

# Feedbacks and responses of coral calcification on the Bermuda reef system to seasonal changes in biological processes and ocean acidification

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**Abstract.** Despite the potential impact of ocean acidification on ecosystems such as coral reefs, surprisingly, there is very limited field data on the relationships between calcification and seawater carbonate chemistry. In this study, contemporaneous in situ datasets of seawater carbonate chemistry and calcification rates from the high-latitude coral reef of Bermuda over annual timescales provide a framework for investigating the present and future potential impact of rising carbon dioxide ( $\text{CO}_2$ ) levels and ocean acidification on coral reef ecosystems in their natural environment. A strong correlation was found between the in situ rates of calcification for the major framework building coral species *Diploria labyrinthiformis* and the seasonal variability of  $[\text{CO}_3^{2-}]$  and aragonite saturation state  $\Omega_{\text{aragonite}}$ , rather than other environmental factors such as light and temperature. These field observations provide sufficient data to hypothesize that there is a seasonal “Carbonate Chemistry Coral Reef Ecosystem Feedback” (CREF hypothesis) between the primary components of the reef ecosystem (i.e., scleractinian hard corals and macroalgae) and seawater carbonate chemistry. In early summer, strong net autotrophy from benthic components of the reef system enhance  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  conditions, and rates of coral calcification due to the photosynthetic uptake of  $\text{CO}_2$ . In late summer, rates of coral calcification are suppressed by release of  $\text{CO}_2$  from reef metabolism during a period of strong net heterotrophy. It is likely that this seasonal CREF mechanism is present in other tropical reefs although attenuated compared to high-latitude reefs such as Bermuda.

Due to lower annual mean surface seawater  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  in Bermuda compared to tropical regions, we anticipate that Bermuda corals will experience seasonal periods of zero net calcification within the next decade at  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  thresholds of  $\sim 184 \mu\text{moles kg}^{-1}$  and 2.65. However, net autotrophy of the reef during winter and spring (as part of the CREF hypothesis) may delay the onset of zero NEC or decalcification going forward by enhancing  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$ . The Bermuda coral reef is one of the first responders to the negative impacts of ocean acidification, and we estimate that calcification rates for *D. labyrinthiformis* have declined by  $>50\%$  compared to pre-industrial times.

## 1 Introduction

Coral reefs are highly productive and biologically diverse ecosystems showing signs of deterioration or undergoing community structure changes due to a host of anthropogenic and natural factors such as bleaching, resource depletion, changing sedimentation rates and turbidity, eutrophication, cyclone damage, and natural climate variability such as El Niño Southern Oscillation (e.g., Hughes, 1994; Smith and Buddemeier, 1992; Wilkinson, 2000; Buddemeier et al., 2004; Edmunds, 2007; Edmunds and Elahi, 2007). In addition to these environmental pressures, the ability of coral reefs to calcify, produce calcium carbonate ( $\text{CaCO}_3$ ) and provide framework structures as habitat may also be adversely affected by the oceanic uptake of anthropogenic  $\text{CO}_2$  (Sabine et al., 2004) and gradual ocean acidification (Broecker et al., 1971; Bacastow and Keeling, 1973; Kleypas et al., 1999a; Royal Society, 2005; Orr et al., 2005; Kleypas et al., 2006;



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Doney, 2006; Doney et al., 2009; Kleypas and Yates, 2009). For example, over the last few decades, seawater dissolved inorganic carbon (DIC) and partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) have increased while pH has decreased (Bates et al., 1996a; Winn et al., 1998; Bates, 2007; Bates and Peters, 2007; Santana-Casiano et al., 2007; Dore et al., 2009). Given predicted atmospheric  $\text{CO}_2$  stabilization scenarios of  $\sim 750$  ppm or higher (IPCC, 1996, 2001, 2007; Clarke et al., 2007), surface ocean pH is expected to decrease by 0.3–0.5 during this century and beyond (Caldeira and Wickett, 2003, 2005), with concomitant reduction in ocean carbonate ion ( $[\text{CO}_3^{2-}]$ ) concentration and saturation states ( $\Omega$ ) with respect to carbonate minerals such as calcite ( $\Omega_{\text{calcite}}$ ), and aragonite ( $\Omega_{\text{aragonite}}$ ). In addition, experimental, field and model studies suggest that the dissolution of carbonate sediments and structures will increase as  $\Omega$  values decline in the future (Wollast et al., 1980; Andersson et al., 2003; Morse et al., 2006; Andersson et al., 2006, 2007, 2009).

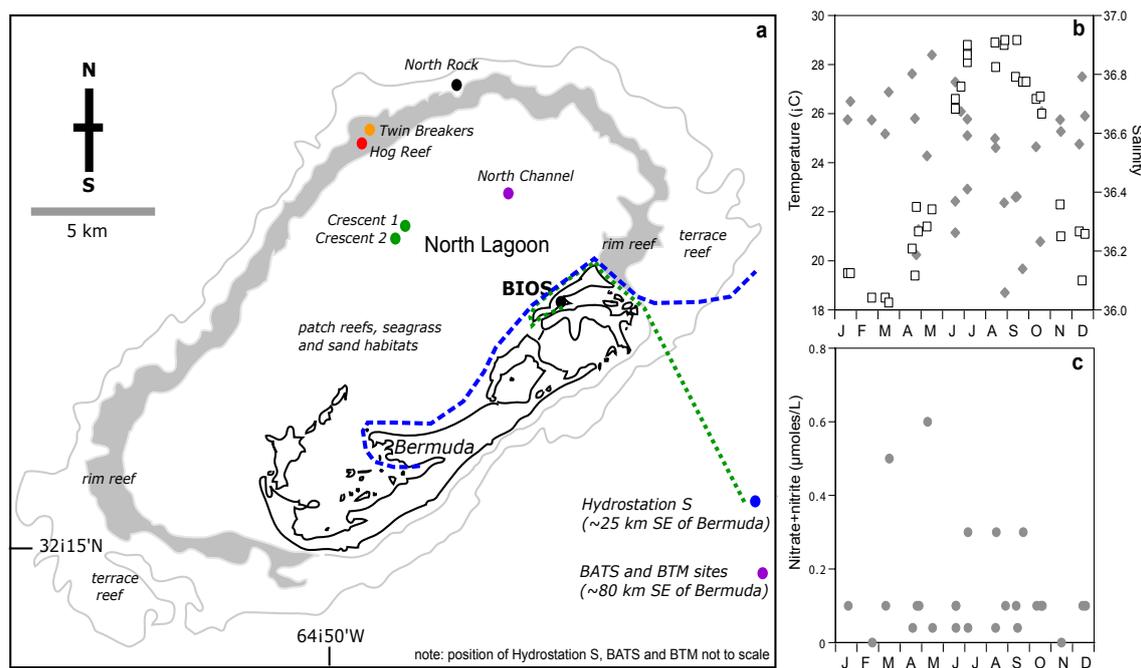
Experimental studies have shown that the ability and the rate at which coral reefs calcify decrease as a result of ocean acidification, decreasing seawater  $[\text{CO}_3^{2-}]$  and  $\Omega$  (e.g., Gattuso et al., 1999; Marubini and Atkinson, 1999; Marubini and Thake, 1999; Langdon et al., 2000; Langdon, 2001; Langdon and Atkinson, 2005; Marubini et al., 2008). Observations from coral colonies and coral reef community mesocosms exposed and equilibrated with high levels of atmospheric  $\text{CO}_2$  ( $\sim 500$ – $700$  ppm) and lowered  $[\text{CO}_3^{2-}]$  concentration (with lower values of  $\Omega_{\text{aragonite}}$ ) have generally shown reduction in the rates of coral calcification. However, a singular, predictable response of corals to changes in seawater  $\text{CO}_2$  chemistry has not emerged from these experimental studies. Instead, a wide range in the reduction of coral calcification rates in response to elevated  $\text{CO}_2$  conditions (i.e., typically doubling seawater  $p\text{CO}_2$  from present-day conditions to  $700 \pm 100$   $\mu\text{atm}$ ) has been observed in experiments studying “community” mesocosms (e.g.,  $-19$  to  $-58\%$ ; Leclercq et al., 2000; Langdon, 2001; Leclercq et al., 2002; Langdon et al., 2003; Langdon and Atkinson, 2005; Jokiel et al., 2008) and individual coral species (e.g., Amat, 2002; Marubini et al., 2001, 2003; Renegear and Riegel, 2005; Schneider and Erez, 2006; Fine and Tchenov, 2007; Marubini et al., 2008; Guinotte and Fabry, 2008).

