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**Dynamics of
seawater carbonate
chemistry**

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Dynamics of seawater carbonate chemistry, production, and calcification of a coral reef flat, Central Great Barrier Reef

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Abstract

Ocean acidification is projected to shift coral reefs from a state of net accretion to one of net dissolution this century. Presently, our ability to predict global-scale changes to coral reef calcification is limited by insufficient data relating seawater carbonate chemistry parameters to in situ rates of reef calcification. Here, we investigate natural trends in carbonate chemistry of the Davies Reef flat in the central Great Barrier Reef on diel and seasonal timescales and relate these trends to benthic carbon fluxes by quantifying net ecosystem calcification (nec) and net community production (ncp). Results show that seawater carbonate chemistry of the Davies Reef flat is highly variable over both diel and seasonal timescales. pH (total scale) ranged from 7.92 to 8.17, $p\text{CO}_2$ ranged from 272 to 542 μatm , and aragonite saturation state (Ω_{arag}) ranged from 2.9 to 4.1. Diel cycles in carbonate chemistry were primarily driven by ncp, and warming explained 35% and 47% of the seasonal shifts in $p\text{CO}_2$ and pH, respectively. Daytime ncp averaged $36 \pm 19 \text{ mmol C m}^{-2} \text{ h}^{-1}$ in summer and $33 \pm 13 \text{ mmol C m}^{-2} \text{ h}^{-1}$ in winter; nighttime ncp averaged -22 ± 20 and $-7 \pm 6 \text{ mmol C m}^{-2} \text{ h}^{-1}$ in summer and winter, respectively. Daytime nec averaged $11 \pm 4 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ in summer and $8 \pm 3 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ in winter, whereas nighttime nec averaged 2 ± 4 and $-1 \pm 3 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ in summer and winter, respectively. Net ecosystem calcification was positively correlated with Ω_{arag} for both seasons. Linear correlations of nec and Ω_{arag} indicate that the Davies Reef flat may transition from a state of net calcification to net dissolution at Ω_{arag} values of 3.4 in summer and 3.2 in winter. Diel trends in Ω_{arag} indicate that the reef flat is currently below this calcification threshold 29.6% of the time in summer and 14.1% of the time in winter.

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1 Introduction

Atmospheric carbon dioxide ($p\text{CO}_2$) has increased from approximately 280 ppm to 390 ppm since the start of the industrial revolution due to anthropogenic activities such as the burning of fossil fuels, cement production, and land use changes (IPCC, 2007).

5 Approximately 30% of the carbon dioxide emitted each year into the atmosphere is absorbed by the world's surface oceans, causing a shift in the seawater carbonate chemistry (Canadell et al., 2007; Sabine et al., 2011). On entry into the ocean, CO_2 reacts with seawater via the following net chemical reaction:



10 As a result, concentrations of aqueous carbon dioxide, $[\text{CO}_2]_{\text{aq}}$, and bicarbonate, $[\text{HCO}_3^-]$, increase, while the concentration of carbonate, $[\text{CO}_3^{2-}]$, and the pH of seawater decrease (Broecker et al., 1979; Caldeira and Wickett, 2003; Sabine et al., 2004); this process is referred to as ocean acidification. Since preindustrial times, CO_2 uptake by the surface ocean waters has lowered seawater pH by approximately 0.1 units, which

15 equates to an increase in acidity (i.e., the hydrogen ion concentration) of approximately 30%. Carbonate ion concentrations in surface waters have simultaneously decreased by 11% and 15% in the tropics and Southern Ocean respectively (Orr et al., 2005). Further reductions in pH of 0.3–0.5 units are projected by the end of this century as the oceans continue to absorb anthropogenic CO_2 (Sabine et al., 2004; IPCC, 2007).

20 A decrease in $[\text{CO}_3^{2-}]$ results in a decrease in the saturation state of calcium carbonate (CaCO_3), defined as:

$$\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K'_{\text{sp}}, \quad (2)$$

where K'_{sp} is the solubility product for a particular mineral phase of CaCO_3 (e.g. aragonite, calcite). Aragonite is the dominant biogenic form of CaCO_3 secreted by many

25 reef-building organisms, including corals. If $\Omega > 1$, seawater is supersaturated with respect to CaCO_3 , and conditions are favorable for CaCO_3 precipitation; conversely, if

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$\Omega < 1$, seawater is undersaturated with respect to CaCO_3 and the dissolution of CaCO_3 is favored. The surface waters of the tropical oceans are currently supersaturated with respect to aragonite ($\Omega_{\text{arag}} = 4.0 \pm 0.2$, mean \pm SD); however, Ω_{arag} has steadily declined from a calculated 4.6 ± 0.2 one-hundred years ago and is expected to continue declining to 3.1 ± 0.2 by the year 2065 and 2.8 ± 0.2 by 2100 (Kleypas et al., 1999).

Experimental results and models suggest that increases in atmospheric CO_2 and the associated declines in $[\text{CO}_3^{2-}]$ and Ω_{arag} of the ocean's surface waters will reduce rates of calcification on coral reefs (Gattuso et al., 1999; Langdon et al., 2000; Langdon and Atkinson, 2005; Anthony et al., 2008). Simultaneously, rates of bioerosion (Tribollet et al., 2009) and dissolution (Halley and Yates, 2000) are expected to increase. Because reef growth ultimately depends on the balance between constructive (e.g. CaCO_3 deposition) and destructive (e.g. bioerosion, dissolution, etc.) processes, there is concern that corals may be approaching a critical threshold, beyond which their ability to effectively form reefs will be severely compromised. Presently, our ability to predict global-scale changes to coral reef calcification is limited by insufficient data relating $p\text{CO}_2$, pH, $[\text{CO}_3^{2-}]$, and/or Ω to in situ rates of reef calcification.

Ocean acidification projections are based on trends from data collected in open ocean environments (Doney et al., 2009; Feely et al., 2009; Zeebe et al., 2012) and their implications for shallow, near-shore environments, such as coral reefs, are poorly understood. Coral reefs can naturally experience large fluctuations in seawater carbonate chemistry on both diurnal (Ohde and van Woeseik, 1999; Shamberger et al., 2011; Shaw et al., 2012) and seasonal (Bates et al., 2010; Gray et al., 2012) timescales. The coral reef carbon cycle is mainly driven by two biological processes, organic carbon metabolism (photosynthesis and respiration) and inorganic carbon metabolism (calcification and dissolution). The extent to which these processes alter the carbonate chemistry of the overlying water column is a function of numerous environmental factors, including benthic community composition (Anthony et al., 2011), biological activity (which can vary with temperature, light and nutrient availability), physical forcing (e.g. temperature, salinity), tidal regime, water depth, and residence time (Falter et al., 2008,

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2013). As a result, chemical conditions can vary from reef to reef and often differ from open ocean conditions. For example, Shaw et al. (2012) demonstrated that $p\text{CO}_2$ and pH values on the Lady Elliot Island reef flat (Great Barrier Reef, Australia) can range from preindustrial values ($\sim 100 \mu\text{atm } p\text{CO}_2$ and pH 8.6) to future ocean acidification scenarios ($\sim 1300 \mu\text{atm } p\text{CO}_2$ and pH 7.6) over the course of a day. Understanding the significance of ocean acidification projections in the context of this background variability is imperative to gauging the susceptibility of reef ecosystems to projected changes in ocean chemistry.

