (after Guinotte *et al.*, 2006). The color coding provides an indication of the conditions for coral calcification (Langdon *et al.*, 2003; Langdon and Atkinson, 2005). Subtropical regions would decrease from an optimal degree of saturation level >4 to marginal levels <3.0. These conditions will have significant impacts on the ability of coral reef ecosystems to maintain their structures against the forces of erosion and dissolution. For deep-water scleractinian corals, vertical migration of the aragonite saturation horizons means that more than 70% of these corals would be subjected to undersaturated conditions by 2100 (Guinotte *et al.*, 2006).

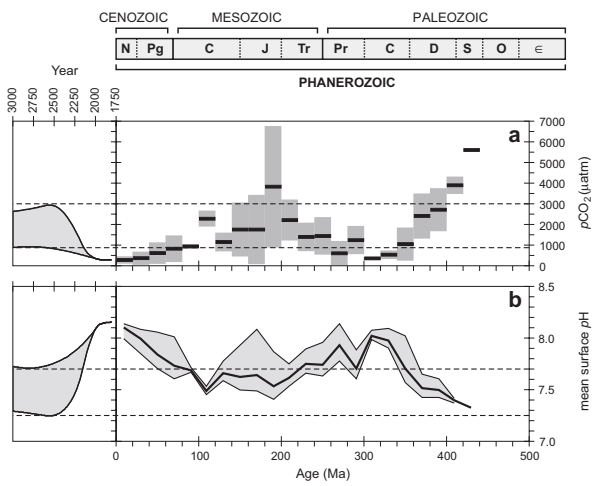


Figure 1–5: Geologic history (right-hand side of figure) and projection (left-hand side) of (a) atmospheric pCO_2 and (b) modeled changes in pH over the same time period. Horizontal dashed lines indicate the range of predicted pCO_2 peak atmospheric CO_2 concentration over the next century. Dark lines are average historical pCO_2 values, while gray shading indicates ± one standard deviation. Reprinted from Ridgwell and Zeebe (2005), with permission from Elsevier.

mated to have been only about 70–160 ppmv, which may be too low to have caused the dramatic temperature increase recorded by marine organisms. This has led to speculation about the sources of the light carbon, whether CH_4 oxidation occurred in the ocean or atmosphere (Dickens, 2001; Zachos *et al.*, 2003), and whether other mechanisms (e.g., ocean circulation changes (Tripati and Elderfield, 2005)) could have contributed to the warming. Thus while the PETM may provide clues toward our understanding of rapid perturbations to the global carbon cycle, this period may not be an ideal analog for present-day changes due to fossil fuel combustion.

The geologic record suggests that even earlier in Earth history, carbonate sedimentation was abruptly interrupted during periods of rapid increases in pCO_2. For example, a rapid volcanogenic increase in pCO_2 at the Triassic-Jurassic boundary (Palfy, 2003) coincides with a major extinction event, a worldwide interruption of carbonate sedimentation, and an evolutionary replacement of aragonite with calcite (Palfy, 2003; Hautmann, 2004). Furthermore, there is evidence that groups of calcifying organisms have become more or less dominant over geologic time, depending on CO_2 levels, and is likely linked to their utilization of dominant carbonate species in the ocean. For example, comparison of atmospheric CO_2 fluctuation from the Cambrian through the Cenozoic, to dominance trends for cyanobacterial and algal calcifiers, demonstrate that cyanobacteria dominate during periods of high CO_2, while algae dominate in periods of relatively lower CO_2, when HCO_3^- is more abundant (Yates and Robbins, 2001).

1.3 History of the CO_2-Marine Calcification Issue

The realization that atmospheric CO_2 concentrations can affect marine calcification rates emerged about 40 years ago (**Table 1.2**). Probably the first paper to address this issue was that of Wally Broecker and Taro Takahashi (Broecker and Takahashi, 1966), who based their conclusions on a time series of carbon system measurements over the Bahamas Bank. In the following decade, several authors presented calculations suggesting that the surface ocean would become undersaturated with respect to calcite by the year 2000, and that this would likely affect shell formation in many marine calcifying organisms (Fairhall, 1973a, 1973b; Zimen and Altenhein, 1973). However, these early calculations did not properly account for the carbon system equilibrium in seawater, and later calculations revealed that atmospheric CO_2 concentrations would have to reach nearly ten times that of

pre-industrial levels to cause calcite undersaturation in the tropical oceans (Whitfield, 1974; Skirrow and Whitfield, 1975).

In the 1980s, predictions based on field studies of the carbonate system in the Pacific Ocean forecast that surface waters of the North Pacific would become undersaturated with respect to aragonite (which is more soluble than calcite) sometime in the 21st century (Feely and Chen, 1982; Feely *et al.*, 1984; Feely *et al.*, 1988). At the same time, laboratory and field studies demonstrated that calcification rates in many marine organisms varied in response to the *degree* of $CaCO_3$ saturation, even in supersaturated waters. Smith and Buddemeier (1992) explicitly stated that increased CO_2 could cause seawater chemistry changes that would lead to reduced calcification rates, and numerous laboratory studies showed that calcification rates of reef-building corals and algae could decline by 10–50% under doubled CO_2 conditions (Gattuso *et al.*, 1998b; Langdon *et al.*, 2000; Leclercq *et al.*, 2000; Marubini *et al.*, 2001; Leclercq *et al.*, 2002; Langdon *et al.*, 2003; Marubini *et al.*, 2003; Langdon and Atkinson, 2005). Similarly, experiments with laboratory cultures and field populations revealed that calcification rates of two coccolithophore species decreased by 9–29% when pCO_2 was two times higher than pre-industrial levels (Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Sciandra *et al.*, 2003; Delille *et al.*, 2005; Engel *et al.*, 2005).

1.4 The Next Step—Development of a Research Strategy

Several previous workshops and meetings were explicitly dedicated to addressing how marine biological processes (primarily calcification) will respond to future changes in ocean CO_2 chemistry. A U.S. JGOFS workshop on marine calcification (Iglesias-Rodriguez *et al.*, 2002) focused on the effects on open ocean calcifiers and how reduced calcification would affect the ocean carbon cycle. In May 2004, the Scientific Committee on Oceanic Research (SCOR) and the Intergovernmental Oceanographic Commission (IOC) of UNESCO sponsored the symposium *The Ocean in a High-CO_2 World* that addressed the "biological and biogeochemical consequences of increasing atmospheric and oceanic CO_2 levels, and possible strategies for mitigating atmospheric increases." This workshop identified priority research areas regarding organismal and ecosystem responses to increased CO_2, and also recommended approaches to study them from small-scale laboratory experiments to large-scale field experiments, and modeling (Cicerone *et al.*, 2004). The Royal Society Report, *Ocean Acidification Due to Increasing Atmospheric Carbon Dioxide* (Royal Society, 2005), described the potential impacts of ocean acidification on ocean ecosystems and the resulting socio-economic impacts on the global economy. The report recommended that these potential risks to the ocean environment be considered by national and international policy makers involved in discussions of climate change issues. A recent report by the Integrated Marine Biogeochemistry and Ecosystem Research program of the IGBP (IMBER, 2005) lists "the effects of increasing CO_2 levels and decreasing pH" as a major scientific issue, with three priorities: (1) the effects of CO_2-driven changes in carbonate chemistry, (2) the effects of pH changes on the speciation of nutrients and trace metals, and (3) the sensitivity of organisms to changes in pH and CO_2.

The present report summarizes findings from a workshop (hereafter referred to as the "St. Petersburg Workshop") jointly sponsored by NOAA, NSF, and the USGS entitled "The Effects of Increased Atmospheric CO_2 on Coral Reefs and Other Marine Calcifiers," held in St. Petersburg, Florida, 18–20 April 2005. Some fifty participants gathered to address the next steps toward understanding the future of marine calcification and calcifying communities:

- identification of specific, testable hypotheses;
- evaluation of existing and promising methodologies for testing those hypotheses; and
- recommendations for streamlining research, from coordination of research across agencies to identification of specific locations where the most information can be obtained.

We present the scientific basis for building a realistic research strategy for understanding the interactions between ocean carbonate chemistry and marine calcification, and ultimately toward predicting marine ecosystem response to future increases in atmospheric CO_2. Although marine calcification occurs in virtually every marine environment, the focus of this document is on shallow benthic calcifying ecosystems (primarily coral reefs) and planktonic calcifying organisms (primarily planktonic foraminifera, coccolithophorids, and euthecosomatous (shelled) pteropods).

1.5 The Overall Scientific Issues

The St. Petersburg Workshop was stimulated by a need to consolidate current understanding of future changes in seawater carbonate chemistry and the response of marine calcification to those changes; and

Table 1.2: Chronological summary of significant research findings relevant to the relationship between carbonate chemistry of seawater and marine calcification.

Reference	Finding
Broecker and Takahashi, 1966	Illustrated dependency of calcification rates on $CaCO_3$ saturation state, in field study across the Bahama Banks
Smith and Pesret, 1974	Illustrated interaction between calcification and carbonate chemistry in Fanning Island Lagoon
Zimen and Altenhein, 1973 Fairhall, 1973a	Predicted increasing atmospheric CO_2 concentrations would cause surface ocean to become undersaturated with respect to calcite by year 2000
Skirrow and Whitfield, 1975 Whitfield, 1975	Corrected calculations showed that calcite undersaturation would not occur until atmospheric CO_2 was 10x pre-industrial levels
Feely and Chen, 1982 Feely *et al.*, 1984	Predicted surface waters of northern Pacific Ocean could become undersaturated with respect to aragonite in the 21st century
Smith and Roth, 1979 Borowitzka, 1981 Agegian, 1985 Gao *et al.*, 1993	Multiple studies illustrated that calcification rates in corals and coralline algae vary with the degree of $CaCO_3$ saturation
Smith and Buddemeier, 1992	Review called attention to potential role of decreasing $CaCO_3$ saturation state on future coral calcification rates
Gattuso *et al.*, 1998b	First controlled experiment showing calcification rate in a coral decreases with decreasing saturation state
Gattuso *et al.*, 1999a	Predicted 9–30% reduction in calcification rates between years 1990 and 2100
Kleypas *et al.*, 1999	Predicted that globally, coral reef calcification will decline by 14–30% under doubled CO_2 conditions
Marubini and Thake, 1999 Marubini *et al.*, 2001 Marubini *et al.*, 2003	Multiple studies showed effects of lower pH (or decreased carbonate ion concentration) on calcification in individual corals
Langdon *et al.*, 2000 Langdon *et al.*, 2003	Showed significant decline in calcification in CO_2 manipulations of the Biosphere 2 coral reef mesocosm. Illustrated that calcification rates were controlled by the ion concentration product of $[Ca^{2+}]$ and $[CO_3^{2-}]$ rather than pH, pCO_2, or $[CO_3^{2-}]$ alone.
Leclercq *et al.*, 2000 Leclercq *et al.*, 2002	Coral mesocosm studies showed decline in calcification under increased atmospheric CO_2 conditions
Riebesell *et al.*, 2000 Zondervan *et al.*, 2001 Riebesell, 2004	Showed significant reductions in calcification of two coccolithophorid species under increased atmospheric CO_2 conditions
Lough and Barnes, 2000	Analyzed dozens of *Porites* cores which did not reveal significant decline in coral calcification between early 20th and late 20th century
Feely *et al.*, 2004 Sabine *et al.*, 2004	Synthesized observations from 10 years of ocean carbon chemistry measurements; established role of oceans as carbon sink; addressed future changes in calcium carbonate saturation state profiles
Orr *et al.*, 2005	Predicted surface waters of Southern Ocean and subarctic Pacific will become undersaturated with respect to aragonite by year 2100

to identify the most important unknowns. This issue naturally cuts across physical, chemical, biological, and geological disciplines. Considerable effort has gone into understanding the patterns of open ocean carbonate chemistry and biogeochemical feedbacks to the global carbon cycle; and some major findings have arisen from that effort (e.g., quantitative estimates of ocean carbon uptake (Sabine *et al.*, 2004); the potential role of calcium carbonate as mineral ballast for organic carbon to the deep sea (Armstrong *et al.*, 2002; Klaas and Archer, 2002; Barker *et al.*, 2003)). Much less effort has gone into investigating the response of marine calcifying organisms to future changes in carbonate chemistry, and almost no research has tackled the longer timescales necessary to determine ecosystem responses.

Many benthic and planktonic calcifiers of both neritic and pelagic communities display a similar response to increased CO_2 forcing. There are important differences between the two (**Table 1.3**) that will dictate different approaches toward assessing the potential effects of reduced calcification on ecosystem structure and function, and how the effects could cascade to other ecosystems and the ocean carbon cycle. However, there is opportunity for researchers of planktonic and benthic communities to exchange

ideas and technology and thus streamline their respective research. For the most part, planktonic and benthic calcification are addressed separately in this report. Regardless of differences between the two groups, there are certainly common questions:

1. What are the most important hypotheses within the overall question of "What are the ecological consequences of increasing atmospheric CO_2 on marine calcifying organisms and communities?"
2. What information is currently available for synthesis and guiding future research?
3. What information can be gained from monitoring natural temporal and spatial variations?
4. What scientific hypotheses will require testing with experimental manipulations in the field and laboratory?
5. Which ocean regions will be first to experience large changes in carbonate chemistry? Over what timescales?
6. What are the technical needs to address these research questions in these environments?
7. Based on the above, what are the priority research areas?
8. Where can we take advantage of existing observing systems, and with what technology, for both monitoring and experimental testing of hypotheses? Where can we capitalize on existing efforts by developing partnerships?

1.6 Relevant U.S. Agencies and Programs

1.6.1 National Science Foundation (NSF)

Determining the effects of rising atmospheric CO_2 on marine ecosystems—an interdisciplinary challenge—has relevance in several National Science Foundation programs, and particularly within the Division of Ocean Sciences (OCE). The Biological Oceanography Program supports investigations of the biology, ecology, and biogeochemistry of planktonic and benthic systems of both the open ocean and coastal regions, while the Chemical Oceanography Program has a strong emphasis on the formation and fate of both organic and inorganic geochemical materials. This topic also falls under the Marine Geology and Geophysics (MGG), Earth System History (ESH), and Geobiology and Low-Temperature Geochemistry (GG) programs. MGG considers the genesis, chemistry, and mineralogical evolution of marine sediments, as well as interactions of continental and marine geologic processes; ESH addresses the mechanisms and feedbacks that drive the Earth's climate system and determine its natural variability; and GG promotes studies of the interactions between biological and geological systems at all space and timescales (and several other research objectives relevant to this report). Finally, NSF's Long-Term Ecological Research Program (LTER) supports the type of long-term interdisciplinary research necessary to understand the consequences of decreased calcification rates at the ecosystem scale.

1.6.2 National Oceanic and Atmospheric Administration (NOAA)

On 23 December 2000 the U.S. Congress enacted the Coral Reef Conservation Act of 2000 (CRCA; Public Law 106-562). The CRCA authorized the Secretary of Commerce to establish a National Program and conduct mapping, monitoring, assessment, restoration, scientific research, and other activities that benefited the understanding, sustainable use, and long-term conservation of U.S. coral reef ecosystems. As authorized by the CRCA, the Secretary of Commerce established the National Oceanic and Atmospheric Administration Coral Reef Conservation Program to carry out the mandates laid out in the CRCA, including supporting effective ecosystem-based management and sound science to preserve, sustain, and restore the condition of coral reef ecosystems. NOAA's Coral Reef Conservation Program is implemented by four NOAA line offices—the National Ocean Service (NOS), the National Marine Fisheries Service (NMFS), the National Environmental, Satellite, and Data Information Service (NESDIS), and the Office of Oceanic and Atmospheric Research (OAR). In June 2002 NOAA, in collaboration with the United States Coral Reef Task Force, published "A National Coral Reef Action Strategy" as required by the CRCA to: provide information on major threats and needs; identify priority actions to achieve the goals outlined in the National Action Plan and the CRCA; and track progress in achieving these goals and objectives. Regarding research, the National Action Strategy identified two needs: (1) conduct strategic research to provide critical information on the underlying causes of reef decline; and (2) increase understanding of the social and economic factors of conserving coral reefs.

1.6.3 U.S. Geological Survey (USGS)

The USGS mission is to provide sound scientific knowledge and information needed to understand environmental quality and preservation on regional,

Table 1.3: Comparison of benthic and planktonic calcifying ecosystems.

	Benthic	**Planktonic**
Ecology		
Habit	Mostly stationary or sedentary as adults; $CaCO_3$ accumulation provides structural ecosystem framework	Nonstationary; $CaCO_3$ accumulation physically separate from ecosystem
Domain	Continental shelves <100 m deep; mostly at low latitudes	Upper ocean; present data suggest mostly at high latitudes
Nutrient limitation	Usually low	Variable
Light limitation	Many species are photosynthetic or have photosynthetic symbionts	Many species are photosynthetic or have photosynthetic symbionts
Temperature limitation	Directly affected by changing temperature	Indirectly affected by changes in thermal stratification, upwelling
Biodiversity or functional diversity?	High, but differs between ocean basins	High at low latitudes; generally lower at high latitudes
Dominant calcifiers	Low latitudes: coelenterates/algae Temperate latitudes: bryozoans, molluscs, forams, algae	Algae, protists, molluscs
Food web	Mostly primary producers	Primary producers or consumers
Competition	Potential to be outcompeted by noncalcifying species	Potential to be outcompeted by noncalcifying species
Capacity to adapt to elevated pCO_2	No evidence of adaptation in corals, coralline algae	Unknown; short generation times may enhance ability to adapt
Calcification		
Production cycle/generation times?	Relatively constant production; Regeneration times usually years to decades	Variable production cycle from bloom-forming to relatively constant; Regeneration times usually days to months[1]
Mineralogy	Low latitudes: mainly aragonite (corals) and high-Mg calcite (calc. algae) High latitudes: mainly calcite (bryozoans, forams) and mixed arag/calcite (molluscs)	Mainly calcite (coccolith; forams) Some aragonite (pteropods; heteropods) Some high-Mg calcite[2]
Area[3]	$\sim 1 \times 10^{12}$ m^2	$\sim 300 \times 10^{12}$ m^2
Calcification rate[3]	10–180 g C m^{-2} y^{-1}	1–2 g C m^{-2} y^{-1} Wide range in literature for coccolithophores; hard to measure in many planktonic calcifiers
Net $CaCO_3$ production[3]	0.02–0.1 Pg C y^{-1}	0.29–1.1 Pg C y^{-1}
Net $CaCO_3$ accumulation[3]	0.01–0.1 Pg C y^{-1}	0.1 Pg C y^{-1}
Carbonate System Behavior		
pCO_2 variability	High	Low?[4]
Influence of sedimentary processes	High	Low
Carbon Cycling		
Role in carbon cycle	Increases atmospheric CO_2 — "coral reef hypothesis"	Affects C_{org}:C_{CaCO3} of deep ocean

[1] Two coccolithophorid species can have episodic blooms but there are many other species that may be important in terms of $CaCO_3$ flux.
[2] In some regions, such as Sargasso Sea.
[3] Estimates from Milliman and Droxler (1996) and Lee (2001).
[4] At high latitudes there are pronounced differences between summer/winter seasons.

national, and when appropriate, global scales. A number of programs within the USGS address such needs, including the Coastal and Marine Geology Program, Earth Surface Dynamics and Climate Change, and various USGS Biology Programs. Within the marine realm, the Coastal and Marine Geology Program in the USGS recognizes a need for scientific research linking changes in atmospheric CO_2 to marine ecosystem responses because of significant resource management implications. Coastal and marine ecosystems, including coral reefs, bays, and estuaries, and continental margins are particularly sensitive to climatic and CO_2 changes. Therefore, USGS research will continue to provide fundamental information on CO_2 cycling in these societally important areas and these data will feed development of models that describe ecosystem responses to CO_2 changes in the ocean.

1.6.4 Other U.S. Agencies

Several other agencies have programs that are relevant to investigations of changes in carbonate chemistry of the ocean and the effects on marine organisms. The Earth Science mission of the National Aeronautics and Space Administration (NASA) is to "understand and protect our home planet by using the view from space to study the Earth system and improve prediction of Earth system change." Much of NASA's contributions to ocean research are through their support of remotely sensed observations from space-based and sub-orbital platforms, such as SeaWiFS, MODIS/Aqua, QuikSCAT, and TOPEX/Poseidon, to name but a few. NASA also supports basic research and data analysis, modeling, applying research results in decision support, and scientific assessment. Specific applications of satellite-based data to derive calcification rates in both open ocean and shallow water environments are described in section 4.1.4 of this document.

The Environmental Protection Agency (EPA) has a long history of supporting ecosystem research. For example, EPA's National Center for Environmental Research (NCER) sponsors the Science to Achieve Results (STAR) program, which engages scientists and engineers in targeted research that complements existing research within EPA as well as that of other federal agencies. NCER recently sponsored a research program on the "Effects of Climate Change on Ecosystem Services Provided by Coral Reefs and Tidal Marshes." NCER also periodically establishes large research centers in specific areas of national concern, such as the National Center for Caribbean Coral Reef Research (NCORE). NCER lists several "opportunities" presented by these centers that would greatly accelerate research on the effects of ocean acidification on marine calcifiers; these include:

- provide for multidisciplinary interactions in a wide range of scientific areas—informing state-of-the-art research programs for a specific purpose;
- establish a national network that fosters communication, innovation, and research excellence;
- improve study designs, resulting from intra-Center, multi-disciplinary integration and cross-disciplinary work;
- ability to pursue "higher-risk" efforts in methods development, validation, and pilot studies, providing a greater potential for innovation; and
- longer term continuity (i.e., for five years) allows long-term planning and research implementation.

2. Future Carbonate Chemistry of the Oceans

2.1 Open Ocean

2.1.1 Background

THE OCEAN IS THE LARGEST labile reservoir for carbon on decadal to millennial timescales, acting as a variable sink for atmospheric CO_2 and other climate-relevant trace gases (e.g., Siegenthaler and Sarmiento, 1993). Model projections suggest that on millennial timescales the ocean will be the ultimate sink for about 90% of the anthropogenic carbon released to the atmosphere (Archer *et al.*, 1998). On shorter timescales, however, the rate of ocean uptake can vary substantially. Estimates of the ocean CO_2 uptake for the last 20 years amount to about a third of the CO_2 released from fossil fuel burning (Prentice *et al.*, 2001). However, a recent estimate of the ocean anthropogenic CO_2 inventory for the mid 1990s accounts for nearly half of the fossil fuel CO_2 released between 1800 and 1994 (Sabine *et al.*, 2004). The net ocean uptake of anthropogenic carbon appears to be controlled over the historical period and at present by ocean physics (**Figure 2–1**), namely the ventilation and exchange of surface waters with the thermocline and intermediate to deep waters (Sarmiento and Gruber, 2002). The study of purely physical transport processes in the ocean is a huge endeavor in itself and is arguably further advanced than the study of ocean ecosystems and their effect on the carbon cycle.

Distinguishing a human-induced signal from natural decadal variability is often singularly difficult given the relatively short length of most oceanographic data records. Recent geochemical studies indicate a 0.1 unit drop in surface ocean pH and a shoaling of aragonite saturation depths by as much as 200 m since the pre-industrial period (Feely *et al.*, 2004; **Box 2**). Model projections indicate that these chemical changes will accelerate in concert with increases in atmospheric CO_2, and the human signal will become increasingly evident in the near future. A recent study projects that surface waters around Antarctica and the North Pacific could become undersaturated with respect to aragonite by the end of the 21st century (Orr *et al.*, 2005).

Decadal timescale ocean biological responses (e.g., changes in nutrient stocks and community structure) to climate change and ocean acidification are not well characterized. There is, however, evidence for large-scale biogeochemical regime shifts (or perhaps secular trends) (Karl, 1999) and changes in nutrient distributions (Emerson *et al.*, 2001). Under future greenhouse warming climate scenarios, the ocean's physical uptake of anthropogenic carbon is expected to decline over the next few decades because of surface warming, increased vertical stratification, and slowed thermohaline circulation (Sarmiento *et al.*, 1998; Matear and Hirst, 1999). In coupled simulations with simple biogeochemical models, these physical effects are partly compensated by increased uptake from changes in the strength of the natural biological carbon pump. The biogeochemical response is governed by two opposing factors: (1) a reduction in the upward nutrient supply due to increased stratification, which leads to decreased export production of organic matter and CO_2 uptake, and (2) a decrease in the upward vertical flux of dissolved inorganic carbon. The latter factor generally dominates in the present simulations, so that the effect of altered biogeochemistry is a net positive CO_2 uptake. These studies, however, only consider overall productivity and not the potential impact of changes in ecosystem structure if, for example, calcifying organisms were more strongly impacted than other marine producers. Given the low level of biological sophistication used in these early simulations, such projections must be considered preliminary. They do, however, demonstrate the potential sensitivity of the system and pose important questions to be addressed through future research.

2.1.2 Evidence and gaps in current knowledge

A wide variety of mechanisms have been identified that could alter ocean carbon uptake, but in many cases even the sign of the biogeochemical response, let alone the magnitude, is uncertain (Denman *et al.*, 1996; Doney and Sarmiento, 1999). Potential effects include:

- Decreased CO_2 released to the seawater environment because of lower calcification due to anthropogenic CO_2 uptake (Gattuso *et al.*, 1999b;

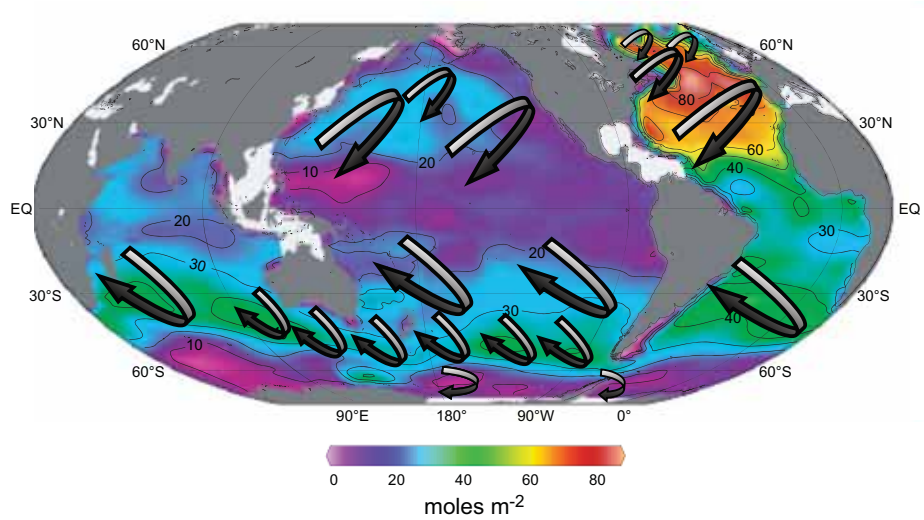


Figure 2–1: Comparison of estimated mode, intermediate, and deep water formation regions (Talley, 1999) and regions with large column inventories of anthropogenic CO_2 (Sabine *et al.*, 2004). The largest arrows indicate deep and bottom water formation regions, the medium-size arrows are intermediate water formation regions, and the smallest arrows indicate mode water formation regions. The water mass formation regions are areas where anthropogenic CO_2 is moved into the ocean interior.

Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Barker *et al.*, 2003);

- Altered carbon export rates because of lower vertical nutrient supply and in some regions enhanced, effective-surface-layer light supply leading to often opposing regional changes in primary productivity (Bopp *et al.*, 2001);
- Alterations in the spatial patterns of carbon uptake and export due to stratification-induced changes in community composition of marine biomes (Boyd and Doney, 2002);
- Altered carbon uptake and export in high nitrate-low chlorophyll (HNLC) regions such as the Southern Ocean, and possible changes in subtropical nitrogen fixation, due to changes in dust deposition and iron fertilization; and
- Decoupling of carbon and macronutrient cycling because of shifts in the elemental stoichiometry of surface export and differential subsurface remineralization.

Accounting for such hypotheses in future climate projections is problematic given our current understanding and modeling tools (Doney, 1999; Falkowski *et al.*, 2000).

Calcium carbonate is thought to play a role in organic carbon transport to the deep ocean (Armstrong *et al.*, 2002; Klaas and Archer, 2002), but the mechanism for this has not been determined (Passow, 2004). Predictions of the response of the ocean carbon cycle to increased atmospheric CO_2 are thus poorly constrained. Reduced calcification and/or increased calcium carbonate dissolution in the ocean will increase its capacity to take up atmospheric CO_2. A complete shutdown of calcification would lower surface ocean pCO_2 by about 10–20 μatm (Gruber *et al.*, 2004) and oceanic uptake of CO_2 would slightly *increase*. However, calcium carbonate is also thought to serve as a "ballast" for organic carbon transport to the deep ocean (Armstrong *et al.*, 2002); so a reduction in ballast could *decrease* ocean uptake of CO_2.

Mechanisms for dissolution of particulate inorganic carbon (PIC) in the water column, above the aragonite and calcite saturation horizons, are poorly understood. The dissolution of PIC affects the carbonate chemistry of the water column, and thus affects the rate of carbon uptake from the atmosphere, the calcification rates of organisms, and the translocation of carbon to deeper depths. PIC composition, grainsize, aggregation (Jackson, 1990; Jackson and Burd, 1998), sinking rate (e.g., Pilskaln *et al.*, 1998; Berelson, 2002), and carbonate saturation state of the water column are all factors affecting PIC dissolution, as well as biological factors such as microbial activity, ingestion by organisms, and the presence of biologically produced materials such as transparent exopolymer particles (TEP) (Passow, 2002). These processes and how they will change in response to future CO_2 increases must be better understood in order to obtain a global carbonate budget and to predict the future state of ocean seawater chemistry. Without

this understanding, we cannot close the global carbonate budget or have a proper understanding of how ecosystem changes might impact the calcium carbonate cycle. Similarly, the role of PIC dissolution in open oceans needs to be quantified; e.g., what are the rates of change in carbonate dissolution?

