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Ocean acidification hot spots: Spatiotemporal dynamics of the seawater CO_2 system of eastern Pacific coral reefs

Derek P. Manzello

Marine Biology and Fisheries, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida

Abstract

Seawater CO_2 system dynamics were assessed from eastern Pacific reef sites in Panamá over 5 consecutive years (2003–2008) and twice in the Galápagos Islands (2003 and 2009). The seawater CO_2 system was highly variable in time and space, but was explained by physical forcing from meteorological (seasonal rainfall) and oceanographic (upwelling, tides) processes interacting with diurnal reef metabolism. Galápagos coral reef communities are naturally exposed to the highest ambient partial pressure of CO_2 (pCO_2) and lowest aragonite saturation (Ω_{arag}) values documented for any coral reef environment to date. During upwelling in the Galápagos, mean pCO_2 and mean Ω_{arag} at five different sites ranged from 53.1 to 73.5 Pa and 2.27 to 2.86, respectively. Values of pCO_2 and Ω_{arag} ranged from 21.0 to 48.7 Pa and 2.47 to 4.18, respectively, on the Saboga Reef in the seasonally upwelling Gulf of Panamá, with the highest pCO_2 and lowest Ω_{arag} values occurring during upwelling. The Uva Reef, in the nonupwelling Gulf of Chiriquí of Pacific Panamá, had mean Ω_{arag} values that were always significantly greater than those at the Saboga Reef. Diurnal changes in the seawater CO_2 system from reef metabolism on the Uva Reef were magnified at low tide and highly significant differences were measured over depths as shallow as 15 m because of the shallow thermocline that is pervasive throughout the eastern Pacific. These naturally high-CO_2 reefs persist near the Ω_{arag} distributional threshold for coral reefs and are thus expected to be the first and most affected by ocean acidification.

Approximately one-third of all the CO_2 released into the atmosphere since the industrial revolution has been absorbed by the oceans (Sabine et al. 2004). This ongoing and accelerating uptake of atmospheric CO_2 is causing a drop in seawater pH at the global scale (Orr et al. 2005), resulting in an acidification of the surface ocean (Caldeira and Wickett 2003). Ocean acidification results in a decrease in seawater $[CO_3^{2-}]$ and, consequently, a decrease in the saturation state (Ω) of carbonate minerals ($\Omega = [CO_3^{2-}][Ca^{2+}]/K'_{sp}$, where K'_{sp} is the solubility product for a carbonate mineral). Acidification is expected to reduce coral reef calcification and increase reef dissolution, and the relative rates of change will likely be a function of the partial pressure of CO_2 (pCO_2) in surface seawater, which is near equilibrium with pCO_2 in the atmosphere (Kleypas et al. 1999; Langdon et al. 2000; Yates and Halley 2006). Despite these concerns, there have been a limited number of studies on the seawater CO_2 system of reef waters at the spatial and temporal scales necessary to resolve the sources of ambient variability.

Two biological processes drive the carbon cycle on coral reefs: organic carbon metabolism (photosynthetic fixation and respiration) and inorganic carbon metabolism (precipitation and dissolution of calcium carbonate [$CaCO_3$]). Total inorganic carbon (TCO_2, or dissolved inorganic carbon) is decreased by 1 mole due to the production of 1 mole of organic matter or $CaCO_3$. On the other hand, TCO_2 is increased by 1 mole due to the dissolution of 1 mole of $CaCO_3$ or oxidation of organic carbon via respiration. The total alkalinity (TA) of seawater does not change significantly because of the organic carbon metabolism that normally occurs on a reef (Gattuso et al. 1999). TA is affected by inorganic carbon metabolism and is decreased by 2 equivalents for every mole of $CaCO_3$ produced and increased by 2 equivalents for every mole of $CaCO_3$ dissolved.

The limited number of field studies on the seawater CO_2 system of coral reef waters is primarily an artifact of the difficulty associated with making these measurements. At least two of the four carbonate parameters (TCO_2, TA, pH, pCO_2) must be measured concurrent with salinity and temperature to calculate the entire CO_2 system of seawater. For the biogeochemical processes that dominate coral reef environments, the best approach is to measure TCO_2 and TA to directly gauge changes on the seawater CO_2 system from photosynthesis, respiration, calcification, and dissolution, which may or may not be coupled. This requires discrete bottle sampling and laboratory analysis as in situ autonomous instrumentation does not yet exist for these parameters.

Early studies that assessed the CO_2 dynamics of coral reef waters were focused on community metabolic performance, whereas more recent investigations have been concerned with whether coral reefs act as sinks or sources of atmospheric CO_2. Short-term field studies have been done primarily in the western Pacific (Suzuki and Kawahata 2003). Two long-term time-series measurements of carbonate chemistry exist: the Hawaiian Ocean time-series and the Bermuda-Atlantic time-series (Gruber et al. 2002; Brix et al. 2004), but these measurements are taken in oceanic waters at a considerable distance from coral reefs. Therefore, there is a

* Corresponding Author: Derek.Manzello@noaa.gov

Present address: Cooperative Institute of Marine and Atmospheric Sciences, Rosenstiel School, University of Miami, Miami, Florida

need for long-term sampling (i.e., multiple years) of the carbonate system from coral reef waters to establish baseline conditions by which to gauge the anticipated future change from ocean acidification.

Surface waters in many parts of the eastern tropical Pacific (ETP) have lower pH, lower Ω, and higher pCO_2 values relative to the rest of the tropics because CO_2-enriched deep waters are upwelled to the surface layers along the shallow thermocline (Takahashi et al. 1997; Manzello et al. 2008). The intensity of this upwelling varies regionally and strongly influences reef development across the ETP (reviewed by Cortés 1997). This unique oceanography of the ETP makes it an exemplary natural laboratory to study the effects of high-CO_2 conditions on coral reef ecosystem processes and response to disturbance (Manzello 2009).

Seawater CO_2 system dynamics were assessed from eastern Pacific reef sites in Panamá over 5 consecutive years (2003–2008) and twice in the Galápagos Islands (2003 and 2009). Sampling in Panamá was designed to capture the ambient variability of the seawater CO_2 system due to diurnal, seasonal, and tidal cycles, whereas data from Galápagos are limited to daylight hours because of the logistic difficulties associated with working in the remote archipelago. Average CO_2 system data collected during daylight hours were previously presented for Panamá and Galápagos (Manzello et al. 2008). The data presented here confirm the limited data previously presented and illustrate finer-scale trends and processes with additional data from 2008 and 2009 for Panamá and Galápagos, respectively.

Methods

ETP oceanography—The Galápagos Islands are situated along the equatorial front where the northwesterly flowing Peru Current mixes with the more tropical water mass from the north (Fiedler and Talley 2006). Sea surface temperatures (SSTs) ranging from 21°C to 26°C and salinities from 33 to 35 are typical for Galápagos coral reef communities (Glynn 2003). The Galápagos Islands experience a cool and dry period from June to November when upwelling is most pronounced, whereas a warm and wet period with dampened upwelling occurs from December to May (Wellington et al. 2001).

