

Impacts of ocean acidification in naturally variable coral reef flat ecosystems

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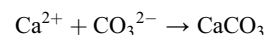
[1] Ocean acidification leads to changes in marine carbonate chemistry that are predicted to cause a decline in future coral reef calcification. Several laboratory and mesocosm experiments have described calcification responses of species and communities to increasing CO₂. The few in situ studies on natural coral reefs that have been carried out to date have shown a direct relationship between aragonite saturation state (Ω_{arag}) and net community calcification (G_{net}). However, these studies have been performed over a limited range of Ω_{arag} values, where extrapolation outside the observational range is required to predict future changes in coral reef calcification. We measured extreme diurnal variability in carbonate chemistry within a reef flat in the southern Great Barrier Reef, Australia. Ω_{arag} varied between 1.1 and 6.5, thus exceeding the magnitude of change expected this century in open ocean subtropical/tropical waters. The observed variability comes about through biological activity on the reef, where changes to the carbonate chemistry are enhanced at low tide when reef flat waters are isolated from open ocean water. We define a relationship between net community calcification and Ω_{arag} , using our in situ measurements. We find net community calcification to be linearly related to Ω_{arag} , while temperature and nutrients had no significant effect on G_{net} . Using our relationship between G_{net} and Ω_{arag} , we predict that net community calcification will decline by 55% of its preindustrial value by the end of the century. It is not known at this stage whether exposure to large variability in carbonate chemistry will make reef flat organisms more or less vulnerable to the non-calcifying physiological effects of increasing ocean CO₂ and future laboratory studies will need to incorporate this natural variability to address this question.

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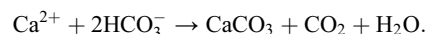
1. Introduction

[2] The ocean has absorbed approximately 50% of anthropogenic carbon dioxide (CO₂) that has been released to the atmosphere from fossil fuel burning and cement production since the beginning of the industrial revolution [Sabine *et al.*, 2004]. This has led to a decline in oceanic pH of 0.1 units, equivalent to ~30% increase in hydrogen ion concentration ([H⁺]). The surface ocean pH is predicted to decline by a further 0.3–0.5 units this century [Caldeira and Wickett, 2003, 2005; McNeil and Matear, 2007]. The increase in [H⁺] causes a decline in carbonate ion concentration ([CO₃²⁻]) and in the saturation state of calcium carbonate (CaCO₃), which may reduce the ability of marine calcifiers to produce CaCO₃ [Orr *et al.*, 2005].

[3] Coral reefs are composed of large amounts of CaCO₃, produced biogenically through the process of calcification [Kleypas and Yates, 2009]



or



[4] Corals produce the mineral form of CaCO₃ as aragonite, and laboratory and mesocosm studies have shown that the calcification rate of coral reef communities and a number of calcifying species is directly related to the aragonite saturation state (Ω_{arag}) or [CO₃²⁻] [e.g., Gattuso *et al.*, 1998b; Langdon and Atkinson, 2005; Langdon *et al.*, 2000; Leclercq *et al.*, 2000, 2002; Marubini *et al.*, 2001]. However, a recent study has also suggested that it is a change in bicarbonate ion concentration ([HCO₃⁻]), that occurs with changing carbonate chemistry, that is the major factor controlling coral calcification [Jury *et al.*, 2010].

[5] Coral calcification may also be strongly influenced by other environmental parameters. Corals have been found to have an optimal temperature, above and below which calcification declines [Clausen and Roth, 1975; Marshall

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and Clode, 2004]. Coral calcification has been shown to increase with increasing irradiance levels, up to a point at which light becomes saturating [Barnes, 1982; Marubini et al., 2001]. Laboratory and mesocosm experiments have also shown decreases in calcification rates in response to enriched nutrient levels [Langdon and Atkinson, 2005, and references therein]. Aside from environmental parameters, calcification is also controlled through active regulation of internal pH at the site of calcification, where this process is dependent on the energetic status of the corals [Cohen and Holcomb, 2009; Venn et al., 2011].

[6] Global-scale predictions of changes to coral reef calcification have previously been made based on the laboratory response of coral species to changes in carbonate chemistry [Kleypas et al., 1999]. The use of single species data to predict ecosystem responses has limitations, as there are inter-species differences in the calcification response to changing environmental conditions. More recent global predictions have been based on in situ relationships between community calcification and carbonate chemistry [Silverman et al., 2009]. Coral reef carbonate chemistry varies at both seasonal [Bates, 2002; Bates et al., 2010; Drupp et al., 2011] and diurnal timescales [Bates et al., 2001; Drupp et al., 2011; Kayanne et al., 1995; Ohde and van Woessik, 1999; Shamberger et al., 2011]. Diurnal variability on shallow coral reef flats can be particularly large (diurnal pH range of 7.8–8.7 for a reef flat in Okinawa [Ohde and van Woessik, 1999]) and the in situ natural variability in carbonate chemistry can be utilized to investigate coral reef community calcification. The few studies that have attempted to relate community calcification to carbonate chemistry in situ for natural coral reefs have found varied responses [Ohde and van Woessik, 1999; Shamberger et al., 2011; Silverman et al., 2007]. More studies investigating natural community responses are required across a range of different reefs, with varying species composition and environmental conditions, to enable more accurate prediction of the effects of ocean acidification on coral reef ecosystems.

[7] In this study we investigate seasonal and diurnal variability in carbonate chemistry at Lady Elliot Island (LEI) reef flat, southern Great Barrier Reef, Australia. The large diurnal variability we observed allowed us to determine how in situ community calcification of a natural coral reef responds to varying carbonate chemistry, providing valuable insight on how the relationships described in laboratory and mesocosm studies may translate to natural coral reefs. After investigating the natural variability of carbonate conditions within the spectrum of conditions found at LEI, we focus on how community coral reef calcification changes under the naturally varying conditions of carbonate chemistry, temperature, nutrients and net community production, in an environment where physical conditions favor the expression of these changes. We then utilize these results to predict possible changes in CaCO_3 production over the next century for a pristine coral reef flat, which will contribute to our understanding of how coral reefs will respond globally to ocean acidification.

2. Methods

2.1. Study Site

[8] LEI (24°07'S, 152°43'E) is the southernmost island of the Great Barrier Reef and is part of the Capricorn-Bunker

group of islands. Like many islands in this region of the Great Barrier Reef, LEI is a coral cay with a surrounding shallow reef flat. The coral cay has an area of 0.54 km² and is located approximately 80 km off the coast of mainland Australia [Chivas et al., 1986] in waters that are not influenced by coastal inputs and are typically oligotrophic [Weeks et al., 2010]. The reef flat surrounding the island has a length of 1.2 km (NE-SW), width of 0.8 km (SE-NW) and an area of 1.2 km² [Kench and Brander, 2006]. There is a reef rim that is elevated above the height of the reef flat, so that at low tide waters on the reef flat are isolated from offshore waters (Figure 1). The reef flat comprises two main lagoons that are separated with eroding cay rock and cement pavement (Figure 1). The prevailing wind direction is from the south-east and the tidal regime is semidiurnal. The tidal range of spring and neap tides are 1.7 and 0.9 m respectively [Jago et al., 2007].

[9] Sampling was conducted at two main sites, one on the reef flat in the southern lagoon and one off the reef edge in the surrounding offshore waters (Figure 1). The water depth at our sampling location on the reef flat varied from approximately 40 to 180 cm. Reef flat residence time was short with most water on the reef flat exchanging with the offshore water each tidal cycle. As yet there are no documented studies of the reef flat coral community at LEI, however, we observed that the southern lagoon had a sand bottom with high (we estimate approximately 40%) coral cover throughout.

2.2. Water Sampling and Analysis

[10] Sampling occurred for a two-week period in each season starting in the austral spring of 2009 and ending in winter 2010 (Table 1). Sampling was conducted daily over each of the sampling periods at the offshore site to determine the properties of the waters surrounding LEI. Higher frequency samples (multihourly) were also taken at a site on the reef flat to determine diurnal variability in reef flat chemistry (Table 2). The first batch of samples, taken in spring 2009 to determine diurnal variability, were collected each hour for 3 consecutive days, similar to previous studies that measured carbonate chemistry diurnal variability [e.g., Kayanne et al., 1995; Yates et al., 2007]. After examining the spring results it was apparent that tide height was an important factor regulating the reef flat carbonate chemistry. On consecutive days, tide times are only ~50 min apart and therefore the range of diurnal variability as influenced by tides cannot be determined with only 3 consecutive days of sampling. For subsequent seasons, sampling on the reef flat occurred over 24 h periods, evenly spaced at 3–4 days of a two-week sampling period, in order to sample through a range of tidal conditions (Table 1). The first sampling trip also revealed rapid changes in reef flat chemistry during low tide, but slow changes at high tide. Therefore sampling on subsequent trips occurred hourly around the low tide, but only every 2–3 h at high tide.