Dissolution of open-ocean carbonate sediments needs further study. Over glacial-interglacial timescales, preservation and dissolution of $CaCO_3$ in ocean sediments act to maintain a constant ocean alkalinity ("calcium carbonate compensation") that provides a significant negative feedback on changes in atmospheric CO_2 (Archer, 1996). On shorter timescales, the rates of dissolution are too slow to effectively counter the current increase in atmospheric CO_2. However, dissolution rates of these sediments are likely to increase as the saturation horizons of the carbonate minerals begin to shoal and expose more sediments to undersaturated conditions, which will affect the rates of alkalinity fluxes across the water-sediment interface. Similar to the controls on PIC dissolution in the water column, a variety of factors can affect benthic dissolution rates, from organic carbon content (Jahnke *et al.*, 1994) to bioturbation and dissolution in the guts of deposit feeders (Jansen and Ahrens, 2004). Factors that affect solubility and dissolution kinetics of carbonate sediments are also not fully understood (Gehlen *et al.*, 2005a, b). Predicting how the rates of carbonate sediment dissolution may change in response to water column chemical changes and how this will affect carbonate chemistry of the overlying water column are important objectives toward improved understanding of the global $CaCO_3$ budget.

2.2 Coastal Ocean

2.2.1 Background

Little attention has been given to the role of the carbon cycle of shallow-water ocean margins and their modeling in the context of global change, despite their documented importance in the global carbon cycle (Gattuso *et al.*, 1998a; Ver *et al.*, 1999; Chen, 2003; Chen *et al.*, 2003; Chen *et al.*, 2004). The shallow-water ocean environment (i.e., bays, estuaries, lagoons, banks, and continental shelves) constitutes only 7% of global ocean surface area, but supports approximately 10–30% of the world's marine primary production. Eighty percent of inputs from land to sea are deposited here, and 85% of organic carbon and 45% of inorganic carbon are buried in the ocean margin sediments (Gattuso *et al.*, 1998a; Wollast, 1998; Chen *et al.*, 2003). Carbonate accumulation in coral reef environments alone accounts for an estimated 20–30% of the global ocean accumulation (Milliman and Droxler, 1996). Ocean margins are also heavily impacted by human activities, as nearly 40% of the global population lives within 100 km of the coastline (Cohen *et al.*, 1997). Since the onset of the Industrial Revolution, burning of fossil fuels and land-use changes have caused substantial increases in both atmospheric CO_2 concentration and in the delivery of organic matter and nutrients to ocean margins (Mackenzie, 2003). Such changes could alter the role of this system and considerably affect important processes such as air-sea CO_2 exchange.

Model calculations for a "business as usual" CO_2 emissions scenario suggest that global coastal ocean seawater marine carbon chemistry could change significantly and that the saturation state of the surface waters with respect to aragonite and calcite could decline 45% by the year 2100 and 73% by the year 2300 (Caldeira and Wickett, 2005; Andersson *et al.*, 2006). Because of this and increases in water temperature, the $CaCO_3$ production rate (mainly biogenic calcification) in coastal seawater could decrease by 40% by 2100 and by 90% by 2300 (**Figure 2–2**). By 2150, because of increases in atmospheric CO_2, temperature and loading of the coastal ocean with nutrients and organic carbon, the $CaCO_3$ production rate in the global coastal ocean is predicted to fall below the $CaCO_3$ dissolution rate; that is, $CaCO_3$ would be dissolving faster than it is being produced (Andersson *et al.*, 2006).

2.2.2 Evidence and gaps in current knowledge

Pre-industrial carbon cycling in the coastal zone is not well understood because human activity has already significantly altered the natural carbon cycle. Without a clear understanding of how the coastal carbon system operated prior to human alteration, it is difficult to understand how the system will change in the future. For example, we do not fully understand the potential role of sediment (including suspended sediment) dissolution in benthic environments.

Measurements of coastal zone carbon fluxes are currently insufficient to determine the response of coastal carbonate systems. At present it is difficult to determine from either syntheses of field observations or modeling whether global coastal ocean waters are a net source or sink of CO_2 to the atmosphere. This is particularly true in tropical and subtropical zones and estuaries. Upscaling of air-water CO_2 fluxes measured in the coastal ocean is hampered by the poorly con-

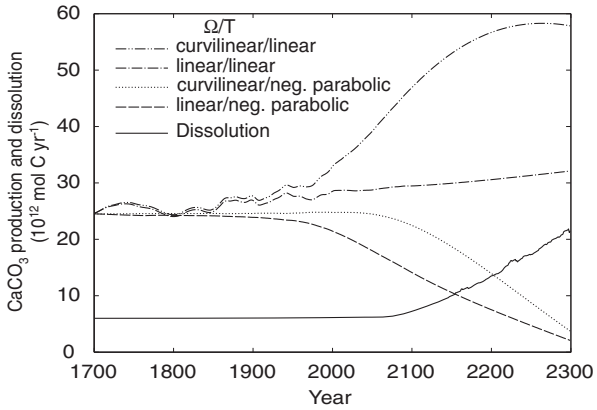


Figure 2–2: Model calculations showing changes in $CaCO_3$ production and dissolution rates in global coastal ocean surface waters depending on various relationships between carbonate production rate, temperature (T), and saturation state (Ω). For the most likely scenario of a linear relationship between saturation state and production and a negative parabolic relation between production and temperature, the calculations indicate that by 2150 under a business as usual scenario, global coastal ocean carbonates will be dissolving faster than they are produced. Reprinted from Andersson *et al.* (2006) with permission from the American Journal of Science.

strained estimate of the surface area of inner estuaries (Borges, 2005), and some regions are net sinks and others net sources of CO_2 to the atmosphere. Coastal oceans are characterized by extreme spatial and temporal heterogeneity, and by high rates of primary production, fluxes from land, and burial of organic and inorganic carbon. Quantifying these rates and detecting a response to CO_2 forcing are difficult and require a well-designed, coordinated monitoring network. As atmospheric CO_2 continues to rise, there is a strong need for such data to (1) resolve the direction and magnitude of the CO_2 flux in coastal waters, (2) assess the effects of the rise on the carbonate saturation state of coastal waters, and (3) identify response of coral and other shallow-water carbonate ecosystems to this perturbation. Estimates from modeling are not very robust at present but suggest that the global coastal ocean several hundred years ago was a net source of atmospheric CO_2, and has recently or will soon become a net sink (Mackenzie *et al.*, 2004; Andersson *et al.*, 2005).

3. Calcification/Dissolution Response

Research into the effects of increased atmospheric CO_2 on marine calcifiers has concentrated on two research questions: (1) how do calcification rates vary with calcium carbonate saturation state, and (2) what are the effects of changing calcification and dissolution rates on the ocean carbon cycle and the capacity of the ocean to take up CO_2 from the atmosphere? How decreased calcification rates affect biological functioning or organism survival, however, is essentially unstudied. Carbonate dissolution also remains poorly determined; i.e., the controls on dissolution rates in the water column and in sediments, how dissolution affects alkalinity fluxes, and the potential role of dissolution in buffering the carbonate system.

Biogenic calcification[1] evolved sometime during the Cambrian period, coincident with a sudden rise in Ca^{2+}. Because high Ca^{2+} is toxic to cellular processes, it has been proposed that calcification may have arisen 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 (**Table 3.1**). Predictions about how reduced calcification will affect organisms are therefore based on the fact that secretion of calcium carbonate by organisms serves some function (or multiple functions) that benefits the organism.

3.1 Coral Reefs and Other Benthic Calcifying Systems

The major benthic calcifying organisms on coral reefs are corals, calcifying macroalgae, benthic foraminifera, molluscs, and echinoderms (**Figure 3–1**). In the tropics, scleractinian corals and calcareous green and red algae are important to the building and cementation of the massive carbonate framework that forms the habitat for coral reef organisms. In colder deep (50–1000 m) waters of the continental shelves and offshore canyons, deep-sea corals build carbonate thickets or groves of high complexity that provide habitat for many other organisms. To date, studies of the effects of elevated CO_2 have been confined to a few species of coral and/or algae, and there remain large voids in our knowledge of the physiological and ecological impacts of increasing pCO_2 on other benthic calcifiers such as benthic foraminifera, echinoderms, molluscs, and deep-sea corals. For example, some deep-sea corals will experience waters with $\Omega_{arag} < 1$ as early as 2020 (Guinotte *et al.*, 2006); these organisms may thus be impacted by undersaturated waters before we can determine their potential ecological and economical importance as fish habitat.

The following addresses the evidence and gaps in our current knowledge of how increasing ocean acidification will affect benthic calcifying ecosystems in terms of: (1) calcification response, (2) organism response, (3) ecosystem response, and (4) dissolution and reef-building response. We focus here on coral reefs and other benthic calcifying systems of the tropics, but many other calcifying systems should be included in future studies. Some temperate shelves, for example, support a wealth of benthic calcifiers and calcifying communities, many of which are of economic importance either directly (shellfish) or indirectly (supporting fish habitat and fisheries). Finally, although not addressed here, calcification by benthic microbial communities is recognized as a potentially important component of the overall $CaCO_3$ budget. Microbial communities are of particular interest because they tend to have biologically induced rather than biologically controlled calcification (Weiner and Dove, 2003), and are thus more likely to respond to changing carbonate chemistry.

3.1.1 Calcification response

Multiple taxa of benthic calcifiers have shown a significant calcification response to carbonate chemistry. Most studies have concentrated on reef-associated taxa such as coralline red algae (articulate and encrusting) and hermatypic corals (branching, massive, and solitary). The two most soluble phases of the $CaCO_3$ mineralogy (aragonite and high-Mg calcite) are represented in this suite. Decreases in calcification rates across a suite of benthic species and calcifying systems range from 3% to 60% for a doubling

[1] Biological precipitation of $CaCO_3$, which is often termed "biocalcification" or, given that almost all $CaCO_3$ precipitation is biologically induced or mediated, simply "calcification."

Table 3.1: Proposed functions of calcification in organisms. Not all suggested functions are supported by experimental evidence.

Function	Planktonic	Benthic
Protection	all groups	all groups
Buoyancy regulation	coccolithophores, foraminifera	
Light modification	coccolithophores	corals
Provide protons for conversion of HCO_3^- to CO_2 for photosynthesis	coccolithophores	calcareous algae?
Facilitate bicarbonate-based photosynthesis	coccolithophores	
Aid in capture of prey	foraminifera	
Reproduction	foraminifera, some pteropod species	corals?
Prevention of osmotically induced volume changes	coccolithophores	
Extension into hydrodynamic regime		corals, calc. algae, bryozoans
Anchoring to substrate		corals, calc. algae, bryozoans
Competition for space		corals, calc. algae, bryozoans

in pCO_2 (34% reduction in saturation state) (**Figure 1–4**). The average response of corals is a 30% decline in calcification in response to a doubling in pCO_2 (**Table 1.1**).

Exposure to elevated CO_2 can affect physiology as well as calcification rate in many other benthic organisms. Several studies have demonstrated physiological stress in organisms exposed to very high pCO_2 levels that would be expected from direct CO_2 disposal in the ocean (see, for example, the special issue on ocean sequestration of CO_2 (Brewer *et al.*, 2004)). Two recent studies have investigated both physiological and calcification effects of long-term exposure of molluscs and sea urchins to much lower elevations of CO_2. Specimens of *Mytilus galloprovincialis* that were maintained for three months at pH = 7.3 (consistent with a pCO_2 of about 1900 μatm) experienced a significant reduction in growth, as well as shell dissolution, in response to reduced haemolymph bicarbonate levels (Michaelidis *et al.*, 2005). In another study, specimens of two species of sea urchin (*Hemicentrotus pulcherrimus* and *Echinometra mathaei*) and one gastropod mollusc (*Strombus luhuanus*) that were exposed for six months to CO_2 levels elevated by 200 ppmv over normal levels had smaller size and body weight, and in *E. mathaei* a thinning of the $CaCO_3$ tests was observed (Shirayama and Thornton, 2005). Many other calcifying taxa are important ecologically, economically, and as components of the marine $CaCO_3$ cycle (e.g., calcareous green algae, echinoderms, benthic molluscs and foraminifera, bryozoans, ahermatypic corals), but few have been tested for their physiological and calcification responses to elevated CO_2.

The interactive effects of saturation state, temperature, light, and nutrients, are important factors in calcification rates of reef organisms. Human activities are causing changes in all of these factors and light, temperature, and nutrients have all been demonstrated to affect calcification rates of corals, either singly or in combination with saturation state. As described below, there are very few studies that have examined the combined effects of these variables, and the results have been difficult to interpret.

Coral calcification responds to both light and saturation state but the effects do not seem to be strongly interactive, as coral calcification decreases under increased pCO_2 conditions over the full range of light intensity that corals experience (Marubini *et al.*, 2001), and dark calcification shows the same sensitivity.

Only two studies have tested the combined temperature-saturation state effect on coral calcification, and these have produced confusing results. Reynaud *et al.* (2003) observed a strong interaction between temperature and saturation state while Langdon and Atkinson (2005) observed little or no interaction. Coral calcification increases with increasing temperature up to a thermal optimum and then declines rapidly (Coles and Jokiel, 1977; Jokiel and Coles, 1977; Marshall and Clode, 2004; Al-Horani, 2005). As a result, increasing temperature could mask, partially offset, or reinforce the effect of elevated pCO_2, depending on where the temperature falls on the bell-shaped calcification-temperature response curve.

Two studies have measured the effects of combined nutrient concentrations and saturation state on corals. In one experiment, the calcification rate in *Porites porites* was more sensitive to changes in aragonite saturation state under increased nutrient conditions (Marubini and Thake, 1999), while in another, calcification rates of the corals *P. compressa* and *Mon-*

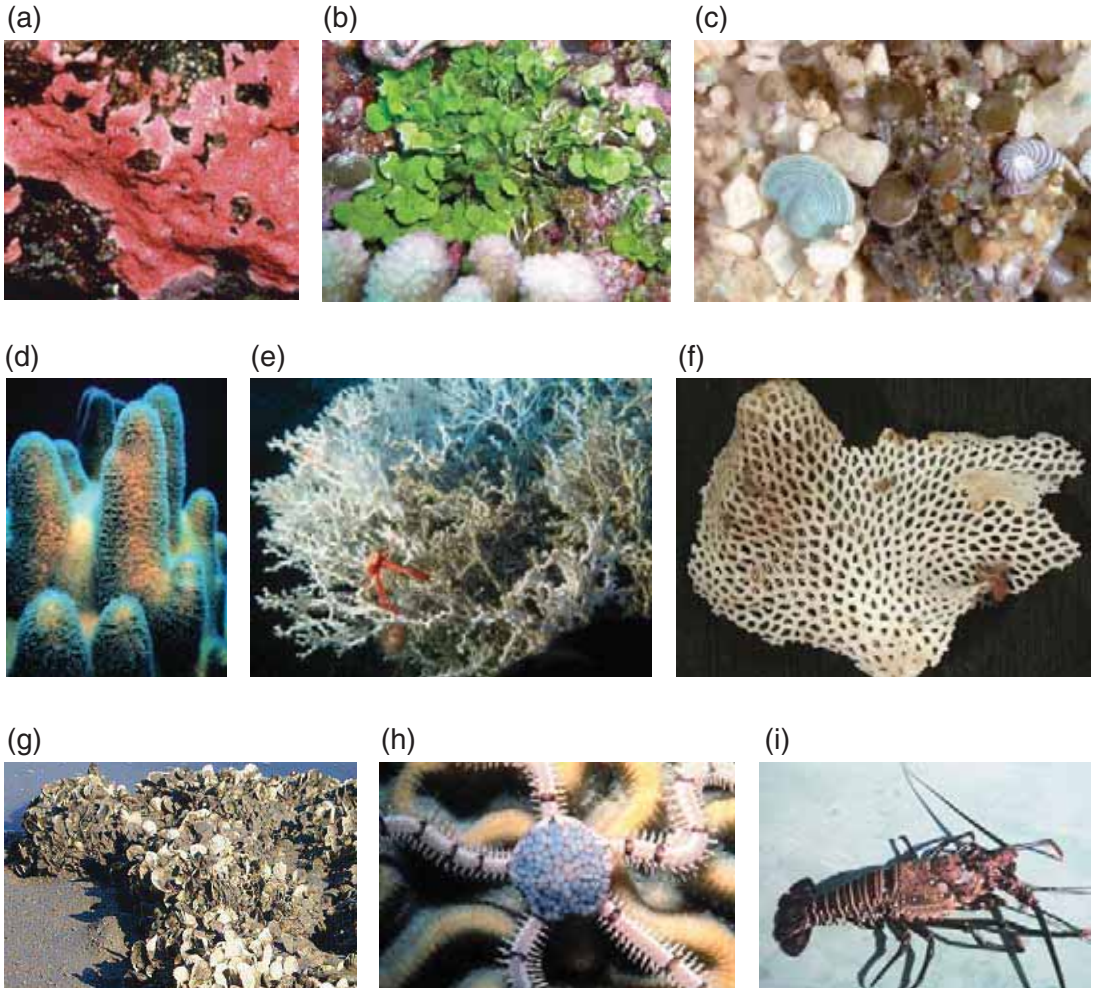


Figure 3–1: Representatives of major benthic calcifiers: (a) coralline algae (photo by Nancy Sefton; courtesy NOAA/CORIS); (b) *Halimeda* (photo by James Watt; courtesy NOAA/NMFS); (c) benthic foraminifera (courtesy P. Hallock); (d) reef-building coral (*Dendrogyra cylindrus*; Cmdr William Harrigan, NOAA Corps; courtesy Florida Keys National Marine Sanctuary); (e) deep-water coral (*Lophelia pertusa*; from 413 m depth off North Carolina. Large red crab is *Eumunida picta*; urchin below it is *Echinus tylodes*; courtesy S.W. Ross, K. Sulak, and M. Nizinski); (f) bryozoan (courtesy NOAA/Ocean Explorer); (g) mollusc (oyster reef; courtesy South Carolina Department of Natural Resources); (h) echinoderm (brittle star; Larry Zetwoch; Florida Keys National Marine Sanctuary); (i) crustacean (lobster; Dr. James P. McVey, NOAA Sea Grant Program). The calcification responses of many of these groups have not been investigated.

tastraea capitata were much less sensitive to changes in saturation state under increased nutrient conditions. The experimental designs of these two studies were very different, however, which is a likely factor in the mixed results.

Identification of a "CO_2 signal" is difficult because calcification rates in the field are a response to multiple variables (light, temperature, nutrients, etc.), and particularly to rising temperature. If seawater chemistry was the only variable affecting calcification, then calcification records from corals and other organisms should show a decrease in calcification over the past century. While some individual calcification records from massive corals do reveal a decrease in calcification rate over the past century, on average they do not (Lough and Barnes, 1997, 2000), and this is believed to reflect the effects of other variables on calcification. In particular, calcification rates in these and other massive corals show a strong correlation with temperature (Lough and Barnes, 1997, 2000; Bessat and Buigues, 2001; Carricart-Ganivet, 2004).

Boron isotopic analysis of a massive *Porites* coral core from Flinders Reef in the southwest Pacific indicates that seawater pH in this region fluctuated between about 7.9 and 8.2 units over the last 300 years, in 50-year cycles consistent with circulation changes associated with the Interdecadal Pacific Oscillation (Pelejero *et al.*, 2005). The authors also found that calcification rates for this core were not correlated with the derived pH values.

Carbonate chemistry measurements of waters overlying reefs and reef flats often show extreme diurnal variability, due to the effects of calcification-dissolution and photosynthesis-respiration of the coral community (Gattuso *et al.*, 1993b; Kayanne *et al.*, 1995; Frankignoulle *et al.*, 1996; Bates *et al.*, 2001; Kayanne *et al.*, 2005). Such high variability illustrates that many factors affect seawater chemistry both spatially and temporally on coral reefs, and attributing a change in calcification rate to a single factor is difficult. Future experiments that monitor diurnal to seasonal environmental fluctuations on a coral reef and compare them to calcification rates of resident organisms (e.g., as recorded in coral cores) would certainly shed light on the cumulative impact of multiple variables on coral calcification.

The relationship between photosynthesis and calcification in benthic calcifiers remains poorly understood. There is strong evidence that calcification rates in coralline algae and corals are enhanced by photosynthesis, with a mean light:dark ratio of about 3 (Gattuso *et al.*, 1999a), but the stimulating mechanism remains poorly known (Cohen and McConnaughey, 2003). The assumption that photosynthetic removal of CO_2 simply elevates the carbonate saturation state (Goreau, 1959) does not seem to hold. The opposite notion—that calcification stimulates photosynthesis by supplying CO_2—has also been proposed but is not widely accepted (Gattuso *et al.*, 2000; Cohen and McConnaughey, 2003; McConnaughey, 2003; Cohen, 2004; Marshall and Clode, 2004), although a recent study supports it (Schneider and Erez, 2006). Finally, photosynthesis and calcification may not be connected through carbonate chemistry, but rather because photosynthesis provides energy for calcification (Muscatine, 1990), or because calcification stimulates nutrient uptake (Cohen and McConnaughey, 2003).

Based on a small number of studies, net photosynthetic rates of corals show either no response to increased pCO_2 or a slight increase (Burris *et al.*, 1983; Goiran *et al.*, 1996; Langdon and Atkinson, 2005; Schneider and Erez, 2006). There is also empirical evidence that photosynthesis and calcification vary inversely when exposed to elevated CO_2 or nutrients (Hoegh-Guldberg and Smith, 1989; Stambler *et al.*, 1991; Marubini and Davies, 1996; Marubini and Thake, 1999; Langdon and Atkinson, 2005). Clearly, research is required on the molecular and biochemical pathways of the photosynthesis-calcification relationship before the effect of environmental changes on coral physiology can be deciphered.

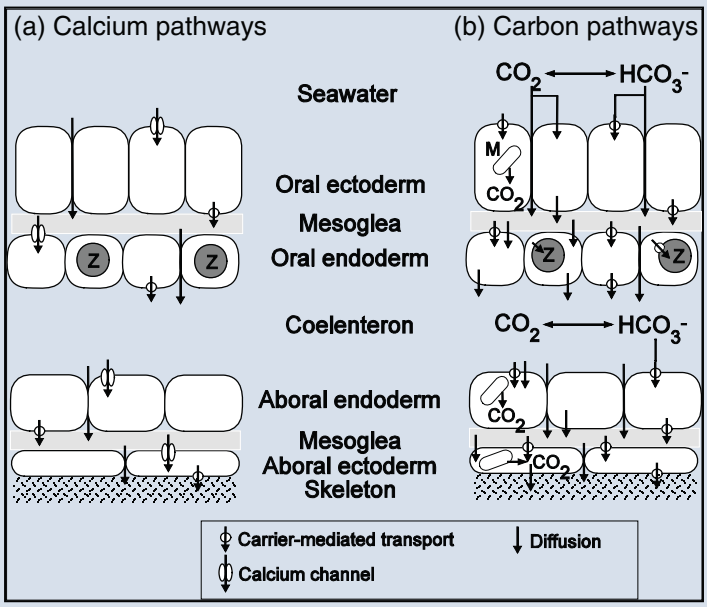
Identifying the various calcification mechanisms across taxa can streamline efforts to understand future responses to saturation state. The degree of biological control of calcification varies between taxonomic groups. The most passive mechanism, termed "biologically induced calcification" (Lowenstam and Weiner, 1989), occurs as a consequence of an organism's metabolic effects on the environment (e.g., photosynthesis absorbs CO_2 and raises saturation state). Calcification in most benthic calcifiers, including corals, is "biologically controlled," that is, cellular processes are directly involved in mineral nucleation, growth, and placement (Weiner and Dove, 2003). Even amongst taxa with biologically controlled calcification, the degree of control varies considerably. Calcification rates in those taxa with biologically induced or weakly controlled calcification are likely to be more sensitive to seawater chemistry changes than in other groups. For example, the mineralogy, skeletal amounts, and overall volumes of $CaCO_3$ produced by "hypercalcifiers" (e.g., corals, coccolithophores, and phylloid algae) have varied over geologic time in concert with changes in the seawater Mg:Ca ratio (Stanley and Hardie, 1998; Stanley *et al.*, 2005).

Beyond this broad classification, some of the biocalcification processes of corals can be pieced together from existing studies. For example, both dark and light calcification in corals are affected by a change in saturation state of the seawater, which implies that there is either significant exchange with the external environment or some indirect control by the external seawater chemistry on the carbonate chemistry of the internal calcifying space (**Box 3**). While HCO_3^- is the preferred substrate for coral photosynthesis (Al-Moghrabi *et al.*, 1996; Goiran *et al.*, 1996; Allemand *et al.*, 1998), coral calcification uses both HCO_3^- from seawater and metabolic CO_2 as sources of carbon (Erez, 1978; Furla *et al.*, 2000). Most models assume that the calcifying fluid is isolated from external seawater. This is supported by microelectrode observations that show that the pH of the calcifying space is elevated relative to external waters (as high as 9.3) (Al-Horani *et al.*, 2003) and by the well-known fractionation of oxygen and carbon isotopes in the calcifying fluid.

The component of the carbonate system—CO_3^{2-}, saturation state, pH—that controls calcification rate has not been adequately determined. Although biochemical studies fail to provide any evidence that

Box 3—Coral Calcification

Coral calcification was reviewed by Gattuso *et al.* (1999a), Cohen and McConnaughey (2003), and Allemand *et al.* (2004). A coral is a colonial organism made up of many polyps. The anatomy of a polyp can be simply described as a "bag" enclosing a coelenteric cavity or gut open to the surrounding seawater by a mouth. The walls of the polyp are made of two single-cell thick epithelial layers, the ectoderm (outer layer) and the endoderm (inner layer), separated by a thin connective layer, the mesoglea. The two layers against the skeleton are the aboral endoderm and ectoderm, and the two layers in closest contact to seawater are the oral endoderm and ectoderm. A schematic of the polyp geometry is shown below. In reality, the geometry is much more complex; the coelenteric cavities of neighboring polyps are connected, the shape of the "bag" conforms to the complex skeletal structure of the calyx or calcium carbonate "cup" that each polyp occupies, the "bag" is compartmentalized into mesenteries and tentacles, and it contains cilia that are capable of generating water movement.



(a) Calcium and (b) carbon pathways involved in calcification and photosynthesis in scleractinian corals. Anatomy is greatly simplified. The extracytoplasmic calcifying fluid is located between the aboral ectoderm and the skeleton. Every possible pathway is shown; the actual transport mechanisms for each of the four cell layers can be transcellular or paracellular, or a combination of both. M = mitochondria; Z = zooxanthellae. Reprinted from Gattuso *et al.* (1999a).

The zooxanthellae, symbiotic plant cells, are mainly located in the oral endoderm. The zooxanthellae supply during the day much of the polyp's energy requirements through the process of photosynthesis. Calcification occurs in the extracellular calcifying fluid (ECF) located between the aboral ectoderm and the dead skeleton. The cells of the aboral ectoderm, called calicoblastic cells, are thought to be intimately involved in skeletogenesis, the process whereby crystals of calcium carbonate produced by calcification are grown into the complex architecture characteristic of each coral species. The distance separating the processes of photosynthesis and calcification is approximately 25 μm.

The diagram summarizes the many pathways via which calcium ion and inorganic carbon could reach the site of calcification. For each there are diffusive or active pathways that have been demonstrated by physiological and pharmacological studies. Diffusive pathways involve molecular diffusion through the lateral cell junctions termed paracellular transport while active pathways occur via an energy-dependent transcellular transport mechanism. The chemical composition of the coelenteric fluid is influenced by photosynthesis, calcification, and advective exchange of seawater through the mouth and transepithelial transport of ions by enzyme-mediated mechanisms. This fluid in turn supplies the Ca^{2+} and inorganic carbon to the ECF. The source and pathways of inorganic carbon are particularly complex because they can exist in three different forms and can be produced metabolically within the cells in addition to diffusing into the cells from the seawater or being actively transported in the form of $[HCO_3^{2-}]$. Several studies suggest that metabolic CO_2 is the major source of carbon for calcification (Erez, 1978; Furla *et al.*, 2000). The current model of coral calcification emphasizes the active uptake of Ca^{2+} from the coelenteric fluid by calicoblastic cells in which two major transporter proteins, the Ca^{2+}-channel allowing Ca^{2+} entry into the cells and the Ca^{2+}-ATPase allowing its active secretion toward the site of calcification, have been characterized and localized (Allemand *et al.*, 2004). It has been demonstrated that these cells are responsible for the secretion of macromolecules, called organic matrix, involved in the control of calcification (Puverel *et al.*, 2005).

CO_3^{2-} plays a direct role in coral calcification, results from experiments that specifically control the concentrations of the various components of the carbonate system (e.g., maintaining constant pH while varying $[CO_3^{2-}]$) suggest that coral calcification responds to $[CO_3^{2-}]$ rather than pH or some other component of the surrounding seawater environment (Langdon, 2002; Schneider and Erez, 2006). Many calcification data sets are well described by the rate law: $R = k(\Omega - 1)^n$, where R is rate of calcification, k is the rate constant, Ω is the saturation state, and n is the order of reaction. Two data sets have shown that an increase in $[Ca^{2+}]$ has the same effect on calcification as an increase in $[CO_3^{2-}]$ (Gattuso *et al.*, 1998b; Langdon *et al.*, 2000), lending support to the hypothesis that it is the ion concentration product, $[Ca^{2+}][CO_3^{2-}]$, and not the change in carbonate chemistry per se that is affecting the rate of calcification. In normal seawater, $[Ca^{2+}]$ is much higher than $[CO_3^{2-}]$ and is not considered limiting to calcification. Changes in Ω are thus primarily a function of $[CO_3^{2-}]$ changes.

3.1.2 Organism response

How decreased calcification rates will affect the long-term survival of benthic calcifiers is unknown. The effects of reduced calcification on an organism's fitness and survivorship have been hypothesized based on the perceived functions of $CaCO_3$ in that organism. In corals and coralline algae, for example, skeletal growth is thought to elevate the organism above the substrate and into higher light and better flow conditions, provide anchoring/rigidity against hydrodynamic forces, increase competitiveness for space, increase light gathering, and provide protection (**Table 3.1**). Reproductive success of some coral species could be affected by slower or more fragile growth. Reproductive maturity in *Goniastrea aspera*, for example, is achieved by size rather than age (Sakai, 1998a, b), and increased skeletal fragmentation in *Acropora palmata* can promote asexual propagation, but can also lower the potential for sexual reproduction of the species (Lirman, 2000).

