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CO_3^{2-} concentration and pCO_2 thresholds for calcification and dissolution on the Molokai reef flat, Hawaii

K. K. Yates and R. B. Halley

U.S. Geological Survey, Center for Coastal and Watershed Studies, St. Petersburg, FL 33701, USA

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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 μatm and ranged from 467 to 1003 μatm. The average CO_3^{2-} threshold value was 152±24 μmol kg^{-1}, ranging from 113 to 184 μmol 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.

Correspondence to: K. K. Yates
(kyates@usgs.gov)

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:

$$CO_2 + H_2O \rightarrow H_2CO_3, \quad \text{(R1)}$$

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:

$$H_2CO_3 \rightarrow H^+ + HCO_3^-, \text{ and } CO_3^{2-} + H^+ \rightarrow HCO_3^-. \quad \text{(R2)}$$

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 $CO^{2-}_{3\,C/D=1}$ 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).

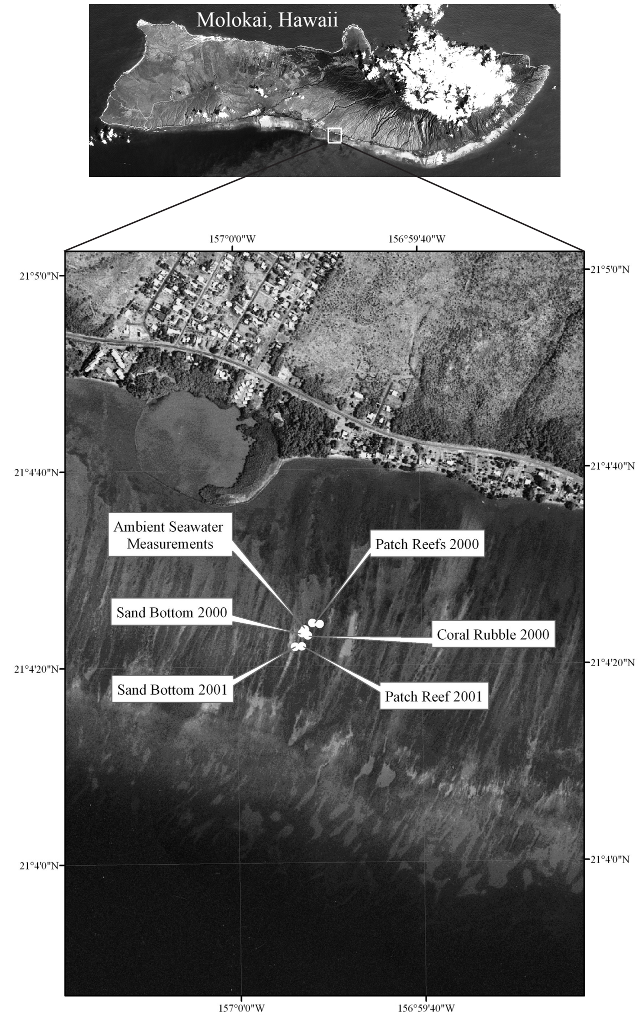

Fig. 1. Study sites for measurement of calcification and dissolution on patch reefs, sand bottom and coral rubble of the Molokai reef flat. Landsat TM satellite images courtesy of U.S. Geological Survey, Southwest Geographic Science Team.

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. 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 μm

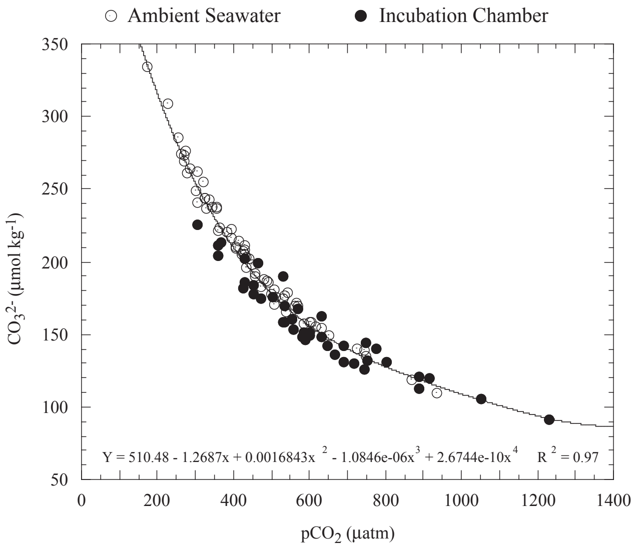

Fig. 2. pCO_2 and CO_3^{2-} concentrations of ambient seawater on the Molokai reef flat near incubation chamber study sites from 13–14 October 2000, from 20–29 July 2001, and from 16–19 June 2003 (open circles), and from all measurements inside the incubation chamber (solid circles).