The widely ranging experimental response of scleractinian corals to elevated  $\text{CO}_2$  conditions, decreasing seawater  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$ , likely reflects the complex interaction of factors that influence calcification such as light, temperature, coral host-endosymbiotic zooxanthellae interactions, species specific responses, life history, experimental design, and seawater carbonate chemistry. The influence of environmental factors on coral calcification is not clearly demonstrated and somewhat contradictory. In early studies, Goreau (1959) suggested that zooxanthellae photosynthesis would lower internal  $p\text{CO}_2$ , enhancing  $\text{CaCO}_3$  saturation and precipitation of  $\text{CaCO}_3$  at internal sites of coral calcification. Field studies have subsequently indicated that rates of cal-

cification are 3–5 times greater in the light than in the dark (Gattuso et al., 1999), with a coupling of photosynthesis and calcification.

Field studies of the seawater carbonate chemistry of coral reef ecosystems have focused mainly on  $\text{CO}_2$  variability and air-sea  $\text{CO}_2$  gas exchange (e.g., Broecker and Takahashi, 1966; Gattuso et al., 1993, 1995, 1996, 1997; Kayanne et al., 1995, 1996, 2005; Kawahata et al., 1997, 2000; Bates et al., 2001; Bates, 2002), rather than relationships between coral calcification,  $[\text{CO}_3^{2-}]$ ,  $\Omega_{\text{aragonite}}$  and other environmental factors. In a few studies, decreased rates of calcification have been observed on coral reef ecosystems associated with decreases in seawater  $[\text{CO}_3^{2-}]$  conditions (e.g., diurnal timescales, Suzuki et al., 1995; Yates and Halley, 2003, 2006; seasonal timescales, Silverman et al., 2007; Manzello, 2008). Under scenarios of future ocean acidification, it has been proposed that the combination of reduced rates of calcification and increased rates of  $\text{CaCO}_3$  dissolution could result in coral reefs transitioning from net accumulation to a net loss in  $\text{CaCO}_3$  material (“decalcification”) during this century (e.g., Andersson et al., 2005, 2006, 2007, 2009; Hoegh-Guldberg et al., 2007; Manzello et al., 2008; Kleypas and Yates, 2009; Silverman et al., 2009). The balance of  $\text{CaCO}_3$  production and dissolution can be defined as net ecosystem calcification (NEC). It is generally considered that  $\text{CaCO}_3$  production occurs at saturation state values  $>1$ , while dissolution of a particular carbonate mineral phase occurs when  $\Omega$  with respect to this phase is  $<1$ . The transition from positive to negative net ecosystem calcification (NEC = calcification-dissolution) occurs at “critical threshold values” (Kleypas et al., 2001; Yates and Halley, 2006) of seawater  $p\text{CO}_2$ ,  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  when NEC = 0. The transition is complicated due to the fact that individual coral species and other reef calcifiers may have different “critical threshold values” compared to the entire coral reef ecosystem that is influenced by a spectrum of hard coral and other marine calcifier responses as well as bioerosion and sediment dissolution.

As stated earlier, there is very limited field data on the relationships between calcification and seawater carbonate chemistry (Suzuki et al., 1995; Ohde and van Woesik, 1999), particularly over seasonal to annual timescales (Silverman et al., 2007; Manzello, 2008) and relevant reef spatial scales. The geographic distribution of coral reefs is generally dictated by light availability, sea surface temperature and by  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$ , with the high-latitude Bermuda coral reef at the geographic limit of this ecosystem (Kleypas et al., 1999a, b, 2001; Fig. 1). In this paper, we demonstrate seasonal relationships between in situ rates of coral calcification, seawater carbonate chemistry (i.e.,  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$ ) and other environmental parameters at Hog Reef, a previously studied coral reef site within the Bermuda coral reef ecosystem (Bates et al., 2001; Bates, 2002). Furthermore, offshore data collected at the Bermuda Atlantic Time-series Study (BATS) site,  $\sim 80$  km SE of Bermuda (Steinberg et al., 2001; Bates, 2007; Fig. 1) are used to constrain our estimates



**Fig. 1.** Location of rim and terrace reefs of Bermuda, the North Lagoon and island of Bermuda, and seasonal changes in temperature, salinity and nitrate+nitrite. (a) Two reef sites, Hog Reef (red symbol) and Twin Breakers (orange symbol), were chosen as representative of the broad rim reefs that enclose lagoonal waters of the North Lagoon. The North Lagoon contains patch coral reefs and extensive sand area, with two sites (Crescent 1 and 2; green symbol) representative of patch reefs. The track of weekly underway, shipboard sampling from the R/V *Atlantic Explorer* (green dashed line) and M/V *Oleander* (blue dashed line) are shown. The offshore Hydrostation S (blue symbol), Bermuda Atlantic Time-series Study (BATS; purple symbol) and Bermuda Testbed Mooring (BTM) sites are also shown (Bates, 2007). The CARIOCA  $p\text{CO}_2$  buoy was deployed at Hog Reef from 2002 to 2003; (b) seasonal changes in temperature ( $^{\circ}\text{C}$ ; open squares) and salinity (grey diamond) at the North Channel site in the North Lagoon from 2001 to 2006, and; (c) seasonal changes in nitrate+nitrite ( $\mu\text{moles kg}^{-1}$ ) at the North Channel site in the North Lagoon from 2001 to 2006. North Channel WQMP data courtesy of Drs Richard Owen and Ross Jones (MEP, 2006; <http://www.bios-mep.info/>; executive summary).

of net ecosystem calcification (NEC) and net ecosystem production (NEP) in an improved method compared to previous studies (Bates, 2002). These contemporaneous datasets provide a framework for investigating the present and future potential impact of rising  $p\text{CO}_2$  and ocean acidification on coral reef ecosystems in their natural environment. Furthermore, we evaluate the critical threshold values of  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  at which chemical conditions may no longer be favourable for calcification on the Bermuda coral reef and the timing of these thresholds in response to future acidification of the oceans. In addition, we describe the evidence for a “Carbonate Chemistry Coral Reef Ecosystem Feedback” (CREF hypothesis), a case where there is a seasonal feedback between the primary components of the reef ecosystem (i.e., scleractinian hard corals and macroalgae) and  $\text{CaCO}_3$  saturation states that enhance and suppress calcification rates at different times of the year. Diurnal enhancement and suppression of  $[\text{CO}_3^{2-}]$  and coral calcification by photosynthesis and respiration, respectively, have been modelled for the Shiraho Reef in the Ryukyu Islands by Suzuki et al., 1995 using short-term in situ observations (i.e., one daytime and one nighttime collection of data).

## 2 Methods and materials

### 2.1 Physiographic setting of the Bermuda coral reef

Bermuda has a geographically isolated subtropical coral reef ecosystem ( $\sim 1000 \text{ km}^2$ ), with a shallow central lagoon (i.e., North Lagoon) containing patch reefs, partly surrounded with a flank of outer rim and terrace reefs (Dodge and Vainys, 1977; Morris et al., 1977; Dodge et al., 1984, 1985; Logan et al., 1994) and the island of Bermuda ( $55 \text{ km}^2$ ) to the south (Fig. 1). The marine ecology of Bermuda is dominated by calcifying organisms, while the island’s seamount is capped by Quaternary limestones and marine carbonate sediments.

Waters of the Bermuda coral reef continuously exchange with offshore waters of the North Atlantic Ocean surrounding Bermuda (Bates et al., 2001; Bates 2002). The typical residence time of water on the rim reef is approximately 1–4 days (Morris et al., 1977), while water residence times are longer in the North Lagoon ( $\sim 5$ –10 days) (R. J. Johnson, tide and wind mixing model, D. Kadko, unpublished  $^7\text{Be}$  tracer data).

