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Effect of calcium carbonate saturation of seawater on coral calcification

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Abstract

The carbonate chemistry of seawater is usually not considered to be an important factor influencing calcium-carbonate-precipitation by corals because surface seawater is supersaturated with respect to aragonite. Recent reports, however, suggest that it could play a major role in the evolution and biogeography of recent corals. We investigated the calcification rates of five colonies of the zooxanthellate coral *Stylophora pistillata* in synthetic seawater using the alkalinity anomaly technique. Changes in aragonite saturation from 98% to 585% were obtained by manipulating the calcium concentration. The results show a nonlinear increase in calcification rate as a function of aragonite saturation level. Calcification increases nearly 3-fold when aragonite saturation increases from 98% to 390%, i.e., close to the typical present saturation state of tropical seawater. There is no further increase of calcification at saturation values above this threshold. Preliminary data suggest that another coral species, *Acropora* sp., displays a similar behaviour. These experimental results suggest: (1) that the rate of calcification does not change significantly within the range of saturation levels corresponding to the last glacial-interglacial cycle, and (2) that it may decrease significantly in the future as a result of the decrease in the saturation level due to anthropogenic release of CO_2 into the atmosphere. Experimental studies that control environmental conditions and seawater composition provide unique opportunities to unravel the response of corals to global environmental changes.

Keywords: Scleractinan corals; calcification; carbonate chemistry; global change

1. Introduction

Human activities increase the atmospheric CO_2 partial pressure (pCO_2), mostly through fossil fuel utilization, cement production and biomass burning. Approximately half of the released CO_2 remains in the atmosphere, presently increasing pCO_2 at a rate of 0.4% yr^{-1} (Houghton et al., 1996). The remaining CO_2 is stored in terrestrial biomass by photosynthetic CO_2 uptake and in the ocean through air–sea CO_2 exchange which tends to equilibrate pCO_2 across the air–sea interface. The amount of CO_2 stored in both sinks is not well known (Sarmiento, 1995) but it appears that the global ocean presently increases its storage of CO_2 by 1.7 ± 0.9 Pg C yr^{-1}

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(Keeling et al., 1996). CO_2 uptake by surface seawater increases the concentration of dissolved inorganic carbon and decreases pH. The saturation of seawater with respect to calcium carbonate (calcite and aragonite) is defined as the ratio of the ion activity product to the stoichiometric solubility product (Morse and Mackenzie, 1990).

If the saturation equals 100%, the solid and solution are in equilibrium; if it is lower than 100%, the solution is undersaturated and dissolution can occur; and if it is greater than 100%, the solution is supersaturated and precipitation can occur (Morse and Mackenzie, 1990). The aragonite saturation state decreases as a function of decreasing pH and it has been estimated that a doubling of the preindustrial pCO_2 could reduce tropical sea surface carbonate saturation levels to about two-thirds of present values (Smith and Buddemeier, 1992).

Seawater carbonate chemistry also displayed significant changes in the past. It is virtually certain that the oceanic surface waters have been supersaturated or saturated with respect to calcite and aragonite since early Precambrian time (Holland, 1984). However, evolution of calcifying organisms and the appearance of the various forms of calcium carbonate (calcite, aragonite, Mg–calcite) in the geologic record have been linked to the evolution of saturation levels in the oceanic geochemical system (Mackenzie and Agegian, 1989). In terms of more recent changes, the estimated decrease of surface water pH by 0.2 ± 0.1 units in the tropical Atlantic and Pacific Oceans between glacial age and the Holocene (Sanyal et al., 1995) has certainly affected the carbonate saturation level.

Such past, present and future changes in the seawater carbonate chemistry may have several implications for rates of photosynthetic CO_2 fixation (photosynthesis) and $CaCO_3$ precipitation (calcification) of marine organisms and ecosystems. CO_2 fertilization may increase productivity, as has been shown in most terrestrial plants and certain marine macrophytes (Bowes, 1993). It has also been repeatedly suggested during the past few years that carbonate saturation state may control calcification both at the ecosystem and organism scales because the rate of deposition of a mineral from solution is controlled, at the cellular level, by the degree of saturation in addition to solubility, nucleation and crystal growth (Mann, 1986). Broecker and Takahashi (1966) discussed the possibility of saturation control on the precipitation of calcium carbonate on the Bahama banks. Smith and Pesret (1974) investigated the community metabolism of the Fanning Island atoll lagoon and suggested that the carbonate mineral saturation state may influence the rate of $CaCO_3$ precipitation in calcifying ecosystems. This possibility has been discussed further (e.g., Smith and Buddemeier, 1992; Buddemeier, 1994; Buddemeier and Fautin, 1996a,b; Holligan and Robertson, 1996), although there remains a paucity of experimental data on coral reef organisms, and the most definitive experimental information has been obtained on marine calcareous algae (Mackenzie and Agegian, 1989; Gao et al., 1993a) and zoospores of freshwater algae (Hepperle and Krienitz, 1997). Additionally, some authors have assumed that community calcification in coral reefs is a linear function of aragonite saturation (Suzuki et al., 1995).

