



Possible effects of ocean acidification on coral reef biogeochemistry: topics for research

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ABSTRACT: This paper is a short review of recent literature on how ocean acidification may influence coral reef organisms and coral reef communities. We argue that it is unclear as to how, and to what extent, ocean acidification will influence calcium carbonate calcification and dissolution, and affect changes in community structure of present-day coral reefs. It is critical to evaluate the extent to which the metabolism of present-day reefs is influenced by mineral saturation states, and to determine a threshold saturation state at which coral communities cease to function as reefs.

KEY WORDS: Ocean acidification · Climate change · Coral reefs · Biogeochemistry

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INTRODUCTION

Ocean acidification is the progressive increase in hydrogen ions (H^+) in the world's oceans as a result of rising partial pressure of atmospheric carbon dioxide (CO_2), i.e. a decrease in seawater pH, where $pH = -\log_{10}[H^+]$; see Dickson (1984) for a review of the different pH scales for seawater. As atmospheric carbon dioxide has increased as a result of the burning of fossil fuels, increasing amounts of CO_2 have entered the ocean and reacted with water (Sabine et al. 2004). When CO_2 gas reacts with water, carbonic acid is formed and the ocean becomes progressively more acidic ($CO_2 + H_2O = H_2CO_3 = HCO_3^- + H^+ = CO_3^{2-} + 2H^+$), driving the CO_2 chemical equilibrium toward CO_2 and HCO_3^- , reducing CO_3^{2-} , the carbonate ion.

Several oceanic feedback loops buffer pH, but presently these buffering mechanisms are considered relatively small, and will not counteract the falling pH over the next 100 yr (Andersson et al. 2006, 2007). CO_2 gas influx and efflux between oceans and atmosphere are large terms in the overall oceanic carbon budget, with substantial errors (Houghton 2007). Nevertheless, the scientific community has observed an estimated decrease of 0.1 pH units in the surface ocean in the last 100 yr and current trends in atmospheric CO_2 partial

pressure project a further change of 0.3 to 0.4 pH units over the next 100 yr (Sabine et al. 2004, Orr et al. 2005). The above calculations are based on a stable total alkalinity. Thus, over the next 100 yr, CO_2 gas dissolved in tropical oceans is expected to increase 200 to 250 %, and CO_3^{2-} is expected to decrease 35 to 50 %, reducing the saturation state of seawater with respect to calcium carbonate minerals (Orr et al. 2005).

The saturation state of seawater for a mineral (Ω) is a measure of the thermodynamic potential for the mineral to form or to dissolve; specifically it is the product of the concentrations (or activities) of the reacting ions that form the mineral (Ca^{2+} and CO_3^{2-}), divided by the product of the concentrations of those ions when the mineral is at equilibrium (K_{sp}), that is, when the mineral is neither forming nor dissolving:

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \quad (1)$$

when $\Omega > 1.0$, the formation of the mineral is thermodynamically favorable; when $\Omega < 1.0$, the dissolution of the mineral is favorable. Aragonite Ω (Ω_{arag}) of surface seawater is expected to decrease throughout the tropics from the present-day values of 3 to 3.5 to 2 to 2.5 in 100 yr; and the ratio of dissolved CO_2 gas to CO_3^{2-} will increase by a factor of 4 (Orr et al. 2005).

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Based on principles of thermodynamics, the rate of formation of carbonates is positively correlated to Ω ; this pervading principle has been central to biological and chemical production, distribution and dissolution of carbonates in the oceans (Feely et al. 2004, Zachos et al. 2005), as well as tropical coastal seas (Broecker et al. 2001, Morse et al. 2003). Thus, there has been a long standing observation that the distribution of coral reefs is highly correlated to Ω_{arag} in the ocean, implying that the limits of coral reef formation may not be controlled solely by temperature, light, salinity or substrate availability (Grigg 1982, Smith & Buddemeier 1992, Buddemeier & Fautin 1996). Further investigations have explicitly stated that Ω_{arag} , together with light and temperature, set boundaries for coral reef biogeography (Kleypas et al. 1999a). The present paper will discuss the effects of ocean acidification on coral reefs from the above estimates of changes in pH and CO_2 equilibria.

