Coral reefs modify their seawater carbon chemistry – case study from a barrier reef (Moorea, French Polynesia)

JOAN A. KLEYPAS*, KENNETH R. N. ANTHONY† and JEAN-PIERRE GATTUSO‡§

*Climate and Global Dynamics and Integrated Science Program, National Center for Atmospheric Research, PO Box 3000, Boulder, CO 80307-3000, USA, †Australian Institute of Marine Science, PMB 3 Townsville MC, Townsville, 4810, Qld Australia, ‡INSU-CNRS, Laboratoire d'Océanographie de Villefranche, B.P. 28, 06234, Villefranche-sur-mer Cedex, France, §UPMC Univ. Paris 06, Observatoire Océanologique de Villefranche, 06230, Villefranche-sur-mer, France

Abstract

Changes in the carbonate chemistry of coral reef waters are driven by carbon fluxes from two sources: concentrations of CO_2 in the atmospheric and source water, and the primary production/respiration and calcification/dissolution of the benthic community. Recent model analyses have shown that, depending on the composition of the reef community, the air-sea flux of CO_2 driven by benthic community processes can exceed that due to increases in atmospheric CO_2 (ocean acidification). We field test this model and examine the role of three key members of benthic reef communities in modifying the chemistry of the ocean source water: corals, macroalgae, and sand. Building on data from previous carbon flux studies along a reef-flat transect in Moorea (French Polynesia), we illustrate that the drawdown of total dissolved inorganic carbon (C_T) due to photosynthesis and calcification of reef communities can exceed the draw down of total alkalinity (A_T) due to calcification of corals and calcifying algae, leading to a net increase in aragonite saturation state (Ω_a). We use the model to test how changes in atmospheric CO_2 forcing and benthic community structure affect the overall calcification rates on the reef flat. Results show that between the preindustrial period and 1992, ocean acidification caused reef flat calcification rates to decline by an estimated 15%, but loss of coral cover caused calcification rates to decline by at least three times that amount. The results also show that the upstream–downstream patterns of carbonate chemistry were affected by the spatial patterns of benthic community structure. Changes in the ratio of photosynthesis to calcification can thus partially compensate for ocean acidification, at least on shallow reef flats. With no change in benthic community structure, however, ocean acidification depressed net calcification of the reef flat consistent with findings of previous studies.

Keywords: carbonate chemistry, coral reefs, ocean acidification

Received 27 May 2011 and accepted 18 July 2011

Introduction

Seawater carbon chemistry of coral reef environments changes in response to both intrinsic and extrinsic processes. Coral reef communities have long been known to alter their own seawater chemistry, through processes of photosynthesis, respiration, calcification, and dissolution (Smith, 1973). Seawater carbon chemistry is also altered by air-sea exchange of CO_2 between the atmosphere and surface mixed layer.

Ocean acidification, the alteration of CO_2 carbon chemistry, is a result of the latter process; i.e., increasing CO_2 concentration in the atmosphere is driving more CO_2 into the ocean surface layer via air-sea exchange (Broecker *et al.*, 1979; Smith & Buddemeier, 1992; Sabine *et al.*, 2004).

Compared to coral reef environments, the carbon chemistry of ocean seawater is not subject to a high degree of biological alteration, and is thus more closely linked to atmospheric CO_2 concentrations. Once open ocean waters flow onto a reef, however, coral community processes can dramatically alter the carbon chemistry (Smith & Pesret, 1974; Gattuso *et al.*, 1993; Kayanne *et al.*, 1995; Anthony *et al.*, 2011). The capacity of one reef community to alter its seawater carbon chemistry can have consequences for the calcification capacity of another community downstream, and can affect the vulnerability of the reef ecosystem to ocean acidification.

The increase in atmospheric CO_2 thus affects both the carbon chemistry of the ocean source water flowing onto coral reefs, as well as air-sea CO_2 gradient of reef waters (the higher atmospheric CO_2 concentration slows the rate of CO_2 degassing). The latter process is slow (Frankignoulle *et al.*, 1996) and not considered a major factor in determining day-to-day variability in coral reef seawater chemistry.

Correspondence: Joan A. Kleypas, tel. + 303 497 8111, fax + 303 497 1700, e-mail: kleypas@ucar.edu

The community composition of a coral reef can greatly alter the carbon chemistry of seawater flowing across the system (e.g., Kinsey, 1985). In a recent accompanying article (Anthony *et al.*, 2011) we demonstrate theoretically and experimentally how corals and macroalgae produce contrasting effects on the carbon chemistry of reef water downstream. After considerable debate in the literature on whether coral reefs were net CO_2 sources or sinks to the atmosphere (Crossland *et al.*, 1991; Gattuso *et al.*, 1996a), it was recognized that, with the exception of algal-dominated zones, the effects of reef calcification on CO_2 chemistry outweigh the effects of organic carbon production, so that reefs are net sources of CO_2 to the atmosphere (see reviews of Gattuso *et al.*, 1999; Andersson & Mackenzie, 2004). In this study we field test this model and further explore the role of reef community changes in modifying reef water chemistry and how benthic carbon fluxes will interact with ocean acidification.

This article builds on a series of carbon flux studies conducted on the Tiahura Barrier Reef Flat at Moorea, French Polynesia, in 1991 and 1992. These studies aimed to understand the effects of coral community metabolism on the seawater carbon system, as well as to resolve the net effect of reef metabolism on air-sea CO_2 fluxes. Two studies were conducted within benthic chambers to measure the primary production and calcification of carbonate sands (Boucher *et al.*, 1998) and a macroalgal community (Gattuso *et al.*, 1997). Another used a Lagrangian approach to measure community metabolism as water flowed across a continuum of coral community types on the reef flat from the forereef to the backreef (Gattuso *et al.*, 1996b); and yet another measured the air-sea fluxes of CO_2 of reef flat waters (Frankignoulle *et al.*, 1996). These studies produced models linking both organic carbon production (*p*) and inorganic carbon production (*g*) via their response to irradiance.

Herein, we integrate the results of these flux studies within a model calibrated to reproduce the Gattuso *et al.* (1996b) results to address a key question: what is the significance of reef community composition in modifying the carbon chemistry of seawater as it flows across shallow-water reef communities? We explore further the importance of changes in coral vs. macroalgal abundances in modifying the seawater carbon system. Lastly, we explore how ocean acidification will interact with the primary production and calcification of different reef communities, and what will be the implications for patterns of reef water carbon chemistry.

Methods

We modeled the effects of photosynthesis-respiration and calcification-dissolution on seawater chemistry as offshore water traversed over coral/algae/sediment communities along the same Tiahura reef flat transect studied by Gattuso *et al.* (1996b). The carbon flux due to photosynthesis-respiration was modeled as a function of irradiance, while the carbon flux due to calcification-dissolution was modeled as a function of both light and aragonite saturation state (Ω_a). Air-sea carbon fluxes were also calculated according to Wanninkhof (1992).