The role of calcification in multiple life stages may play a critical role in organism survival. For many organisms, the function of $CaCO_3$ varies with life cycle stage (e.g., planktonic stages, recruitment), but almost all studies of CO_2 effects on calcification have focused on adults. One study (Agegian, 1985) noted that recruitment of coralline algae on aquarium walls was reduced in experiments with elevated pCO_2, and another (Green *et al.*, 2004) found that newly settled larvae of the mollusc *Mercenaria mercenaria* experienced higher shell dissolution and mortality rates when the pore-water interface was undersaturated with respect to aragonite.

Several years may be necessary to determine whether benthic calcifiers can adapt or acclimate to different carbonate chemistry conditions. There is no experimental evidence from either single organisms or multispecies mesocosms that corals or coralline algae can acclimate or adapt to lowered saturation state. However, most experiments have been conducted over hours to months, and based on isotopic evidence corals appear to calcify with natural "biorhythms" for up to two years after being introduced into a new environment (P. Swart, personal communication). Another unexplored mechanism for adaptation may be to secrete less soluble skeletons. The solubility of high-Mg calcite, for example, increases with increasing Mg content, and several taxa are known to vary the Mg content of their skeletons in response to several environmental variables (Chave, 1954; Stanley *et al.*, 2002). This ability to secrete skeletons with lower Mg content (and lower solubility) provides some organisms the potential to "adapt" to decreasing saturation state. Finally, some species may be able to adapt to lower calcification rates by adopting different morphologies or growth strategies.

3.1.3 Ecosystem response

The effects of changing calcification and dissolution on reef ecosystem functioning are unknown. This includes (1) the interactions of organisms, (2) food web dynamics, (3) basic cycling of carbon and nutrients through the ecosystem, and (4) the services that these ecosystems provide. The role of inorganic cementation in stabilization of organisms, communities, and reef structures has not been quantified; nor has the extent to which inorganic cementation may be affected by a lowered saturation state. Inorganic cementation is considered another component of ecosystem development, as it plays a role in the resilience of coral skeletons and reef structures.

The effects of reduced saturation state on bioerosion rates are unknown. Bioerosion is another prevalent, natural process in coral communities. All benthic calcifiers experience skeletal bioerosion simultaneously with growth, from a wide variety of both chemical and physical bioeroders, both macroscopic (e.g., molluscs and sponges) and microscopic (e.g., fungi and microalgae). Will bioerosion rates change in response to lower calcification rates, or increase in the presence of less dense skeletal material; and how will this affect the structure and functioning of benthic ecosystems?

3.1.4 Dissolution and reef-building response

The role of reef-building in coral reef ecosystem functioning is complex and not fully understood. Reef-building supports many functions of a coral 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 diversity, and (4) the structural influence on the local hydrodynamic regime. A better understanding of the second point, in particular, is key to predicting coral reef community response to elevated CO_2.

Dissolution in reef environments is expected to increase. Net carbonate dissolution is observed in many reef environments at night when respiration elevates the local pCO_2 of the water column. Measured dissolution rates range from 0.1–20 mmol $CaCO_3$ m^{-2} h^{-1} and average 2 ± 5 mmol $CaCO_3$ m^{-2} h^{-1} (**Table 3.2**). Dissolution is likely occurring all the time in sediments and carbonate framework of the reef but is only evident at night when it is not masked by a higher rate of carbonate precipitation. Mass loss of red algal carbonate substrates (18% Mg-calcite) embedded in Florida reef tract sediments suggest a dissolution rate of 10–19 mmol $CaCO_3$ m^{-2} d^{-1} of this most soluble form of biogenic carbonate.

Rates of dissolution in the sediments and reef framework are expected to increase as the overlying water becomes less supersaturated. This is because respiratory CO_2 produced by microorganisms living in the sediments produces a profile of saturation state that is initially equal to the overlying water at the sediment-water interface and then declines to undersaturation with increasing depth. As the saturation state of the overlying water declines due to uptake of anthropogenic CO_2, the pore water profile of saturation state will become more uniform. This will cause the saturation horizon to rise closer to the surface, and the degree of undersaturation in the deeper sediments will increase. The combined result is likely to be more dissolution and a greater flux of Ca^{2+} and CO_3^{2-} ions into the overlying water.

Model calculations that account for changing saturation state of the overlying water, and the organic carbon and mineral characteristics of the sediments, predict that by the year 2300 under a business-as-usual scenario, dissolution of carbonate minerals, particularly of high-Mg calcite, will increase by more than 200% (Andersson *et al.*, 2006).

Conditions controlling sediment dissolution (including suspended sediment) and the potential impact on coral reef carbonate chemistry are poorly understood. Increased dissolution of coral reef sediments (particularly high-Mg calcite) may provide some buffering of the carbonate system in coral reef waters that have low exchange rates with the open ocean. Modeling of this process, however, has shown that dissolution of shallow-water carbonates will not significantly counteract the effects of rising CO_2 (Andersson *et al.*, 2003). Quantifying the effects of dissolution would greatly benefit from better determination of the thermodynamic constants for high-Mg calcite, which can vary by an order of magnitude.

Reef building requires reef calcification to exceed reef dissolution, but dissolution is likely to exceed calcification at some threshold value of pCO_2. Coral reefs by definition produce more calcium carbonate than is removed, but reef-building is expected to decrease in the future as calcification rates decline and dissolution rates increase (Kleypas *et al.*, 2001). The net response of coral reef calcification to changing seawater chemistry 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. To predict how rates of reef building will change in the future, the calcium carbonate budgets of coral reefs, particularly across environmental gradients, need to be better quantified.

The threshold pCO_2 value where dissolution exceeds calcification will vary from reef to reef with changes in community structure and environmental conditions. In experiments where calcification and dissolution were measured using sealed enclosures placed over the reef or associated seafloor, the threshold value where calcification = dissolution occurred at pCO_2 levels of 467–1003 μatm (Yates and Halley, submitted).

3.2 Coccolithophores, Foraminifera, Pteropods, and Other Planktonic Calcifying Organisms and Systems

The major planktonic calcifying organisms are coccolithophores and foraminifera, both of which secrete calcite, and euthecosomatous pteropods, which form shells of aragonite (**Figure 3–2**). While many other calcifying invertebrate and protist taxa also have planktonic stages, these three groups largely account for the majority of the total $CaCO_3$ produced by planktonic organisms. The major planktonic calcifying groups differ with respect to size, trophic level, generation time, and other biological attributes (**Ta-**

Table 3.2: Carbonate dissolution rates reported from reef environments and mesocosms.

	$CaCO_3$ dissolution rate			
Location	**mmol m^{-2} h^{-1} at night**	**mmol m^{-2} night^{-1}**	**mmol m^{-2} 24 h^{-1}**	**Source**
Moorea sandy bottom reef flat and lagoon	0.8	9.4	2.4	Boucher *et al.*, 1998
Hawaiian patch reef 22% coral cover	1.5∗	17.7		Yates and Halley, 2003
Hawaiian patch reef 10% coral cover	1.1∗	13.0		"
Hawaiian coral rubble	1.2∗	14.1		"
Hawaiian sand bottom	0.3∗	3.3		"
Florida patch reef 10% coral cover	0.5∗	5.5		"
Florida patch reef top	0.1∗	1.1		"
Florida seagrass	0.4∗	4.7		"
Florida sand bottom	0.3∗	3.0		"
Reunion Island Back reef zone summer	7.0			Conand *et al.*, 1997
Rib Reef flat, GBR in March	4.0		97.0	Barnes and Devereux, 1984
Biosphere 2 mesocosm hi Mg-calcite sediments	0.2∗		4.7	Langdon *et al.*, 2000
One Tree Island, GBR back reef zone	3.0∗			Kinsey, 1978
Monaco mesocosm sand community	0.8∗			Leclercq *et al.*, 2002
Florida Bay	0.8		19.0	Walter and Burton, 1990
Average	**2.3**	**8.0**	**42.6**	
Standard deviation	**4.8**	**5.5**	**42.0**	

* derived rates

Table 3.3: Characteristics of major calcifying groups.

Group	**Trophic Level**	**Mineral Form**	**Generation Time**	**Approx. No. of Extant Species**
Coccolithophores	autotrophic	calcite	day(s)	200
Foraminifera	heterotrophic many with autosymbionts	calcite	weeks	35
Euthecosomatous pteropods	heterotrophic	aragonite	Months to >1 year?	34
Coralline algae	autotrophic	high-Mg calcite	days	~20 genera
Halimeda	autotrophic	aragonite	weeks	25–30
Zooxanthellate corals	hetotrophic with autosymbionts	aragonite	months–years	~1000

ble 3.3). However, quantitative data on the distribution and abundance of these major groups are lacking, and estimates of their contributions to global calcification rates are poorly constrained. Analysis of sediment trap data indicates that the relative proportion of each of these major groups varies regionally. For example, at the Ocean Flux Program (OFP) site in the Sargasso Sea, the total $CaCO_3$ fluxes at 1500 and 3200 m of 8.0 g m^{-2} y^{-1} consist primarily of calcite (75–79%) composed mainly of foraminifera and coccolithophores with a lesser amount of aragonite (13–15%) produced by planktonic pteropod and heteropod snails (1.2 g m^{-2} y^{-1}), and high-Mg calcite (8–10%) possibly produced by bryozoans attached to floating *Sargassum* (Deuser and Ross, 1989; Fabry and Deuser, 1991) (**Table 3.4**). In contrast, at the high-latitude site of Ocean Station Papa in the North Pacific, the aragonite flux of a single pteropod species was 2.5 g $CaCO_3$ m^{-2} y^{-1}, about twice the total aragonite flux in the Sargasso Sea (Tsurumi *et al.*, 2005).

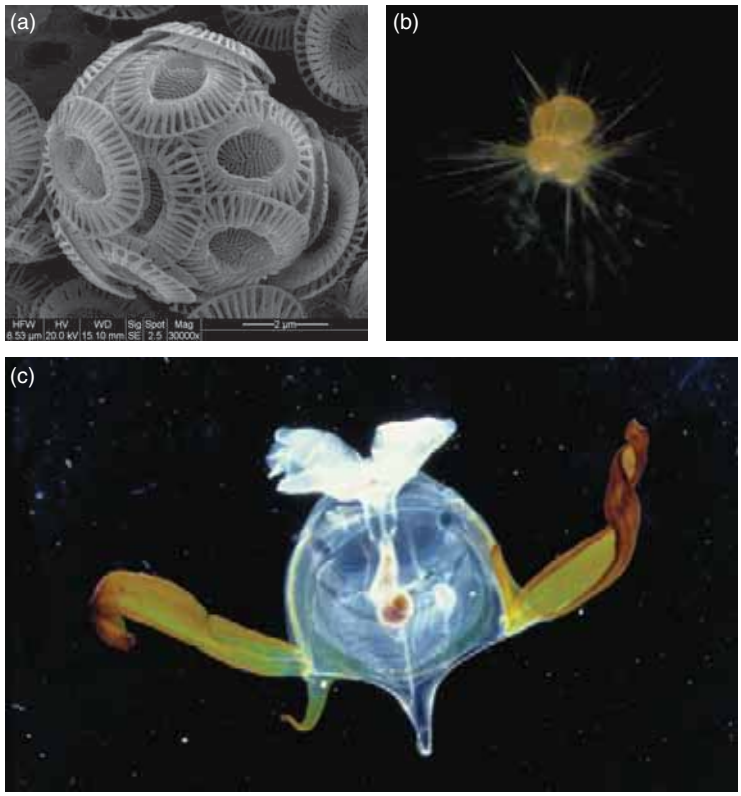


Figure 3–2: Representatives of major planktonic calcifiers: (a) the coccolithophore *Emiliania huxleyi* (courtesy V. Fabry) ; (b) planktonic foraminifer (courtesy A. Alldredge); and (c) the euthecosomatous pteropod *Cavolinia tridentata* (courtesy V. Fabry).

Table 3.4: Contributions of various planktonic groups and $CaCO_3$ mineral phases to the total $CaCO_3$ fluxes measured with sediment traps at 1500 and 3200 m in the Sargasso Sea (after Deuser and Ross, 1989 and Fabry and Deuser, 1991).

	Calcite[a]		Aragonite[b]		High-Mg calcite[c]		
Depth (m)	**Flux ($g\ m^{-2}\ y^{-1}$)**	**% of total $CaCO_3$**	**Flux ($g\ m^{-2}\ y^{-1}$)**	**% of total $CaCO_3$**	**Flux ($g\ m^{-2}\ y^{-1}$)**	**% of total $CaCO_3$**	**Total $CaCO_3$ flux ($g\ m^{-2}\ y^{-1}$)**
1500	6.0	75	1.2	15	0.8	10	8.0
3200	6.3	79	1.1	13	0.6	8	8.0

[a] Primarily foraminifera and coccoliths
[b] Pteropod and heteropod shells
[c] Containing >5 mole% $MgCO_3$

The physical, chemical, and biological factors that drive biogenic calcification and population dynamics in coccolithophores, foraminifera, and pteropods are little understood. To date, few studies have investigated the response of planktonic calcifiers to elevated pCO_2, and most of these have involved a single coccolithophore species, *Emiliania huxleyi*. There are clear needs for research on the physiological and ecological impacts of increasing pCO_2 on planktonic calcifying organisms and marine systems, and these are presented below. The evidence and gaps in our current knowledge of how increasing ocean acidification will affect planktonic calcifiers are addressed below in terms of: (1) calcification response, (2) organism response, (3) ecosystem response, and (4) dissolution.

3.2.1 Calcification response

Calcification in three major groups of planktonic calcifiers—coccolithophores, foraminifera, and pteropods—has been shown to respond to changes in the carbonate system. However, most studies

have been performed on bloom-forming coccolithophores, and there are very limited observations of other planktonic groups. Several laboratory and field studies show that two coccolithophore species have reduced calcification rates at elevated pCO_2, even when the calcite saturation state is >1 (Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Zondervan *et al.*, 2002; Sciandra *et al.*, 2003; Delille *et al.*, 2005; Engel *et al.*, 2005). In a mesocosm bloom experiment with *E. huxleyi* cultured at glacial, present-day, and year 2100 CO_2 values, organic carbon production did not change, but calcification decreased under the projected year 2100 levels (Delille *et al.*, 2005). Contrary to findings in laboratory experiments (e.g., Riebesell *et al.*, 2000), no malformations of the coccospheres were observed, but coccospheres and coccoliths were smaller and coccoliths weighed less when grown under high pCO_2 levels (Engel *et al.*, 2005). In laboratory experiments with three species of planktonic foraminifera, shell mass in two species decreased as the carbonate ion concentration of seawater decreased (Spero *et al.*, 1997; Bijma *et al.*, 1999; Bijma *et al.*, 2002). Data for a single species of shelled pteropod suggest that net shell dissolution occurs in live pteropods when the aragonite saturation is forced to <1 (Feely *et al.*, 2004; Orr *et al.*, 2005).

The response of planktonic calcifying organisms to elevated pCO_2 is likely to vary between and within taxonomic groups. The limited number of studies and species investigated, however, preclude identification of widespread or general trends. Furthermore, all data collected from foraminifera and pteropods to date have come from mature specimens. Hence, there is a need for quantitative, direct measurements of calcification rates over a range of taxa and life stages, as well as over a range of elevated pCO_2 values.

While the relationship between calcification and carbonate ion concentration appears to be linear in corals, the response of other major groups of planktonic calcifiers may not be linear, and additional studies are needed to better determine the nature of the response. Some experimental data suggest, for example, that calcification in coccolithophores and foraminifera may respond asymptotically to carbonate ion concentration, implying that reduction of the carbonate saturation state below a threshold value will lead to large decreases in calcification rates.

The synergistic impacts of increased pCO_2 with light, nutrients, and temperature are largely unknown. For example, de Villiers (2005) found that shell weight of marine foraminifera was better correlated with "optimum growth conditions" defined by a suite of environmental factors than by saturation state alone. Light intensity was shown to be an important factor in laboratory experiments with *E. huxleyi*, with calcification rates decreasing with increasing CO_2 concentrations only under saturating light intensities (Zondervan *et al.*, 2002). Nutrient limitation may also be important, as experiments with *E. huxleyi* cultured under nitrogen limitation showed that calcification rates decreased with increasing CO_2, but that organic carbon production decreased only in response to limited nitrogen (Sciandra *et al.*, 2003) (in contrast to nitrogen replete experiments which show an increase in organic carbon production under increased pCO_2 (Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Zondervan *et al.*, 2002; Delille *et al.*, 2005; Engel *et al.*, 2005)). Finally, trace metal limitation has been shown to affect *E. huxleyi* calcification and growth (Schulz *et al.*, 2004). Iron limitation affected both calcification and organic carbon production, while zinc was limiting to organic carbon production but not to calcification.

Calcification and photosynthesis in coccolithophores and foraminifera are poorly understood. The few studies on the relationship between calcification and photosynthesis in these two groups suggest that the two processes may not be coupled. In laboratory experiments with *E. huxleyi*, calcification does not stimulate photosynthesis (Paasche, 1964; Herfort *et al.*, 2002) and, although calcification rates are greater in light than in dark, increased rates of calcification are not necessarily accompanied by higher photosynthetic rates (Paasche, 1964; Herfort *et al.*, 2004; Rost and Riebesell, 2004). In foraminifera, photosynthesis by symbiotic algae enhances calcification (e.g., Anderson and Faber, 1984; Lea *et al.*, 1995); however, calcification rates in symbiont-bearing species are similar to those of nonsymbiont foraminifera and photosynthesis is not necessary for calcification (Zeebe and Sanyal, 2002).

The molecular and physiological mechanisms that control the calcification response in planktonic organisms to changes in the CO_2 system are poorly understood. Results from several studies indicate that the substrate for calcification in *E. huxleyi* is HCO_3^- (cf., Paasche, 2001), which *increases* under elevated pCO_2 conditions, suggesting that calcification in this coccolithophore should increase under high CO_2 conditions, rather than decrease as observed. In foraminifera, one hypothesis is that if HCO_3^- is the substrate, then a proton pump is required to remove excess H^+ formed during calcification, and the pump does not operate as efficiently when external pH is lower (Zeebe and Sanyal, 2002). In addition, it is unclear why calcification rates in foraminifera decrease in response to surrounding seawater carbonate chemistry when the pH at the shell surface ranges from 8.8 during the daytime when symbiont photo-

synthesis is active, to 7.9 when respiration processes dominate (Rink *et al.*, 1998).

The suite of planktonic calcifiers includes larval stages of many benthic invertebrates but almost no information exists on how these early calcifying stages may be affected by decreased carbonate saturation state. Larval stages of two sea urchins showed smaller calcitic skeletons, as well as decreased developmental rates and larval size, under high pCO_2 conditions (Kurihara and Shirayama, 2004).

3.2.2 Organism response

It is not known whether planktonic calcifiers require calcification to survive (Seibel and Fabry, 2003). The response will almost certainly vary among taxa and the function of the $CaCO_3$ precipitation (**Table 3.1**). For example, if $CaCO_3$ provides protection, then the species may be more subject to predation or microbial infections; if $CaCO_3$ provides ballast, then the species may be less able to maintain its position in the water column. Some coccolithophore species have a non-calcifying stage in their life cycles (e.g., Green *et al.*, 1996; Houdan *et al.*, 2004) and many laboratory cultures of coccolithophores grow well without calcifying (cf. Paasche, 2001). In field samples, the presence of such naked coccolithophore cells cannot readily be identified by traditional microscopy, but may be accomplished with the use of molecular markers, such as immunofluorescence probes (e.g., Campbell *et al.*, 1994).

The capacity for planktonic organisms to adapt to lower saturation states (or reduced calcification rates) has not been investigated. The few studies of the response of planktonic calcifying organisms to increased pCO_2 and decreased carbonate saturation state have been short term, and have not detected adaptations that would allow organisms to calcify at "normal" rates under decreased saturation states. Natural variation within species and sister species indicates that some species may be favored over others. For example, specimens of the foraminifer *Globigerina bulloides* from Chatham Rise (east of New Zealand) are much larger and heavier than those from Catalina Island (west of California), despite the waters around Catalina Island having a higher CO_3^{2-} concentration. One explanation is that *G. bulloides* may be a complex of sister species (Darling *et al.*, 2000); and "adaptation" in the future may reflect replacement by species better adapted to lower saturation state.

While little is known about the ability of planktonic calcifiers to adapt to the high pCO_2 ocean of the future, there is evidence suggesting that at least one coccolithophore species may have the capacity to adapt to changing pCO_2 over long time periods. Experimental manipulations show that *Calcidiscus leptoporus* exhibits highest calcification rates at present-day CO_2 levels, with malformed coccoliths and coccospheres at both lower and higher pCO_2 (Langer *et al.*, in press). However, since no malformed coccoliths are observed in sediments from the Last Glacial Maximum (when pCO_2 levels were about 200 ppm), the authors conclude that *C. leptoporus* has adapted to present-day CO_2 levels.

Long-term impacts of elevated pCO_2 on reproduction, growth, and survivorship of planktonic calcifying organisms have not been investigated. Existing studies on the impacts of ocean acidification on calcareous plankton have been short-term experiments, ranging from hours to weeks. Chronic exposure to increased pCO_2 may have complex effects on the growth and reproductive success of $CaCO_3$-secreting plankton. No studies have investigated the possibility of differential impacts with life stage or age of the organism.

3.2.3 Ecosystem response

If reduced calcification decreases a calcifying organism's fitness or survivorship, then such calcareous species may undergo shifts in their latitudinal distributions and vertical depth ranges as the CO_2/carbonate chemistry of seawater changes (Seibel and Fabry, 2003). To date, no quantitative data exist with which to test this hypothesis. This emphasizes the need for high-quality data on the vertical distributions and abundances of foraminifera, shelled pteropods, and coccolithophores, particularly in those oceanic regions which are expected to experience the greatest changes in carbonate saturation states.

The potential impacts of increased CO_2 on planktonic ecosystem structure and functions are unknown. It is possible that CO_2-sensitive species will be outcompeted by non-calcifying species and/or those not sensitive to elevated pCO_2. The synergistic effects of elevated pCO_2 with other stressors such as increased water column stratification and decreased upwelling could result in substantial changes in species diversity and abundances in many regions. Species interactions may be altered on multiple trophic levels, potentially impacting ecosystem productivity as well as the cycling of organic carbon and carbonate carbon.

3.2.4 Dissolution response

Decreased saturation states can affect both the production and dissolution of biogenic $CaCO_3$, yet most studies have neglected dissolution rates. One study observed dissolution of the aragonitic shells of live pteropods exposed to a degree of aragonite undersaturation that is projected to occur in surface waters of the Southern Ocean by 2100 under the IPCC business-as-usual CO_2 emissions scenario (IS92a) (Feely *et al.*, 2004; Orr *et al.*, 2005).

$CaCO_3$ dissolution is substantial in the upper water column, but little is known about the mechanisms that control this dissolution or how they may change with future increased CO_2. Dissolution rates are unexpectedly high in the upper ocean, even in supersaturated waters. From mass balance estimates, up to 70% of the export production of calcite and aragonite dissolves before it reaches the lysocline (Milliman *et al.*, 1999; Feely *et al.*, 2002; Feely *et al.*, 2004), and process studies in the equatorial Pacific and Arabian Sea suggest that 75–80% of the calcite flux dissolves in the upper 800–900 m of water (Balch and Kilpatrick, 1996; Balch *et al.*, 2000). Several mechanisms for these high dissolution rates have been proposed but have not been adequately quantified or tested. Mechanisms include microbial processes (e.g., Buitenhuis *et al.*, 1996; Troy *et al.*, 1997; Schiebel, 2002) and dissolution in acidic zooplankton guts (Bishop *et al.*, 1980; Harris, 1994; Pond *et al.*, 1995). Improved understanding of these processes is needed to predict how upper ocean dissolution rates will change with increased ocean acidification.

3.3 Linkages Between Communities and Ecosystems

Calcifying organisms affect processes in different communities and ecosystems, thereby creating linkages between marine systems. For example, species diversity in the deep ocean has been linked to surface ocean productivity (Gage and Tyler, 1991). Thus, if increased pCO_2 decreases calcification rates and abundance of calcifying planktonic organisms in the upper ocean, there could be cascading effects on deep sea biodiversity and ecology. Further examples of the connectivity between ecosystems are the lateral, offshore transport of alkalinity from shallow coral reef systems to the open ocean (Sabine *et al.*, 1995; Mackenzie *et al.*, 2004), and between sea-grass beds and coral reefs (Burdige and Zimmerman, 2002). Such community and ecosystem linkages are undoubtedly important in the overall cycling of carbon and nutrients across large spatial scales, but are among the least understood aspects of the calcium carbonate cycle.

3.4 Effects on Carbon Cycle

3.4.1 The coral reef hypothesis

Shallow-water deposition of calcium carbonate has changed dramatically with the flooding and drying of continental shelves during glacial-interglacial fluctuations in sea level. The "coral reef hypothesis" (Berger, 1982) states that flooding of continental shelves during postglacial sea level rise provided large surface areas for reef growth and $CaCO_3$ production, which released significant amounts of CO_2 to the atmosphere. Several modeling efforts confirm that this mechanism is probably a significant component of the global carbon cycle (Opdyke and Walker, 1992; Archer *et al.*, 2000), including one that estimates that the 20 ppmv increase in atmospheric CO_2 in the late Holocene was primarily due to increased shallow water $CaCO_3$ deposition (Ridgwell *et al.*, 2003).

3.4.2 The open-ocean $CaCO_3$ budget

The biological pump removes carbon from surface waters in organic ("soft tissue pump") and inorganic ("hard tissue pump") forms. The inorganic form is predominantly $CaCO_3$. Although both pumps transport carbon from the surface to the deep ocean, their net effect on the partitioning of CO_2 between the atmosphere and the ocean is different. While the hard tissue pump increases pCO_2 of the surface ocean and thus decreases its ability to absorb atmospheric CO_2, the soft tissue pump has the opposite effect. Thus, changes in the carbon export ratio between the hard and soft tissue pumps may have major consequences for the upper ocean pCO_2 and the air-sea CO_2 flux. Furthermore, only the soft tissue pump is directly coupled to the biological uptake of nitrogen, phosphorus, and iron. Growing evidence suggests a linkage between the vertical remineralization length-scales of organic matter and the sinking fluxes of $CaCO_3$ and biogenic silica. While the basic chemical and biological processes driving both biological pumps are known, current understanding of the environmental factors that control variations in the ratio between both pumps remains limited.

Quantitative accounting of the global $CaCO_3$ budget was first addressed by Milliman (1993) and Milliman and Droxler (1996), and those estimates continue to be refined (Iglesias-Rodriguez *et al.*, 2002; Feely *et al.*, 2004). Elements of this budget were derived through a variety of techniques, including direct

measurements (e.g., calcification rates, sediment calculations). Pelagic $CaCO_3$ production is estimated to be between 0.5 and 2.0 Pg C y^{-1}, based on direct measurements and modelling studies. Alkalinity-based estimates seem to narrow this estimate down to between 0.72 Pg C y^{-1} (Morse and Mackenzie, 1990) and 1.1 ± 0.3 Pg C y^{-1} (Lee, 2001); while the globally integrated trap-based estimate of $CaCO_3$ flux at 2000 m is 0.41 Pg C y^{-1} (Iglesias-Rodriguez *et al.*, 2002). This suggests that at least half of the pelagic production dissolves in the water column, between 100–1500 m depth. $CaCO_3$ accumulation rates at the seafloor (data from some 3000 deep-sea cores (Catubig *et al.*, 1998) indicate a present-day global measured accumulation rate of 0.1 Pg C y^{-1}, which implies that about 90% of surface $CaCO_3$ production dissolves in the water column, at the sediment-seawater interface, or within the sediment column.

3.4.3 Composition of the open-ocean $CaCO_3$ flux

Calcifying organisms in the open ocean are represented by at least ten different phyla including coccolithophorids, planktonic foraminifera, and pteropods, and the life cycles of each affects their potential contribution to the carbonate flux. The distribution of coccolithophorids in the oceans is not well mapped, but some general patterns are known. *Emiliania huxleyi* and *Gephyrocapsa oceanica* are cosmopolitan species that can form large blooms visible in satellite imagery (Brown and Yoder, 1994). *Florisphaera profunda* lives in the deep photic zone (about 150–200 m) in low to mid latitudes, and can be extremely abundant in low- to mid-latitude sediments (Winter and Siesser, 1994). *Coccolithus pelagicus* is a cold-water species dominant from sub-polar to polar waters in the northern Atlantic (McIntyre and Bé, 1967). *Calcidiscus leptoporus* ranges from equatorial to polar waters, although it never constitutes a large part of the living flora (McIntyre and Bé, 1967).

Satellite observations suggest that the greatest spatial extent of surface coccolithophorid blooms are in subpolar and polar regions and are largely represented by *E. huxleyi* (Brown and Yoder, 1994; Balch *et al.*, 2005). While *E. huxleyi* is the numerically dominant coccolithophore species on a global basis, in situ data suggest that other coccolithophore species such as *Coccolithus pelagicus* in the North Atlantic or *Florisphaera profunda* in the tropics may also be important components of the $CaCO_3$ flux in those regions (Broerse *et al.*, 2000).

The contribution of heterotrophic calcifiers to the open-ocean carbonate flux has often been overlooked (understandably so, as it is much easier to parameterize calcifying primary producers as a function of nutrients, light, etc. than higher trophic-level calcifiers such as pteropods and planktonic foraminifera). Foraminifera tend to produce flux pulses of calcite that are related to their reproduction cycles (Bijma, 1991; Bijma and Hemleben, 1994; Bijma *et al.*, 1994; Schiebel *et al.*, 1997) and are difficult to detect. Most, if not all, spinose planktonic foraminifera seem to follow a lunar or semi lunar reproduction cycle (Spindler *et al.*, 1979; Bijma *et al.*, 1990; Erez *et al.*, 1991). Non-spinose species have probably longer cycles (Hemleben *et al.*, 1989). In at least a few spinose species, two modes of carbonate transport have been distinguished (Bijma and Hemleben, 1994) associated with juvenile and adult mortality. Due to high juvenile mortality, a large number of smaller shells sink in association with the cytoplasm. The cytoplasm counteracts the negative buoyancy of the shell and the spines provide "drag," hence the shells settle slowly and bacterial infestation might result in dissolution and break up of the shells at intermediate depth. Adult specimens that undergo gametogenesis produce spineless and empty shells that have an additional carbonate phase ("gametogenetic calcite," up to 30% by weight) that causes the shells to sink rapidly into the abyss (Bé, 1980).