There are 2 possible major effects of the changing ratio of CO_2 gas to CO_3^{2-} on coral reefs: (1) changes in organism and community rates of calcification and dissolution, and (2) changes in relative metabolism of autotrophs, cyanobacteria and bacteria, which in turn have the potential to alter community structure and biogeochemical cycles.

CALCIFICATION

Impact of decreasing saturation state on organismic calcification rates

Saturation state has been shown to affect growth in calcifying green algae, crustose coralline algae and corals (reviewed by Kleypas & Langdon 2006). The first estimates of total pre-industrial to 2100 reef calcification decreases were 17 to 40% (Gattuso et al. 1999, Kleypas et al. 1999b). With increasing sea surface temperature (SST) and reduced Ω , there is concern that coral reefs may soon reach a threshold of 'no return', losing corals and other calcifiers, becoming dead carbonate platforms covered in macro-algae (Hoegh-Guldberg et al. 2007). Several studies have observed thresholds of coral growth and coral reef development at $\Omega = 3.0$ to 3.3 based on the geographic distribution of coral reefs (Kleypas et al. 1999b, Guinotte et al. 2003, Hoegh-Guldberg et al. 2007, Buddemeier et al. 2008). Considering the enormity of the postulated impact, it is crucial to continue research into how Ω influences the growth of a variety of different taxa. There are many questions remaining to be answered, however, before thresholds of growth/calcification can be established. For example, responses of coral to Ω vary between experiments (see Langdon & Atkinson 2005, their

Fig. 9). Thus, we suggest several avenues of research (next subsections), all towards understanding how Ω affects the basic calcification mechanism, and trying to establish some confidence in a particular value of Ω at which reefs might degrade.

Saturation state versus co-varying parameters

Although coral calcification is unquestionably influenced by Ω , it is not clear whether calcification is also responding to other co-varying parameters, such as pH, HCO_3^- or pCO_2 . For example, in some cultures of *Emiliania huxleyi* (a carbon-limited coccolithophore) grown under high pCO_2 and high nutrients, inorganic and organic carbon production and cell size were enhanced despite the decrease in calcite Ω (Ω_{calc}) (Iglesias-Rodriguez et al. 2008). Thus, concerns have arisen regarding experiments using only HCl to decrease pH, without further addition of bicarbonate to offset the drop in total alkalinity. Achieving reduced pH by CO_2 bubbling or by combinations of both acid and bicarbonate to maintain constant alkalinity, is thought to better mimic future CO_2 scenarios.

The extent to which increased dissolved inorganic carbon (DIC) can counteract the effect of decreasing Ω on coral calcification is considered moderate (Kleypas & Langdon 2006) because (1) HCO_3^- (the substrate for photosynthesis) will increase only about 14% under doubled pCO_2 conditions; (2) increased pCO_2 is usually assumed to have little or no effect on photosynthesis (Reynaud et al. 2003, Schneider & Erez 2006); (3) it is not evident that an increase in photosynthesis will necessarily lead to increased calcification (discussed by Kleypas & Langdon 2006). Some studies have, however, shown an enhancement of coral growth (calcification) after an increase in DIC (Marubini & Thake 1999, Schneider & Erez 2006, Herfort et al. 2008), suggesting that the ambient DIC concentration of seawater may limit the calcification rates of hermatypic corals. In some experiments, an increase in DIC concentration also resulted in an increase in photosynthesis (Herfort et al. 2008, Marubini et al. 2008). Marubini et al. (2008) recently reported that *Stylophora pistillata* nubbins grew faster in bicarbonate-enriched seawater independent of pH conditions (pH 7.6 to 8.2). Thus, it is essential that studies of coral calcification and acidification report details of the DIC parameters and not only pH.

Mechanism of coral calcification

Inadequate understanding of the mechanism of coral calcification limits our ability to provide an accurate prediction of the effect of increasing atmospheric CO_2

(Gattuso et al. 1999). It is still not well understood how the elemental composition and physical chemistry of the external environment interacts with biological control under different saturation state conditions (Cohen et al. 2006). In hermatypic corals, the supply of Ca^{2+} , as well as HCO_3^- derived from host tissue respiration (via a carbonic anhydrase), are biologically controlled (Allemand et al. 2004). Geochemical models (e.g. Adkins et al. 2003, Gaetani & Cohen 2006, Sinclair & Risk 2006), however, have considered diffusion of CO_2 across the calcicoblastic epithelium, and passive entry of seawater, e.g. through pericellular channels (see Cohen & McConnaughey 2003). The level of control of skeletal organic compounds (the organic matrix synthesized by the calcicoblastic cells) over the chemistry and growth of coral skeleton is also a topic of debate (Meibom et al. 2007). Thus, considering these models of coral calcification, there is still some question as to why external concentrations of carbonate should have such a strong effect on calcification.

