

CO₂ partial pressure controls the calcification rate of a coral community

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Abstract

Previous studies have demonstrated that coral and algal calcification is tightly regulated by the calcium carbonate saturation state of seawater. This parameter is likely to decrease in response to the increase of dissolved CO₂ resulting from the global increase of the partial pressure of atmospheric CO₂. We have investigated the response of a coral reef community dominated by scleractinian corals, but also including other calcifying organisms such as calcareous algae, crustaceans, gastropods and echinoderms, and kept in an open-top mesocosm. Seawater *p*CO₂ was modified by manipulating the *p*CO₂ of air used to bubble the mesocosm. The aragonite saturation state (Ω_{arag}) of the seawater in the mesocosm varied between 1.3 and 5.4. Community calcification decreased as a function of increasing *p*CO₂ and decreasing Ω_{arag} . This result is in agreement with previous data collected on scleractinian corals, coralline algae and in a reef mesocosm, even though some of these studies did not manipulate CO₂ directly. Our data suggest that the rate of calcification during the last glacial maximum might have been 114% of the preindustrial rate. Moreover, using the average emission scenario (IS92a) of the Intergovernmental Panel on Climate Change, we predict that the calcification rate of scleractinian-dominated communities may decrease by 21% between the pre-industrial period (year 1880) and the time at which *p*CO₂ will double (year 2065).

Keywords: calcification, coral community, coral reefs, *p*CO₂

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Introduction

Calcification plays a major role in the global carbon cycle over geological time (Opdyke & Walker 1992) and is a major process enabling coral reefs, one of the most diverse ecosystems, to thrive in tropical shallow waters (Birkeland 1997). Complex interactions exist between calcification and dissolved inorganic carbon (DIC) which comprises three species (dissolved CO₂: CO₂ + H₂CO₃; bicarbonate: HCO₃⁻; and carbonate ions: CO₃²⁻) related according to the following equilibrium:



Their respective proportions are controlled by the following equilibrium constants K_0 , K_1 and K_2 (*p*CO₂ = CO₂ partial pressure):

$$K_0 = \frac{p\text{CO}_2}{[\text{CO}_2]} \quad K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} \quad K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}. \quad (2-4)$$

These constants depend on temperature, salinity and pressure (DOE 1994). The process of calcification modifies the seawater DIC system by releasing 0.6 mole of CO₂ (Frankignoulle *et al.* 1994) and removing 2 mole of bicarbonate (Smith & Key 1975) for each mole of calcium carbonate precipitated. CaCO₃ dissolution has an opposite effect on the DIC system.

Theoretical considerations and experiments performed on calcifying organisms indicate that calcification is regulated by the seawater DIC chemistry. Indeed, the availability of CO₃²⁻ plays a critical role in controlling the calcium carbonate precipitation (Smith & Buddemeier 1992; Kleypas *et al.* 1999; see, for review, Gattuso *et al.* 1999). Therefore, calcification is also modified by changes in DIC induced by the steady increase of atmospheric *p*CO₂ due to anthropogenic inputs (Houghton *et al.* 1996).

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The upper layers of the oceans tend to equilibrate with the atmosphere; their $p\text{CO}_2$ increases (Brewer *et al.* 1997; Winn *et al.* 1998; Goyet *et al.* 1999) leading to a decrease of the carbonate concentration and of the calcium carbonate saturation state (Ω). These changes might lead to a drop of the rate of calcium carbonate deposition on reefs.

Previous experiments on the effect of the aragonite saturation state, Ω_{arag} , on the rate of calcification of marine organisms did not directly manipulate atmospheric $p\text{CO}_2$ or the CO_2 concentrations used were far above predicted values for the next century (Smith & Roth 1979; Gao *et al.* 1993). In the other studies, the modification of the seawater CaCO_3 saturation state was achieved by adding sodium bicarbonate, sodium carbonate and/or calcium chloride (Borowitzka 1981; Gao *et al.* 1993; Langdon *et al.* 1998, submitted; Marubini & Thake 1999), by using calcium-modified artificial seawater (Gattuso *et al.* 1998a) or by manipulating pH (Aegeian 1985; Mackenzie & Aegeian 1989; Gao *et al.* 1993; Marubini & Atkinson 1999). Nevertheless, these studies demonstrated that calcification is tightly controlled by Ω .