Organic carbon production

To formally integrate carbon fluxes driven by organic and inorganic production as a function of time of day, we used both photosynthesis-irradiance and calcification-irradiance curves (Chalker, 1981). Net organic production (*p*) was calculated based on the saturated exponential light response equation:

$$p = p_{max}(1 - e^{-E/E_k}) + p_{dark} \tag{1}$$

where *p* is rate of net production (mmol CO_2 m^{-2} h^{-1}), p_{max} is maximum rate of net production (mmol CO_2 m^{-2} h^{-1}) and p_{dark} is net production rate in the absence of light, i.e., respiration. All production rates are in units of mmol CO_2 m^{-2} h^{-1}. *E* is irradiance in (µmol photons m^{-2} s^{-1}) at the sea surface for a given time of day, as determined by:

$$E(t) = E_{noon} \sin(\pi t/H_{day}) \tag{2}$$

where E_{noon} is noon (max) irradiance, E_k is the irradiance where the photosynthesis curve begins to saturate with respect to irradiance, and H_{day} is the length of day in hours.

Inorganic carbon production

Calcium carbonate production (*g*) is a function of both irradiance and Ω_a. To be consistent with the empirical model of the original studies at Moorea we express the light response of calcification using the saturated exponential light response equation:

$$g = g_{max}(1 - e^{-E/E_k}) + g_{dark} \tag{3}$$

where *g* and g_{max} are the net and maximum rate of $CaCO_3$ production, respectively, and g_{dark} is net $CaCO_3$ production rate in the absence of light (all in mmol $CaCO_3$ m^{-2} h^{-1}). Assuming that the shape of the calcification-irradiance response (i.e., E_k) is not influenced by variation in Ω_a, g_{max} and g_{dark} can be described as power functions with respect to Ω_a:

$$g_{max} = k_{day}(\Omega_a - 1)^n \tag{4a}$$

$$g_{dark} = k_{night}(\Omega_a - 1)^n \tag{4b}$$

where k_{day} and k_{night} are the regression coefficients for day and night calcification rates, respectively. Previous studies indicate that the reaction order, *n*, does not vary with irradiance (Marubini *et al.*, 2001) or between day and night (Schneider & Erez, 2006; Anthony *et al.*, 2011). Hence, *g* as a function of *E* and Ω_a can be expressed as

$$g = k_{day}(\Omega_a - 1)^n (1 - e^{-E/E_k}) + k_{night}(\Omega_a - 1)^n \qquad (5)$$

In the above model, dissolution would occur once Ω_a drops below a value of 1.0, yet in reality, it likely occurs at values >1.0, because of the presence of high-Mg calcite in reef sediments, which is usually more soluble than aragonite (Morse et al., 2006), and because respiration of organic matter can cause sediment porewaters to become undersaturated with respect to aragonite. We do not, however, include an explicit term for dissolution, as model fitting using the g vs. Ω_a response for communities with corals implicitly includes dissolution (g is net calcification), and is not significantly improved when the dissolution term is explicitly included (Anthony et al., 2011). For simplicity in our parameter fitting, we assumed that the reaction order, n, was equal to 1.0 (i.e., the relationship between the calcification rate and Ω_a is linear), which is consistent with the meta-analysis of Langdon & Atkinson (2005).

Tiahura barrier reef flat

The Tiahura reef flat is located on the northwest side of Moorea. Moorea is located near an M2 amphidromic point, so that the tides are dominated by the S2 (solar, 12 h period) and the tidal range is small (<0.5 m). Offshore waters typically flow over the reef flat toward the back reef, and into deeper channels that return the water behind and alongside the reef. Water depths across the reef flat are fairly uniform, about 1–2 m depth. Diurnal fluctuations in temperature are small (Gattuso et al., 1996b) and not included as a variable in the calculations. Coral cover on the Tiahura reef flat declined from about 35% to 18% between 1979 and 1982 due to *Acanthaster planci* infestations, with particular reductions in branching forms such as the genera *Acropora* and *Pocillopora* (Bouchon, 1985). In 1996, the percent coral cover on the reef flat was about 14%.

Changes in water chemistry were simulated for water flowing from just offshore the Tiahura reef flat to just off the back-reef, along the same transect sampled by Gattuso et al. (1996b) (Fig. 1). The transect length was about 400 m, and at a typical flow rate of 15 cm s^{-1}, water traveled the length of the transect in about 0.7 h. Average water depth along the transect was 1.3 m.

The modeling scheme is an adaptation of the model described in Anthony et al. (2011) (Fig. 2). As seawater flows from point A to point B along the transect, the changes in seawater chemistry were recalculated every meter as a function of the net carbon fluxes of the underlying benthic community (Eqns 1 and 5) and the air-sea CO$_2$ flux. Air-sea CO$_2$ fluxes were calculated according to Wanninkhof (1992) based on the wind speed and the pCO$_2$ gradient across the air-sea interface. The concentration of dissolved inorganic carbon (C_T) and total alkalinity (A_T) were adjusted according to the net uptake/release of carbon and A_T, and the seawater chemistry was recalculated.

The benthic community structure along the transect was partitioned into relative areal abundances of sand/sediment (including rubble), algae (turf and macroalgae), and calcifiers

Fig. 1 (a) NASA astronaut image of Moorea, French Polynesia (photo ID: ISS006-E-39837; image courtesy of the Image Science & Analysis Laboratory, NASA Johnson Space Center; http://eol.jsc.nasa.gov). (b) Tiahura reef flat in Moorea, showing approximate locations of original transect followed by Gattuso et al. (1996b) (solid red line) and transect for community composition analyses of R. Galzin (personal communication; black boxes; stations 8 and 17 are labeled) (Google Maps image).

(corals/coralline algae), based on data collected by Dr. René Galzin (Fig. 3; data provided by René Galzin) during the same year as the reef flat metabolism studies. For each of these benthic community components, both production (p) and calcification (g) were calculated and adjusted to reflect their relative contributions to the total carbon fluxes within a grid cell area. The Galzin data did not provide species composition, but a 1982 survey of the Tiahura barrier reef flat showed a dominance of *Porites* species [esp. *Porites lobata*, *Porites lutea*, and *Porites (Napapora) irregularis*] following a 1980–82 *Acanthaster* infestation that had eliminated the previously abundant *Acropora* and *Pocillopora* species (Bouchon, 1985). The macroalgae species consisted mostly of *Turbinaria ornata* and *Sargassum* spp. (Gattuso et al., 1996b); seagrasses were not present.

Organic production rates

Corals, sediments, and algae all contribute to organic carbon production in the model (Table 1). For organic production of the sediments (p_s), we used the production equation provided by Boucher et al. (1998). For algae (p_a), we considered the production equation derived for a typical macroalgae-dominated community (*Padina* sp.) on the Tiahura fringing reef flat (Gattuso et al., 1997); but adjusted these values higher to reflect
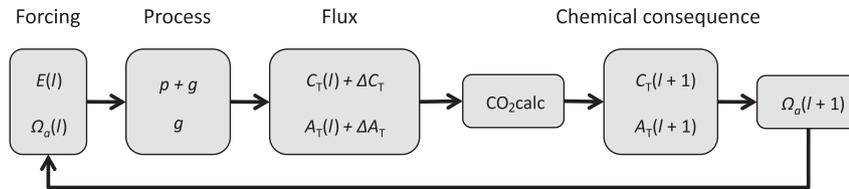
Fig. 2 Main steps in the model for calculating changes in the CO_2-system in seawater as a function of production (p) and calcification (g) of the coral, algae and sand components. As water flows from one grid cell to the next (l), fluxes in C_T and A_T, as determined from Eqns (1) and (2), are used as input into CO_2CALC to recalculate the CO_2-system parameters, including Ω_a. Figure modified from Lagrangian model used by Anthony *et al.* (2011).
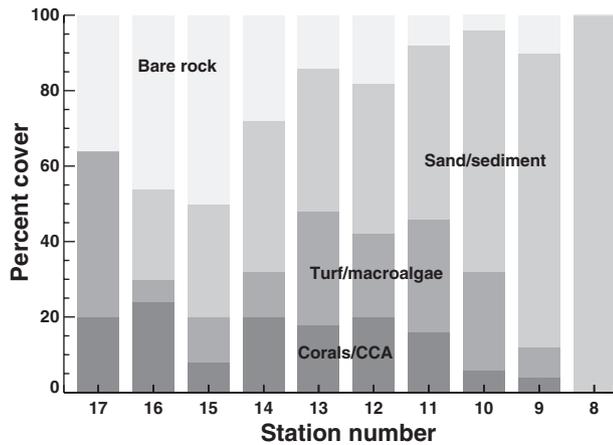