Even though calcification observed under light is greater than that under dark conditions (reviewed by Gattuso et al. 1999), the relationship between calcification and Ω appears to have a similar slope in both the light and the dark (Ohde & Hossain 2004, Schneider & Erez 2006). One interpretation of this evidence is that a simple diffusion pathway must exist, possibly revealing an increase in the flux of bicarbonate from enhanced light respiration (see discussion in Marubini et al. 2008). Based upon morphological evidence, the calcicoblastic cell layer is regarded as a 'tight' epithelium, reducing the ability of Ca^{2+} and CO_3^{2-} to diffuse away via a paracellular route (Clode & Marshall 2002). An increase in outward diffusion of carbonate when external carbonate is low cannot be dismissed, however. A decrease in pH may affect different cellular processes, e.g. anionic permeability (Gattuso et al. 1999), or pH regulation during the calcification process (Marubini et al. 2008). Indeed, H^+ ions produced during calcium carbonate precipitation ($\text{HCO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 + \text{H}^+$) are removed from the calcification sites by an energy-dependent carrier (Ca^{2+} -ATPase), thereby increasing Ω (see reviews by Cohen & McConnaughey 2003, Allemand et al. 2004).

Studies are needed that focus on the physico-chemical characteristics of the sub-calicoblastic space under different saturation state conditions, or on actual morphological features connecting the calcicoblastic cells to seawater. For example, Tambutté et al. (2007) report that some tissues calcifying at the highest rates in *Stylophora pistillata* consist only of ectodermal cell-layers separated by mesoglea. It would be informative to determine whether these observations give more clues about the mechanism of coral calcification. The magnitude of the response to low Ω seems to be constant

between coral species (Marubini et al. 2003). There should be, however, further effort to compare taxa with differing sensitivities to external saturation state.

Interaction with other parameters

Hermatypic coral calcification is a strong function of light (Gladfelter 1984, Allemand et al. 2004), shows temperature optima (Marshall & Clode 2004), and is affected by nutrients (Tanaka et al. 2007) and particulate feeding (Houlbrèque et al. 2003), yet there are no studies on the effects of Ω that adequately control all 4 of these variables. The magnitude of the effect of Ω on calcification increases with increasing light and temperature (Marubini et al. 2001, Reynaud et al. 2003). When nutrients are added to the waters surrounding corals, however, the corals become less sensitive to Ω (Atkinson et al. 1995, Langdon & Atkinson 2005, selected data from their Fig. 5), perhaps because symbiotic dinoflagellates (*Symbiodinium* spp.) enhance calcification by providing the biochemical precursors of the organic matrix (Muscatine et al. 2005). Nutrient loading, typical of that seen in the field, increased the Ω threshold for calcification of a mixed coral community from 1.5 to 1.0 (recent experiments, unpublished, Fig. 1). This coral community dominates in Hawaii, and calcifies at $\Omega < 3.0$,