Smith and Buddemeier (1992) concluded that: ''we clearly know very little about the links between atmospheric CO_2, marine benthic productivity, and marine calcification; and available information is partially contradictory. Growth-rate and metabolic experiments that carefully and explicitly define and control aqueous CO_2 chemistry are required...''.

The objective of the present paper is to investigate the effect of calcium carbonate saturation state on the calcification rate of two reef-building corals maintained under controlled laboratory conditions. Since manipulation of saturation state by changing the inorganic carbon system equilibrium might have confounding effects on coral photosynthesis and its effect on calcification, the experiments controlled saturation state through the calcium concentration in artificial seawater.

2. Materials and methods

Branches were cut from six different parent colonies of the zooxanthellate scleractinian corals *Stylophora pistillata* (Esper, 1797) and one parent colony of *Acropora* sp. several months prior to the experiments, attached to nylon string and suspended in aquaria supplied with Mediterranean seawater (exchange rate: ca 2% h^{-1}). The healing process took

3–4 weeks, after which the specimens were completely surrounded by living tissue. Specimens were approximately rod-like in form, with dimensions in the range of 3–5 cm and skeletal weights in the range of 7.2–25.7 g. Culture conditions were: $S = 38.5$; temperature = 27 ± 0.5°C; aragonite saturation = ca. 360%, photosynthetic photon flux density = ca. 450 μmol m^{-2} s^{-1} (metal halide lamp, Philips HPIT 1000 W); photo-period = 12:12.

For an experimental run, five branches of *S. pistillata* (one from each parent colony) and one branch of *Acropora* sp. were transferred into individual 250-ml beakers and incubated for 2.5 h in synthetic seawater (SSW) of controlled aragonite saturation level, under environmental conditions otherwise similar to the culture conditions. Another branch of *S. pistillata*, sampled from a different parent colony, served as a control and was simultaneously incubated in Millipore (0.45 μm) filtered Mediterranean seawater at the same temperature and light conditions. The total experimental sequence consisted of five such runs, at aragonite saturation levels of 390, 98, 585, 293 and 195%, in the sequence indicated.

The incubation media were stirred continuously and a transparent plastic film was placed over each beaker in order to reduce evaporation. SSW was freshly prepared, a few hours prior to the experiments, as described by DOE (1994) but adapted to a salinity of 38.5 and an inorganic carbon content of 2.008 mmol kg^{-1}. The calcium concentration was set to 25, 50, 75, 100 or 150% the natural concentration (ca. 11.4 mmol kg^{-1}). SSW composition was determined as follows (Table 1): (1) the concentration of $CaCl_2$ was set according to the desired aragonite saturation level, (2) both Na_2CO_3 and HCl were added in order to obtain the desired values (i.e., close to Mediterranean levels) of dissolved inorganic carbon (DIC) and total alkalinity (TA) and (3) the NaCl concentration was then adjusted to respect the chlorinity (and the salinity).

All chemicals used were reagent grade (Merck). $CaCl_2$ and $MgCl_2$ were added volumetrically, using a Mettler DL 70 titrator, after accurate determination of densities and concentrations of stock solutions (Mohr titration). HCl (0.1 N) was also added volumetrically. TA was checked on freshly prepared SSW; experimental values were within 2 μeq kg^{-1} of the theoretical values. Preliminary experiments showed that the stability of a SSW saturated at 300% with respect to aragonite was longer than 24 h. Strontium concentration was measured using an ICP-MS; it was much lower in SSW than in Mediterranean seawater (0.9 vs. 105 μmol kg^{-1}).