An increasing number of studies are characterizing in situ trends in seawater carbonate chemistry and calcification rates in natural reef communities to develop relationships between carbonate parameters and biological processes; these relationships are used to estimate ‘thresholds’ at which reef systems transition from net accretion to net dissolution. To date, studies indicate that thresholds vary between reefs (Silverman et al., 2009; Shamberger et al., 2011), substrate types (Yates and Halley, 2006), and years (Yates and Halley, 2006), complicating our ability to predict global trends. $p\text{CO}_2$ thresholds for the Eilat Reef in the Red Sea are estimated to be as low as 560 ppm (Silverman et al., 2009) while reefs in Kaneohe Bay, Hawaii are not expected to dissolve until $p\text{CO}_2$ reaches nearly 900 μatm (Shamberger et al., 2011). More studies investigating natural community responses and relationships between in situ carbonate chemistry and fundamental biological processes are required to develop accurate predictions of the effects of ocean acidification on coral reef ecosystems.

Here, we investigate natural trends in carbonate chemistry of the Davies Reef flat (central Great Barrier Reef) on both diel and seasonal timescales. We relate these trends to benthic carbon fluxes by quantifying net ecosystem calcification (nec) and net community production (ncp). Automated water samplers were deployed to document diel cycling in reef carbonate chemistry, and nec and ncp were measured using a Lagrangian approach. Relationships between nec and Ω_{arag} are calculated to estimate the threshold Ω_{arag} value at which the Davies Reef flat transitions from net calcification to net dissolution.

2 Methods

2.1 Study site

Davies Reef (18°50' S, 147 °38' E) is an open, lagoonal reef located in the mid-shelf of the central Great Barrier Reef, Australia (Fig. 1). The reef is located approximately 90–100 km Northeast of Townsville, Queensland. Davies Reef is approximately 6 km long and 2.7 km wide; the reef flat faces the SE direction, and is approximately 300 m wide. The prevailing wind direction is from the southeast, and the tidal regime is semidiurnal. Current behaviour on the reef flat is determined by the interaction of wind, tide and surface slope (Frith, 1983). Water flow across the reef flat is tidally dominated when the wind speed falls below ~ 10 knots. Tidal reversals occur such that reef flat currents flood from the lagoon to the reef crest and ebb from the crest to the lagoon (Frith, 1983). There is a wet season during summer from approximately November through April and a dry season during winter from approximately May through October.

2.2 Water sampling and analysis

2.2.1 Fixed stations

An automated water sampler (Fig. 2) was deployed on the protected (lagoonal) side of the reef flat (Fig. 1) to document diurnal variability in reef flat carbonate chemistry. The approximate depth of the water sampler was 0.5 m but varied with tides. The sampler was programmed to collect discrete water samples at 2 h intervals, by pumping reef water into pre-poisoned (0.05 % HgCl₂ by volume to inhibit biological activity; Dickson, 2007) 250 mL borosilicate bottles. Bottles were filled with reef water at a flow rate of ~ 2 mL s⁻¹ (~ 2 min per sample). The sampler was programmed to flush the lines for 30 s prior to filling a new sample bottle to avoid contamination of new samples with “old” water. Bottles were retrieved every 12 h and new, pre-poisoned bottles were deployed.

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The sampler was deployed from 17–27 January 2012 in austral summer and 29 July–6 August 2012 in austral winter.

2.2.2 Transects

Net ecosystem calcification (nec) and net community production (ncp) of the Davies reef flat were measured using a Lagrangian approach. This method involves measuring total alkalinity (A_T) and dissolved inorganic carbon (C_T) immediately before a parcel of water traverses the reef flat and immediately downstream of the reef community. The change in A_T and C_T was corrected for the transit time and water depth profile to produce a net rate at which the community altered the chemistry of the overlying water column (Eqs. 3, 4, 5). This method is limited to environments that experience unidirectional flow of water, and it has been widely applied to reef flats that experience unidirectional flow during incoming/outgoing tides or due to waves breaking across a reef crest (Langdon et al., 2010). If the study site consists of biological zones that are broad and perpendicular to the direction of water flow, lateral mixing is considered an insignificant source of error (Langdon et al., 2010).

Lagrangian transport was measured by following water parcels using a small boat and a hand-held GPS (2–5 m precision) to record the location of the parcel as it traversed the reef flat. Water parcels were identified using fluorescein dye during the day and drifters (60 cm tall and 75 cm wide) at night. Discrete water samples were taken in duplicate at the beginning and end of each transect. Samples were taken in 250 mL borosilicate bottles filled at the water's surface and immediately poisoned with 125 μ L $HgCl_2$ (0.05 % by volume) to inhibit biological activity. Water depth was measured using a hand-held depth sounder alongside of the dye patch/drifter at regular intervals along each transect and averaged. Transects were repeated many times over the course of several days in order to develop a composite diel curve of calcification and production.

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2.2.3 Carbonate Chemistry

Water samples were transported to the Australian Institute of Marine Science (AIMS) where they were analyzed for total alkalinity (A_T) and dissolved inorganic carbon (C_T) using a VINDTA 3C[®] (Versatile INstrument for the Determination of Total dissolved inorganic carbon and Alkalinity, Marianda, Kiel, Germany) and a UIC CO₂ coulometer detector (UIC Inc., Joliet, USA). Accuracy was checked against certified seawater reference material (from A. Dickson, Scripps Institute of Oceanography, Batch 106). $p\text{CO}_2$, pH_T (total scale), and aragonite saturation state (Ω_{arag}) were calculated as a function of the measured salinity, temperature, A_T , and C_T using the program CO2SYS (from E. Lewis, Brookhaven National Laboratory/Lewis and Wallace, 1998); dissociation constants for carbonate and boric acid determined by Mehrbach et al. (1973) as refit by Dickson and Millero (1987), and the dissociation constant for boric acid determined by Dickson (1990).

2.2.4 Physical conditions

Temperature, light (PAR at 0.8 m depth), and wind data were obtained from the AIMS Weather Station at Davies Reef (<http://data.aims.gov.au/>), and salinity data were obtained from the Integrated Marine Observing System (IMOS 2012).