On a global basis, it is generally assumed that euthecosomatous pteropods constitute 10–15% of the total $CaCO_3$ flux (Fabry and Deuser, 1991; Milliman, 1993; Milliman and Droxler, 1996), although few studies have provided high-quality quantitative information on annual pteropod mass fluxes. In most ocean areas, pteropod aragonite dissolves in the water column or soon after reaching the seafloor, and does not accumulate in sediments. In polar and subpolar regions, the aragonitic shells of pteropods are important components of the $CaCO_3$ flux (e.g., Accornero *et al.*, 2003; Collier *et al.*, 2000; Honjo *et al.*, 2000; Tsurumi *et al.*, 2005), and can include mass sedimentation of pteropods after the summer growing season.

3.5 Misconceptions

The previous sections have outlined the current state of knowledge of ocean carbonate chemistry and the effects of ocean acidification on calcifying marine organisms. These issues are complicated and have led to several misconceptions about the future response of marine calcifiers to increasing atmospheric CO_2, which we address here.

Misconception 1. Increasing atmospheric CO_2 will *increase* rather than decrease pH of marine waters

This argument is based on an incorrect assumption that the coupled processes of photosynthesis and calcification increase pH of the water. Release of CO_2 via calcification on reefs, for example, generally exceeds CO_2 uptake by photosynthetic processes, so that reef waters tend to have elevated pCO_2 and lower pH than surrounding oceanic waters (Gattuso *et al.*, 1996a; Gattuso *et al.*, 1996b; Gattuso *et al.*, 1997; Kawahata *et al.*, 1997; Gattuso *et al.*, 1998a; Gattuso *et al.*, 1999a; Gattuso *et al.*, 1999b; Kawahata *et al.*, 2000; Suzuki *et al.*, 2001; Suzuki *et al.*, 2003). Although biological processes can modify the carbonate system in seawater (see section 4.1), the thermodynamic effect of increasing atmospheric CO_2 on surface ocean pH outweighs the ability of marine photosynthesis to take up that excess CO_2 and thus raise the pH (see below for related discussion). Long-term measurements of the carbonate system in seawater illustrate that ocean pH is decreasing (sections 1.1 and 2.1).

Misconception 2. CO_2 fertilization of zooxanthellae will lead to an increase in coral calcification

A common misconception is that an increase in CO_2 will increase photosynthesis of coral symbionts, which will then enhance coral calcification. This is based on two assumptions about the coral/algal symbiotic relationship: (a) that zooxanthellar photosynthesis will increase with rising CO_2, and (b) that increased photosynthesis increases calcification rates.

The first assumption assumes that, like land plants, zooxanthellae use CO_2 as the substrate for photosynthesis, so an increase in CO_2 concentrations will increase photosynthesis. Seagrasses are an example of a marine plant that also directly uses CO_2 for photosynthesis and which may benefit from increased CO_2 concentrations (Zimmerman *et al.*, 1997; Invers *et al.*, 2001; Invers *et al.*, 2002). However, almost all marine autotrophs, including zooxanthellae, are algae that primarily use HCO_3^- for photosynthesis, and HCO_3^- concentrations will increase only about 14% under doubled CO_2 conditions. Photosynthetic rates of corals have shown little to no response to increased pCO_2 (Burris *et al.*, 1983; Goiran *et al.*, 1996; Langdon and Atkinson, 2005; Schneider and Erez, 2006).

The second assumption is based on the fact that zooxanthellate corals calcify about 3x faster in the light than in the dark (Gattuso *et al.*, 1999a). The photosynthetic activity of zooxanthellae is the chief source of energy for the energetically expensive process of calcification, and much evidence suggests that calcification rates generally rise in direct proportion to increases in rates of primary production both at the organismal and community scale (Gattuso *et al.*, 1999a), at least under normal conditions. Although a shutdown in photosynthesis leads to slower calcification rates, the inverse—that an increase in photosynthesis will lead to increased calcification—is not evident. In virtually all studies that have measured both photosynthesis and calcification in corals, any stimulation of photosynthesis by increased pCO_2 was accompanied by a decrease rather than an increase in calcification (for example):

1. Reynaud *et al.* (2003) exposed *Stylophora pistillata* to two levels of pCO_2 (380 and 750 μatm) and two temperatures (25 and 28°C). There was no significant increase in symbiont photosynthesis with a doubling in pCO_2 at either temperature. At 25°C there was also no significant change in calcification. However, at 28°C they observed a 50% decrease in calcification.
2. Langdon *et al.* (2003) subjected a coral reef community in a mesocosm to pCO_2 of 400 and 660 μatm for one to two months of preconditioning and then measured the rates of net primary production and calcification for seven days. They found no significant change in the rate of net primary production and an 85% decrease in calcification.
3. Langdon and Atkinson (2005) exposed an assemblage of *Porites compressa* and *Montipora capitata* in an outdoor flume to two pCO_2 levels (380–460 and 733–789 μatm), and observed the rates of symbiont net primary production and calcification. At the higher pCO_2 level, they found a 22–26% increase in the rate of net primary production and a 44–80% decrease in calcification, depending on the time of year.

In all but one case a doubling in pCO_2 resulted in a 40–80% decrease in calcification (in the exceptional case there was no significant change in calcification). Such results may be due to competition between zooxanthellae and the host for the same internal pool of dissolved inorganic carbon—a mechanism first suggested to explain the observation that nutrient enrichment stimulates photosynthesis but causes a decrease in calcification (Hoegh-Guldberg and Smith, 1989; Stambler *et al.*, 1991; Marubini and Davies, 1996; Marubini and Atkinson, 1999; Ferrier-Pagés *et al.*, 2000).

Misconception 3. Warmer water temperatures will significantly offset decreases in saturation state

Two consequences of rising atmospheric CO_2 affect the seawater CO_2 system: (1) increasing partial pres-

sure of CO_2 drives more CO_2 into seawater, but (2) the greenhouse effect also warms the ocean, and warmer waters can hold less CO_2. However, the ameliorating effect of warming is small. At constant temperature of 27°C and a typical oceanic A_T of 2300 μmol kg^{-1}, a doubling in pCO_2 results in a 37% decrease in carbonate saturation state. If one includes the effect of a 5°C warming in ocean temperature over the same period (an extreme case) the net decrease in saturation state would be 25%.

Misconception 4. The effect of global warming on calcification will outweigh the effects of decreased saturation state

Records from massive coral colonies in the Western Pacific (Lough and Barnes, 1997, 2000; Bessat and Buigues, 2001) and Caribbean (Carricart-Ganivet, 2004) do not show a decrease in calcification in recent decades as would be expected from increased atmospheric CO_2 concentrations, but rather a statistically significant positive correlation with temperature. This has led some to conclude that, under future ocean temperature and chemistry conditions, the effects of increasing temperature on coral calcification will outweigh the effects of decreasing carbonate saturation state and coral calcification will increase rather than decrease (McNeil *et al.*, 2004). This conclusion ignores three important points (Kleypas *et al.*, 2005). First, the calcification response of corals to temperature almost always follows a Gaussian function rather than a linear function (Coles and Jokiel, 1977; Houck *et al.*, 1977; Jokiel and Coles, 1977; Marshall and Clode, 2004), and will reverse once the optimum temperature is reached (the optimum temperature is often close to ambient summertime temperatures). Second, the temperature increase necessary to outweigh the effects of ocean acidification exceeds the threshold for coral bleaching (1–2°C above average maximum), which will shut down coral calcification rather than enhance it. Indeed, given the recent increase in coral bleaching episodes, further increases in tropical sea surface temperature are considered a major threat to the future of coral reefs (Wilkinson, 2004). Third, the temperature:calcification relationship from massive corals, which are longer-lived and more tolerant of environmental perturbations, may not be representative of the bulk of reef-building species.

Temperature is certainly a major control on metabolism and growth, and the above misconception simply arises from extrapolating the positive benefits of temperature beyond biological thresholds. This highlights the need to study coral calcification response to the combination of rising temperature and declining saturation state within a wide range of coral taxa.

Misconception 5. Carbonate dissolution in coral reef sediments will buffer the overlying seawater

Dissolution of carbonate minerals releases alkalinity and increases the carbonate saturation state of the surrounding water column. Dissolution is a prevalent process in reef environments (see section 3.2.2), but the misconception relates to the extent to which dissolution can bring the system toward pre-industrial conditions. Empirical evidence illustrates that dissolution rates are much slower than calcification rates and do not fully restore the carbonate chemistry of coral reef systems (Gattuso *et al.*, 1995, 1996a; Kawahata *et al.*, 1997; Gattuso *et al.*, 1999b; Kawahata *et al.*, 2000; Suzuki *et al.*, 2003). Total alkalinity and carbonate saturation state of most reef waters primarily reflect the balance between precipitation and dissolution of $CaCO_3$. Total alkalinity and saturation state are both lower in reef waters than in the nearby open ocean, and the magnitude of the difference is proportional to the residence time of water on the reef. The departure from oceanic conditions is small in systems with short residence times, but can be significant in lagoons or on reefs with long residence times (Gattuso *et al.*, 1997; Boucher *et al.*, 1998; Conand *et al.*, 1997; Yates and Halley, 2006a,b), illustrating that rates of dissolution are much slower than rates of calcification.

With increased pCO_2, net calcification rates on coral reefs are likely to decline, partly due to slower calcification rates and partly due to faster dissolution. At some point in time and space, we can expect that some reef systems will shift from net calcification to net dissolution; i.e., shift from being a sink to a source of alkalinity to the surrounding ocean (see Section 3.1).

3.6 Critical Research Needs

Based on the identified knowledge gaps listed above, the St. Petersburg Workshop participants identified critical research needs. Although the following list is not exhaustive, we believe it captures the most pressing research needs for the next 5–10 years.

- Determine the calcification response to increased CO_2 in additional species of coccolithophores, foraminifera, and shelled pteropods, and benthic calcifiers such as corals (including cold-water corals), coralline algae, foraminifera, molluscs, and echinoderms. Where applicable, studies should address calcification within mul-

tiple life stages of organisms. In particular, experiments to quantify the effect of elevated pCO_2 on calcification in two major groups—shelled pteropods and deep-sea scleractinian corals—are considered urgent. These two aragonite-secreting organisms will be the first to experience carbonate saturation states <1 within their current geographical ranges;

- Discriminate the various mechanisms of calcification within calcifying groups through physiological experiments, and thus better understand the cross-taxa range of responses to changing seawater chemistry;
- Continue experimental studies that combine multiple variables affecting calcification in marine organisms: saturation state, light, temperature, and nutrients, and extend the range of calcifying groups tested;
- Combine laboratory experiments with field studies. Analogous to the CO_2 enrichment experiments performed in terrestrial systems, develop and deploy technology for continuous field monitoring and experiments. Focus on multiple oceanic areas, including regions where substantial changes in seawater CO_2 chemistry will occur in the near future (e.g., Southern Ocean), regions where naturally high pCO_2 conditions are found (e.g., Galápagos Islands), and regions that are readily accessible or have on-going, related monitoring programs (e.g., Station Papa, HOTS, BATS, Florida Keys, CREWS stations);
- Characterize the diurnal and seasonal cycles of the carbonate system on coral reefs, including a commitment to long-term monitoring. Focus on collecting information from a variety of ocean settings that cover the important environmental ranges and seawater chemistry conditions, as well as the range of reef settings (e.g., well-mixed open ocean versus lagoonal) and reef zones (e.g., forereef, reef flat, lagoonal);
- In concert with above, monitor in situ calcification and dissolution in planktonic and benthic organisms, with better characterization of the key environmental controls on calcification, and supplement and cross-check present-day measurements with coral skeletal records of calcification and skeletal geochemical proxies (stable isotopes, metals, etc.);
- Incorporate ecological questions into observations and experiments; e.g., How does a change in calcification rate affect the ecology and survivorship of an organism? At the ecosystem scale, what are the ecological differences between communities with and without calcifying species?
- Improve the accounting of coral reef and open ocean carbonate budgets through combined measurements of biogenic $CaCO_3$ production, seawater chemistry, $CaCO_3$ dissolution and accumulation, and, in near-shore environments, bioerosion and off-shelf export of $CaCO_3$.
- Apply biogeochemical and ecological modeling to quantify the mechanisms that contribute to the carbonate system, and to guide future sampling and experimental efforts.
- Develop protocols for the various methodologies used in seawater chemistry and calcification measurements. Establish the pros and cons of each procedure, and, when possible, how each measurement can be related to the others.

The following section summarizes the research techniques and designs to be considered when addressing these research needs.

4. A Guide to Improve Research on Increasing Atmospheric CO_2 on Marine Calcifiers

4.1 Field Monitoring and Surveys

4.1.1 What variables should be monitored?

Precipitation and dissolution of $CaCO_3$ occurs both inorganically and through biological processes. $CaCO_3$ precipitation is driven mainly by organisms, with inorganic cementation contributing a fraction of the total oceanic $CaCO_3$ precipitation. $CaCO_3$ dissolution is primarily an inorganic process, although microbial films, borings, and bioerosion may play a significant role in determining dissolution rates. $CaCO_3$ precipitation/dissolution thus lies along a continuum of biological and inorganic processes, and therefore many variables need to be considered when monitoring a system's calcification response to increased atmospheric pCO_2.

Monitoring the inorganic carbon system requires measuring at least two of the following: pCO_2, DIC, pH, A_T, as well as temperature and salinity. In regions where calcification rates are high and water exchange is low, measurements of the calcium ion may also be required. Calculation of air-sea CO_2 exchange rates also require measurements of atmospheric and oceanic CO_2 concentrations, barometric pressure, and wind speed. Other important physical variables include surface seawater temperature and salinity.

Field monitoring of ecosystems should minimally include calcification rates of key individual organisms, community structure, and, if appropriate, primary production and sedimentary characteristics (mineralogical composition, accumulation rates, and dissolution rates). Calcification rates should include measurements of both extension rates and density. In planktonic systems, the vertical distributions of calcifying organisms should be tracked and related to vertical profiles of the $CaCO_3$ saturation state. When measuring ecological response, it is important to also monitor the response of multiple life stages of organisms, including larval recruitment, age to sexual maturity, and fecundity. Biological measurements of calcification in the field should be closely coupled with measurements of the seawater CO_2 chemistry.

The temporal and spatial scales over which monitoring should be conducted vary widely across environments. The coastal ocean requires high-frequency monitoring because of high spatial and temporal variability (**Figure 4–1**). High-frequency monitoring of the reef waters of Ishigaki, Palau, and South Florida, for example, revealed rapid and large fluctuations (e.g., a diurnal range in pCO_2 an order of magnitude greater than that of adjacent open-ocean waters) that allowed an analysis of how various physical and biological factors affected organic and inorganic carbon cycling in coastal systems (Kayanne *et al.*, 2005; Yates and Halley, 2006b). Monitoring of coastal waters should be augmented with measurements from nearby offshore waters, preferably from a reference station (e.g., time-series station ALOHA as an open-ocean reference for coastal environments of Hawaii, and the BATS station as a reference for those of Bermuda).

4.1.2 Priority environments for future monitoring or research

Organisms/Ecosystems. Priority ecosystems for studying the effects of increased CO_2 on marine calcification include those with high calcification rates or where calcification is an integral part of the ecosystem, and organisms or ecosystems which may be particularly threatened by lowered $CaCO_3$ saturation states. Because calcification is often linked to photosynthesis, studies of the effects of CO_2 on marine calcification have concentrated on photosynthetic organisms, and have thus been confined to the photic zones of the ocean, although many calcifying organisms are not phototrophic.

In neritic regions, the major benthic calcifiers are the reef-forming organisms (corals and calcareous algae), the aragonite secreting algal species of the genus *Halimeda,* benthic foraminifera, bryozoans, molluscs, and echinoderms (**Figure 3–1**). Coral reefs have received the most attention regarding the effects of changing saturation state. Reefs and *Halimeda* bioherms have high calcification rates, a wide distribution in the tropics, and produce the bulk of continen-

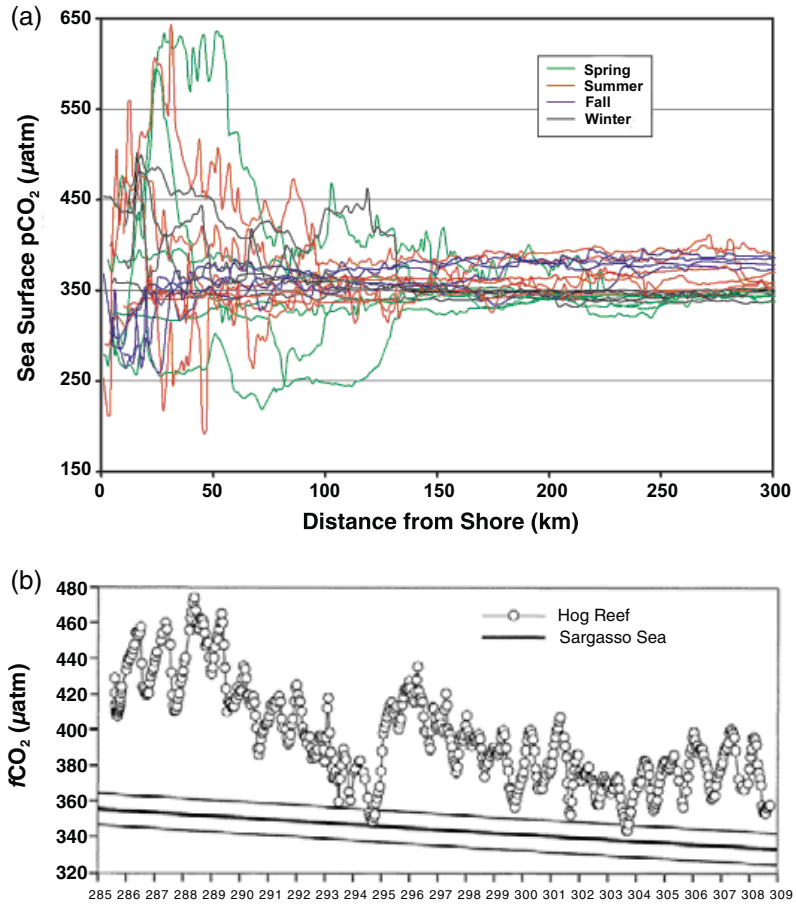


Figure 4–1: pCO_2 variability of surface waters: (a) pCO_2 variability in surface waters across the continental margin of the west coast of the United States, showing the high degree of variability in coastal upwelling regions out to a distance of about 150 km from the coast (courtesy Francisco Chavez; modified from Pennington *et al.*, in press); and (b) Time series of seawater fCO_2 from Hog Reef Flat in Bermuda, and the Sargasso Sea. The curve for the Sargasso Sea reflects the mean seawater fCO_2 observed over 1994–1998 (reprinted from Bates *et al.*, 2001; copyright by the American Society of Limnology and Oceanography, Inc.).

tal shelf $CaCO_3$ production and accumulation (Milliman and Droxler, 1996). Deep-water coral bioherms are another important neritic calcifying ecosystem. These corals are non-photosynthetic, and occur on continental slopes often at depths near the saturation horizon. These bioherms may be particularly vulnerable to shoaling of the saturation horizon (Guinotte *et al.*, 2006).

In the open ocean, the major planktonic calcifiers are coccolithophores, foraminifera, and pteropod molluscs (**Figure 2–2**), and members within each of these groups are considered sensitive to carbonate saturation. Coccolithophorids are calcitic, autotrophic, and are often the most prominent planktonic calcifiers, in part because of their visibility in surface waters during blooms, and because of their estimated importance in global calcium carbonate budgets. Planktonic foraminifera are calcitic and heterotrophic, although many species have photosynthetic symbionts, and are widely distributed latitudinally. Pteropods are aragonitic, heterotrophic, planktonic gastropods widely distributed in the oceans and may be quantitatively important in maintaining the alkalinity flux in several major ocean regions (Betzer *et al.*, 1984; Fabry, 1990). While all of the major planktonic calcifiers most frequently occur in the upper 500 m, baseline data on their present-day vertical distributions and abundances are insufficient to detect possible changes that may result from ocean acidification.

Natural gradients. Natural gradients in carbonate chemistry can affect biological calcification rates, as well as inorganic processes of dissolution and perhaps inorganic cementation (**Table 4.1**). The obvious

gradients in $CaCO_3$ saturation are with latitude and depth (**Figure 4–2**), but there are also gradients associated with major upwelling regions and biological processes (Feely *et al.*, 2004).

Depth gradients in seawater carbonate chemistry occur as a consequence of (1) biological processes that take up carbon, such as photosynthetic organic carbon production and calcium carbonate production, (2) remineralization of those products through respiration and dissolution, and (3) physical processes that mix the surface ocean and increase air-sea CO_2 exchange. The typical profile of carbonate chemistry in the open ocean is where alkalinity increases rapidly with depth (due to the solubility pump), as does dissolved inorganic carbon (due to the organic carbon pump). The distribution of planktonic organisms with depth gradients in carbonate chemistry are essentially unknown, although rates of dissolution of their shells with depth have been investigated (Byrne *et al.*, 1984; Feely *et al.*, 1988). Obvious targets for future monitoring are the depths of the aragonite, calcite, and high-Mg saturation horizon. The depth distribution of carbonate chemistry parameters on coral reefs or other benthic calcifying ecosystems has not been investigated.

Latitudinal gradients in seawater carbonate chemistry in the surface ocean occur primarily in concert with temperature change. Because the surface ocean is so well mixed, processes that affect alkalinity and air-sea CO_2 exchange also affect the rate of CO_2 uptake by the surface ocean, but the effects on latitudinal gradients in carbonate chemistry are secondary to those of ocean temperature and physics (Takahashi *et al.*, 1997).

In a few areas, upwelling processes bring deep CO_2-rich waters to the surface, and this dominates surface carbonate chemistry. The best example of this is the equatorial upwelling region in the eastern Pacific (Feely *et al.*, 2002). pCO_2 in the Galápagos Islands often exceeds 500 μatm (Millero *et al.*, 1998; Sakamoto *et al.*, 1998), with high spatial and temporal variability. Coral reefs in the Galápagos are considered marginal in terms of their development, probably owing to many factors such as cooler temperature and low diversity, but the role of lower saturation state of the waters should also be considered.

Natural gradients in carbonate chemistry also occur because of calcification itself, which draws down the alkalinity. Broecker and Takahashi (1966) documented such a gradient on the Bahama Banks, and a recent study (Kawahata *et al.*, 2000) documented a similar gradient between open ocean waters and those of the Great Barrier Reef lagoon.

Some information about possible future changes can be gained by examining how calcium carbonate production varies across these natural gradients. At higher latitudes, for example, corals and other reef-building organisms exist and even comprise coral reef communities, but their carbonate accumulation (i.e., the balance between $CaCO_3$ production and its removal) is not sufficient to build reefs. Carbonate production also decreases dramatically with depth, presumably because of light limitations, as the main $CaCO_3$-producing organisms are photosynthetic or have photosynthetic endosymbionts.

The main disadvantage of using natural gradients to examine the control of carbonate saturation state on $CaCO_3$ production, within both the planktonic and benthic environments, is the difficulty of finding regions where carbonate chemistry does not co-vary with other parameters that affect calcification rates (e.g., temperature, irradiance, nutrients). Temperature, for example, decreases with depth, latitude, and in upwelling regions. Irradiance also decreases with latitude and depth, but less so in upwelling regions. Where gradients are due to calcification, such as in coral reef regions, the carbonate chemistry gradient reflects an alkalinity change as well as changes in DIC, and thus does not exactly mimic the carbonate chemistry changes expected from increased pCO_2.

Practical considerations. Because biological processes dominate marine calcification, environmental monitoring should include not only carbonate chemistry parameters, but also parameters that affect biological processes. These include oceanographic parameters such as temperature, irradiance, hydrodynamics, and nutrients; and atmospheric parameters such as surface winds and pressure. Carbonate chemistry parameters are routinely measured as part of the International Repeat Hydrography and Carbon Program (Feely *et al.*, 2005), and at a handful of open ocean time-series stations (**Table 4.2**). A few of the time-series stations have monitored seawater chemistry for more than a decade.

Several efforts are currently underway to expand these observations in the coastal zone and in specific ecosystems. For example, the implementation strategy for the Ocean Carbon and Climate Change report (Doney *et al.*, 2004) calls for expanding CO_2 system measurements at existing time-series stations, and augmenting additional time-series sites and moored buoys with automated CO_2 system measurements. Also, NOAA is establishing monitoring stations in several tropical coral reef locations as part of the Integrated Coral Observing Network/Coral Reef Early Warning System (ICON/CREWS; **Figure 4–3**). Existing ICON/CREWS stations collect both meteorological and oceanographic data, and could easily be augmented with autonomous carbon system instrumentation.

Table 4.1: Major processes that create natural gradients in seawater carbonate chemistry.

Process	Effects on carbonate parameters	Notes	Gradients
Physical			
atmospheric pCO_2	controls air-sea equilibrium CO_2	equilibrium generally achieved within 1 year	minor; CO_2 is well mixed in the atmosphere
temperature	determines CO_2 solubility	solubility decreases with increasing temperature	latitude and depth
pressure	determines CO_2 solubility	solubility increases with increasing pressure	
upwelling	delivers CO_2-rich waters to surface	also cold and nutrient-rich	upwelling gradients
$CaCO_3$ dissolution	removes CO_2 releases alkalinity	through reaction $CaCO_3 + CO_2 + H_2O \rightarrow 2HCO_3^- + Ca^{2+}$	depth, and other carbonate chemistry gradients
Biological			
photosynthesis	removes CO_2	through formation of organic matter	depth, and other irradiance gradients
respiration	releases CO_2	through remineralization of organic matter	biological—mostly microbial
calcification	decreases alkalinity increases CO_2	through reaction $2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + H_2O$	biological—across calcifying zones

4.1.3 Skeletal records and isotopic/ elemental analyses

Calcification records from corals and other calcifying organisms. Skeletal records provide climatological and oceanographic histories as well as information about the response of the organism to environmental change (e.g., changes in calcification rates). A wealth of potential information on coral calcification exists within the large inventory of coral cores collected in recent decades. Such measurements tend to be confined to a few massive species of corals, such as *Porites*, *Montastrea*, and *Diploria*. Branching corals, by nature of their growth form, do not offer a clear yearly record of skeletal growth. Some calcitic sponges also record environmental information in their skeletons (Böhm *et al.*, 2002).

Annual density bands in massive corals allow retrospective monitoring of coral growth rates over several centuries and can provide information about the response of such corals to environmental stress and change. The most easily measured growth parameter in coral skeletons is annual linear extension rate, which can be measured from X-radiographs of coral slices, but deriving annual calcification rates also requires measuring skeletal density (**Figure 4–4**). This can be measured using gamma densitometry (Chalker and Barnes, 1990) and optically from X-radiographs (Helmle *et al.*, 2002). Calcification rate is thus calculated as the product of skeletal extension and skeletal density. It is probable that changes in coral calcification rate will be reflected as changes in density in some species, and in linear extension in others. In some species, such as the commonly used Indo-Pacific coral, *Porites*, variations in annual calcification rate are dominated by changes in linear extension rate and the latter (most easily measured parameter) can be used as a proxy for calcification rate (Lough and Barnes, 2000).

In recent years, most studies using massive corals have focused on geochemical records contained within the coral skeletons rather than analyses of coral growth rates. Although extracting geochemical proxies for various climatic and environmental parameters is important, there is a large number of massive coral cores already collected that could be exploited to assess possible changes in coral growth due to changing carbonate chemistry (see coral records data base at NOAA Paleoclimatology Data Center, `http://www.ncdc.noaa.gov/paleo/index.html`). Such existing coral material could be used for retrospective coral growth analyses, including annual density, extension, and calcification. These would provide long-term information on changes in coral growth rates, important baselines for assessing future changes, and would also allow spatial comparisons between regions. Coral calcification rates vary with average water temperature, and in several massive species have so far responded more to rising water temperature than to changes

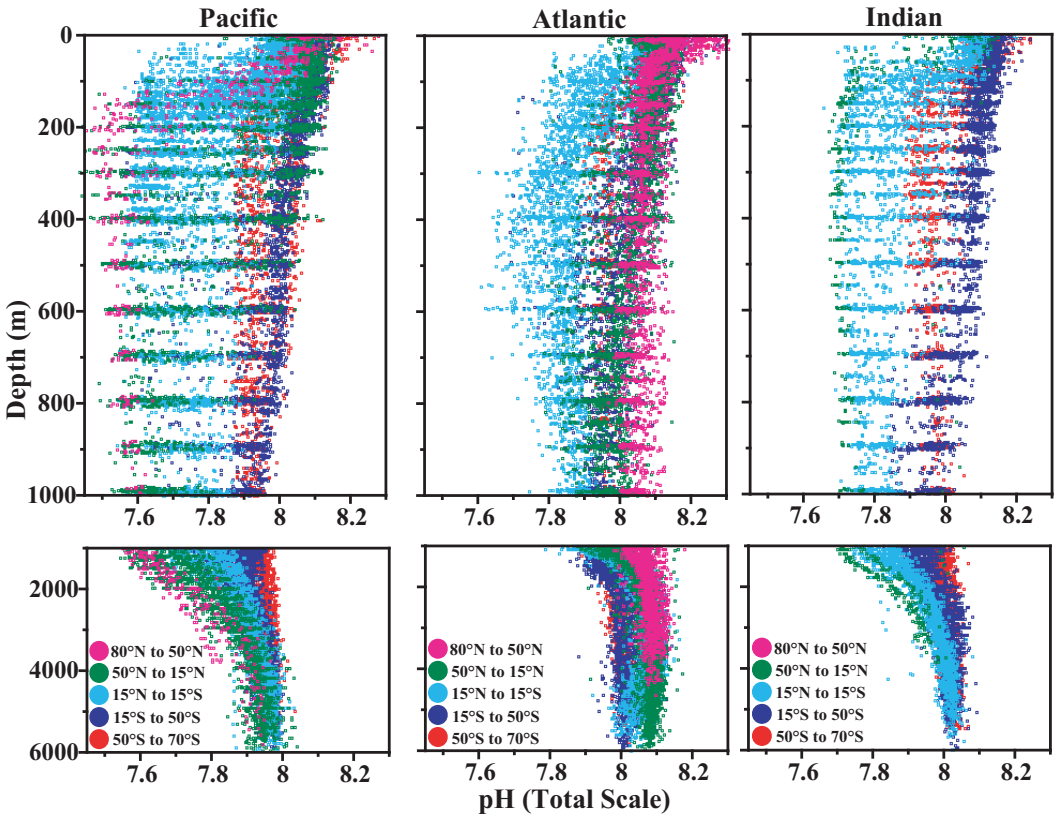


Figure 4–2: Natural gradients in ocean pH (total scale) across the Pacific, Atlantic, and Indian Ocean basins, showing the natural variation with both depth and latitude, for the period 1990–1998. Data from GLODAP (`http://cdiac.esd.ornl.gov/oceans/glodap/Glodap_home.htm`); after Feely *et al.* (submitted).

in ocean chemistry (Lough and Barnes, 2000; Bessat and Buigues, 2001). Observed and modeled future changes in water temperature and ocean chemistry would allow targeting of particular regions where, for example, either parameter is more or less important. Coral growth rates could then be analyzed either from the existing international archive or through collection of new coral cores. Future efforts to document calcification histories should also include both non-massive coral species and other major calcifiers.