Parameters of the inorganic carbon system were calculated using the CO_2 constants from Goyet and Poisson (1989), the CO_2 solubility coefficient from Weiss (1974) and the aragonite saturation constants from Morse et al. (1980). The pH electrode (Orion, 81-02) was calibrated daily using TRIS and AMP buffers (Dickson, 1993) and pH was expressed on the seawater scale (SWS).

Rates of calcification were estimated from the changes in total alkalinity (TA) during the course of

Table 1
Composition (mol kg^{-1}) of synthetic seawater (SSW) based on the recipe provided by DOE (1994) (SSD) and adapted for inorganic carbon

	SSD	SSW		Comment
		50% Ca	100% Ca	
NaCl	0.453893	0.463532	0.452136	$[NaCl]_{SSW} = [NaCl]_{SSD} + 2([CaCl_2]_{SSD} - [CaCl_2]_{SSW}) - [HCl]_{SSW}$
$CaCl_2$	0.011396	0.005698	0.011396	$[CaCl_2]_{SSW} = 0.01$ (%sat) $[CaCl_2]_{SSD}$
KCl	0.011231	0.011231	0.011231	
Na_2SO_4	0.031064	0.031064	0.031064	
$MgCl_2$	0.058113	0.058113	0.058113	
Na_2CO_3	0	0.002008	0.002008	$[Na_2CO_3]_{SSW} = DIC$
HCl	0	0.001757	0.001757	$[HCl]_{SSW} = 2DIC - TA$

DIC: dissolved inorganic carbon; TA: total alkalinity; %sat: aragonite saturation.
Salinity = 38.5, DIC = 2008 μmol kg^{-1}, TA = 2259 μeq kg^{-1}.

the incubation using the alkalinity anomaly technique (Smith and Key, 1975) and normalized with the protein content. TA was measured using a potentiometric titration as described by Gattuso et al. (1993). Upon completion of all experiments, proteins were solubilized in 1 N NaOH at 90°C for 30 min. Samples were allowed to cool, neutralized with 1 N HCl and the protein content was measured using the method given by Bradford (1976) against a series of bovine gamma globulin standards. The response curve of the rate of calcification vs. aragonite saturation was modelled using nonlinear regression techniques with the shareware package MacCurveFit 1.3. Statistical testing was performed with JMP 3.1.6 (SAS Institute, Cary, USA). Results are reported as mean ± standard error of the mean (SE). N is the sample size.

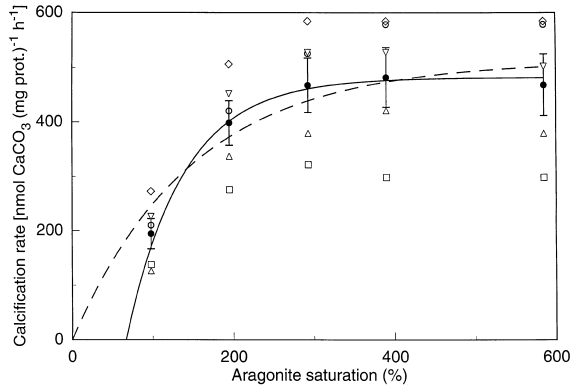

Fig. 1. Calcification rate of colonies of *S. pistillata* as a function of aragonite saturation (open symbols). Average calcification rates (●) are displayed ±1 standard error of the mean. The average relationships forced (dashed line) or not forced (continuous line) through the origin are shown. The corresponding curve fitting parameters are given in Table 3.

3. Results

Experimental results are summarized in Table 2. The calcification rate of the control colony of *S. pistillata* changed by only 13% (at most) during the course of the experiment [20 days; 784–882 nmol $CaCO_3$ (mg prot.)$^{-1}$ h^{-1}] and was, on average, 833 ± 18 nmol $CaCO_3$ (mg prot)$^{-1}$ h^{-1} ($N = 6$). The rate of calcification of *S. pistillata* and *Acropora* sp. ranged from 126 to 584 nmol $CaCO_3$ (mg prot)$^{-1}$ h^{-1} depending on the colony and the incubation medium. *Acropora* sp. and *S. pistillata* calcified at a similar rate (paired *t*-test; $P = 0.55$).

The rate of calcification of all colonies of *S. pistillata* increased as a function of increasing aragonite saturation and reached a saturation plateau at aragonite saturation ranging between 426% and 585% (Fig. 1). The relationship is well described by exponential functions, forced through the origin or not, with coefficients of determination higher than 0.92 (Table 3).