Hard coral cover on the Bermuda rim and terrace regions of the reef system typically ranges between 15 and 70% (Fig. 1; CARICOMP, 1997a, b, 2000) including the areally dominant calcareous sand and seagrass ecosystems of the North Lagoon. Over the last couple of decades, Bermuda's rim reefs have maintained long-term average of 21% coral cover varying between 18–23% year to year (MEP, 2006; R. J. Jones, unpublished data, [http://www.bios-mep.info/NEW%20site/Sub\\_Program\\_2c.htm](http://www.bios-mep.info/NEW%20site/Sub_Program_2c.htm)) with macroalgae varying between 5 and 15%. The dominant coral reef taxa are *Diploria labyrinthiformis* and *D. strigosa*, with *Montastrea franksii*, *M. cavernosa*, *Porites astreoides*, and *Millepora al-cicornis* being significant components of the reef ecosystem. *D. labyrinthiformis* and *strigosa* are arguably the dominant species and constitutes 25–35% of the reef hard coral cover.

## 2.2 Seawater carbonate chemistry considerations

The complete seawater carbonic acid system (i.e.,  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ ) can be calculated from a combination of two carbonate system parameters, DIC, TA,  $p\text{CO}_2$  and pH, along with temperature and salinity. Here,  $p\text{CO}_2$  is the partial pressure of  $\text{CO}_2$  in equilibrium with seawater, while pH is expressed on the total seawater scale. DIC is defined as (Zeebe and Wolf-Gladrow, 2001; Dickson et al., 2007):

$$\text{DIC} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1)$$

where  $[\text{CO}_2^*]$  represents the concentration of all unionized carbon dioxide, whether present as  $\text{H}_2\text{CO}_3$  or as  $\text{CO}_2$ . The total alkalinity of seawater (TA) is defined as:

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + \\ & [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{HS}^-] + [\text{NH}_3] + \dots \\ & - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - \dots \end{aligned} \quad (2)$$

where  $[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \text{B}(\text{OH})_4^-$  are the principal components of seawater TA.

Calcium carbonate ( $\text{CaCO}_3$ ) mineral production and dissolution is governed by the following chemical reaction:



$\text{CaCO}_3$  production and dissolution rates vary as a function of saturation state ( $\Omega$ ). For corals and other calcifying marine organisms whose carbonate mineralogy is aragonite, the seawater saturation state with respect to this mineral phase is defined as the ion concentration product of calcium and carbonate ions divided by the stoichiometric solubility product,  $K_{\text{sp}}^*$  (aragonite), which is a function of temperature, salinity and pressure (Mucci, 1983), thus:

$$\Omega_{\text{aragonite}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] / K_{\text{sp}}^* (\text{aragonite}) \quad (4)$$

## 2.3 Seawater DIC, TA and $p\text{CO}_2$ observations

During 2002 and 2003, seawater samples were collected regularly at Hog Reef (~2 m deep). Samples for DIC and TA were drawn from a Niskin sampler into clean 0.5 dm<sup>3</sup> size Pyrex glass reagent bottles, using established gas sampling protocols (Bates et al., 1996a). A headspace of <1% of the bottle volume was left to allow for water expansion and all samples were poisoned with 100  $\mu\text{l}$  of saturated  $\text{HgCl}_2$  solution to prevent biological alteration. Bottles were sealed with ground-glass stoppers and Apiezon silicon vacuum grease. Rubber bands were placed around the lip of the bottle and stopper to provide positive closure. Samples were returned to BIOS for analysis.

DIC was measured by a gas extraction/coulometric technique (see Bates et al., 1996a, b for details), using a SOMMA (Single-Operator Multi-Metabolic Analyzer) to control the pipetting and extraction of seawater samples and a UIC  $\text{CO}_2$  coulometer detector. The precision of DIC analyses of this system is typically better than 0.025% (~0.4  $\mu\text{moles kg}^{-1}$ ) based on duplicate and triplicate analyses of >2000 seawater samples analyzed at BIOS from 1992 to present. Seawater certified reference materials (CRM's; prepared by A.G. Dickson, Scripps Institution of Oceanography) were analyzed to ensure that the accuracy of DIC was within 0.03% (~0.5  $\mu\text{moles kg}^{-1}$ ). Salinity was determined analytically using a SeaBird SBE-9 conductivity sensor and calibrated against salinity collected at the ocean time-series BATS (Steinberg et al., 2001). In situ temperature was measured with a platinum thermistor ( $\pm 0.05^\circ\text{C}$ ) and temperature logger. TA was determined by potentiometric titration with HCl (see Bates et al., 1996a, b for details). CRM samples were also analyzed for TA and these values were within 0.15% (~2–3  $\mu\text{moles kg}^{-1}$ ) of certified TA values reported by A.G. Dickson (<http://andrew.ucsd.edu/co2qc/index.html>).

A time-series of seawater  $p\text{CO}_2$  was collected at Hog Reef using an autonomous CARIOCA (CARbon Interface Ocean Atmosphere) buoy (Merlivat and Brault, 1998; Bates et al., 2000, 2001). The CARIOCA buoy was deployed twice during the 2002–2003 period. Initially, the CARIOCA buoy was deployed on the 16 October 2002 (day 287 of the year) and recovered on the 20 January 2003 (day 20 of the year) after breaking its mooring line. Instrument repair and calibration delayed the subsequent deployment and the CARIOCA buoy was deployed on the 26 April 2003 (day 116 of the year). In anticipation of the passage of Hurricane Fabian over Bermuda (5 September 2003; day 247), the CARIOCA buoy was moved from Hog Reef to a protected inshore site (Ferry Reach) off BIOS's dock on the 28 August 2003 (day 239).

The CARIOCA buoy collected hourly measurements of seawater temperature,  $p\text{CO}_2$  and fluorescence from an intake at 2 m depth. Seawater temperature data was measured using two Betatherm thermistors with an accuracy of 0.05  $^\circ\text{C}$ . Tri-butyl tin (TBT) tubing was used internally and a copper plate was mounted at the seawater intake of

the CARIOCA buoy; both were used to reduce the possibility of biofouling affecting the  $p\text{CO}_2$  sensor. Seawater  $p\text{CO}_2$  measurements were conducted using an automated spectrophotometric technique (Hood et al., 1999; Bates et al., 2001; <http://www.lodyc.jussieu.fr/carioca/>). CARIOCA buoy  $p\text{CO}_2$  measurements were calibrated in the laboratory prior to deployment using a Licor infrared  $\text{CO}_2$  analyzer (Model 6262) and  $\text{CO}_2$ -in-air gas standards. Seawater was pumped in parallel through an equilibrator-Licor analyzer system and the CARIOCA exchanger cell. Linear regression curves of the spectrophotometric and Licor  $p\text{CO}_2$  data were calculated and subsequently used to determine  $p\text{CO}_2$  from spectrophotometric absorbance and temperature data.

In this study,  $p\text{CO}_2$ ,  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  were calculated from in situ DIC and TA data sampled from Hog Reef. The carbonic acid dissociation constants of Mehrbach et al. (1973), as refit by Dickson and Millero (1997), were used to determine seawater  $p\text{CO}_2$  and other carbonate parameters, using the equations of Zeebe and Wolf-Gladrow (2001). In addition, the  $\text{CO}_2$  solubility equations of Weiss (1974), and dissociation constants for borate (Dickson, 1990), and phosphate (DOE, 1994) were used. DIC and TA data was also recalculated as salinity normalized DIC (i.e., nDIC) and alkalinity (i.e., nTA) using a salinity of 36.6. This correction accounts for the DIC changes imparted by local precipitation and evaporation (Bates et al., 1996a).

Meteorological data were collected each hour from the island of Bermuda by the Bermuda Weather Service. Wind speed data were corrected to 10 m using the equations of Smith (1988). Observations of net shortwave downward radiation were also used (Dutton, 2007). Net shortwave radiation,  $Q_{\text{sw}}$ , was determined from observations of cloud cover,  $C_f$ , and theoretical extraterrestrial solar radiation,  $E_t$ , using a model of Beriland (1960) and Dobson and Smith (1980):

$$Q_{\text{sw}} = T_r E_t (a C_f) \quad (5)$$

where  $T_r$  is the transmission coefficient and  $a$  is the cloud correction factor. The values for  $T_r$  and  $a$  have been measured at 0.89 and 0.67 in the Sargasso Sea surrounding Bermuda (Johnson, 2003). The theoretical extraterrestrial solar radiation,  $E_t$ , was determined using standard astronomical formulae for the solar constant, solar elevation and ephemeris to account for seasonality and diurnality (equations from Payne, 1972; Partridge, 1976; Watt Engineering Ltd, 1978; Duffie and Beckman, 1991). Photosynthetically available radiation (PAR) at the ocean surface is  $\sim 45\%$  of estimated total insolation or  $Q_{\text{sw}}$  (Baker and Frouin, 1987).