cellulose nitrate filters, poisoned with 100 μL 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 μm 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 μmol kg^{-1}. While precision of repeated measurements was good, a large discrepancy was observed between our measured SRM values (Batch #4, 2354.0 μmol kg^{-1}; Batch #5, 2355.0 μmol kg^{-1}; and Batch #6, 2401.0 μmol kg^{-1}) and reported values for SRMs (Batch #4, 2359.0 μmol kg^{-1}; Batch #5, 2347.0 μmol kg^{-1}; and Batch #6, 2357.0 μmol kg^{-1}) resulting in differences between measured and reported values of 5 μmol kg^{-1}for Batch #4 (n=6), 8 μmol kg^{-1} for Batch #5 (n=4), and 44 μmol 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 μmol kg^{-1}. Measurement of CRMs from Batch #59 (n=6) yielded a value of 2220.0 μmol kg^{-1} which was only 1.0 μmol kg^{-1}lower than the reported value for Batch #59 of 2221.0 μmol 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):

$$G(\text{mmol CaCO}_3\,\text{m}^{-2}4\,\text{h}^{-1}) = {}^1/_2\,\Delta\text{TA}(\text{mmol m}^{-2}4\,\text{h}^{-1}) \times \text{SHARQ volume (m}^3)/\text{SHARQ surface area (m}^2). \quad (1)$$

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 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 (μmol kg^{-1})	pH	G (mmol $CaCO_3$ m^{-2} 4 h^{-1})	TCO_2 (μmol kg^{-1})	CO_3^{2-} (μmol kg^{-1})	pCO_2 (μatm)	Ω_C	Ω_A	Avg. PAR (μmol 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 μatm, and CO_3^{2-} concentrations ranged from 92 to 226 μmol kg^{-1} (Table 1). Ambient seawater pCO_2 ranged from 170 to 935 μatm, and CO_3^{2-} concentrations ranged

Table 2. Carbonate system parameters for ambient seawater measurements.

Date	Time (hh:mm)	Salinity	Temp. (°C)	TA (μmol kg^{-1})	pH	TCO_2 (μmol kg^{-1})	CO_3^{2-} (μmol 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	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

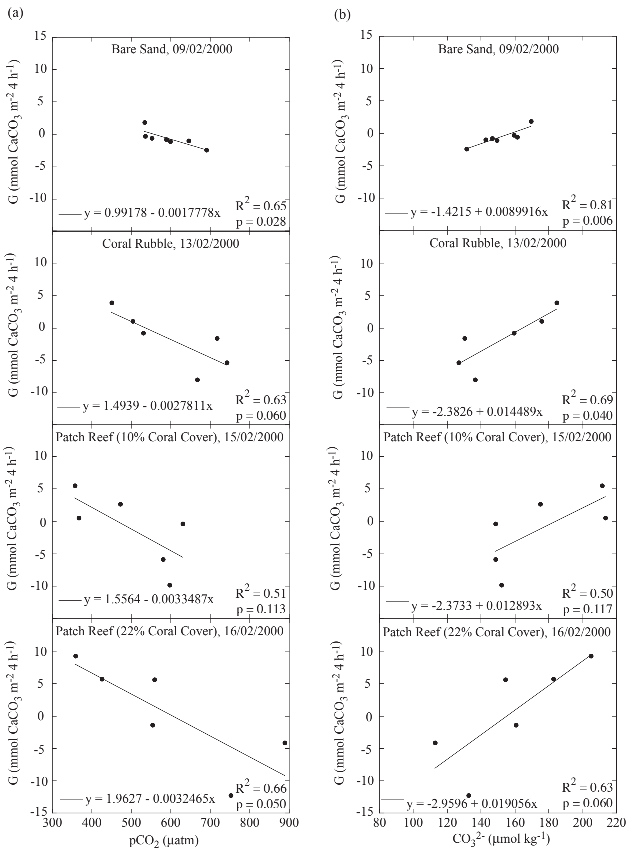

Fig. 3. Rates of calcification/dissolution (G) vs. pCO_2 **(a)** and CO_3^{2-} concentrations **(b)** for all substrate types measured in 2000. Positive values indicate calcification. Negative values indicate dissolution.