Stable isotopes and other environmental proxies. The use of stable isotopes and trace elements from $CaCO_3$ skeletal material has been common in environmental reconstructions, particularly of temperature and salinity, and more recently of carbonate chemistry (**Figure 4–5**). Several geochemical tracers have been used to reconstruct past environmental conditions. For example, massive dissolution events that occurred in the past have been examined using both isotopes ($\delta^{18}O$, $\delta^{13}C$, $\delta^{11}B$) and trace elements (U/Ca, Sr/Ca, Mg/Ca) to describe the environmental setting and to reveal mechanisms for the dissolution events. $\delta^{13}C$ of corals and sponges has also been developed as a proxy for the penetration of anthropogenic pCO_2 in the ocean (Quinn *et al.*, 1998; Böhm *et al.*, 2002). In addition, the $\delta^{13}C$ of skeletal material may reflect differences in physical mixing in environments, since pCO_2 in closed systems tends to show greater changes than in open-ocean environments (P. Swart, personal communication; **Figure 4–6**).

Skeletal chemistry can also record ocean carbonate chemistry. For example, the Zn/Ca ratio in benthic forams appears to covary with the carbonate ion concentration of bottom waters (Marchitto *et al.*, 2000; Marchitto *et al.*, 2005). More widely used as a proxy for ocean pH is the boron isotope ratio (Sanyal *et al.*, 1995; Sanyal *et al.*, 2001). A recent analysis raises concerns about large uncertainties in the technique (Pagani *et al.*, 2005); however, boron isotope fractionation in corals has been shown to be strongly dominated by pH control (Reynaud *et al.*, 2004), and a recent analysis of boron isotopes in a massive coral from the western Coral Sea provided multi-century, annually resolved reconstructions of pH (Pelejero *et al.*, 2005) (**Figure 4–5b**). The signal appeared to reflect variations in ocean circulation and flushing rate

Table 4.2: Locations where carbonate chemistry parameters are currently or have been routinely measured.

Location	Ocean	Lat.	Lon.	Time Period	Frequency (per year)
Atlantic Ocean					
Ocean Weather Station M	Norwegian Sea	66°N	2°E	1992–present	4
Irminger Sea	Irminger Sea	60°N	36°W	1990–present	limited
Ocean Weather Station Bravo	Labrador Sea	57°N	53°W	1980s–present	1
BATS (Bermuda-Atlantic Time-series)	NW Atlantic	31°50′N	64°10′W	1988–present	12
Hydrostation S	N Pacific	31°50′N	64°10′W	1983–present	12
ESTOC (European Station for Time-series in the Ocean Canary Islands)	NE Atlantic	29°N	16°W	1994–present	12
CARIACO (CArbon Retention In A Colored Ocean)	Atlantic	10°30′N	64°40′W	1995–present	intermittent
DYFAMED (Dynamics of Atmospheric Fluxes in the Mediterranean sea)	Mediterranean	43°25′N	7°52′E	1995–1997 2003–present	intermittent 4
Pacific Ocean					
OSP/Line P (Ocean Station PAPA)	Gulf of Alaska	50°N	145°W	1970s–present	4
KNOT (Kyodo N Pacific Ocean Time-series)	N Pacific	44°N	155°E	1999–2002	12
HOT (Hawaii Ocean Time-series)	Pacific	22°45′N	158°00′W	1988–present	12
TAO/TRITON mooring (pCO_2 only)	Tropical Pacific	2°S	170°W	1997–present	continuous
"	"	0°S	170°W	2005–present	continuous
"	"	0°	155°W	1997–present	continuous
"	"	0°	140°W	2003–present	continuous
"	"	0°	125°W	2003–present	continuous
Kuroshio Extension Observatory (pCO_2 only)	N Pacific	32°18′N	144°30′E	2006–present	continuous
Kaneohe Bay, Oahu Hawaii	N Pacific	21°24′N	157°W	2005–present	continuous
Monterey Bay, California	N Pacific	36°48′N	122°W	1989–present	12
Santa Monica Bay, California	Pacific	33°56′N	118∘43′W	2001–present	continuous
Indian/Southern Oceans					
KERFIX	Indian Ocean	50°S	68°E	1990–1995	intermittent

related to natural, approximately 50-year climatic oscillations. The variations of approximately 0.3 pH units equate to a variation in Ω_{arag} of approximately 3–4.5, but had no apparent impact on coral extension or calcification rates. The authors concluded that this *Porites* coral was well adapted to maintain its calcification over the natural range of variability. Application of this technique to *Porites* from around the Indo-Pacific basin and to other corals elsewhere should provide an exciting source of data on the response of corals to a wide range of natural saturation states.

An important need in correlating skeletal records with environmental change requires a combination of experimental and sclerochronological studies. Both calcification and isotopic records from free-living corals should be compared with those from massive corals used in experimental studies to understand how well the techniques capture the relationship, for example, between pH and calcification.

4.1.4 Remote sensing

Satellite observations can be used to estimate the distribution of particulate inorganic carbon (PIC, which is primarily composed of $CaCO_3$), in the global oceans (**Figure 4–7a**). This includes calcite biomass of coccolithophores (in the upper 20 m of the ocean), suspended PIC due to phenomena such as whitings and resuspended PIC in the coastal ocean, and submerged accretions in shallow tropical coral reefs. Satellite and airborne remote sensing tools, once calibrated against field measurements of PIC, can be used to investigate long-term changes in abundance and lateral ex-

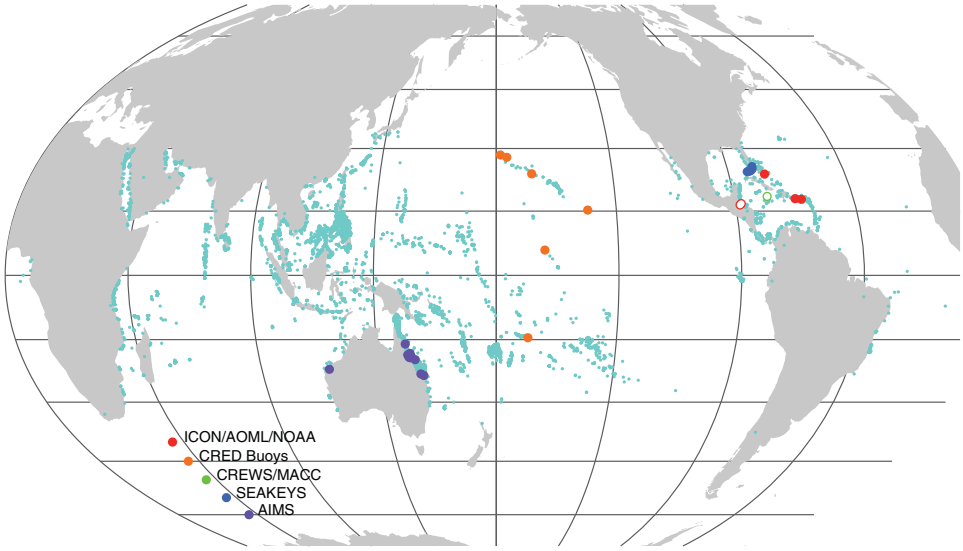


Figure 4–3: Existing and proposed stations within NOAA's Coral Reef Conservation Program; ICON = Integrated Coral Observing Network; AOML = Atlantic Oceanographic and Meteorological Laboratory (NOAA); CREWS = Coral Reef Early Warning System; CRED = Coral Reef Ecosystem Division (NOAA); MACC = Mainstreaming Adaptation to Climate Change; AIMS = Australian Institute of Marine Science. Solid symbols are existing sites; open symbols are proposed sites (data courtesy Eric Stabenau and Jim Hendee, NOAA/AOML).

port. New instruments that will become available in the next 10 years will provide better spatial and temporal resolution, and development and application of these data should prioritize quantifying $CaCO_3$ production in both the open and coastal oceans.

Remote sensing of suspended calcite. This is a relatively new addition to the suite of space-based measurements available to oceanographers. NASA has kept ocean color sensors in space beginning with the Coastal Zone Color Scanner (CZCS) mission from 1978–1986, and continuing with the Sea Wide Field of view Sensor (SeaWiFS; 1997–2004), and the Moderate resolution Imaging Spectrometer (MODIS; 1999–present) aboard the Terra (1999–present) and Aqua (2002–present) platforms. Originally considered as "contamination" in the ocean color spectrum, suspended PIC (mainly calcite from coccolithophores and other micron-sized particles, rather than forams and pteropods; Balch *et al.*, 1996) can now be quantified through 2-band and 3-band PIC algorithms of remotely sensed water-leaving irradiances (**Box 4**). These techniques are mainly limited to coccolithophorid blooms, and can only estimate $CaCO_3$ standing stock rather than $CaCO_3$ production. However, these advances provide a valuable baseline for tracking changes in the upper few meters of the water column, and for quantifying $CaCO_3$ production in the future.

Remote sensing of $CaCO_3$ production in benthic communities. Previous studies based on very few in situ measurements demonstrated that shallow tropical coral reefs may be both sources and sinks of carbon depending on the patchiness of the community components (corals, algae, sediments), and on the condition of the reef (Kayanne *et al.*, 2005). Further, short-term perturbations (rainfall, river discharge) may invalidate the assumption that carbonate equilibrium of seawater above reefs is principally controlled by respiration, photosynthesis, and solution and calcification of the reef. Assessing these conditions requires tools that address both large-scale as well as local forcings and changes in the reef over both short and longer time periods. Satellite observations have the potential to address these questions, and also obtain reliable estimates of the total extent of calcification and associated biogeochemistry by:

1. Better defining spatial constraints of locations and surface area of shallow tropical reef communities;
2. Assessing the diversity of habitats associated with coral reefs around the world, and quantifying the carbonate content and calcification associated with each;
3. Assessing disturbance on reefs, from regional-scale climatic/environmental factors to local-scale anthropogenic and natural phenomena; and assessing the resistance and resilience of coral communities to perturbation;

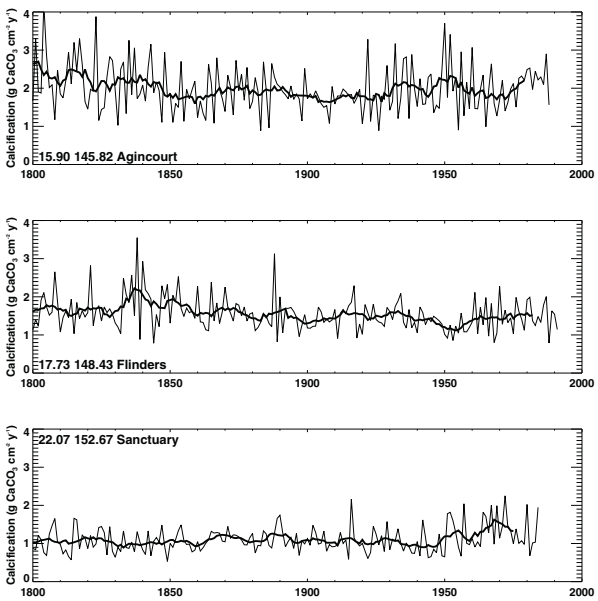


Figure 4–4: Calcification records from massive *Porites* corals of several outer reefs of the Great Barrier Reef. The thin line indicates raw data; thick line is a running 10-year average; data obtained from Lough and Barnes (2000; `http: // coris.noaa.gov / metadata / records / html/ paleoclimatology_masthead_2001.html`). Calcification records reflect decrease in calcification with increasing latitude, as well as very different calcification trends over the last century.

4. Detecting change in calcification rates and other biogeochemical impacts on communities and the water column at local, regional, and global scales.

A variety of strategies can be used to address these questions. One strategy would be to map global coral reef communities using high-resolution LANDSAT 7 ETM+, IKONOS, and other high spatial resolution satellite images. A basic global coral reef LANDSAT 7 ETM+ dataset has been assembled under NASA's Millennium Coral Reef Mapping Project (**Figure 4–7b**). Such high-resolution imagery, if complemented with time series of specific oceanographic environmental variables around selected reefs (e.g., temperature, sea-surface height, rainfall, wind speed and direction, phytoplankton pigment, colored dissolved organic matter and suspended solid concentrations, photosynthetically active radiation, cloud cover), allows assessment of the effects of large-scale processes, from short-term weather events to long-term climate forcing, that may cause stress and/or affect coral reef $CaCO_3$ budgets.

A number of representative reefs should be selected where in situ air-sea CO_2 fluxes are to be measured at least seasonally. Pairing these measurements with high-resolution satellite images will enable large-scale integration and scaling-up of metabolic rate estimates (**Box 5**), rates of export of suspended sediment plumes from shallow water to deep areas, and biogeochemical impacts on the overlying water column and vice versa.

4.2 Experimental Approaches

Testing the response of calcifying organisms to increased CO_2 concentrations has primarily been conducted under controlled, laboratory conditions. Most of these experiments have also been conducted over short periods (days to weeks), and otherwise have not been designed to detect adaptation or acclimation. Given the scarcity of data on many marine organisms, workshop participants expressed a real need to continue laboratory-based experiments, and to establish guidelines for designing such experiments. Such guidelines should include recommendations and standards for:

1. acclimatization periods for organisms;
2. length of experiments;
3. methods for manipulating carbonate chemistry;
4. ranges for carbonate chemistry manipulations; and
5. measuring and reporting of seawater chemistry and calcification rates.

For example, experimental manipulations should cover the natural range of atmospheric CO_2 conditions between the minima of past glacial periods through the values predicted from different emissions scenarios and ocean models (e.g., 180–2000 ppmv; Caldeira and Wickett, 2003), while ensuring that the other carbonate chemistry variables are maintained within the associated natural ranges.

Experimental approaches to advance our understanding of the future of $CaCO_3$-secreting organisms requires a suite of experimental designs spanning a range of space and timescales (**Table 4.3**). These and other approaches are roughly outlined below based on whether they are generally laboratory-based, microcosm/mesocosm-based, or field-based.

4.2.1 Laboratory experiments

Most research on calcification of marine calcifiers to increased CO_2 has been laboratory based. Additional laboratory work is necessary to expand our knowledge of calcification response across the major planktonic calcifying groups (corals, benthic calcifying algae, coccolithophorids, foraminifera, pteropods,

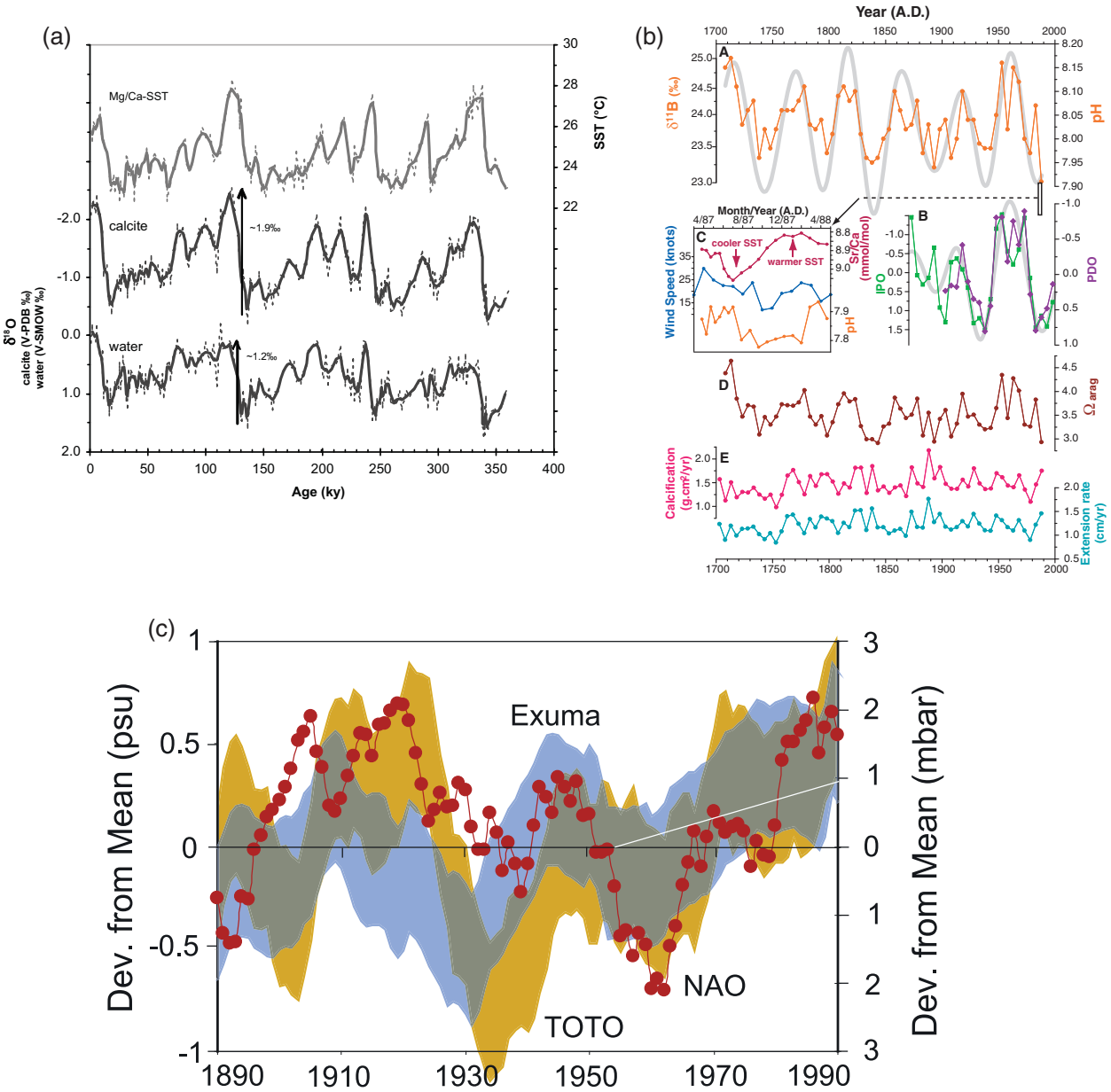


Figure 4–5: Environmental records from calcifying organisms: (a) A 350-ky paleo-SST record from deep-sea sediments at Cocos Ridge based on δ^{18}O isotope and Mg/Ca ratios of the planktonic foram *Globigerinoides ruber*; dashed lines are measured and calculated data while heavy lines are filtered to remove higher frequency components (reprinted from Lea *et al.*, 2002, with permission from Elsevier); (b) A 300-y reconstruction of surface-ocean pH at Flinders Reef, Australia, based on boron isotope (δ^{11}B) data retrieved from a 300-y-old *Porites* coral. Gray line in top figure is the Interdecadal Pacific Oscillation (IPO). Also shown are aragonite saturation state (Ω_{arag}) calculated from the boron isotope-derived pH and assuming constant alkalinity, and the measured extension and calcification rates of the corals (reprinted from Pelejero *et al.*, 2005, copyright AAAS). (c) A 100-y paleo-salinity record for the North Atlantic, based on a combination of Sr/Ca and δ^{18}O isotope from the aragonitic sclerosponge *Ceratoporella nicholsoni* (reprinted from Rosenheim *et al.*, 2005 with permission from *Geophys. Res. Lett.*).

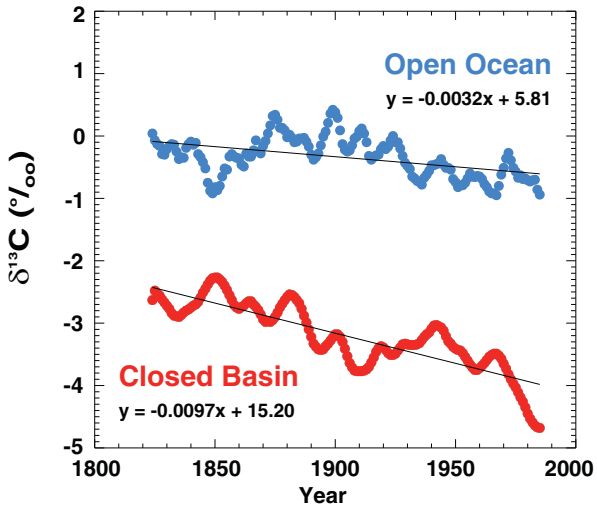


Figure 4–6: δ^{13}C records from South Florida coral skeletons, one from a well-mixed open ocean setting, and the other from a closed basin with restricted circulation. The closed system coral shows changes in δ^{13}C that is 5x greater than that of the open system (figure courtesy of Peter Swart, University of Miami).

echinoderms), and determine the various mechanisms of calcification. Priority should be given to molecular and physiological studies of species within these major groups to determine:

1. transport mechanisms of ions to the site of calcification;
2. efficiency of the proton pump;
3. pH at the site of calcification;
4. how the above are affected by changes in pH and carbonate system parameters of seawater; and
5. the interaction of carbonate chemistry with other environmental parameters, such as temperature, nutrient concentrations, and light.

Laboratory studies should continue to investigate both the photosynthesis-respiration and calcification-dissolution responses of calcifiers to combinations of saturation state, temperature, light, and nutrients. Field monitoring should be used to guide these studies; e.g., using organisms that show natural variations in calcification rates between different geographic regions.

Genomic sequencing of key calcifying organisms may lead to the identification of genes involved in calcification and how they are regulated by environmental parameters such as pCO_2, temperature, light, and nutrients. Since 2004, the National Human Genome Research Institute of the National Institutes of Health has been considering proposals to sequence a coral genome, and solicited recommendations of which species to use. Most coral researchers prefer *Porites lobata* as the likely candidate, because it is widespread and well researched, but other well-studied "lab rat" species have also been recommended (e.g., species of *Acropora*, *Montastrea*, and *Pocillopora*). Among planktonic calcifiers, the mitochondrial genome of *E. huxleyi* was the first to be sequenced (Sanchez Puerta *et al.*, 2004) and additional genomic sequencing is being conducted through the Department of Energy's Microbial Genomics Program (`http://www.jgi.doe.gov/sequencing/why/microbesseq.html`). Because of the genetic diversity and the possibility of pseudo-cryptic speciation in coccolithophores and foraminifera (De Vargas *et al.*, 1999), markers need to be developed for different genotypes, so that changes in dominance due to competition and/or adaptation can be tracked during experiments.

Cultured strains of coccolithophores may have low genetic diversity, and experiments with such cultures can lead to biased results. Thus, there is a need to broaden the genetic diversity of culture stocks. Some cultured strains of calcifiers actually lose their ability to calcify (cf. Paasche, 2001), but it has not been determined whether this is a laboratory artifact or a natural adaptation that occurs in the field.

Finally, there is a need to commit to long-term experiments (>1 year), for the major calcifying taxa, and particularly benthic species that require a year to form a complete skeletal band. Studies to determine the calcification response of deep-water corals (non-symbiont bearing corals that form deep-water reefs and support important fisheries) to increased CO_2 are also recommended.

4.2.2 Aquaria, flumes, microcosms, and mesocosms

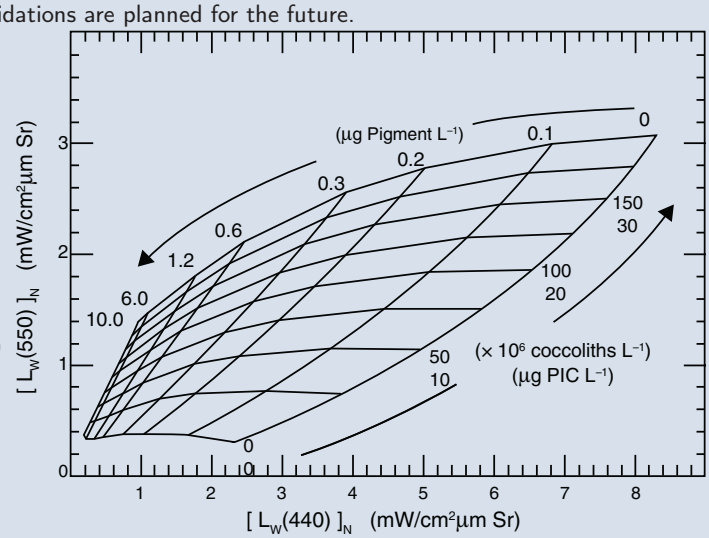
Microcosms are small, aquarium-sized (<1 m^3) experimental systems that allow species assemblages and environmental conditions to be controlled. Mesocosms are larger (>1 m^3) with less control on the ecosystems and environmental conditions. Mesocosms range from very large aquaria, to corrals and bags, to natural enclosures with known dimensions, physics, and chemistry. In general, the larger the system, the greater its complexity and the difficulty to control it; for example, many mesocosm experiments occur under natural lighting and temperature conditions.

Most physiological studies of planktonic calcifiers have been conducted on single species in aquaria or physiological chambers with tightly controlled envi-

Box 4—Recent Advances in Remote Sensing Techniques to Measure Suspended Calcite

Determination of suspended calcite from satellite imagery has been performed with algorithms that rely on either two remotely sensed reflectances or three. The 2-band PIC algorithm relies on absolute remote-sensing reflectance of the 440 nm and 550 nm wavelengths (not ratios). The normalized water-leaving radiance (L_W) is related to the absorption and scattering properties of the biogenic components of the water, phytoplankton, and their associated detritus (Gordon *et al.*, 1988). Balch *et al.* (1991) showed that the backscattering coefficient at 436 and 546 nm of detached coccoliths could be approximated along with the wavelength dependence of calcite backscattering. The 2-band PIC algorithm iteratively solves for both chlorophyll (Chl) and calcite concentrations (C_{CC}) using a standard ratio algorithm as well as the absolute water-leaving irradiances, but is sensitive to chlorophyll concentration (sensitivity of radiances to C_{CC} decreases by ~2x from high to low Chl; see figure below). The 2-band algorithm produces (1) coccolith concentration (assumed to be *Emiliania huxleyi* coccoliths), (2) equivalent PIC concentration, and (3) chlorophyll concentration. The conversion of coccolith concentration to suspended PIC is based on the carbon content in coccoliths, 0.2 pg PIC coccolith^{-1} (Balch *et al.*, 1991; Fernandez *et al.*, 1993; Balch *et al.*, 1999); however, PIC per coccolith can vary with environmental conditions (Paasche *et al.*, 1996; Paasche, 1999), and represents a potential source of error.

A 3-band calcite algorithm (670, 765, and 865 nm) has been devised that reduces errors associated with chlorophyll and CDOM (chromophoric dissolved organic matter) (Gordon *et al.*, 2001; Balch *et al.*, 2005). SeaWiFS trials of this algorithm in dense coccolithophore blooms show promise, and without contaminating effects of chlorophyll and CDOM. Ongoing validation activities for both the 2-band and 3-band algorithms are demonstrating that the two algorithms produce similar results, and further validations are planned for the future.



$[L_W(550)]_N$ as a function of $[L_W(440)]_N$ for various combinations of chlorophyll and C_{CC} (coccolith concentration). The less sloped lines are lines of constant C_{CC} ranging from 0 (bottom) to 200 × 10^9 coccoliths m^{-3} (top) in steps of 25 × 10^9 coccoliths m^{-3}. The more sloped lines are lines of constant chlorophyll. The chlorophyll concentrations are 0.03, 0.1, 0.2, 0.3, 0.6, 1, 2, and 6 mg m^{-3} from right to left (see isopleth markings). From Balch *et al.* (2005).

ronmental conditions. Investigations of the collective response of planktonic calcifying communities to increases in pCO_2 require microcosm or mesocosm experiments; for example, the mesocosm "bag" experiments on induced *E. huxleyi* blooms (**Figure 4–8**) (Delille *et al.*, 2005) could measure not only primary production and calcification, but also the vertical fluxes of organic and inorganic carbon in the water column. Other species may be well suited for mesocosm studies similar to those on *E. huxleyi*. Pteropods may be good candidates, as they can be collected and placed in mesocosm bags, and have long life cycles for extended study. Foraminifera are thought to be poor candidates for mesososms because they normally occur in low densities, and the environmental conditions to induce population explosions are poorly known.