2.3 Calculations

Changes in seawater carbon chemistry between upstream and downstream sampling points can be used to calculate net ecosystem calcification (nec) and net community production (ncp) rates. In most coral reef systems, changes in total alkalinity (A_T) are caused primarily by calcification and dissolution of CaCO₃ whereby two moles of A_T are consumed (produced) for every mole of CaCO₃ produced (dissolved). Accordingly,

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net ecosystem calcification, nec, ($\text{mmol CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$) can be calculated as:

$$\text{nec} = -0.5\rho h \frac{\Delta A_T}{\Delta t} \quad (3)$$

where ΔA_T is the change in total alkalinity between the upstream and downstream locations (mmol kg^{-1}), ρ is the seawater density (kg m^{-3}), h is the water depth (m), and Δt is the duration of the transect (h).

C_T is affected by calcification, dissolution, photosynthesis, respiration. Net community production, ncp, ($\text{mmol C m}^{-2} \text{ h}^{-1}$) can be calculated using changes in C_T after taking into account nec and gas exchange:

$$\text{ncp} = -h\rho \frac{(\Delta C_T - 0.5\Delta A_T)}{\Delta t} - kS(\rho\text{CO}_2^w - \rho\text{CO}_2^a) \quad (4)$$

where ΔC_T is the change in dissolved inorganic carbon between the upstream and downstream locations (mmol kg^{-1}), and the term $kS(\rho\text{CO}_2^w - \rho\text{CO}_2^a)$ approximates gas exchange where k is the gas transfer velocity, S is the solubility of CO_2 calculated as a function of salinity and temperature, and $(\rho\text{CO}_2^w - \rho\text{CO}_2^a)$ is the difference in ρCO_2 between the surface ocean and the atmosphere. All other parameters are defined as above. The wind speed parameterization of Ho et al. (2006) was used to calculate k , which ranged from 5.8 to 16.7 cm h^{-1} , with a mean of 10.3 cm h^{-1} . Resulting gas exchange estimates were small in comparison to ncp, ranging from -0.11 to 0.13 $\text{mmol C m}^{-2} \text{ h}^{-1}$. Because gas exchange averaged 0.32% of ncp (ranging from 0% to 1.9%), this term was treated as negligible, simplifying the equation to the following:

$$\text{ncp} = -h\rho \frac{(\Delta C_T - 0.5\Delta A_T)}{\Delta t} \quad (5)$$

Pearson's correlations were computed to assess the relationship between nec and aragonite saturation state (Ω_{arag}).

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2.4 Light response curves

Productivity- and calcification-irradiance curves were fitted to data using linear or non-linear curve fitting (Graphpad Prism 5.0 for Mac OS X) (Gattuso et al., 1996). The exponential function $y = a[1 - \exp(-x/b)] + c$ produced the best fit for the productivity-irradiance curve, and the calcification-irradiance curve was modeled using a linear function.

2.5 Benthic community structure

Benthic surveys were conducted in both summer and winter to characterize the underlying community structure of the reef flat site. Five, 200 m transects were laid on the reef flat perpendicular to the reef front, spaced 50 m apart. Photographs were taken of 0.5 m² quadrats at 5 m intervals (40 photos per transect). Photos were analyzed using Coral Point Count software with excel extensions (CPCe) using 20 random points per quadrat. The benthos was assigned to one of five main categories: (1) live coral; (2) algae (including macroalgae, turf, and cyanobacteria); (3) coralline algae (CCA); (4) CaCO₃ substrate including sand, CaCO₃ rock (e.g. old, dead coral), and/or rubble (i.e., substrate with the potential to undergo dissolution); (5) and “other”, including sponges, gorgonians, zoanthids, giant clams, etc. Where morphologic forms of CaCO₃ (e.g. rubble, CaCO₃ rock) were covered with biologically active groups (e.g. turf, coralline algae, cyanobacteria), the biologically active group was scored.

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3 Results

3.1 Physical conditions

3.1.1 Summer

Noontime irradiance, as measured at 0.8 m depth, ranged from 563–1240 $\mu\text{mol m}^{-2} \text{s}^{-1}$, averaging $1099 \pm 186 \mu\text{mol m}^{-2} \text{s}^{-1}$. Winds were predominantly from the East/Southeast and averaged 12 ± 3 knots (ranging from 3–24 knots). The tidal height ranged from 0.5–3.5 m. Average temperature was $28.5 \pm 0.2^\circ\text{C}$ (ranging from 28.1°C to 28.9°C) and salinity was 35.0 ± 0.1 . All values are mean ± 1 SD.

3.1.2 Winter

Noontime irradiance ranged from 772–1023 $\mu\text{mol m}^{-2} \text{s}^{-1}$, averaging $908 \pm 99 \mu\text{mol m}^{-2} \text{s}^{-1}$. Winds were predominantly from the East/Southeast and averaged 12 ± 3 knots (ranging from 4–19 knots). The tidal height ranged from 0.5–3.4 m. Average temperature $22.4 \pm 0.1^\circ\text{C}$ (ranging from 22.1°C to 22.7°C) and salinity was 35.6 ± 0.1 . All values are mean ± 1 SD.

3.2 Diel patterns in seawater carbonate chemistry

C_T and $p\text{CO}_2$ were highest just before dawn, following a steady increase throughout the night and lowest just before dusk following a steady decrease during the day (Fig. 3). Diel patterns in pH_T and aragonite saturation state (Ω_{arag}) mirrored those for C_T and $p\text{CO}_2$ but with highs at dusk and lows at dawn (Fig. 3). Tides resulted in small diel changes in temperature and salinity of approximately 1°C and < 0.1 units, respectively. All measured and calculated physical and chemical parameters are presented in Table 1.

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3.3 Biological activity

A total of 47 net ecosystem calcification (nec) and net community production (ncp) rates were calculated over both seasons. Details of Lagrangian transects are given in Table 2.

3.3.1 Summer

Net ecosystem calcification (nec) ranged from 5 to 17 mmol CaCO₃ m⁻² h⁻¹ during the day, averaging 11 ± 4 mmol CaCO₃ m⁻² h⁻¹. At night, nec ranged from -3 to 7 mmol CaCO₃ m⁻² h⁻¹, averaging 2 ± 4 mmol CaCO₃ m⁻² h⁻¹. There was a positive correlation between nec and Ω_{arag}, Pearson $r = 0.522$, $n = 16$, $p = 0.038$ (Fig. 8). Average net daily calcification, based on a 12 : 12 light dark cycle, was 6.5 mmol CaCO₃ m⁻² h⁻¹.

Net community production (ncp) ranged from 9 to 62 mmol C m⁻² h⁻¹ during the day, averaging 36 ± 19 mmol C m⁻² h⁻¹. At night, ncp ranged from -50 to 1 mmol C m⁻² h⁻¹, averaging -22 ± 20 mmol C m⁻² h⁻¹ (i.e., net respiring).