The control colony of *S. pistillata* incubated in Mediterranean seawater (aragonite saturation ≈ 360%) calcified at a significantly higher rate than the colonies incubated in artificial seawater with arago-

Table 2
Rate of calcification [nmd $CaCO_3$ (mg prot)$^{-1}$h^{-1}] of colonies of *S. pistillata* (five specimens from different parent colonies) and *Acropora* (one specimen) as a function of aragonite saturation

Species	Aragonite saturation (%)				
	98	195	293	390	585
S. pistillata					
Sp1	272.5	506.1	584.0	584.0	584.0
Sp2	210.2	420.5	525.6	578.2	578.2
Sp3	126.4	337.1	379.2	421.4	379.2
Sp4	226.1	452.2	527.5	527.5	502.4
Sp5	137.7	275.5	321.4	298.4	298.4
Mean ± SE	194.6 ± 25.2	398.3 ± 37.6	467.5 ± 45.5	481.9 ± 49.6	468.4 ± 51.4
Acropora sp.	214.3	500.1	535.8	428.7	428.7

SE: standard error of the mean.

Table 3
Nonlinear regression parameters of the relationship between the calcification rate and the aragonite saturation

Function	a	b	c	n	r^2
$y = a(1-\exp(-x/b))+c$					
Sp1	1323 ± 218	69 ± 8	-723 ± 223	5	0.997
Sp2	906 ± 90	115 ± 14	-312 ± 98	5	0.996
Sp3	1245 ± 573	64 ± 20	-846 ± 582	5	0.98
Sp4	1460 ± 589	61 ± 16	-938 ± 597	5	0.99
Sp5	1148 ± 858	51 ± 20	-842 ± 864	5	0.98
Average	1214 ± 92	72 ± 11	-732 ± 111	–	–
$y = a(1-\exp(-x/b))$					
Sp1	619 ± 38	134 ± 27	–	5	0.96
Sp2	637 ± 49	190 ± 38	–	5	0.98
Sp3	432 ± 60	165 ± 65	–	5	0.92
Sp4	549 ± 46	135 ± 37	–	5	0.94
Sp5	321 ± 28	126 ± 38	–	5	0.92
Average	512 ± 59	150 ± 12	–	–	–

n = Number of samples; r = correlation coefficient; mean $\pm$ asymptotic standard error. The average values are shown as mean $\pm$ standard error of the mean.

nite saturation of 390% (833 ± 18 vs. 482 ± 50 nmol $CaCO_3$ (mg prot)$^{-1}$ h^{-1}; Welch ANOVA, $P = 0.002$), but the differences within experimental specimens were well within the range of natural variability in calcification rates (Buddemeier and Kinzie, 1976).

4. Discussion

Our results demonstrate that manipulating calcium carbonate saturation through changes in calcium concentration has a highly significant short-term effect on coral calcification. The work of Marubini and Atkinson (pers. comm.) and Langdon et al. (pers. comm.), which address similar issues by manipulation of carbonate concentration in natural seawater, arrived at essentially the same overall conclusion. For the experiments described here, the rate of calcification appears to increase exponentially as a function of increasing aragonite saturation state above the 100% saturation level, and reaches a plateau at saturation values greater than 300%.

Curve-fitting can provide useful descriptions of the data. The first relationship derived from the experimental data is a three-parameter saturated exponential function. Extrapolation of this relationship at saturation levels lower than those used in the present study indicates that calcification is 0 when aragonite saturation is 66%. Such extrapolation does not agree with the observation that some azooxanthellate scleractinians are known to calcify in deep-sea environments, and with the observations of Marubini and Atkinson (pers. comm.), who have shown that colonies of the coral *Porites compressa* calcify at saturation states $< 50\%$. It is probable that the decrease of calcification in seawater undersaturated with respect to aragonite is not as dramatic. Fitting a two-parameter function to the data makes it possible to force the line to 0 (Fig. 1). The lack of experimental data at low saturation values prevents choice of one fitting function rather than the other. In the rest of the discussion we will use the three-parameter function as a predictive function for environments with saturation state $> 100\%$ since (1) it provides the best fit to the data, as shown by the high r^2 and (2) the response of calcification to saturation levels below 100% is relevant to overall understanding of the mechanisms of calcification control, but is not a major factor in the role of neritic carbonate production in global carbon cycle and its changes over time.