Two separate gulfs with differing physical characteristics occur off the coast of Pacific Panamá: the Gulf of Chiriquí and Gulf of Panamá (Fig. 1). Both gulfs experience a wet and a dry season that is controlled by the position of the intertropical convergence zone (Glynn and Maté 1997). During the wet season (end of April to mid-December), oceanographic conditions in the surface layers are similar in both gulfs, with SSTs ranging from 27.5°C to 29°C and salinities from 29.5 to 33.5 (Glynn and Maté 1997; D'Croz and O'Dea 2007). In the dry season (mid-December to the end of April), the surface waters in the Gulf of Panamá are advected offshore by the funneling of the NE tradewinds through the low-lying isthmus of eastern Panamá and upwelling occurs. During upwelling in the Gulf of Panamá, SST decreases to 18–24°C, whereas salinities increase to > 33 (Glynn and Maté 1997). The Gulf of Chiriquí does

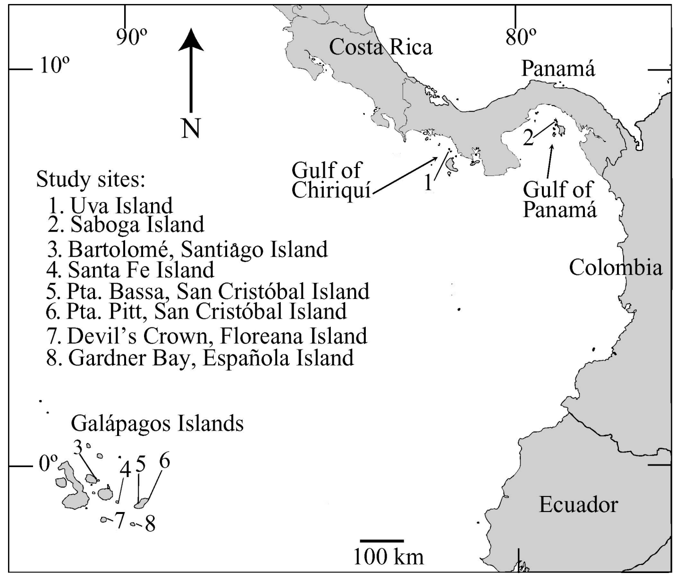

Fig. 1. Map of eastern tropical Pacific (ETP) showing location of study sites in Pacific Panamá and Galápagos Islands.

not experience classical upwelling because the mountainous topography of western, mainland Panamá blocks the NE tradewinds; impeding the advection of surface waters offshore (D'Croz and O'Dea 2007). As a result, oceanographic conditions in the surface layers of the Gulf of Chiriquí are warm year-round with dry season SSTs comparable with those in the wet season and dry season salinities generally stable around 33 (Glynn and Maté 1997; D'Croz and O'Dea 2007). Although traditional upwelling does not occur in the Gulf of Chiriquí, there is measurable shoaling of the already shallow thermocline to shallow depths of 15 m or less in the dry season (Manzello et al. 2008). Recent observations suggest that thermocline shoaling may be more common in the Gulf of Chiriquí than was previously appreciated (D'Croz and O'Dea 2007; Manzello et al. 2008).

Seawater sampling—Seawater samples were collected by hand in 500-mL borosilicate glass bottles with a scuba setup. Seawater was collected from four separate islands totaling five sites in Galápagos on 13–18 May 2003 (sites 3–7 in Fig. 1). This sampling was repeated in 2009 (24 April–01 May) with the addition of another site at Gardner Bay, Española (Fig. 1). Samples were obtained from the Uva Reef in Panamá's Gulf of Chiriquí (Fig. 1) during three wet (14–19 September 2003, 19–22 September 2006, and 30 July–05 August 2007) and three dry seasons (06–14 March 2004, 12–19 March 2005, and 15–22 March 2006). Seawater samples were obtained at the Saboga and Contadora (adjacent to Saboga) Reefs in the Gulf of Panamá (Fig. 1) during one dry (21 March 2005) and two wet seasons (07–09 August 2007 and 04–05 December 2008). Galápagos samples were collected from former reef sites (Manzello 2009) and conditions were generally favorable during all sampling excursions in 2003 and 2009. Samples in Panamá were taken at shallow depths (1–6 m) over the reef to

Table 1. Seawater CO_2 system, depth, temperature, and salinity measured discretely at reef sites in (I) Galápagos, (II) Uva Reef, Gulf of Chiriquí, Pacific Panamá, and (III) Saboga Reef, Gulf of Panamá, Pacific Panamá. Values split by (A) day and (B) night by season. Mean and standard error of the mean (±SEM) reported. Seawater scale (sws) used for pH values.

Site	Season	n	Depth (m)	Temp. (°C)	Salinity	TCO_2 (μmol kg^{-1})	TA (μeq kg^{-1})	pCO_2 (Pa)	pH (sws)	Ω_{arag}
(I) Galápagos										
(A) Day	All	45	4.9(0.96)	25(—)	34.98(0.017)	2072.7(4.90)	2308.5(3.69)	58.5(2.28)	7.91(0.014)	2.74(0.071)
	Cool	24	6.3(1.68)	25(—)	35.07(0.014)	2091.2(5.27)	2299.3(5.39)	66.5(2.67)	7.86(0.015)	2.46(0.072)
	Warm	21	3.4(0.67)	25(—)	34.88(0.014)	2051.5(5.89)	2318.9(3.95)	49.4(2.73)	7.97(0.016)	3.07(0.085)
(II) Uva Reef Gulf of Chiriquí										
(A) Day	All	84	2.6(0.22)	28.9(0.11)	31.97(0.15)	1797.3(9.17)	2093.0(8.61)	41.0(1.41)	8.01(0.010)	3.53(0.062)
	Dry	48	2.5(0.34)	28.8(0.19)	33.10(0.04)	1852.7(8.23)	2148.8(7.23)	45.0(2.18)	7.98(0.015)	3.53(0.092)
	Wet	36	2.6(0.24)	28.9(0.06)	30.47(0.08)	1723.3(8.39)	2018.5(6.30)	35.8(1.04)	8.04(0.012)	3.53(0.080)
(B) Night	All	37	1.2(0.12)	28.5(0.16)	31.82(0.218)	1831.4(9.54)	2092.8(12.48)	46.6(0.98)	7.96(0.008)	3.15(0.056)
	Dry	20	1.1(0.05)	28.4(0.30)	32.97(0.034)	1878.3(6.11)	2157.5(4.37)	46.3(1.40)	7.97(0.011)	3.34(0.065)
	Wet	17	1.5(0.26)	28.7(0.03)	30.46(0.138)	1776.3(6.47)	2016.7(8.12)	46.8(1.41)	7.95(0.011)	2.94(0.062)
(III) Saboga Reef Gulf of Panamá										
(A) Day	All	32	4.0(0.33)	25.7(0.66)	29.7(0.543)	1717.3(30.97)	1969.1(29.73)	36.7(1.31)	8.04(0.012)	2.98(0.056)
	Dry	12	3.7(0.33)	21.0(—)	33.40(0.038)	1932.7(8.02)	2176.6(7.00)	42.8(1.19)	8.01(0.010)	2.79(0.054)
	Wet	20	4.2(0.49)	28.6(0.11)	27.47(0.272)	1588.1(11.72)	1844.5(10.69)	33.0(1.45)	8.05(0.016)	3.09(0.074)
(B) Night	Wet	4	1.0(—)	27.5(—)	26.89(0.015)	1614.1(1.83)	1829.5(2.14)	39.2(0.88)	7.99(0.008)	2.64(0.043)