3.3.2 Winter

Net ecosystem calcification (nec) ranged from 2 to 14 mmol CaCO₃ m⁻² h⁻¹ during the day, averaging 8 ± 3 mmol CaCO₃ m⁻² h⁻¹. At night, nec ranged from -4 to 4 mmol CaCO₃ m⁻² h⁻¹, averaging -1 ± 3 mmol CaCO₃ m⁻² h⁻¹ (i.e. net dissolution). There was a strong positive correlation between nec and Ω_{arag}, Pearson $r = 0.497$, $n = 29$, $p = 0.006$ (Fig. 8). Average net daily calcification, based on a 12 : 12 light dark cycle, was 3.5 mmol CaCO₃ m⁻² h⁻¹, approximately half that of summer.

Net community production (ncp) ranged from 1 to 52 mmol C m⁻² h⁻¹ during the day, averaging 33 ± 13 mmol C m⁻² h⁻¹. At night, ncp ranged from -14 to 5 mmol C m⁻² h⁻¹, averaging -7 ± 6 mmol C m⁻² h⁻¹ (i.e. net respiring), and approximately a third of the summer rate.

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3.4 Light response curves

Best fits for productivity- and calcification-irradiance curves are presented in Fig. 9.

3.5 Benthic surveys

Percent cover of major benthic groups did not change significantly from summer to winter (Table 3).

4 Discussion

4.1 Trends in carbonate chemistry

Seawater carbonate chemistry observed at the Davies Reef flat was highly variable over both diel and seasonal timescales. pH_T ranged from 7.92 to 8.17, ρCO_2 ranged from 272 to 542 μatm , and Ω_{arag} ranged from 2.9 to 4.1. These ranges are consistent with those reported for other studies of extensive shallow-water reef flat systems (Shaw et al., 2012, Table 3). Diel cycles of ρCO_2 and Ω_{arag} are largely driven by rates of primary production (Anthony et al., 2011; Kleypas et al., 2011; Shamberger et al., 2011; Shaw et al., 2011) such that photosynthetic uptake of CO_2 during the day results in an elevated saturation state when calcification is at its highest (Fig. 5). This coupling of primary production and calcification is shown in Fig. 7. While the light-dark cycle fundamentally controls the phase of the diel carbonate cycle via primary production, the amplitude of the cycle is influenced by a variety of factors including benthic community composition, tidal regimes, water depth, and residence time. The effect of tides on the amplitude of diel cycling is highly visible in Fig. 4b. The larger of the two mixed diurnal tides resulted in greater changes in Ω_{arag} , while the smaller diurnal tide resulted in a dampened signal.

Seasonal variability in pH_T , ρCO_2 , and Ω_{arag} is the result of both physical processes (e.g. temperature forcing) and biological processes driving variation in nec and

n_{cp}. Temperature effects were examined using sensitivity analyses whereby in situ pH_T, pCO₂, temperature, and salinity were used as input parameters to the program CO₂SYS (Lewis and Wallace, 1998), and pH_T and pCO₂ were recorded as outputs at the mean seasonal temperature (see Gray et al., 2012). Temperature-adjusted data indicate that 0.03 units of the 0.06 pH_T unit seasonal change (47 %) (Table 1) and 19 μatm of the 56 μatm seasonal pCO₂ change (35 %) were due to cooling from 28.5 °C in summer to 22.3 °C in winter.

4.2 Diel and seasonal variation in biological activity

In general, nec and n_{cp} increased throughout the day and decreased into the evening (Fig. 5). The reef flat generally showed positive nec during the day and negative nec at night. Daytime nec and n_{cp} were slightly higher in summer than in winter, a finding that is consistent with numerous prior studies (e.g. Shamberger et al., 2011, Table 2). Net calcification continued at low rates at night in summer, but net dissolution occurred at low rates at night in winter.

Net ecosystem calcification was positively correlated to Ω_{arag} with similar relationships observed for both summer and winter (Fig. 8). These findings are consistent with previous studies that report no seasonal effect on the relationship between nec and Ω_{arag} (Langdon and Atkinson, 2005; Shaw et al., 2012). Ω_{arag} explains 25–27 % of the variance in nec (Fig. 8). While we did not observe values of Ω_{arag} lower than 2.9, dissolution occurred at night in waters that remained supersaturated with respect to calcium carbonate. Dissolution in supersaturated waters has been reported previously in other reef systems (Yates and Halley, 2006) and is believed to be the result of undersaturation in pore waters, bioerosion of sediments by endolithic microbes and boring forams, and/or dissolution of more soluble forms of calcium carbonate (e.g. high-Mg calcite) (Yates and Halley, 2006; Santos et al., 2012).

Average nighttime respiration in summer (-22 ± 20 mmol C m⁻² h⁻¹) was approximately 3-fold higher than in winter (-7 ± 6 mmol C m⁻² h⁻¹). This difference was primarily driven by two night transects in summer that yielded anomalously high respiration

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5 rates ($> 40 \text{ mmol C m}^{-2} \text{ h}^{-1}$). One of these transects was conducted at approximately 00:30 h, and the other was conducted at approximately 19:40 h (Fig. 5b). While these rates are high in comparison to the other nighttime data from this study, comparable rates of nighttime respiration have been reported for the Kaneohe Bay barrier reef (Shamberger et al., 2011), and we have little reason to believe that these transects are unrepresentative. By omitting the two anomalous transects, summer nighttime respiration ranged from -19 to $1 \text{ mmol C m}^{-2} \text{ h}^{-1}$, averaging $-10 \text{ mmol C m}^{-2} \text{ h}^{-1}$, which are comparable to winter values.

10 Assuming a 12:12 light dark cycle, the average net daily nec was $6.5 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ in summer and $3.5 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ in winter. When scaled up, these values yield a net daily calcification rate of $156 \text{ mmol (15.6 g) CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$ in summer and $84 \text{ mmol (8.4 g) CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$ in winter and an annual calcification rate of $4.27 \text{ kg CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$ (assuming 0.5 yr or 178 days at each net rate). This annual calcification rate is consistent with the average calcification rate of $4 \pm 0.7 \text{ kg m}^{-2} \text{ CaCO}_3 \text{ yr}^{-1}$ reported to occur widely in Indo-Pacific coral reef flat environments (Kinsey, 1985). The average summer daytime net calcification in this study, $11 \pm 4 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$, is also similar to values reported for GBR sites with comparable coral cover during similar times of year; Silverman et al. (2012) reported average summer daytime net calcification for the One Tree Island reef flat (13.7% coral cover) as $11.4 \pm 7.4 \text{ mmol CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$.

4.3 Historical comparisons

25 Assessing historical trends in reef community metabolism is often complicated by a lack of baseline data, including data on changes in benthic community composition. Nonetheless, at least two recent studies conducted on the Great Barrier Reef address long-term trends in carbon cycling on coral reefs. Carbon turnover rates of the One Tree Island reef were originally studied in the 1970s and 1980s (Kinsey, 1978, 1979) and more recently by Silverman et al. (2012). Silverman et al. (2012) report drastic

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reductions in net calcification ($\sim 44\%$) that are primarily attributed to a threefold increase in nighttime dissolution rates. In contrast, Shamberger et al. (2011) report rates of net ecosystem calcification for reefs in Kaneohe Bay that are comparable to values reported from the 1970s. These findings were surprising given that $p\text{CO}_2$ was substantially lower and Ω_{arag} was higher in the 1970s (Kinsey, 1985).