Fig. 3 Percent cover of the four main community types at stations along the Tiahura transect, based on original community survey work of R. Galzin (personal communication): corals and crustose coralline algae; turf algae and macroalgae; sand and sediment; and bare rock. Station locations are indicated in Fig. 1.

more productive algal communities, such as turf algae, which constituted about 75% of the algae on the reef flat (Galzin data). Estimates of coral production (p_c) were not available for any of the Tiahura coral communities; we therefore estimated p_{cmax} and p_{cdark} based on the production and respiration rates reported from a variety of sources. We relied in particular on production rates reported by Nakamura & Nakamori (2009) for incubations of various coral communities on a reef flat in the Ryukyus, which we adjusted to reflect 100% coral cover. Our p_c equation produces a maximum value of 55 mmol C m^{-2} h^{-1}, which falls between the average value of 64 mmol C m^{-2} h^{-1} derived from the coral communities studied by Nakamura & Nakamori (2009), and the value of 42 mmol C m^{-2} h^{-1} obtained from flume experiments with *Acropora aspera* (Anthony *et al.*, 2011).

CaCO₃ production rates

Both coral communities and sediments play a role in $CaCO_3$ fluxes on reefs (Table 2). While the Gattuso *et al.* (1996b) measurements reflect the integrated $CaCO_3$ production of all communities along the Tiahura transect (g), $CaCO_3$ production

rates were not measured separately for the coral component of the reef community (g_c). Similarly to the p_{cmax} and p_{cdark} estimates obtained above, we estimated g_{cmax} and g_{cdark} based on other measurements (e.g., scaling the *in situ* measurements of Nakamura & Nakamori (2009) to 100% cover). g_{cmax} and g_{cdark} were estimated at 29.7 mmol $CaCO_3$ m^{-2} h^{-1} and 9.9 mmol $CaCO_3$ m^{-2} h^{-1}, respectively. These coral community values are slightly higher than the g_{max} of 28.5 mmol $CaCO_3$ m^{-2} h^{-1} reported for entire reef flats (Gattuso *et al.*, 1998), and more than twice the g_{max} value determined for the Tiahura transect (10.5 mmol $CaCO_3$ m^{-2} h^{-1}). Maximum irradiance, E_{noon}, was set at the value for Moorea (2200 μmol photons m^{-2} s^{-1}), and E_k was around 600 μmol photons m^{-2} s^{-1}.

The calcification rate of Tiahura reef flat sediments (g_s) was much lower than that of the coral/mixed communities, and was the only community component that exhibited net dissolution, which occurred during the nighttime (Boucher *et al.*, 1998). We fixed g_{sdark} at -0.8 mmol $CaCO_3$ m^{-2} h^{-1} (the nighttime dissolution rate determined by Boucher *et al.* (1998) based on the assumption that nighttime dissolution rates were driven more strongly by organic matter respiration in the sediments than by saturation state of the overlying water column. The maximum value of g_s was estimated at 1.8 mmol $CaCO_3$ m^{-2} h^{-1}. At $\Omega_a = 4.3$, the rate constant, k_{day}, was estimated at 0.8 mmol $CaCO_3$ m^{-2} h^{-1}.

Calcification and production within each reef cell

Total rates of calcification, g, and organic production, p, within each 1×1 m reef cell were determined as:

$$p = \sum_{i=1}^{j} (p_i \cdot f_i) \qquad (6)$$

$$g = \sum_{i=1}^{j} (g_i \cdot f_i) \qquad (7)$$

where i is the contributing community component, f is the percent cover of that community component and j is the total number of components.

Transect simulations were run over a 24-h period, and results were compared with the integrated values for the entire reef flat, p and g obtained by Gattuso *et al.* (1996b). Source seawater conditions were set at a constant temperature (27.1 °C), salinity (36), pCO_2 (326 μatm), and pH (8.11, total

scale), consistent with the average conditions of offshore water reported by Gattuso *et al.* (1996b). Atmospheric pCO$_2$ was set at 350 ppm. Based on these conditions, A_T was determined to be 2378 μeq kg^{-1} and Ω_a was approximately 4.3 (based on CO$_2$CALC software; Robbins *et al.* (2011)).

Simulations were initially run using the reported current speed for the Tiahura field study (~15 cm s^{-1}). However, this flow rate proved too fast to produce rates of calcification and production in the simulations of seawater chemistry along the transect, and the best fit to the data was obtained when using a flow rate of 7 cm s^{-1}. This need to decrease the flow rate (i.e., increase residence time of the water) indicates that either the estimated flow rate was too high or the carbon fluxes used in the model equations were too low. In the latter case, the carbon fluxes used here are near the maxima reported by others (Tables 1 and 2). We therefore concluded that the difference is most likely due to an overestimation of the flow rate, which is plausible since surface drifter measurements may overestimate depth-averaged current speeds (Falter *et al.*, 2008). For all simulations, the flow rate was thus set at 7 cm s^{-1}.

Following model verification, we examined how changes in both reef community structure and atmospheric CO$_2$ forcing affected overall reef metabolism. Table 3 lists the conditions of each simulation. Five community structure configurations were tested: (1) the '1992 baseline' configuration, where community structure was set according to the Galzin data (Fig. 2,3); (2) an algae-coral configuration where algae were segregated to the seaward edge of the reef flat and coral at the landward edge, separated by sand; (3) a coral-algal configuration where coral were segregated to the seaward edge of the reef flat and algae at the landward edge, separated by sand; (4) a pre-1992 configuration where coral cover increased by 2.5-fold relative to 1992 levels (Bouchon, 1985); and (5) an increased algal cover configuration where algal cover was increased by 2.5-fold. For each of these community structure configurations, the model was run at three different CO$_2$-chemistry conditions: (1) the '1992 baseline' state; (2) the preindustrial state; and (3) the doubled preindustrial state.

