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

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# CO$_3^{2-}$ concentration and pCO$_2$ thresholds for calcification and dissolution on the Molokai reef flat, Hawaii

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**Abstract.** The severity of the impact of elevated atmospheric pCO$_2$ to coral reef ecosystems depends, in part, on how seawater pCO$_2$ affects the balance between calcification and dissolution of carbonate sediments. Presently, there are insufficient published data that relate concentrations of pCO$_2$ and CO$_3^{2-}$ to in situ rates of reef calcification in natural settings to accurately predict the impact of elevated atmospheric pCO$_2$ on calcification and dissolution processes. Rates of net calcification and dissolution, CO$_3^{2-}$ concentrations, and pCO$_2$ were measured, in situ, on patch reefs, bare sand, and coral rubble on the Molokai reef flat in Hawaii. Rates of calcification ranged from 0.03 to 2.30 mmol CaCO$_3$ m$^{-2}$ h$^{-1}$ and dissolution ranged from –0.05 to –3.3 mmol CaCO$_3$ m$^{-2}$ 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 pCO$_2$ 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 pCO$_2$. Threshold pCO$_2$ and CO$_3^{2-}$ values for individual substrate types showed considerable variation. The average pCO$_2$ threshold value for all substrate types was 654±195 $\mu$atm and ranged from 467 to 1003 $\mu$atm. The average CO$_3^{2-}$ threshold value was 152±24 $\mu$mol kg$^{-1}$, ranging from 113 to 184 $\mu$mol kg$^{-1}$. Ambient seawater measurements of pCO$_2$ and CO$_3^{2-}$ indicate that CO$_3^{2-}$ and pCO$_2$ threshold values for all substrate types were both exceeded, simultaneously, 13% of the time at present day atmospheric pCO$_2$ concentrations. It is predicted that atmospheric pCO$_2$ will exceed the average pCO$_2$ threshold value for calcification and dissolution on the Molokai reef flat by the year 2100.

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## 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 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; Marubini et al., 2001, 2003; Anderson et al., 2003; Langdon et al., 2003; Reynaud et al., 2003; Langdon and Atkinson, 2005; Renegar and Riegl, 2005) 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 CO$_2$ 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 pCO$_2$ and CO$_3^{2-}$ 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 $pCO_2$, $CO_3^{2-}$ concentrations, and the balance between calcification and dissolution in natural reef settings to accurately predict the impact of elevated atmospheric $CO_2$.

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 $Ca^{2+}$ and $CO_3^{-2}$ divided by the stoichiometric solubility product ($Ksp^*$) (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:

$$CO_2 + H_2O \rightarrow H_2CO_3, \tag{R1}$$

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:

$$H_2CO_3 \rightarrow H^+ + HCO_3^-, \text{ and } CO_3^{2-} + H^+ \rightarrow HCO_3^-. \tag{R2}$$
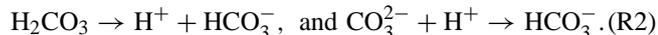
Thus, an increase in $pCO_2$ and a reduction in $CO_3^{2-}$ concentration result in a reduction of saturation state. Inorganic dissolution of carbonate sediments presumably occurs when saturate state is less than one.

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 (Kleypas 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 have decreased 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 and Loya, 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 $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$. 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 $CO_{3\,C/D=1}^{2-}$ and $pCO_{2\,C/D=1}$) 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 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) × 0.6 m (h)), constructed of an aluminum frame and a clear, 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 (±0.1°C) probes.
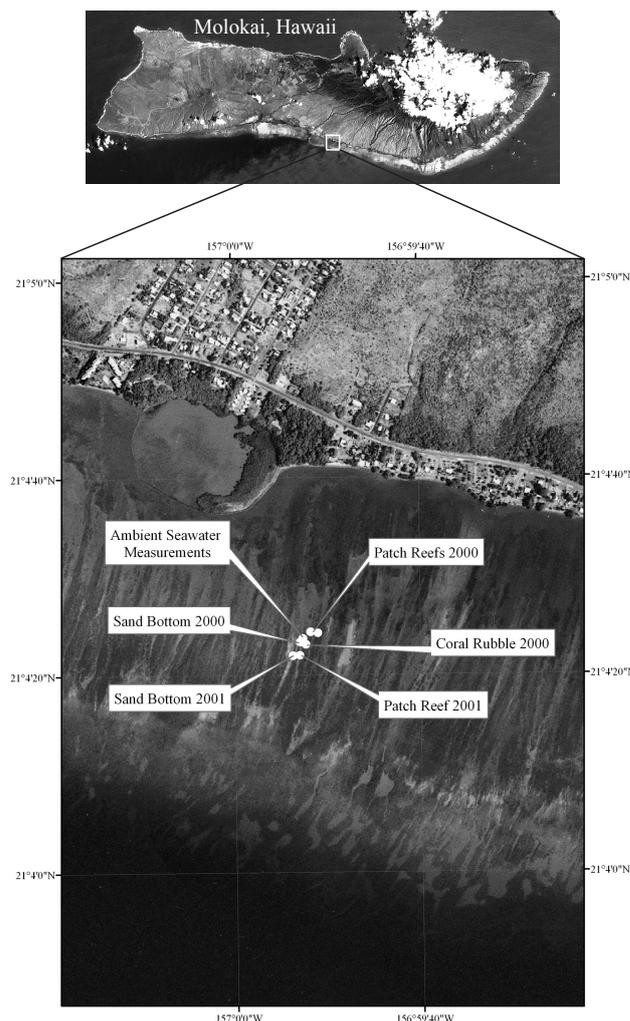


**Fig. 1.** Study sites for measurement of calcification and dissolution on patch reefs, sand bottom and coral rubble of the Molokai reef flat. Landsat TM satellite images courtesy of U.S. Geological Survey, Southwest Geographic Science Team.

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 $\mu$m
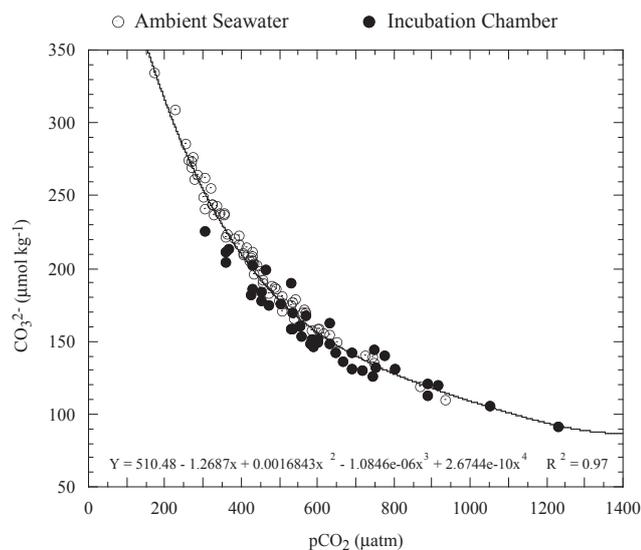
**Fig. 2.** $pCO_2$ and $CO_3^{2-}$ concentrations of ambient seawater on the Molokai reef flat near incubation chamber study sites from 13–14 October 2000, from 20–29 July 2001, and from 16–19 June 2003 (open circles), and from all measurements inside the incubation chamber (solid circles).

cellulose nitrate filters, poisoned with $100 \mu L$ saturated mercuric chloride, and stored in borosilicate glass bottles sealed with ground glass stoppers and Apiezon$^{©}$ grease.

