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**CO₃²⁻ concentration
and pCO₂ thresholds**

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CO₃²⁻ concentration and pCO₂ thresholds for calcification and dissolution on the Molokai reef flat, Hawaii

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Abstract

The severity of the impact of elevated atmospheric $p\text{CO}_2$ to coral reef ecosystems depends, in part, on how seawater $p\text{CO}_2$ affects the balance between calcification and dissolution of carbonate sediments. Presently, there are insufficient published data that relate concentrations of $p\text{CO}_2$ and CO_3^{2-} to in situ rates of reef calcification in natural settings to accurately predict the impact of elevated atmospheric $p\text{CO}_2$ on calcification and dissolution processes. Rates of net calcification and dissolution, CO_3^{2-} concentrations, and $p\text{CO}_2$ were measured, in situ, on patch reefs, bare sand, and coral rubble on the Molokai reef flat in Hawaii. Rates of calcification ranged from 0.003 to 0.23 $\text{g CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ and dissolution ranged from -0.005 to $-0.33 \text{ g CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$. Calcification and dissolution varied diurnally with net calcification primarily occurring during the day and net dissolution occurring at night. These data were used to calculate threshold values for $p\text{CO}_2$ and CO_3^{2-} at which rates of calcification and dissolution are equivalent. Results indicate that calcification and dissolution are linearly correlated with both CO_3^{2-} and $p\text{CO}_2$. Threshold $p\text{CO}_2$ and CO_3^{2-} values for individual substrate types showed considerable variation. The average $p\text{CO}_2$ threshold value for all substrate types was $654 \pm 195 \mu\text{atm}$ and ranged from 467 to $1003 \mu\text{atm}$. The average CO_3^{2-} threshold value was $152 \pm 24 \mu\text{mol kg}^{-1}$, ranging from 113 to $184 \mu\text{mol kg}^{-1}$. Ambient seawater measurements of $p\text{CO}_2$ and CO_3^{2-} indicate that CO_3^{2-} and $p\text{CO}_2$ threshold values for all substrate types were both exceeded, simultaneously, 13% of the time at present day atmospheric $p\text{CO}_2$ concentrations. It is predicted that atmospheric $p\text{CO}_2$ will exceed the average $p\text{CO}_2$ threshold value for calcification and dissolution on the Molokai reef flat by the year 2100.

1. Introduction

Experimental results and models suggest that rising atmospheric CO_2 and resulting decreases in saturation state with respect to carbonate minerals in the ocean's surface

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waters will cause a decrease in rates of calcification on coral reefs by the middle of the 21st century (Gattuso et al., 1999; Kleypas et al., 1999; Mackenzie et al., 2000; Langdon et al., 2000; Leclercq et al., 2000, 2002; Anderson et al., 2003) and an increase in rates of dissolution of carbonate sediments (Barnes and Cuff, 2000; Halley and Yates, 2000; Andersson et al., 2003). Reduced calcification and loss of carbonate sediment may inhibit the ability of coral reefs to keep up with rising sea level (Smith and Kinsey, 1976), cause premature “erosion” of coral reef structure (Kleypas et al., 2001), and inhibit the ability of corals and other calcifying reef builders to compete with more opportunistic benthic species including algae and sponges. The severity of the impact of elevated CO₂ on coral reef systems depends, in part, upon the balance between coral reef calcification and dissolution of reef sediments. Development of predictive capabilities that describe this balance requires in situ characterization of seawater carbonate chemistry and calcification rates in natural reef communities of varying composition in order to place constraints on the range of pCO₂ and CO₃²⁻ at which rates of sediment dissolution exceed rates of calcification. Rates of calcification on coral reefs have been well characterized through in situ measurements made in numerous coral reef systems over the past four decades (e.g. Kinsey, 1972, 1978, 1979, 1985; Smith, 1973, 1981; Atkinson and Grigg, 1984; Barnes and Devereux, 1984; Smith et al., 1985; Conand et al., 1997; Gattuso et al., 1997; Boucher et al., 1998; Yates and Halley, 2003). However, there is insufficient published data for quantifying the relation among in situ pCO₂, CO₃²⁻ concentrations, and the balance between calcification and dissolution in natural reef settings to accurately predict the impact of elevated atmospheric CO₂.

Many studies have demonstrated a close correlation between the rate of calcification by marine organisms and aragonite saturation state (Borowitzka, 1981; Gao et al., 1993; Langdon et al., 1998, 2000; Gattuso et al., 1998; Marubini and Thake, 1999; Marubini and Atkinson, 1999; Marubini et al., 2003; Leclercq et al., 2000; Langdon and Atkinson, 2005) whereby rate of calcification decreases with decreasing saturation state. Saturation state with respect to carbonate minerals is calculated as the product of the concentrations of Ca²⁺ and CO₃²⁻ divided by the stoichiometric solubility prod-

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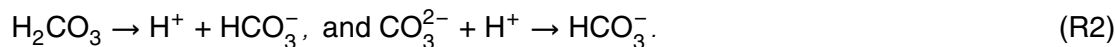
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uct (K_{sp}^*) (Andersson et al., 2003), and is, thus, dependant upon the distribution of inorganic carbon species in seawater (H_2CO_3 , HCO_3^- , and CO_3^{2-}). The distribution of inorganic carbon species is regulated, in part, by changes in seawater pH (Stumm and Morgan, 1981). As atmospheric pCO_2 increases and equilibrates with seawater, carbonic acid is generated via:



causing a reduction in pH and a shift in carbonate speciation that reduces the concentration of CO_3^{2-} and increases the concentration of HCO_3^- via:



Thus, an increase in pCO_2 and a reduction in CO_3^{2-} concentration result in a reduction of saturation state. Inorganic dissolution of carbonate sediments occurs when saturate state is less than one.

Diurnal variation in calcification and dissolution with net calcification occurring during the day and net dissolution occurring at night in surface waters that remain supersaturated with respect to calcite and aragonite has long been recognized (Kinsey, 1978; Barnes and Devereux, 1984; Gattuso et al., 1993, 1997; Conand et al., 1997; Boucher et al., 1998; Yates and Halley, 2003, 2006). Earlier studies (Kinsey et al., 1978; Barnes and Devereux, 1984; Gattuso et al., 1993) indicate that calcification during the day typically exceeded dissolution during the night resulting in net carbonate sediment production during 24 h time periods, or that calcification occurred during both day and night (Smith, 1973). More recent studies provide many examples of reef areas in which dissolution is now exceeding calcification resulting in a net loss of carbonate sediment from the system over 24 h time periods (Conand et al., 1997 – back reef zone during summer only; Gattuso et al., 1997; Boucher et al., 1998; Yates and Halley, 2003, 2006). Saturation state in the tropics has decreased, on average, from 4.6 to 4.0 over the past century (Kleyepas et al., 1999) and atmospheric pCO_2 has increased from 338 to 375 ppm at the Mauna Loa Observatory in Hawaii from 1980 to 2003 (Keeling and Whorf,

2004). However, detailed studies on corals from the Great Barrier Reef show no indication of decreasing calcification rates since the industrial revolution (McNeil et al., 2004; Pelejero et al., 2005). Whether or not rates of coral reef calcification or dissolution of carbonate sediments in shallow reef environments has already increased over the past half century remains to be determined.

Dissolution in shallow, saturated surface waters has been attributed to numerous processes (Peyre-Venec, 1987; Lazar, 1991; Peyrot-Clausade, 1995; Sabine and Mackenzie, 1995; Charpy-Roubaud et al., 1996; Yates and Halley, 2006). Gattuso et al. (1996) suggested that sediments could have a significant contribution to reef chemistry as sinks of carbon due to the fact that dissolution of calcium carbonate consumes CO_2 through the reaction $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$. However, Andersson et al. (2003) provide model evidence indicating that dissolution of carbonate sediments will not buffer the global shallow-water marine environment against changes in pCO_2 because of the rapid mixing rate and large reservoir size of the coastal ocean. Whether or not calcium carbonate dissolution will buffer coral reef organisms against the impact of rising CO_2 and decreasing saturation states in localized areas with longer water residence times, or whether dissolution will simply promote the demise of reef building by removal of carbonate sediment from the reef system remains controversial.