## 2.4 In situ coral colony calcification or skeletal growth rates

The buoyant weight technique (e.g., Jokiel et al., 1978, Davies 1989, 1990), a non-destructive method commonly used to determine calcification and growth of hermatypic corals (e.g., Dodge et al., 1984, 1985; Marubini et al., 2001,

2003; Abramovich-Gottlieb et al., 2003), was used to determine in situ skeletal growth of *D. labyrinthiformis* at several sites across the Bermuda reef including Hog Reef, Twin Breakers and Crescent Reef (Fig. 1). At each site, coral colonies ( $n = 8$ ) of *D. labyrinthiformis* were transplanted on racks and secured to the reef sites in a block design. Approximately every three months, colonies were transported to BIOS and weighed in water using the buoyant weight technique. The dry weight of the coral specimen in air is

$$W_a = W_w / (1 - (\rho_w / \rho_s)) \quad (6)$$

where  $W_a$  and  $W_w$  are the dry and wet (or buoyant) weights respectively, and  $\rho_w$  and  $\rho_s$  are the densities of seawater and specimen respectively (Jokiel, 1978; Langdon et al., 2010). With this method, the skeletal weight of the coral colony can be estimated from its buoyant weight in seawater whose density has been accurately determined, thereby providing a simple, non-destructive method for recording integrated coral skeletal growth (or calcification rate) over seasonal timescales. The calcification rate ( $G$ ) or skeletal growth for *D. labyrinthiformis* is given by:

$$G_{\text{diploria}} = \Delta W_a / \Delta t \quad (7)$$

where  $\Delta W_a$  is the change in dry skeletal weight and  $\Delta t$  is the number of days between weighings. Thus, skeletal growth is expressed as weight increase per g weight ( $\text{CaCO}_3$  plus very minor contributions from tissue) for each coral colony and expressed as  $\text{mg CaCO}_3 \text{ g}^{-1} \text{ d}^{-1}$  (Table 1). Skeletal growth rate per unit area was also calculated from weight changes and determination of individual coral colony surface area (determined at the end of deployment) expressed as  $\text{mg CaCO}_3 \text{ cm}^{-2} \text{ d}^{-1}$  (Table 1).

## 3 Results

The coral reefs of Bermuda experience large seasonal changes in physical conditions, such as light and temperature, seawater carbonate chemistry and calcification rates (Fig. 2). At the summer solstice, day and night length was  $\sim 14$  and  $\sim 10$  h, respectively, and reversed at the winter solstice (CARICOMP, 1997a, b, 2000). Net shortwave radiation ( $Q_{\text{sw}}$ ) and sea surface temperature showed distinct seasonality as observed previously (Bates, 2002). Light conditions were highly variable seasonally (Fig. 2a). For example,  $Q_{\text{sw}}$  had a seasonal minima of  $\sim 2000\text{--}3000 \text{ W m}^{-2}$  in the December 2002 and January 2003 period, and a seasonal maxima of  $\sim 6000\text{--}8000 \text{ W m}^{-2}$  in the June–August 2003 period (Fig. 2a). The period of highest  $Q_{\text{sw}}$  occurred around the June solstice period (Julian Day, JD  $\sim 150\text{--}165$ ).

Surface temperatures at Hog Reef decreased from mid-summer maxima of  $\sim 27^\circ\text{C}$  in 2002 to a winter minima of  $\sim 20^\circ\text{C}$  in the January to March 2003 period (Fig. 2a). These seasonal changes are similar to those typically observed on the Bermuda reef (Fig. 1b). Subsequently, a mid-summer

**Table 1.** Natural seawater  $[\text{CO}_3^{2-}]$  variability observed at coral reef sites. Diurnal and seasonal  $[\text{CO}_3^{2-}]$  values were calculated using average alkalinity and pH observed on the Eilat coral reef by Silverman et al., 2007.

Date	Timescale	Diurnal $[\text{CO}_3^{2-}]$ range & amplitude ( $\mu\text{moles kg}^{-1}$ )	Seasonal $[\text{CO}_3^{2-}]$ range & amplitude ( $\mu\text{moles kg}^{-1}$ )	Source
Okinawa, site 1 (Japan)	1d	~144–350 (~200)	NA	Ohde and Woesik, 1999
Hog Reef (Bermuda)	38d	~200–270 (~10–30)	NA	Bates et al., 2001
Ferry Reach (Bermuda)	1d	~180–260 (80)	~200–280 (70)	Bates (unpubl. data)
North Lagoon	1994–1998	NA	~220–280 (60)	Bates, 2002
Eilat	2001–2002	~320–390	~309–364	Silverman et al., 2007

maxima of  $\sim 30^\circ\text{C}$  was observed in August 2003 a couple of months after the seasonal solar input maxima. For context, winter temperatures on the Bermuda coral reef are typically  $1\text{--}2^\circ\text{C}$  cooler than the surrounding offshore Sargasso Sea (Bates, 2002, 2007).

Inorganic nutrient concentrations across the Bermuda coral reef are low. For example, nitrate+nitrite concentrations are typically less than  $0.1 \mu\text{moles kg}^{-1}$  (MEP, 2006; <http://www.bios-mep.info/>; executive summary only; Fig. 1c) and similar to oligotrophic conditions observed in offshore waters at BATS (Steinberg et al., 2001). Freshwater inputs to the North Lagoon from the island of Bermuda are negligible and there is an absence of major sources of pollutants (e.g., anthropogenic nutrients). Bermuda reef surface salinity, typically has a seasonal range of  $\sim 36.0$  to  $36.8$ , with slightly fresher conditions occurring during summertime (MEP, 2006; Fig. 1b) and similar to offshore conditions (Steinberg et al., 2001).

Wind speeds experienced by the Bermuda coral reef were also generally higher during the winter due to the regular passage of cold fronts originating from North America (Fig. 2b). Similar seasonal changes in windspeed have been observed at the BATS site offshore (Bates, 2007). The major event recorded in the windspeed data were sustained high winds of  $\sim 120$  mph ( $\sim 200$  kph) during the passage of Hurricane Fabian over the island of Bermuda on the 5 September 2003 (JD 247; Fig. 2b).

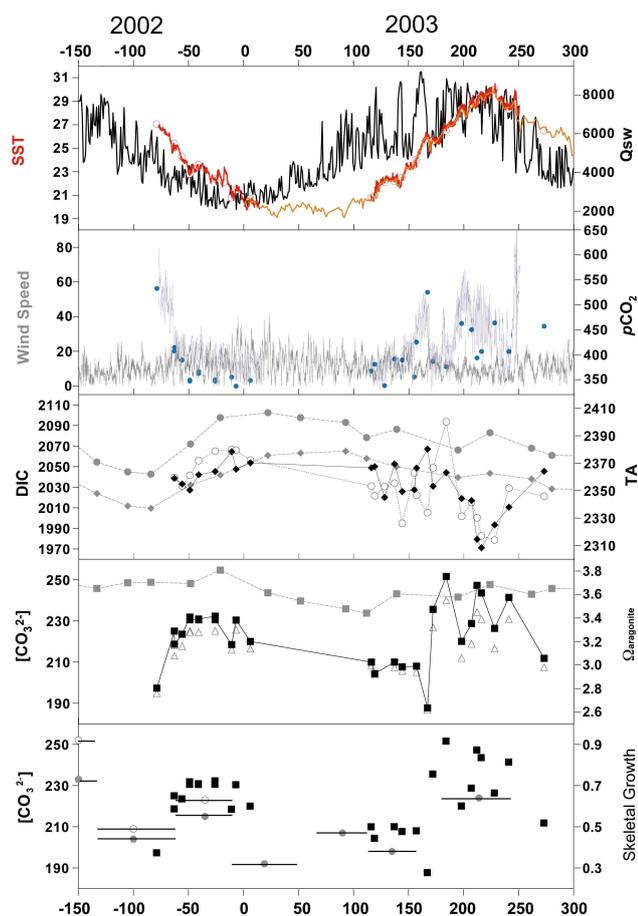
Seawater carbonate chemistry observed at Hog Reef was also highly variable over seasonal timescales. Since the source of Bermuda coral reef waters is the surrounding Sargasso Sea, the variability of Hog Reef carbonate chemistry can be compared with contemporaneous carbonate chemistry data observed at the offshore BATS site. For the 2002–2003 period, surface seawater  $p\text{CO}_2$  ranged from low wintertime values ( $\sim 300\text{--}360 \mu\text{atm}$ ) to summertime values exceeding  $550 \mu\text{atm}$  (Fig. 2b). In comparison, seawater  $p\text{CO}_2$  values at the BATS site had a seasonal range of  $\sim 300\text{--}420 \mu\text{atm}$  (Bates, 2007), with the major difference observed during the summertime, when seawater  $p\text{CO}_2$  was significantly higher on the Bermuda coral reef. The continuous observations