[11] Surface seawater samples were collected for total dissolved inorganic carbon (DIC), total alkalinity (TA) and dissolved phosphate (PO_4^{3-}) and nitrate (NO_3^-) analyses. DIC and TA samples were drawn into 500 mL borosilicate glass bottles and preserved with 200 μL of saturated mercuric chloride (HgCl_2) solution. Nutrient samples were filtered through a 0.45 μm filter and frozen. Samples were then transported and analyzed at the Marine Laboratories at

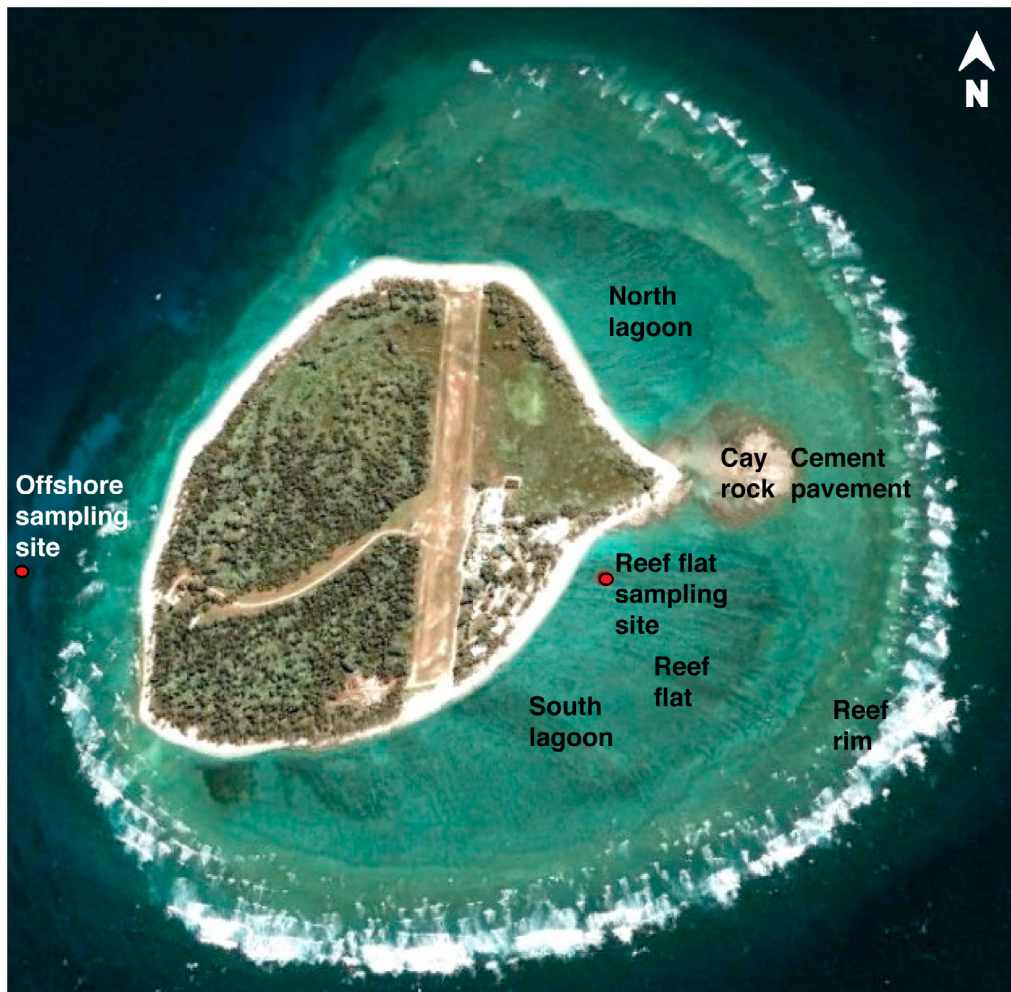


Figure 1. Map of Lady Elliot Island and reef, showing the reef flat sampling site (24.114S, 152.717E) and offshore sampling site (24.114°S, 152.711°E).

CSIRO, Hobart, Australia. At the time of sampling, in situ salinity and temperature measurements were taken using a conductivity, temperature, depth (CTD) logger (RBR Ltd, model XR-420).

[12] DIC and TA were both analyzed as prescribed by the *Guide to Best Practices for Ocean CO₂ Measurements* [Dickson *et al.*, 2007]. DIC analysis was performed coulometrically using a Single-Operator Multi-Parameter Metabolic Analyzer (SOMMA) and TA using the open cell method of acidimetric titration. Samples were analyzed in batches at the end of each season. The precision of the DIC analyses for each season (spring to winter) based on replicate samples were ± 0.8 (n = 13), ± 1.4 (n = 13), ± 1.8 (n = 12)

and ± 1.2 $\mu\text{mol kg}^{-1}$ (n = 14) respectively. Similarly the precision of the TA analyses for each season were ± 1.9 (n = 13), ± 2.0 (n = 13), ± 2.2 (n = 12) and ± 1.1 $\mu\text{mol kg}^{-1}$ (n = 14). The quality of the measurements was confirmed by analyzing certified reference materials (CRMs; provided by Dr A. Dickson, Scripps Institute of Oceanography) twice daily. The precision of CRM replicates for each season for DIC were ± 0.6 (n = 14), ± 1.3 (n = 11), ± 1.8 (n = 12) and ± 0.8 $\mu\text{mol kg}^{-1}$ (n = 12) and for TA were ± 1.7 (n = 18), ± 1.1 (n = 19), ± 1.4 (n = 20) and ± 0.9 $\mu\text{mol kg}^{-1}$ (n = 13).

Table 1. Sampling Dates

Season	Offshore Sampling	Reef Flat Sampling
Spring 2009	6–19 Nov	7–9 Nov
Summer 2010	30 Jan to 11 Feb	30–31 Jan, 3–4 Feb, 6–7 Feb, 9–10 Feb
Autumn 2010	19 Apr to 1 May	18–19 Apr, 21–22 Apr, 25–26 Apr, 29–30 Apr
Winter 2010	20 Jul to 1 Aug	19–20 Jul, 23–24 Jul, 29–30 Jul

Table 2. Seasonal Range in Reef Flat Properties

Parameter	Season			
	Spring	Summer	Autumn	Winter
Temperature ($^{\circ}\text{C}$)	21.9–25.4	25.0–31.2	23.1–28.7	17.6–25.9
Salinity	32.26–35.51	34.89–35.82	34.77–35.59	34.32–35.81
DIC ($\mu\text{mol kg}^{-1}$)	1783–2234	1636–2394	1450–2264	1412–2174
TA ($\mu\text{mol kg}^{-1}$)	2169–2374	2122–2538	1922–2429	2012–2397
pH	7.59–8.29	7.60–8.34	7.69–8.49	7.74–8.56
pCO ₂ (μatm)	186–1271	150–1325	89–996	70–892
Ω_{arag}	1.13–4.84	1.45–6.08	1.59–6.46	1.62–6.01
[NO ₃ ⁻] ($\mu\text{mol L}^{-1}$)	0.11–3.36	0.38–16.98	0.11–4.09	0.20–5.88
[PO ₄ ³⁻] ($\mu\text{mol L}^{-1}$)	0.02–0.29	0.07–0.75	0.05–0.40	0.10–0.38

Measurements were corrected based on the difference between the measured and the certified values of the CRMs, which were always within $2 \mu\text{mol kg}^{-1}$ for DIC and $6 \mu\text{mol kg}^{-1}$ for TA. Phosphate and nitrate concentrations were both determined on frozen samples by flow injection analysis using a Lachat FIA nutrient analyzer (precision of $0.02 \mu\text{M}$), following standard procedures outlined in the WOCE manual [Gordon *et al.*, 1994].

2.3. Calculations

2.3.1. Seawater Carbonate System

[13] Measurements of DIC, TA, temperature and salinity were used to calculate the system of carbonate parameters for each sample using the CO2SYS program (D. Pierrot *et al.*, MS Excel program developed for CO2 system calculations, http://cdiac.ornl.gov/ftp/co2sys/CO2SYS_calc_XLS/, Carbon Dioxide Information Analysis Center, 2006). Calculations were made using the total hydrogen ion concentration scale, the carbonic acid dissociation constants of Mehrbach *et al.* [1973] as refit by Dickson and Millero [1987], and the K_{SO4} for the bisulfate ion from Dickson [1990]. Calcium carbonate saturation state is defined as $\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}}$, where K_{sp} is the solubility product constant for the various forms of CaCO_3 (e.g., aragonite and calcite). K_{sp} values used in the calculations were from Mucci [1983].