We present calcification and dissolution rates measured in situ, relative to pCO_2 and CO_3^{2-} concentrations for representative substrate types of the Molokai, Hawaii reef flat, and have determined threshold values for pCO_2 and CO_3^{2-} at which rates of calcification and dissolution are equivalent. These threshold values (which we denote as $\text{CO}_{3,C/D=1}^{2-}$ and $\text{pCO}_{2,C/D=1}$) indicate the CO_3^{2-} and pCO_2 concentrations that must be surpassed to cause a transition from net calcification to net dissolution for each substrate type. Understanding diurnal, seasonal, inter-annual, species composition, and geographic effects on threshold values of seawater parameters that affect the balance between calcification and dissolution is critical for development of numerical predictive capabilities that will describe the impact of elevated CO_2 on reef systems. The range of threshold values reported for this very limited data set is intended to provide a first

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approximation of the natural range of values that might be encountered only on the Molokai reef flat and do not reflect spatial or temporal variation. Our range of threshold values represents only a small contribution to a much larger database of similar measurements that must be acquired to adequately characterize calcification and dissolution processes in natural reef systems.

2. Methods

Rates of calcification and dissolution were measured on representative substrate types of the Molokai reef flat from 9–17 February 2000, from 23–24 July 2001, and from 28–29 July 2001 using a large incubation chamber and the alkalinity anomaly technique (Smith and Key, 1975). The reef flat is approximately 1 km wide and shallow, with water depths ranging from 1 to 2 m. Substrate types measured in this study were located approximately 0.8 km off-shore, and included sand bottom, coral rubble, and patch reefs with 10% or 20% live coral cover located on sand (Fig. 1). Sand bottom consisted of medium to coarse grain carbonate sand of approximately 40% magnesian calcite containing 20 to 24% MgCO_3 . The mineralogy of the sand was determined by XRD analysis using a Bruker Endeavor D-4 x-ray diffractometer. Coral rubble was colonized by coralline algae including *Porolithon* sp. and *Hydrolithon* sp., and by a thin veneer of algal turf. Patch reefs were dominated by scleractinian corals (including *Porites lobata*, *Porites compressa*, *Montipora capitata*, and *Pocillopora* sp.), several species of coralline algae, and calcareous algae *Halimeda discoidea*. Percentage of coral cover was determined by measurement of the circumference of all live coral colonies within the incubation chamber. Carbonate system parameters, salinity, and temperature were measured in ambient seawater every 4 h throughout the duration of 24-h time periods from 13–14 October 2000, from 20–29 July 2001, and from 16–19 June 2003. Ambient seawater measurements were performed in the same general location as incubation chamber measurements (Fig. 1).

An incubation chamber (4.9 m (l) × 2.4 m (w) × 1.2 m (h)), constructed of an alu-

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minum frame and a clear, 10-mil vinyl tent fitted over the frame, was placed over each substrate type to isolate the water mass over the seafloor from ambient water. Detailed methodology on use of this incubation chamber, known as the Submersible Habitat for Analyzing Reef Quality (or SHARQ, U.S. patent #6,467,424 B1), can be found in Yates and Halley (2003). The vinyl tent was sealed to the seafloor by laying sand bags on a seal-flap around the perimeter of the incubation chamber to prevent leakage of water into or out of the tent. A submersible pump (246 LPM) was mounted to the aluminum frame and connected to a circulation system to maintain turbulent flow inside of the chamber. Oscillatory motion inside of the incubation chamber was achieved by translation of wave motion through the flexible tent structure. Water was diverted from the chamber's circulation system, using a secondary booster pump (44 LPM), to a flow-through analytical system located on a fixed platform at the water's surface. The water was then pumped back into the chamber after analysis in a closed-loop system. Salinity, temperature, and pH were measured continuously in the incubation chamber by the flow-through analytical system using an Orion Ross pH electrode (± 0.005 pH unit), and Orion conductivity (± 0.1 psu) and temperature ($\pm 0.1^\circ\text{C}$) probes. All probes were fitted into a PVC manifold attached to the flow-through analytical system, and data were logged every one-minute throughout the duration of 24-h incubation periods on each substrate type. pH electrodes were calibrated using Tris seawater buffers prepared at an ionic strength of 0.7 and scaled to the free-hydrogen-ion concentration scale (pH_f) (Millero, 1996). Conductivity probes were calibrated using standards acquired from the USGS Ocala National Water Quality and Research Laboratory. Fluorescein dye was injected into the incubation chamber during each deployment to determine incubation chamber volume, mixing rate, and leakage as described previously by Yates and Halley (2003). Water samples (500 mL) for total alkalinity analyses were removed from a sampling port in the incubation chamber's flow-through analytical system every 4 h throughout incubation periods, pressure filtered through $0.45\ \mu\text{m}$ cellulose nitrate filters, poisoned with $100\ \mu\text{L}$ saturated mercuric chloride, and stored in borosilicate glass bottles sealed with ground glass stoppers and Apiezon[®] grease.

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Throughout the duration of 24 h time periods, ambient seawater was measured, in situ, for salinity, temperature, and pH every 4 h using Orion conductivity (± 0.1 psu) and temperature ($\pm 0.1^\circ\text{C}$) probes, and an Orion Ross pH electrode (± 0.005 pH unit). Water samples for total alkalinity analyses were collected concurrently with salinity, temperature, and pH measurements using a peristaltic pump connected to a 145 mm filtration apparatus. Five hundred milliliter water samples were pressure filtered ($0.45\ \mu\text{m}$ cellulose nitrate filters), prepared, and stored using the same technique as described for incubation chamber water samples. Analytical measurements and water samples were collected within the upper 0.5 m of the water column.

Total alkalinity was measured on water samples collected in 2000 and 2001 by Gran titration using the automated titration system, methods, and equations described in detail in Millero et al. (1993) and Yates and Halley (2006). Standardized (~ 0.25 M) HCl used for titrations and standardized reference materials (SRM's) used to determine the reliability of alkalinity measurements were provided by Dr. Frank Millero (University of Miami, Rosenstiel School of Marine and Atmospheric Science). SRM's and replicate measurements were performed approximately once every ten samples. Measurement of 12 sets of replicate seawater samples yielded average precision of $0.9\ \mu\text{mol kg}^{-1}$. While precision of repeated measurements was good, a large discrepancy was observed between our measured SRM values (Batch #4, $2354.0\ \mu\text{mol kg}^{-1}$; Batch #5, $2355.0\ \mu\text{mol kg}^{-1}$; and Batch #6, $2401.0\ \mu\text{mol kg}^{-1}$) and reported values for SRMs (Batch #4, $2359.0\ \mu\text{mol kg}^{-1}$; Batch #5, $2347.0\ \mu\text{mol kg}^{-1}$; and Batch #6, $2357.0\ \mu\text{mol kg}^{-1}$) resulting in differences between measured and reported values of $5\ \mu\text{mol kg}^{-1}$ for Batch #4 ($n=6$), $8\ \mu\text{mol kg}^{-1}$ for Batch #5 ($n=4$), and $44\ \mu\text{mol kg}^{-1}$ for Batch #6 ($n=3$). Correction factors were determined from the measured and reported SRM values and used to correct TA measurements.