Other studies have previously shown that calcification changes as a function of calcium concentration in several taxonomic groups. For example, the rates of calcification and photosynthetic $^{14}CO_2$ fixation increase as a function of external Ca^{2+} concentration in cells harvested from the exponential growth phase of a high-calcifying strain of the coccolithophorid *Emiliania huxleyi* (Nimer et al., 1996). The rates of photosynthesis and calcification are closely coupled, and are saturated at 10 mM Ca^{2+} compared with the Ca^{2+} concentration of 8 mM in seawater. Lea et al. (1995) also suggested that the calcification rate of the foraminiferan *Orbulina universa* is proportional to the degree of carbonate saturation.

There is little direct information on the effect of the carbonate saturation state on coral calcification (Smith and Buddemeier, 1992). Several authors demonstrated, however, that the seawater calcium concentration has a significant effect on calcification (e.g., Yamazato, 1966 in Swart, 1979; Chalker, 1981; Krishnaveni et al., 1989; Ip and Krishnaveni, 1991; Tambutté et al., 1996). Most studies showed that the

rate of calcification follows a saturation kinetics but the calcium concentration at which the saturated rate is reached encompasses a rather wide range: 10–25 mM Ca^{2+}. It is difficult to draw conclusions on the effect of saturation state from these studies because they did not control, measure, or report the parameters of the inorganic carbon system which prevents derivation of the aragonite saturation levels from calcium concentrations. An artificial seawater formula recently designed for chemical oceanography (DOE, 1994) was used in the present study. It permitted strict control of pH, dissolved inorganic carbon and total alkalinity of the incubation medium thereby avoiding any effect of parameters other than saturation state on the rate of calcification.

Our results are in agreement with those obtained on the calcareous alga *Porolithon gardineri* by Agegian (1985) (see also Mackenzie and Agegian, 1989). The linear growth rate of this species was measured under controlled environmental conditions in which the calcite saturation state was changed by manipulating the seawater pH. It displayed a twofold increase when the saturation state increased from 100 to 800%. There was, however, no evidence of a saturation kinetics as the increase appears to be linear over this range of calcite saturation.

Differences in the strontium concentration between normal and artificial seawater of similar aragonite saturation level, may explain that the rate of calcification was lower in the synthetic than in the Mediterranean seawater. Strontium is incorporated into the coral skeleton and its deposition is linear with respect to Sr^{2+} concentration (Ip and Krishnaveni, 1991). Additionally, Chalker (1976) and Ip and Krishnaveni (1991) have suggested that strontium can be a competitive inhibitor of calcification, although it has been suggested that Sr^{2+} and Ca^{2+} deposition appear to involve different biochemical pathways (Ip and Krishnaveni, 1991).

The effect of the seawater saturation state on calcification may explain the distribution of calcifying and noncalcifying Cnidaria (Buddemeier and Fautin, 1996a). Sea anemones are found at greater depth than are corals, which is consistent with the decrease of calcium carbonate saturation as a function of depth and the resulting solubility of $CaCO_3$ at depth (Buddemeier and Fautin, 1996b). Additionally, the latitudinal range of reef-building (zooxanthellate) corals is narrower than the distribution of either symbiotic sea anemones or non reef-building (azooxanthellate) corals, which implies that symbiotic calcification is latitudinally restricted whereas neither algal symbioses nor coral calcification are individually limited. Buddemeier and Fautin (1996a) acknowledged that temperature is an important factor controlling biogeography but made the points that saturation state may also be involved, and that the latitudinal distribution of saturation state is qualitatively similar to that of temperature. Kleypas (1997) has recently demonstrated that the latitudinal distribution of reefs can also be reproduced using light as a controlling variable. The results of the present study provide experimental support for the hypothesis that saturation state is important, as do the results of Atkinson and Marubini (pers. comm.), but it remains impossible at this stage to estimate the relative importance of temperature, saturation state, and light as controls on the distribution of corals.

The occurrence of coral reefs and the distribution of most reef-building (= hermatypic) corals are limited to the tropics and subtropics (Veron, 1995), and encrusting red algae are more heavily calcified in temperate than in cold water (see Lowenstam and Weiner, 1989) Such distribution is traditionally explained by temperature limitation at higher latitudes (Veron, 1995). An increase in the extent of biomineralization across a latitudinal temperature gradient has been observed in the scales and bones of marine fish (Moss, 1963). These differences were attributed to a decreased calcium concentration in the low-salinity Arctic waters. King and Schramm (1982) also suggested that the calcium ion concentration and not salinity per se affects calcification rates of the Baltic sea coralline alga *Phymatolithon calcareum.* Lastly, $CaCO_3$ precipitation over the Bahama Banks (the so-called 'whitings') is strongly correlated with the degree of supersaturation (Broecker and Takahashi, 1966). Opdyke and Wilkinson (1993) have correlated the accumulation of Holocene reefal carbonates with saturation state.