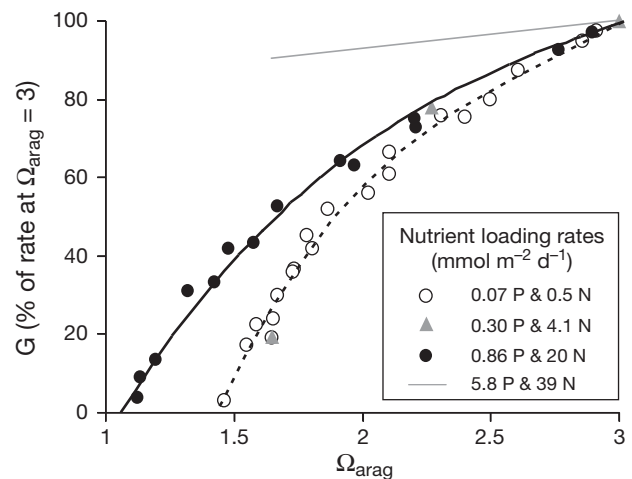


Fig. 1. Effect of nutrient loading on coral calcification rate (G). Coral communities (0.3 m^2 ; *Montipora capitata*, *Porites compressa* and *Pocillopora damicornis*) were placed in a wave flume with equal light, gross primary production, water motion and initial aragonite saturation state (Ω_{arag}). Nutrient loading was varied from extremely low values to those representative of field conditions. The closed black circles (black line) represent communities that were given natural nutrient loading rates and the open circles (dashed line) are low nutrient conditions. The grey triangles and the grey line are data from Langdon & Atkinson (2005) for a nutrient loading experiment with the same species. Data are normalized to $\Omega_{\text{arag}} = 3.0$ for intercomparison. The nutrient loading rates are in the key

contrary to calcification threshold values stated in Budemeier et al. (2008). Also, nutrient loading as particles often increases skeletal growth (Bongiorni et al. 2003, Houbrèque et al. 2003, Shafir et al. 2006), but no study to date has assessed the possible interactions between feeding and Ω . It is our suspicion that many experiments have been performed in low light, relatively starved conditions, with extremely low pH. Future studies should report nutrient and particulate loading as well as optimal light intensities in order to assess the nutritional status of the corals. More research is needed on the effects of Ω , under natural field conditions, for a variety of coral reef calcifying organisms (Schneider & Erez 2006). These are difficult experiments and require improved facilities to control the environmental variables. Data on a variety of taxa may then be synthesized to present a threshold at which corals do not grow (and at which changes in community structure may prove to be unavoidable).

Anthony et al. (2008) reported increased sensitivity of corals to bleaching as a result of acidified seawater conditions. One possible explanation for the loss of zooxanthellae is that high CO_2 reduces the efficiency of Ru-BisCO (maximum activity at pH 9) to react with oxygen radicals, leaving more oxygen radicals to stimulate bleaching in coral tissue. Other interpretations may relate to the greater efficiency of *Symbiodinium* spp. under carbon-rich conditions, and the resulting compensatory reduction in symbiont number (i.e. bleaching). These observations are contrary to published experiments and observations in which corals were grown at very low pH (7.2 to 7.8) without bleaching (Atkinson et al. 1995, Marubini & Atkinson 1999). Clearly, there appears to be a diversity of responses from corals that requires further investigation.

Community calcification

Are communities of corals showing effects of Ω in the field? This question was addressed by Kinsey in the 1970s. He tried to find some latitudinal variation in calcification, correlating with mean temperature and Ω , and instead developed the concept of standard metabolism and reef zonation, controlled largely by hydrodynamics (Kinsey 1979, 1985). Kinsey made a strong case that community structure and corresponding zonation gave characteristic rates of calcification (reviewed in Atkinson & Falter 2003). Calcification rates vary by an order of magnitude within a coral reef, from areas that have rich coral communities to other areas that are flat and just consist of sand. The higher the 3-dimensional relief of the benthic community, the greater is primary productivity and calcification. In general, daily calcification rates are about 15 to 20% of the gross primary

production (Kinsey 1985, Gattuso et al. 1999). Thus, coral reef calcification and coral calcification are strongly a function of gross productivity, even at the scale of a polyp (Al-Horani et al. 2005). It is now assumed that reef calcification is proportional to both gross primary productivity and Ω (Nakamura & Nakamori 2007), but it is not clear to what extent Ω actually affects a whole reef. When a lack of storm damage allows the maintenance of high productivity community structure, by lack of storm damage, rising sea-level and warming temperatures may be more important than small changes in Ω . These issues are clearly important and should be the focus for future research.