Results

The choice of parameters within the various flux equations (Tables 1 and 2) produced chemistry changes along the Tiahura transect similar to those measured in the 1992 studies (Fig. 4). Changes in A_T varied dramatically throughout the day. At night, the A_T draw down was minimal, while respiration contributed to a considerable increase in C_T, so that the resulting Ω_a decreased slightly from 4.45 to 4.32. Conversely, during maximum solar radiation, the decreases in both A_T and C_T were high, but the photosynthetic drawdown in C_T was much greater than the calcification drawdown of A_T, which resulted in an elevation in Ω_a as seawater flowed from offshore to the backreef (from 4.45 to 4.8). The ranges in ΔA_T and ΔC_T values over the course of the 24-h cycle ($\Delta A_T = -20$ to -3 mmol kg^{-1}; $\Delta C_T = -55$ to 10 mmol kg^{-1}) (Fig. 5) were similar to those measured

by Gattuso *et al.* (1996b) ($\Delta A_T = -20$ to -2 mmol kg^{-1}, $\Delta C_T = -56$ to 10 mmol kg^{-1}). The diurnal range in seawater pCO$_2$ from the model (280–342 μatm), however, was smaller than the range reported by Frankignoulle *et al.* (1996) for the Tiahura barrier reef flat in July 1992 (240–390 μatm). This may be partly due to differences in how pCO$_2$ was calculated in the model vs. the Frankignoulle *et al.* (1996) study. The model values were calculated using A_T and C_T on the total pH scale, and the Frankignoulle *et al.* (1996) values were calculated using A_T and pH on the seawater scale. It may also be partly due to differences in the timing of the two field studies: the Frankignoulle *et al.* (1996) air-sea flux study was collected about a week after the Gattuso *et al.* (1996b) study that was used to tune our model.

The simulations illustrate the effects of both atmospheric CO$_2$ forcing and community structure on the overall CaCO$_3$ production capacity of the Tiahura reef flat (Fig. 6). For simulated pre-industrial (year 1880) levels of atmospheric CO$_2$, the net daily rate of reef calcification was about 20% higher than at 1992 levels (assuming a 1992 benthic composition, Fig. 6a vs. f). In contrast, increasing coral cover 2.5-fold (from 14% to 30%) within the 1992 simulation resulted in a 140% increase in the net daily rate of calcification (Fig. 6j vs. f). Thus, the model indicates that the decrease in coral cover on the Moorea Reef flat (which occurred prior to the 1992) had a much stronger impact on reef calcification than did the degree of ocean acidification between 1880 and 1992.

Segregation of corals and algae altered the $A_T : C_T$ ratio along the reef flat, but had a relatively minor impact on the net daily rate of reef calcification. At all three levels of atmospheric CO$_2$ forcing, segregation of algae near the reef front resulted in a slight increase (<3.0%) in total overall calcification relative to the 1992 community structure (Fig. 6c,h,m vs. a,f,k, values are hourly rates integrated over a 24-h cycle). Segregation of corals near the reef front led to slight decrease (<2%) in the daily integrated calcification rates (Fig. 6b,g,l).

Increasing the percent coral cover naturally led to increased reef calcification. Increasing algal cover 2.5-fold had little overall effect on the net calcification at lower CO$_2$ conditions, but led to a 5% increase in net calcification under doubled CO$_2$ conditions.

Discussion

Our study illustrates the role of benthic primary producers and calcifiers in altering the seawater chemistry as it flows over reef communities. In the mixed coral/algal community of the Tiahura reef flat, the draw down of C_T by the reef flat communities more than compensates for drawdown of A_T, leading to an

Table 1 Equations and parameter values derived from measured production rate (*p*) on the Tiahura reef flat and of various reef communities (p_a, p_c, p_s)

Community	Parameter values	Maximum value	Notes
Tiahura reef flat (*p*)		$p = p_{max}(1 - e^{-E_0/E_k}) + p_{dark}$	
Reef flat	$p_{max} = 91$ $p_{dark} = -25$ $E_k = 686$	62.30 (80)	1991 summer; Lagrangian; Gattuso *et al.* (1993)*
Reef flat	$p_{max} = 90$ $p_{dark} = -31$ $E_k = 321$	58.88 (75)	1992 winter; Lagrangian; Gattuso *et al.* (1996b)*
Macroalgae (p_a)		$p_a = p_{amax}(1 - e^{-E_0/E_k}) + p_{adark}$	
Tiahura *Padina* sp.	$p_{amax} = 27$ $p_{adark} = -10$ $E_k = 243$	16.60 (20)	1992 winter; *in situ* incubation, back reef; Gattuso *et al.* (1997)*
Chnoospora sp.	$p_{amax} = 96$ $p_{adark} = -13$ $E_k = 500$	83.00	Flume study; Anthony *et al.* (2011)
Macroalgae	$p_{amax} = 80$ $p_{adark} = -25$ $E_k = 500$	55.0	This study
Coral communities (p_c)		$p_c = p_{cmax}(1 - e^{-E_0/E_k}) + p_{cdark}$	
Coral communities	$p_{amax} = 92$ $p_{adark} = -28$ $E_k = 250$	64.00 (72.04)	2006/2007; *in situ* incubations, sites 5, 6, 7; Nakamura & Nakamori (2009)
Acropora aspera	$p_{cmax} = 79$ $p_{cdark} = -37$ $E_k = 250$	42.0	Flume study; Anthony *et al.* (2011)
Coral	$p_{cmax} = 80$ $p_{cdark} = -25$ $E_k = 250$	55.0	This study
Sand/sediment (p_s)		$p_s = p_{smax}(1 - e^{-E_0/E_k}) + p_{sdark}$	
Tiahura sand/sediment	$p_{smax} = 12.3$ $p_{sdark} = -3.5$ $E_k = 696$	8.28 (14)	1992 winter; *in situ* incubation; Boucher *et al.* (1998)*
Sand/sediment	$p_{smax} = 12.3$ $p_{sdark} = -3.5$ $E_k = 696$	8.28	This study

p and *k* are in mmol m^{-2} h^{-1}. All irradiance (*E*) values are in μmol photons m^{-2} s^{-1}. Maximum values, in mmol m^{-2} day^{-1}, are provided based on estimated noontime irradiance (E_0) = 2200 μmol photons m^{-2} s^{-1}; values in parentheses are the highest measured values reported in the original references.
*Note that equations provided by Tiahura references were based on surface irradiance (E_0). All other equations were based on *in situ* irradiance (*E*).

increase in Ω_a downstream. Ideally, having *in situ* measurements of the organic and CaCO$_3$ production of the various communities across the Tiahura reef flat would have been optimal. Nonetheless, our selection of values for the various equations, which were constrained by the range of estimates for coral and algal communities, was sufficient to simulate the integrated reef flat measurements of Gattuso *et al.* (1996b).

Our model simulations of CO$_2$-system chemistry on the Tiahura reef flat in 1992 illustrate a net flux of atmospheric CO$_2$ into the reef waters, but when we account for air-sea pCO$_2$ gradient of the source water

Table 2 Equations and parameter values derived from measured calcification rates (g) on the Tiahura reef flat and of various reef flat communities (g_c, g_s)