2.3.2. Community Metabolism

[14] For an hour before low tide to an hour after low tide, the reef flat is isolated from offshore waters, thereby restricting oceanic mixing-driven changes in carbonate properties. Biological processes can strongly influence the reef flat water chemistry during these ‘slack water’ periods along with evaporation and rainfall. The normalization of the concentration of carbonate species to a constant salinity can be used to account for the effects of evaporation and precipitation. Calcification rates can then be calculated using the slack-water alkalinity anomaly method [Langdon *et al.*, 2010]. It is assumed in the slack-water alkalinity anomaly method that the change in alkalinity is uniform with depth. We performed conductivity, temperature, depth (CTD) profiles from the surface to the bottom to ensure that there was no gradient over the shallow depth (0.4 m) of the reef flat at low tide and found that temperature varied by $<1^\circ\text{C}$ and salinity varied by <0.05 units. We also took a pair of alkalinity samples from the surface and bottom during low tide and found a difference of $0.5 \mu\text{mol kg}^{-1}$, which is lower than the precision we obtained for duplicate samples. We therefore believe that the physicochemical properties are vertically homogenous at low tide on the reef flat.

[15] We calculated the net community calcification rate (G_{net} ($\text{mmol m}^{-2} \text{h}^{-1}$)) according to equation (1) for the slack water periods, which occurred twice daily

$$G_{\text{net}} = \frac{-0.5\Delta\text{TA}d\rho}{\Delta t}, \quad (1)$$

where ΔTA is the change in salinity-normalized total alkalinity ($\mu\text{mol kg}^{-1}$), d is the water depth (m), ρ is the density of the seawater (kg L^{-1}), and Δt is the time interval (h) between observations made on the reef flat over a slack water period. Seawater density was calculated at each time period from the measured in situ salinity and temperature using the equation of state of seawater.

[16] This method calculates net community calcification, which is the difference between gross community calcification and dissolution. Net community calcification incorporates the CaCO_3 that is produced from calcification by all calcifying organisms within the study site as well as dissolution of CaCO_3 sands, where sediment-water exchange may influence the chemistry of the overlying seawater. The alkalinity anomaly method cannot directly partition the importance of calcification or dissolution. Negative G_{net} values occur when there is net dissolution.

[17] Net community production (P_{net} ($\text{mmol C m}^{-2} \text{h}^{-1}$), i.e., photosynthesis – respiration) was calculated during slack water periods from the change in DIC (equation (2))

$$P_{\text{net}} = \frac{\Delta\text{DIC}d\rho}{\Delta t} - G_{\text{net}} + F_{\text{CO}_2}, \quad (2)$$

where ΔDIC is the change in salinity-normalized DIC ($\mu\text{mol kg}^{-1}$) over the time period (Δt) and F_{CO_2} ($\text{mmol C m}^{-2} \text{h}^{-1}$) is the air-sea flux of CO_2 . F_{CO_2} was calculated using the CO2calc program [Robbins *et al.*, 2010], using the wind speed parameterization of Ho *et al.* [2006] and wind speed measurements from the Australian Government Bureau of Meteorology station at LEI (<http://www.bom.gov.au/>).

[18] A total of 56 net community calcification and production rates were calculated over all four seasons. G_{net} was related to P_{net} and the following environmental parameters using bivariate Pearson correlations: Ω_{arag} , temperature, $[\text{NO}_3^-]$, $[\text{PO}_4^{3-}]$ and $[\text{HCO}_3^-]$. G_{net} was related to P_{net} and Ω_{arag} using multiple linear regression.

2.3.3. Ω_{arag} and Calcification Projections

[19] Ω_{arag} values of the offshore waters were projected from 1880 (preindustrial) to 2100 using the IS92a ‘business-as-usual’ CO_2 emissions scenario [Intergovernmental Panel on Climate Change, 2001]. It was assumed that $p\text{CO}_2$ tracks the atmospheric concentration, where this has been shown to be valid for non-upwelling regions of the tropics/subtropics [Takahashi *et al.*, 2009]. The calculations were performed with CO2SYS (Pierrot *et al.*, MS Excel program, 2006), assuming constant TA, temperature and salinity. Projected G_{net} values were calculated for the same time period, using the Ω_{arag} projections and the observed relationship between G_{net} and Ω_{arag} (equation (5)).

3. Results and Discussion

3.1. Diurnal Variability in Seawater CO_2 and Carbonate Chemistry

[20] Large diurnal variability was observed in Ω_{arag} during each season on the LEI reef flat, and the magnitude of the changes was similar for each season (Table 2 and Figure 2). The Ω_{arag} values increased during the day and decreased at night (Figures 3 and 4). This is likely due to the drawdown of CO_2 during the day from net photosynthesis and release at night from net respiration, as also shown by a decrease (increase) in $p\text{CO}_2$ and DIC, and an increase (decrease) in pH, during the day (night) (Figure 5). There was also a draw down of TA during the day as a result of net calcification (Figure 5). Most biological production on coral reef flats is benthic [Gattuso *et al.*, 1998a], such that changes in carbonate chemistry are amplified at low tide and diluted at high tide, where high tide chemical conditions largely resemble

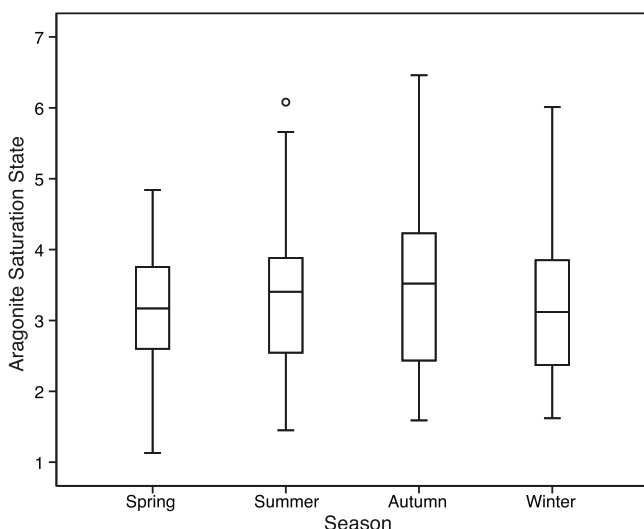


Figure 2. Reef flat diurnal variability in Ω_{arag} over each season. The box length shows the interquartile range and the small circle represents outliers.

those of the offshore water (Figure 3). The maximum spring Ω_{arag} value was lower than during the other seasons likely because low tide sampling always occurred near dawn or dusk.

[21] The Ω_{arag} values that we measured on LEI reef flat ranged from 1.13 to 6.46, which is larger than the variability measured in previous studies of carbonate chemistry on coral reefs [e.g., Manzello, 2010; Ohde and van Woessik, 1999; Santos et al., 2011; Shamberger et al., 2011] (see Table 3). This may be because most other sites from other studies were deeper and therefore changes in seawater chemistry resulting from metabolic processes would be diluted [Bates et al., 2001]. The largest variation previously reported in Ω_{arag} was 1.83 to 6.36 on a reef flat near Okinawa, Japan [Ohde and van Woessik, 1999]. These diurnal changes in reef water chemistry were similar to our study and were also attributed to changes in CO_2 resulting from the balance between photosynthesis and respiration. The depth of the sampling site in the study by Ohde and van Woessik [1999] was 18 cm compared with the minimum of 40 cm in this study and based on depth alone the variation at LEI would be expected to be lower than at Okinawa. The larger range of Ω_{arag} recorded at LEI could be explained by higher levels of biological production or a greater number of sampled seasons and times in our study. The minimum Ω_{arag} observed at LEI ($\Omega_{\text{arag}} = 1.1$) is also lower than the previous lowest recorded value of 1.54 from the Galápagos, although the mean Ω_{arag} at Galápagos was lower (mean Ω_{arag} of 2.7 in the Galápagos compared with 3.6 at LEI) [Manzello, 2010].

3.2. Coral Reef Community Calcification

[22] Coral reef community calcification is expected to decline as a result of changes in seawater carbonate chemistry via increasing atmospheric CO_2 [Kleypas and Yates, 2009]. However, calcification in coral species and coral reef communities can also be affected by temperature and nutrient concentrations [e.g., Langdon and Atkinson, 2005; Marshall and Clode, 2004; Silverman et al., 2007]. Calcification rates are also higher during light than dark periods and have been

found to be correlated with photosynthesis in both individuals and communities [Gattuso et al., 1999]. The relationship between carbonate chemistry and temperature, nutrients and photosynthesis, which also vary naturally over short time-scales, are investigated below.