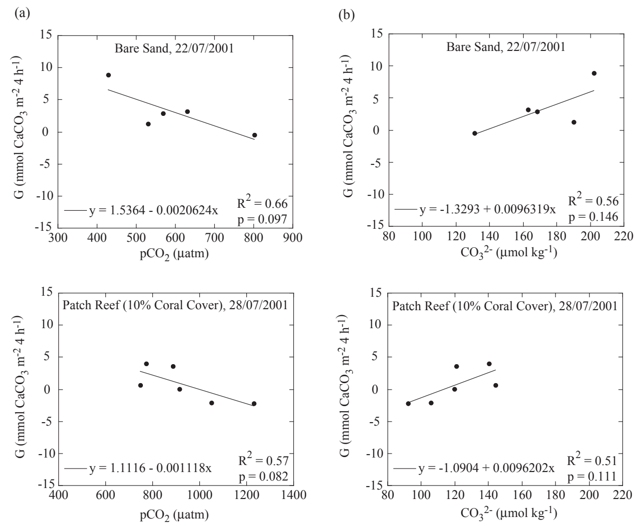

Fig. 4. Rates of calcification/dissolution (G) vs. pCO_2 **(a)** and CO_3^{2-} concentrations **(b)** for all substrate types measured in 2001. Positive values indicate calcification. Negative values indicate dissolution.

from 110 to 335 μmol 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 $CO^{2-}_{3\,C/D=1}$. Net dissolution occurred when pCO_2 exceeded $pCO_{2\,C/D=1}$, or when CO_3^{2-} fell below $CO^{2-}_{3\,C/D=1}$. Threshold $pCO_{2\,C/D=1}$ and $CO^{2-}_{3\,C/D=1}$ values for each substrate type are listed in Table 3. All $CO^{2-}_{3\,C/D=1}$ 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.

$CO^{2-}_{3\,C/D=1}$ and $pCO_{2\,C/D=1}$ varied considerably among substrate types and between years of data collection (Table 3). The average $CO^{2-}_{3\,C/D=1}$ 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 $CO^{2-}_{3\,C/D=1}$ 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 $CO^{2-}_{3\,C/D=1}$ 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 $CO^{2-}_{3\,C/D=1}$ 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 $CO^{2-}_{3\,C/D=1}$ 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	$CO^{2-}_{3\,C/D=1}$ (μmol kg^{-1})	% time below $CO^{2-}_{3\,C/D=1}$ Oct. 2000	July 2001	June 2003	$pCO_{2\,C/D=1}$ (μatm)	% 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 $\pm$ 1 std. dev.	152$\pm$24	11.3$\pm$24	5.7$\pm$5	23.0$\pm$18	654$\pm$195	17.7$\pm$27	8.7$\pm$8	29.0$\pm$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.

$CO^{2-}_{3\,C/D=1}$ 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 $CO^{2-}_{3\,C/D=1}$ 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$\pm$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 $CO^{2-}_{3\,C/D=1}$ varies considerably among substrate types, and it is likely that $pCO_{2\,C/D=1}$ and $CO^{2-}_{3\,C/D=1}$ 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 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 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

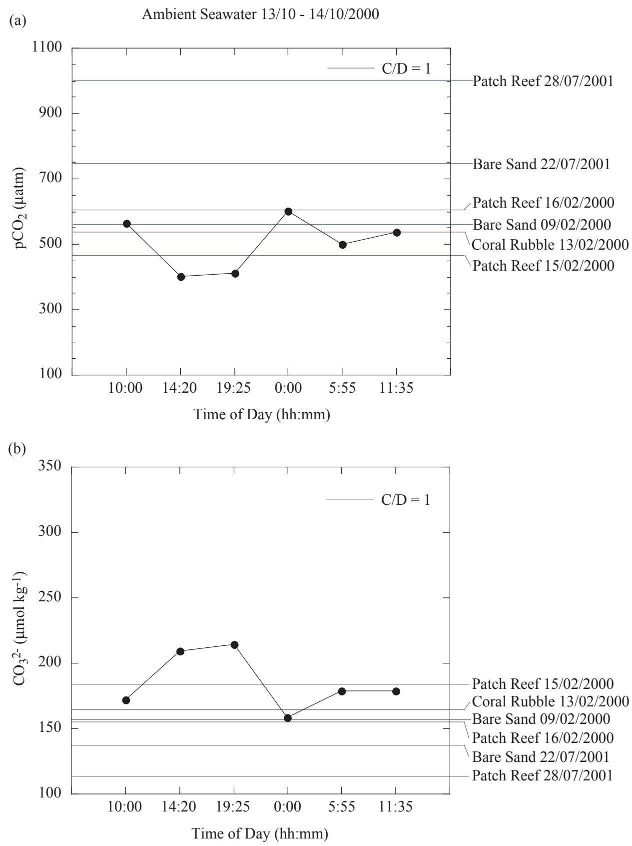

Fig. 5. Ambient seawater measurements of pCO_2 and CO_3^{2-} concentrations from 13–14 October 2000. Horizontal lines represent threshold pCO_2 and CO_3^{2-} values from each substrate type whereby the rate of calcification is equivalent to the rate of dissolution.