Evidence of an effect of Ω on community calcification in the field is still scarce. In a seasonal study, calcification was correlated to Ω (Silverman et al. 2007), however, Ω was also correlated to seasonal changes in temperature, light and nutrients, and it was difficult to identify the forcing parameter. The model for calculating calcification was also based on salinity changes between nearshore and offshore sampling sites and made all variables dependent. Yates & Halley (2006), using a large closed chamber on a reef flat in Hawaii, reported rates of dissolution and calcification as a function of Ω . Their results were quite variable and it was difficult to set a single Ω threshold value. They showed an enhancement of calcification at high Ω , but it is not clear in their study whether calcification was responding to increased productivity or elevated Ω within the chamber. Studies on growth of large *Porites* spp. in the Great Barrier Reef show both inter-decadal increases and decreases in calcification per surface area (Cooper et al. 2008). These data are difficult to interpret on an ecological basis (see Lough 2008, this Theme Section). As a single coral head grows larger (more convoluted and oblique to the light field) light absorption per area decreases (Stambler & Dubinsky 2005). This effect probably reduces calcification per surface area of the coral, even though calcification per planar area of reef may be increasing. There is large variability in environmental light quantity and quality due to day-length, cloud-cover and water turbidity, thus changes in calcification rate per surface area of coral tissue can change daily, seasonally, and even within decades, making it difficult to link coral growth to changes in temperature and Ω .

One of the key issues underlying our understanding of the impact of ocean acidification is how to evaluate the impact of Ω on reef calcification under field conditions. Field studies must obviously involve measurement of light, productivity and respiration. We suggest a comprehensive experiment involving several reefs with different Ω s, to determine how the relationship between primary productivity and calcification is

affected or controlled by temperature, Ω and nutrient input. If calcification is decreasing with respect to Ω , then on a large reef scale, independent of detailed community structure, we should be capable of producing a derivative calcification ratio, G:P (slope of calcification = $f(\text{gross primary production})$) related to Ω . With present technology, it is possible to evaluate calcification and productivity on large reef scales, combining all zones and communities by using a combination of *in situ* measurements, hydrodynamic models and remote sensing products. *In situ* chemical measurements and accurate hydrodynamic models (e.g. Lowe et al. 2008) can be used to measure calcification rates of large areas of coral reefs and remote sensing products are being developed for reef productivity (Hochberg & Atkinson 2007).

Dissolution of calcium carbonates

The solubilities of high-Mg carbonates from natural reef environments are not well determined (Morse et al. 2006). These carbonates are abundant on reefs and form a significant part of the framework, thus, it is important to determine the Ω or pH at which these minerals will dissolve. There are conflicting views as to the extent to which the Ω of overlying seawater can influence dissolution in sediments. Manzello et al. (2008) showed increased dissolution in the Eastern Tropical Pacific, suggesting that this is from low-pH upwelled water, while Andersson et al. (2007) showed high-Mg calcites were dissolving in Bermuda from natural changes in Ω , but with little difference compared to other places; they pointed out the influence of naturally low pH in sediments. A primary direction of research is to understand the dissolution of these carbonates in a natural system.

Bio-erosion by endolithic phototrophs, which inhabit every available carbonate substrate, should also be better quantified. The endolithic chlorophyte *Ostreobium quekettii* increased its depth of penetration under $p\text{CO}_2$ of 750 μatm (Tribollet et al. in press), suggesting increased biogenic carbonate dissolution under high $p\text{CO}_2$.

EFFECTS ON BIOGEOCHEMICAL CYCLES, AND COMMUNITY STRUCTURE SHIFTS

Carbon and nutrients

It is very likely that increased CO_2 will alter the relative growth and efficiency of different groups of organisms (Phytoplankton, Riebesell et al. 2007; Cyanophytes, Levitan et al. 2007; Seagrass, Palacios &

Zimmerman 2007). For example, the net photosynthetic rates of epilithic coralline algae decreased in 750 μatm $p\text{CO}_2$, while endolithic communities remained constant (Tribollet et al. 2006). Increased $p\text{CO}_2$ may stimulate growth of algae that do not have carbon-concentrating mechanisms (Kaplan & Reinhold 1999). It is usually assumed that macro-algae as a group will exhibit little photosynthetic response to increasing $p\text{CO}_2$, because most of them possess carbon-concentrating mechanisms. However, some species are carbon-limited with the current levels of dissolved inorganic carbon in seawater (see references in Zou 2005). It is also suggested that the energy used for carbon-concentrating mechanisms can be used for growth when $p\text{CO}_2$ is high (Levitan et al. 2007).