Community	Parameter values	Maximum value	Notes
Tiahura reef flat (g)		$g = a\,E_0 + b$	
Reef flat	$a = 0.006$ $b = -6.7$	19.9 (25)	1991 summer; Lagrangian; Gattuso *et al.* (1993)
		$g = g_{max}(1 - e^{-E_0/E_k}) + g_{dark}$	
Reef flat	$g_{max} = 10.66$ $g_{dark} = 2.88$ $E_k = 87$	13.54 (16)	1992 winter; Lagrangian; Gattuso *et al.* (1996b)
Coral communities (g_c)		$g_c = g_{cmax}(1 - e^{-E_0/E_k}) + g_{cdark}$ where: $g_{cmax}, g_{cdark} = k\,(\Omega_a - 1)^n$	
Coral communities	g_{cmax}: $k = 9.0$ $n = 1$ $E_k = 400$ g_{cdark}: $k = 3.0$ $n = 1$	31.8 (35.6) (when $\Omega_a = 3.65$)	2006/2007; *in situ* incubations, sites 5, 6, 7; Nakamura & Nakamori (2009)
Coral communities	g_{cmax}: $k = 9.0$ $n = 1$ $E_k = 400$ g_{cdark}: $k = 3.0$ $n = 1$	39.6 (when $\Omega_a = 4.3$)	This study
Sand/sediment (g_s)		$g_s = g_{smax}(1 - e^{-E_0/E_k}) + g_{sdark}$	
Tiahura sand/sediment	$g_{smax} = 10.66$ $g_{sdark} = -0.80$ $E_k = 560$	1.26 (1.7)	1992 winter; *in situ* incubation; Boucher *et al.* (1998)
		$g_s = g_{smax}(1 - e^{-E_0/E_k}) + g_{sdark}$ where: $g_{smax} = k\,(\Omega_a - 1)^n$	
Sand/sediment	g_{smax}: $k = 0.80$ $n = 1$ $E_k = 560$ $g_{sdark} = -0.80$	1.8	This study

g and k are in mmol m^{-2} h^{-1}; all irradiance (E) values are in µmol photons m^{-2} s^{-1}. Maximum values are based on estimated noontime irradiance ($E_0 = 2200$ µmol photons m^{-2} s^{-1}); values in parentheses are the highest measured values reported in the original references.

(pCO$_2$ = 325 µatm, vs. atmospheric pCO$_2$ = 350 µatm), the reef processes reduced the air-sea pCO$_2$ gradient from 25 to 24 µmol kg^{-1}, and thus acted as a small source of CO$_2$ to the atmosphere. This is consistent with the findings of Gattuso *et al.* (1996b) and Frankignoulle *et al.* (1996). Changing the atmospheric forcing or the algae-coral and coral-algae configuration did not affect the reef's role as a CO$_2$ source. Changes in the percent coral and algal cover, however, did affect whether the reef flat was a source or sink of CO$_2$. As expected, increasing the percent coral cover intensified the reef's role as a net source of CO$_2$, while the reef acted as a net CO$_2$ sink when the percent algae cover was increased.

**Table 3** Carbonate chemistry conditions used in model simulations

Simulation	Year	pCO$_{2(aq)}$ (μatm)	pCO$_{2(air)}$ (ppmv)	Temperature (°C)	% Cover Coral	Algae	Sand	Community structure
a	1880	255	280	27.1	14	19	46	1992 baseline
b	1880	255	280	27.1	14	19	46	Algae-coral
c	1880	255	280	27.1	14	19	46	Coral-algae
d	1880	255	280	27.1	14	47.5	38.5	Algae × 2.5
e	1880	255	280	27.1	30	19	46	Coral × 2.5
f	**1992**	**325**	**350**	**27.1**	**14**	**19**	**46**	**1992 baseline**
g	1992	325	350	27.1	14	19	46	Algae-coral
h	1992	325	350	27.1	14	19	46	Coral-algae
i	1992	325	350	27.1	14	47.5	38.5	Algae × 2.5
j	1992	325	350	27.1	30	19	46	Coral × 2.5
k	2050	535	560	29.1	14	19	46	1992 baseline
l	2050	535	560	29.1	14	19	46	Algae-coral
m	2050	535	560	29.1	14	19	46	Coral-algae
n	2050	535	560	29.1	14	47.5	38.5	Algae × 2.5
o	2050	535	560	29.1	30	19	46	Coral × 2.5

'1992 baseline' community structure indicates reef communities are arranged according to community survey data of R. Galzin (personal communication; see Fig. 3); 'algae-coral' indicates the communities are segregated with algae upstream of coral; and 'coral-algae' indicates the communities are segregated with corals upstream of algae; 'algae × 2.5' indicates 2.5× normal% algal cover, and 'coral × 2.5' indicates 2.5× normal% coral cover. Note that total percent cover does not always equal 100% because bare rock (~20% of the reef flat) was not included in the simulations. In the coral × 2.5 and algae × 2.5 cases, sand cover was only reduced if total cover exceeded 100%. All simulations were initialized at A_T = 2378 μeq kg^{-1} and nutrient-free conditions. Simulation 'f' is the reference condition, tuned to the 1992 Tiahura reef flat conditions. Results of these simulations are shown in Fig. 6.
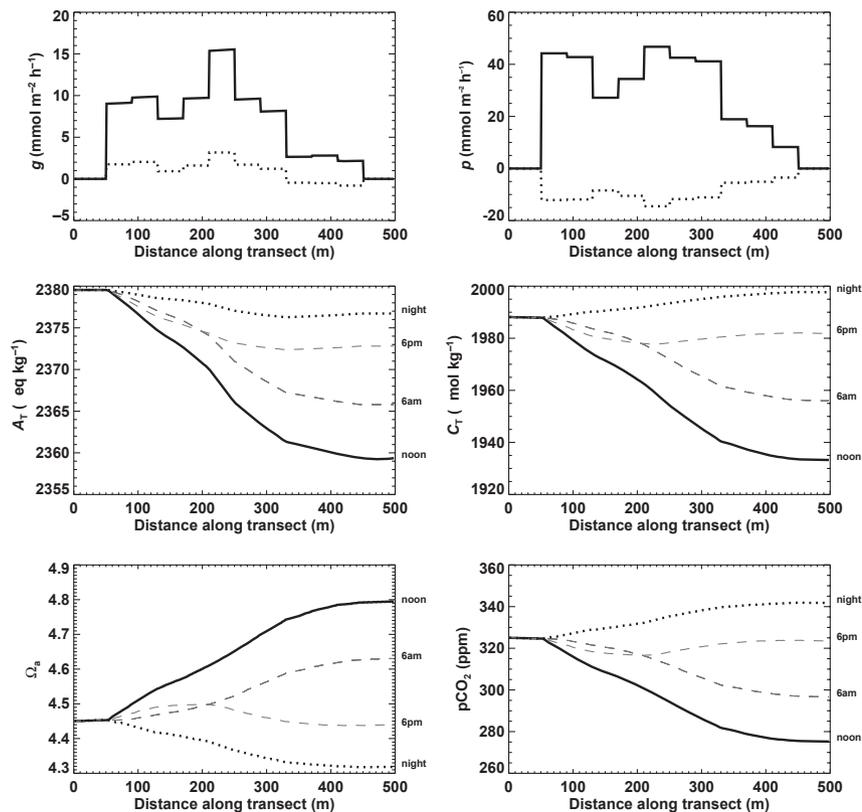
Fig. 4 Modeled changes in *g*, *p*, A_T, C_T, Ω_a, and pCO$_2$ on the Tiahura reef flat, from seaward to leeward, for 1992 conditions reported by Gattuso *et al.* (1996b). Profiles of the changes are shown for noon (solid line), nighttime (dotted line), and 06:00 and 18:00 (dashed line).
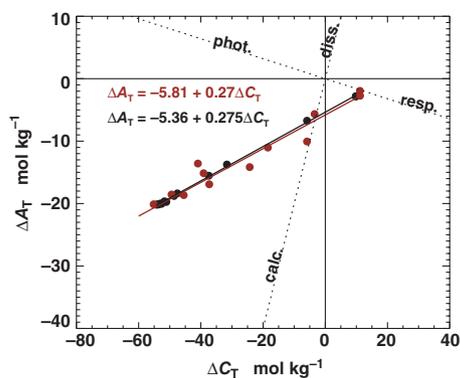
Fig. 5 Changes in A_T vs. C_T, on the Tiahura reef flat for 1992 conditions. Red dots represent the net changes in A_T and C_T at end of each field transect reported in Gattuso *et al.* (1996b); dots with the highest (least negative) ΔA_T and ΔC_T are nighttime values while those at the lowest (most negative) ΔA_T and ΔC_T are noontime values. Red line is the linear regression determined by Gattuso *et al.* (1996b). Black dots represent net changes in A_T and C_T at end of each hourly transect run by the model; black line is the linear regression determined using the model. Dotted lines show the expected changes under photosynthesis (phot.) and respiration (resp.) alone, or calcification (calc.) and dissolution (diss.) alone.