Studies of the calcification response of benthic calcifiers have mostly been measured with individual species in aquaria or chambers, but a few studies have included microcosm studies of communities dominated by corals (Leclercq *et al.*, 2000, 2002; Reynaud *et al.*, 2003; Yates and Halley, 2003), mesocosms dominated by corals and/or coralline algae (Langdon *et al.*, 2000; Yates and Halley, 2003) and coral-lined flumes (Langdon and Atkinson, 2005) (**Figure 4–9**). Usually the experiments are carried out under controlled conditions in the laboratory, but some have been conducted in situ using microcosm-size chambers (e.g., Dodge *et al.*, 1984; Gattuso *et al.*, 1993a)

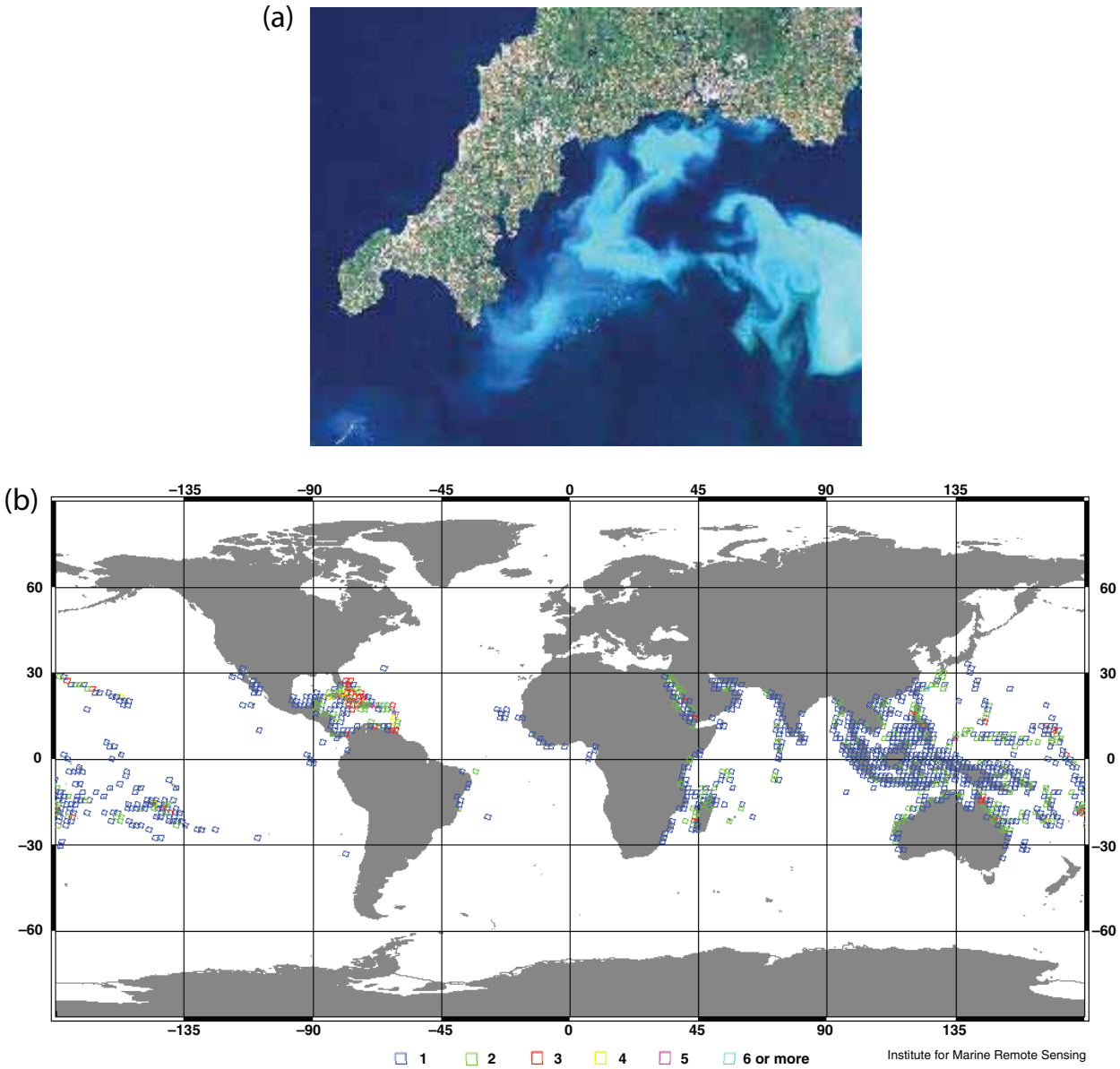


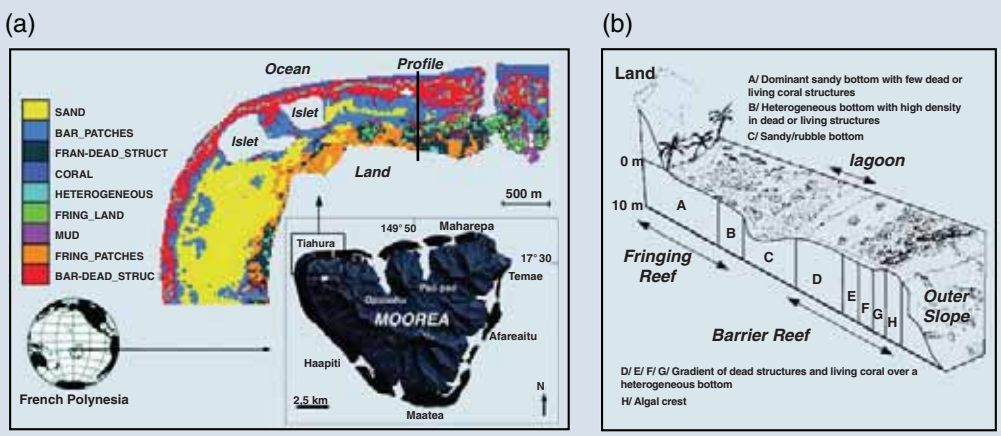
Figure 4–7: Remote sensing of marine calcium carbonate. (a) Remotely sensed image of a coccolithophorid bloom (image courtesy of Steve Groom and Andrew Wilson, Plymouth Marine Laboratory). (b) Location of shallow tropical coral reefs. Numbers of images in the LANDSAT-7 ETM+ holdings of the Millennium Coral Reef Mapping Project are shown as squares of different colors. Each square represents a LANDSAT-7 ETM+ scene. From University of South Florida, France's Institut de Recherche pour le Développement, and NASA's Johnson Space Center and the Goddard Space Flight Center (image courtesy of Frank-Muller Karger; see `http://imars.usf.edu/corals/index.html` and `http://eol.jsc.nasa.gov/reefs/`).

or enclosures such as the SHARQ (Submerged Habitat for Analyzing Reef Quality) chamber system developed by the USGS (Yates and Halley, 2003). Besides reef-building corals and coralline algae, other critical groups of benthic calcifiers that should be investigated include major carbonate producers such as *Halimeda*, and key ecosystem components such as benthic forams and deep-water corals.

All of these laboratory and in-situ approaches are overlapping in scale, and many of the pressing research questions identified in Section 3 will be best answered through multiple approaches. Scaling is an important concern when designing these systems, particularly when considering the timescales over which organisms can acclimatize or adapt to new conditions. Most planktonic calcifiers are microscopic and have generation times of days to

Box 5—Remote Sensing Applications to Coral Reef Production and Calcification

Remote sensing can be used to scale up coral reef production and calcification measurements to reef scales. Below is a classification of Moorea Island (French Polynesia) reefs (a and b) produced using high-resolution remote sensing data (Andréfouët and Payri, 2001). The main zonation patterns of the reefs are clearly visible, showing large sedimentary areas of low productivity (yellow), coral-dominated regions (blue), etc. Profiles of gross production and calcification are also shown along the profile plotted over the map (the corresponding reef is stylized in the upper-right panel). Excess production (gross production minus respiration) for the first full-resolution profile (i) is slightly positive for the barrier reef. Profiles are averaged at 100 and 300 m resolutions (h, f), and for the entire reef width (d). The spatial variability of metabolism is still distinct at 300 m resolution, which is easily accessible by LANDSAT or IKONOS imagery. At the island scale (over 35 km^2 of coral reef environment) metabolic performances were estimated for gross production (93,560 10^3 kg C y^{-1}), excess production (10,017 10^3 kg C y^{-1}), and calcification (165,348 10^3 kg $CaCO_3$ y^{-1}) (figures reprinted from Andréfouët and Payri, 2001, with kind permission from Springer Science and Business Media).



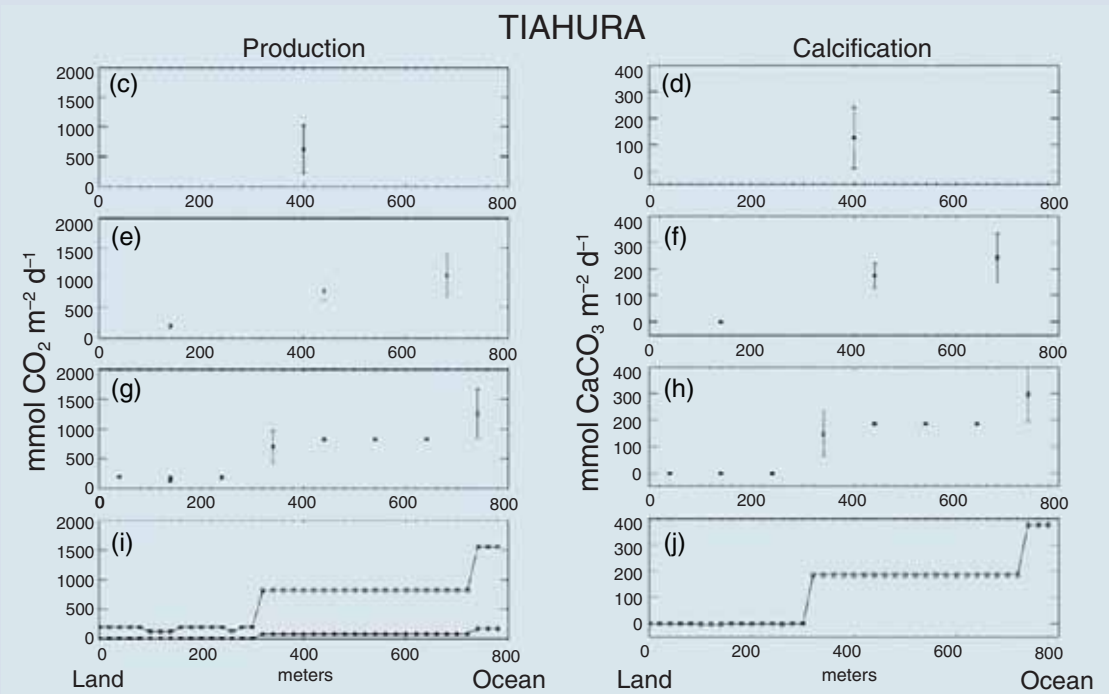


Table 4.3: What will it take to answer the pressing questions? Major research questions regarding the response of marine calcifiers to increased atmospheric CO_2, and the primary types of experiments and experimental settings necessary to address those questions.

Calcification Response	Types of Experiments	Experimental Settings
Organisms		
Determine the relationship between photosynthesis and calcification.	Physiological Biochemical	Laboratory manipulations
Discriminate mechanisms of calcification within calcifying groups; identify cross-taxa range of responses to changing seawater chemistry.	Physiological Biochemical	Laboratory manipulations
Measure response of other taxa and other life stages to elevated pCO_2.	Physiological Skeletal records	Laboratory manipulations Field monitoring Field manipulations
Determine interactive effects of multiple variables that affect calcification in organisms: saturation state, light, temperature, nutrients.	Physiological Skeletal records	Laboratory manipulations Mesocosm manipulations Field monitoring Modeling
Test for adaptation: Several years may be necessary to determine whether calcifying taxa can adapt or acclimate to different carbonate chemistry conditions.	Physiological monitoring Skeletal records	Laboratory manipulations Field manipulations and monitoring
Ecosystems		
Determine how calcification in organisms affects: (1) species interactions, (2) food webs, (3) regional productivity, (4) carbon and nutrient cycling through the ecosystem, and (5) ecosystem services.	Ecosystem monitoring Ecosystem manipulations	Mesocosm manipulations Field monitoring and manipulations Ecosystem modeling
Determine role of inorganic cementation in resiliency of coral skeletons and reef structures and how inorganic cementation will be affected by lowered saturation state.	Geochemical Documentation of cementation patterns versus environment	Laboratory studies
Determine how bioerosion rates will be affected by reduced saturation state.	Bioerosion studies Ecosystem manipulations	Field surveys Field manipulations
Dissolution and Carbonate Budgets		
Quantify dissolution rates and chemical mass balances in pelagic systems, and characterize factors that control them.	Biogeochemical	Laboratory Field
Quantify $CaCO_3$ budgets of coral reefs, *Halimeda* bioherms, and temperate and cool-water benthic carbonate-producing systems.	Sedimentological and geochemical surveys and monitoring	Field Modeling
Commit to long-term monitoring for detecting response of the seawater carbonate system to continued increases in CO_2, across a variety of planktonic and benthic settings.	Geochemical	Field Measurements
Determine role of excess $CaCO_3$ production ("reef building") in supporting: (1) vertical accretion, (2) spatial complexity that supports diversity, (3) depth gradient that also supports diversity, and (4) structural influence on hydrodynamic regime.	Combined ecological, environmental and geological studies	Field measurements and manipulations Modeling
Determine the dissolution = calcification threshold in benthic calcifying communities, and how it varies under different environmental conditions.	Geochemical Seawater chemistry monitoring	Field measurements and manipulations Modeling

(a)

(b)

Figure 4–8: Experimental setup for measuring *E. huxleyi* calcification under different environmental conditions. (a) Laboratory experiments with a "chemostat" (Sciandra *et al.*, 2003) (photo courtesy of J.-P. Gattuso, CNRS). (b) Mesocosms in Norway (Delille *et al.*, 2005; Engel *et al.*, 2005) (photo courtesy of Ulf Riebesell, GEOMAR).

months, so that the potential for genetic adaptation is greater than for slower-growing macroinvertebrates that dominate benthic systems. Microcosm and mesocosm experiments of many benthic organisms may require timescales of a year or more to determine the potential rates of acclimation and adaptation to elevated pCO_2.

4.2.3 Field experiments

Manipulative field experiments have the advantage of closely mimicking the real world, and may be one of the few ways to obtain realistic assessments of the ecological consequences of decreased calcification rates. Field experiments avoid the problem of co-variation between important parameters (temperature, saturation state, and light), and biases introduced in controlled laboratory experiments. For example, a field experiment where a patch of water in the open ocean or overlying a benthic community is enriched with pCO_2 while keeping all other variables natural would provide key insights into future responses of the calcifying community, particularly in terms of subtle changes such as species interactions, community structure, bioerosion, and dissolution.

Ideally, experimental field settings should range from naturally enclosed water bodies (natural embayments, lagoons) to open ocean. Such experiments (particularly the open-boundary experiments) are difficult to conduct because the environmental variable of interest—seawater carbonate chemistry—is difficult to control, as are other conditions such as temperature, nutrients, and light. Those environmental variables that cannot be controlled will have to be monitored and then factored into the overall response. Field studies should, therefore, be augmented with controlled laboratory and mesocosm experiments.

Two types of field experiments that could be adapted for examining calcification response of planktonic communities include (1) the IronEx and similar experiments where a large patch of seawater was fertilized with iron, and then tracked and monitored for several weeks to examine community and biogeochemical response (Martin *et al.*, 1994; Coale *et al.*, 1996; Boyd *et al.*, 2000; Coale *et al.*, 2003) (**Figure 4–10a**); and (2) FACE (Free Air Carbon dioxide Enrichment), the terrestrial field experiments which increase ambient CO_2 concentrations using controlled inputs of CO_2 directed toward the center of an experimental plot (Hendrey and Kimball, 1994) (**Figure 4–10b**). "CO_2Ex" studies could be conducted at a variety of scales in benthic communities, particularly with restricted water masses (from patch reefs to atoll lagoons and large embayments). A CO_2Ex study could be performed within a planktonic calcifying community, although additional manipulations may be necessary to induce calcifiers to bloom. For benthic calcifying systems, coral reef lagoons (e.g., within an atoll) are one example of naturally enclosed systems in which CO_2 chemistry manipulations could be contained.

An ocean version of a FACE experiment requires considerable engineering design, mainly because of challenges associated with hydrodynamics and with CO_2 supply to the water column. Some progress in such designs has been made already (**Figure 4–11**; Kirkwood *et al.*, 2005). A FACE-like experiment for shallow benthic systems would be easier than in the open ocean, as it could be permanently secured to the ocean floor and the organisms would remain in place (as opposed to open ocean systems, in which a system would have to be deployed and maintained within a bloom of calcifiers in order to obtain measurable results).

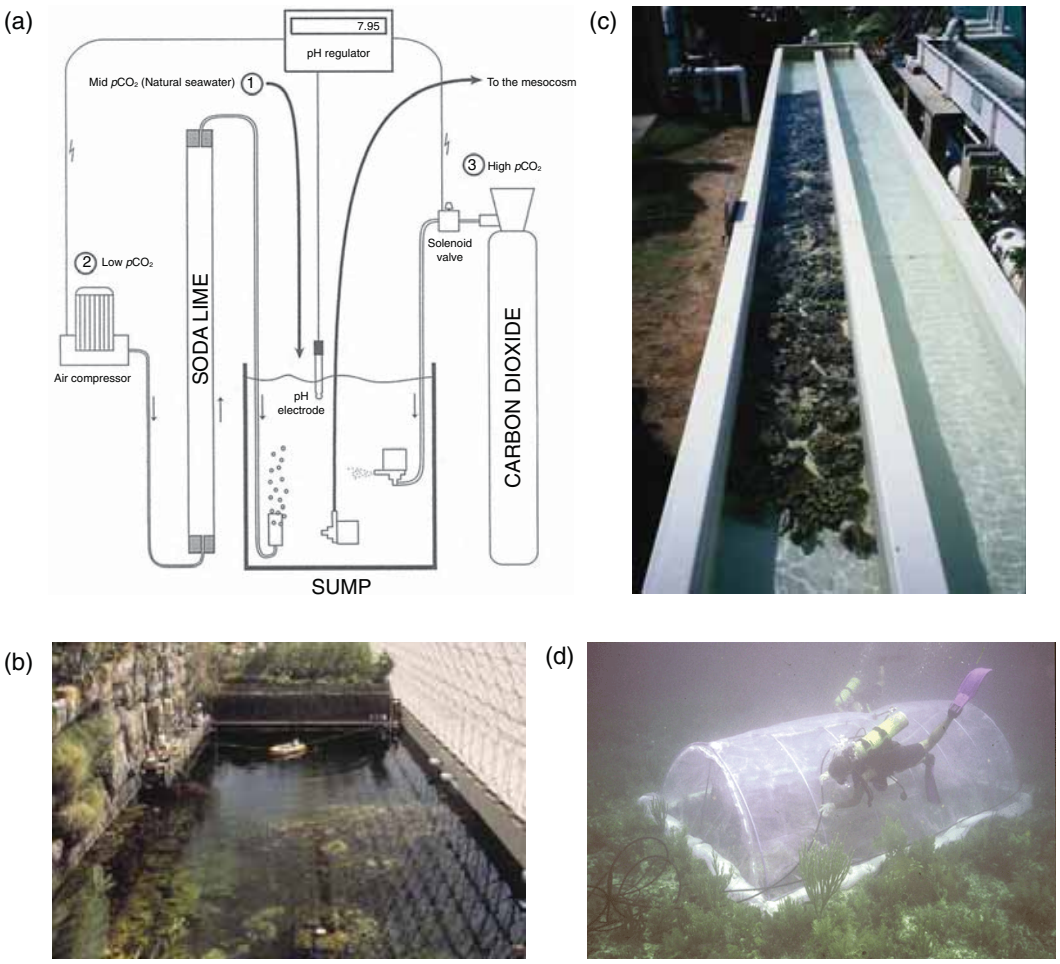


Figure 4–9: Mesocosm experiments for conducting calcification experiments on benthic communities. (a) Diagram of the Monaco coral community microcosm (reprinted from Leclercq *et al.*, 2002; copyright by the American Society of Limnology and Oceanography, Inc.). (b) Biosphere 2 coral reef mesocosm (Langdon *et al.*, 2000; Langdon *et al.*, 2003). (c) Hawaii Marine Biological Institute flume studies on coral communities (Langdon and Atkinson, 2005). (d) SHARQ (Submersible Habitat for Analyzing Reef Quality) chamber experiments conducted in situ (reprinted from Yates and Halley, 2003, with kind permission from Springer Science and Business Media).

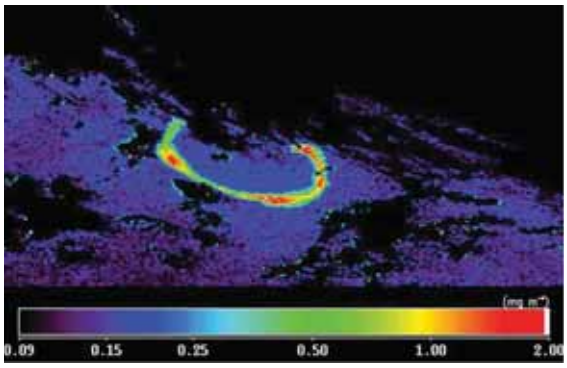
Both CO_2Ex and FACE-like experiments require pumping large quantities of CO_2 into seawater. This is a technological challenge, and may also be harmful in some environments. Alternatively, technology and techniques to conduct CO_2-*removal* experiments (e.g., to mimic ice-age concentrations) should also be considered in future design.

4.2.4 Target organisms for research

Most research on marine calcifiers has been on three major taxa: coccolithophorids, foraminifers, and scleractinian corals. Continued research on these groups is likely because they are ecologically and biogeochemically important, but also to take advantage of the existing database. Research on many other groups is badly needed, however. Little research has been conducted on organisms that secrete high-Mg calcite, or commercially important species such as bivalves and crustaceans. Selection of target species for laboratory experiments should consider a range of features (**Table 4.4**), including:

1. ecological importance;
2. different calcification mechanisms (i.e., from organisms with low biological control over calcification to those with high biological control);
3. different skeletal structures (e.g., dense versus porous);
4. different mineralogies (e.g., aragonite versus high-Mg calcite);

(a)



(b)

Figure 4–10: Examples of large-scale field experiments that could be modified for open-ocean studies on calcifying communities: (a) Satellite picture of a phytoplankton bloom in the Southern Ocean induced by iron fertilization during the SOIREE experiment (from `http://www.awi-bremerhaven.de/Biomeer/southern-ocean-top01-e.html`); and (b) the Free-Air Carbon-dioxide Enrichment (FACE) experimental design for terrestrial systems.

5. different capacities for adaptation (e.g., from variable and/or marginal environments); and
6. ease of culture.

For example, the coccolithophorid *E. huxleyi* is the best-studied of the planktonic calcifiers, owing to its prominence in the open ocean, its importance in marine ecosystems and biogeochemical cycling, and the relative ease of maintaining it in culture. Many aspects of *E. huxleyi* physiology are well understood, but the underlying mechanisms of its calcification are not. Many common coccolithophore species differ substantially from *E. huxleyi* in calcification and other physiological processes, and the response of such species to decreased carbonate saturation state should be investigated. Among benthic organisms, massive *Porites* and branching *Stylophora pistillata* and *Acropora* spp. are often considered the "lab rats" among corals, but many other benthic calcifiers should be considered target species for future research.

Many organisms within these groups have multiple life stages, but most studies have concentrated on adults. Calcification could play a critical role in planktonic larval stages (e.g., ballast or protection), and when benthic organisms initially calcify to a substrate at the time of settlement (see "Organism Response" under Section 3.1).

4.2.5 Dissolution in the water column and sediments

Both field and laboratory measurements are useful and necessary to understand rates and processes affecting carbonate dissolution. In some basic ways, our understanding of carbonate dissolution is limited; for example, there is still debate concerning the kinetic expression defining the relationship between calcite dissolution and degree of saturation (Morse and Arvidson, 2002; Gehlen *et al.*, 2005a). Aragonite and high-Mg calcite dissolution kinetics are even more poorly understood. Measuring dissolution in the field has been tackled in both the water column and in sediments. In the open ocean, quantification of carbonate particle dissolution may be achieved using an array of techniques:

1. *Hanging particles on a wire* and determining dissolution rates over time (Peterson, 1966; Troy *et al.*, 1997). An advantage of this approach is its elegant simplicity. A drawback is that the impact of hydrodynamics and fouling are difficult to assess and that a mooring is required.
2. *Sediment trap fluxes* provide a measure of net dissolution. The change in flux between two trap horizons, in a simple 1-dimensional mass balance, defines the rate of dissolution between two depths in the water column (Walsh *et al.*, 1988; Feely *et al.*, 2002). This approach can be widely applied throughout the global ocean as there are data from many trap arrays, yet the 1-dimensional flux assumption is problematic, especially in assessing trap data from depths shallower than 1000–2000 m. Hence, obtaining an accurate measurement of dissolution in the shallow ocean requires the use of traps free of hydrodynamic biases. Neutrally buoyant traps may provide a partial solution to this dilemma. Another problem with trap budget approaches is the difficulty in assessing whether captured particles swam or fell into the trap.
3. *Water chemistry mass balance.* Feely *et al.* (2004) provides a clever method of establishing disso-

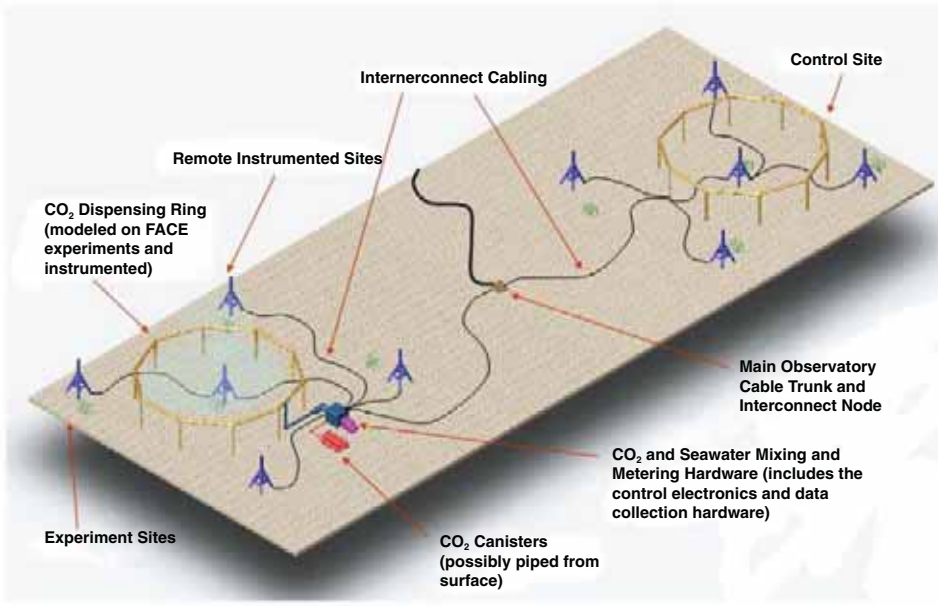


Figure 4–11: Diagram of FACE-like technology adapted for benthic marine studies (figure reprinted from Kirkwood *et al.*, 2005, courtesy of Bill Kirkwood and Peter Brewer, MBARI).

lution rates in parcels or discrete water masses. Here, the age of a water mass is established from tracer modeling (Chlorofluorocarbons, tritium, ^{14}C) and the "in-growth" of "excess" alkalinity or calcium is determined. The method to define the excess alkalinity in a water mass is not simple—it relies on two model-dependent determinations—but its applicability to deriving global estimates of dissolution makes it a powerful tool.

4. *Particle tracers.* The mass of foraminifera tests (Broecker and Clark, 1999) has been used as a proxy for dissolution (simple weight loss) as has the change in Mg/Ca ratios in forams. While these proxies have been more often applied to studies of carbonate dissolution within sediments, they may also serve to constrain dissolution as it occurs within the water column.
5. *Bulk water measurements.* Capturing a volume of water, incubating it, and determining the change in carbonate chemistry is a direct measure of dissolution or precipitation rate (Byrne *et al.*, 1984; Feely *et al.*, 1988; Buitenhuis *et al.*, 1996). This approach requires high precision measurements to detect the small changes in the CO_2/carbonate system that occur during incubation.

Field methods to study carbonate dissolution on the sea floor include both "active" experimentation which captures reactions occurring over timescales of days, and integrative measurements which capture reactions occurring over much longer timescales, often integrating processes that have been active over hundreds to thousands of years.

1. *Benthic flux chambers* are deployed in situ to capture and incubate water in contact with the sediment-water interface. Changes in alkalinity and/or calcium with time provide a direct measure of sea floor dissolution rates (Berelson *et al.*, 1994; Jahnke *et al.*, 1994; Martin and Sayles, 1996). This approach has had limited application in the field and some consider chamber fluxes suspect due to hydrodynamic interferences and because dissolution is determined over short timescales.
2. *In situ microelectrode profiles* of pH and/or pCO_2 have been applied to study carbonate diagenesis in sediments (Hales *et al.*, 1994). Data are interpreted with the use of transport-reaction models to predict carbonate dissolution rates, and resulting flux estimates are subject to the uncertainties inherent in model assumptions.
3. *Proxies for dissolution,* including those mentioned above, provide a measure of dissolution occurring on the timescale of sediment accumulation, mixing, and sample resolution. Other proxies for dissolution include the degree of foram fragmentation, trace metal ratios (McCorkle *et al.*, 1995), and the ratio between more soluble and less soluble species.

Table 4.4: Examples of targeted organisms and taxa for research on impacts of increasing atmospheric CO_2 on calcification. Note that a lack of notes under "Cons" does not necessarily indicate the taxon is highly suitable for research, but rather a lack of information in this regard.

Taxon	Pros	Cons
Planktonic		
Coccolithophores	Abundant with global distributions Some species are bloom-forming and blooms can be induced Some species are easy to maintain in lab Importance in carbon cycle Potential importance in food webs Some species well studied Common in calcareous sediments	Complex life cycles Difficult to identify species without using SEM
Planktonic foraminifera	Abundant and widespread Calcification mechanism in many taxa uncomplicated by photosynthesis Some species can be cultured in lab Common in calcareous sediments	Difficult to culture
Euthecosomatous pteropods	Widespread and regionally abundant Importance in carbon cycle Importance in food webs Only aragonitic member of the major planktonic calcifiers Calcification mechanism uncomplicated by symbiotic algae	Normal behavior is often disrupted in captivity
Benthic		
Halimeda	Abundant and widespread in tropics Simple calcification mechanism Easy to maintain in lab Prolific calcifier Importance in carbon cycle	
Coralline algae	Abundant and widespread Secrete most soluble form of $CaCO_3$ Easy to maintain in lab Importance in carbon cycle Reef-builder	
Benthic foraminifera	Abundant and widespread Important component of carbonate sediments Symbiotic and asymbiotic forms High-Mg and low-Mg taxa Some species well studied and easy to maintain in the lab Diverse calcification mechanisms Diverse habitats (infaunal, epifaunal, sessile, motile)	
Zooxanthellate coral, *Stylophora pistillata*	Abundant and widespread Easy to maintain in lab Established history in laboratory experiments	Branching coral—not well suited to skeletal records Typically non-reef-forming
Zooxanthellate coral, massive *Porites* spp.	Abundant and widespread Calcification rates and isotopic signals recorded in skeletal bands Major reef-builder	Slow-growing Difficult to culture and maintain
Azooxanthellate corals	Calcification mechanism uncomplicated by symbiotic algae Some species form significant deep-water reefs Some species may occur near saturation horizon (most vulnerable) Low environmental variability may allow clean signal of calcification rate changes over time	Slow-growing Usually non-reef-building Ability to culture unknown?
Echinoderms	Abundant and widespread Can be maintained in culture (larvae of some species are used in bioassay work) High-Mg calcite	

Table 4.4: Continued.