of seawater  $p\text{CO}_2$  at Hog Reef also showed considerable diurnal variability of  $\sim 20\text{--}100 \mu\text{atm}$ . In contrast, diurnal variability at the BATS site is significantly attenuated ( $\sim 5\text{--}25 \mu\text{atm}$ ; Bates et al., 2000, 2001). In other coral reef systems, diurnal to seasonal seawater  $p\text{CO}_2$  ranged from as low as  $\sim 100 \mu\text{atm}$  to as high as  $1000 \mu\text{atm}$ , the largest amplitude in seawater  $p\text{CO}_2$  typically observed in the shallower reefs. These previous studies have typically observed seawater  $\text{CO}_2$  and associated variables over a few days only or with transects across reef systems (e.g., Smith, 1973; Smith and Key, 1975; Gattuso et al., 1993; Kayanne et al., 1995, 1996; Frankignoulle et al., 1996; Kawahata et al., 1997, 2000; Ohde and van Woesik, 1999; Suzuki and Kawahata, 2003).

Surface DIC at Hog Reef had a seasonal variability of  $\sim 100 \mu\text{moles kg}^{-1}$ , with a maxima of  $\sim 2070 \mu\text{moles kg}^{-1}$  and minima of  $\sim 1970 \mu\text{moles kg}^{-1}$  observed during the summer of 2003 (Fig. 2c). When compared to contemporaneous BATS DIC data, in general, Hog Reef DIC data generally follows (within  $\sim 20 \mu\text{moles kg}^{-1}$ ) seasonal changes of DIC observed at the BATS site (Fig. 2c). However, during the summer of 2003, Hog Reef DIC became depleted by as much as  $30\text{--}40 \mu\text{moles kg}^{-1}$  relative to DIC at the BATS site.

Total alkalinity at Hog Reef varied seasonally by  $\sim 100 \mu\text{moles kg}^{-1}$  (Fig. 2c), with considerable differences observed between Hog Reef and offshore at BATS. For example, Hog Reef TA was generally lower by  $\sim 20\text{--}40 \mu\text{moles kg}^{-1}$  compared to BATS TA for most of 2002 and 2003. However, during the summer of 2003, Hog Reef TA and DIC were depleted by  $\sim 60\text{--}80 \mu\text{moles kg}^{-1}$  and  $30\text{--}40 \mu\text{moles kg}^{-1}$ , respectively, compared to offshore concentrations at BATS (Fig. 2c). The depletion of Hog Reef TA and DIC had an approximate ratio of  $\sim 2:1$ , similar to theoretical predictions that the formation of  $\text{CaCO}_3$  decreases TA and DIC in a ratio of  $2:1$  due to the uptake of  $[\text{Ca}^{2+}]$  and  $[\text{CO}_3^{2-}]$  (Eqs. 1–3).

The seasonal values of  $[\text{CO}_3^{2-}]$  observed at Hog Reef ranged from  $190$  to  $250 \mu\text{moles kg}^{-1}$ , a smaller range than changes observed on other reefs (Table 1; Fig. 2d). Hog Reef



**Fig. 2.** Time-series of physical, chemical and biological variables from the coral reefs of Bermuda from August 2002 to October 2003. **(a)** Surface temperature ( $^{\circ}\text{C}$ ) and short wave radiation ( $Q_{\text{sw}}$ ;  $\text{W m}^{-2}$ ) from the coral reefs of Bermuda. Surface temperature was collected hourly at Hog Reef ( $\sim 15$  km NW of the island of Bermuda) using a CARIOCA buoy (red line), and daily average from a temperature logger at 5 m deep (orange line). The red diamond symbols denote surface temperature collected during visits to Hog Reef. The daily short wave radiation ( $Q_{\text{sw}}$ ) was calculated from meteorological measurements collected hourly from the island of Bermuda by the Bermuda Weather Service. **(b)** Wind speed (grey line; mph) and surface seawater  $p\text{CO}_2$  ( $\mu\text{atm}$ ; blue line). Wind speed was collected hourly from the island of Bermuda by the Bermuda Weather Service. The blue diamond symbols denote values of seawater  $p\text{CO}_2$  determined from DIC and alkalinity measurements. **(c)** Time-series of DIC (black diamond;  $\mu\text{moles kg}^{-1}$ ) and alkalinity (open circle;  $\mu\text{moles kg}^{-1}$ ) from Hog Reef. The grey diamond and circle denote DIC and TA observed offshore at the BATS site. **(d)** Time-series of  $[\text{CO}_3^{2-}]$  (black square;  $\mu\text{moles kg}^{-1}$ ) and  $\Omega_{\text{aragonite}}$  (open triangle) from Hog Reef. The grey square denote  $[\text{CO}_3^{2-}]$  observed offshore at the BATS site. **(e)** Time-series of  $[\text{CO}_3^{2-}]$  (black square;  $\mu\text{moles kg}^{-1}$ ) and in situ skeletal growth rate (i.e.,  $G_{\text{diploria}}$ ; Hog Reef and open diamond, Twin Breakers;  $\text{mg CaCO}_3 \text{g}^{-1} \text{d}^{-1}$ ) for the massive coral *Diploria labyrinthiformis* from Hog Reef and Twin Breakers. The horizontal bars denote length of time for each in situ skeletal growth determination.

$[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  values were generally lower by  $\sim 30$ – $70$   $\mu\text{moles kg}^{-1}$  and  $\sim 0.3$  (not shown) relative to offshore  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  values at BATS, with the exception of a few occurrences during early summer 2003 (JD  $\sim 180$ – $210$ ) (Fig. 2d).

The annual range of skeletal growth rates (i.e.,  $G_{\text{diploria}}$ ) was  $\sim 0.28$ – $0.65$   $\text{mg CaCO}_3 \text{g}^{-1} \text{d}^{-1}$  for *D. labyrinthiformis* colonies (Table 2). Skeletal growth rates per unit area ranged from  $0.40$ – $0.96$   $\text{mg CaCO}_3 \text{cm}^{-2} \text{d}^{-1}$  for the same *D. labyrinthiformis* colonies (Table 2). The highest rates were observed at Hog Reef for the period of July–August 2003 and lowest rates during the wintertime (Fig. 2e; Table 2). In situ skeletal growth rates for *D. labyrinthiformis* colonies deployed at Twin Breakers were also seasonally similar and included in Fig. 2d (with the period of in situ colony deployment denoted by the horizontal bars). Twin Breakers is assumed to have similar seasonal changes in carbonate chemistry to Hog Reef due to their close proximity. At both sites, in situ skeletal growth or calcification rates covaried with seasonal changes of  $[\text{CO}_3^{2-}]$  (Fig. 2e) and  $\Omega_{\text{aragonite}}$  (not shown).