capture variability due to time of day (i.e., reef metabolism) and tidal state when conditions were calm with low wind speeds. Wind speeds are generally low in the Gulf of Chiriquí and conditions were usually calm on the Uva Reef as it is located in a protected embayment of Uva Island. Although the Gulf of Panamá experiences greater wind speeds in the dry season relative to the Gulf of Chiriquí, conditions were calm during all collections. Tidal amplitude in the Gulf of Chiriquí and Gulf of Panamá is 3–5 and 3–6 m, respectively, with the greatest tides occurring in the dry season (Glynn and Maté 1997). Tidal amplitude in Galápagos is on the order of 3 m, but is less important given the less restricted nature of reef sites there.

In the Gulf of Chiriquí, samples were also taken from a "deep" location (15 m) on the Uva Reef and offshore in the surface open ocean at a distance of at least 1 km away from any shoreline. Deep samples were obtained in March 2006, September 2006, and August 2007, whereas offshore samples were taken in March 2005 and August 2007. All seawater samples were immediately preserved with 200 μL of saturated $HgCl_2$ solution. Seawater temperature at the time of sampling for the Panamá sites was obtained from in situ HOBO (Onset Corp.) thermistors fixed on the reefs that logged temperature every half hour. CO_2 system calculations for Saboga Reef in 2005 use 21°C because in situ data were unavailable and this was considered an appropriate modal SST for upwelling pulses (D'Croz and O'Dea 2007). The CO_2 system for the Galápagos sites was calculated using 25°C to compare both sampling years as in situ data were not available. Satellite-derived advanced very-high resolution radiometer (AVHRR) SSTs were obtained online from the National Oceanographic and Atmospheric Administration (http://coralreefwatch.noaa.gov/satellite/current/sst_series_24reefs.html). AVHRR SSTs have been shown to be a good proxy for Galápagos sites and were used to compare temperatures across sampling periods (Wellington et al. 2001).

TCO_2 was measured coulometrically, whereas TA was determined using a gran titration sensu Langdon et al. (2000). The accuracy and precision of the TCO_2 and TA measurements were always less than 4 and 2 μmol kg^{-1} and 3 and 2 μequiv. kg^{-1}, respectively, and were verified with certified reference materials distributed by A. Dickson (Scripps Institute of Oceanography). Duplicate samples were taken (n = 25 pairs) and paired t-tests showed that preservation did not differ between duplicate samples as values for TCO_2 and TA of duplicates normalized to salinity were no different. Measurement of TA and TCO_2 allowed the calculation of seawater pCO_2, pH, and Ω_{arag}. The carbonate parameters (pCO_2, pH, and Ω_{arag}) were calculated with the CO2SYS computer program (Lewis and Wallace 1998) using the dissociation constants of Mehrbach et al. (1973) for carbonic acid as refit by Dickson and

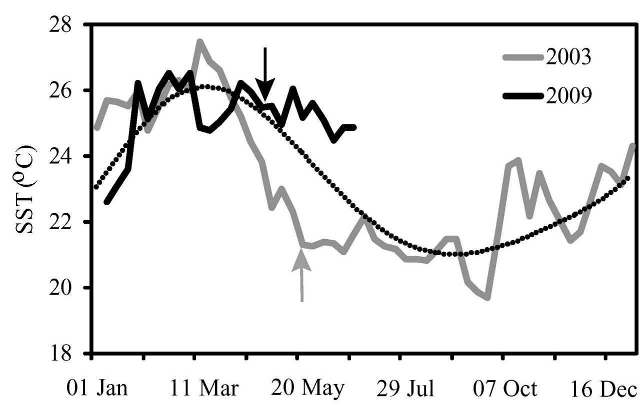

Fig. 2. Sea surface temperatures (SSTs) for Galápagos in 2003 and 2009 relative to average conditions from 2001–2008. Timing of sampling indicated by black and gray arrows for 2009 and 2003, respectively.

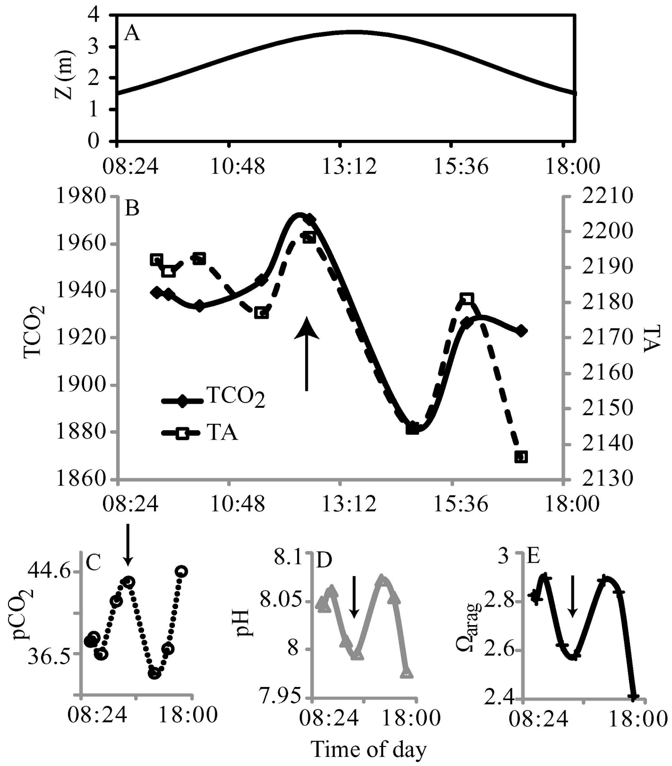

Fig. 3. (A) Tidal height, (B) TCO_2, TA, (C) pCO_2, (D) pH, and (E) Ω_{arag} coincident with upwelling of subthermocline water advected by high tide onto the Saboga Reef, Gulf of Panamá, 21 March 2005. Arrows on plot indicate upwelled water pulse.