4.1. Inferences on the effect of $CaCo_3$ saturation on calcification in the past

The saturation of calcium carbonate in seawater is essentially controlled by the concentration of cal-

cium and carbonate ions (neglecting the effect of changes in salinity and temperature at this stage). It is mostly dependent on CO_3^{2-} on short time scales as Ca^{2+} concentration is two orders of magnitude higher than CO_3^{2-} concentration. For time scales longer than a million years (i.e., longer than the residence time of calcium in the sea), shifts in both Ca^{2+} and in CO_3^{2-} ion concentrations need to be considered (Broecker and Peng, 1982).

There is some information suggesting that the calcium concentration has increased dramatically between 2 and 1 Ga (Kempe and Kazmierczak, 1994). It has been proposed that the onset of skeletal biomineralization at the Precambrian–Cambrian boundary was a detoxification response to an environmental calcium shock (Kazmierczak et al., 1985). Bengtson (1994) rejected that proposal because it appears to clash with evidence of substantial $CaCO_3$ precipitation in sedimentological records from the Middle Archean. Other studies have proposed that changes in $CaCO_3$ saturation had profound impacts on the biology of the early ocean. For example, it has been suggested that the decline of Proterozoic stromatolites could, in part, be related to a reduction in carbonate saturation through time (Grotzinger, 1994). According to Grotzinger (1994), the advent of calcification in the terminal Proterozoic and earliest Cambrian did not substantially change the calcium carbonate saturation state of seawater.

The more recent history of the calcium content of seawater shows that it has decreased during the last 20 million years, but that the carbonate content increased in similar proportions; the carbonate saturation was therefore roughly the same during the 5–20-million-year time period (Broecker and Peng, 1982; see also Lasaga, 1985). Note, however, that the magnitude of the recent changes in the calcium content are poorly known; Opdyke and Wilkinson (1988) suggested that it did not depart from the average value of the last 150 million years by more than 20%.

There is comparatively more information on the chemistry of tropical surface water during the last glacial–interglacial period than there is from the distant past. The atmospheric pCO_2 was approximately 80 μatm lower 18 kyr ago than during the preindustrial period (200 vs. 280 μatm). Since the ocean surface is, on the long term, essentially in equilibrium with the atmosphere, such a large-scale change in pCO_2 is likely to have had a profound effect on the seawater inorganic carbon system (Archer and Maier-Reimer, 1994). This was recently demonstrated using the isotopic composition of borates incorporated into foraminiferan shells as a proxy record of oceanic pH. Sanyal et al. (1995) estimated that the pH of tropical surface water was 0.2 ± 0.1 higher during the last glacial age than during the Holocene.

We estimate that aragonite saturation during the last glacial period, calculated using the estimated pCO_2 (200 μatm) and total alkalinity (2457 μeq kg^{-1}; Broecker and Peng, 1982), was 566% compared to 446% in the late 1800s (Table 4). This estimate of the seawater carbonate chemistry during the glacial time requires a difference in pH of 0.12 unit, which is consistent with the paleo-pH data proposed by Sanyal et al. (1995). The rate of calcification of *S. pistillata* is essentially constant for aragonite saturation states between 400% and 600% (Fig. 1). Our experimental data suggest therefore that

Table 4
Carbonate chemistry of tropical surface seawater in glacial and interglacial periods

	Glacial	Preindustrial	Present	Future 1 ($\times 2$ pCO_2)	Future 2 ($pCO_2 = 1000$)
pH (SWS)	8.29	8.17	8.08	7.93	7.71
TA (μeq kg^{-1})	**2457**	**2350**	**2350**	**2350**	**2350**
pCO_2 (μatm)	**200**	**280**	**360**	**560**	**1000**
Aragonite saturation (%)	566	446	387	293	192

Secondary parameters (standard fonts) were computed from primary parameters (in bold). The estimate of TA during the glacial time is from Broecker and Peng (1982). TA was held constant at its preindustrial value from the late 1800s onwards. Temperature and salinity were set at 25°C and 35, respectively.

the deposition of $CaCO_3$ by scleractinian corals may not have changed significantly in response to the decrease in aragonite saturation that occurred during the last 18 kyr. The decrease in tropical sea surface temperature by 3–6°C during the last glacial maximum is likely to have diminished $CaCO_3$ deposition.