The results of this study are partly consistent with the results of Barnes (1983, 1988) whereby seasonality in community productivity and calcification were evaluated by floating an instrument package carrying pH and oxygen electrodes across the Davies Reef flat. Barnes reported seasonal variations in productivity and calcification of the Davies Reef flat, with net productivity averaging 45% higher, and net calcification averaging 30–40% higher in summer than in winter (Barnes, 1988). Daily net calcification rates of the reef flat were $16\text{ g CaCO}_3\text{ m}^{-2}\text{ d}^{-1}$ in summer (1981) and $11.9\text{ g CaCO}_3\text{ m}^{-2}\text{ d}^{-1}$ in winter (1984), compared to 15.6 g (summer) and 8.4 g (winter) $\text{CaCO}_3\text{ m}^{-2}\text{ d}^{-1}$ in the present study. Barnes also reported higher rates of respiration in summer, an observation that is consistent with the present study. Barnes attributed the seasonality in community productivity to seasonal shifts in community composition, whereby epilithic algal blooms occurred in summer and died in winter. Seasonal shifts in algal biomass (or other benthic community groups) were not observed in the present study. The seasonal differences in community metabolism measured here are likely due to the warmer temperatures in summer driving higher rates of calcification and productivity. Other contributing factors may have been light and/or nutrients; in the present study, average noontime irradiance was slightly higher in summer ($1099\text{ }\mu\text{mol m}^{-2}\text{ s}^{-1}$) than winter ($908\text{ }\mu\text{mol m}^{-2}\text{ s}^{-1}$). Nutrient levels were not measured, however, and cannot be excluded as a source of seasonal differences. In Barnes' study, both light and temperature were elevated in summer and may have also been a contributing factor to the seasonal differences that were reported; however, the influence of these factors on seasonal differences was not addressed.

Differences in methodology and technology preclude a robust assessment of changes in reef metabolism over time. However, these studies indicate that while some

reefs (One Tree Island) may have experienced drastic changes in net calcification over time, others, including Kaneohe Bay and Davies Reef, may have been less heavily affected.

4.4 Implications of the A_T - C_T relationship

5 The effect of community metabolism on the saturation state of the overlying water column can be observed in Fig. 6. Vectors indicate the theoretical effects of photosynthesis-respiration and calcification-dissolution on A_T and C_T : for every mol of organic carbon produced (via photosynthesis), one mol of C_T is consumed, and A_T remains unchanged; for every mol of CaCO_3 produced (calcification), A_T decreases
10 by 2 mol and C_T decreases by 1 mol. Because photosynthesis-respiration (ncp) and calcification-dissolution (nec) affect A_T and C_T differently, the slope of the A_T - C_T relationship indicates the balance between these two processes (i.e. the nec:ncp ratio). The nec:ncp ratio is given by $\frac{1}{[(2/m)^{-1}]}$, where m is the slope of the A_T - C_T line. The slope of the omega isopleths in Figure 6 is approximately 0.93 in A_T - C_T space, which
15 corresponds to a nec:ncp ratio of 0.87. Generally, if the slope of the A_T - C_T relationship approximates the slope of the omega isopleths, biological activity shifts points along a given isopleth and does not alter the saturation state of the overlying water column. Alternatively, if the A_T - C_T relationship crosses the isopleths (i.e. the slope of the A_T - C_T relationship is less than the slope of the isopleths), biological activity will increase the saturation state during the day and decrease the saturation state during the night. The
20 slopes of the A_T - C_T relationships for Davies Reef are 0.37 and 0.46 for summer and winter, respectively, which correspond to nec:ncp ratios of 0.23 for summer and 0.30 for winter, indicating that daytime biological activity increases the saturation state of the water with time. The slope of the A_T - C_T relationship may prove a valuable indicator of reef function because it reflects the balance between calcification and production; phase shifts (e.g. from coral-dominated to algal-dominated systems) and/or significant
25

stress events (e.g. bleaching) would be expected to be reflected in this slope, possibly rendering it a useful parameter for broad-scale reef monitoring programs.

4.5 Estimating thresholds and implications of ocean acidification

Linear correlations were calculated between net calcification rate and Ω_{arag} for summer and winter (Fig. 8). The Ω_{arag} values at which the trend-lines cross zero on the y -axis indicate “thresholds” at which the community transitions from net calcification to net dissolution. The corresponding Ω_{arag} thresholds for summer and winter are 3.39 and 3.23, respectively. It should be noted, however, that only 25–27 % of the variation in nec is explained by Ω_{arag} so thresholds are associated with substantial error. Figure 4 shows the diurnal variation in Ω_{arag} by season. Using this data, we have estimated the percentage of time that Ω_{arag} naturally falls below the threshold for net calcification (according to Yates and Halley, 2006). Accordingly, ambient Ω_{arag} is below the calcification threshold for the Davies Reef flat 29.6 % of the time in summer and 14.1 % of the time in winter. Based on this relationship, one would expect more nighttime dissolution in summer than in winter (Fig. 4). We observed dissolution in 2 out of 6 summer nighttime transects; however, average mean nighttime calcification was positive. This may indicate a deviation from the above relationship or a lack of replication for nighttime transects in summer. Thresholds can provide a valuable tool to assess ecosystem function on individual reef scales; however, threshold values can vary widely between reefs (Shamberger et al., 2011), substrate types (Yates and Halley, 2006), and years (Yates and Halley, 2006), rendering generalizations complicated at best.

As ocean acidification drives the gradual decline of CO_3^{2-} and Ω_{arag} , mean values of incoming water masses will lower. Consequently, the percentage of time spent below threshold values (favoring reef dissolution) will increase and the percentage of time spent above threshold values (favoring reef accretion) will decrease, driving changes in the overall carbon budget on reefs. This assumes that relationships between CO_3^{2-} , Ω_{arag} , and community calcification hold as we move into the future and that reef organisms demonstrate little capacity to acclimatize and/or adapt to changing chemical

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conditions (thereby altering the relationship between CO_3^{2-} , Ω_{arag} , and calcification). Presently, our understanding of the ability of reef organisms to acclimatize and/or adapt to ocean acidification is poorly developed. Additional field studies are needed that relate trends in reef carbonate chemistry to rates of calcification in natural settings; such studies will help establish ocean carbon chemistry baselines that will inform future change and will assist the development of predictive capabilities to assess the future of coral reefs in a changing environment.