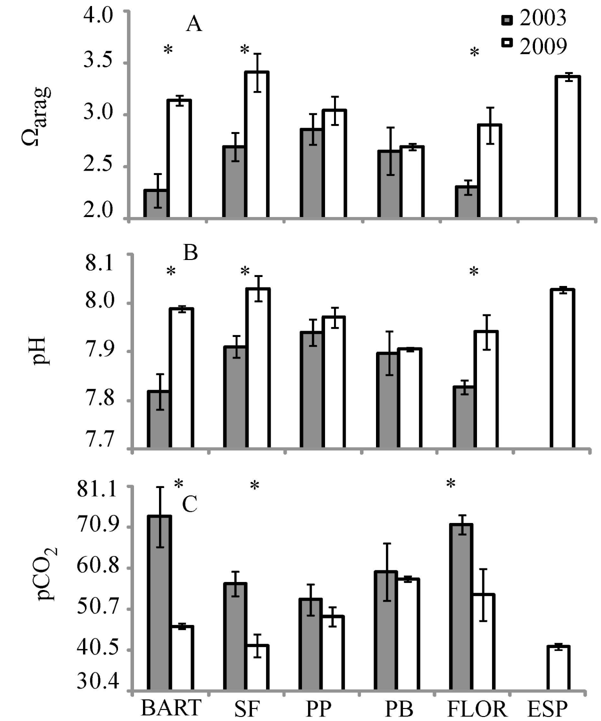

Fig. 4. (A) Ω_{arag}, (B) pH, and (C) pCO_2 measured at Galápagos coral reef sites in 2003 and 2009. BART, Bartolomé; SF, Santa Fe; PP, Punta Pitt; PB, Punta Bassa; FLOR, Floreana; ESP, Española.

Millero (1987), and Dickson (1990) for boric acid. Aragonite saturation (Ω_{arag}) was calculated according to Mucci (1983). Calculated values of pCO_2 were converted from microatmospheres to Pascals by multiplying microatmospheres by a factor of 0.101325.

The nonparametric Mann–Whitney *U*-test was used for statistical comparisons between two groupings (i.e., site, season, day vs. night, tidal state), whereas the Kruskal–Wallis one-way analysis of variance (nonparametric) was used when more than two groups were compared. An alpha level of 0.05 was used for significance in all statistical tests. For the Panamá sites, data were compared across temporal (day vs. night, tidal state, dry vs. wet season) and spatial gradients (reef, deep, offshore). These data were split into a high- or low-tide category on the basis of their proximity to the high and low tide on a given day, and day vs. night values were split on the basis of local sunrise and sunset, which generally occurs at 06:00 h and 18:00 h local time. Last, data were compared between and within individual sampling periods when possible.

Results

Between-site differences: ETP—Galápagos salinity, TCO_2, TA, and pCO_2 were significantly greater, whereas pH and Ω_{arag} were significantly lower when pooled values were compared with the Panamá sites (Mann–Whitney *U*-tests, $p < 0.05$, Table 1). Sampling in the Galápagos in 2003 and 2009 occurred coincident with SSTs near the climatological minimum and maximum, respectively (Fig. 2). As a result, an approximation of the full-season cycle of the seawater CO_2 system was inferred from these results. The highest pCO_2 and lowest Ω_{arag} values occur during the cool part of the climatological cycle when upwelling is most pronounced. Ω_{arag} values from the Galápagos in 2003 were significantly lower than all other ETP sites ($p < 0.01$). Values of pCO_2 are still high in Galápagos during the warm part of the seasonal cycle, but Ω_{arag} values are similar to what is observed at the Saboga Reef in the Gulf of Panamá during the wet season (Table 1). Galápagos mean Ω_{arag} values during the warm period in 2009 (3.07) were no different from the wet season Ω_{arag} values at the Saboga Reef (3.09). Upwelling pulses can significantly lower Ω_{arag} and raise pCO_2 at the Saboga Reef during the dry season (Fig. 3), but this upwelling occurs in pulses and is less chronic than that in Galápagos. As a result, values of pCO_2 and Ω_{arag} in the Gulf of Panamá remain lower and higher, respectively, than what is observed in the Galápagos (Table 1).

Between- and within-site differences: Galápagos—Mean pCO_2 was > 50.7 Pa for all Galápagos sites in 2003, but between 40.5 and 60.8 Pa during the warmer conditions of 2009 (Fig. 4). Mean SST during the time of sampling in 2003 (21.2°C) was 4°C cooler than it was in 2009 (25.2°C, Fig. 2). Mean Ω_{arag} values for all sites in 2003 were very low (2.27–2.86), but higher in 2009 (2.69–3.41, Fig. 4). Significant differences in TCO_2, pCO_2, pH, salinity, and Ω_{arag} were observed when the 2003 and 2009 data were

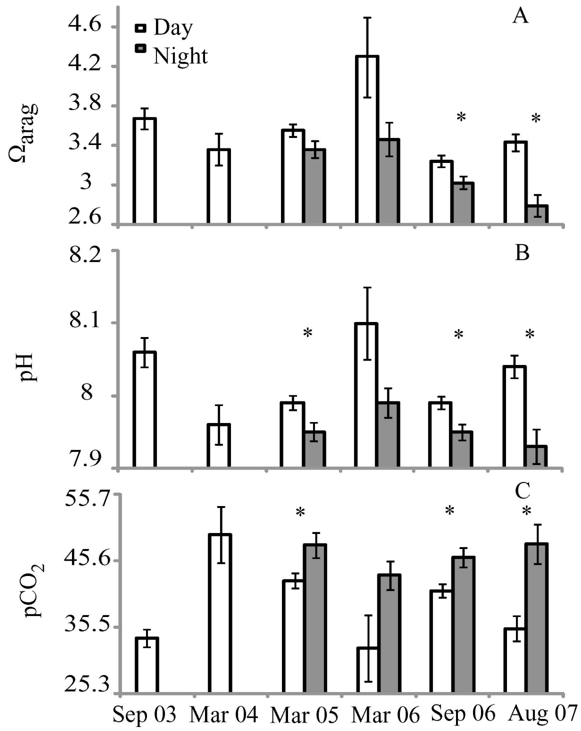

Fig. 5. Day vs. night values for (A) Ω_{arag}, (B) pH, and (C) pCO_2 measured at the Uva Reef, Gulf of Chiriquí, Panamá. Statistically significant differences indicated with a star. The March 2006 values are from a small sample size ($n = 4$) with mean ($\pm$ SEM) $pCO_2 = 32.3$ (5.07), $\Omega_{arag} = 4.30$ (0.41), and pH = 8.10 (0.050) because two of the samples were taken at < 1 m over the reef flat during a very low tide at midday (*see* Fig. 7A). Significance of day vs. night difference for three parameters in March 2006 and Ω_{arag} in March 2005 was $0.5 < p < 0.1$.

compared for the Bartolomé, Santa Fe, and Floreana sites ($p < 0.05$, Fig. 4), but TA was no different. The San Cristóbal sites (Punta Bassa and Punta Pitt) were no different in 2003 and 2009. Unlike the other islands in 2009, localized upwelling was occurring at San Cristóbal during sampling, which likely explains why the carbonate system data were no different from 2003.