3.2.1. Relationship to Temperature

[23] Unlike previous studies on corals [Marshall and Clode, 2004; Reynaud et al., 2004] and coral reefs [Silverman et al., 2007], we found no significant relationship between temperature and community G_{net} (Table 4). This is further shown in Figure 6, where the G_{net} values calculated for each season were similar, whereas temperature varied significantly between the seasons. In any one season, temperature and Ω_{arag} are directly related (Pearson correlation, $p < 0.05$ for all seasons), where both parameters increase during the day and decrease at night. A positive relationship between G_{net} and Ω_{arag} could lead to an observed correlation between G_{net} and temperature, which was observed in our summer and autumn data (significant Pearson correlations, $p < 0.05$). However, when data from all seasons are combined, temperature and Ω_{arag} become uncoupled, with G_{net} related to Ω_{arag} but not temperature. This is in agreement with the in situ coral reef community study by Silverman et al. [2007], who suggest that their observed positive correlation between temperature and G_{net} is mainly due to the effects of temperature on Ω_{arag} .

[24] Our results showed no obvious relationship between net calcification and temperature at the community scale for LEI reef flat. However, calcification rates in some species may be related to temperature, as found in experimental studies on individual coral species [Marshall and Clode, 2004; Reynaud et al., 2004]. We therefore caution against extrapolating results from any one species in order to predict changes in total coral reef community calcification [e.g., McNeil et al., 2004].

3.2.2. Relationship to Nutrients

[25] Previous laboratory studies have shown that coral calcification decreases when corals are exposed to nutrient concentrations that are enriched above the levels found naturally in oligotrophic tropical/subtropical waters [Ferrier-Pagès et al., 2000; Marubini and Davies, 1996; Stambler et al., 1991]. This is believed to occur because nutrient enrichment leads to an increase in zooxanthellae concentration, which in turn leads to a reduction in the availability of DIC for calcification [Langdon and Atkinson, 2005; Stambler et al., 1991]. We find no relationship between nutrients and G_{net} under natural in situ nutrient concentrations (Table 4). LEI is a sufficient distance from both the Australian mainland and any large rivers that discharge high levels of nutrients into the inner Great Barrier Reef lagoon, such that nutrient conditions are typically oligotrophic [Furnas et al., 2005]. Although the reef flat has elevated nutrient concentrations for short periods of time from respiration at nighttime low tide (Table 2), the offshore mean seasonal nitrate and phosphate concentrations are low, ranging from 0.12 to 0.68 and 0.06–0.10 μM , respectively.

3.2.3. Relationship to Carbonate Chemistry

[26] We observe that G_{net} is directly related to Ω_{arag} (Table 4), consistent with other studies on coral reef communities [e.g., Langdon and Atkinson, 2005; Langdon et al., 2000; Yates and Halley, 2006]. A recent single-species coral study by Jury et al. [2010] suggests that the availability of

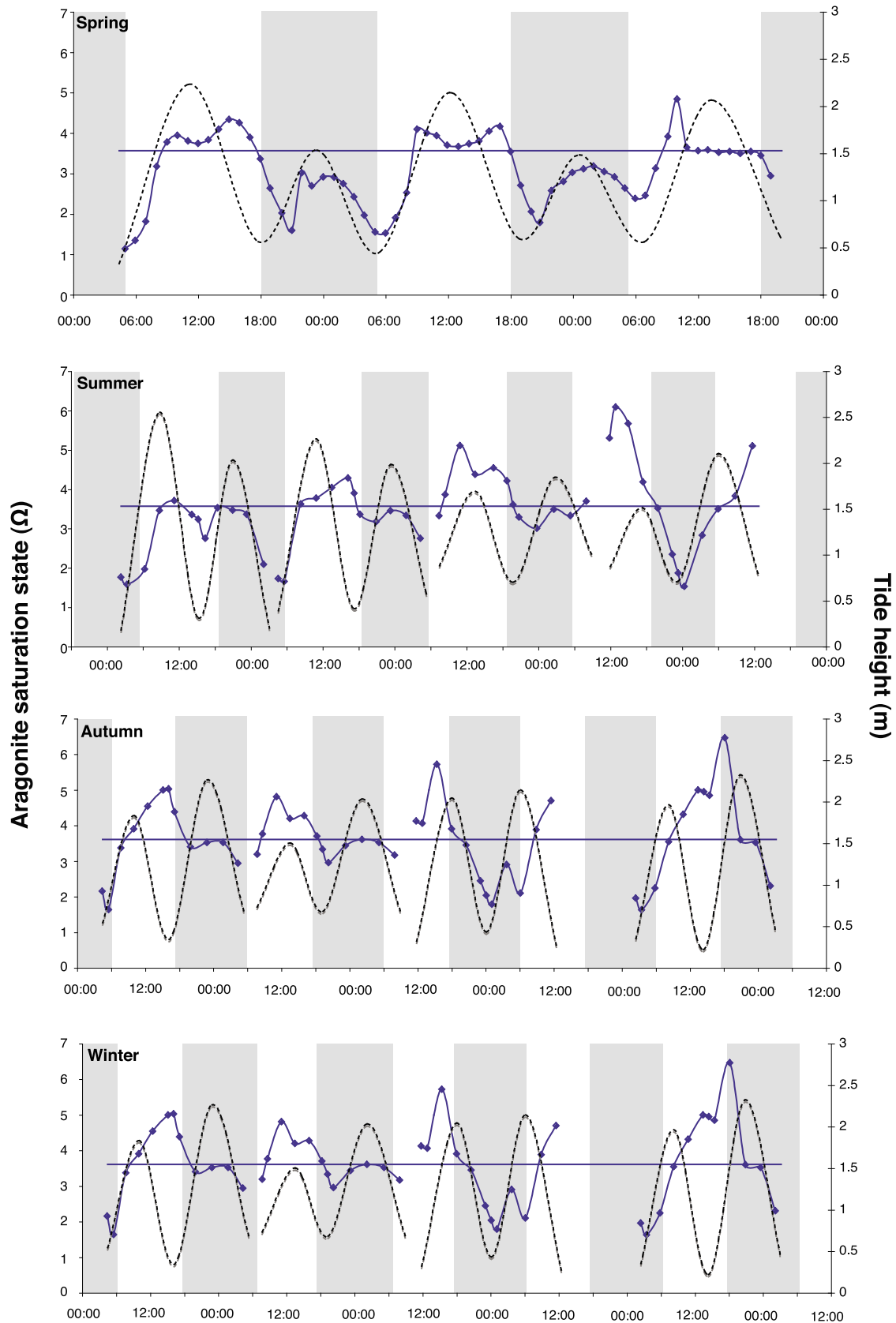


Figure 3. Daily time series of reef flat Ω_{arag} for each season. Ω_{arag} is shown in blue, where reef flat measurements are shown in blue diamonds connected with solid line and offshore values are shown as a solid horizontal line in each season. Tide height is shown in dotted black and nighttime periods are shaded.

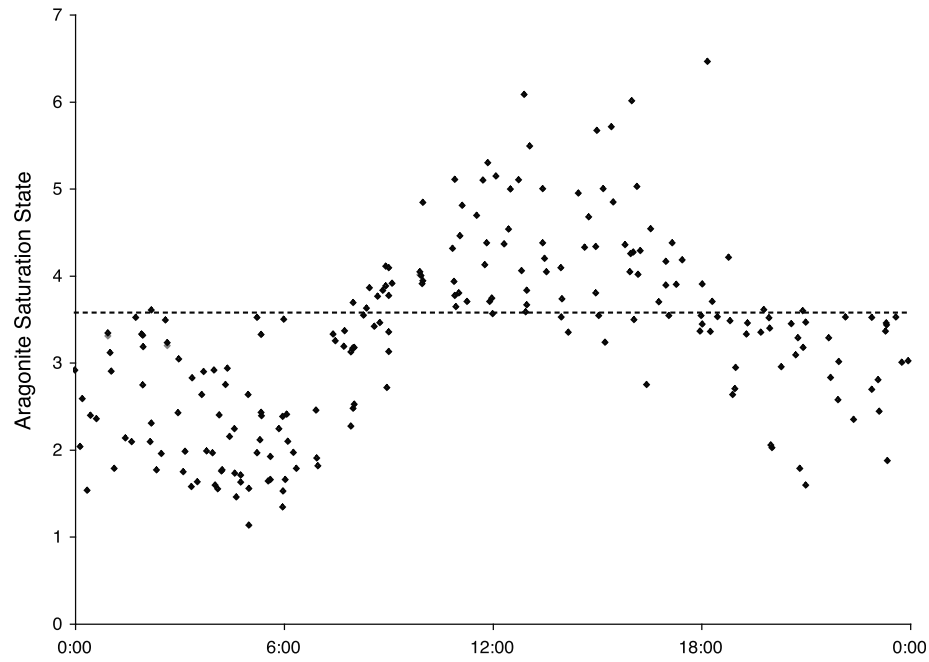


Figure 4. Variation in reef flat Ω_{arag} with time. Data points are from all seasons. Mean nearby offshore conditions are shown by the dotted line.