Supplementary material related to this article is available online at:
[http://www.biogeosciences-discuss.net/10/7641/2013/
bgd-10-7641-2013-supplement.zip](http://www.biogeosciences-discuss.net/10/7641/2013/bgd-10-7641-2013-supplement.zip).

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Table 1. Seasonal averages (mean \pm 1 SD) and ranges of measured* and calculated physical and chemical parameters.

	T^* °C	S^*	A_T^* $\mu\text{mol kg}^{-1}$	C_T^* $\mu\text{mol kg}^{-1}$	pH_T	pCO_2 μatm	Ω_{arag}	CO_3^{2-} $\mu\text{mol kg}^{-1}$	n
Summer									
Mean \pm 1 SD	28.5 \pm 0.2	35.0 \pm 0.1	2276 \pm 16	1954 \pm 25	8.03 \pm 0.03	404 \pm 40	3.7 \pm 0.2	228 \pm 13	227
Range			2213–2304	1878–2018	7.92–8.10	325–542	2.9–4.1	181–253	
Winter									
Mean \pm 1 SD	22.3 \pm 0.1	35.6 \pm 0.1	2294 \pm 13	1985 \pm 19	8.09 \pm 0.02	348 \pm 24	3.4 \pm 0.1	217 \pm 9	211
Range			2212–2322	1887–2028	8.03–8.17	275–420	3.0–3.8	195–245	

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Table 2. Length, depth, velocity, and sample size (n) of Langrangian transects by season.

	Length m	Depth m	Velocity cm s^{-1}	n , daytime (sample times)	n , nighttime (sample times)
Summer					
Mean \pm 1 SD	210 \pm 59	1.7 \pm 0.5	11.6 \pm 5.7	10 (09:30–16:00)	6 (19:00–03:30)
Range	85–316	1.1–2.8	4.2–22.5	–	–
Winter					
Mean \pm 1 SD	193 \pm 55	1.9 \pm 0.4	10.1 \pm 3.8	20 (09:00–15:30)	11 (19:00–23:00)
Range	77–397	1.2–2.6	3.1–17.5	–	–

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Table 3. Percent cover (Mean \pm 1 SD) of major benthic groups on the Davies Reef flat by season. Benthos was assigned to one of five categories: (1) live coral; (2) algae, including macroalgae, turf, and cyanobacteria; (3) coralline algae; (4) CaCO₃ substrate, including sand, CaCO₃ rock (e.g. old, dead coral), and/or rubble (i.e., substrate with the potential to undergo dissolution); and (5) “other”, including sponges, gorgonians, zoanthids, etc. When morphologic forms of CaCO₃ (e.g. rubble, CaCO₃ rock) were covered with biologically active groups (e.g. turf, coralline algae, cyanobacteria), the biologically active group was scored.

	Live Coral	Algae	Coralline algae	CaCO ₃ substrate	“Other”
Summer	10 \pm 2	58 \pm 3	8 \pm 4	22 \pm 5	< 2
Winter	8 \pm 2	56 \pm 3	9 \pm 3	24 \pm 3	< 3

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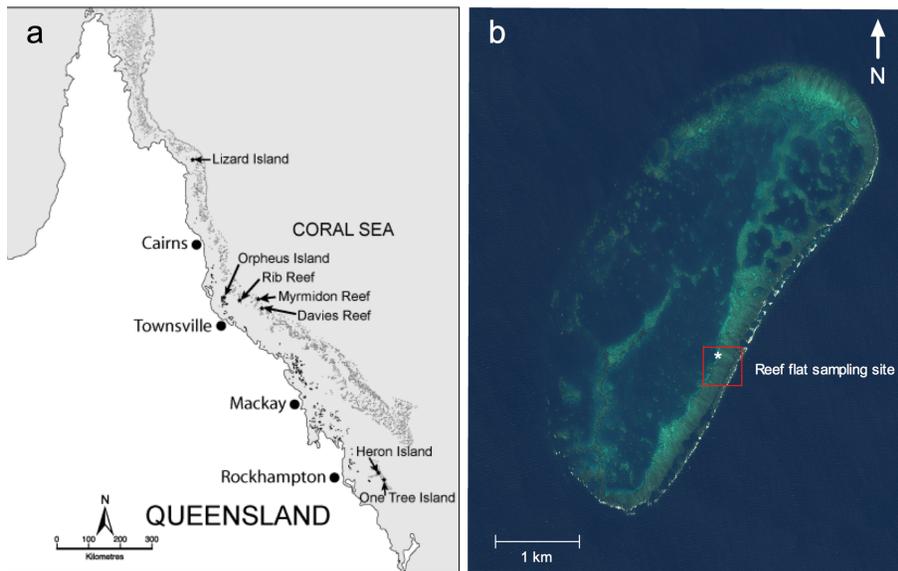


Fig. 1. (a) Map of Queensland, Australia, showing the location of Davies Reef within the Central Great Barrier Reef (www.imos.org). (b) Quickbird image of Davies Reef ($18^{\circ}50' \text{ S}$, $147^{\circ}38' \text{ E}$) with the reef flat study area denoted by a red square. The asterisk denotes the location of the automated water sampler. Lagrangian transects were conducted within the 300 m^2 sampling box.

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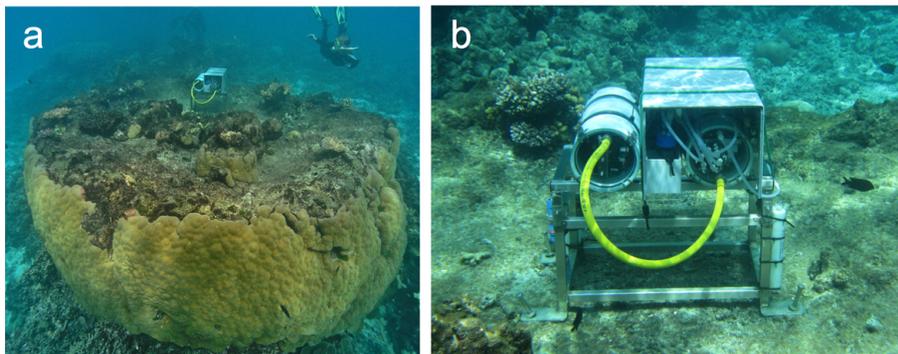


Fig. 2. Automated water sampler that was deployed at the lagoonal edge of the reef flat for 10 days in austral summer (17–27 January 2012) and 9 days in winter (29 July–6 August 2012). The sampler collected discrete water samples at 2 h intervals during the course of each deployment for the analysis of total alkalinity (A_T) and dissolved inorganic carbon (C_T). Photo credit: E. Matson.