Total alkalinity for water samples collected in 2003 was measured using the spectrophotometric method, analytical system, and equations described in detail in Yao and Byrne (1998) and Yates and Halley (2006). Accuracy of our spectrophotometric alkalinity measurements was determined by comparison to Certified Reference Material

(CRM) from the laboratory of Dr. Andrew Dickson (Scripps Institution of Oceanography), see Dickson et al. (2003). Measurement of 4 sets of replicate seawater samples yielded average precision of $0.4 \mu\text{mol kg}^{-1}$. Measurement of CRMs from Batch #59 ($n=6$) yielded a value of $2220.0 \mu\text{mol kg}^{-1}$ which was only $1.0 \mu\text{mol kg}^{-1}$ lower than the reported value for Batch #59 of $2221.0 \mu\text{mol kg}^{-1}$.

The method of measuring carbonate sediment production and dissolution used in this study, known as the alkalinity anomaly technique (Smith and Key, 1975), provides a measure of net carbonate sediment production defined as gross carbonate production minus dissolution of carbonate sediments. Rates of net calcification and dissolution (G) in the incubation chamber were calculated for each 4-h interval between total alkalinity measurements during chamber incubation periods using the equation from Yates and Halley (2003):

$$G (\text{g CaCO}_3 \text{ m}^{-2} \text{ 4 h}^{-1}) = \frac{1}{2} \Delta\text{TA} (\text{mol m}^{-2} \text{ 4 h}^{-1}) \times \text{SHARQ volume (m}^3\text{)} / \text{SHARQ surface area (m}^2\text{)} \times \text{molecular weight of CaCO}_3 (\text{g mol}^{-1}). \quad (1)$$

Carbonate system parameters, including TCO_2 , CO_3^{2-} concentration, pCO_2 , and saturation state of calcite (Ω_C) and aragonite (Ω_A), were calculated using CO2SYS (Lewis and Wallace, 1998) for both incubation chamber and ambient seawater data sets. Dissociation constants K_1 and K_2 were from Merbach et al. (1973) refit by Dickson and Millero (1987), and KSO_4 was from Dickson (1990). Total alkalinity values and corresponding in situ pH, salinity, and temperature measurements were used to derive the remaining carbonate system parameters.

3. Results

Rates of net calcification and dissolution (G) for incubation chamber measurements are listed in Table 1. Calcification is denoted by positive numbers, and dissolution is

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denoted by negative numbers. Carbonate system and physical parameters for both incubation chamber and ambient seawater measurements are listed in Tables 1 and 2. Note that ambient seawater measurements were only collected concurrently with incubation chamber measurements for the 2001 data sets. Rates of net calcification for 4 h measurement periods ranged from 0.010 to 0.930 g CaCO₃²⁻ m⁻² 4 h⁻¹, and rates of dissolution ranged from -0.020 to -1.330 g CaCO₃²⁻ m⁻² 4 h⁻¹. Rates of net calcification and dissolution calculated over the duration of daylight and night hours are available in Yates and Halley (2003) for data sets collected during 2000. Net dissolution was observed for all substrate types primarily during the night in both 2000 and 2001 data sets. Highest rates of calcification were observed during the day for a patch reef with 20% live coral cover measured during February of 2000. While the highest rate of dissolution for a single 4 h period of time was observed for sand bottom substrate measured in July of 2001, the patch reef with 20% live coral cover showed highest rates of dissolution, in general, during the night.

Incubation chamber pH ranged from 7.72 to 8.22, and ambient seawater pH ranged from 7.82 to 8.42 for all measurements. Incubation chamber pCO₂ ranged from 303 to 1229 μatm, and CO₃²⁻ concentrations ranged from 92 to 226 μmol kg⁻¹ (Table 1). Ambient seawater pCO₂ ranged from 170 to 935 μatm, and CO₃²⁻ concentrations ranged from 110 to 335 μmol kg⁻¹ (Table 2). Carbonate ion concentrations and pCO₂ for 41 out of 43 four-hour incubation chamber measurements were within the range of CO₃²⁻ concentrations and pCO₂ observed for ambient seawater (Fig. 2). Two data points collected during 28 through 29 July 2001 on the patch reef with 10% live coral cover had pCO₂ measurements higher than (and CO₃²⁻ measurements lower than) the observed range of values for ambient seawater (Fig. 2). These same two data points also had slightly lower pH than that observed in ambient seawater.

Linear correlations were calculated between calcification rate and pCO₂, and calcification rate and CO₃²⁻ concentration for each substrate type (Figs. 3 and 4). The point at which the trend-lines cross zero on the y-axes indicates the transition from net calci-

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5 fication to net dissolution and the pCO₂ and CO₃²⁻ values at which rates of calcification and dissolution are equivalent such that the ratio of calcification to dissolution equals one (C/D=1). We refer to the pCO₂ and CO₃²⁻ concentrations at the point where C/D=1 as threshold values denoted as pCO_{2,C/D=1} and CO_{3,C/D=1}²⁻. Net dissolution occurred
10 when pCO₂ exceeded pCO_{2,C/D=1}, or when CO₃²⁻ fell below CO_{3,C/D=1}²⁻. Threshold pCO_{2,C/D=1} and CO_{3,C/D=1}²⁻ values for each substrate type are listed in Table 3. All CO_{3,C/D=1}²⁻ and pCO_{2,C/D=1} values were within the range of CO₃²⁻ and pCO₂ values measured in ambient seawater with the exception of the patch reef measured in 2001. CO_{3,C/D=1}²⁻ and pCO_{2,C/D=1} varied considerably among substrate types and between
15 years of data collection (Table 3). The average CO_{3,C/D=1}²⁻ for all substrate types was 152±24 μmol kg⁻¹, and the range was from 113 to 184 μmol kg⁻¹. The average pCO_{2,C/D=1} was 654±195 μatm, ranging from 467 to 1003 μatm. The highest CO_{3,C/D=1}²⁻ and lowest pCO_{2,C/D=1} values corresponded to a patch reef with 10% live coral cover that was measured in February of 2000. However, a similar patch reef with 10% live coral cover measured in July of 2001 exhibited the lowest CO_{3,C/D=1}²⁻
20 and highest pCO_{2,C/D=1} suggesting that considerable seasonal variability in calcification and dissolution thresholds may exist. Insufficient data is available at this time to quantify seasonal or interannual variation in CO_{3,C/D=1}²⁻ and pCO_{2,C/D=1}.

25 Figures 5, 6, and 7 show the diurnal variation in ambient seawater pCO₂ and CO₃²⁻ concentrations measured during October of 2000, July of 2001, and June of 2003, respectively, and the threshold values for pCO_{2,C/D=1} and CO_{3,C/D=1}²⁻ for each substrate type. In general, ambient seawater pCO₂ decreased during the day and increased during the night, while CO₃²⁻ increased during the day, and decreased during the night. We have estimated the percentage of time that pCO₂ and CO₃²⁻ concentrations in ambient seawater data sets naturally surpassed the pCO_{2,C/D=1} and CO_{3,C/D=1}²⁻ thresholds

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for calcification and dissolution calculated from incubation chamber measurements for each substrate type (Figs. 5, 6, and 7, and Table 3). The percent of time during which pCO_{2,C/D=1} and CO_{3,C/D=1}²⁻ were simultaneously surpassed during ambient seawater measurements in October 2000, July 2001, and June 2003 ranged from 0 to 59% with an average of 13.2±18%. Note, however, that these estimates have a high degree of error that is difficult to quantify because ambient seawater and incubation chamber measurements were not collected concurrently for two of the three data sets, pCO_{2,C/D=1} and CO_{3,C/D=1}²⁻ varies considerably among substrate types, and it is likely that pCO_{2,C/D=1} and CO_{3,C/D=1}²⁻ varies at each location on, at least, seasonal time scales. These estimates are a first approximation to indicate the potential amount of time that dissolution may be occurring in the ambient reef flat environment at present day atmospheric pCO₂ conditions. The accuracy of such estimates will improve as additional in situ measurements of threshold conditions for calcification and dissolution are acquired, and seasonal variation is characterized.