Faster growth under high $p\text{CO}_2$ may increase C:N:P ratios of macro-algae, further providing relatively low quality food to herbivores. Uptake of phosphate and nitrogen compounds are generally under hydrodynamic control (Atkinson & Falter 2003), thus it is unlikely that increased net production would stimulate increased nitrogen uptake. If this response occurs, then coral reefs may shift to higher export of organic matter, deposition and bacteria remineralization in back-reef areas, creating zones of anoxia. There may also be more export of dissolved organic matter. This scenario would suggest less carbon of higher quality moving up and through the foodweb. On the other hand, it is also quite possible that increased growth of nitrogen fixing cyanobacteria may enhance nitrogen fixation (Levitan et al. 2007). Nitrogen fixation can be a large source of nitrogen to some reefs, thus an increase in nitrogen fixation may further enhance photosynthetic efficiencies and net production. There may be major shifts in the biogeochemistry of reefs, yet we know very little how nutrient cycles are presently coupled to carbon cycles, nor how different groups of algae compete for scarce nutrients.

Community structure

The recruitment rate and growth of crustose coralline algae is severely inhibited under elevated $p\text{CO}_2$, suggesting changes in benthic community structure may occur owing to the impact of ocean acidification on recruitment and competition for space (Kuffner et al. 2008, Jokiel et al. 2008). At a shallow coastal site in the Mediterranean where vents of volcanic carbon dioxide reduce seawater pH (pH 7.8 to 7.9), non-calcareous algae proved to be resilient to naturally high $p\text{CO}_2$, replacing typical rocky shore communities (pH 8.1 to 8.2) with >60% cover of Corallinaceae (Hall-Spencer et al. 2008). In the mesocosm experiment performed by Jokiel et al. (2008), however,

the space made available from the reduction in crustose coralline algae cover was not colonized by non-calcifying algae (e.g. turfs). Any advantage of non-calcifying algae under high $p\text{CO}_2$ could be offset by increased herbivory (Jokiel et al. 2008). With reductions in crustose coralline algae, coral recruitment may be affected (Hoegh-Guldberg et al. 2007), but coral spawning and recruitment were not affected under elevated $p\text{CO}_2$ (Jokiel et al. 2008). Some scleractinian coral species were also found to survive from decalcification as polyps in the laboratory, including normal gametogenesis (Fine & Tchernov 2007).

These experiments are just the beginning to our understanding of the complex response of coral reefs to ocean acidification. Undoubtedly, ocean acidification will create major shifts in community structure that will certainly affect communities of grazers. We suggest developing an enclosed high- $p\text{CO}_2$ natural coral reef mesocosm, in which synergistic effects of different organisms responding to changes in water chemistry can be observed. In this way, organismal calcification, growth and competition can be compared with changes in community structure. Also direct measurements and observations of calcium carbonate mineral dissolution in sediments can be achieved.

RECOMMENDATIONS FOR RESEARCH

A coordinated research effort is required to understand and ascertain whether a decrease in Ω will alter the community structure and function of coral reefs. It is now accepted that dissolved inorganic carbon species are very important chemical parameters of the function of a variety of key taxa comprising coral reefs, but our understanding is limited and quantification almost non-existent. The next challenge is to understand how both organismal and community metabolism interact with dissolved inorganic carbon chemistries. This effort will require a new generation of experimental facilities and instrumentation for reefs. Some suggestions for research directions are to:

- (1) continue to evaluate the effects of bicarbonate and carbonate ions on growth and calcification of key taxa, under environmental realistic conditions of light, temperature, nutrients and dissolved inorganic carbon;
- (2) study the morphology of carbonate calcification, looking for the structural detail at the sites of calcification;
- (3) develop an improved model for coral calcification;
- (4) conduct studies on high-Mg carbonate solubility constants for naturally occurring carbonates on coral reefs;
- (5) develop several natural coral reef mesocosms, complete with sediments, to observe whole system changes and community structure competition;

- (6) develop a program to evaluate the relationships between community metabolism and calcification at several coral reefs with different Ω s, and test whether present naturally-varying Ω drives community calcification rates;

- (7) expand efforts in monitoring basic CO_2 parameters on a number of coral reefs worldwide, in conjunction with basic community structure data. These do not have to be continuous but must span decades;

- (8) study effects of pH on a variety of algae, including endoliths, as well as key species of nitrogen fixing cyanobacteria.

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