Taxon	Pros	Cons
Bryozoans	Abundant and widespread Both shallow-water and deep-water taxa Aragonite, high-Mg calcite, and calcite taxa	
Molluscs	Abundant and widespread Some species house zooxanthellae Many species commercially important Some taxa easy to culture (e.g., several bivalve taxa are aquacultured) Calcification rates and isotopic signals recorded in skeletal bands Some taxa secrete aragonite and calcite in proportions that may reflect saturation state	

4. *The amount of* C_{org} raining to the sea floor affects the rate of carbonate dissolution (Emerson and Bender, 1981; Archer and Maier-Reimer, 1994). Subtle changes in how much organic matter gets mixed into surface sediments, as opposed to sitting in a fluff layer on top of the sediments, is thought to be an important factor in controlling net dissolution.
5. *The mass balance approach*, which determines net dissolution as the balance between sedimentation and burial rates, generally requires a loss term. Mass balances constructed over short time periods for a section of sea floor and water column require high-frequency determinations of carbonate parameters and good control on water circulation. This approach could be more frequently applied as technologies improve in Doppler current meters and pCO_2 and pH detectors.

In addition to the methods listed above, there are emerging research needs that will require creative research designs. At the smallest biological scales in ocean ecosystems, the role of viruses, bacteria, and *Archaea* in affecting carbonate precipitation, dissolution, or preservation is poorly known, but likely important (Fabry and Robbins, 1994; Robbins *et al.*, 1997; Yates and Robbins, 1999). Methods to measure dissolution inside the guts of zooplankton and larger organisms should be refined (Bishop *et al.*, 1980; Harris, 1994; Milliman *et al.*, 1999), and measurements of particle dissolution in the water column require better ways of estimating particle residence time in different water masses.

4.3 Target Regions for Research

Potential locations of future research studies were recommended at the St. Petersburg Workshop. These recommendations were based on several factors, including:

1. ecologically important systems (e.g., high biodiversity, food-chain support);
2. ecological systems particularly sensitive to carbonate chemistry changes;
3. regions likely to experience the most dramatic change in carbonate chemistry (e.g., high latitudes, deep-sea coral reefs near the aragonite saturation horizon);
4. regions which already experience high pCO_2, or have strong natural gradients in carbonate chemistry (see section 4.1.2);
5. regions that permit combined pelagic and benthic experiments;
6. remoteness from human activities;
7. regions with existing long-term environmental information (existing time-series stations, LTER sites);
8. regions with existing infrastructure for performing the research (e.g., marine laboratories, ocean observing systems).

Based on these criteria, some regions identified as being particularly suitable for future field research. The list below is biased toward coral reef locations, which were the priority benthic ecosystem considered at the workshop; however, we stress the need to also consider temperate calcifying environments. Among the pelagic systems, workshop participants focused on high-latitude regions, particularly those most likely to experience undersaturated surface waters within decades, and regions with natural gradients in CO_2 chemistry.

Galápagos Islands (0°30′N 91°W). The Galápagos Archipelago in the eastern Pacific lies in a region of strong equatorial upwelling. pCO_2 of upwelled wa-

ters is naturally high (often exceeding 500 μatm), and in many locations these waters penetrate the thermocline and reach the surface, particularly along the western sides of the islands. Anecdotal evidence supports the notion that lower saturation states of these waters may have been a factor in the marginal coral reef development here (although other factors, such as low water temperature, certainly play a role as well). The Galápagos Archipelago also has strong lateral gradients in carbonate chemistry which could be taken advantage of in experimental designs, and offers the opportunity to study both planktonic and benthic calcifying systems, and sedimentation (sedimentation rates at Cocos Ridge are about 15 cm ky^{-1}). There are existing research facilities and low levels of human influence. All of the major groups of planktonic calcifiers commonly occur here and have high species diversity. Coral reefs of the Galápagos experienced severe bleaching during the 1982–1983 El Niño event, and moderate bleaching in the 1997–1998 event. While many of the reefs experienced dramatic bioerosion following these events, coral recruitment continues and offers the opportunity to examine coral reef development in an elevated-pCO_2 environment.

Bahamas Bank (22–27°N 72–75°W). In contrast to the Galápagos, the Bahamas Bank is a region where saturation states are naturally high, although strong gradients do occur across the Banks because of calcification processes that draw down the alkalinity (e.g., Broecker and Takahashi, 1966; Broecker *et al.*, 2001). This region has been a Mecca for carbonate research, as there is a suite of biologically produced and inorganically precipitated carbonates (ooids and whitings). Ocean chemistry has been measured nearly annually at various locations in the Bahamas since 1980 (Frank Millero, University of Miami, personal communication). It is also a region of high ecological importance and most of the Bahama Islands experience low human impact. Several research stations are active in the Bahamas (e.g., Perry Institute for Marine Science on Lee Stocking Island; the Bahamian Field Station on San Salvador Island) and offer good infrastructure for supporting research and monitoring.

Florida Keys and Dry Tortugas (24°25′–25°45′N 80–83°W). The primary advantage of conducting research in the Florida Keys is access to excellent research facilities and expertise on the carbonate system from various Florida marine science laboratories. While most of the Keys are heavily impacted by human activities, the Dry Tortugas are more remote and isolated from land activities.

Bermuda (32°20′N 64°40′W) and **Hawaiian Islands** (19–28°N 155–177°W). Both Bermuda and the Hawaiian Islands are located in mid-ocean gyres, and have extensive coral reefs. Bermuda is located at the northern limit of reef development in the Atlantic, while the Hawaiian Islands extend across nearly 10° latitude. Both locations have a long history of reef and oceanic research, and have time-series stations that have tracked open ocean carbonate chemistry for more than 15 years (HOT and BATS, see **Table 4.2**). Each site has well-equipped laboratories for carbonate chemistry analyses. Bermuda's coral reefs have been studied for more than a century, with intensive ecological studies being conducted since the 1960s, mainly through the Bermuda Biological Station for Research (BBSR). Several studies have already been conducted on the carbonate chemistry of Bermudan reef waters (Bates *et al.*, 2001; Bates, 2002). Hawaiian coral reefs are similarly well studied, particularly those of Kaneohe Bay, site of the Hawaiian Institute of Marine Biology research station, where experiments have been conducted on the effects of increased pCO_2 on coral calcification (Langdon and Atkinson, 2005). NOAA has recently established an extensive monitoring program in Kaneohe Bay and the NW Hawaiian Islands.

Many other coral reef locations may be well suited for research on the effects of increased pCO_2 on calcifying communities. These include the Great Barrier Reef, French Polynesia (which has recently established a Long-Term Ecological Research site), and Ryukyu Islands of Japan, among many other coral reef regions.

Deep-sea coral communities. Deep-sea coral communities are distributed throughout the world oceans, in relatively constant environments, and usually at 200–600 m depth. Deep-sea corals are non-zooxanthellate, slow-growing, and can live for over a century. Because of the low environmental variability, the long-lived nature of the corals, and their proximity to carbonate saturation horizons, these communities may be ideal for monitoring changes in saturation state.

Southern Ocean. In the Southern Ocean, the aragonite saturation horizon is expected to shoal from a mean present-day depth of 730 m to the surface in less than 100 y (Orr *et al.*, 2005). The very large changes in carbonate chemistry that this high latitude region will experience make it a high priority study area. The McMurdo and Palmer Stations in Antarctica have excellent research facilities for monitoring field populations of both planktonic and benthic calcifiers, and conducting manipulative experiments.

Subarctic Pacific. Similar to the Southern Ocean, parts of the subarctic Pacific are expected to experience aragonite undersaturation in surface waters within 100 years (Orr *et al.*, 2005); calcite undersaturation is predicted to lag that of aragonite by 50 to 100 years. The major planktonic calcifying groups com-

monly occur here and occasionally experience population explosions (e.g., coccolithophores, pteropods). Ocean Station Papa and the Line P have a long history of hydrographic and biological measurements, and researchers at Canada's Institute of Ocean Science (IOS) have monitored carbonate chemistry for many years. The ongoing monitoring activities by IOS, coupled with the large changes in carbonate saturation states that are expected to occur within the 21st century, make this an ideal region to study planktonic calcification and dissolution processes.

Large Scale Mesocosm Facilities, Bergen, Norway. This facility at the Marine Biological Station of the University of Bergen consists of nine polyethylene enclosures moored to a raft in the Raunefjorden (60.3°N, 5.2°E). In previous experiments, the volume of each enclosure was 11 m^3 or 20 m^3. The enclosures are filled with fjord water and coccolithophore blooms are induced by addition of nutrients. This mesocosm facility provides the ability to manipulate complex ecosystems in a semi-natural setting, providing a critical bridge between laboratory studies and mesoscale in situ experiments.

4.4 Modeling Opportunities and Needs

Modeling will be an important component of future research on CO_2 effects on marine calcifiers. Such modeling efforts need to focus on three arenas:

1. physical and chemical environment (hydrodynamics, sediments, carbonate system);
2. biological and ecological response (physiological response; community interactions);
3. coupling of global-coastal processes.

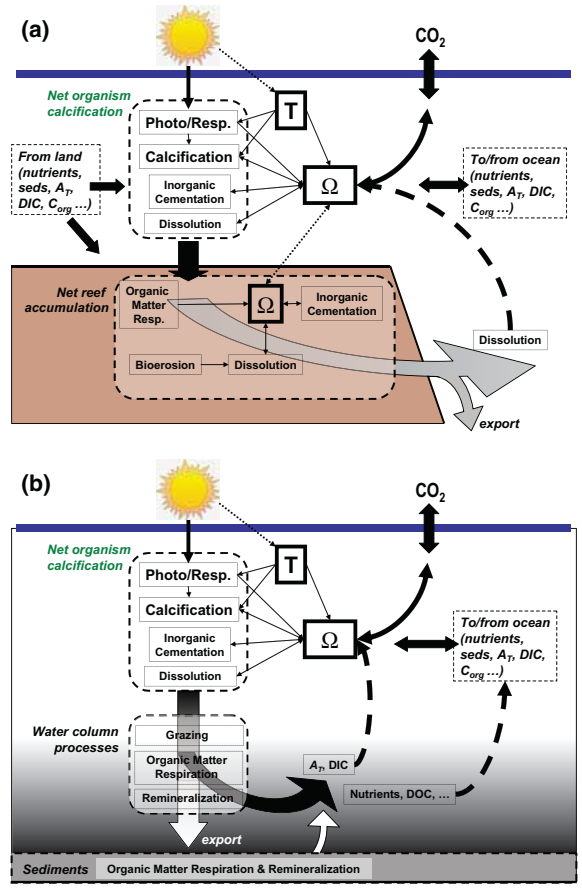


Figure 4–12: Comparison of the major processes that need to be considered in modeling the carbonate system in (a) a shallow benthic system (<100 m depth) and (b) an open ocean system (up to 6000 m depth). These are oversimplified representations. For example, the dissolution component in both systems involves complicated processes that include differences in mineralogies, organic matter respiration, etc.

4.4.1 *Current modeling efforts*

Modeling efforts of the ocean carbon system have focused on the biogeochemical response of the global carbon cycle to increased CO_2, and the consequent feedbacks to future atmospheric CO_2 concentrations (**Box 6**; **Figure 4–12**). Global models of the open-ocean system can capture the main physical and biogeochemical processes that control the marine carbon cycle. For the present-day ocean, global models simulate large-scale regional changes in saturation state and saturation horizons that roughly match observed changes. Such models can therefore guide laboratory and field studies and make predictions of large-scale changes over at least the 21st century. These models are designed only for the open ocean, however, and they do not include coastal processes. Also the ecological components of the models are probably too simple to adequately predict biogenic calcium carbonate production under higher atmospheric CO_2 levels.

Few coastal carbon system models have been developed. Coastal modeling is inherently more difficult than open-ocean modeling, because, in addition to water column processes and air-sea gas exchange, coastal models must include land-based inputs and sediment interactions (**Figure 4–12a**) as well as much higher spatial and temporal variability. Coastal models must also be validated site by site. One example of a coastal biogeochemical model is the Shallow Ocean Carbon Model (SOCM) developed by Fred Mackenzie and colleagues (e.g., Andersson *et al.*, 2003). This

Table 4.5: Priority modeling needs, example topics, and whether the question relates primarily to physical-chemical or biological-ecological questions.

Modeling Priority	Example Topics	Physical-Chemical	Biological-Ecological
Guidance on field design	• best regions for monitoring/experiments	×	×
	• constraining ranges of measurements, expected variability in parameters	×	×
	• determining best frequency/spatial scale for data collection	×	×
Dissolution and remineralization	• C_{org}:C_{CaCO3} rain ratio	×	×
	• settling rates	×	×
	• controls on dissolution rates within the water column	×	×
	• changes in carbonate chemistry profile with depth	×	
Sedimentary response	• sedimentation rates	×	×
	• advection of alkalinity from sediments to coastal and open ocean	×	
	• mineralogical controls on sedimentary response	×	×
	• hydrodynamic controls on fluxes (especially flow through porous media)	×	
	• relative effects of organic matter respiration on dissolution versus changing saturation state of overlying water column	×	×
Mineralogical	• conditions affecting the balance between calcification/dissolution	×	×
	• kinetics of high-Mg calcite precipitation and dissolution	×	×
Organism response	• organism production, respiration, calcification rates	×	×
	• competitiveness		×
	• potential role of adaptation		×
	• changes in reproductive success		×
Ecosystem response	• community production, respiration, calcification rates	×	×
	• competitive interactions		×
	• predator-prey interactions		×
	• cascading effects due to removal of key calcifiers		×
Global-coastal model coupling	• need for coupling coastal processes with open ocean	×	×
	• to what extent can shallow water sediments affect global changes in carbonate saturation (open ocean, coastal)?	×	×
	• scaling up from local/regional to global	×	×
	• driving regional models with global model	×	×
	• incorporating more realistic coastal circulation; predicting future changes in circulation	×	

model could be adapted for studying both future biogeochemical changes in coastal carbonate systems, and ecosystem response to those changes.

Even fewer models have addressed $CaCO_3$ production at smaller scales, varying from the organism to the ecosystem, or how changes in calcification rates might affect future ecosystem composition and functioning. For example, some coral species propagate by skeletal fragmentation. If reduced calcification leads to less dense skeletons, would this increase propagation of this species, and if so how would such changes affect long-term community composition? In the pelagic realm, can we use ecological modeling to predict how a change in pteropod abundance or distribution (Orr *et al.*, 2005) would affect food webs that depend on them?

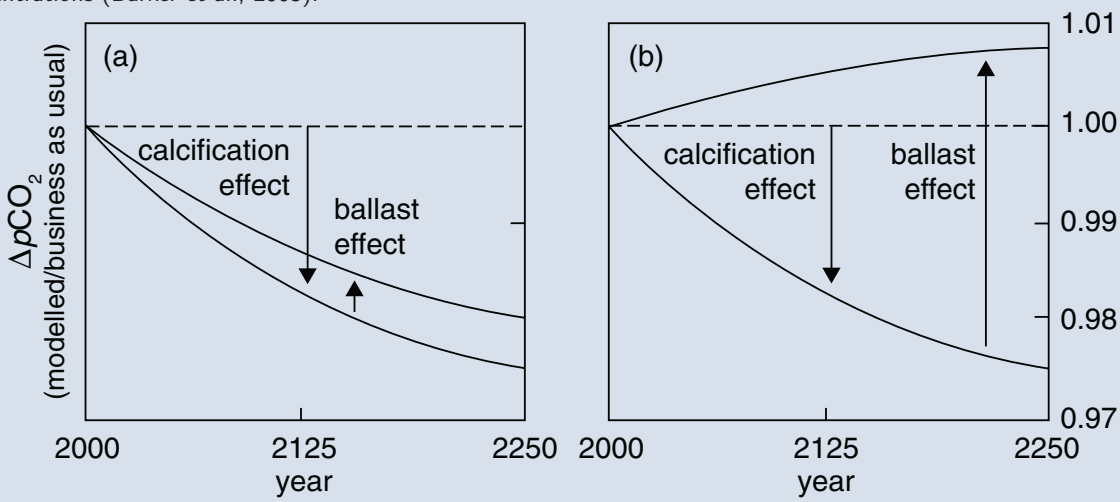
4.4.2 *Modeling priorities*

A successful research strategy requires modeling be included from the outset. In the early stages, models can guide research design (experiments and observations; sensitivity tests to bound particular processes), and field designs should specifically address activities for model validation. The obvious first step toward this greater integration of modeling is to conduct a census of available models—hydrodynamic through ecological—and data available for input and valida-

Box 6—Current Modeling of $CaCO_3$ Processes Within the Global Carbon Cycle

Most modeling efforts addressing calcium carbonate production have focused on the role of $CaCO_3$ production, export, and dissolution on the marine carbon cycle. The state-of-the-art technique for predicting biogenic $CaCO_3$ production is ecosystem modeling (imbedded within ocean general circulation models) that typically contain two to five functional types of phytoplankton (Moore *et al.*, 2002; Bopp *et al.*, 2003; Aumont and Bopp, in press). $CaCO_3$ export (and its ratio with POC) may be modeled as competition between a functional calcifier and the other plankton (e.g., silicifiers) where dominance is determined by differential grazing pressures and physical oceanographic conditions. However, the calcifier is always patterned after the bloom-forming coccolithophore *E. huxleyi*, which may or may not be the dominant producer of $CaCO_3$.

The traditional alternative to complex ecosystem formulations, taken in box models and many global circulation models, has been to prescribe either a spatially (and temporally) invariant ratio between $CaCO_3$ and particulate organic carbon ($CaCO_3$:POC) production (Broecker and Peng, 1986; Yamanaka and Tajika, 1996; Archer *et al.*, 1998), or to estimate the $CaCO_3$:POC ratio based on temperature and/or opal production (Archer *et al.*, 2000; Heinze, 2004). However, none of the above methods (ecosystem or alternatives) are capable of predicting a response of calcification and carbonate export to surface ocean acidification. Several recent attempts have been made to address this and incorporate a response of the $CaCO_3$:POC rain ratio to surface ocean carbonate chemistry. These model parameterizations have been based on the deviation from modern surface ocean conditions of either CO_2 partial pressure (Heinze, 2004) or carbonate ion concentrations (Barker *et al.*, 2003).



Example of modeling the combined effects of reduced calcification and reduced $CaCO_3$ ballast on atmospheric pCO_2: (a) reduced calcification acts to lower atmospheric pCO_2, while reduced $CaCO_3$ ballasting of organic carbon acts to increase atmospheric pCO_2; (b) the same calculations but allowing for increased dissolution and remineralization rates (20% shorter remineralization length scales). Reprinted from Barker *et al.* (2003), with permission from the Royal Society of London.

tion. For example, a number of coastal models designed for estuaries can be modified to study coastal calcification processes, but as yet do not include the carbonate system.

Most of the priorities for modeling (**Table 4.5**) parallel concerns noted elsewhere in this document. Workshop participants recommended four main areas of model development needed to tackle these priorities:

1. *Streamlining and standardization:* Develop standard computer codes for addressing specific needs (calcification, dissolution) and make them available to the community;
2. *Hydrodynamics:* Conduct a census of coastal hydrodynamic models that could be adapted for use in coastal carbon cycle modeling;
3. *Ecological modeling:* Conduct a census of ecological models that can be used in carbon cycle modeling. Some of the complex ecosystem models already available for coastal systems could be adapted to examine effects of reduced calcification. This census should be conducted for both benthic and pelagic systems, as well as for models that couple the two; and
4. *Intensive modeling:* Select a high-intensity study area where detailed modeling can be validated and used to examine the most important processes with sufficient modeling complexity.

5. Technology Needs and Standardization of Measurements

5.1 Carbonate Chemistry

5.1.1 Carbonate system measurements

THE CARBONATE CHEMISTRY of seawater is so complex that it can be a challenge to accurately measure changes and attribute observed changes to specific mechanisms. One of the key carbon species to quantify for calcification studies is the carbonate ion concentration ($[CO_3^{2-}]$). At this time $[CO_3^{2-}]$ cannot be directly measured. Laboratory studies are underway to develop a method for optically measuring $[CO_3^{2-}]$, but it will be a few years before this is an operational technique. Currently there are four measurable parameters: CO_2 partial pressure (pCO_2), total alkalinity (A_T or TA), total dissolved inorganic carbon (DIC), and pH. Using the thermodynamic dissociation constants and assumptions about the composition of seawater as a function of salinity, the distribution of all the carbonate species can be calculated from the concentrations of any two of these measurable quantities.

The most common measurements for open-ocean discrete water samples are DIC and A_T. DIC is typically measured using a coulometric titration with a semi-automated sample delivery system. The most common system, a single-operator multi-parameter metabolic analyzer (SOMMA), is fitted with a 20- to 30-mL pipette and calibrated by filling a gas loop with a known volume of pure CO_2 gas, then introducing the gas into the carrier gas stream and performing coulometric titration (Johnson *et al.*, 1987; Johnson and Wallace, 1992; Johnson *et al.*, 1993; Johnson *et al.*, 1998). Some systems are calibrated by analyzing sodium carbonate standards. DIC systems that are not coupled with a semi-automated sample analyzer typically introduce the sample manually with a pipette or a syringe. Typical open-ocean accuracy and precision are ±1–2 μmol/kg.

A_T measurements are made by potentiometric titration (using a titrator and a potentiometer). A_T can be determined either by characterizing a full titration curve (Brewer *et al.*, 1986; Millero *et al.*, 1993; DOE, 1994; Ono *et al.*, 1998) or by a single-point titration (Perez and Fraga, 1987). Common analytical differences between systems are in the volume of sample analyzed, the use of either an open or closed titration cell, and the calibration methods. Results can also be obtained from different curve-fitting techniques such as Gran plots, nonlinear fitting, or single-point analysis. Typical open-ocean accuracy and precision are ±2–4 μmol/kg.

Two different types of instruments are typically used to measure discrete pCO_2 samples. The main difference between the systems is the sample size. One system uses ~500 mL samples equilibrated by bubbling a recirculated 50 mL headspace gas through the sample. There is also a small volume technique which equilibrates a 10 mL headspace with a 120 mL sample. With each, an aliquot of seawater is equilibrated at a constant temperature of either 4 or 20°C with a head space of known initial CO_2 content. Subsequently, the head space CO_2 concentration is determined by a nondispersive infrared (NDIR) analyzer or by quantitatively converting the CO_2 to CH_4 and analyzing the concentration using a gas chromatograph (GC) with a flame ionization detector. The initial pCO_2 in the water is determined after correcting for loss (or gain) of CO_2 during the equilibration process. This correction can be significant for large initial pCO_2 differences between the head space and the water, and for systems with a large head-space-to-water volume ratio (Chen *et al.*, 1995). Estimates of precision based on duplicate samples range from 0.1 to 1%,depending on pCO_2 level and the measurement procedure, with higher pCO_2 levels on the small volume system (>700 μatm), being the least reproducible (Chen *et al.*, 1995).

The pH of seawater can be determined using pH electrodes, or more precisely, by a spectrophotometric method (Clayton and Byrne, 1993). The spectrophotometric technique involves adding a pH sensitive indicator (usually m-cresol purple) to a fresh seawater sample and looking at the relative absorbance of the protonated and un-protonated species using either a scanning or diode array spectrophotometer. Variability in the spectrophotometer response is corrected by looking at wavelengths outside of the range

of the indicating dye. The results are also a function of the temperature and pressure of the sample at the time of measurement. Seawater pH is not a common open ocean measurement because samples cannot be preserved and must be measured soon after collection, but it does provide a key variable for calcification studies. The estimated accuracy of the spectrophotometric method is ±0.002, although individual precision estimates using this technique may be much better.

Although these techniques are very useful for mesocosm or water column studies from ships, some of the studies outlined in this report require sampling at much higher frequencies or over longer temporal ranges. These measurements can be obtained with autonomous instruments. Carbon researchers have been making high-resolution surface pCO_2 measurements from moving ships for decades using semi-autonomous instruments. These typically use an equilibrator that equilibrates a small, fixed volume of air with essentially an infinite volume of water. The equilibrated air is then analyzed in a manner similar to the discrete pCO_2 measurement using either an infrared detector or a GC (e.g., Wanninkhof and Thoning, 1993; Feely *et al.*, 1998). These systems are regularly calibrated by analyzing gas from a series of known CO_2 concentrations. This technology has also been adapted for use on moorings with a surface buoy.

Underway shipboard pH measurements have also been made using the spectrophotometric method. This technique mixes a colorimetric dye into a flowing seawater stream which is then run through the spectrophotometer. The system is "calibrated" by looking at the wavelengths that are not affected by the dye. This basic principle has also been adapted for a variety of autonomous instruments. The most common instruments determine seawater pCO_2 by taking a dye solution with a known alkalinity and allowing it to equilibrate with ambient seawater conditions. The CO_2 that diffused into the dye solution changes the pH, which is determined with a spectrophotometer. Using the known A_T and measured pH, the pCO_2 of the seawater can be calculated.

Continuous-flow-through analyzers have been developed for DIC (Kimoto *et al.*, 2002) and A_T (Watanabe *et al.*, 2004), for use in shallow-water coastal zones. The continuous DIC analyzer strips CO_2 from an acidified sample, and the CO_2 is then measured with an NDIR analyzer. The flow-through A_T analyzer is based on continuous potentiometric measurements. These systems can measure DIC and A_T at frequencies of 1–5 minutes, with precisions and accuracies of about 2 μmol kg^{-1} in the laboratory (Watanabe *et al.*, 2004). These instruments have been incorporated into an integrated carbonate chemistry monitoring system that additionally measures temperature, pH conductivity, and dissolved oxygen (Kayanne *et al.*, 2002). The integrated system has been used successfully to obtain continuous measurements on reef flats from an anchored boat in Ishigaki and Palau for 6–10 days (Kayanne *et al.*, 2005). The spectrophotometric method has also been adapted for making underway A_T and DIC measurements by comparing acidified water samples to un-acidified samples. Although a few prototype systems have been demonstrated to work, they have not been developed for common oceanographic use.

Moorings and drifting buoys provide another effective way to obtain high temporal resolution data over extended periods, but they have the additional challenge of very limited power and space that typically are not a problem on ships. Variations on the basic principles described for the ship-board systems are also being investigated for the development of autonomous carbon measurements. Two basic types of instruments have been adapted for long-term, truly autonomous deployments in the ocean. One class of instrument uses the spectrophotometric technique to measure pCO_2 in seawater (e.g., Merlivat and Brault, 1995; DeGrandpre *et al.*, 2002). These instruments have been successfully deployed for at least six months in both open-ocean and coastal environments. Although the current commercially available systems are set up to measure pCO_2, they can be easily adapted to measure pH. Another type of instrument that has been successfully deployed in both open-ocean and coastal environments for at least six months is based on the NDIR analyzer (e.g., Friederich *et al.*, 1995). These systems are very similar to the underway ship-board systems in that they equilibrate a large volume of water with a relatively small volume of air and then measure the CO_2 in the equilibrated air.

High resolution data from autonomous systems have been shown to resolve rapid changes in the carbonate system of water overlying the reefs, results which are difficult to obtain through discrete sampling (e.g., `http://www.pmel.noaa.gov/co2/coastal/kbay/`). To fully constrain the carbon system at least two carbon system parameters need to be measured. Although systems are available for pCO_2 and pH, these two parameters co-vary so strongly that they do not make the ideal pair to measure. Several groups are working to develop autonomous DIC and A_T systems that can be deployed on moorings. These systems will allow a more thorough examination of the short-term controls on the carbonate system over extended periods.

5.1.2 Standardization of carbon system measurements

A key to high quality, reproducible carbon measurements is routine analysis of carbon standards. In a recent compilation and quality assessment of global ocean carbon data, the single most useful source of information about data quality was based on the analysis of Certified Reference Materials (CRMs) (Sabine *et al.*, 2005). The mean of a series of CRM analyses conducted over the course of a cruise provides a direct link to the manometric[1] standard for DIC and a critical tool for comparison with data from other cruises where CRMs were also run.

This analysis also provides a useful comparison between multiple instruments being run on a cruise. The standard deviation of the mean CRM results provides an assessment of the long-term stability and precision of the instrument(s). Examination of at least daily CRM analyses can provide a good record of the consistency of the measurements throughout the cruise and can identify when potential offsets might have occurred. The CRMs are intended as a secondary standard to validate the accuracy of the primary calibration, but in the event of a catastrophic failure in the calibration system, the CRMs, together with a good history of CRM analyses on that instrument when the calibration system was working, may provide a way of manually calibrating the instrument. CRMs are currently certified for DIC and A_T and are available at `http://andrew.ucsd.edu/co2qc/`. For this reason, A_T and DIC are the currently preferred measurable carbon system parameters for defining the carbonate system.

5.2 Calcification and Dissolution Rates

5.2.1 Benthic organisms and ecosystems

A wide range of methods to measure calcification rates are available depending on the temporal and spatial scale of the question being asked (**Table 5.1**). Calcification rates in living corals and other benthic organisms are obtained by three basic means: (1) measurement of the uptake of ^{45}Ca into the skeleton; (2) change in the mass of skeleton over time (e.g., buoyant weight technique); and (3) the alkalinity anomaly technique, which estimates calcification rate by tracking changes in alkalinity of some known volume of surrounding seawater. While the ^{45}C methods are thought to yield values closer to the gross rate of calcification (at least when measured over very short time periods), the buoyant weight and alkalinity anomaly methods yield net calcification values; i.e., gross calcification minus dissolution. The buoyant weight and alkalinity anomaly methods have the advantage of being nondestructive.