The response of organisms to changes in Ω is relatively well documented. However, there is little information on the response of natural reef communities to changes in Ω : one study investigated the response of a reef flat in Japan (Ohde & van Woessik 1999) and one study investigated the response of a reef mesocosm (Langdon *et al.* 1998; submitted).

The present paper provides information on the response of calcification of a reef community, maintained under controlled conditions, to direct and rapid manipulation of $p\text{CO}_2$. The results are used to predict future changes in reef calcification using the average emission scenario (IS92a) of the Intergovernmental Panel on Climate Change (IPCC). This scenario forecasts that atmospheric $p\text{CO}_2$ will reach a value of $560 \mu\text{atm}$, i.e. twice the preindustrial value, in 2065 and $700 \mu\text{atm}$ in 2100 (Houghton *et al.* 1996).

Materials and methods

The experimental reef community included coral sand and calcareous rocks on which were growing scleractinian corals [2 *Acropora* spp. (20 cm and 15 cm in diameter, respectively), 1 *Favia* sp. (5 cm), 1 *Porites* sp. (20 cm), 1 *Montipora* sp. (35 cm), 1 *Galaxea fascicularis* (12 cm), 1 *Trachiphyllia geoffroyi* (10 cm), 1 *Turbinaria mesenterina* (10 cm)], sea anemones (*Entaeacmea quadricolor* and *Aiptasia* sp.) and some calcareous red algae (mainly *Neogoniolithon* spp. and *Hydrolithon* spp.). It also included 2 *Dascyllus trimaculatus* (damselfish) and 1 *Zebrasoma scopas* (brown tang). The microfauna included small crustaceans, polychaetes and gastropods. This community was held in a glass aquarium

($0.58 \text{ m} \times 0.58 \text{ m} \times 0.58 \text{ m}$). The substratum (surface area = 0.34 m^2) was a live sand system: a carbonate sand layer (0.05 m thick) separated the main seawater reservoir (150 L) from a small volume (15 L) of confined and stagnant water (Jaubert 1989). We assumed that this water body acted as interstitial water and was part of the community. The aquarium contained mediterranean seawater (salinity = 38.0) pumped at a depth of 50 m, passed through a sand filter and heated to $26 \pm 1^\circ\text{C}$ with a temperature controller (Réna, Biotherm 2000). Seawater was renewed at a rate of $50\% \text{ h}^{-1}$ to prevent any change in its composition. Light was provided by a 400-W Daylight metal halide lamp (Osram HQI-T/D) that ran on a 12:12 h photoperiod. Irradiance (= photosynthetic photon flux density) was measured using a quantum 4π sensor (LI-193SA, LI-COR Inc.) and was $230 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$. Water motion in the main reservoir was ensured by a 600-l h^{-1} centrifugal pump (Réna, C40) and gas exchange was promoted by 2 air stones fitted either to an air pump (Réna 301) or to a gas blender which was used to increase $p\text{CO}_2$. Aquarium windows were cleaned daily to control algal growth.

Seawater input was shut down during measurements of calcification. 24 h incubations ($N = 19$) were performed under normal ($N = 7$), low ($N = 5$) and high ($N = 7$) $p\text{CO}_2$ in order to get a wide range of aragonite saturation values. This was achieved by using a gas blender (series 850, Signal Instrument Co. Ltd) in combination with a gas divider (821S, Signal Instrument Co. Ltd) or a CO_2 -scrubber filled with soda lime. The $p\text{CO}_2$ of the air used to aerate the mesocosm was checked using an infra-red gas analyser (LI-6262, LI-COR Inc.). Incubations under normal $p\text{CO}_2$ started around mid-day; the air used to aerate had a $p\text{CO}_2$ of $380 \mu\text{atm}$. Incubations under high $p\text{CO}_2$ started in the morning, after bubbling the mesocosm with CO_2 -rich ($700 \mu\text{atm}$) air through the preceding night. Dark respiration and CO_2 -rich air resulted in a seawater $p\text{CO}_2$ above normal values. Incubations under low CO_2 started in the evening, after the mesocosm being bubbled with CO_2 -free ($2 \mu\text{atm}$) air throughout the day. Net photosynthesis and CO_2 -free air resulted in a seawater $p\text{CO}_2$ below normal values. Water temperature was measured ($\pm 0.05^\circ\text{C}$) and logged every minute (Seamon, Hugin). pH was measured using a glass combination electrode (Orion, model 8102SC) that was calibrated before each experiment against Sea Water Scale (SWS) buffers: TRIS and AMP (DOE 1994). pH data were averaged over a minute and logged (LI-1000, LI-COR Inc.). Seawater was sampled every 1 to 6 h (200 mL), filtered on $0.45 \mu\text{m}$ membranes (cellulose nitrate membrane filters, Whatman Ltd) and stored at 4°C pending total alkalinity (TA) determination. TA was determined by potentiometric titrations using an automatic titrator (DL25, Mettler) and the calcification rate was estimated