Our model results support the findings of Anthony *et al.* (2011) that coral reef communities can have a strong impact on the chemistry of reef waters. Large variations in reef seawater chemistry have been observed at multiple reef sites [beginning with the early studies of Smith and colleagues (e.g., Smith, 1973; Smith & Pesret, 1974; Smith & Key, 1975), Kinsey (1978), and others (Gattuso *et al.*, 1993; Kayanne *et al.*, 1995; Bates *et al.*, 2001; Ohde & Hossain, 2004; Kayanne *et al.*, 2005; Frankignoulle *et al.*, 1996)], and this raises the question of whether or not coral reefs will be affected by ocean acidification. The ability of our model to capture the changes in seawater chemistry on the Tiahura reef flat allows us to explore this question further, by examining the relative impacts of CO_2 forcing vs. changes in community structure on coral reef metabolic performance.

Effects of increasing CO_2

Despite the daily variations in seawater chemistry on the Tiahura reef flat, simulated net calcification on the reef flat responded to changes in atmospheric CO_2 forcing. Based on our formulations of g_c and g_s, and assuming no change in coral cover, the net reef calcification rate in 1992 was about 85% the 1880 rates. Also, the 2050 simulation (assuming a doubling of atmospheric CO_2 relative to 1880: 560 ppm) indicated the net calcification rate would be about 60% of the 1880 rates. Thus, changes in seawater chemistry of the source water due to ocean acidification are likely to significantly affect

net calcification on the reef. These modeled calcification rate decreases are in line with those predicted by others (Gattuso *et al.*, 1999; Kleypas *et al.*, 1999; Hoegh-Guldberg *et al.*, 2007; Anthony *et al.*, 2008; Silverman *et al.*, 2009). However, our simulations do not include two potentially important factors. First, we assume that primary production by macroalgae or corals is not stimulated by elevated pCO_2 (see, for example, Anthony *et al.*, 2008; Diaz-Pulido *et al.*, 2010). An increase in production would draw down some of the CO_2 absorbed from the atmosphere and offset the decreases in calcification (see discussion below). Second, we do not include the effects of $CaCO_3$ dissolution in our equations, except for the base rate of nighttime dissolution in the carbonate sediments. This value is small and assumed to be unresponsive to ocean acidification, but $CaCO_3$ dissolution rates are expected to increase with ocean acidification, particularly in sediments with high-Mg calcite sediments (Andersson *et al.*, 2009), and because of an expected increase in microbial bioerosion rates (Tribollet *et al.*, 2009).

Effects of reef communities

Spatial distribution of algae and coral communities. Recent papers have demonstrated that CO_2-drawdown by photosynthetic algae and plants can affect calcification rates of nearby calcifying species (Semesi *et al.*, 2009a; Semesi *et al.*, 2009b). Our model simulations with segregated algae and coral communities were used to test the significance of coral-algal distributions on the overall community calcification rates. The segregation of algae upstream of corals resulted in slightly higher calcification rates as C_T drawdown by algae upstream led to an increase in Ω_a of the water over corals downstream, but the benefit of the segregation was highly dependent on overall algae and coral abundances on the reef flat. For example, in the 1992 simulation, segregation of the algae upstream resulted in only a 2.5% increase in calcification rates downstream. If algae were segregated to the upstream location and its coverage increased 2.5-fold (simulation not shown), then net reef calcification increased 5.8%. This indicates that modest increases in calcification rates on the reef flat could be obtained by a phase shift to macroalgae upstream of coral communities. Based on the production equations employed in our simulations, however, algal growth would have to be increased by more than fivefold to make up for the reduction in calcification due to ocean acidification. Increasing the percent algae cover in a dispersed configuration on the reef flat (see Fig. 6d,i,n) did not produce the same results. An important point about the effects of the spatial distribution of algae and corals on chemistry of the reef waters is its dependence
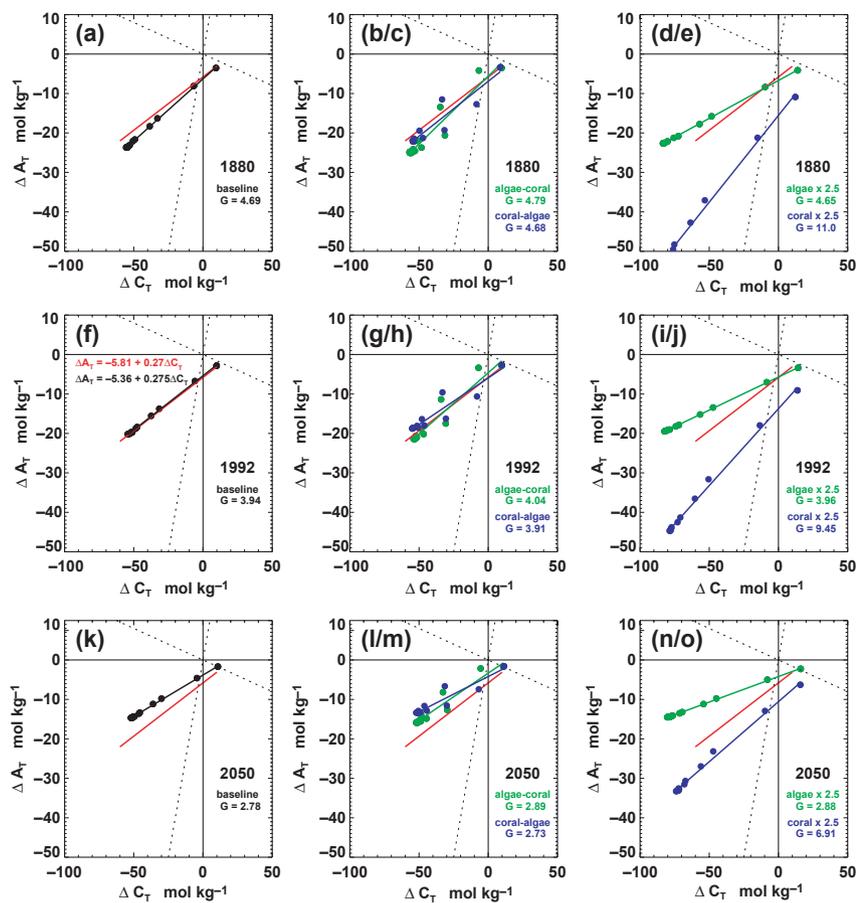
Fig. 6 Changes in A_T vs. C_T, under different atmospheric forcing and reef community configurations. Letters in upper left corner coincide with simulations listed in Table 3. '1992 baseline' community structure indicates reef communities are arranged according to community survey data of R. Galzin (personal communication; see Fig. 3); 'algae-coral' indicates the communities are segregated with algae upstream of coral; and 'coral-algae' indicates the communities are segregated with corals upstream of algae; 'algae × 2.5' indicates 2.5× normal percent algal cover, and 'coral × 2.5' indicates 2.5× normal percent coral cover. Hourly rate of calcification, integrated over a 24-h cycle for the entire reef flat (*G*), is provided in mmol $CaCO_3$ m^{-2} h^{-1}. All simulations were initialized at A_T = 2378 μeq kg^{-1}, C_T = 1990 μmol m^{-2} h^{-1} and nutrient-free conditions. Simulation 'f' is the reference condition, adjusted to the 1992 Tiahura reef flat conditions (the same as shown in Fig. 5).

on the volume of the overlying water column. The Moorea reef flat is shallow (~1.3 m), and the benthic carbon and alkalinity fluxes have a marked effect on the seawater chemistry. The fluxes of reef communities in deeper water will be more diluted if the overlying water column is well mixed, which is typical for most reef environments.