## 4 Discussion

### 4.1 Estimates of annual rates of in situ coral calcification

Previous studies of Bermuda corals such as *D. labyrinthiformis* and *Porites astreoides*, have been shown to accrete narrow, high density bands of  $\text{CaCO}_3$  during the summer, and wider low-density bands during the fall to spring (Logan and Tomascik, 1991; Cohen et al., 2004). If the in situ skeletal growth rates observed at Hog Reef are scaled up, we estimate that the calcification rate per unit area of the rim reef (i.e.,  $G_{\text{reef}}$ ) ranged from  $\sim 1.3$  to  $3.2$   $\text{g CaCO}_3 \text{m}^{-2} \text{d}^{-1}$ , using the following equation:

$$G_{\text{reef}} = G_{\text{diploria}} \cdot \alpha \beta \quad (8)$$

where  $G_{\text{diploria}}$  is skeletal growth rate (expressed as  $\text{mg CaCO}_3 \text{cm}^{-2} \text{d}^{-1}$ ) scaled up to a  $\text{m}^{-2}$  area (i.e.,  $1 \text{m}^2 = 10\,000 \text{cm}^2$ ).  $\alpha$  is a multiplier value that varies between 0 and 1 that is a function of the planar surface area of the reef. Here,  $\alpha = 0.21$  given that Bermuda's rim reefs have a long-term average of 21% coral cover. However, the actual surface area is larger due to the complex/hemispherical geometry of coral colony surface area. Thus in Eq. (8),  $\beta$  is a multiplier that accounts for the complex/hemispherical geometry of coral colony surface area, which is set at 1.57 assuming an ideal hemisphere for coral colony shape. Thus, for example, if a skeletal growth rate of  $0.96 \text{mg CaCO}_3 \text{cm}^{-2} \text{d}^{-1}$  is used, and 21% coral cover assumed (i.e.,  $\alpha = 0.21$ ), the  $G_{\text{reef}}$  rate is  $3.2 \text{g CaCO}_3 \text{m}^{-2} \text{d}^{-1}$  (i.e.,  $0.96 \text{mg CaCO}_3 \text{cm}^{-2} \text{d}^{-1} \times 10\,000 (\text{cm}^2) \times 0.21 \times 1.57$ ). In

**Table 2.** In situ rates of skeletal growth of *Diploria labyrinthiformis* from Hog Reef on the rim reef of Bermuda.

Date	Day of year	<i>n</i>	Skeletal Growth (mg CaCO <sub>3</sub> g <sup>-2</sup> d <sup>-1</sup> )	Skeletal Growth (mg CaCO <sub>3</sub> cm <sup>-2</sup> d <sup>-1</sup> )	SST (°C)	<i>Q<sub>sw</sub></i> (W m <sup>-2</sup> d <sup>-1</sup> )
1 Jul 2002–21 Aug 2002	181–237	8	0.73 ± 0.09	0.87 ± 0.20		6773 ± 1209
21 Aug 2002–19 Oct 2002	233–301	7	0.44 ± 0.08	0.74 ± 0.18	26.0 ± 0.7 <sup>b</sup>	5217 ± 1328
29 Oct 2002–22 Dec 2002	301–356	8	0.55 ± 0.15	0.92 ± 0.21	23.1 ± 0.9	3138 ± 701
22 Dec 2002–17 Feb 2003	356–48	8	0.32 ± 0.08	0.46 ± 0.15	20.2 ± 0.6	3014 ± 542
4 Mar 2003–22 Apr 2003	63–115	8	0.47 ± 0.08	0.72 ± 0.07	20.0 ± 0.5	4985 ± 999
22 Apr 2003–4 Jun 2003	116–154	8	0.43 ± 0.11	0.59 ± 0.09	22.2 ± 0.8	5890 ± 1800
1 Jul 2003–5 Sep 2003	181–247	8	0.64 ± 0.05 <sup>a</sup>	0.96 ± 0.15	28.4 ± 0.9	7368 ± 963
5 Sep 2003–6 Nov 2003	247–314	8	0.79 ± 0.11 <sup>c</sup>	0.69 ± 0.18	26.3 ± 1.1	4485 ± 1082

Note: standard deviation of skeletal growth rates, sea surface temperature (SST) and *Q<sub>sw</sub>* are also shown in the Table.

<sup>a</sup> Several of the coral specimens had moderate signs of bleaching potentially suppressing coral skeletal growth;

<sup>b</sup> surface temperatures only available for day of year 288–301;

<sup>c</sup> in situ during Hurricane Fabian.

parts of the rim reef, coral cover can be up to 70%, for which the *G<sub>reef</sub>* rate would be ~4.4 to 10.6 g CaCO<sub>3</sub> m<sup>-2</sup> d<sup>-1</sup>. In this calculation, we also assume that the skeletal growth rates for other coral species present at Hog Reef were similar to *D. labyrinthiformis*, and that other calcifying organisms such as coralline algae do not contribute substantially to this estimate of calcification rate. Calcification rates on other reefs can vary by a couple of orders of magnitude but the calcification rate estimated for the Bermuda coral reef is at the lower end of the typical observed range for other reefs (~<2–40 g CaCO<sub>3</sub> m<sup>-2</sup> d<sup>-1</sup>; e.g., Kinsey, 1985; Pichon 1997; Gattuso et al., 1993, 1996, 1999; Barnes and Lazar, 1993; Yates and Halley, 2006; Silverman et al., 2007). The annual rate of calcification per unit area of the reef is estimated at Hog Reef to range between 0.5 and 1.2 kg CaCO<sub>3</sub> m<sup>-2</sup> year<sup>-1</sup>, slightly lower than the average calcification rate of 4 ± 0.7 kg CaCO<sub>3</sub> m<sup>-2</sup> year<sup>-1</sup> reported for other coral reefs (Kinsey, 1985). Benthic turf and fleshy macroalgae distributions were not directly measured at Hog Reef, but typically constitute <5–15% of the reef cover (MEP, 2006; [http://www.bios-mep.info/NEW%20site/Sub\\_Program\\_2c.htm](http://www.bios-mep.info/NEW%20site/Sub_Program_2c.htm)). The highest macroalgal biomass is typically observed coincident with the period of highest solar irradiance in June (Smith, S. R., personal communication), a seasonal feature typically observed on other reefs (Gattuso et al., 1997).

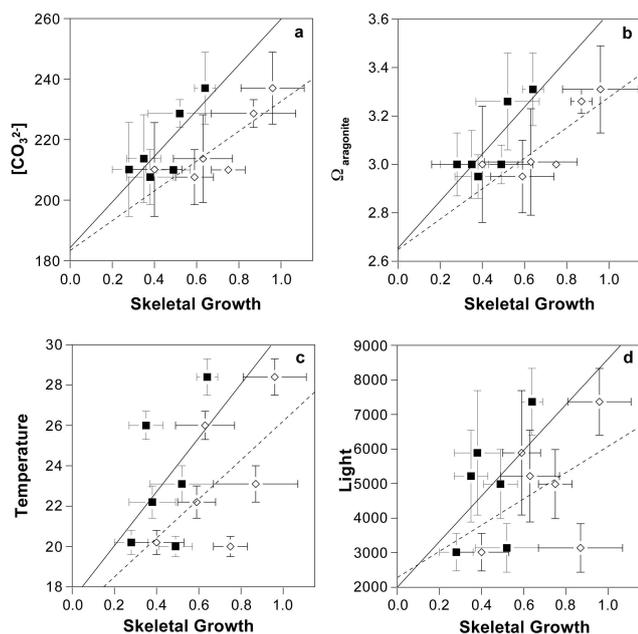
#### 4.2 Seasonal covariance of coral calcification and carbonate chemistry on the Bermuda coral reef

There are few datasets that can be used to test relationships between coral calcification and carbonate chemistry under natural conditions. Our results from the Bermuda coral reef indicate that calcification rates of *D. labyrinthiformis* at Hog Reef and Twin Breakers covaried seasonally with [CO<sub>3</sub><sup>2-</sup>] and Ω<sub>aragonite</sub>. Mean in situ skeletal growth rates had a

range of ~0.28–0.65 mg CaCO<sub>3</sub> g<sup>-1</sup> d<sup>-1</sup> while [CO<sub>3</sub><sup>2-</sup>] and Ω<sub>aragonite</sub> varied by ~40 μmoles kg<sup>-1</sup> and 0.4 respectively (Fig. 3). Despite a limited number of observations, in situ skeletal growth rates (either expressed as weight increase or per unit area) were well correlated with mean [CO<sub>3</sub><sup>2-</sup>] and Ω<sub>aragonite</sub> (Fig. 3a and b), with *r*<sup>2</sup> of ~0.68. Similar findings have been shown in the natural environment (Silverman et al., 2007, 2009) and in vitro experiments with other coral species (Marubini et al., 2003; Schneider and Erez, 2006).