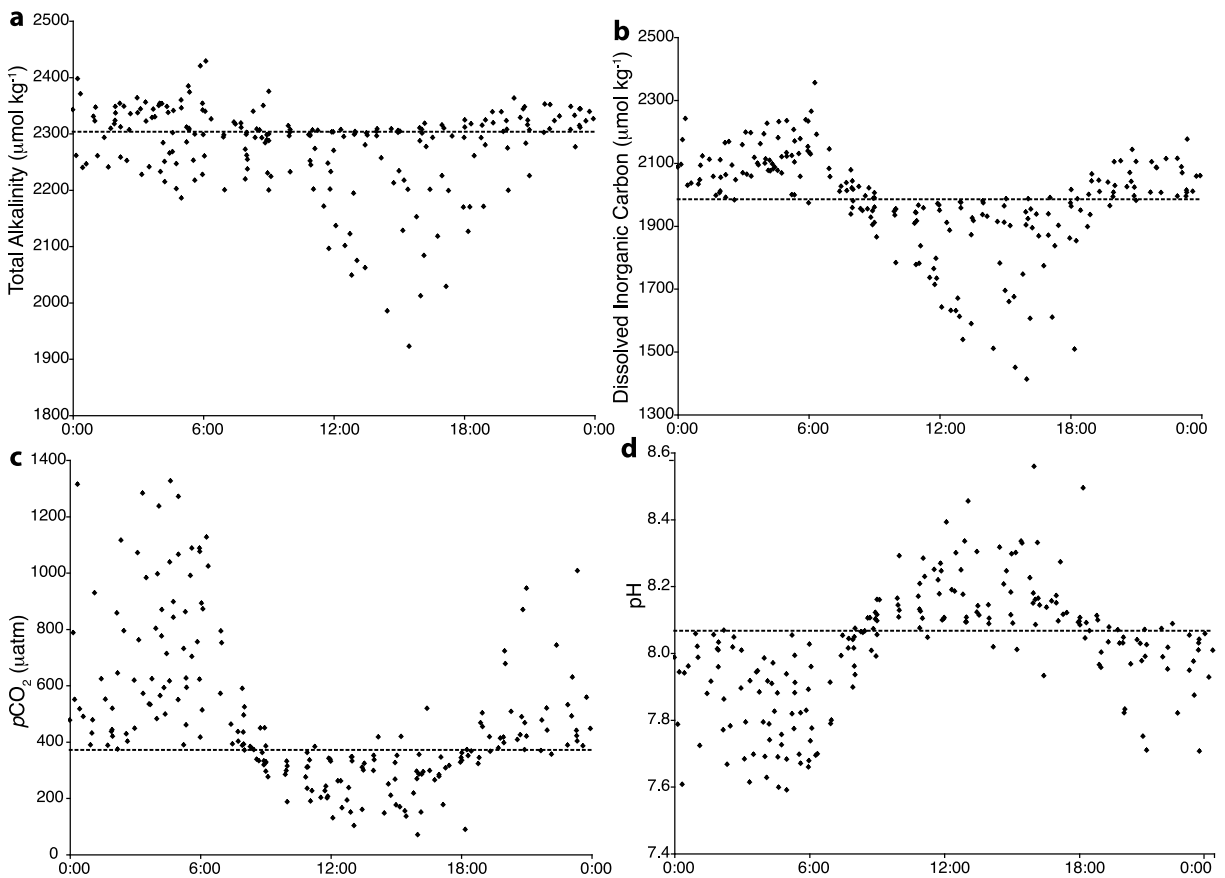


Figure 5. Daily temporal variability in (a) total alkalinity, (b) dissolved inorganic carbon, (c) $p\text{CO}_2$ and (d) pH. Data points show reef flat data from all seasons. Mean nearby offshore conditions are shown by the dotted line (measured offshore TA values ranged from 2278 to 2319 $\mu\text{mol kg}^{-1}$ and DIC from 1977 to 2003 $\mu\text{mol kg}^{-1}$).*

Table 3. Comparison of Observed Coral Reef Ω_{arag} Ranges

Study Site	Range of Ω_{arag}	Reference
Lady Elliot Island Reef Flat	1.13–6.46	This study
Nature Reserve Reef, Gulf of Eilat, northern Red Sea	3.67–4.41 ^a	Silverman <i>et al.</i> [2007]
Rukan-sho, Okinawa	1.83–6.36	Ohde and van Woessik [1999]
Molokai reef flat, Hawaii	1.9–5.4	Yates and Halley [2006]
Kaneohe Bay Barrier Reef, Hawaii	1.97–3.85	Shamberger <i>et al.</i> [2011]
Galápagos	1.54–3.70 ^b	Manzello [2010]
Gulf of Panamá	2.52–4.18	Manzello [2010]
Gulf of Chiriquí, Panamá	1.60–5.07	Manzello [2010]
Hog Reef, Bermuda	2.6–3.6 ^a	Bates <i>et al.</i> [2010]

^aOnly includes seasonal variations, not diurnal variability.

^bDaytime measurements only.

HCO_3^- may be the most important chemical factor determining calcification rates in coral reefs, where calcification increases with increasing $[\text{HCO}_3^-]$. For our results we observed the opposite relationship, with G_{net} decreasing with increasing $[\text{HCO}_3^-]$ (Table 4). Our observed relationship between G_{net} and $[\text{HCO}_3^-]$ likely occurs because of the strong inverse relationship between $[\text{HCO}_3^-]$ and Ω_{arag} (Table 4), and suggests that Ω_{arag} is a more important determinant of calcification at the community scale. Jokiel [2011] has also suggested that $[\text{H}^+]$ may be the key parameter driving the observed calcification response to changes in carbonate chemistry. Our in situ data from LEI show pH and Ω_{arag} are strongly correlated ($r = 0.97$), thus resulting in a similar correlation between pH and G_{net} ($r = 0.58$) and between Ω_{arag} and G_{net} ($r = 0.57$). We cannot decouple pH and Ω_{arag} variability in our in situ data, so it is not possible to further evaluate Jokiel's "proton flux hypothesis" [Jokiel, 2011].

[27] G_{net} ($\text{mmol m}^{-2} \text{h}^{-1}$) is linearly related to Ω_{arag} as described in equation (3), where Ω_{arag} can explain 32% of the variance in G_{net} (Figure 7)

$$G_{\text{net}} = 3.53\Omega_{\text{arag}} - 6.14. \quad (3)$$

[28] Similar relationships between G_{net} and Ω_{arag} were observed for all seasons (Figure 7). This is in agreement with a previous study in a coral reef mesocosm that found no significant change in the G_{net} – Ω_{arag} relationship between winter and summer [Langdon and Atkinson, 2005].

3.2.4. Factors Controlling Ω_{arag}

[29] Carbonate equilibria constants in seawater are a function of temperature and salinity and changes in these parameters can alter seawater Ω_{arag} and influence the relationship between Ω_{arag} and G_{net} . Figure 8 shows the mean diurnal in situ Ω_{arag} curve, along with the diurnal curves for Ω_{arag} that

were calculated while holding each of temperature, salinity, TA and DIC parameters constant. When either temperature or salinity are held constant, the diurnal curve is almost identical to the in situ Ω_{arag} curve, indicating that in situ temperature and salinity variability have negligible contribution to diurnal Ω_{arag} variability. When TA and DIC are held constant, the calculated Ω_{arag} varies from the in situ value, indicating that it is variability in these parameters that drives Ω_{arag} variability. Diurnal variability in TA and DIC is in turn driven by diurnal changes in biological processes (Section 3.1.).

3.2.5. Combined Effects of Ω_{arag} and Net Community Production

[30] We found that G_{net} is significantly positively correlated with P_{net} on the LEI reef flat (Table 4 and Figure 9), consistent with several other studies that have shown coral reef community calcification is related to photosynthesis [Gattuso *et al.*, 1999, and references therein]. The correlation between G_{net} and P_{net} shown here is stronger than the correlation between G_{net} and Ω_{arag} , suggesting that P_{net} may be a stronger influence on G_{net} over diurnal time-scales than Ω_{arag} . Both P_{net} and Ω_{arag} are higher during day than night, and relationships between G_{net} and Ω_{arag} that are derived from diurnal reef data [e.g., Yates and Halley, 2006] may have a large signal driven by diurnal changes in P_{net} , rather than Ω_{arag} .