Between- and within-site differences: Panamá—Upwelling in the Gulf of Panamá during the dry season is reflected in the significantly higher salinity, TCO_2, and TA, but significantly lower temperature and Ω_{arag} at the Saboga Reef relative to the Uva Reef in the Gulf of Chiriquí (Table 1). A pulse of upwelled subthermocline water was advected onto the Saboga Reef in the Gulf of Panamá in March 2005, causing TCO_2, TA, and pCO_2 to increase while pH and Ω_{arag} declined (Fig. 3). Values of pCO_2 and Ω_{arag} within the subthermocline upwelled water were $\sim$ 44.6 Pa and $\leq$ 2.6, respectively. The warmer surface layer had pCO_2 and Ω_{arag} values of $\sim$ 36.5 Pa and $\sim$ 2.9, respectively. The data obtained likely are a result of tidal pumping causing a shoaling of the thermocline as it is located very near the ocean surface in the Gulf of Panamá during the dry season (D'Croz and O'Dea 2007).

Although classical upwelling does not occur in the Gulf of Chiriquí, it was hypothesized that increased shoaling of the shallow thermocline during the dry season would raise TCO_2 and pCO_2 while lowering pH and Ω_{arag}. Indeed, pCO_2 values were significantly higher and pH values significantly lower during the dry season at the Uva Reef ($p < 0.01$, Table 1). The higher variance in temperature during the dry season at the Uva Reef is also indicative of thermocline shoaling (Table 1). However, daytime Ω_{arag} values were identical during both the wet and dry season. This is due to the effect of salinity. In the dry season, although TCO_2 is greater, TA is higher as well. Thus, while pCO_2 increases, Ω_{arag} remains high because of the high

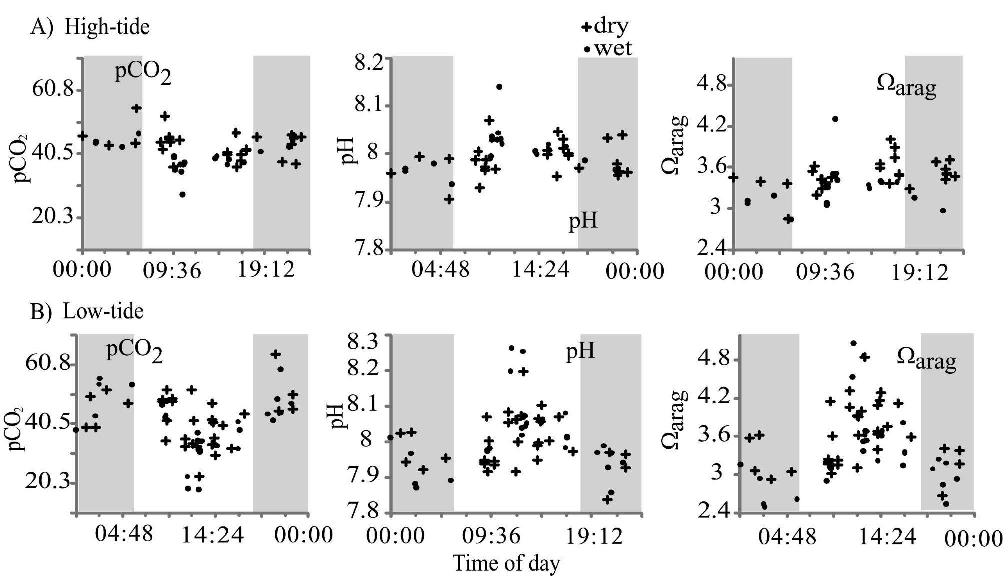

Fig. 6. (A) High- and (B) low-tide values of pCO_2, pH, and Ω_{arag} split by season and plotted against time of day for all data from the Uva Reef. *x*-axis values are time of day and shaded areas show night time period.

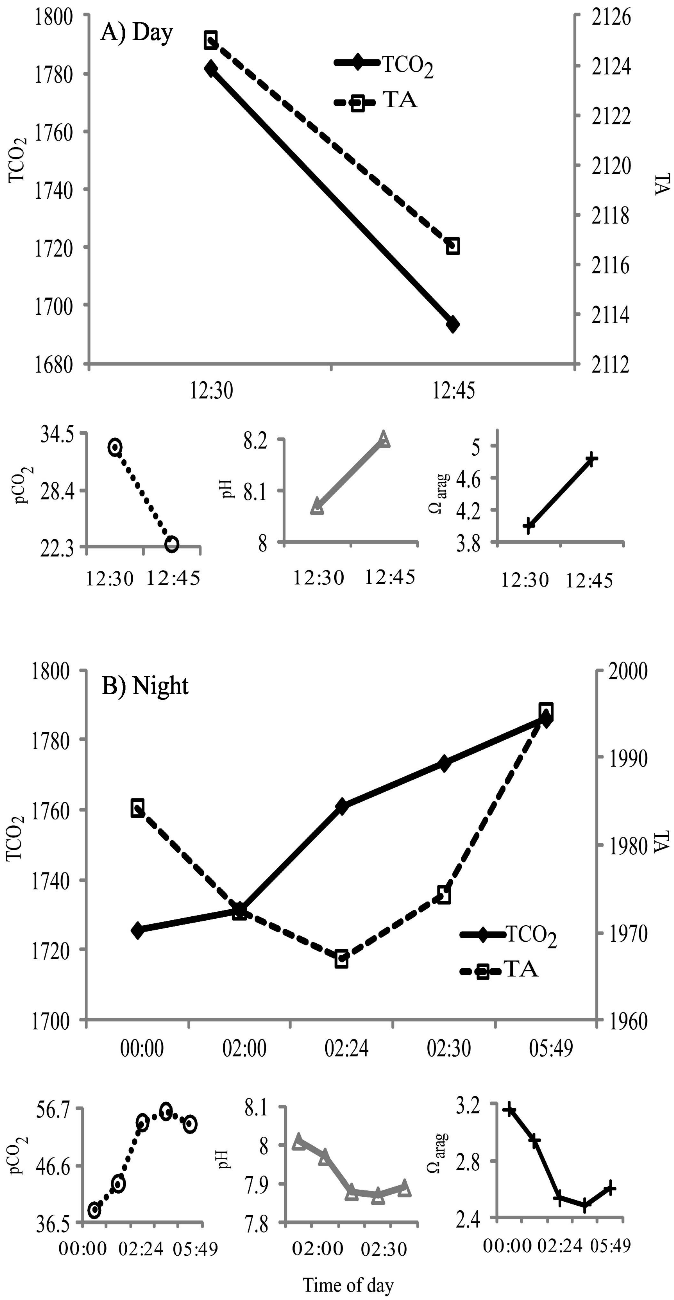

Fig. 7. Effect of slack low tide on seawater CO_2 system at the Uva Reef during the (A) day and (B) night. Slack low tide occurred at 11:59 h and 02:04 h local time on (A) 18 March 2006 and (B) 05 August 2007, respectively. *x*-axis values are time-of-day samples obtained.