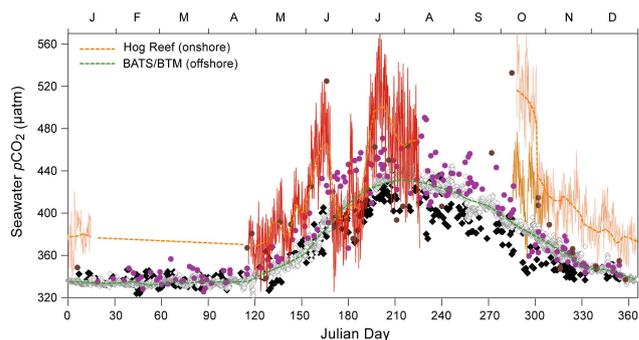
The correlation between in situ skeletal growth and other environmental factors were less statistically significant. For example, mean temperatures during each in situ skeletal growth measurement at Hog Reef were weakly correlated with rates of in situ skeletal growth (Fig. 3c). In the Eilat reef, coral community calcification is well correlated with temperature (Silverman et al., 2007), while in other reef systems, the highest seasonal rates of calcification have been observed a few degrees below the seasonal temperature maximum (e.g., Abramovitch-Gottlieb et al., 2003; Marshall and Clode, 2004). In Sect. 4.4, we show that net heterotrophy induced by other components of the reef ecosystem appears to suppress Ω<sub>aragonite</sub> and rates of coral calcification during periods of the summertime. As a result, in situ skeletal growth rates are weakly correlated with temperature on the Bermuda reef.

There was a poor correlation between in situ skeletal growth of *D. labyrinthiformis* and mean shortwave radiation (i.e., *Q<sub>sw</sub>*; Fig. 3c). This is perhaps surprising since other studies have shown a strong coupling between light and calcification (e.g., Gattuso and Jaubert, 1990; Marubini et al., 2003; Schneider and Erez, 2006). Short-term (<2 h) in vitro chamber experiments using *D. labyrinthiformis* colonies recovered from Hog Reef and acclimatized at BIOS, showed a strong coupling between light (~200–1400 μE m<sup>-2</sup> s<sup>-1</sup>) and zooxanthellae photosynthesis and respiration rates (as expressed as oxygen production or consumption). If *Q<sub>sw</sub>* is



**Fig. 3.** Relationship between in situ skeletal growth rate of *D. labyrinthiformis* (i.e., *G. diplorea*) at Hog Reef against mean  $[\text{CO}_3^{2-}]$ ,  $\Omega_{\text{aragonite}}$ , temperature and light conditions observed at Hog Reef. Skeletal growth rates are expressed either as  $\text{mg CaCO}_3 \text{ g}^{-1} \text{ d}^{-1}$  (black square) or as skeletal growth rate per unit surface area ( $\text{mg CaCO}_3 \text{ cm}^{-2} \text{ d}^{-1}$ ; open diamond). **(a)** Relationship between in situ skeletal growth rate of *D. labyrinthiformis* and average  $[\text{CO}_3^{2-}]$  (observed at Hog Reef during the concurrent skeletal growth rate measurement time period.) Regression statistics were:  $75.77x + 184.2$ ,  $r^2 = 0.68$  (skeletal growth rate per colony weight) and  $49.30x + 183.3$ ,  $r^2 = 0.69$  (skeletal growth rate per unit surface area). **(b)** Relationship between in situ skeletal growth rate of *D. labyrinthiformis* and average  $\Omega_{\text{aragonite}}$  observed at Hog Reef during the concurrent skeletal growth measurement time period. Regression statistics were:  $0.976x + 2.65$ ,  $r^2 = 0.68$  (skeletal growth rate per colony weight) and  $0.629x + 2.65$ ,  $r^2 = 0.68$  (skeletal growth rate per unit surface area). The 95% confidence levels for the zero skeletal growth intercept was 2.22–3.08 and 2.21–3.08, respectively. **(c)** Relationship between in situ skeletal growth rate of *D. labyrinthiformis* and temperature ( $^{\circ}\text{C}$ ) observed at Hog Reef during the concurrent skeletal growth measurement time period. Regression statistics were:  $13.44x + 17.36$ ,  $r^2 = 0.28$  (skeletal growth rate per colony weight) and  $9.655x + 16.56$ ,  $r^2 = 0.35$  (skeletal growth rate per unit surface area). **(d)** Relationship between in situ skeletal growth of *D. labyrinthiformis* and average light ( $\text{W m}^{-2}$ ) observed at Hog Reef during the concurrent skeletal growth measurement time period. Regression statistics were:  $6617.8x + 2001.4$ ,  $r^2 = 0.27$  (skeletal growth rate per colony weight) and  $3791.8x + 2281.1$ ,  $r^2 = 0.21$  (skeletal growth rate per unit surface area).

an appropriate proxy for coral photosynthesis, our in situ observations would suggest a weak coupling between coral photosynthesis and calcification. However, while  $Q_{\text{sw}}$  is a good proxy for the seasonally integrated mean light conditions at Hog Reef,  $Q_{\text{sw}}$  may not accurately reflect variability



**Fig. 4.** Annual composite and comparison of surface seawater  $p\text{CO}_2$  data ( $\mu\text{atm}$ ) collected over the last twelve years from the coral reef of Bermuda and offshore in the North Atlantic Ocean at BATS and the Bermuda Testbed Mooring (BTM). All seawater  $p\text{CO}_2$  datasets have been adjusted to the year 2006 using the long-term trend of  $+1.7 \mu\text{atm year}^{-1}$  observed at the BATS site in the North Atlantic Ocean from 1983–2006 (Bates, 2007). Coral reef seawater  $p\text{CO}_2$  datasets include: (1) surface seawater  $p\text{CO}_2$  from October 2002 to January 2003 collected hourly at Hog Reef using a CARIOCA buoy (red line); (2) surface seawater  $p\text{CO}_2$  from April 2002 to September 2003 hourly at Hog Reef using a CARIOCA buoy (peach line); (3) surface seawater  $p\text{CO}_2$  from October 1998 to November 1998 hourly at Hog Reef using a CARIOCA buoy (orange line) (Bates et al., 2001); (4) surface seawater  $p\text{CO}_2$  (brown closed circles) calculated from surface DIC and alkalinity samples collected at Hog Reef from July 2002 to November 2003; (5) daily mean surface seawater  $p\text{CO}_2$  (purple closed circle) collected along the southeastern terrace and rim coral reefs of the North Lagoon, Bermuda, from the R/V *Weatherbird II* during  $\sim 150$  cruises between 1994 and 1998. Offshore seawater  $p\text{CO}_2$  datasets include: (6) surface seawater  $p\text{CO}_2$  (grey open diamond) from November 2005 to December 2006 collected every 3 h at the BTM site [C. L. Sabine and N. R. Bates, unpub. data] and; (7) daily mean surface seawater  $p\text{CO}_2$  (black closed diamond) collected every 2 min at the BATS site from the R/V *Weatherbird II* during  $\sim 150$  cruises between 1994 and 1998 (Bates, 2007).

of in situ PAR over shorter time-scales. With limited data, we cannot statistically confirm either a strong coupling or uncoupling of light and calcification for corals at Hog Reef. Similar weak correlation between coral calcification and seasonal changes in shortwave radiation have been shown for other reefs primarily due to the seasonal lag of several months between peak solar input, and seawater temperatures and coral calcification (e.g., Silverman et al., 2007).

#### 4.3 Potential mechanisms coupling seawater carbonate chemistry and coral calcification

The field data collected from the Bermuda coral reef indicates that the highest rates of calcification occurred when  $[\text{CO}_3^{2-}]$  in the external reef environment was at seasonally high concentrations (while  $[\text{HCO}_3^-]$  was at seasonally low

values). However, it remains unclear why calcification in corals responds to changes of seawater carbonate chemistry in the external natural environment.