[31] However, mesocosm studies [Langdon and Atkinson, 2005; Langdon *et al.*, 2000; Leclercq *et al.*, 2000] and longer-term field studies [Silverman *et al.*, 2007], where Ω_{arag} and P_{net} can be decoupled have shown that carbonate chemistry is also an important determinant of coral reef community calcification. In order to partition the effects of P_{net} and Ω_{arag} on G_{net} , we perform a multiple linear regression analysis. Combining our data from all seasons of sampling at LEI we determined a relationship for G_{net} as a function of Ω_{arag}

Table 4. Correlations Between Net Community Calcification, Production and Seawater Parameters

	G_{net} ($\text{mmol m}^{-2} \text{h}^{-1}$)	Ω_{arag}	Temperature (°C)	$[\text{HCO}_3^-]$ ($\mu\text{mol kg}^{-1}$)	$[\text{NO}_3^-]$ ($\mu\text{mol L}^{-1}$)	$[\text{PO}_4^{3-}]$ ($\mu\text{mol L}^{-1}$)
G_{net} ($\text{mmol m}^{-2} \text{h}^{-1}$)	1					
Ω_{arag}	0.57 ^a	1				
Temperature (°C)	0.26	0.57 ^a	1			
$[\text{HCO}_3^-]$ ($\mu\text{mol kg}^{-1}$)	−0.64 ^a	−0.96 ^a	−0.50	1		
$[\text{NO}_3^-]$ ($\mu\text{mol L}^{-1}$)	0.01	−0.34 ^a	0.18	0.29	1	
$[\text{PO}_4^{3-}]$ ($\mu\text{mol L}^{-1}$)	−0.11	−0.57 ^a	−0.02	0.50 ^a	0.94 ^a	1
P_{net} ($\text{mmol C m}^{-2} \text{h}^{-1}$)	0.66 ^a	0.45 ^a	0.16	−0.40 ^a	−0.18	−0.26

^aCorrelation is significant at the 0.05 level.

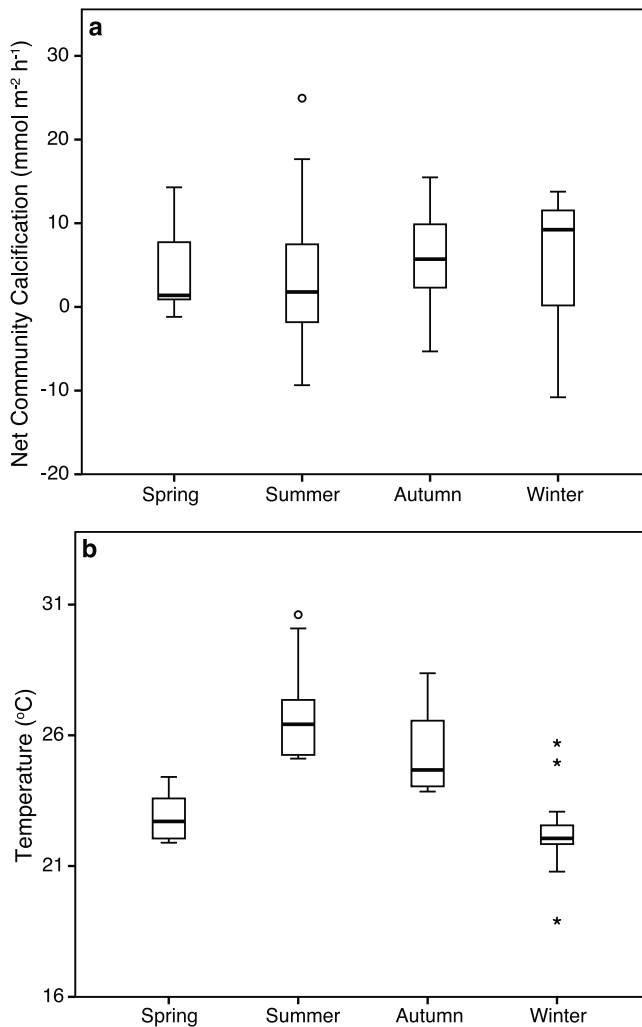


Figure 6. Seasonal variability in (a) net community calcification rates calculated for each season using the slack-water alkalinity anomaly method, and (b) corresponding seawater temperature. The box length shows the interquartile range, small circles represent outliers and asterisks represent extreme outliers.

and P_{net} that accounts for 53% of the variance in G_{net} (equation (4))

$$G_{\text{net}} = 2.14\Omega_{\text{arag}} + 0.19P_{\text{net}} - 1.59. \quad (4)$$

[32] Although there is a significant positive correlation between P_{net} and Ω_{arag} , the correlation is weaker than that between either variable and G_{net} (Table 4). Furthermore, when developing the regression relationship for which Ω_{arag} and P_{net} are both significant parameters (equation (4)), the variance inflation factor is low ($\text{VIF} = 1.25$). VIF describes the influence of collinearity on the variance of a coefficient in a regression relationship, where the low VIF found here indicates that multicollinearity is not adversely influencing the model.

[33] Photosynthesis and respiration have been shown to be approximately in balance for a number of coral reefs [Gattuso et al., 1998a] and within coral reef mesocosm

experiments [Falter et al., 2001]. By integrating our average hourly P_{net} values for all the data over a diel cycle, we calculate a P_{net} value of $0.7 \text{ mmol m}^{-2} \text{ h}^{-1}$, indicating that photosynthesis and respiration are almost balanced. Coral photosynthesis and respiration have also been shown to be insensitive to changes in carbonate chemistry [Schneider and Erez, 2006]. If we assume that photosynthesis and respiration are balanced (i.e., $P_{\text{net}} = 0$) on interannual time scales, then changes to calcification that will occur from ocean acidification can be determined based on a simplification of equation (4) as follows (equation (5)):

$$G_{\text{net}} = 2.14\Omega_{\text{arag}} - 1.59. \quad (5)$$

[34] The $G_{\text{net}}-\Omega_{\text{arag}}$ relationship we present here falls within the range of community coral reef studies from the Biosphere 2 mesocosm [Langdon et al., 2003] and with previous in situ coral reef studies [Ohde and van Woessik, 1999; Shamberger et al., 2011; Silverman et al., 2007] (Figure 10).

3.3. Community Calcification Thresholds

[35] There are few studies that have been performed in situ on coral reefs that relate coral reef community calcification to changes in carbonate chemistry. Silverman et al. [2007] studied the response of community calcification to temperature, nutrients and carbonate chemistry in the Gulf of Eilat, northern Red Sea, and provided one of the first in situ relationships between community calcification and Ω_{arag} . A global-scale modeling study based on the Gulf of Eilat data suggests that coral reefs may undergo net dissolution with a doubling of preindustrial CO_2 [Silverman et al., 2009]. However, reef calcification rates in the Gulf of Eilat responded more strongly to Ω_{arag} than previously predicted in single-species and mesocosm studies, and the discrepancy between laboratory studies and this field study is currently

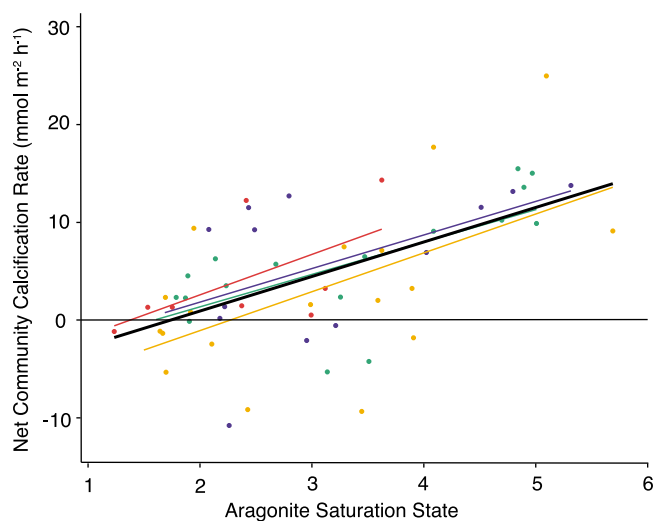


Figure 7. Relationship between reef flat community calcification and Ω_{arag} for each season. Spring, summer, autumn and winter are shown in red, orange, green and blue, respectively. The line of best fit for all data (equation (3)) is shown in black.