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 ($\pm 0.1$) and temperature ($\pm 0.1°C$) probes, and an Orion Ross pH electrode ($\pm 0.005$ 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 $\mu m$ 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 ($\sim 0.25$ M) HCl used for titrations and standardized reference materials (SRM's) used to determine the reliability of alkalinity measurements were provided by F. 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 $\mu mol kg^{-1}$. While precision of repeated measurements was good, a large discrepancy was observed between our measured SRM values

(Batch #4, 2354.0 $\mu mol kg^{-1}$; Batch #5, 2355.0 $\mu mol kg^{-1}$; and Batch #6, 2401.0 $\mu mol kg^{-1}$) and reported values for SRMs (Batch #4, 2359.0 $\mu mol kg^{-1}$; Batch #5, 2347.0 $\mu mol kg^{-1}$; and Batch #6, 2357.0 $\mu mol kg^{-1}$) resulting in differences between measured and reported values of 5 $\mu mol kg^{-1}$ for Batch #4 (n=6), 8 $\mu mol kg^{-1}$ for Batch #5 (n=4), and 44 $\mu mol kg^{-1}$ 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 A. Dickson (Scripps Institution of Oceanography), see Dickson et al. (2003). Measurement of 4 sets of replicate seawater samples yielded average precision of 0.4 $\mu mol kg^{-1}$. Measurement of CRMs from Batch #59 (n=6) yielded a value of 2220.0 $\mu mol kg^{-1}$ which was only 1.0 $\mu mol kg^{-1}$ lower than the reported value for Batch #59 of 2221.0 $\mu mol kg^{-1}$.

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 from the difference in total alkalinity ($\Delta TA=TA_{initial}-TA_{final}$) at the beginning and end of each incubation period using the equation from Yates and Halley (2003):

$$G(mmol\, CaCO_3\, m^{-2}4\, h^{-1}) = {}^1/_2 \Delta TA(mmol\, m^{-2}4\, h^{-1})$$
$$\times SHARQ\ volume\ (m^3)/SHARQ\ surface\ area\ (m^2). \quad (1)$$

Carbonate system parameters, including $TCO_2$, $CO_3^{2-}$ concentration, $pCO_2$, and saturation state of calcite ($\Omega_C$) and aragonite ($\Omega_A$), were calculated using CO2SYS (Lewis and Wallace, 1998) for both incubation chamber and ambient seawater data sets. Dissociation constants K1 and K2 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 denoted by negative numbers. Carbonate system and physical parameters for both incubation chamber and ambient seawater

**Table 1.** Carbonate system parameters for incubation chamber measurements.

| Description | Time (hh:mm) | Salinity | Temp. (°C) | TA ($\mu$mol kg$^{-1}$) | pH | G (mmol CaCO$_3$ m$^{-2}$ 4 h$^{-1}$) | TCO$_2$ ($\mu$mol kg$^{-1}$) | CO$_3^{2-}$ ($\mu$mol kg$^{-1}$) | pCO$_2$ ($\mu$atm) | $\Omega_C$ | $\Omega_A$ | Avg. PAR ($\mu$mol photons m$^{-2}$ s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sand Bottom | 19:00 | 33.7 | 24.7 | 2217 | 8.11 | – | 1956 | 186 | 429 | 4.5 | 3.0 | – |
| 9/2–10/2/2000 | 23:00 | 33.7 | 24.4 | 2218 | 8.03 | –0.2 | 2000 | 159 | 535 | 3.9 | 2.5 | 0 |
| | 3:00 | 33.7 | 23.8 | 2222 | 8.00 | –0.8 | 2025 | 147 | 589 | 3.6 | 2.3 | 0 |
| | 7:00 | 33.7 | 23.6 | 2236 | 7.94 | –2.4 | 2066 | 131 | 690 | 3.2 | 2.1 | 0 |
| | 11:00 | 33.7 | 24.2 | 2243 | 8.00 | –1.1 | 2043 | 149 | 598 | 3.6 | 2.4 | 713 |
| | 15:00 | 33.7 | 26.1 | 2232 | 8.04 | 1.9 | 1999 | 170 | 533 | 4.1 | 2.7 | 1551 |
| | 19:00 | 33.7 | 25.1 | 2235 | 8.03 | –0.6 | 2016 | 161 | 551 | 3.9 | 2.6 | 536 |
| | 23:00 | 33.7 | 24.5 | 2241 | 7.97 | –1.0 | 2053 | 142 | 645 | 3.5 | 2.3 | 0 |
| Coral Rubble | 13:00 | 34.2 | 26.0 | 2166 | 8.00 | – | 1958 | 152 | 583 | 3.7 | 2.4 | – |
| 13/2–14/2/2000 | 17:00 | 34.2 | 27.4 | 2142 | 8.09 | 3.9 | 1881 | 185 | 450 | 4.5 | 3.0 | 1163 |
| | 21:00 | 34.2 | 25.9 | 2147 | 8.03 | –0.8 | 1926 | 159 | 530 | 3.9 | 2.5 | 74 |
| | 1:00 | 34.2 | 24.9 | 2195 | 7.95 | –8.0 | 2013 | 137 | 666 | 3.3 | 2.2 | 0 |
| | 5:00 | 34.2 | 24.2 | 2227 | 7.91 | –5.3 | 2063 | 127 | 742 | 3.1 | 2.0 | 0 |
| | 9:00 | 34.2 | 24.0 | 2236 | 7.92 | –1.6 | 2067 | 130 | 717 | 3.1 | 2.1 | 139 |
| | 13:00 | 34.2 | 25.8 | 2230 | 8.06 | 1.1 | 1987 | 176 | 503 | 4.3 | 2.8 | 1432 |
| Patch Reef (10% | 9:30 | 35.0 | 24.9 | 2177 | 8.09 | – | 1926 | 178 | 452 | 4.3 | 2.8 | – |
| Coral Cover) | 13:30 | 35.0 | 26.7 | 2145 | 8.17 | 5.5 | 1839 | 212 | 357 | 5.1 | 3.4 | 1540 |
| 15/2–16/2/2000 | 17:30 | 35.0 | 27.8 | 2141 | 8.16 | 0.6 | 1833 | 214 | 367 | 5.2 | 3.4 | 1003 |
| | 21:30 | 35.0 | 26.7 | 2125 | 8.07 | 2.7 | 1877 | 175 | 472 | 4.2 | 2.8 | 23 |
| | 1:30 | 35.0 | 24.9 | 2160 | 7.99 | –5.8 | 1956 | 148 | 580 | 3.6 | 2.3 | 0 |
| | 5:30 | 35.0 | 24.8 | 2218 | 7.99 | –9.8 | 2012 | 152 | 597 | 3.6 | 2.4 | 0 |
| | 9:30 | 35.0 | 25.3 | 2221 | 7.97 | –0.4 | 2020 | 149 | 631 | 3.6 | 2.4 | 237 |
| Patch Reef (22% | 14:15 | 35.0 | 24.9 | 2161 | 8.22 | – | 1833 | 226 | 303 | 5.4 | 3.6 | – |
| Coral Cover) | 18:15 | 35.0 | 26.7 | 2105 | 8.16 | 9.3 | 1808 | 205 | 358 | 4.9 | 3.3 | 752 |
| 16/2–17/2/2000 | 22:15 | 35.0 | 27.8 | 2114 | 8.01 | –1.4 | 1889 | 161 | 553 | 3.9 | 2.6 | 1 |
| | 3:49 | 35.0 | 26.7 | 2187 | 7.91 | –12.2 | 2011 | 133 | 752 | 3.2 | 2.1 | 0 |
| | 7:49 | 35.0 | 24.9 | 2211 | 7.84 | –4.1 | 2071 | 113 | 888 | 2.7 | 1.8 | 16 |
| | 11:49 | 35.0 | 24.8 | 2178 | 8.01 | 5.6 | 1966 | 154 | 558 | 3.7 | 2.4 | 1035 |
| | 14:20 | 35.0 | 25.3 | 2144 | 8.10 | 5.8 | 1883 | 183 | 426 | 4.4 | 2.9 | 1624 |
| Sand Bottom | 7:00 | 34.3 | 25.0 | 2277 | 7.95 | – | 2088 | 143 | 688 | 3.5 | 2.3 | – |
| 23/7–24/7/2001 | 11:00 | 34.3 | 27.7 | 2258 | 7.99 | 3.2 | 2038 | 163 | 630 | 4.0 | 2.6 | – |
| | 15:00 | 34.3 | 29.3 | 2250 | 8.06 | 1.3 | 1987 | 190 | 530 | 4.6 | 3.1 | – |
| | 19:00 | 34.3 | 28.0 | 2197 | 8.12 | 8.9 | 1911 | 202 | 429 | 4.9 | 3.3 | – |
| | 23:00 | 34.3 | 27.0 | 2276 | 8.10 | –13.3 | 1999 | 199 | 462 | 4.8 | 3.2 | – |
| | 3:00 | 34.3 | 26.3 | 2259 | 8.02 | 2.9 | 2030 | 168 | 568 | 4.1 | 2.7 | – |
| | 7:00 | 34.3 | 26.2 | 2262 | 7.89 | –0.5 | 2094 | 131 | 802 | 3.2 | 2.1 | – |
| Patch Reef (10% | 11:00 | 34.4 | 27.0 | 2250 | 8.10 | – | 1978 | 195 | 465 | 4.7 | 3.1 | – |
| Coral Cover) | 15:00 | 34.4 | 28.4 | 2226 | 7.91 | 4.0 | 2042 | 140 | 773 | 3.4 | 2.3 | 1274 |
| 28/7–29/7/2001 | 19:00 | 34.4 | 28.6 | 2222 | 7.92 | 0.7 | 2031 | 144 | 747 | 3.5 | 2.3 | 777 |
| | 23:00 | 34.4 | 27.5 | 2221 | 7.84 | 0.1 | 2071 | 120 | 914 | 2.9 | 1.9 | 0 |
| | 3:00 | 34.4 | 26.6 | 2234 | 7.79 | –2.1 | 2109 | 106 | 1050 | 2.6 | 1.7 | 0 |
| | 7:00 | 34.4 | 26.0 | 2247 | 7.72 | –2.2 | 2147 | 92 | 1229 | 2.2 | 1.5 | 0 |
| | 11:00 | 34.4 | 26.9 | 2226 | 7.85 | 3.6 | 2074 | 121 | 887 | 2.9 | 1.9 | 968 |