values of TA and high values of TCO_2. In the wet season, there is no shoaling of the thermocline and surface salinity is significantly diluted by rainfall and river discharge, resulting in significantly lower TCO_2 and TA values ($p < 0.01$, Table 1). Greater input of freshwater as rainfall and runoff in the Gulf of Panamá during the wet season results in salinity, TCO_2, TA, and Ω_{arag} being significantly depressed relative to the Gulf of Chiriquí ($p < 0.05$, Table 1). The Gulf of Panamá receives less rainfall than the Gulf of Chiriquí, but the more restricted nature of the Gulf of Panamá appears to limit mixing with oceanic seawater leading to the greater dilution (D'Croz and O'Dea 2007).

The seawater CO_2 system of the Uva Reef was significantly different between day and night ($p < 0.05$, Table 1) because of diurnal metabolism. When photosynthesis and calcification co-occur during the day, TCO_2 is depleted faster than TA under most circumstances (Suzuki and Kawahata 2003), which causes a decline in pCO_2 but an increase in pH and Ω_{arag}. When calcification and respiration occur at night in the absence of photosynthesis, values of pCO_2 increase, while pH and Ω_{arag} decrease. Indeed, TCO_2 and pCO_2 were always greater, whereas pH and Ω_{arag} were always lower at night relative to the day (Fig. 5, Table 1). This same trend was observed in the limited data from the Gulf of Panamá (Table 1).

The effect of reef metabolism on the seawater CO_2 system was magnified at low tide (Fig. 6). To illustrate this further, the effects of the coincidence of a low tide with midday and midnight on the seawater CO_2 system at the Uva Reef are shown in Fig. 7. The mean values of the CO_2 system parameters organized within tidal state by time of day and season for the Uva Reef are presented in Table 2.

Spatial variability deep and offshore of the Uva Reef—The greatest spatial differences in the seawater CO_2 system around the Uva Reef occurred with depth as the offshore samples were generally comparable with those taken on the reef, albeit the reef samples had a much higher variance relative to those taken offshore (Tables 1A, 3). Values offshore of the Uva Reef in the Gulf of Chiriquí were more variable than those at depth. Pooled values of TCO_2, TA, and pCO_2 were significantly greater, whereas pH and Ω_{arag} were significantly lower at depth relative to the reef and offshore samples ($p < 0.01$, Tables 1A, 3A). Deep waters on the Uva Reef are similar during the day to the seawater overlying the reef at night. The high pCO_2 and low Ω_{arag} at only 15 m (Table 3) are indicative of just how shallow the thermocline is throughout the ETP, even in nonupwelling locations. However, significant differences between the reef and deep samples were not always observed within each individual sampling period (e.g., wet season pH, pCO_2, and Ω_{arag} values in September 2006) even though TCO_2, TA, temperature, and salinity were always significantly different ($p < 0.05$). This likely reflects the deeper thermocline during the wet season (D'Croz and O'Dea 2007).

Discussion

To accurately characterize the potential threat faced by a particular reef from accelerating ocean acidification, the ambient diurnal variability must be understood alongside the seasonal cycle, or climatology of the seawater CO_2 system. Eastern Pacific reefs are unique in that they are routinely exposed to upwelled waters with naturally high CO_2. Reefs in Pacific Panamá experience a large tidal range of up to 6 m and this large tidal amplitude significantly interacts with diurnal reef metabolism. This study reconfirms that Galápagos coral reef communities are naturally exposed to the highest ambient pCO_2 and lowest Ω_{arag} documented for any coral reef environment to date

Table 2. Seawater CO_2 system, depth, temperature, and salinity measured discretely at the Uva Reef, Gulf of Chiriquí, Pacific Panamá during (A) day and (B) night grouped by tidal state. Mean (±SEM) reported. Seawater scale (sws) used for pH values.

Time	Season	Tidal state	*n*	Depth (m)	Temp. (°C)	Salinity	TCO_2 (μmol kg^{-1})	TA (μeq kg^{-1})	pCO_2 (Pa)	pH (sws)	Ω_{arag}
(A) Day											
	All	High	37	3.7(0.39)	28.4(0.21)	32.18(0.228)	1828.4(13.06)	2112.7(13.80)	43.5(2.15)	7.99(0.014)	3.40(0.086)
		Low	47	1.7(0.15)	29.2(0.09)	31.82(0.196)	1772.7(11.67)	2077.4(10.49)	39.1(1.85)	8.02(0.014)	3.63(0.086)
	Dry	High	22	3.7(0.62)	28.2(0.35)	33.25(0.070)	1886.0(9.10)	2169.2(10.88)	47.7(3.29)	7.97(0.022)	3.38(0.138)
		Low	26	1.6(0.25)	29.3(0.13)	32.98(0.040)	1824.5(10.36)	2131.6(8.45)	42.6(2.89)	8.00(0.020)	3.65(0.121)
	Wet	High	15	3.7(0.37)	28.7(0.05)	30.60(0.146)	1744.0(6.58)	2030.0(11.17)	37.3(0.78)	8.03(0.009)	3.43(0.073)
		Low	21	1.9(0.15)	29.1(0.09)	30.38(0.088)	1708.6(12.78)	2010.3(6.98)	34.8(1.68)	8.06(0.019)	3.61(0.124)
(B) Night											
	All	High	17	1.0(0.0)	28.7(0.28)	32.15(0.292)	1837.2(13.47)	2113.3(16.97)	44.5(0.94)	7.97(0.008)	3.31(0.066)
		Low	20	1.5(0.22)	28.4(0.19)	31.53(0.310)	1826.5(13.66)	2075.6(17.49)	48.3(1.54)	7.94(0.012)	3.02(0.075)
	Dry	High	11	1.0(0.0)	28.7(0.44)	33.01(0.046)	1872.0(8.92)	2160.8(4.89)	44.7(1.41)	7.98(0.011)	3.45(0.069)
		Low	9	1.1(0.11)	28.0(0.39)	32.92(0.049)	1886.0(7.86)	2153.6(7.80)	48.3(2.53)	7.95(0.019)	3.20(0.106)
	Wet	High	6	1.0(0.0)	28.6(0.05)	30.59(0.088)	1773.4(9.80)	2025.6(12.65)	44.0(0.81)	7.97(0.007)	3.06(0.054)
		Low	11	1.7(0.38)	28.7(0.03)	30.39(0.209)	1777.8(8.76)	2011.8(10.60)	48.4(2.00)	7.93(0.016)	2.87(0.086)

(Table 4). The seawater chemistry during upwelling is similar to what is expected for the entire tropical surface ocean with a tripling of atmospheric CO_2 (Manzello 2009). Not surprisingly, reef development is scant in this highly marginal environment and ephemeral on geological timescales (Manzello 2009). Binding calcium carbonate cements do not precipitate above trace levels in this low-Ω_{arag} environment and rates of bioerosion are the highest measured for any reef in the world (Manzello et al. 2008). The Santa Fe site had the highest abundances of inorganic aragonite cement of all Galápagos sites in that study, and, not unexpectedly, this site had the highest Ω_{arag} for all sites in 2009 (Fig. 4). This suggests that the trace amounts of cement observed in Galápagos samples likely precipitate during the warm period of the seasonal cycle when Ω_{arag} is highest.