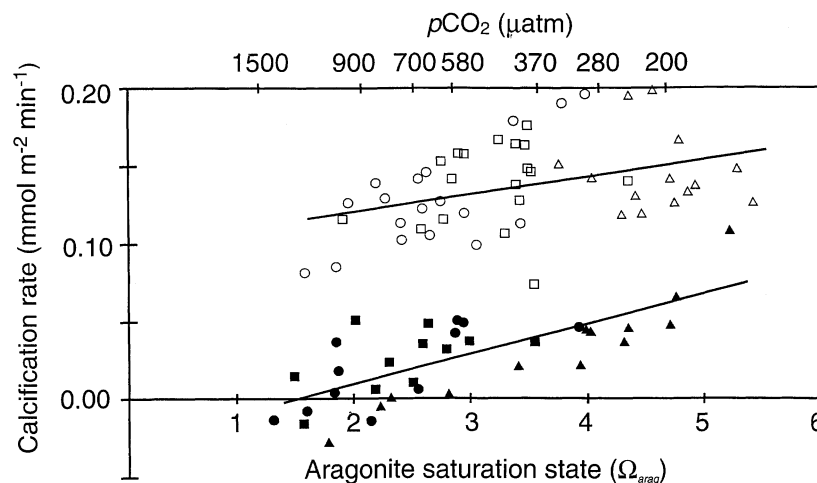


Fig. 1 Calcification rate of the reef community, in the light (open symbols) and dark (filled symbols) as a function of the aragonite saturation state and $p\text{CO}_2$. Symbol shape indicates data collected in the low (\triangle and \blacktriangle), normal (\square and \blacksquare) and high (\circ and \bullet) $p\text{CO}_2$ treatments.

from ΔTA using the alkalinity anomaly technique (Smith & Key 1975). Measurements of pH and TA were used, together with the computation of the carbonate equilibrium constants, to derive the concentration of the carbonate species (DOE 1994). The aragonite saturation state was calculated as follows:

$$\Omega_{\text{arag}} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{arag}}}, \quad (5)$$

where $[\text{Ca}^{2+}]$ is the calcium concentration (set to 10 mmol kg^{-1}), $[\text{CO}_3^{2-}]$ is the carbonate concentration (in mmol kg^{-1}) derived from pH and TA measurements, K_{arag} is the equilibrium constant for aragonite (Mucci 1983).

The Ω_{arag} values of the preindustrial period, years 2065 and 2100, used in this work were from Gattuso *et al.* (1999; Table 1).

Results

Total alkalinity dropped from 2.5 to $\approx 2.0 \text{ mEq kg}^{-1}$ during the course of a 24-h incubation; such change had no effect on the rate of community calcification ($r = 0.34$, $N = 50$, $P = 0.014$ for calcification in the light and $r = 0.21$, $N = 35$, $P = 0.24$ for calcification in the dark). $p\text{CO}_2$ ranged from $134 \mu\text{atm}$ to $1813 \mu\text{atm}$ as a result of photosynthesis, respiration or $p\text{CO}_2$ manipulations and resulted in a wide range of Ω_{arag} (1.3–5.4). Significant changes in the rate of community calcification were associated with these changes in $p\text{CO}_2$ (Fig. 1). Net community calcification was significantly correlated with Ω_{arag} both during daylight (light calcification = $9.8 \times 10^{-2} + 1.2 \times 10^{-2} \cdot \Omega_{\text{arag}}$, $r = 0.39$, $N = 50$, $P = 0.006$) and at night (dark calcification = $-3.0 \times 10^{-2} + 2.0 \times 10^{-2} \cdot \Omega_{\text{arag}}$, $r = 0.74$, $N = 35$, $P < 0.001$). The calcification rate found for the present day value of Ω_{arag} (4.3) was $0.15 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ min}^{-1}$

during the light period and $0.05 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ min}^{-1}$ in the dark. This corresponds to an integrated net inorganic flux of $53 \text{ mol CaCO}_3 \text{ m}^{-2} \text{ y}^{-1}$ or $5.3 \text{ kg CaCO}_3 \text{ m}^{-2} \text{ y}^{-1}$.