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 0.1 to 9.3 mmol CaCO$_3^{2-}$ m$^{-2}$ 4 h$^{-1}$, and rates of dissolution ranged from –0.2 to –13.3 mmol CaCO$_3^{2-}$ 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 pCO$_2$ ranged from 303 to 1229 $\mu$atm, and CO$_3^{2-}$ concentrations ranged from 92 to 226 $\mu$mol kg$^{-1}$ (Table 1). Ambient seawater pCO$_2$ ranged from 170 to 935 $\mu$atm, and CO$_3^{2-}$ concentrations ranged

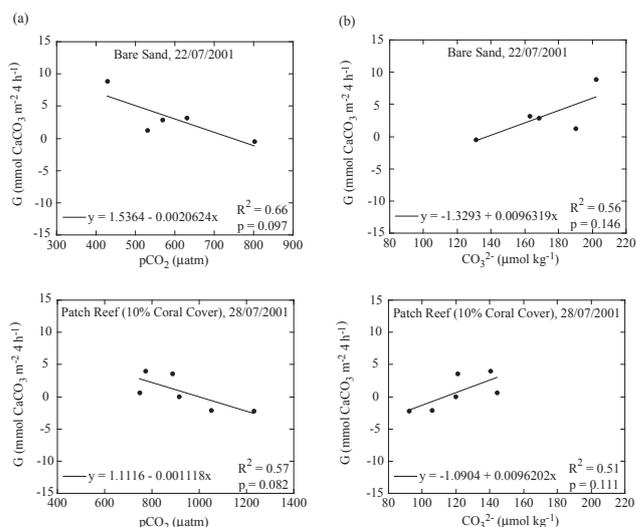**Table 2.** Carbonate system parameters for ambient seawater measurements.