4. Discussion

Orr et al. (2005) report that tropical and subtropical seawater will become undersaturated with respect to carbonate minerals when pCO₂ reaches 1700 and 2800 μatm, respectively. However, we observed net dissolution rates of carbonate sediments during the night that exceeded net calcification during the day on representative substrate types of the Molokai reef flat at pCO₂ and CO₃²⁻ values that were within the range of those measured in ambient seawater at present day atmospheric pCO₂ conditions of 380 ppmv (Houghton, 2001). Our results and results of other researchers (Conand et al., 1997; Gattuso et al., 1997; Boucher et al., 1998) indicate that a considerable amount of dissolution is already naturally occurring in shallow waters of reef environments. Our night-time dissolution rates (calculated per hour, -0.005 to -0.33 g CaCO₃²⁻ m⁻² h⁻¹) fall within the range of those observed by previous researchers.

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Gattuso et al. (1997) measured community metabolism on a fringing reef at Moorea (French Polynesia) over 24 h time periods. Community net calcification showed a strong diurnal pattern with net calcification occurring during the day ($1.24 \text{ g CaCO}_3 \text{ m}^{-2}$) and net dissolution occurring during the night ($-1.33 \text{ g CaCO}_3 \text{ m}^{-2}$, or approximately $-0.11 \text{ g CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$) resulting in dissolution of $-0.09 \text{ g CaCO}_3 \text{ m}^{-2} \text{ 24 h}^{-1}$. The saturation state of surface water ranged from 2.84 to 4.38 and dissolution was attributed to lower saturation state in pore waters of the sediment due to release of respiratory CO₂, and possibly due to boring sponges. Boucher et al. (1998) measured the contribution of soft bottoms to productivity and calcification on the Tiahura barrier reef of Moorea, French Polynesia. They observed dissolution at night that exceeded calcification during the day resulting in slight net dissolution of $-0.24 \text{ g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$ and mean night dissolution rates of -0.06 to $-0.07 \text{ g CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$. Conand et al. (1997) reported night-time dissolution rates during the summer on the back reef of Reunion Island in the Indian Ocean of up to $-2.5 \text{ g CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ that resulted in net dissolution of $-9 \text{ g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$. Earlier studies (Kinsey, 1978; Barnes and Devereux, 1984) observed higher night-time dissolution rates of -0.1 to $-0.4 \text{ g CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ on One Tree Island Reef (Kinsey, 1978), and approximately $-0.8 \text{ g CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ on the Rib Reef (Barnes and Devereux, 1984) of the Great Barrier Reef in Australia, however day-time calcification exceeded night-time dissolution in these studies.

Moderate correlation of our calcification and dissolution rates with surface water pCO₂ and CO₃²⁻ (r^2 from 0.50 to 0.81) and diurnal variation in calcification and dissolution corresponding to day and night, respectively, suggests that variation in carbonate system parameters as a result of photosynthesis and respiration on the shallow reef flat may facilitate calcification and dissolution (Schmalz and Swanson, 1969; Yates and Halley, 2006). Leclercq et al. (2002) measured dark dissolution of -0.081 to $-0.048 \text{ g CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ in a coral reef mesocosm with pCO₂ manipulated to 411, 647, and $918 \mu\text{atm}$. Coral reef community calcification decreased with decreasing aragonite saturation state both day and night. Sand community calcification decreased with decreasing aragonite saturation state during the day, but no correlation with aragonite

saturation state existed at night suggesting that night dissolution was not correlated with saturation state, rather it was a function of the interstitial aragonite saturation state due to low pH and elevated CO₂ from bacterial respiration in sediments. This is contrary to our observations of a linear correlation between calcification and dissolution on sand communities relative to surface water pCO₂ and CO₃²⁻.

The fact that dissolution occurred in waters that remained supersaturated with respect to carbonate minerals indicates that either dissolution of magnesian carbonates (which are more soluble in seawater than calcite and aragonite) occurred, that simple carbonate thermodynamic equilibrium with respect to pCO₂ and carbonate ion species was not the sole process causing dissolution, or that some combination of magnesian carbonate dissolution and non-equilibrium dissolution of carbonate sediment occurred. Sabine and Mackenzie (1995) measured higher alkalinity values as a result of dissolution of resuspended carbonate sediments in surface waters of Penguin Bank, a mid-depth bank extending 45 km southwest of the western end of Molokai with an average depth 60 m. Saturation state of Penguin Bank waters was 4.4 times oversaturated with respect to aragonite, and they attributed the signature to dissolution of high-mg calcite.

We calculated stoichiometric solubility products ($K^*_{sp} = mCa^{2+} mCO_3^{2-}$ reported as $-\log K^*_{sp}$ in Table 3) for the dissolving carbonate mineral phase at each substrate type by assuming that mineral saturation state is equal to one when the rate of calcification is equivalent to dissolution (C/D=1), that the Ca²⁺ concentration in seawater was 10.3M (Morse and Mackenzie, 1990), and by using our threshold CO_{3,C/D=1}²⁻ values (Table 3). It is important to note, however, that dissolution likely began before the calcification/dissolution threshold was reached (i.e. C/D=1) because we measured net calcification resulting from the combined processes of calcium carbonate precipitation and dissolution. Therefore, our $-\log K^*_{sp}$ calculations most likely represent maximum values that underestimate solubility. Our values for $-\log K^*_{sp}$ ranged from 5.72 to 5.93 with an average of 5.81. This range of variation is similar to the range of variation observed by Busenberg and Plummer (1989) for a variety of biogenic magnesian calcites. Mucci (1983) reports K^*_{sp} for aragonite and calcite at 25°C and a salinity of 35 that

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correspond to $-\log K^*_{sp}$ of 6.18 and 6.37, respectively. Stumm and Morgan (1981) report K^*_{sp} for aragonite and calcite in seawater of 6.05 and 6.20, respectively. Our $-\log K^*_{sp}$ values were lower than those reported for aragonite in seawater suggesting that dissolution of magnesian calcite occurred.

5 Solubility of magnesian calcites in seawater is poorly understood (Sabine and Mackenzie, 1995). Busenberg and Plummer (1989) performed one of the most comprehensive studies of magnesian calcite dissolution and report $-\log K^*_{sp}$ values for biogenic magnesian calcites ranging from 19 to 0.8 mol% $MgCO_3$ content of 8.16 to 8.46, respectively. Mackenzie et al. (1983) provide a review of experimentally determined magnesian calcite solubilities with lowest $-\log K^*_{sp}$ values from Plummer and Mackenzie (1974) of approximately 7.20 for magnesian calcite with 23 mol% $MgCO_3$.
10 However, all of these measurements were made in distilled water. Only a few values of $-\log K^*_{sp}$ have been calculated from dissolution studies on biogenic magnesian calcites in seawater (Chave and Schmalz, 1966; Land, 1967; Weyl, 1967), and these
15 range from approximately 8.05 to 8.62 (Mackenzie et al., 1983). However, these reported values of $-\log K^*_{sp}$ for magnesian calcites in seawater are greater than $-\log K^*_{sp}$ for calcite and aragonite in seawater (Mucci, 1983; Stumm and Morgan, 1981), and higher than values reported for magnesian calcite dissolution in distilled water (Plummer and Mackenzie, 1974). Thus, reported K^*_{sp} values for magnesian calcites
20 remain contradictory. Our estimates of $-\log K^*_{sp}$ indicate that magnesian calcites in natural systems are much more soluble than previously determined, or that non-equilibrium processes are facilitating mineral dissolution.