The rate of net community calcification was always higher in the light than in the dark. The light to dark calcification ratio varied as a function of the aragonite saturation state. It was 2.4 at $\Omega_{\text{arag}} = 4.9$ (preindustrial value), 2.9 at $\Omega_{\text{arag}} = 4.3$ and 5 at $\Omega_{\text{arag}} = 3$ (predicted value for the year 2100).

The rate of calcification was integrated over 24 h and expressed as a percentage of the maximum rate measured ($\Omega_{\text{arag}} = 5.4$). The linear relationship between this relative rate of calcification and Ω_{arag} ($Y = 28.5 + 13.2 \cdot \Omega_{\text{arag}}$) was calculated from the parameters of the linear regressions presented in Fig. 1. The calcification rate, in percentage terms relative to the rate at $\Omega_{\text{arag}} = 4.9$, is plotted in Fig. 2 together with data compiled by Gattuso *et al.* (1999). Some data sets of this compilation were not used because of the narrow range of Ω_{arag} investigated or because they were related to temperate algae. Data derived from Marubini & Thake (1999) and data presented by Ohde & van Woesik (1999) are also plotted.

Discussion

Calcification rates measured in the coral mesocosm are of the same order of magnitude as those reported for reef flat communities (Smith 1973; Kinsey 1983; Smith 1995; Gattuso *et al.* 1998b). This emphasizes that coral mesocosms are good models that can be used to investigate the behaviour of natural reef communities (Jaubert *et al.* 1995; Leclercq *et al.* 1999) and allows the extension of our results to natural communities of similar composition.

TA dropped from 2.5 to $\approx 2.0 \text{ mEq kg}^{-1}$ during the course of a 24-h incubation as a consequence of

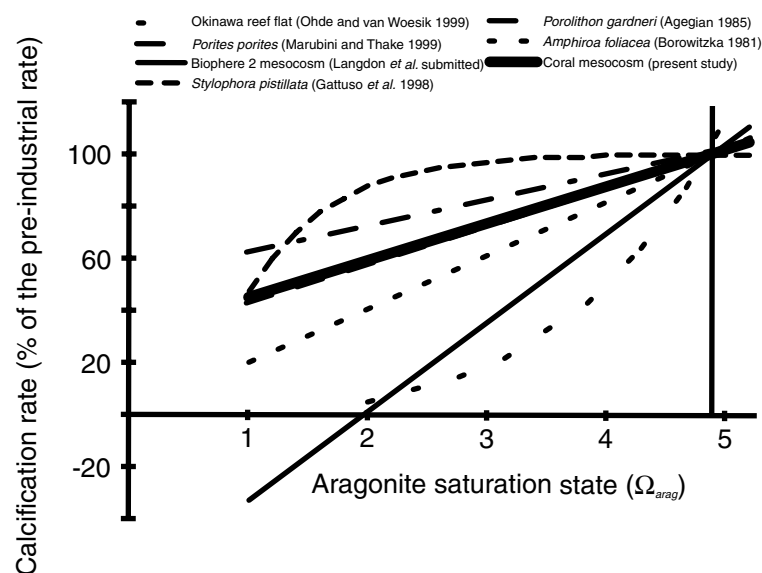


Fig. 2 Relative calcification rate as a function of Ω_{arag} for scleractinian corals, calcareous algae and coral communities. Previous data are from the review of Gattuso *et al.* (1999) and from Marubini & Thake (1999). Data for *Porites porites* were derived from tables 2 (p.717) and 5 (p.719, Control vs. Control + DIC) of Marubini & Thake (1999) using eqn (5) of the present work. The vertical line shows the preindustrial Ω_{arag} (4.9).

calcification by the coral community in a relatively small volume of seawater. Such variation does not occur on coral reefs where TA typically decreases by a few tens of $\mu\text{Eq kg}^{-1}$ in flow respirometry experiments.