| Date | Time (hh:mm) | Salinity | Temp. (°C) | TA ($\mu$mol kg$^{-1}$) | pH | TCO$_2$ ($\mu$mol kg$^{-1}$) | CO$_3^{2-}$ ($\mu$mol kg$^{-1}$) | pCO$_2$ ($\mu$atm) | $\Omega_C$ | $\Omega_A$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 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 | 28.8 | 2245 | 8.28 | 1846 | 277 | 273 | 6.8 | 4.5 |
| | 19:00 | 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 | 3.8 |
| | 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 | 2284 | 8.11 | 2008 | 198 | 446 | 4.8 | 3.2 |
| | 11:00 | 34.3 | 26.9 | 2273 | 8.29 | 1881 | 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 | 2283 | 8.13 | 1987 | 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 |
| | 21:36 | 36.2 | 26.3 | 2197 | 8.11 | 1917 | 196 | 433 | 4.7 | 3.1 |
| 17/6/2003 | 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 |
| 18/6/2003 | 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 |
| 19/6/2003 | 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 |
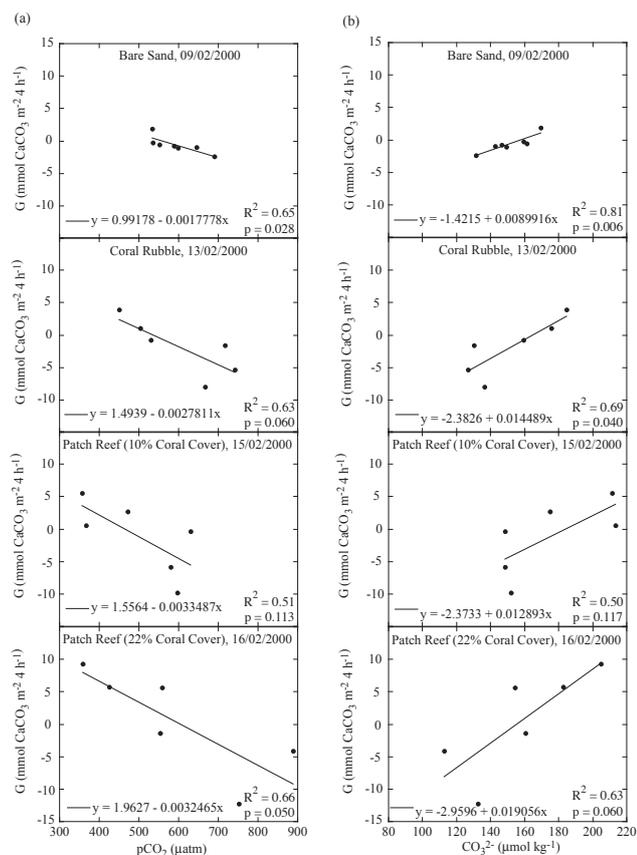
**Fig. 3.** Rates of calcification/dissolution (G) vs. $pCO_2$ **(a)** and $CO_3^{2-}$ concentrations **(b)** for all substrate types measured in 2000. Positive values indicate calcification. Negative values indicate dissolution.



**Fig. 4.** Rates of calcification/dissolution (G) vs. $pCO_2$ **(a)** and $CO_3^{2-}$ concentrations **(b)** for all substrate types measured in 2001. Positive values indicate calcification. Negative values indicate dissolution.

from 110 to 335 $\mu$mol kg$^{-1}$ (Table 2). Carbonate ion concentrations and $pCO_2$ for 41 out of 43 four-hour incubation chamber measurements were within the range of $CO_3^{2-}$ concentrations and $pCO_2$ 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 $pCO_2$ measurements higher than (and $CO_3^{2-}$ 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 $pCO_2$, and calcification rate and $CO_3^{2-}$ 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 calcification to net dissolution and the $pCO_2$ and $CO_3^{2-}$ 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 $pCO_2$ and $CO_3^{2-}$ 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 when $pCO_2$ exceeded $pCO_{2\,C/D=1}$, or when

$CO_3^{2-}$ 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 $CO_3^{2-}$ and $pCO_2$ 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 years of data collection (Table 3). The average $CO_{3\,C/D=1}^{2-}$ for all substrate types was 152±24 $\mu$mol kg$^{-1}$, and the range was from 113 to 184 $\mu$mol kg$^{-1}$. The average $pCO_{2\,C/D=1}$ was 654±195 $\mu$atm, ranging from 467 to 1003 $\mu$atm. 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 $CO_{3\,C/D=1}^{2-}$ 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 $pCO_{2\,C/D=1}$.

Figures 5, 6, and 7 show the diurnal variation in ambient seawater $pCO_2$ and $CO_3^{2-}$ 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 $pCO_2$ decreased during the day and increased during the night, while $CO_3^{2-}$ increased during the day, and decreased during the night. We have estimated the percentage of time that $pCO_2$ and $CO_3^{2-}$ concentrations in ambient seawater data sets naturally surpassed the $pCO_{2\,C/D=1}$ and

**Table 3.** Percent of time ambient seawater $CO_3^{2-}$ concentration and $pCO_2$ surpassed thresholds for C/D=1.

| Description | $CO_{3\,C/D=1}^{2-}$ ($\mu$mol kg$^{-1}$) | % time below $CO_{3\,C/D=1}^{2-}$ Oct. 2000 July 2001 June 2003 | | | $pCO_{2\,C/D=1}$ ($\mu$atm) | % time above $pCO_{2\,C/D=1}$ Oct. 2000 July 2001 June 2003 | | |
|---|---|---|---|---|---|---|---|---|
| Sand Bottom 2000 | 157 | 0[a] | 5[a] | 21[a] | 562 | 13 | 11 | 28 |
| Coral Rubble 2000 | 164 | 9[a] | 8[a] | 33[a] | 537 | 24 | 13 | 43 |
| Patch Reef 10% 2000 | 184 | 59[a] | 15[a] | 53[a] | 467 | 69 | 21 | 64 |
| Patch Reef 20% 2000 | 155 | 0[a] | 5[a] | 19[a] | 605 | 0 | 7 | 26 |
| Sand Bottom 2001 | 138 | 0[a] | 1 | 10[a] | 748 | 0 | 0[a] | 10 |
| Patch Reef 2001 | 113 | 0[a] | 0[a] | 2 | 1003 | 0 | 0 | 0[a] |
| Average ± 1 std. dev. | 152±24 | 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 $CO_3^{2-}$ and $pCO_2$ thresholds were, simultaneously, surpassed.