25 Other processes that may contribute to dissolution include bioerosion from endolithic microbes and boring foraminifera (Lazar, 1991; Peyrot-Clausade, 1995; Peyre'-Venec, 1987), under-saturated pore water conditions in the sediment due to bacterial respiration and oxidation of organic matter (Charpy-Roubaud et al., 1996), increased pCO_2 as a result of respiration of benthic organisms (Yates and Halley, 2006), and dissolution of magnesian calcite which is more soluble in seawater than calcite or aragonite (Sabine and Mackenzie, 1995). Despite the fact that most of these processes primarily take

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place in sediment pore waters, advection and diffusion can transfer alkalinity across the sediment water interface imparting a chemical signature to surface water (Walter et al., 1993). It is likely that the calcification/dissolution signatures that we observed result from a combination of high-mg calcite dissolution and other sediment pore water processes.

It is predicted that atmospheric $p\text{CO}_2$ will reach $560 \mu\text{atm}$ by 2065, and $700 \mu\text{atm}$ by 2100 (Houghton et al., 1996) surpassing the average $p\text{CO}_2$ threshold value of $654 \mu\text{atm}$ that we calculated for our study sites on the Molokai reef flat. At present day atmospheric $p\text{CO}_2$ of 380 ppmv, ambient seawater $p\text{CO}_2$ on the Molokai reef flat ranged from 170 to $935 \mu\text{atm}$, and individual $p\text{CO}_2$ threshold values for all substrate types (ranging from 467 to $1003 \mu\text{atm}$) were exceeded, on average, 18% of the time during measurement of ambient seawater chemistry. Ambient seawater $p\text{CO}_2$ measurements were higher than atmospheric $p\text{CO}_2$ (380 ppmv) 66% of the time. Our linear correlation between calcification/dissolution rates and $p\text{CO}_2$, and our calculated $p\text{CO}_2$ threshold values suggest that not only will rates of dissolution increase with increasing $p\text{CO}_2$, but the amount of time that $p\text{CO}_2$ threshold values for dissolution are exceeded will increase resulting in considerable loss of carbonate sediments on reefs.

While insufficient data exists to fully characterize spatial and temporal trends in threshold values for $p\text{CO}_2$ and CO_3^{2-} , our data indicate that these values vary considerably among substrate types, and on similar substrate types during different time periods. There are many potential causes of variability in threshold $p\text{CO}_2$ and CO_3^{2-} values that remain to be quantified. These causes include variation in metabolic performance due to community composition (Gattuso et al., 1997), seasonal variation in calcification and dissolution rates, variation in sediment composition, degree of biologic control on calcification and dissolution mechanisms, and mixing rate of water masses overlying substrate areas. Any combination of these processes may result in variable threshold values. As more in situ measurements of threshold values are made, researchers may be able to place constraints on the typical ranges of observed threshold values for the purpose of modeling potential rates of dissolution at future, elevated

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atmospheric pCO₂ levels.

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Table 1. Carbonate system parameters for incubation chamber measurements.

Description	Time (hh:mm)	Salinity	Temp. (°C)	TA ($\mu\text{mol kg}^{-1}$)	pH	G	TCO ₂ (g CaCO ₃ m ⁻² 4 h ⁻¹)	CO ₃ ²⁻ ($\mu\text{mol kg}^{-1}$)	pCO ₂ ($\mu\text{mol kg}^{-1}$)	Ω_c (μatm)	Ω_a
Sand Bottom 9/2–10/2/2000	19:00	33.7	24.7	2217	8.11	–	1956	186	429	4.5	3.0
	23:00	33.7	24.4	2218	8.03	–0.020	2000	159	535	3.9	2.5
	3:00	33.7	23.8	2222	8.00	–0.080	2025	147	589	3.6	2.3
	7:00	33.7	23.6	2236	7.94	–0.240	2066	131	690	3.2	2.1
	11:00	33.7	24.2	2243	8.00	–0.110	2043	149	598	3.6	2.4
	15:00	33.7	26.1	2232	8.04	0.190	1999	170	533	4.1	2.7
	19:00	33.7	25.1	2235	8.03	–0.060	2016	161	551	3.9	2.6
	23:00	33.7	24.5	2241	7.97	–0.100	2053	142	645	3.5	2.3
Coral Rubble 13/2–14/2/2000	13:00	34.2	26.0	2166	8.00	–	1958	152	583	3.7	2.4
	17:00	34.2	27.4	2142	8.09	0.390	1881	185	450	4.5	3.0
	21:00	34.2	25.9	2147	8.03	–0.080	1926	159	530	3.9	2.5
	1:00	34.2	24.9	2195	7.95	–0.800	2013	137	666	3.3	2.2
	5:00	34.2	24.2	2227	7.91	–0.530	2063	127	742	3.1	2.0
	9:00	34.2	24.0	2236	7.92	–0.160	2067	130	717	3.1	2.1
	13:00	34.2	25.8	2230	8.06	0.110	1987	176	503	4.3	2.8
	Patch Reef (10% Coral Cover) 15/2–16/2/2000	9:30	35.0	24.9	2177	8.09	–	1926	178	452	4.3
13:30		35.0	26.7	2145	8.17	0.550	1839	212	357	5.1	3.4
17:30		35.0	27.8	2141	8.16	0.060	1833	214	367	5.2	3.4
21:30		35.0	26.7	2125	8.07	0.270	1877	175	472	4.2	2.8
1:30		35.0	24.9	2160	7.99	–0.580	1956	148	580	3.6	2.3
5:30		35.0	24.8	2218	7.99	–0.980	2012	152	597	3.6	2.4
9:30		35.0	25.3	2221	7.97	–0.040	2020	149	631	3.6	2.4
Patch Reef (22% Coral Cover) 16/2–17/2/2000		14:15	35.0	24.9	2161	8.22	–	1833	226	303	5.4
	18:15	35.0	26.7	2105	8.16	0.930	1808	205	358	4.9	3.3
	22:15	35.0	27.8	2114	8.01	–0.140	1889	161	553	3.9	2.6
	3:49	35.0	26.7	2187	7.91	–1.220	2011	133	752	3.2	2.1
	7:49	35.0	24.9	2211	7.84	–0.410	2071	113	888	2.7	1.8
	11:49	35.0	24.8	2178	8.01	0.560	1966	154	558	3.7	2.4
	2:20	35.0	25.3	2144	8.10	0.580	1883	183	426	4.4	2.9
	Sand Bottom 23/7–24/7/2001	7:00	34.3	25.0	2277	7.95	–	2088	143	688	3.5
11:00		34.3	27.7	2258	7.99	0.320	2038	163	630	4.0	2.6
15:00		34.3	29.3	2250	8.06	0.130	1987	190	530	4.6	3.1
19:00		34.3	28.0	2197	8.12	0.890	1911	202	429	4.9	3.3
23:00		34.3	27.0	2276	8.10	–1.330	1999	199	462	4.8	3.2
3:00		34.3	26.3	2259	8.02	0.290	2030	168	568	4.1	2.7
7:00		34.3	26.2	2262	7.89	–0.050	2094	131	802	3.2	2.1
Patch Reef (10% Coral Cover) 28/7–29/7/2001		11:00	34.4	27.0	2250	8.10	–	1978	195	465	4.7
	15:00	34.4	28.4	2226	7.91	0.400	2042	140	773	3.4	2.3
	19:00	34.4	28.6	2222	7.92	0.070	2031	144	747	3.5	2.3
	23:00	34.4	27.5	2221	7.84	0.010	2071	120	914	2.9	1.9
	3:00	34.4	26.6	2234	7.79	–0.210	2109	106	1050	2.6	1.7
	7:00	34.4	26.0	2247	7.72	–0.220	2147	92	1229	2.2	1.5
	11:00	34.4	26.9	2226	7.85	0.360	2074	121	887	2.9	1.9

Table 2. Carbonate system parameters for ambient seawater measurements.