It is expected that increased stratification and surface warming that accompany strong El Niño–Southern Oscillation (ENSO) events in Galápagos raise Ω_{arag} because of the combined effects of CO_2 off-gassing to and equilibration with the atmosphere in addition to the thermodynamic increase in Ω_{arag} that occurs at higher temperatures (Millero 2007). As a result, coral reef communities in Galápagos may actually experience an increase in calcification due to the hypothesized increase in Ω_{arag} during mild to moderate ENSO events. This would only occur up to the thermal tolerance of the reef-building corals, which is equivalent to sustained SSTs in excess of the climatological monthly maximum by 1–2°C for a month or more (Glynn 1993). When thermal anomalies of this magnitude or greater occur, mass coral bleaching, which is the loss of the endosymbiotic algae or their pigments within the coral tissues, results. Severe ENSO events like that observed in 1982–1983 and 1997–1998 are associated with thermal anomalies of 3–5°C for several months (Wellington et al. 2001). The 1982–1983 ENSO caused a mass mortality of up to 99% of reef corals in Galápagos (Glynn 1990). Thus, the potential increase in calcification that may occur during mild to moderate ENSO events may be insignificant relative to the large-scale mortality that can occur during severe ENSO events. Furthermore, it is possible that any possible benefits experienced from ENSO-induced increases in Ω_{arag} may be erased during the La Niña phase where upwelling intensifies and SSTs cool drastically. It is expected that during La Niña periods Ω_{arag} values would be lower than those observed during the cool sampling period in 2003.

Table 3. Seawater CO_2 system, depth, temperature, and salinity measured adjacent to the Uva Reef, Gulf of Chiriquí at (A) deep (15 m depth) and (B) offshore sites pooled and split by season. Mean (±SEM) reported. Note that the term "deep" is relative to the shallow reef samples (<6 m). Seawater scale (sws) used for pH values.

Site	Season	*n*	Depth (m)	Temp. (°C)	Salinity	TCO_2 (μmol kg^{-1})	TA (μeq kg^{-1})	pCO_2 (Pa)	pH (sws)	Ω_{arag}
(A) Deep										
	All	13	17.0(0.43)	25.9(0.77)	33.18(0.268)	1931.0(17.98)	2187.5(15.36)	48.6(1.67)	7.96(0.012)	3.05(0.093)
	Dry	8	16.7(0.40)	25.0(1.14)	33.81(0.087)	1967.4(11.34)	2225.9(4.29)	48.6(1.50)	7.96(0.012)	3.06(0.131)
	Wet	5	17.6(0.93)	27.4(0.30)	32.18(0.359)	1872.6(27.89)	2126.0(15.95)	48.6(3.95)	7.95(0.026)	3.05(0.140)
(B) Offshore										
	All	8	1.0(0.0)	29.0(0.13)	31.72(0.450)	1805.5(23.36)	2086.3(28.16)	42.4(1.76)	7.99(0.015)	3.37(0.115)
	Dry	4	1.0(0.0)	29.3(0.11)	32.88(0.019)	1863.0(2.39)	2160.7(1.45)	43.3(0.47)	7.99(0.004)	3.56(0.028)
	Wet	4	1.0(0.0)	28.7(0.08)	30.56(0.230)	1748.0(18.28)	2012.0(3.21)	41.4(3.71)	7.99(0.031)	3.18(0.191)

Table 4. CO_2 system parameters of eastern Pacific coral reef sites compared with values for other Pacific reef sites. Galápagos values normalized to 25°C for comparison because of lack of in situ temperature data. Seawater scale (sws) used for pH values.

Location, time of day	pCO_2 (Pa) mean (±SEM)	Range	pH_{sws} mean (±SEM)	Range	Ω_{arag} mean (±SEM)	Range	Reference
Eastern Pacific							
Galápagos, day, cool	66.5(2.67)	45.6–108.5	7.86(0.015)	7.65–7.99	2.46(0.072)	1.54–3.14	This study
Galápagos, day, warm	49.4(2.73)	37.3–98.7	7.97(0.016)	7.70–8.07	3.07(0.085)	1.74–3.70	This study
Panamá							
Gulf of Panamá, day, dry season	42.8(1.19)	34.9–48.7	8.01(0.010)	7.95–8.08	2.79(0.054)	2.47–3.15	This study
Gulf of Panamá, day, wet season	33.0(1.45)	21.0–43.7	8.05(0.016)	7.95–8.23	3.09(0.074)	2.65–4.18	This study
Gulf of Panamá, night, wet season	39.2(0.88)	37.7–41.7	7.99(0.008)	7.96–8.00	2.64(0.043)	2.52–2.72	This study
Gulf of Chiriquí, day, dry season	45.0(2.18)	22.6–104.4	7.98(0.015)	7.63–8.20	3.53(0.092)	1.60–5.05	This study
Gulf of Chiriquí, day, wet season	35.8(1.04)	18.2–47.2	8.04(0.012)	7.94–8.26	3.53(0.080)	2.90–5.07	This study
Gulf of Chiriquí, night, dry season	46.3(1.40)	37.6–64.4	7.97(0.011)	7.84–8.04	3.34(0.065)	2.67–3.71	This study
Gulf of Chiriquí, night, wet season	46.8(1.41)	38.7–59.3	7.95(0.011)	7.86–8.01	2.94(0.062)	2.49–3.24	This study
Central and western Pacific							
Majuro Atoll, day	32.6(0.58)	25.8–38.4	8.11(0.006)	8.04–8.18	4.04(0.044)	3.61–4.59	Suzuki et al. 1997*
Moorea, day and night	42.4(2.23)	28.2–55.3	8.04(0.002)	7.90–8.19	4.14(–)	2.96–5.65	Gattuso et al. 1997†
Palau	42.0(1.94)	35.2–46.8	8.00(0.016)	7.96–8.06	3.61(0.082)	3.48–3.92	Watanabe et al. 2006‡
GBR Lagoon, day and night	36.6(0.22)	33.7–39.6	8.06(0.002)	8.03–8.09	3.89(0.019)	3.72–4.14	Suzuki et al. 2001§
Hawai'i, day	38.4(2.20)	17.2–75.4	8.06(0.019)	7.80–8.31	3.72(0.126)	2.2–5.4	Yates and Halley 2006‖
Hawai'i, night	53.0(2.57)	30.8–94.7	7.94(0.017)	7.70–8.12	2.89(0.093)	1.7–3.9	Yates and Halley 2006‖
Japan							
Okinawa, day	18.3(1.09)	7.4–35.9	8.36(0.018)	8.12–8.58	5.43(0.080)	4.09–6.36	Ohde and van Woesik 1999¶
Okinawa, night	76.1(4.08)	43.2–108.7	7.86(0.022)	7.70–8.05	2.65(0.115)	1.83–3.67	Ohde and van Woesik 1999¶
Shiraho Reef, day	37.6(1.38)	14.6–67.0	8.03(0.012)	7.80–8.26	3.89(0.078)	2.32–5.53	Nakamura and Nakamori 2009#
Shiraho Reef, night	52.8(1.52)	34.1–93.4	7.92(0.009)	7.71–8.06	3.22(0.057)	2.15–4.17	Nakamura and Nakamori 2009#