$CO_{3\,C/D=1}^{2-}$ thresholds 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 $pCO_2$ 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 under-saturated with respect to carbonate minerals when $pCO_2$ reaches 1700 and 2800 $\mu$atm, 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 $pCO_2$ and $CO_3^{2-}$ values that were within the range of those measured in ambient seawater at present day atmospheric $pCO_2$ 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
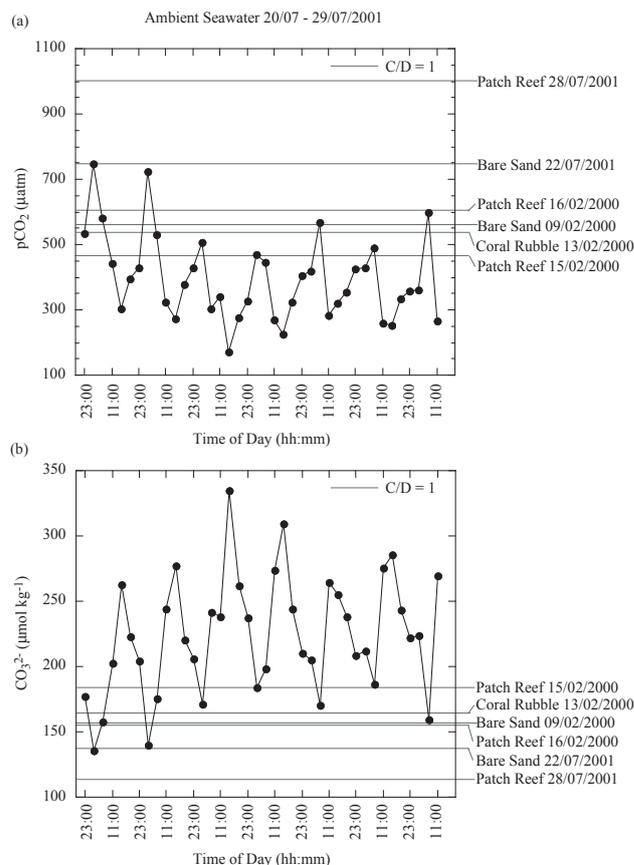
night-time dissolution rates (calculated per hour, –0.05 to –3.3 mmol $CaCO_3^{2-}$ m$^{-2}$ h$^{-1}$) fall within the range of those observed by previous researchers. Gattuso et al. (1997) measured community metabolism on a fringing reef at Moorea (French Polynesia) over 24 h time periods. Community net calcification showed a strong diurnal pattern with net calcification occurring during the day (12.4 mmol $CaCO_3$ m$^{-2}$) and net dissolution occurring during the night (–13.3 mmol $CaCO_3$ m$^{-2}$, or approximately -1.1 mmol $CaCO_3$ m$^{-2}$ h$^{-1}$) resulting in dissolution of –0.9 g $CaCO_3$ m$^{-2}$ 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 $CO_2$, 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 –2.4 mmol $CaCO_3$ m$^{-2}$ d$^{-1}$ and mean night dissolution rates of –0.6 to –0.7 mmol $CaCO_3$ m$^{-2}$ 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 –25.0 mmol $CaCO_3$ m$^{-2}$ h$^{-1}$ that resulted in net dissolution of –90.0 mmol $CaCO_3$ m$^{-2}$ d$^{-1}$. Earlier studies (Kinsey, 1978; Barnes and Devereux, 1984) observed higher night-time dissolution rates of –1.0 to –4.0 mmol $CaCO_3$ m$^{-2}$ h$^{-1}$ on One Tree Island Reef (Kinsey, 1978), and approximately –8.0 mmol $CaCO_3$ m$^{-2}$ 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 $pCO_2$ and $CO_3^{2-}$ ($r^2$ 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
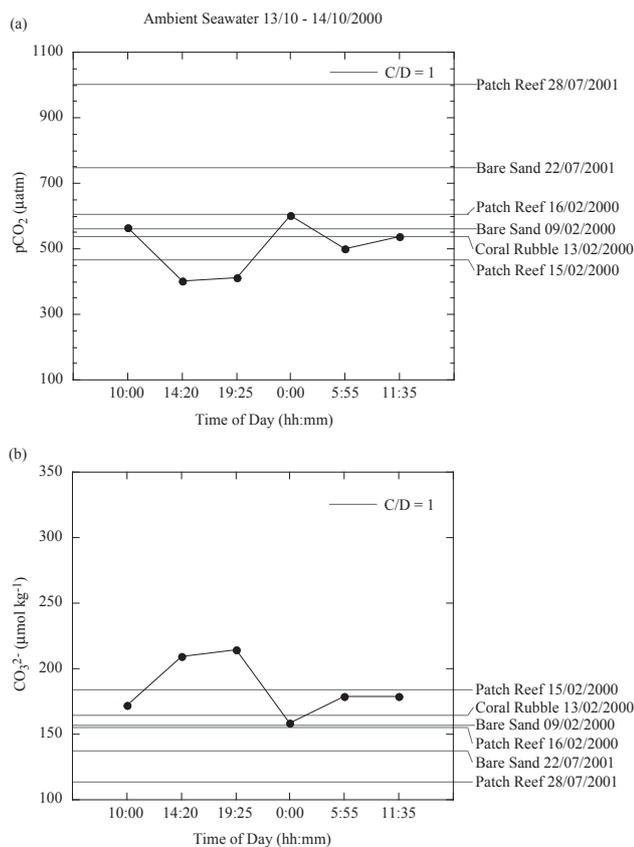
**Fig. 5.** Ambient seawater measurements of $pCO_2$ and $CO_3^{2-}$ concentrations from 13–14 October 2000. Horizontal lines represent threshold $pCO_2$ and $CO_3^{2-}$ values from each substrate type whereby the rate of calcification is equivalent to the rate of dissolution.
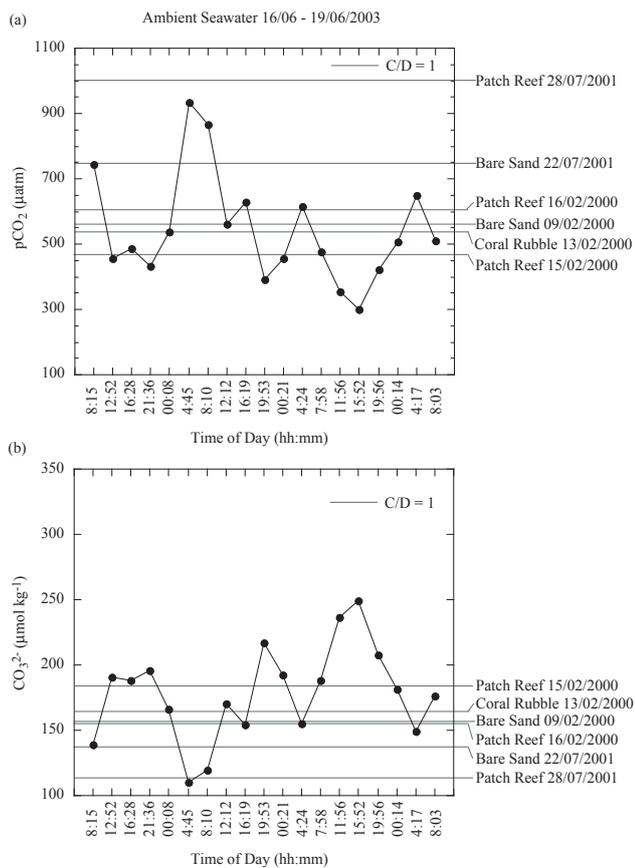
**Fig. 6.** Ambient seawater measurements of $pCO_2$ and $CO_3^{2-}$ concentrations from 20–29 July 2001. Horizontal lines represent threshold $pCO_2$ and $CO_3^{2-}$ values from each substrate type whereby the rate of calcification is equivalent to the rate of dissolution.

facilitate calcification and dissolution (Schmalz and Swanson, 1969; Yates and Halley, 2006). Ohde and van Woesik (1999) measured (in situ) rates of coral reef metabolism and seawater carbonate system parameters on the Rukansho reef in Okinawa. Their results showed diurnal cycles in reef calcification and carbonate system parameters including (pH, $pCO_2$, total alkalinity, and carbonate mineral saturation state) similar to the trends observed in our study. Although they report very low rates of calcification during the night, they observed no dissolution. Ohde and van Woesik (1999) also showed the dependence of calcification on saturation state (whereby calcification increases with increasing saturation state) and suggested that the changes in calcification rate and saturation state driven by organic carbon production and respiration respond to changes in pH and $pCO_2$. This is consistent with our observations. Leclercq et al. (2002) measured dark dissolution of –0.8 to –0.5 mmol $CaCO_3$ m$^{-2}$ h$^{-1}$ in a coral reef mesocosm with $pCO_2$ manipulated to 411, 647, and 918 $\mu$atm. Coral reef community calcification decreased with decreasing aragonite saturation state both day and night. Sand community calcification decreased with de-

creasing 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 $CO_2$ 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 $pCO_2$ and $CO_3^{2-}$.