Date	Time (hh:mm)	Salinity	Temp. (°C)	TA ($\mu\text{mol kg}^{-1}$)	pH	TCO ₂ ($\mu\text{mol kg}^{-1}$)	CO ₃ ²⁻ ($\mu\text{mol kg}^{-1}$)	pCO ₂ (μatm)	Ω _c	Ω _a
13/10/2000	10:00	34.1	25.8	2306	8.03	2073	172	564	4.2	2.8
	14:20	33.9	26.7	2243	8.15	1949	209	403	5.1	3.4
	19:25	35.6	25.9	2293	8.14	1990	214	411	5.1	3.4
14/10/2000	0:00	33.8	25.0	2292	8.00	2080	158	601	3.9	2.5
	5:55	34.3	24.6	2286	8.07	2041	179	499	4.3	2.8
	11:35	34.9	25.9	2298	8.05	2053	179	539	4.3	2.9
20/7/2001	23:00	33.8	26.1	2287	8.05	2046	177	535	4.3	2.8
21/7/2001	3:00	33.8	25.7	2266	7.92	2091	135	748	3.3	2.2
	7:00	33.8	25.1	2255	8.01	2042	158	583	3.8	2.5
	11:00	33.8	26.4	2284	8.12	2003	202	441	4.9	3.3
22/7/2001	15:00	34.3	27.4	2293	8.25	1919	263	303	6.4	4.2
	19:00	34.3	26.9	2294	8.16	1981	223	393	5.4	3.6
	23:00	34.3	26.3	2270	8.13	1986	204	430	5.0	3.3
23/7/2001	3:00	34.3	26.0	2259	7.93	2076	140	723	3.4	2.2
	7:00	34.3	25.9	2270	8.05	2029	175	531	4.3	2.8
	11:00	34.3	27.4	2242	8.22	1893	244	323	5.9	3.9
15/00	34.3	26.8	2245	8.28	1846	277	273	6.8	4.5	
	18:00	34.3	27.7	2223	8.16	1910	220	380	5.4	3.6
	23:00	34.3	26.8	2261	8.13	1974	206	429	5.0	3.3
24/7/2001	3:00	34.3	24.0	2268	8.06	2033	171	506	4.1	2.7
	7:00	34.3	24.6	2271	8.24	1927	242	304	5.8	3.9
	25/7/2001	11:00	34.3	26.7	2271	8.21	1934	238	341	5.8
15:00	34.3	28.1	2204	8.43	1712	335	170	8.2	5.4	
	19:00	34.3	27.1	2228	8.27	1851	262	276	6.4	4.2
	23:00	34.3	26.3	2247	8.22	1909	237	326	5.8	3.8
26/7/2001	3:00	34.3	25.5	2234	8.09	1979	184	469	4.5	2.9
	7:00	34.3	25.7	2294	8.11	2008	198	446	4.8	3.2
	11:00	34.3	26.9	2273	8.29	1861	274	269	6.6	4.4
15:00	34.1	28.7	2264	8.35	1817	309	225	7.5	5.0	
	19:00	34.1	27.6	2237	8.22	1889	244	323	5.9	3.9
	23:00	34.1	26.9	2244	8.14	1948	210	405	5.1	3.4
27/7/2001	3:00	34.1	26.4	2257	8.13	1969	205	419	5.0	3.3
	7:00	34.1	26.0	2288	8.03	2057	170	567	4.1	2.7
	11:00	34.1	27.1	2268	8.27	1889	265	285	6.5	4.3
15:00	34.1	28.9	2250	8.23	1885	256	319	6.2	4.2	
	19:00	34.4	28.8	2236	8.19	1896	238	355	5.8	3.9
	23:00	34.4	28.0	2232	8.13	1938	208	427	5.1	3.4
28/7/2001	3:00	34.4	27.2	2293	8.13	1967	212	428	5.1	3.4
	7:00	34.4	26.2	2265	8.08	2008	186	490	4.5	3.0
	11:00	34.4	27.0	2256	8.30	1860	275	261	6.7	4.4
15:00	34.4	28.1	2252	8.31	1839	286	253	7.0	4.6	
	17:00	34.4	28.2	2237	8.21	1890	243	335	5.9	3.9
	23:00	34.4	27.1	2206	8.18	1889	222	359	5.4	3.6
29/7/2001	3:00	34.4	26.3	2249	8.18	1932	224	362	5.4	3.6
	7:00	34.4	25.8	2252	8.00	2037	159	600	3.9	2.5
	11:00	34.4	26.4	2265	8.29	1877	270	268	6.5	4.3
16/6/2003	8:15	35.8	26.4	2235	7.92	2050	139	744	3.3	2.2
	12:52	35.9	27.6	2164	8.09	1892	191	457	4.6	3.0
	16:28	36.1	27.1	2213	8.07	1948	188	488	4.5	3.0
17/6/2003	21:36	36.2	26.3	2197	8.11	1917	196	433	4.7	3.1
	0:08	36.2	25.5	2193	8.03	1961	166	538	4.0	2.6
	4:45	36.2	25.1	2206	7.82	2069	110	935	2.6	1.7
8:10	35.3	26.0	2212	7.85	2060	120	868	2.9	1.9	
	12:12	36.4	26.8	2214	8.02	1976	170	561	4.1	2.7
	16:19	36.1	27.4	2173	7.97	1960	155	629	3.7	2.5
19:53	36.0	26.4	2246	8.15	1936	217	391	5.2	3.4	
	0:21	36.0	25.6	2241	8.09	1969	192	456	4.6	3.0
	4:24	35.3	25.2	2256	7.99	2045	156	616	3.7	2.5
7:58	35.3	25.3	2274	8.08	2012	188	477	4.5	3.0	
	11:56	36.0	27.1	2258	8.19	1918	237	353	5.7	3.8
	15:52	35.8	27.1	2205	8.24	1842	249	301	6.0	4.0
19:56	35.9	26.4	2253	8.13	1958	208	423	5.0	3.3	
	0:14	35.9	25.7	2252	8.06	1999	181	507	4.3	2.9
	4:17	35.2	25.1	2260	7.97	2060	149	651	3.6	2.4
8:03	35.3	25.7	2232	8.05	1987	176	511	4.2	2.8	

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Table 3. Percent of time ambient seawater CO₃²⁻ concentration and pCO₂ surpassed thresholds for C/D=1.

Description	CO _{3,C/D=1} ²⁻ (μmol kg ⁻¹)	-log K*sp	% time below CO _{3,C/D=1} ²⁻			pCO _{2,C/D=1} (μatm)	% time above pCO _{2,C/D=1}		
			Oct. 2000	July 2001	June 2003		Oct. 2000	July 2001	June 2003
Sand Bottom 2000	157	5.79	0 ^a	5 ^a	21 ^a	562	13	11	28
Coral Rubble 2000	164	5.77	9 ^a	8 ^a	33 ^a	537	24	13	43
Patch Reef 10% 2000	184	5.72	59 ^a	15 ^a	53 ^a	467	69	21	64
Patch Reef 20% 2000	155	5.80	0 ^a	5 ^a	19 ^a	605	0	7	26
Sand Bottom 2001	138	5.85	0 ^a	1	10 ^a	748	0	0 ^a	10
Patch Reef 2001	113	5.93	0 ^a	0 ^a	2	1003	0	0	0 ^a
Average ±1 std. dev.	152±24	5.81±.07	11.3±24	5.7±5	23.0±18	654±195	17.7±27	8.7±8	29.0±23
Total hours	–	–	25.6 h	156.0 h	71.6 h	–	25.6 h	156.0 h	71.6 h

^a percent of time both CO₃²⁻ and pCO₂ thresholds were, simultaneously, surpassed.