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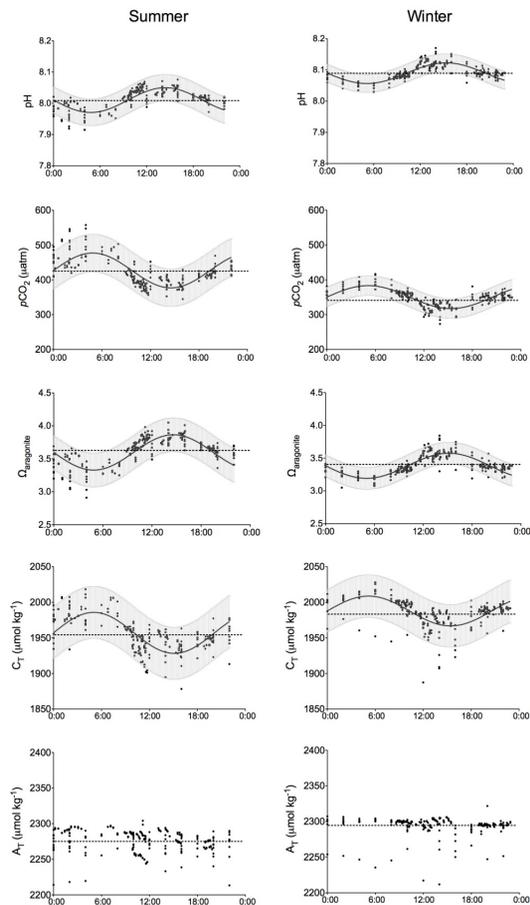


Fig. 3. Caption on next page.

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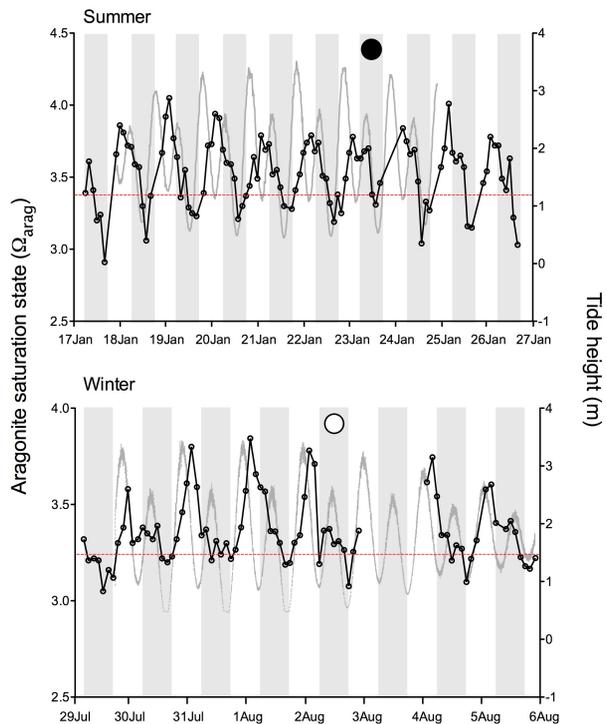


Fig. 4. Daily times series of aragonite saturation state (Ω_{arag}) of the Davies Reef flat in summer (January) and winter (August), 2012. Data were collected using an automated water sampler that was deployed at the lagoonal edge of the reef flat. Light and dark cycles are denoted by shading, and moon phases are indicated by open (full moon) and closed (new moon) circles. Tide height is indicated by the grey line. The red dashed line corresponds to the calculated Ω_{arag} thresholds when the community transitions from net calcification to net dissolution (see text for details). Gaps in the data correspond to when the instrument was removed from the reef for maintenance.

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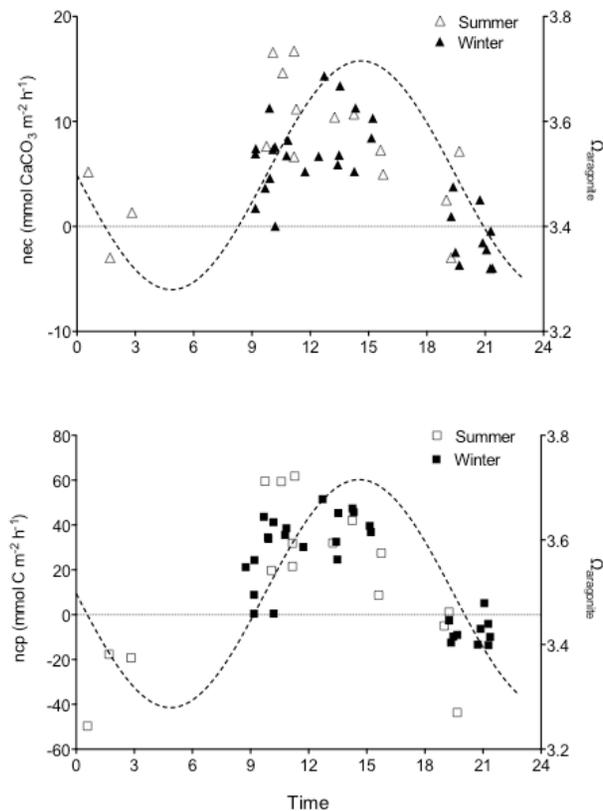


Fig. 5. Net ecosystem calcification (nec) and net community production (ncp) of the Davies Reef flat by season. Dashed line represents the combined (summer and winter) diurnal trend in aragonite saturation state (Ω_{arag}) as modeled from data in Fig. 3.

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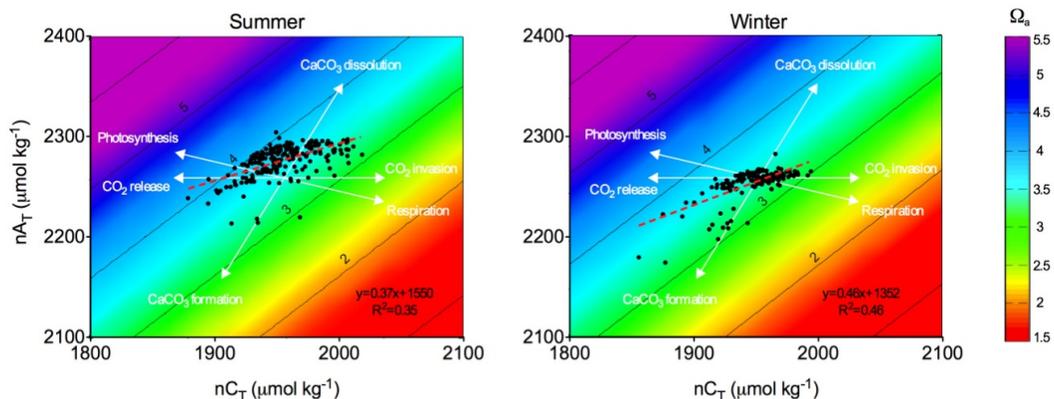


Fig. 6. Total alkalinity versus dissolved inorganic carbon diagrams by season. Vectors illustrate the theoretical effects of photosynthesis, respiration, calcification, and dissolution on A_T , C_T , and Ω_{arag} . Omega isopleths correspond to 28.3°C in summer and 22.5°C in winter. A_T and C_T data were normalized to a salinity of 35 (nA_T and nC_T , respectively) by multiplying A_T and C_T data by the ratio of 35 to the measured in situ salinity. Data points show all reef flat data collected by water samplers and lagrangian transects. The slope of the A_T – C_T relationship is less than the slope of the omega isopleths, indicating that biological activity during the day elevates the saturation state of the overlying water column, benefiting calcification and partially offsetting the effects of ocean acidification. See text for details.