It is fairly well known that biogenic calcification is enhanced by light during the day through a number of processes discussed in Gattuso et al. (1999) and Barnes and Chalker (1990). Our study was not designed to discriminate among the combined effect of light and $pCO_2$ on day-time rates of calcification. A plot of our day-time rates of calcification on the Molokai reef flat versus average photosynthetically active radiation (PAR) for each incubation period, results in a linear correlation with $R^2=0.44$ and p=0.001 suggesting that light imparted some degree of control on calcification. Marubini et al. (2001) demonstrated the combined long and short-term effect of irradiance on calcification in

**Fig. 7.** Ambient seawater measurements of $pCO_2$ and $CO_3^{2-}$ concentrations from 16–19 June 2003. Horizontal lines represent threshold $pCO_2$ and $CO_3^{2-}$ values from each substrate type whereby the rate of calcification is equivalent to the rate of dissolution.

experimental studies on *Porites compressa* from Kaneohe Bay, HI. This particular coral species was one of the dominant species in our incubation chamber experiments. Marubini et al. (2001) derived a hyperbolic tangent function for irradiance vs. calcification curves (similar to the function that describes the relationship between photosynthesis and irradiance) that showed an asymptote at $10 \, \mathrm{mol \, photons \, m^{-2} \, d^{-1}}$ beyond which calcification rate no longer increased with increasing irradiance. They suggest that calcification is light enhanced through photosynthesis over the short-term by production of a chemical environment conducive to calcification, and over the long-term by production of energy for organic matrix production. The maximum PAR during their experiments was only $700 \, \mu\mathrm{mol \, photons \, m^{-2} \, s^{-1}}$. Saturation light intensities for photosynthesis by many species of coral reef organisms range from approximately 600 to $1180 \, \mu\mathrm{mol}$ photons $\mathrm{m^{-2} \, s^{-1}}$ (Barnes and Devereux, 1984; Carpenter, 1985; Griffith et al., 1987). Chalker (1981) presents a similar curve for instantaneous light-enhanced calcification.

Maximum surface PAR reached $2500 \, \mu\mathrm{mol \, photons \, m^{-2}}$ $\mathrm{s^{-1}}$ and maximum seafloor PAR reached $2000 \, \mu\mathrm{mol \, photons}$

$\mathrm{m^{-2} \, s^{-1}}$ during our reef flat experiments. However, we did not observe saturation of calcification rates at higher light intensities during our study, suggesting that light was not the only controlling factor of day-time calcification in our experiments. Furthermore, night-time dissolution is not dependent upon light. In our study we observed a great deal of dissolution, often with light:dark, calcification:dissolution ratios of less than 1.0. Our calcification:dissolution ratios were, generally, much lower than the median value of 3.0 reported in Gattuso et al. (1999) for light enhanced calcification. It is likely that light imparted some degree of control on calcification and dissolution indirectly through photosynthesis and respiration. We observed a $CO_2$ decrease and $CO_3^{2-}$ increase as calcification increased during the day, and $pCO_2$ continued to increase during the night even as dissolution increased. This can occur when the amount of $CO_2$ generated and consumed by respiration and photosynthesis is much greater than the amount generated and consumed by calcification and dissolution. Photosynthesis and respiration force the system out of equilibrium with respect to calcification and dissolution because $CO_2$ generated by calcification is consumed by photosynthesis, and $CO_2$ consumed by dissolution is replaced by $CO_2$ from respiration. We used this relationship to our advantage so we could use natural changes in $pCO_2$ and $CO_3^{2-}$ resulting from photosynthesis and respiration to look at calcification and dissolution over a range of concentrations. Future experiments need to de-convolve the combined impact of light and $pCO_2$ on calcification.

The fact that dissolution occurred in waters that remained supersaturated with respect to aragonite and calcite 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 $pCO_2$ and carbonate ion species was not the sole process causing dissolution, that dissolution occurred in the pore waters of seafloor sediments, or that some combination of magnesian carbonate dissolution, non-equilibrium dissolution of carbonate sediments, and pore water dissolution 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 of 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. However, Langdon et al. (2000) measured rates of calcification and dissolution of sediments in the Biosphere-2 that were dominated by tests of the red coralline alga *Amphiroa* sp. consisting of magnesian calcite containing 22% $MgCO_3$. They indicate that dissolution only occurred when the aragonite saturation state was less than 1.3. In our experiments, aragonite saturation state did not decrease below 1.5 suggesting that dissolution likely occurred in under-saturated pore waters of shallow surface sediments. Under-saturated pore water conditions can result

from bacterial respiration and oxidation of organic matter (Charpy-Roubaud et al., 1996). Burdige and Zimmerman (2002) measured carbonate dissolution rates in the pore waters of shallow ooilitic sands in the Bahamas ranging from 0.01 mmol m$^{-2}$ d$^{-1}$ for bare sand to 0.94 mmol m$^{-2}$ d$^{-1}$ for sand covered with dense seagrass. Our sand bottom study sites were also devoid of seagrass, however our dissolution rates were several orders of magnitude greater than those observed by Burdige and Zimmerman. It is also possible that dissolution may have resulted from bioerosion of sediments by endolithic microbes and boring foraminifera (Vogel et al., 2000; Lazar and Loya, 1991; Peyrot-Clausade, 1995; Peyre'-Venec, 1987).

Our incubation chamber system measures net changes as a result of processes in the surface water, reef structure, and shallow sediments. Our experiments were not designed to discriminate which dissolution processes occurred (pore water dissolution, endolithic and other bioeroding organisms, High-Mg Calcite dissolution, etc.). While it is likely that dissolution occurred in the pore water of shallow surface sediments because aragonite saturation state did not decrease below 1.5, it is unknown as to what the carbonate speciation was in these pore waters, or how deep within the sediments this interaction occurred. Advection and diffusion can transfer alkalinity across the sediment water interface imparting a chemical signature to surface water (Walter et al., 1993). Our experiments suggest that if dissolution occurred in shallow pore waters, then shallow pore water chemistry responded to diurnal changes in surface water chemistry to some unknown depth depending on porosity, permeability, and advection/diffusion. The threshold values we report for the Molokai reef flat are the surface water $pCO_2$ and $CO_3^{2-}$ concentrations that forced the system (surface and shallow pore water combined) towards dissolution.

It is predicted that atmospheric $pCO_2$ will reach 560 $\mu$atm by 2065, and 700 $\mu$atm by 2100 (Houghton et al., 1996) surpassing the average $pCO_2$ threshold value of 654 $\mu$atm that we calculated for our study sites on the Molokai reef flat. At present day atmospheric $pCO_2$ of 380 ppmv, ambient seawater $pCO_2$ on the Molokai reef flat ranged from 170 to 935 $\mu$atm, and individual $pCO_2$ threshold values for all substrate types (ranging from 467 to 1003 $\mu$atm) were exceeded, on average, 18% of the time during measurement of ambient seawater chemistry. Ambient seawater $pCO_2$ measurements were higher than atmospheric $pCO_2$ (380 ppmv) 66% of the time. Our linear correlation between calcification/dissolution rates and $pCO_2$, and our calculated $pCO_2$ threshold values suggest that not only will rates of dissolution increase with increasing $pCO_2$, but the amount of time that $pCO_2$ 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 $pCO_2$ 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 $pCO_2$ 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 atmospheric $pCO_2$ levels.