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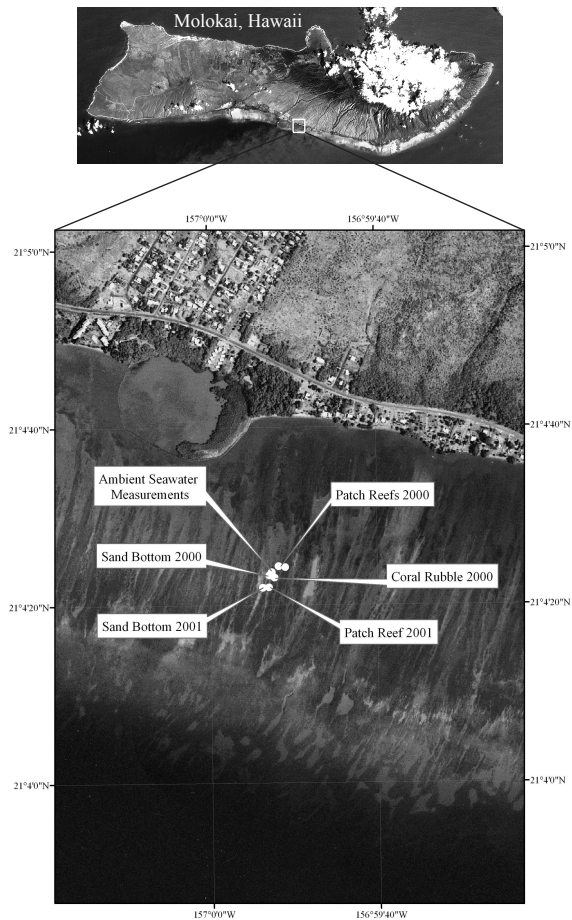


Fig. 1. Study sites for measurement of calcification and dissolution on patch reefs, sand bottom and coral rubble of the Molokai reef flat. Landsat TM satellite images courtesy of U.S. Geological Survey, Southwest Geographic Science Team.

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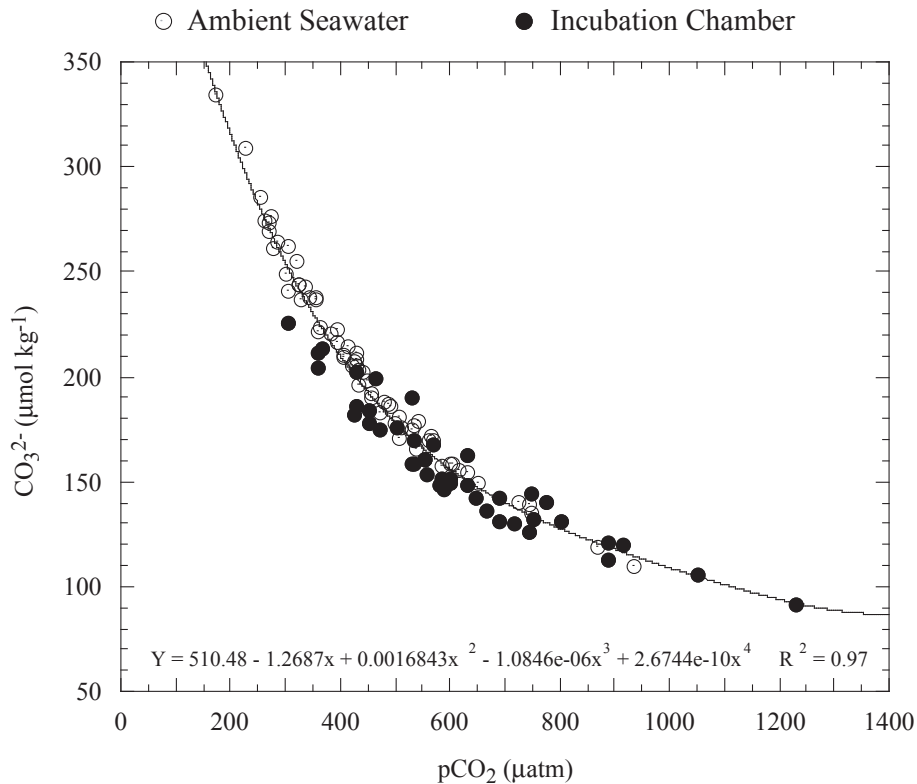


Fig. 2. $p\text{CO}_2$ and CO_3^{2-} concentrations of ambient seawater on the Molokai reef flat near incubation chamber study sites from 13–14 October 2000, from 20–29 July 2001, and from 16–19 June 2003 (open circles), and from all measurements inside the incubation chamber (solid circles).

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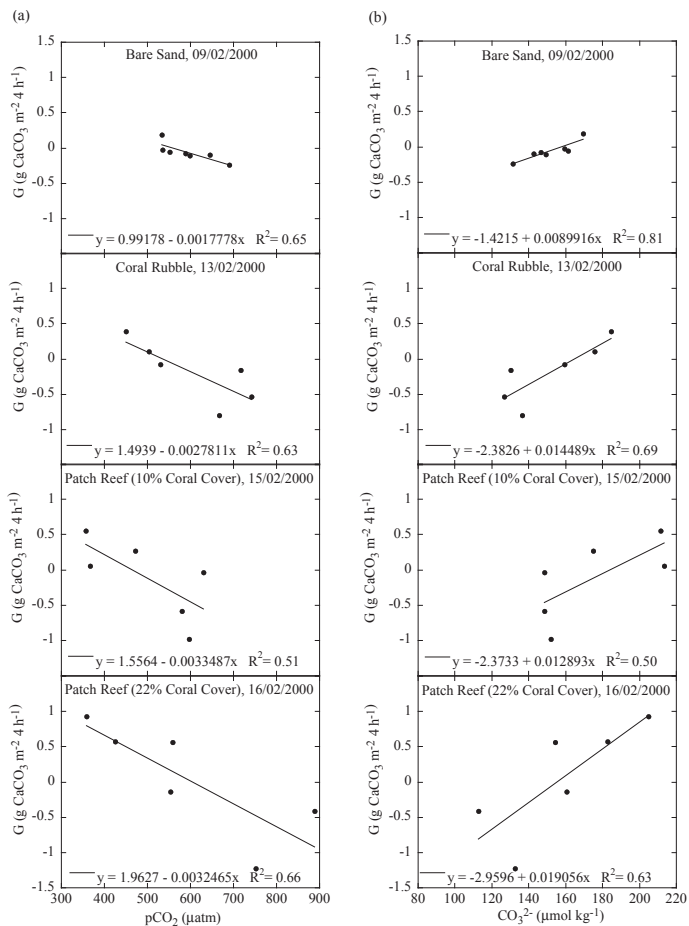


Fig. 3. Rates of calcification/dissolution (G) vs. pCO₂ (a) and CO₃²⁻ concentrations (b) for all substrate types measured in 2000. Positive values indicate calcification. Negative values indicate dissolution.