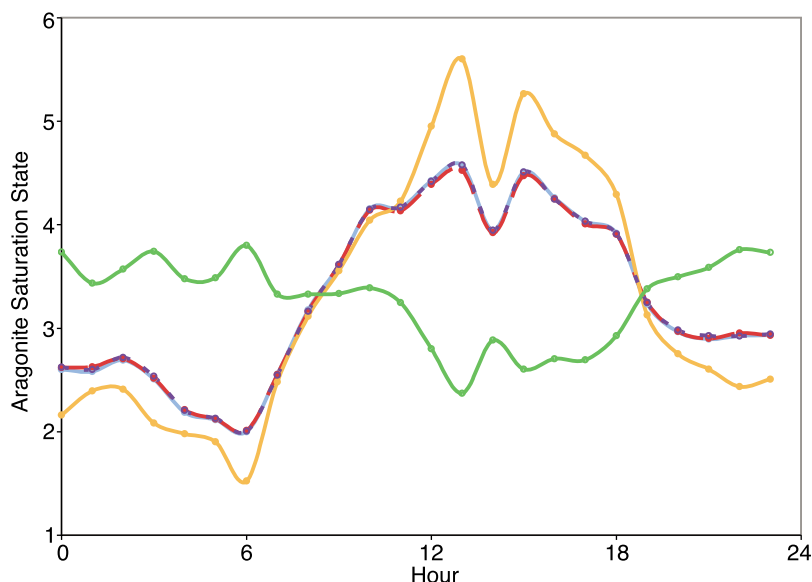


Figure 8. Influence of physical and chemical parameters on the diurnal Ω_{arag} cycle. The dotted purple line represents the reef flat hourly mean in situ Ω_{arag} . Ω_{arag} calculated with a constant salinity, temperature, total alkalinity and dissolved inorganic carbon are represented by solid blue, dashed red, solid orange and solid green lines, respectively.

unresolved [Pandolfi *et al.*, 2011]. A recent in situ community study from Kaneohe Bay, Hawaii [Shamberger *et al.*, 2011], also showed calcification rates that were much higher than those predicted from the relationship of Silverman *et al.* [2009].

[36] Coral reefs throughout the world are expected to show different responses in G_{net} to changes in Ω_{arag} due to different species compositions, with individual species responding differently to changes in carbonate chemistry (e.g., see Figure 9 of Langdon and Atkinson [2005] for a comparison of different coral species and mesocosms). In the Biosphere 2 mesocosm the threshold at which G_{net} equals zero and below which net dissolution will occur was found to be $\Omega_{\text{arag}} = 2.0 \pm 0.2$ [Langdon *et al.*, 2000]. The in situ study by Shamberger *et al.* [2011] found a threshold of $\Omega_{\text{arag}} = 1.65$ and Yates and Halley [2006] calculated a threshold value to be reached when $[\text{CO}_3^{2-}]$ is $155 \mu\text{mol kg}^{-1}$ ($\Omega_{\text{arag}} \sim 2.5$) for Molokai Reef Flat, Hawaii. The data from Yates and Halley [2006] incorporate diurnal changes to carbonate chemistry and G_{net} and therefore may be confounded through effects of photosynthesis on calcification. We estimate a threshold value of $\Omega_{\text{arag}} = 1.74$, based on the relationship of G_{net} and Ω_{arag} in equation (3). However, when accounting for the influence of P_{net} (equation (5)), we get a lower threshold of $\Omega_{\text{arag}} = 0.70$, indicating that the Ω_{arag} threshold value may be overestimated if the effects of P_{net} are not included. Our threshold value of 0.7 is lower than what would be expected from other studies; however, this value is for the mean best fit relationship (equation (5)). There is a large standard error around the intercept (± 2.146) in equation (5), which if taken into account with the standard error around the slope (± 0.66) would result in a threshold Ω_{arag} value that could range from 0 to 2.5.

[37] The threshold values discussed here and in other studies define a threshold for net community calcification and include a balance of both calcification and dissolution.

Dissolution of sediments may occur when the overlying seawater Ω_{arag} exceeds 1, due to high $p\text{CO}_2$ in sediment pore waters from microbial respiration [Andersson and Mackenzie, 2011]. Different forms of CaCO_3 also have differing solubilities, with calcite being least soluble, followed by aragonite, and high-Mg calcite being the most soluble. For example, dissolution of carbonate sediments with high levels of high-Mg calcite can occur at Ω_{arag} of 3.7, compared with dissolution of coralline aragonite, which occurs at Ω_{arag} of ~ 1 [Yamamoto *et al.*, 2011].

[38] Calcifying organisms can also produce CaCO_3 at a rate that exceeds what would be expected based on the external seawater Ω_{arag} through active changes to the

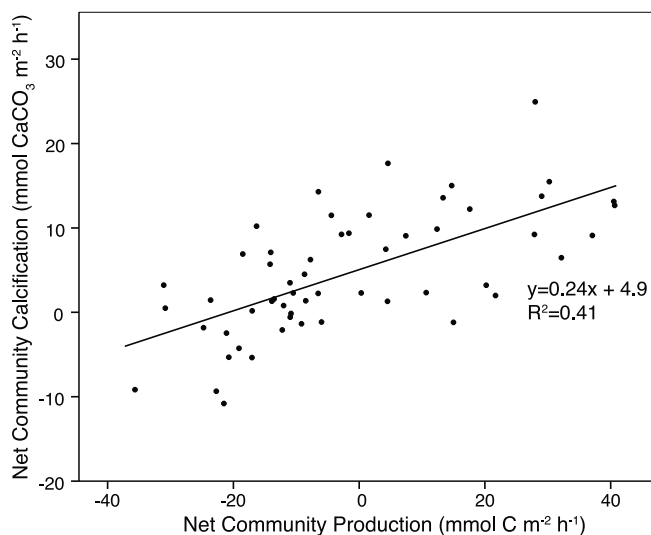


Figure 9. Relationship between net community production and net community calcification during slack water periods at Lady Elliot Island reef flat.

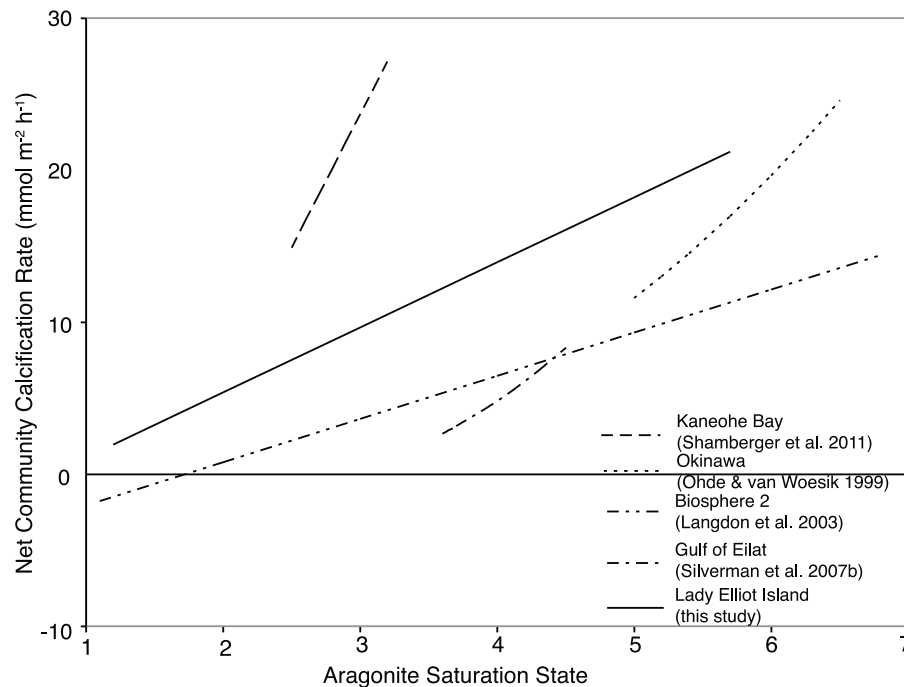


Figure 10. Relationship between net community calcification (G_{net}) and Ω_{arag} . The linear relationship from this study (equation (5)) is shown along with relationships between G_{net} and Ω_{arag} from the Biosphere 2 mesocosm [Kleypas and Yates, 2009; Langdon et al., 2003] and in situ from the Gulf of Eilat [Silverman et al., 2007], Kaneohe Bay [Shamberger et al., 2011] and Okinawa [Ohde and van Woessik, 1999].

seawater chemistry. Calcification by the majority of coral reef calcifiers occurs in locations within the organism that are either isolated or semi-isolated from the surrounding seawater, such that the organism can modify the calcifying fluid to increase the CaCO_3 saturation state and enable precipitation to occur [Cohen and Holcomb, 2009]. Increasing the pH and Ω_{arag} of the calcifying fluid relative to the external seawater is energy intensive and suggests energy derived either autotrophically or heterotrophically is important for calcification [Cohen and Holcomb, 2009]. Therefore, the degree of heterotrophic feeding in different reef flats may contribute to the different observed G_{net} - Ω_{arag} relationships from coral reef community studies. The variability in G_{net} not explained by Ω_{arag} or P_{net} (equation (4)) may also be related to heterotrophic feeding, which was not measured here.