* Values calculated at 25°C from salinity-normalized values of TCO_2 and TA taken from the lagoon ($n = 20$) and reef flat ($n = 2$) over 3 d in September 1994.
† Mean (±SEM), min., and max. values of pCO_2, TA, and pH_{NBS} taken over 2 d in July 1992. Ω_{arag} and pH_{sws} represent average calculated from following pairs: pCO_2, TA; pH, TA; pH, pCO_2.
‡ pCO_2, pH, and Ω_{arag} calculated from mean values of TCO_2, TA, temperature, salinity, and [PO_4^{3-}] taken during five sampling excursions from 1998 to 2002.
§ Values from salinity-normalized values of TCO_2 and TA ($n = 33$) from GBR lagoon in May 1996.
‖ Data broken into day and night categories such that values that occurred near or up to 1 h after sunrise and sunset (e.g., 07:00 h and 17:00 h) were categorized as night and day, respectively, because of lag in carbonate chemistry changes. Data obtained October 2000, July 2001, and June 2003. Values of pH reported on free H^+ scale and were converted to seawater scale. Values reported represent samples taken from ambient seawater, not from within incubation chamber.
¶ Authors provided pCO_2 and Ω_{arag} values. Values of pH at 25°C were given, but scale not indicated. Given high values, it was assumed they were National Bureau of Standards (NBS) scale and converted to the seawater scale accordingly. Data obtained August 1993, June 1994, July 1994, August 1994, and October 1995.
# These values are averaged over data from bare rubble bottom (July 2006), three coral communities (August 2004, June 2006, July 2006, June 2007, July 2007, August 2007), and an algal reef flat (August 2007) incubated within a chamber for 2.75 h. Authors provided fCO_2 and pH_T, which were converted to pCO_2 and pH_{sws}. Values of Ω_{arag} given.

The high variance in the seawater CO_2 system at the Uva Reef was explained by the interaction of diurnal reef metabolism with physical forcing from meteorological (seasonal rainfall) and oceanographic (tides, thermocline shoaling) processes. It is important to understand that the Uva Reef is very small in area (2.5 ha) and does not possess a restricted lagoon even during extreme spring tides when the reef flat can become exposed. This makes it very different compared with the majority of reefs where seawater CO_2 system variability has been studied. Given the routine flushing by semidiurnal tides with large amplitude (≥ 3 m), the residence time of water over the reef, albeit not quantified, is likely short in duration (< 1/2 d). The changes due to reef metabolism occur rapidly (< 6 h) and are erased shortly thereafter by tidal flushing and mixing with oceanic seawater.

The Uva Reef's metabolism had more effect on the seawater CO_2 system at low tide because of the smaller volume of water over the reef (Fig. 6). Bates et al. (2001) hypothesized that a dampening of the CO_2 variability with increasing depth likely explained less variability in Bermuda (6 m) relative to a reef in Okinawa in very shallow water (0.18 m: Ohde and van Woesik 1999). This hypothesis is supported here as there was considerably less influence from reef metabolism at high tide on the Uva Reef when water depth is 4–5 m vs. low tide when the depth of water over the reef is < 1 m (Fig. 6). Increased light attenuation from the greater volume of seawater overlying the reef at high tide may contribute to the dampened metabolic signal by reducing the amount of light available for photosynthesis and light-enhanced calcification. The effect of shallow depths can be seen in the large range in values from this study and that in Okinawa by Ohde and van Woesik (1999, Table 4). The lowest values of pCO_2 and highest values of pH and Ω_{arag} occurred around solar noon at low tide (Fig. 6B).

It has been recently debated if coral reefs are sources or sinks of CO_2 to the atmosphere (Gattuso et al. 1999). Coral-dominated reefs generally appear to be sources of CO_2, whereas algal-dominated reefs may be sinks, albeit temporally on geologic timescales (reviewed by Gattuso et al. 1999). The entire eastern Pacific basin is a major source of CO_2 to the atmosphere from the oceans (Takahashi et al. 1997). Even nonupwelling areas like the Gulf of Chiriquí are sources of CO_2 as shown by the data presented here. By considering what the CO_2 flux would be in the Gulf of Chiriquí with and without the Uva Reef, it was found that at night the reef always acts as a source of CO_2 regardless of tide and season. During the day, this reef acts as a sink in the wet season regardless of tide, but in the dry season it acts as a sink only at low tide. When values are integrated over both seasons and a full 24-h period, the Uva Reef acts as a source of CO_2, which agrees with the findings of Gattuso et al. (1999). Galápagos waters are always a source of CO_2 to the atmosphere, except possibly during strong ENSO events when surface waters warm and stratify, and upwelling stops (Glynn 2003). Limited data (not shown) indicate that Galápagos communities have little if any effect on the seawater CO_2 system. It isn't clear if reefs in the Gulf of Panamá act as sources or sinks because offshore data were not collected, but it is likely that these communities behave in a similar manner as those in the Gulf of Chiriquí because reef community structure is very similar in both Pacific Panamanian gulfs (Glynn and Maté 1997).

It has been hypothesized that reefs in the Galápagos provide a real-world example of the combined thermal and chemical ramifications of climate change on coral reef structure, function, and resilience to disturbance (Manzello 2009). These reefs experience chronically high pCO_2 (low-Ω_{arag}) and are exposed to routine warming disturbances caused by ENSO. These reefs persist near the lower limit of the Ω_{arag} distributional threshold for coral reefs (Kleypas et al. 1999) and it is expected that those environments with the lowest natural Ω_{arag} values will be the first and most affected by ocean acidification (Orr et al. 2005). Galápagos coral communities, with the lowest ambient Ω_{arag} and highest pCO_2 of any coral reef yet studied, are thus ocean acidification hot spots.

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