Percent cover of algae and coral communities. The changes in percent cover of coral and algal communities had the most profound impact on overall calcification rates. Between 1880 and 1992, the estimated 60% reduction in coral cover on the Tiahura reef flat reduced net reef calcification rates by 57%, which is much more than the estimated reduction due to ocean acidification (16%). The implication of these findings is that the impacts of ocean acidification on coral reef calcification during

this century will depend on the spatial and temporal variation in benthic reef composition. A drop in reef calcification (normalized to coral biomass or tissue surface area) can be offset by an increase in relative coral abundance. Conversely, a decline in relative coral abundance expected under intensified warming which causes coral mortality, and ocean acidification which reduces the recruitment of corals and coralline algae (Kuffner *et al.*, 2008; Albright & Langdon, 2011), will lead to accelerated loss of reef calcification (Kleypas *et al.*, 2001; Hoegh-Guldberg *et al.*, 2007; Kleypas & Yates, 2009).

Model assumptions and future research

We made several assumptions in our modeling effort to simulate the seawater chemistry changes on the Tiahura reef flat. First, parameter values were averages

of the broad ranges reported in the literature, and are therefore associated with significant error. Second, the relative contributions of macroalgae and turf algae were not explicitly partitioned in the modeling; nor were the relative contributions to production by corals and algae. This partitioning may be quite different from that in our model. Also, there were no seagrasses on the Tiahura reef flat, but research suggests that seagrasses may have an additional impact on reef seawater chemistry because they enhance the alkalinity flux from sediments (Burdige & Zimmerman, 2002), and they respond to CO_2 fertilization (Palacios & Zimmerman, 2007) while most macroalgae do not (Hurd *et al.*, 2009). Third, by modeling net calcification, we did not differentiate between the relative effects of calcification and dissolution. Understanding the contributions of both processes to the calcium carbonate budget is important, and should be a priority in future studies (Andersson & Mackenzie, 2011). The contributions of ground and pore water fluxes should also be included in future studies, although both are difficult to measure. Finally, although temperature was included in the CO_2-system calculations, it was not included as a factor in the production or calcification equations. Small temperature increases (e.g., <1 °C above climatological maximum) can stimulate coral metabolic rates and coral calcification rates (e.g., Jokiel & Coles, 1990; Lough & Barnes, 1997), and temperature increases can also cause coral bleaching and death (e.g., Eakin *et al.*, 2010). We did not include these effects in our calculations.

Despite these assumptions, our model appears to capture the most significant processes on the Tiahura reef, and has shown that known carbon fluxes of organic and inorganic production by coral reef communities can be used to estimate the net changes in CO_2-chemistry in seawater flowing over a coral reef. Our approach allowed us to examine the relative effects of both reef flat community structure and ocean acidification on the benthos-seawater carbon fluxes, as well as the calcification responses to those changes by communities downstream. The Tiahura reef flat offers a unique combination of geometry, physical oceanography, and benthic ecology that allowed this simple modeling approach.

Acknowledgments

References

Albright R, Langdon C (2011) Ocean acidification impacts multiple life history processes of the Caribbean coral *Porites astreoides*. *Global Change Biology*, **17**, 2478–2487.

Andersson AJ, Mackenzie FT (2004) Shallow-water oceans: a source or sink of atmospheric CO_2? *Frontiers in Ecology and the Environment*, **2**, 348–353.

Andersson AJ, Mackenzie FT (2011) Ocean acidification: setting the record straight. *Biogeosciences Discussions*, **8**, 6161–6190.

Andersson AJ, Kuffner IB, Mackenzie FT, Jokiel PL, Rodgers KS, Tan A (2009) Net loss of $CaCO_3$ from a subtropical calcifying community due to seawater acidification: mesocosm-scale experimental evidence. *Biogeosciences*, **6**, 1811–1823.

Anthony KRN, Kline DI, Diaz-Pulido G, Dove S, Hoegh-Guldberg O (2008) Ocean acidification causes bleaching and productivity loss in coral reef builders. *Proceedings of the National Academy of Sciences of the United States of America*, **105**, 17442–17446.

Anthony KRN, Kleypas JA, Gattuso JP (2011) Coral reefs modify their seawater carbon chemistry – implications for impacts of ocean acidification. *Global Change Biology*, doi: 10.1111/j.1365-2486.2011.02510.x.

Bates NR, Samuels L, Merlivat L (2001) Biogeochemical and physical factors influencing seawater fCO_2, and air-sea CO_2 exchange on the Bermuda coral reef. *Limnology and Oceanography*, **46**, 833–846.

Boucher G, Clavier J, Hily C, Gattuso JP (1998) Contribution of soft-bottoms to the community metabolism (primary production and calcification) of a barrier reef flat (Moorea, French Polynesia). *Journal of Experimental Marine Biology and Ecology*, **225**, 269–283.

Bouchon C (1985) Quantitative study of scleractinian coral communities of the Tiahura Reef (Moorea Island, French Polynesia). *Proceedings of the 5th International Coral Reef Symposium*, **6**, 279–284.

Broecker WS, Takahashi T, Simpson HJ, Peng TH (1979) Fate of fossil fuel carbon dioxide and the global carbon budget. *Science*, **206**, 409–418.

Burdige DJ, Zimmerman RC (2002) Impact of sea grass density on carbonate dissolution in Bahamian sediments. *Limnology and Oceanography*, **47**, 1751–1763.

Chalker BE (1981) Simulating light-saturation curves for photosynthesis and calcification by reef-building corals. *Marine Biology*, **63**, 135–141.

Crossland CJ, Hatcher BG, Smith SV (1991) Role of coral reefs in global ocean production. *Coral Reefs*, **10**, 55–64.

Diaz-Pulido G, Gouezo M, Tilbrook B, Dove S, Anthony KRN (2010) High CO_2 enhances the competitive strength of seaweeds over corals. *Ecology Letters*, **14**, 156–162.

Eakin CM, Morgan JA, Heron SF *et al.* (2010) Caribbean corals in crisis: record thermal stress, bleaching, and mortality in 2005. *PLoS ONE*, **5**, e13969, doi: 13910.11371/journal.pone.0013969.

Falter JL, Lowe RJ, Atkinson MJ, Monismith SG, Schar DW (2008) Continuous measurements of net production over a shallow reef community using a modified Eulerian approach. *Journal of Geophysical Research-Oceans*, **113**, C07035, doi: 07010.01029/02007jc004663.

Frankignoulle M, Gattuso J-P, Biondo R, Bourge I, Copin-Montégut G, Pichon M (1996) Carbon fluxes in coral reefs. 2. Eulerian study of inorganic carbon dynamics and measurement of air-sea CO_2 exchanges. *Marine Ecology Progress Series*, **145**, 123–132.