4.2. Inferences on the effect of $CaCO_3$ saturation on calcification in the future

The present atmospheric pCO_2 is approximately 360 μatm and is increasing at a rate of 0.4% yr^{-1} due to the anthropogenic release of CO_2 (Houghton et al., 1996). The Intergovernmental Panel on Climate Change (IPCC) has made predictions of future atmospheric pCO_2 levels according to a number of scenarios (Houghton et al., 1996), most of which predict a doubling of preindustrial levels within the next century.

CO_2 equilibrates between the surface ocean and the atmosphere through air–sea exchange at the air–water interface. Our calculations predict that seawater pH will decrease from 8.08 at present to 7.93 and 7.71 for pCO_2s values of 560 (i.e., a doubling of the preindustrial value) and 1000 μatm (Table 4). These decreases will drive the aragonite saturation down from its present value (387%) to 293 and 192%, respectively. The relationship between the rate of calcification and aragonite saturation derived in the present paper suggests that calcification may not decrease significantly (461 vs. 476 nmol $CaCO_3$ (mg prot.)$^{-1}$ h^{-1}) at a saturation level corresponding to $pCO_2 = 560$ μatm. However, a significant decrease (14%) may be observed if pCO_2 reaches 1000 μatm (398 vs. 476 nmol $CaCO_3$ (mg prot.)$^{-1}$ h^{-1}). Langdon et al. (pers. comm.) observed much more important changes in Biosphere 2 by manipulating the aragonite saturation through the reef metabolism and additions of carbonate and bicarbonate. They suggest that calcification may decline by 10 and 75% at pCO_2s of, respectively, 560 and 1000 μatm.

It must be noted that additional weathering of terrestrial carbonates is likely to occur under elevated atmospheric pCO_2, thereby increasing Ca^{2+} delivery to the oceans and partly counteracting the decrease in aragonite saturation due to the decrease in pH (Holland, pers. comm. in Riding, 1996).

5. Conclusion

The aragonite saturation state has a significant short-term effect on the rate of calcification of the scleractinian coral *S. pistillata* between 98 and 585%. It is found: (1) that the rate of calcification does not change significantly over a range of saturation levels corresponding to the last glacial-interglacial cycle, and (2) that it may decrease significantly in the future as a result of global environmental changes. It is important to point out the limitations of this prediction. Firstly, the response of only two species was investigated. It can be argued that these species, especially, *S. pistillata*, are not major reef builders. However, results obtained by other groups (Langdon et al., pers. comm.; Marubini and Atkinson, pers. comm.) suggest that the response that we report is valid across a wide range of species, including the major reef building species *P. compressa*. Secondly, only the short-term effect has been investigated. Corals display quite impressive acclimation processes to changes in some environmental parameters (Brown, 1997) and many species have survived the major global environmental cycles of the Quaternary period (Veron, 1995). Thirdly, the saturation state was manipulated by altering the seawater calcium content and not pCO_2. The effect observed in the present study relates therefore to the aragonite saturation per se. It would be interesting to investigate the effect of increased pCO_2 which may also have an effect on photosynthesis of zooxanthellae, the microalgae living in symbiosis in the cells of most reef-building corals. Since photosynthesis has been suggested to stimulate coral calcification (Barnes and Chalker, 1990), an increase of zooxanthellar photosynthesis may counteract the decrease of calcification resulting from decreased aragonite saturation state. Increase of photosynthesis under high pCO_2 has been observed in macroalgae (e.g., Gao et al., 1993b) but the situation is not as clear in zooxanthellate corals. The rate of photosynthesis has never been investigated under elevated pCO_2 but indirect evidence indicates that increased pCO_2 resulting from a decrease in pH (pH_{SWS}: 8.22–7.70, derived empirically) in a closed system slightly inhibits the rate of photosynthesis of colonies of *Galaxea fascicularis* (Allemand, in press). There is clearly a need to pursue experimental studies using controlled envi-

ronmental conditions and seawater composition to unravel the response of corals to global environmental changes.

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