## References

Andersson, A. J., Mackenzie, F. T., and Ver, L. M.: Solution of shallow-water carbonates: an insignificant buffer against rising atmospheric $CO_2$, Geology, 31, 513–516, 2003.

Atkinson, M. J. and Grigg, R. W.: Model of a coral reef ecosystem II: gross and net benthic primary production at French Frigate Shoals, Hawaii, Coral Reefs, 3, 13–22, 1984.

Barnes, D. J. and Cuff, C.: Solution of reef rock buffers seawater against rising atmospheric CO2, in: Proc. 9th Int. Coral Reef Sym. Abstracts: Indonesia, State Ministry for the Environment, edited by: Hopley, D., Hopley, P. M., Tamelander, J., and Done, T., 248 p., 2000.

Barnes, D. J. and Devereux, M. J.: Productivity and calcification on a coral reef: a survey using pH and oxygen electrode techniques, J. Exp. Mar. Biol. Ecol., 79, 213–231, 1984.

Borowitzka, M. A.: Photosynthesis and calcification in the articulated coralline red algae *Amphiroa anceps* and *A. foliacea*, Mar. Biol., 62, 17–23, 1981.

Boucher, G., Clavier, J., Hily, C., and Gattuso, J.-P.: Contribution of soft-bottoms to the community metabolism (primary production and calcification) of a barrier reef flat (Moorea, French Polynesia), J. Exp. Mar. Biol. Ecol., 225, 269–283, 1998.

Charpy-Roubaud, C., Charpy, L., and Sarazin, G.: Diffusional nutrient fluxes at the sediment water interface and organic matter mineralization in an atoll lagoon (Tikehau, Tuamotu Archipelago, French Polynesia), Mar. Ecol. Prog. Ser., 132, 181–190, 1996.

Conand, C., Chabanet, P., Cuet, P., and Letourneur, Y.: The carbonate budget of a fringing reef in La Reunion Island (Indian Ocean): sea urchin and fish bioerosion and net calcification, Proc. 8th Int. Coral Reef Sym., 953–958, 1997.

Dickson, A. G.: Standard potential of the reaction: AgCl(s)+$\frac{1}{2}$H2(g)=Ag(s)+HCl(aq), and the standard acidity constant of the ion HSO4- in synthetic seawater from 273.15 to 318.15 K, J. Chem. Thermodyn., 22, 113–127, 1990.

Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, Deep-Sea Res., 34, 1733–1743, 1987.

Feely, R. A., Byrne, R. H., Betzer, P. R. Gendron, J. F., and Acker, J. G.: Factors influencing the degree of saturation of the surface and intermediate waters of the North Pacific Ocean with respect to aragonite, J. Geophys. Res., 89, 10 631–10 640, 1984.

Gao, K., Aruga, Y., Asada, K., Ishihara, T., Akano, T., and Kiyohara, M.: Calcification in the articulated coralline alga *Corallina pilulifera*, with special reference to the effect of elevated $CO_2$ concentration, Mar. Biol., 117, 129–132, 1993.

Gattuso, J.-P., Pichon, M., Delesalle, B., and Frankignoulle, M.: Community metabolism and air-sea $CO_2$ fluxes in a coral reef ecosystem (Moorea, French Polynesia), Mar. Ecol. Prog. Ser., 96, 259–267, 1993.

Gattuso, J.-P., Frankignoulle, M., Ware, J. R., Smith, S. V., Wollast, R., Buddemeier, R. W., and Kayanne, H.: Coral Reefs and Carbon Dioxide, Science, 271, 1298–1300, 1996.

Gattuso, J.-P., Payri, C. E., Pichon, M., Delesalle, B., and Frankignoulle, M.: Primary production, calcification, and air-sea $CO_2$ fluxes of a macroalgal-dominated coral reef community (Moorea, French Polynesia), J. Phycol., 33, 729–738, 1997.

Gattuso, J.-P., Frankignoulle, M., Bourge, I., Romaine, S., and Buddemeier, R. W.: Effect of calcium carbonate saturation of seawater on coral calcification, Global and Planetary Change, 18, 37–46, 1998.

Gattuso, J.-P., Allemand, D., and Frankignoulle, M.: Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry, Am. Zool., 39, 160–183, 1999.

Halley, R. B. and Yates, K. K.: Will reef sediments buffer corals from increased global $CO_2$, Proc. 9th Int. Coral Reef Sym., Abstracts: Indonesia, State Ministry for the Environment, 2000.

Houghton, J. T., Meira Filho, L. G., Callander, B. A., Harris, N., Kattenberg, A., and Maskell, K.: Climate change 1995. The Science of Climate Change, Cambridge University Press, Cambridge, 1996.

Keeling, C. D. and Whorf, T. P.: Trends Online: a compendium of data on global change, Carbon Dioxide Analysis Center, Oak Ridge National Laboratory, http://cdiac.esd.ornl.gov/ftp/ndp001r7/, 2004.

Kinsey, D. W.: Preliminary observations on community metabolism and primary productivity of the pseudo-atoll reef at One Tree Island, Great Barrier Reef, in: Proc. Symp. Corals and Coral Reefs, Mar. Biol. Assoc. India, 13–22, 1972.

Kinsey, D. W.: Productivity and calcification estimates using slack-water periods and field enclosures, in: Coral Reefs: Research Methods, edited by: Stoddart, D. R. and Johannes, R. E., UNESCO, Monographs on Oceanographic Methodology, No. 5, 439–468, 1978.

Kinsey, D. W.: Carbon turnover and accumulation by coral reefs,

PhD dissertation, University of Hawaii, Honolulu, 248pp., 1979.

Kinsey, D. W.: Metabolism, calcification, and carbon production: system level studies, in: Proceedings 5th Int. Coral Reef Congress, Tahiti, 4, 505–526, 1985.

Kleypas, J. A., Buddemeier, R. W., Archer, D., Gattuso, J.-P., Langdon, C., and Opdyke, B. N.: Geochemical consequences of increased atmospheric $CO_2$ on coral reefs, Science, 284, 118–120, 1999.

Kleypas, J. A., Buddemeier, R. W., and Gattuso, J.-P.: The future of coral reefs in an age of global change, Int. J. Earth Sci., 90, 426–437, 2001.

Langdon, C., Takahashi, T., McConnaughey, T., Anderson, H., and West, H.: Effect of calcium carbonate saturation state on the rate of calcification of an experimental coral reef, Am. Zool., 37, abstract #254, 1998.

Langdon, C., Takahashi, T., Sweeney, C., Chipman, D., Goddard, J., Marubini, F., Aceves, H., Barnett, H., and Atkinson, M. J.: Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef, Global Biogeochem. Cycles, 14, 639–654, 2000.