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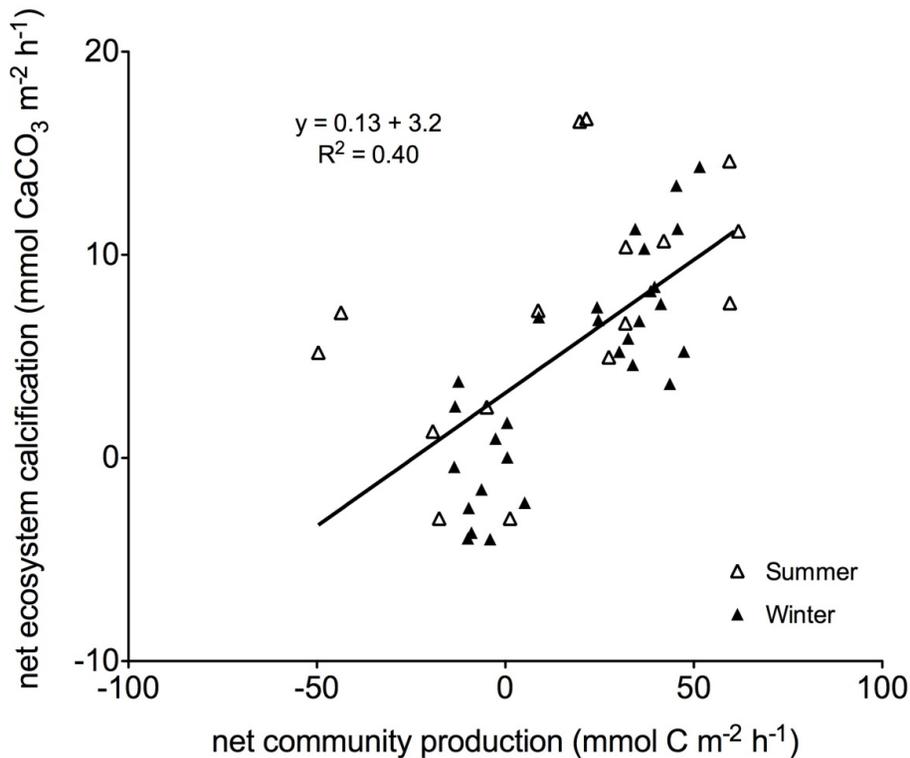


Fig. 7. Relationship between net community production (ncp) and net ecosystem calcification (nec) for combined seasons (summer and winter, 2012) at Davies Reef flat.

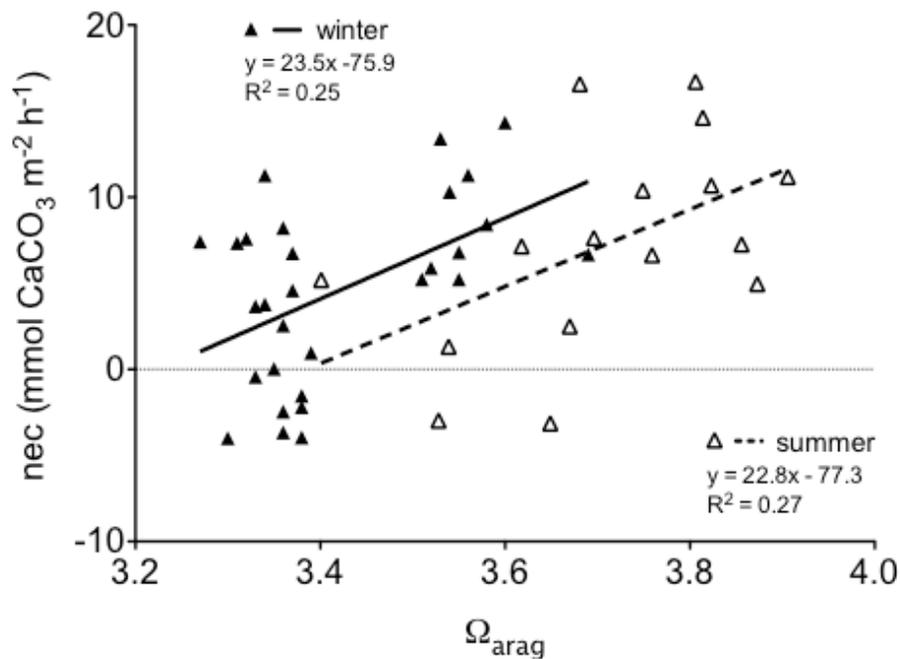


Fig. 8. Relationship between net ecosystem calcification and aragonite saturation state (Ω_{arag}) by season.

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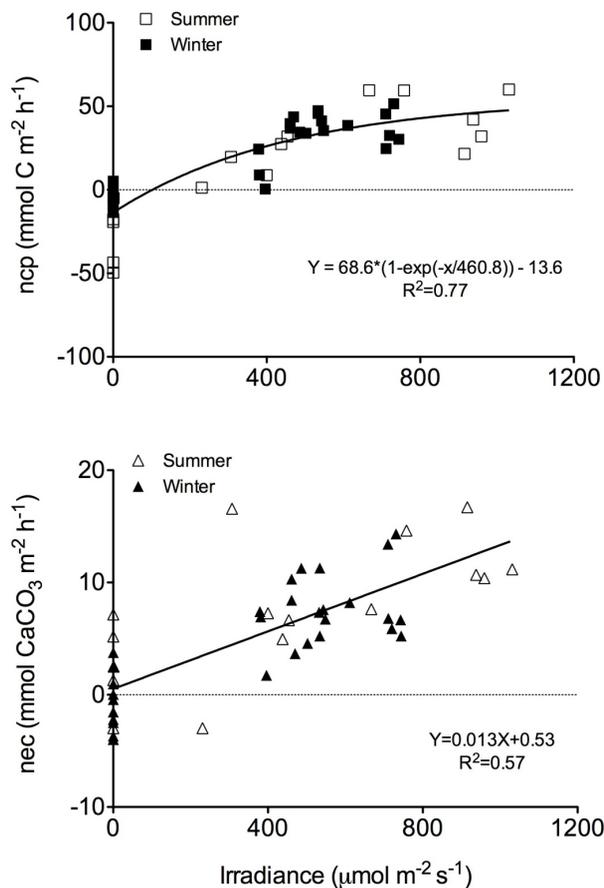


Fig. 9. Community productivity- and calcification-irradiance curves for combined seasons at Davies Reef flat.

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