The most useful unit of calcification rate for ecological and carbon cycle studies is moles of $CaCO_3$ per square meter of planar seafloor per unit time. Calcification rates of organisms are, however, often expressed as or normalized to (a) surface area of the organism being tested, (b) per gram of skeleton, (c) per gram dry weight of tissue, or (d) per gram of protein extracted from the tissue. These normalization methods have the advantage of reducing variability between specimens but make it very difficult to extrapolate the results to the field because statistics on surface area of the organism, grams of skeleton, grams dry weight of tissue, and grams of tissue protein, are generally lacking for natural systems. It is recommended that future studies employ experimental setups such as flumes or mesocosms that permit reporting results in ecologically useful units; i.e., moles $CaCO_3$ per square meter of planar seafloor per unit time. Some intercomparisons have been made between calcification measurements (Smith and Kinsey, 1978; Chisholm and Gattuso, 1991; Tambutté *et al.*, 1995), but many have not and further intercomparisons are recommended to determine their compatibility.

Measurements of coral "growth rates" in the literature usually refer to skeletal extension rates. Although linear extension in the commonly used Indo-Pacific *Porites* spp. is strongly correlated with calcification rate, this correlation does not hold for many other species (Lough and Barnes, 2000; Carricart-Ganivet, 2004) and thus skeletal extension alone is not a reliable proxy for calcification rates. The best records of calcification rates in coral cores or slabs are obtained by combining measurements of both skeletal extension (width) and skeletal density (X-ray radiography, tomography, or gamma densitometry) of annual density bands (e.g., Chalker and Barnes, 1990; Lough and Barnes, 1997). The product of the two measurements yields calcification rates that are typically reported as mass or moles of $CaCO_3$ per square centimeter of coral surface per year.

On geological timescales calcification has been estimated from geometric measurements of reef volume and density of the reef framework. Typically, these entail rather rough estimates based on dated cores, but seismic data can provide 3-dimensional measure-

[1] A DIC-measuring technique that converts DIC to CO_2 and collects it in a known volume so that the pressure of the CO_2 gas can be measured.

Table 5.1: Methods used to measure calcification rates in benthic and planktonic calcifying organisms, populations, and communities; O = organism, P = population, C = community.

Technique	Applicability	Timescale	Examples	Reference
Radioisotope (incorporation of ^{45}Ca or ^{14}C into skeleton)	O,P	minutes to hours	coccolithophores	Paasche, 1964; Balch and Kilpatrick, 1996; Paasche *et al.*, 1996
			pteropods, heteropods	Fabry, 1989, 1990
			foraminifera	Anderson and Faber, 1984; Lea *et al.*, 1995; Erez, 1983
			corals, calc. algae	Goreau, 1963
ΔA_T	O,P,C	minutes to months	coccolithophores	Sikes *et al.*, 1980
			corals	Chisholm and Gattuso, 1991
			coral reef comm.	Smith, 1973
$\Delta[Ca^{2+}]$	O,P,C	minutes to months	corals	Chisholm and Gattuso, 1991; Al-Horani *et al.*, 2003
			coral reef comm.	Debgoswami *et al.*, 1990
Buoyant weight (increase in skeletal mass)	O,P	days to months	corals	Jokiel *et al.*, 1978
pH-O_2	O,P,C	hours	corals	Jacques and Pilson, 1980
			coral reef comm.	Barnes, 1983
Coral density banding (extension between bands × density)	O	months to 100s of years	corals	Lough and Barnes, 2000
Change in particulate inorganic carbon (PIC)	O,P,C	hours to weeks	coccolithophores	Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Sciandra *et al.*, 2003; Delille *et al.*, 2005
Change in particulate $[Ca^{2+}]$	O,P,C	hours to weeks	coccolithophores	van Bleijswijk *et al.*, 1994; Paasche, 1999
Change in shell dimensions or mass	O,P	days to years	pteropods	Redfield, 1939; Kobayashi, 1974; Wells, 1974
			foraminifera	Bijma *et al.*, 1999
Secondary production-instantaneous growth rate method (instantaneous growth rate × stocking stock)	P	days to years	pteropods, heteropods	Fabry, 1989, 1990
			ophiuroids	Migné *et al.*, 1998
			benthic invertebrates	Smith, 1972
Sediment trap	P,C	days to years	foraminifera	Deuser and Ross, 1989
			pteropods, heteropods	Betzer *et al.*, 1984; Fabry and Deuser, 1991
			coccolithophores	
Sedimentological	O,P	months	benthic foraminifera	Langer *et al.*, 1997
Geological (thickness × density/time)	O,P,C	1000s of years	corals	Chave *et al.*, 1972

ments of reef volume that better constrain estimates of $CaCO_3$ accumulation (Ryan *et al.*, 2001).

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. There have been few, if any, studies comparing these different types of measurements.

5.2.2 Planktonic organisms and systems

Accurate measurement of calcification in planktonic organisms is challenging, and workers have used a variety of methods (**Table 5.1**). One commonly used method involves addition of radioisotope ($NaH^{14}CO_3$ or $^{45}CaCl$) to seawater samples that are subsequently incubated, and the incorporation of radioisotope into biogenic $CaCO_3$ is measured with a liquid scintillation counter. This method has the advantage of high sensitivity, and therefore can be used in short-term incubations. Calcification rates must be corrected for the passive exchange of radioisotope with stable calcium or carbon in the shell, however, and this can be problematic if the exchange rate is high relative to the calcification rate. In addition, internal pools of carbon or calcium can result in a lag time before the radioisotope appears in the shell, and accurate calcification rates can only be measured after any internal pools have equilibrated with the ambient seawater (Erez, 2003). A range of radioisotope techniques have been used to measure calcification rates in laboratory cultures, mesocosms, and field populations of coccolithophores (e.g., Paasche, 1964; Paasche and Brubak, 1994; van der Wal *et al.*, 1994; Balch and Kilpatrick, 1996; Delille *et al.*, 2005), foraminifera (e.g., Caron *et al.*, 1981; Erez, 1983; Anderson and Faber, 1984; Lea *et al.*, 1995), and pteropods (Fabry, 1989, 1990). Calcification rates determined with radioisotopes are typically recorded as mass or moles of C or $CaCO_3$, per cell or individual organism, per unit time (e.g., pg C $cell^{-1}$ d^{-1} or μmol $CaCO_3$ $individual^{-1}$ h^{-1}). Radioisotope-derived calcification rates are normalized to chlorophyll in coccolithophores and shell mass in foraminifera and pteropods.

Calcification rates in planktonic foraminifera and pteropods have also been reported as a function of shell size or mass versus time in laboratory experiments (Bijma *et al.*, 1999; Erez, 2003) and in field studies (Redfield, 1939; Kobayashi, 1974; Wells, 1976). One advantage of this method is that it is non-destructive. However, shell size may not be a reliable measure because many species increase the thickness of their tests as they grow rather than shell length or diameter. Use of this method in the field is limited to regions where the same population can be repeatedly sampled over time.

The instantaneous growth rate method of measuring secondary production has been used to estimate aragonite production in pteropods and heteropods (Fabry, 1989, 1990). This method combines short-term calcification rates with the standing stocks of pteropod and heteropod aragonite to estimate production in units of mass or moles $CaCO_3$ m^{-2} d^{-1}. Ideally, instantaneous growth rates should be determined over a range of size classes, unless it is known that the organism's calcification rate is constant throughout its life. Because the instantaneous growth rate method assumes a stable population over the time interval of sampling, its use in planktonic organisms may be best suited to estimate daily rates of production.

In coccolithophores, changes in the concentrations of particulate calcium or inorganic carbon have been used to estimate net calcification rates, typically in units of mass or moles C or $CaCO_3$ per cell or unit volume per day. This method has been used most often in cultures or mesocosms where coccolithophore calcite was the only source of $CaCO_3$ (e.g., van Bleijswijk *et al.*, 1994; Paasche, 1999). Recent advances in estimating the standing stocks of particulate inorganic carbon include in situ measurements using a birefringence method (Guay and Bishop, 2002) and the use of algorithms with satellite data (see section 4.1.4).

Sediment traps have been used extensively to estimate $CaCO_3$ export fluxes in many ocean regions (e.g., Betzer *et al.*, 1984; Fabry and Deuser, 1991; Honjo *et al.*, 1995; Wong *et al.*, 1999). As previously discussed, problems with swimmers and dissolution within the trap can confound $CaCO_3$ flux estimates, particularly when sediment traps are located in the upper 1000 m. The export fluxes measured by sediment traps are necessarily less than $CaCO_3$ production rates because they do not include $CaCO_3$ dissolution fluxes within the water column.

5.2.3 Standardization of calcification measurements

Given the diverse methods and experimental protocols used to measure calcification rates in planktonic and benthic species and systems, there is a need to standardize calcification rate measurements to allow comparison among data sets. A high priority in advancing research on the impacts of anthropogenic CO_2 on calcifying organisms is the formation of a working group charged with evaluating methods

and proposing recommendations for calcification rate measurements of planktonic and benthic organisms in laboratory, mesocosm, and field experiments. The focus of the work group should include evaluating (1) what information each method provides (e.g., gross or net $CaCO_3$ production), and (2) methods for measuring and reporting seawater chemistry and calcification rates. To maximize information exchange, the group should include scientists from both the planktonic and benthic research communities.

5.2.4 Other measurements

Many environmental factors including light (Chalker and Taylor, 1975, 1978; Barnes, 1982; Marubini *et al.*, 2001), temperature (Houck *et al.*, 1977; Coles and Jokiel, 1978; Marshall and Clode, 2004), nutrients (Hoegh-Guldberg and Smith, 1989; Stambler *et al.*, 1991; Marubini and Davies, 1996; Marubini and Thake, 1999; Ferrier-Pagés *et al.*, 2000), water motion (Atkinson *et al.*, 1994; Lesser *et al.*, 1994), food availability, and grazing can affect rates of calcification. All must be carefully controlled or monitored in well-designed experiments to avoid a misinterpretation of the results.

Another important issue is the potential effect of changing pH on the speciation of major elements besides inorganic carbon. Changes in pH can generate a cascade of dissolution and precipitation effects on minerals and chemical species that are often not considered. For example, the sensitivity of Mn and Fe minerals and adsorbed ions to small pH changes can alter their availability in the system, and these potential effects on experimental outcomes should be accounted for or considered.

6. Engaging the Scientific Community and Public

Disseminating research findings about the impacts of CO_2 on marine calcifiers to the general research community, the public, and educators is recognized as a growing responsibility of our community. As public awareness about climate change and impacts on marine ecosystems increases, so does demand for up-to-date and clear information. There are several avenues for informing the wider community, including the media, the internet, and published materials. The oceanographic community has typically used all three approaches.

6.1 Media

The media provides the most direct link between scientists and the community, but the effectiveness of how well the media conveys important scientific findings to the public is often no better than how well the scientists communicate with the media. Unfortunately, the topic of ocean acidification and how it affects marine organisms is complex and requires more explanation than, say, the atmospheric greenhouse affect. To improve our communication with the public, we therefore recommend improving media access to this topic, by involving them in scientific meetings and public discussions of our research results. Involving media students in large research projects (internships) would be a particularly effective way of promoting media accuracy, while providing the students with a unique opportunity in scientific reporting.

6.2 Web

Web-based communication of research results and issues of concern to the community is an increasingly popular education-outreach medium. In order to coordinate and streamline outreach activities we recommend support for a community-wide website dedicated to the impacts of CO_2 and climate on marine calcifiers. It should address the broad scientific issues, highlight new research findings, and provide a teaching resource for education, including K-12 educators. These efforts should also be designed within the scope of the larger U.S. Climate Change Science Program to maximize input for K-12 outreach activities, by identifying new ideas that can be developed and incorporated into a community-wide website.

6.3 Data Resources

Several websites disseminate data for studies on ocean acidification and marine calcification, for example: the Carbon Dioxide Information and Analysis Center (CDIAC; `http://cdiac.esd.ornl.gov/`), which provides a wealth of information and data related to the large-scale ocean carbon system; the NOAA Coral Reef Information System, which provides data on calcification rates derived from *Porites* cores (`http://coris.noaa.gov/metadata/records/html/paleoclimatology_masthead_2001.html`); and the USGS South Florida Information Access website, which provides data on air-sea CO_2 fluxes in Florida Bay (`http://sofia.usgs.gov/projects/geo_monitor/maps/carbon-fluxes/`). However, there is no organized effort to assimilate data resources for research on the effects of ocean acidification on marine biota. Indeed, most information derived from past and future studies on marine calcification response to ocean acidification is typically only available on a researcher-by-researcher basis.

The broad range of information that should be assimilated and made available to researchers includes publications, sampling and experimental protocols, standard hydrographic data, data from experimental results, and modeling resources. Establishing these resources is an important recommendation of this research guide, and will require dedicated resources to organize and distribute published information, obtain and quality control data, and disseminate the information via a central website. These issues should be well thought out and planned prior to any significant undertaking of research on ocean acidification and marine calcification. Successful ocean research programs in the past have benefited greatly by addressing the larger scale needs of data collection and dissemination from the outset of a research design. These programs were successful because expert teams were dedicated to ensuring proper data collection (much of which is expensive and irreproducible) and timely dissemination. We therefore recommend that future research projects include an ex-

plicit commitment to organize data resources relevant to the ocean acidification and marine calcification issue, and to establish protocols for obtaining high-quality data (e.g., standards for collection, reporting, and quality control of inorganic carbon system measurements; standards of calcification measurements; recommended experimental guidelines; as described in Section 5 of this report).

6.4 Teaching Resources

The topic of ocean acidification and its impacts on marine calcifiers is new and with relatively few specialists, and the science can be confusing. Upcoming research efforts will need to entrain young scientists in this area and to inform the public in ways that are understandable and relevant. We recommend that training of new M.S. and Ph.D. scientists and postdoctoral researchers in carbon cycle and marine ecosystem science be promoted by supporting their participation in nearly every aspect of the program and by reserving a certain percentage of slots at meetings and workshops for young scientists.

Emphasis should also be placed on encouraging constituencies and local communities to better understand the impacts of climate change on marine ecosystems, to promote informed decision making, and to increase stakeholder support for and participation in marine ecosystem conservation. Examples of education and outreach activities include: workshops and training programs with constituents to provide access and orientation to current research findings and data; planned development and distribution of educational materials and displays; fostering community involvement in conservation and restoration projects; and hosting two-way discussions with stakeholders to improve mutual understanding of resource needs and management goals.

Developing partnerships with K-12 schools, Centers for Ocean Science Education Excellence (COSEE), the National Sea Grant Program (Sea Grant) and community organizations can use educational resources and encourage stewardship throughout the community by service learning projects and other initiatives that involve teachers and parents in the process of student learning. Education programs should focus on translating the latest research into activities that help students understand the complex interactions of climate and marine ecosystems and the need for scientists from diverse backgrounds. The training of educators in the use of coral reef science and education materials should also be emphasized to ensure the effectiveness of education programs. This could be coordinated through the proposed National Ocean Education Office as recommended by the U.S. Commission on Ocean Policy (2004).

7. Conclusions and Recommendations

7.1 Impacts of Anthropogenic CO_2 in the Oceans

The uptake of anthropogenic CO_2 by the ocean changes the seawater chemistry and will significantly impact biological systems in the upper oceans. Estimates of future atmospheric and oceanic CO_2 concentrations, based on the Intergovernmental Panel on Climate Change (IPCC) emission scenarios and general circulation models indicate that atmospheric CO_2 levels could exceed 500 ppmv by the middle of the 21st century, and 800 ppmv by 2100. Corresponding models for the oceans indicate that by 2100, surface water pH will decrease by approximately 0.4 pH units relative to the preindustrial value, lower than it has been for more than 20 My. The carbonate ion concentration will also decrease by almost 50% relative to preindustrial levels. Such changes will significantly lower the ocean's buffering capacity and, therefore, reduce its ability to accept more CO_2 from the atmosphere.

Recent field and laboratory studies reveal that the carbonate chemistry of seawater has a significant effect on the calcification rates of individual species and communities in both planktonic and benthic habitats. The calcification rates of most calcifying organisms studied to date decrease in response to decreased carbonate ion concentration. This response has been observed in multiple taxonomic groups—from reef-building corals to single-celled protists. Experimental evidence points to a 5–50% reduction in calcification rate under a CO_2 level twice that of the preindustrial. The decreased carbonate ion concentration significantly reduces the ability of reef-building corals to produce their $CaCO_3$ skeletons, affecting growth of individual corals and the ability of the larger reef to maintain a positive balance between reef building and reef erosion. Several groups of calcifying plankton—coccolithophorids (single-celled algae), forams, and pteropods (planktonic molluscs)—also exhibit a reduction in their calcium carbonate structures. Many of these organisms are important components of the marine food web.

The effects of reduced calcification on individual organisms and on ecosystems have not been investigated, however, and have only been inferred from knowledge about the role of calcification in organism and ecosystem functioning. This knowledge is limited because calcification rates have only recently been considered vulnerable to increased atmospheric CO_2. Because calcification provides some advantage (or multiple advantages) to calcifying organisms, decreased calcification is likely to compromise the fitness or success of these organisms and could shift the competitive advantage toward non-calcifiers. There is also little information regarding the capacity of calcifying organisms to adapt to changing seawater chemistry. Coral reef organisms have not demonstrated an ability to adapt to decreasing carbonate saturation state, but experiments so far have been relatively short-term (hours to months). Some planktonic organisms, particularly those with rapid generation times, may be able to adapt to lowered saturation state via natural selection. Planktonic calcifiers that cannot adapt to future changes in seawater chemistry are likely to experience reductions in their geographic ranges, or latitudinal shifts. Decreased calcification in marine organisms is likely to impact marine food webs and, combined with other climatic changes in temperature, salinity, and nutrients, could substantially alter the biodiversity and productivity of the ocean.

Seawater pH is a master variable that impacts the speciation of the carbonate system, nutrients, and other major and trace element species in the oceans. It is largely unknown if, or how, various organisms will adapt to the large-scale pH changes that are anticipated over the next two to three centuries. At present, it is not possible to determine how the community structure will change or how these ecosystem changes might influence future climate feedback mechanisms. It is therefore important to develop new research strategies to better understand the long-term vulnerabilities of sensitive marine organisms to these changes. We are just beginning to understand the complex interactions between large-scale changes in ocean chemistry and marine ecological processes. Clearly, seawater carbonate chemistry is changing over decadal and longer timescales and these changes will impact marine biota.

7.2 Research Needs

Data from across the scientific disciplines support the hypothesis that marine calcification and dissolution are largely controlled by carbonate chemistry, elevating the concern that increasing CO_2 poses a considerable threat to the health of our oceans. But these data are sparse, and extrapolating results from controlled experiments to the natural environment is risky. Several workshops and reports have addressed the overall scientific issues of marine calcification under elevated atmospheric CO_2. The St. Petersburg workshop attempted to summarize these issues, identify the most important gaps in our understanding, and provide guidance toward designing research to address them.

Understanding the biological consequences of ocean acidification and placing these changes in a historical context are in the early stages. Now is the time to coordinate scientific research strategies to maximize scientific findings. This is a complex scientific undertaking, and it is essential that new research is well informed by experimentalists and observationalists in marine chemistry, biology/ecology, and geology; and experts in ocean monitoring and technology, paleoreconstructions, and modelers. It is also essential to entrain young scientists into this field, and to provide them with materials that can help guide their research.

Given the broad array of research needs, participants of the St. Petersburg Workshop recommended a research design that could be logically phased based on criteria such as: (a) the most compelling research needs; (b) research that could be done now versus that which requires longer-term planning; (c) research that requires significant technological development; and (d) research that can take advantage of ongoing field activities. **Table 7.1** lists only the most compelling research needs and should not be considered a complete list of necessary research; nonetheless it offers a framework for coordinating an overall research plan to tackle the issue of marine calcification under increasing atmospheric CO_2. Phase I represents high-priority research needs that can be initiated immediately. Phase II represents research that requires additional long-term planning and coordination, and Phase III represents research that requires some additional technological developments for success.

The St. Petersburg participants agreed on several parallel courses of research for the next 5–10 years. First, sustained observations of changes in the ocean carbon system should be continued. Second, additional field and laboratory investigations into the biological and ecological responses of calcifiers to increasing CO_2 should be conducted. Among these, long-term field manipulation experiments present the most compelling and challenging research needs. Third, these observations and experiments should be founded on a strong set of proven standards for chemical and biological measurements, and should be augmented with paleo-records and proxies that can shed light on the natural response of the system over different timescales. Fourth, simultaneous development of ecosystem models is essential if we are to translate future changes in ocean chemistry and calcification/dissolution rates to ecosystem response.

Many researchers have paved the way along these four courses toward tackling the important questions about calcification and dissolution response to increased ocean acidification. We can build on their efforts to understand the capacity for organisms and ecosystems to adapt to carbonate chemistry changes, and to predict the future of marine calcification and its feedback to the marine carbon cycle and global climate.

7.3 Research Collaborations

Collaborative research on the impacts of enhanced atmospheric CO_2 on ocean chemistry and biology needs to be accelerated at the national and international levels. Emphasis should be placed on developing a better understanding of how changes in the metabolic processes at the cellular level will be manifested within the ecosystem or community structure, and how they will influence the climate feedbacks of the future. A fully integrated system of laboratory, mesocosm, field monitoring, and modeling approaches is required to provide policymakers with informed management strategies that address how humans might best mitigate or adapt to these long-term changes.

Such efforts should complement ongoing research programs in marine biogeochemistry and ecology (e.g., OCCC, Ocean Carbon and Climate Change; SOLAS, Surface Ocean-Lower Atmosphere Study; IMBER, Integrated Marine Biogeochemistry and Ecosystem Research; SCOR, Scientific Committee for Ocean Research; etc.). Many of these programs are international. Indeed, the St. Petersburg workshop and the production of this report included substantial input from our non-U.S. partners and we strongly recommend strengthening these partnerships. Advances in carbon system and calcification measurements, in designing experimental mesocosms, in molecular studies, and in modeling, are among expertise seated across a suite of international labs. Most of the important questions outlined in the report are based on international research efforts, and should

Table 7.1: Key research activities, with a general indication of how they could be coordinated within a phased research plan.

Research Area	Activity	Phase I	Phase II	Phase III
Carbonate system monitoring	Identify key areas for monitoring	×		
	Standardize measurements, reporting	×		
	Coordinate carbonate system monitoring with existing observational systems	×		
	Increase monitoring, particularly in regions with high variability	×	×	×
	Develop technology: autonomous sensors for carbonate system and PIC; remote sensing applications		×	×
	Conduct experiments on dissolution and its response to increased CO_2 (including better understanding of thermodynamic constants for high-Mg calcite)	×	×	×
Physiology of calcification	Conduct experiments to determine the various mechanisms of calcification and the photosynthesis/calcification relationship in autotrophs and in heterotrophs with photosynthetic symbionts	×	×	×
Calcification response and organism response	Develop and standardize methods for measuring calcification rates	×		
	Investigate calcification response across multiple taxa: coccolithophorids; planktonic and benthic forams; pteropods; reef-building and deep-sea corals; *Halimeda*; coralline algae; echinoderms; bryozoans; molluscs	×	×	
	Investigate effects of multiple controls on calcification (e.g., pCO_2, T, light, nutrients)	×	×	
	Investigate potential for organisms to adapt	×	×	×
	Investigate multiple life-stages of organisms	×	×	
	Develop field-based experiments to more realistically simulate pCO_2 effects on calcification		×	
	Develop skeletal proxies for paleo-calcification analysis	×	×	
Ecosystem response	Engage benthic and planktonic ecologists and modelers to identify key needs and design research to address ecosystem response	×		
	Develop and begin long-term monitoring and/or long-term experiments on ecological communities; coordinate with existing ecological monitoring		×	×
	Develop appropriate ecosystem models for planktonic and benthic communities	×	×	×
Biogeochemical response	Open ocean—investigate ecosystem shifts and feedbacks on calcification, sedimentation, carbon cycle	×	×	×
	Quantify "reef-building" and $CaCO_3$ budgets of other benthic systems	×	×	×
	Develop technology such as remote-sensing applications		×	×

be approached with a commitment to nurture these partnerships. In addition, many of the key regions for future research are in international waters, and many interdisciplinary efforts demand that expertise be drawn from beyond U.S. borders. Above all, the urgency of understanding the potential consequences of ocean acidification on marine calcifying ecosystems demands that we design future research on this issue as efficiently as possible, which requires ignoring traditional boundaries so that efforts are complementary rather than duplicated.

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9. Acronyms

AIMS	Australian Institute of Marine Science
BATS	Bermuda-Atlantic Time Series
BBSR	Bermuda Biological Station for Research
CACGP	Commission on Atmospheric Chemistry and Global Pollution (IAMAS)
CARIACO	Carbon Retention in A Colored Ocean
CCSP	U.S. Climate Change Science Program (USGCRP)
CDIAC	Carbon Dioxide Information and Analysis Center (Oak Ridge National Laboratory, USA)
CDOM	colored dissolved organic matter; or chromophoric dissolved organic matter
CNRS	Centre National de la Recherche Scientifique (National Center for Scientific Research) (France)
COSEE	Centers for Ocean Science Education Excellence (NSF, Sea Grant, NOAA, ONR)
CRCA	Coral Reef Conservation Act (USA)
CREWS	Coral Reef Early Warning System (NOAA)
CRM	certified reference material
CSUSM	California State University San Marcos
DIC	dissolved inorganic carbon
DOE	Department of Energy (USA)
DYFAMED	Dynamics of Atmospheric Fluxes in the Mediterranean Sea (France)
EPA	Environmental Protection Agency (USA)
EPA-NCER	EPA National Center for Environmental Research
EPA-STAR	EPA Science to Achieve Results program
ESTOC	European Station for Time-series in the Ocean, Canary Islands (Spain and Germany)
FACE	Free Air Carbon Dioxide Enrichment Program (DOE Office of Biological and Environmental Research)
GC	gas chromatograph
GEOCARB	a model for the evolution of the carbon cycle and atmospheric CO_2 over Phanerozoic time
HOT	Hawaiian Ocean Time-Series
IAMAS	International Association of Meteorology and Atmospheric Sciences
ICON	Integrated Coral Observing Network (NOAA)
ICSU	International Council for Science
IGBP	International Geosphere-Biosphere Programme
IKONOS	High-spatial-resolution commercial satellite (based on “eikon,” the Greek word for “image”)
IMBER	Integrated Marine Biogeochemistry and Ecosystem Research (IGBP-SCOR Project)
IOC	Intergovernmental Oceanographic Commission
IOS	Institute of Ocean Science (Canada)
IPCC	Intergovernmental Panel on Climate Change
IPO	Interdecadal Pacific Oscillation
JGOFS	Joint Global Ocean Flux Survey
KERFIX	Kerguelen Fixed Station; Kerguelen Islands Time-Series Measurement Programme (France-JGOFS); now Climate Océanique à Kerguelen (CLIOKER; component of CLIVAR)
KNOT	Kyodo North Pacific Ocean Time-series (KNOT)
LANDSAT	NASA’s Land Remote-Sensing Satellite
LANDSAT ETM	LANDSAT Enhanced Thematic Mapper
MACC	Mainstreaming Adaptation to Climate change (NOAA)
MBARI	Monterey Bay Aquarium Research Institute
NASA	National Aeronautical and Space Administration (USA)
NCAR	National Center for Atmospheric Research (USA)
NCORE	National Center for Caribbean Coral Reef Research (EPA-NCER)
NDIR	nondispersive infrared
NOAA	National Oceanic and Atmospheric Administration (USA)
NOAA-CRED	NOAA, Coral Reef Ecosystem Division

NOAA-NESDIS	NOAA National Environmental, Satellite, and Data Information Service
NOAA-NOS NOAA	NOAA National Ocean Service
NOAA-OAR NOAA	NOAA Office of Oceanic and Atmospheric Research
NOAA-OGP	NOAA Office of Global Programs
NOAA-PMEL	NOAA Pacific Marine Environmental Lab
NSF	National Science Foundation (USA)
NSF-GG	NSF Geobiology and Low-temperature Geochemistry
NSF-LTER	NSF Long-Term Ecological Research
NSF-MGG	NSF Marine Geology and Geophysics
NSF-OCE-BIO	NSF Ocean Sciences, Biological Oceanography Program
NSF-OCE-CHE	NSF Ocean Sciences, Chemical Oceanography Program
OACES	Ocean-Atmosphere Carbon Dioxide Exchange Study (NOAA)
OCCC	Ocean Carbon and Climate Change (USGCRP-CCSP)
ONR	Office of Naval Research (USA)
OSP	Ocean Station Papa (Canada)
OWS	Ocean Weather Station (Canada)
PETM	Paleocene-Eocene Thermal Maximum
PIC	particulate inorganic carbon
POC	particulate organic carbon
RSMAS	Rosenstiel School of Marine and Atmospheric Science (University of Miami, USA)
SCOR	Scientific Committee on Ocean Research (ICSU; non-governmental)
SHARQ	Submersible Habitat for Analyzing Reef Quality (USGS)
SOCM	Shallow Ocean Carbon Model (Mackenzie)
SOIREE	Southern Ocean Iron Enrichment Experiment (multi-national)
SOLAS	Surface Ocean–Lower Atmosphere Study (IGBP, SCOR, WCRP, CACGP)
SOMMA	single-operator multiparameter metabolic analyzer
TAO-TRITON	Tropical Atmosphere Ocean Project (NOAA) and Triangle Trans-Ocean Buoy Network (Japan)
TEP	transparent exopolymer particles
UNESCO	United Nations Educational, Scientific and Cultural Organization
USGCRP	U.S. Global Change Research Program
USGS	U.S. Geological Survey (USA)
USGS-CCWS	USGS Center for Coastal and Watershed Studies
WCRP	World Climate Research Programme
WOCE	World Ocean Circulation Experiment (WCRP)

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