Langdon, C., Broecker, W. S., Hammond, D. E., Glenn, E., Fitzsimmons, K., Nelson, S. G., Peng, T.-H., Hajdas, I., and Bonani, G.: Effect of elevated $CO_2$ on the community metabolism of an experimental coral reef, Global Biogeochem. Cycles, 17, 1–14, 2003.

Langdon, C. and Atkinson, M. J.: Effect of elevated $pCO_2$ on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment, J. Geophys. Res., 110, C09S07, doi:10.1029/2004JC002576, 2005.

Lazar, B. and Loya, Y.: Bioerosion of coral reefs: a chemical approach, Limnol. Oceanogr., 36, 377–383, 1991.

Leclercq, N., Gattuso, J.-P., and Jaubert, J.: $CO_2$ partial pressure controls the calcification rate of a coral community, Global Change Biol., 6, 329–334, 2000.

Leclercq, N., Gattuso, J.-P., and Jaubert, J.: Primary production, respiration, and calcification of a coral reef mesocosm under increased $CO_2$ partial pressure, Limnol. Oceanogr., 47, 558–564 2002.

Lewis, E. and Wallace, D. W. R.: Program developed for $CO_2$ system calculations, ORNL/CDIAC-105, Carbon dioxide information analysis center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge Tennessee, 1998.

Mackenzie, F. T., Ver, L. M., and Lerman, A.: Coastal zone biogeochemical dynamics under global warming, Int. Geol. Rev., 42, 193–206, 2000.

Marubini, F. and Atkinson, M.: Effect of lowered pH and elevated nitrate on coral Calcification, Mar. Ecol. Prog. Ser., 188, 117–121, 1999.

Marubini, F. and Thake, B.: Bicarbonate addition promotes coral growth, Limnol. Oceanogr., 44, 716–720, 1999.

Marubini, F., Barnett, H., Langdon, C., and Atkinson, M. J.: Dependence of calcification on light and carbonate ion concentration for the hermatypic coral *Porites compressa*, Mar. Ecol. Prog. Ser., 220, 153–162, 2001.

Marubini, F., Ferrier-Pages, C., and Cuif, J. P.: Suppression of skeletal growth in scleractinian corals by decreasing ambient carbonate-ion concentration: a cross-family comparison, Proc. Roy. Soc. London, Ser. B, 270, 179–184, 2003.

McNeil, B., Matear, R., and Barnes, D.: Coral reef calcification and climate change: the effect of ocean warming, Geophys. Res. Lett., 31, L2239, doi:10.1029/2004GL021541, 2004.

Merbach, C., Culberson, C. H., Hawley, J. E., and Pytkowicz, R. M.: Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, Limnol. Oceanogr., 18, 897–907, 1973.

Millero, F. J.: Chemical Oceanography, CRC Press, New York, 1996.

Millero, F. J., Zhang, J., Lee, K., and Campbell, D. M.: Titration alkalinity of seawater, Mar. Chem., 44, 153–165, 1993.

Ohde, S. and van Woesik, R.: Carbon dioxide flux and metabolic processes of a coral reef, Okinawa, Bull. Mar. Sci., 65, 559–576, 1999.

Orr, J. C., Fabry, V. J., Aumont, O., et al.: Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, Nature, 437, 681–686, 2005.

Pelejero, C., Calvo, E., McCullouch, M., Marshall, J., Gagan, M., Lough, J., Opdyke, B.: Preindustrial to modern interdecadal variability in coral reef pH, Science, 309, 2204–2207, 2005.

Peyrot-Clausade, M., Le Campion-Alsumard, T., Hutchings, P., Le Campion, J., Payri, C., and Fontaine, M. C.: Initial bioerosion and bioaccretion on experimental substrates in high island and atoll lagoons (French Polynesia), Oceanol. Acta, 18, 531–541, 1995.

Peyre'-Venec, M. T.: Boring foraminifera in French Polynesia, Coral Reefs, 11, 205–212, 1987.

Renegar, D. A. and Riegl, B. M.: Effect of nutrient enrichment and elevated $CO_2$ partial pressure on growth rate of Atlantic scleractinian coral *Acropora cervicornis*, Mar. Ecol. Prog. Ser., 293, 69–76, 2005.

Reynaud, S., Leclercq, N., Romaine-Lioud, S., Ferrier-Pages, C., Jaubert, J., and Gattuso, J. P.: Interacting effects of $CO_2$ partial pressure and temperature on photosynthesis and calcification in a scleractinian coral, Global Change Biol., 9, 1660–1668, 2003.

Sabine, C. L. and Mackenzie, F. T.: Bank-derived carbonate sediment transport and dissolution in the Hawaiian Archipelago, Aquatic Geochem., 1, 189–230, 1995.

Schmalz, R. F. and Swanson, F. J.: Diurnal variations in the carbonate saturation of seawater, J. Sed. Petrol., 39, 255–267, 1969.

Smith, S. V.: Carbon dioxide dynamics: a record of organic carbon production, respiration, and calcification in the Eniwetok reef flat community, Limnol. Oceanogr., 18, 106–120, 1973.

Smith, S. V.: The Houtman Abrolhos Islands: carbon metabolism of coral reefs at high latitude, Limnol. Oceanogr., 26, 612–621, 1981.

Smith, S. V. and Key, G. S.: Carbon dioxide and metabolism in marine environments, Limnol. Oceanogr., 20, 493–495, 1975.

Smith, S. V. and Kinsey, D. W.: Calcium carbonate production, coral reef growth, and sea level change, Science, 194, 937–939, 1976.

Smith, S. V., Chandra, S., Kwitko, L., Schneider, R. C., Schoonmaker, J., Seeto, J., Tebano, T., and Tribble, G. W.: Chemical stoichiometry of lagoonal metabolism: preliminary report on an environmental chemistry survey of Christmas Island, Kiribati, Technical Report, Joint UH/USF Internat. Sea Grant Programme, 1985.

Stumm, W. and Morgan, M. J.: Aquatic Chemistry, J. Wiley and Sons, Inc., New York, 1981.

Vogel, K., Gektidis, M., Golubic, S., Kiene, W., and Radtke, G.: Experimental studies on microbial bioerosion at Lee Stocking Island, Bahamas and One Tree Islands, Great Barrier Reef, Australia; implications for paleoecological reconstructions, Lethaia, 33, 190–204, 2000.

Walter, L., Bischof, S. A., Patterson, W. P., and Lyons, T. W.: Dissolution and recrystallization in modern shelf carbonates: evidence from pore water and solid phase chemistry, Philos. Trans. R. Soc. Lond., Ser. A, 344, 203–215, 1993.

Yao, W. and Byrne, R. H.: Simplified seawater alkalinity analysis: use of linear array spectrometers, Deep-Sea Res. I, 45, 1383–1392, 1998.

Yates, K. K. and Halley, R. B.: Measuring coral reef community metabolism using new benthic chamber technology, Coral Reefs, 22, 247–255, 2003.

Yates, K. K. and Halley, R. B.: Diurnal variation in rates of calcification and carbonate sediment dissolution in Florida Bay, Estuaries and Coasts, 29, 24–39, 2006.