Previous works have shown that Ω affects the rate of calcification of marine organisms and communities (see review by Gattuso *et al.* 1999). However, in these studies, Ω was not changed by manipulating the seawater carbonate system in a fashion analogous to that occurring since the industrial revolution (increased $p\text{CO}_2$). Rathermore, Ω was changed by directly manipulating the concentrations of bicarbonate, carbonate and/or calcium of natural seawater (Borowitzka 1981; Gao *et al.* 1993; Langdon *et al.* 1998; submitted; Marubini & Thake 1999), by using calcium-modified artificial seawater (Gattuso *et al.* 1998a) or by manipulating pH and TA (Smith & Roth 1979; Agegian 1985; Mackenzie & Agegian 1989; Gao *et al.* 1993; Marubini & Atkinson 1999). The present study demonstrates that the rate of calcification of the coral community decreases in response to a decrease of the seawater aragonite saturation state (Ω_{arag}) resulting from an increase in $p\text{CO}_2$. The fact that a similar result is obtained regardless of the technique used to manipulate Ω_{arag} emphasizes that the calcium carbonate saturation state is a major factor controlling the calcification process. Moreover, since the components of the coral community under study were different in species composition and in proportion from the other experiment performed on a mesocosm (Langdon *et al.* submitted) and that most of the taxa included have not been studied at organism level, our results therefore considerably broaden the taxonomic pool over which the effect of Ω_{arag} on calcification has been demonstrated.

The results presented in this article are relevant to coral-dominated communities with a high rate of inorganic production and are not necessary relevant when considering other, less calcifying, communities such as macrophyte-dominated and sandy areas. Indeed, sandy areas typically exhibit low calcification rates and tend to dissolve under present conditions (Kinsey 1983; Boucher *et al.* 1998). Thus, the net calcification rate of some natural communities could fall below compensation value and lead to net dissolution of the substratum. This could result in a larger decrease of the calcification rate of the whole reef ecosystem than the one reported here. Dissolution consumes CO_2 and increases TA , thereby counteracting the decrease in Ω_{arag} due to increased atmospheric $p\text{CO}_2$. However, this effect is insignificant and can be neglected (Leclercq, Gattuso and Jaubert, unpubl. data).

Although the general response of net calcification to changes in Ω_{arag} is similar across various taxa and communities, there are some differences in the magnitude and shape of the relationship (Fig. 2). The response of our mesocosm is linear and similar to that reported for tropical marine algae (Borowitzka 1981; Agegian 1985; Mackenzie & Agegian 1989) and for *Porites porites* (Marubini & Thake 1999). The response of the Biosphere 2 mesocosm (Langdon *et al.* submitted) is also linear, with a slope greater than that observed in the present study. Such difference might be due to a larger proportion of sandy areas, which could provide increased dissolution. The response of the coral *S. pistillata* to changes in Ω_{arag} is curvilinear as opposed to the linear relationship found in all other systems investigated so far. This response was investigated by manipulating Ω_{arag} through changes in

calcium concentration of synthetic seawater, rather than by modifying the carbonate system (Gattuso *et al.* 1998a). This may have affected calcium transport or some aspect of organic metabolism that would not respond to CO_2 system alterations. The response of a reef flat (Okinawa, Japan) is also curvilinear but exponentially shaped (Ohde & van Woesik 1999). This result is of particular importance since it is the first attempt to study the effect of Ω_{arag} *in situ*. However, its validity remains unclear because the effects of Ω_{arag} and light are superimposed. Since calcification is known to respond to both two parameters, it is difficult to delineate their relative importance on the control of the calcification rate.

Gattuso *et al.* (1999) provide estimates of Ω_{arag} during the last glacial maximum (LGM; 5.9), the preindustrial period (4.9), and years 1990 (4.3), 2065 (3.4) and 2100 (3). It is possible to derive potential changes in calcification from these estimates together with the relationship between net calcification and Ω_{arag} reported here. The results suggest that the calcification rate of coral communities was 114% of the preindustrial rate during the LGM, is presently 91% of the preindustrial value and that it could drop to 79% and 73% of the preindustrial value by years 2065 and 2100, respectively. These predictions are surprisingly close to those provided by Gattuso *et al.* (1999) for both temperate and tropical systems. They predicted that calcification in 2100 could be 78% of the preindustrial calcification. Also, the predicted decrease that we report (21%) is within the range reported by Kleypas *et al.* (1999) for coral reefs (14–30%).

Our work confirms the critical role of dissolved CO_2 in controlling reef calcification. The decrease in calcification as a function of decreasing Ω_{arag} is becoming widely accepted. This, combined with other environmental threats, such as eutrophication and increased seawater temperature, might have a dramatic impact on coral reefs in terms of rate of accretion and capacity to recover after damaging events such as storms or mass mortality following bleaching events.

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