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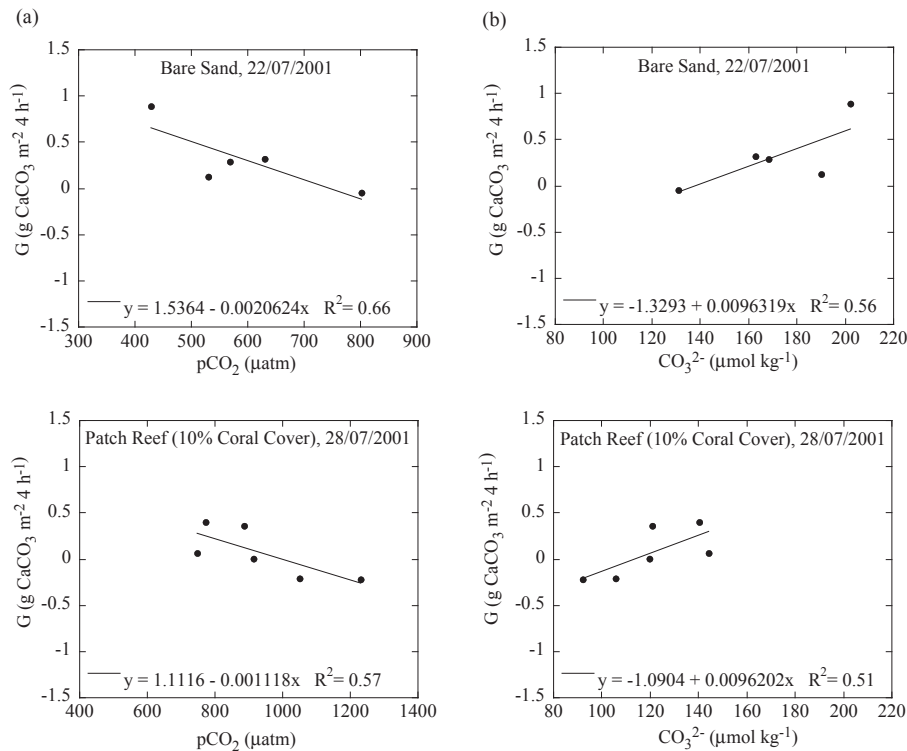


Fig. 4. Rates of calcification/dissolution (G) vs. pCO₂ (a) and CO₃²⁻ concentrations (b) for all substrate types measured in 2001. Positive values indicate calcification. Negative values indicate dissolution.

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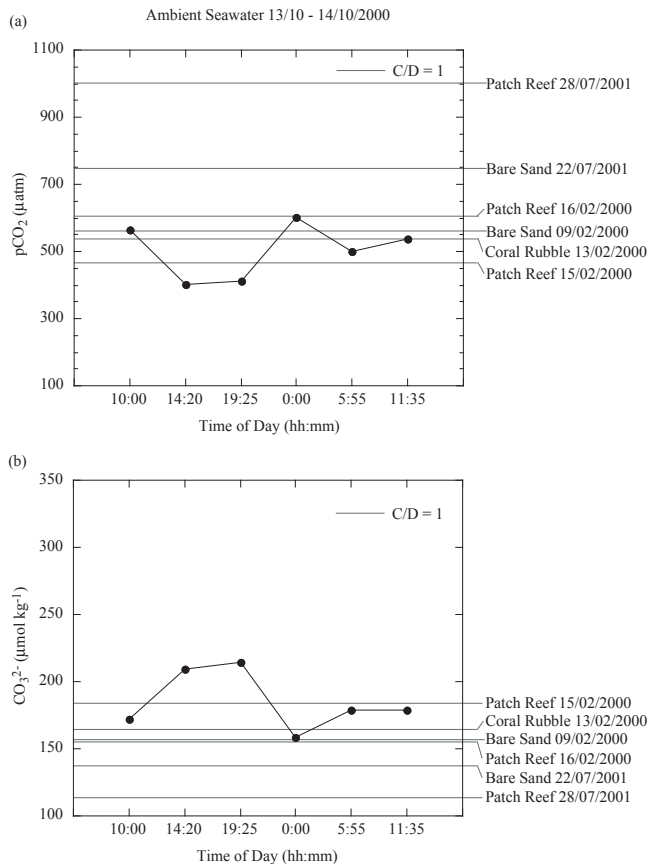


Fig. 5. Ambient seawater measurements of pCO₂ and CO₃²⁻ concentrations from 13–14 October 2000. Horizontal lines represent threshold pCO₂ and CO₃²⁻ values from each substrate type whereby the rate of calcification is equivalent to the rate of dissolution.

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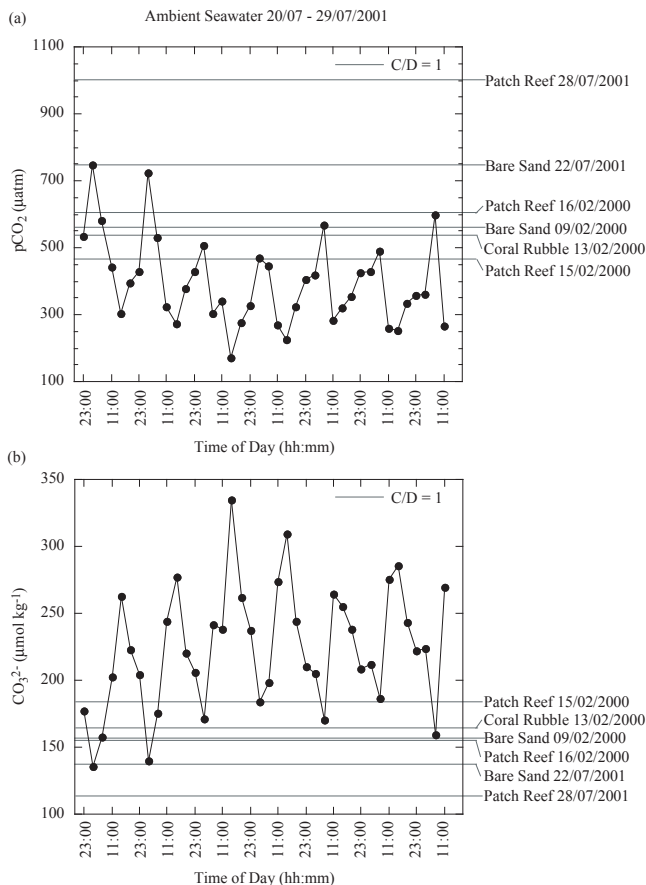


Fig. 6. Ambient seawater measurements of pCO₂ and CO₃²⁻ concentrations from 20–29 July 2001. Horizontal lines represent threshold pCO₂ and CO₃²⁻ values from each substrate type whereby the rate of calcification is equivalent to the rate of dissolution.

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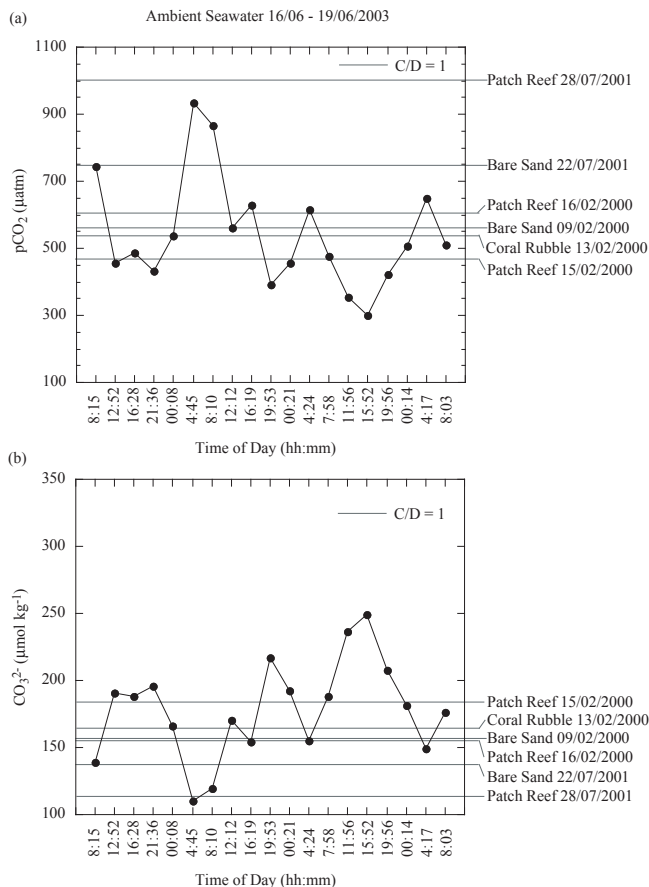


Fig. 7. Ambient seawater measurements of pCO₂ and CO₃²⁻ concentrations from 16–19 June 2003. Horizontal lines represent threshold pCO₂ and CO₃²⁻ values from each substrate type whereby the rate of calcification is equivalent to the rate of dissolution.

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