[39] Experiments on corals have shown a limit to the amount of energy used to actively increase the pH of the calcifying fluid, such that without significant increases in energy in the future coral calcification will decline with the decline in seawater Ω_{arag} [Cohen and Holcomb, 2009]. If we assume that heterotrophic feeding will not change significantly into the future, then the relationship between G_{net} and Ω_{arag} (equation (5)) derived from in situ data for a natural coral reef may be useful in predicting the changes in G_{net} that result from declining Ω_{arag} . Based on equation (5), and using offshore Ω_{arag} values (which approximate mean reef flat values), the calculated present-day (2010) G_{net} at LEI is $145 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$. This value is within the range previously reported for coral reef flats ($14\text{--}340 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$) by Gattuso et al. [1998a]. We predict that G_{net} at LEI is 20% lower than the preindustrial value, coinciding

with a decline in Ω_{arag} from 4.3 to 3.6, and by 2100 ($\Omega_{\text{arag}} = 2.4$) will be 45% of the preindustrial value (Figure 11). Although community calcification is expected to exceed chemical dissolution by 2100, the level of CaCO_3 accretion may no longer exceed the rates of physical and biological erosion, for example from storms or grazing by corallivores [Hoegh-Guldberg et al., 2007]. The decline in community calcification also does not allow us to resolve the different responses of individual species. For example, crustose coralline algae, with high-Mg calcite skeletal material may be particularly sensitive to ocean acidification, whereas other species such as massive *Porites* corals appear to be less sensitive [Fabricius et al., 2011]. Furthermore, these predictions do not take into account the effects of warming and localized stressors that may cause declines in coral reef growth beyond what we predict from ocean acidification alone [Hoegh-Guldberg et al., 2007] or allow for any adaptation to changing environmental conditions [Pistevos et al., 2011; Sunday et al., 2011].

3.4. Does Large Diurnal Variability Imply Vulnerability or Resilience?

[40] In a review of the effects of ocean acidification on echinoderms, Dupont et al. [2010] hypothesize that species and populations naturally exposed to larger variability in carbonate chemistry will have a greater adaptive capacity to future ocean acidification. However, our knowledge of how organisms respond to increasing CO_2 under naturally variable conditions is limited from the lack of perturbation experiments that incorporate natural variability. Kuffner et al. [2008] and Jokiel et al. [2008] have included natural

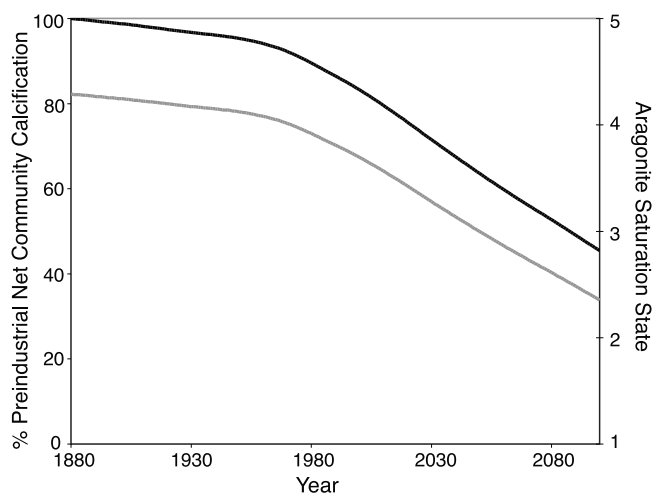


Figure 11. Projected changes in annual mean offshore Ω_{arag} (gray line) and corresponding changes to G_{net} (black line) under business-as-usual CO_2 emissions.

variability in mesocosm experiments and found that coral calcification and growth and recruitment of coralline algae were still significantly adversely affected by CO_2 levels expected by the end of the century under a business-as-usual scenario, despite undergoing large diurnal variations (ΔpH of 0.6). Our in situ observations support these results, where we show that although reef flat organisms are exposed to large carbonate chemistry variability, G_{net} is dependent on Ω_{arag} , and the total daily CaCO_3 production is a balance of both calcification and dissolution. Therefore as Ω_{arag} declines in the future, we predict that calcification will decrease and dissolution increase, leading to an overall decline in community CaCO_3 production.

[41] The high $p\text{CO}_2$ levels that we observed during parts of the day at LEI (up to $1300 \mu\text{atm}$) have been shown to induce negative non-calcifying physiological responses in coral reef organisms during laboratory experiments. *Anthony et al.* [2008] found that bleaching in a species of branching coral and crustose coralline algae was 2–3 times higher under $1000\text{--}1300 \mu\text{atm}$ CO_2 than under control conditions even in the absence of elevated temperatures. Studies of coral reef fish species have also shown key behaviors, such as prey detection and homing ability, to be impaired with exposure to $p\text{CO}_2$ of $550\text{--}950 \mu\text{atm}$ [*Cripps et al.*, 2011; *Devine et al.*, 2011].

[42] There may be multiple reasons why exposure to high CO_2 conditions may be detrimental to coral reef organisms, despite these conditions being within the natural range of conditions experienced on reef flats. First, the exposure time was considerably longer in the experiments (several days to weeks) compared with the exposure of LEI reef flat to high CO_2 conditions, which occurs only for a few hours each day around the nighttime/early morning low tide. In the studies on fish by *Cripps et al.* [2011] and *Devine et al.* [2011], fish were maintained within treatment $p\text{CO}_2$ conditions for several days prior to commencement of the experiment, following the results of *Munday et al.* [2010] who showed a response in larval clownfish and damselfish to high $p\text{CO}_2$ occurred after exposure day 2. Therefore, the pre-exposure of organisms to short-term high CO_2 conditions does not

necessarily imply resilience to persistently high future CO_2 levels.

[43] Second, reef flat organisms may have higher resilience to environmental stressors than organisms from other types of coral reef habitat. A number of studies have compared the susceptibility of corals to thermal stress between different habitat types. A greater tolerance to coral bleaching has been observed for conspecifics on reef flats compared with reef slopes [*Hoeksema*, 1991] and for inshore compared with offshore [*Cook et al.*, 1990], where intraspecific variation may be due to pre-exposure of reef flat and inshore corals to higher temperature variability. Thus, even if the organisms on the LEI reef flat are resilient to future increases in $p\text{CO}_2$, this may not imply that organisms that inhabit different reef habitat types will have a similar level of resilience. Habitat types with high natural variability also do not always exhibit more resilience, as shown in a study by *Berkelmans and Willis* [1999], where no significant difference in bleaching response was observed between reef flat and reef slope populations.

[44] Although large natural variability has been shown to occur in coral reef habitats, much of the work to determine the impacts of ocean acidification on coral reefs has been based on a non-varying view of the carbonate chemistry [*Andersson and Mackenzie*, 2011]. The diurnal range in carbonate chemistry on LEI reef flat exceeds that which is predicted to occur due to anthropogenic carbon emissions. For example, the pH range we observed was 7.6–8.6 units, whereas pH is predicted to decline by 0.3–0.5 units by the end of this century [*Caldeira and Wickett*, 2005]. Therefore, anthropogenic changes to carbonate chemistry or calcification rates, which are both highly variable throughout the day, may be difficult to detect on reef flats and will require a thorough understanding of the underlying natural variability. The exposure of reef flat organisms and communities to underlying natural variability should also be considered in studies that aim to determine the physiological response to increased CO_2 .

4. Conclusions

[45] The diurnal variability in carbonate chemistry observed on LEI reef flat is the largest reported variability for a coral reef, with Ω_{arag} varying from 1.1 to 6.5. This range exceeds the values expected to occur for tropical and subtropical waters over this century. We defined a relationship between net community calcification and Ω_{arag} over this range using in situ measurements and found carbonate chemistry to be an important predictor of net community CaCO_3 production. Measured in situ G_{net} was positively correlated with P_{net} and Ω_{arag} , whereas temperature and nutrient concentrations had no significant effects on G_{net} .

[46] We predict that business-as-usual CO_2 emissions will lead to a decline in preindustrial calcification of 55% by the end of the century. Our results are in agreement with previous in situ community studies that predict a decline in net coral reef community calcification [*Shamberger et al.*, 2011; *Silverman et al.*, 2007]. However, based on the LEI data, including the effect of P_{net} , the threshold Ω_{arag} below which net dissolution occurs may be lower than previously predicted. Future work investigating the response of different natural coral reef communities to carbonate chemistry and an

understanding of why the different systems show different responses will be required in order to make quantitative global predictions about coral reef responses to ocean acidification. It is not known at this stage whether exposure to large variability in carbonate chemistry will make reef flat organisms more or less vulnerable to the non-calcifying physiological effects of increasing ocean CO₂. Laboratory studies that incorporate natural variability will be valuable in addressing this issue.

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