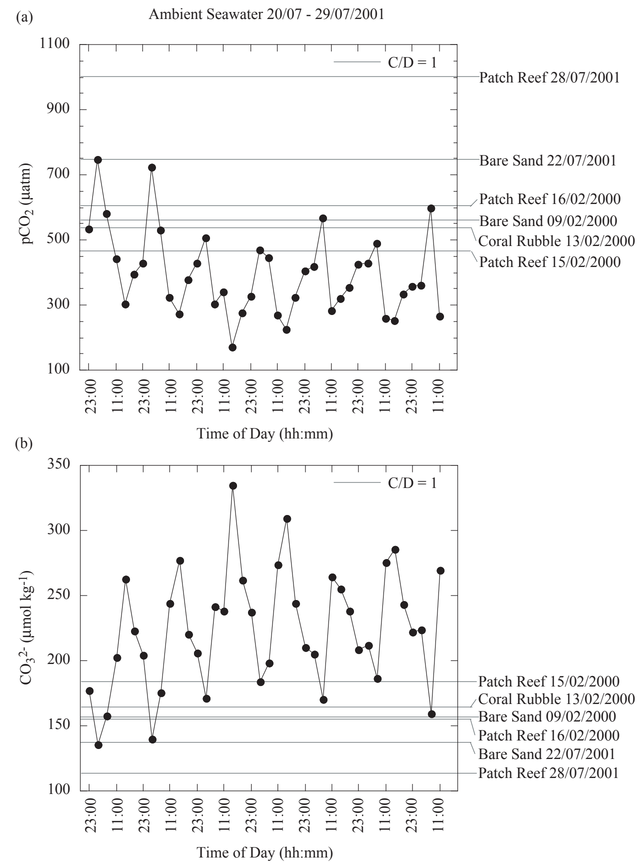

Fig. 6. Ambient seawater measurements of pCO_2 and CO_3^{2-} concentrations from 20–29 July 2001. Horizontal lines represent threshold pCO_2 and CO_3^{2-} values from each substrate type whereby the rate of calcification is equivalent to the rate of dissolution.

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 μatm. 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 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

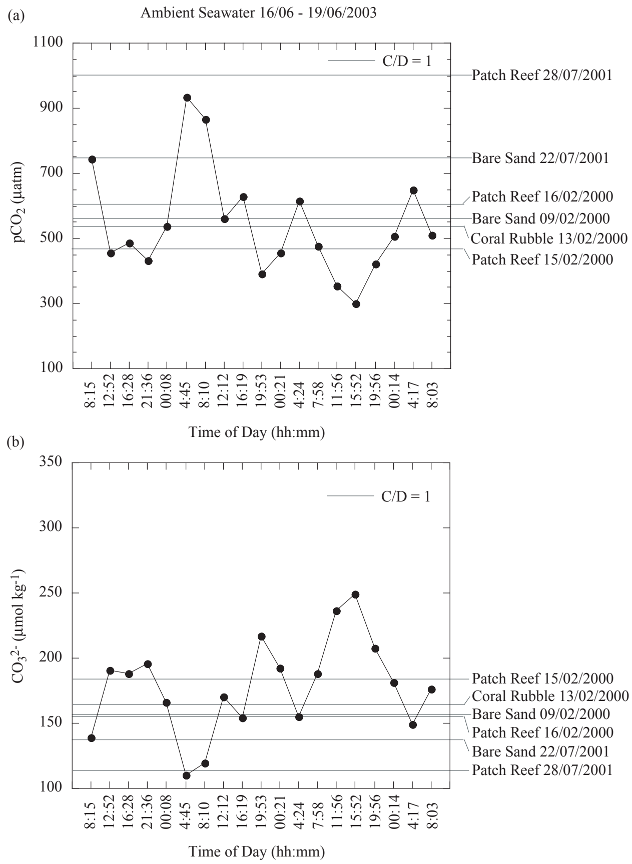

Fig. 7. Ambient seawater measurements of pCO_2 and CO_3^{2-} concentrations from 16–19 June 2003. Horizontal lines represent threshold pCO_2 and CO_3^{2-} values from each substrate type whereby the rate of calcification is equivalent to the rate of dissolution.

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 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 μmol photons m^{-2} s^{-1}. Saturation light intensities for photosynthesis by many species of coral reef organisms range from approximately 600 to 1180 μmol photons 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 μmol photons m^{-2} s^{-1} and maximum seafloor PAR reached 2000 μmol photons 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 μatm by 2065, and 700 μatm by 2100 (Houghton et al., 1996) surpassing the average pCO_2 threshold value of 654 μatm 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 μatm, and individual pCO_2 threshold values for all substrate types (ranging from 467 to 1003 μatm) 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.

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