Gattuso JP, Pichon M, Delesalle B, Frankignoulle M (1993) Community metabolism and air-sea CO_2 fluxes in a coral reef ecosystem (Moorea, French-Polynesia). *Marine Ecology Progress Series*, **96**, 259–267.

Gattuso JP, Frankignoulle M, Smith SV, Ware JR, Wollast R (1996a) Coral reefs and carbon dioxide. *Science*, **271**, 1298.

Gattuso JP, Pichon M, Delesalle B, Canon C, Frankignoulle M (1996b) Carbon fluxes in coral reefs. 1. Lagrangian measurement of community metabolism and resulting air-sea CO_2 disequilibrium. *Marine Ecology Progress Series*, **145**, 109–121.

Gattuso JP, Payri CE, Pichon M, Delesalle B, Frankignoulle M (1997) Primary production, calcification, and air-sea CO_2 fluxes of a macroalgal-dominated coral reef community (Moorea, French Polynesia). *Journal of Phycology*, **33**, 729–738.

Gattuso JP, Frankignoulle M, Wollast R (1998) Carbon and carbonate metabolism in coastal aquatic ecosystems. *Annual Review of Ecology and Systematics*, **29**, 405–434.

Gattuso JP, Allemand D, Frankignoulle M (1999) Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry. *American Zoologist*, **39**, 160–183.

Hoegh-Guldberg O, Mumby PJ, Hooten AJ *et al.* (2007) Coral reefs under rapid climate change and ocean acidification. *Science*, **318**, 1737–1742.

Hurd CL, Hepburn CD, Currie KI, Raven JA, Hunter KA (2009) Testing the effects of ocean acidification on algal metabolism: considerations for experimental designs. *Journal of Phycology*, **45**, 1236–1251.

Jokiel PL, Coles SL (1990) Response of Hawaiian and other Indo-Pacific reef corals to elevated temperature. *Coral Reefs*, **8**, 155–162.

Kayanne H, Suzuki A, Saito H (1995) Diurnal changes in the partial pressure of carbon dioxide in coral reef water. *Science*, **269**, 214–216.

Kayanne H, Hata H, Kudo S *et al.* (2005) Seasonal and bleaching-induced changes in coral reef metabolism and CO_2 flux. *Global Biogeochemical Cycles*, **19**, GB3015.

Kinsey DW (1978) Alkalinity changes and coral reef calcification. *Limnology and Oceanography*, **23**, 989–991.

Kinsey DW (1985) Metabolism, calcification and carbon production. I. Systems level studies. *Proceedings of the 5th International Coral Reef Symposium*, **4**, 505–526.

Kleypas JA, Yates KK (2009) Coral reefs and ocean acidification. *Oceanography*, **22**, 108–117.

Kleypas JA, Buddemeier RW, Archer D, Gattuso JP, Langdon C, Opdyke BN (1999) Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science*, **284**, 118–120.

Kleypas JA, Buddemeier RW, Gattuso JP (2001) The future of coral reefs in an age of global change. *International Journal of Earth Sciences*, **90**, 426–437.

Kuffner IB, Andersson AJ, Jokiel PL, Rodgers KS, Mackenzie FT (2008) Decreased abundance of crustose coralline algae due to ocean acidification. *Nature Geoscience*, **1**, 114–117.

Langdon C, Atkinson MJ (2005) Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment. *Journal of Geophysical Research-Oceans*, **110**, C09S07.

Lough JM, Barnes DJ (1997) Several centuries of variation in skeletal extension, density and calcification in massive *Porites* colonies from the Great Barrier Reef: a proxy for seawater temperature and a background of variability against which to identify unnatural change. *Journal of Experimental Marine Biology and Ecology*, **211**, 29–67.

Marubini F, Barnett H, Langdon C, Atkinson MJ (2001) Dependence of calcification on light and carbonate ion concentration for the hermatypic coral *Porites compressa*. *Marine Ecology Progress Series*, **220**, 153–162.

Morse JW, Andersson AJ, Mackenzie FT (2006) Initial responses of carbonate-rich shelf sediments to rising atmospheric pCO_2 and "ocean acidification": role of high Mg-calcites. *Geochimica et Cosmochimica Acta*, **70**, 5814–5830.

Nakamura T, Nakamori T (2009) Estimation of photosynthesis and calcification rates at a fringing reef by accounting for diurnal variations and the zonation of coral reef communities on reef flat and slope: a case study for the Shiraho reef, Ishigaki Island, southwest Japan. *Coral Reefs*, **28**, 229–250.

Ohde S, Hossain MMM (2004) Effect of $CaCO_3$ (aragonite) saturation state of seawater on calcification of *Porites* coral. *Geochemical Journal*, **38**, 613–621.

Palacios SL, Zimmerman RC (2007) Response of eelgrass *Zostera marina* to CO_2 enrichment: possible impacts of climate change and potential for remediation of coastal habitats. *Marine Ecology Progress Series*, **344**, 1–13.

Robbins L, Hansen M, Kleypas J, Meyla S (2011) CO_2calc: A user-friendly seawater carbon calculator for Windows, Mac OS X, and iOS (iPhone). Florida Shelf Ecosystems Response to Climate Change Project Ocean Acidification Task: U.S. Geological Survey Open File Report 2010-1280, 27 pp.

Sabine CL, Feely RA, Gruber N *et al.* (2004) The oceanic sink for anthropogenic CO_2. *Science*, **305**, 367–371.

Schneider K, Erez J (2006) The effect of carbonate chemistry on calcification and photosynthesis in the hermatypic coral *Acropora eurystoma*. *Limnology and Oceanography*, **51**, 1284–1293.

Semesi IS, Beer S, Bjork M (2009a) Seagrass photosynthesis controls rates of calcification and photosynthesis of calcareous macroalgae in a tropical seagrass meadow. *Marine Ecology Progress Series*, **382**, 41–47.

Semesi IS, Kangwe J, Bjork M (2009b) Alterations in seawater pH and CO_2 affect calcification and photosynthesis in the tropical coralline alga, *Hydrolithon* sp (Rhodophyta). *Estuarine Coastal and Shelf Science*, **84**, 337–341.

Silverman J, Lazar B, Cao L, Caldeira K, Erez J (2009) Coral reefs may start dissolving when atmospheric CO_2 doubles. *Geophysical Research Letters*, **36**, L05606.

Smith SV (1973) Carbon dioxide dynamics: a record of organic carbon production, respiration and calcification in the Eniwetok reef flat community. *Limnology and Oceanography*, **18**, 106–120.

Smith SV, Buddemeier RW (1992) Global change and coral reef ecosystems. *Annual Review of Ecology Evolution and Systematics*, **23**, 89–118.

Smith SV, Key GS (1975) Carbon-dioxide and metabolism in marine environments. *Limnology and Oceanography*, **20**, 493–495.

Smith SV, Pesret F (1974) Processes of carbon dioxide flux in Fanning Island Lagoon. *Pacific Science*, **28**, 225–245.

Tribollet A, Godinot C, Atkinson M, Langdon C (2009) Effects of elevated pCO_2 on dissolution of coral carbonates by microbial euendoliths. *Global Biogeochemical Cycles*, **23**, GB3008.

Wanninkhof R (1992) Relationship between wind-speed and gas-exchange over the ocean. *Journal of Geophysical Research-Oceans*, **97**, 7373–7382.