Early studies suggested that seawater  $\text{HCO}_3^-$  was taken by corals for calcification (Goreau, 1959), with active removal of  $\text{H}^+$  ions from the calcification site to facilitate alkalization of fluids in the coral calcicoblastic layer (e.g., McConnaughey, 1989a, b, 1997, 2004, McConnaughey and Whelan, 1997; Gattuso, 1999; McConnaughey and Cohen, 2004). If coral uptake of  $\text{HCO}_3^-$  is directly proportional to external seawater  $[\text{HCO}_3^-]$ , then it follows that calcification rates should be correlated to  $[\text{HCO}_3^-]$ . However, experimental studies (e.g., Langdon et al., 2000; Marubini et al., 2001) and field data from Hog Reef and other reefs (Silverman et al., 2007, 2009) indicates that calcification rates are strongly correlated with and proportional to  $[\text{CO}_3^{2-}]$ , and inversely correlated with  $[\text{HCO}_3^-]$  (i.e., decreasing calcification rate with increasing  $[\text{HCO}_3^-]$ ). As a potential solution to this conundrum, Marubini et al. (2001) suggested uptake of  $\text{CO}_3^{2-}$  in addition to  $\text{HCO}_3^-$  and, that the pH of the calcifying fluid (calicoblastic layer) would have to be proportionate to external seawater pH. In this scenario, if uptake of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  occurs in proportion to external conditions, external seawater carbonate chemistry can enhance or suppress calcification. For example, at higher external pH conditions (i.e., higher  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$ , and lower  $[\text{HCO}_3^-]$ ), the alkalization of the calcifying fluids would be enhanced by reduced energetic needs to actively remove  $\text{H}^+$  from the calcicoblastic layer produced by dissociation of  $\text{HCO}_3^-$  (or pump  $\text{H}^+$  against a stronger gradient of  $\text{H}^+$  outside the coral). This scenario implies energetic cost for maintaining suitable chemical conditions for calcification when seawater conditions may not be conducive for calcification (Cohen and Holcomb, 2009).

Does this solution agree with field data from Bermuda? At Hog Reef,  $[\text{CO}_3^{2-}]$  has a seasonal range of  $\sim 190\text{--}250 \mu\text{moles kg}^{-1}$  (Fig. 2d), while  $[\text{HCO}_3^-]$  has a range of  $\sim 1720\text{--}1870 \mu\text{moles kg}^{-1}$  (not shown). In summertime, during the highest observed rates of coral calcification, when  $[\text{CO}_3^{2-}]$  is at a seasonal maxima and  $[\text{HCO}_3^-]$  at a seasonal minima, the ratio of  $[\text{HCO}_3^-]:[\text{CO}_3^{2-}]$  is  $\sim 6.8:1$ . In contrast, in wintertime, during the lowest observed rates of coral calcification, when  $[\text{CO}_3^{2-}]$  is at a seasonal minima and  $[\text{HCO}_3^-]$  at a seasonal maxima, the ratio of  $[\text{HCO}_3^-]:[\text{CO}_3^{2-}]$  is  $\sim 9.8:1$ . Thus the ratio of  $[\text{HCO}_3^-]$  to  $[\text{CO}_3^{2-}]$  changes by almost 40% in the natural environment at Hog Reef. In the summertime, the low ratio of  $[\text{HCO}_3^-]$  to  $[\text{CO}_3^{2-}]$  may lessen the need for corals to actively remove  $\text{H}^+$  from the calcicoblastic layer (from the dissociation of  $\text{HCO}_3^-$ ), thereby facilitating alkalization of the calcicoblastic fluids and calcification. In contrast, during winter, the higher seawater proportion of  $[\text{HCO}_3^-]$  relative to  $[\text{CO}_3^{2-}]$ , may mean that there is a greater demand for active removal of  $\text{H}^+$  from the calcicoblastic layer.

Furthermore, with lower external seawater pH and greater  $[\text{H}^+]$ , increased amounts of energy may be required to pump  $\text{H}^+$  against this gradient. Higher energetic demands required to remove  $\text{H}^+$  as suggested by Cohen and Holcomb (2009), combined with lower energy production in winter due to reduced solar input, may make it more difficult for Bermuda corals to alkalize calcicoblastic fluids with lower calcification rates as a result.

If corals do actively take up both  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , changes in zooxanthellae photosynthesis could also enhance or suppress calcification. Since  $\text{HCO}_3^-$  (internally converted to  $\text{CO}_2$  by CA) is the source of inorganic carbon for photosynthesis, increased demand for  $\text{HCO}_3^-$  by increased zooxanthellae photosynthesis (in response to enhanced light conditions) should shift the ratio of  $[\text{HCO}_3^-]:[\text{CO}_3^{2-}]$  to lower values. This should further elevate pH, enhance alkalization, and  $\Omega_{\text{aragonite}}$  conditions in the calcicoblastic layer. Thus, as evidenced by higher calcification rates during summertime for the Bermuda coral reef, photosynthesis and favorable carbonate chemistry changes may act synergistically to enhance rates of coral calcification.

#### 4.4 The carbonate chemistry coral reef feedback (CREF) hypothesis

Seasonal changes in seawater carbonate chemistry of reef systems can be used to evaluate the net ecosystem metabolism (NEM) of the reef and the impact of benthic processes on water overlying the reef system (e.g., Chisholm and Barnes, 1991; Suzuki et al., 1995; Gattuso et al., 1996; Bates, 2002; Silverman et al., 2007; Langdon et al., 2010). Two processes dominate the net ecosystem metabolism of the reef, each with different influence on seawater  $p\text{CO}_2$  and other components of the seawater carbonate system. The first process relates to the balance of coral calcification and dissolution or net ecosystem calcification (NEC). Positive NEC values represent net calcification, while negative NEC values represent net dissolution. In general, calcification release about 0.6 mole of  $\text{CO}_2$  to the surrounding environment per mole of  $\text{CaCO}_3$  precipitated in coral reef systems (Kinsey, 1985; Frankignoulle et al., 1994; Lerman and Mackenzie, 2005). When rates of calcification exceed dissolution (i.e., NEC is positive), the uptake of inorganic carbon into the coral skeleton as  $\text{CaCO}_3$  decreases DIC and TA in a ratio of 1:2, with the net result of  $\text{CO}_2$  production and increase in seawater  $p\text{CO}_2$ . Thus, NEC on most coral reefs results in net production of  $\text{CO}_2$  (Gattuso et al., 1999). In many coral reef systems, higher reef seawater  $p\text{CO}_2$  values compared to offshore conditions have been observed (e.g., Kawahata et al., 2000; Suzuki and Kawahata, 2003), confirming that coral reef metabolism generally acts to increase seawater  $p\text{CO}_2$ . Similar findings were reported from previous short-term observations at Hog Reef (Bates et al., 2001), and across the SE sector of the Bermuda platform (Bates, 2002), and in this paper (Fig. 4).

The second process relates to the balance of photosynthesis and respiration or net ecosystem production (NEP). On a typical coral reef, NEP is dominated by coral/zooxanthellae respiration/photosynthesis, and benthic macroalgal photosynthesis and respiration. In net autotrophic systems, where the rate of photosynthesis or gross primary production ( $P$ ) is greater than rate of respiration ( $R$ ), NEP values are negative and the uptake of  $\text{CO}_2$  decreases DIC only (and seawater  $p\text{CO}_2$  also) and TA remains unchanged (minor changes do occur owing to the uptake of nutrients). In net heterotrophic systems, where  $P < R$ , NEP values are positive,  $\text{CO}_2$  is produced and DIC and seawater  $p\text{CO}_2$  increase over time. In many reef systems, net ecosystem production (NEP) is near zero despite high rates of gross primary production (e.g., Crossland et al., 1991; Gattuso et al., 1999; Ducklow and McAllister, 2004).

In a previous study, Bates (2002) used monthly differences of temperature corrected seawater  $p\text{CO}_2$  between the Bermuda coral reef and offshore values to estimate net productivity (i.e., equivalent to NEP in this study) rates over the annual cycle. In the absence of contemporaneous in situ coral calcification rates, constant rates of calcification over the annual cycle were assumed and used to estimate net productivity. This previous analysis indicated that the Bermuda coral reef was net autotrophic over most of the year (i.e., NEP rates were negative while net heterotrophic conditions occurred in August and September (i.e., Fig. 3 in Bates, 2002).

In this study, NEC and NEP rates for the Bermuda reef were determined using mass balance methods following similar methods to other studies (e.g., Gattuso et al., 1996; Bates, 2002; Silverman et al., 2007). In this approach, observed differences between onshore and offshore seawater carbonate chemistry are used to quantify how reef processes (i.e., calcification, dissolution, photosynthesis and respiration) modify the TA and DIC content of waters overlying the reef, thereby determining the NEM of the reef system. Contemporaneous DIC and TA data from the BATS site (Bates, 2007) and Hog Reef were used for offshore and onshore seawater carbonate chemistry conditions, and both TA and DIC datasets were corrected to a constant salinity of 36.6 to account for local evaporation/precipitation differences between onshore and offshore.

In a mass balance sense, if the rate of NEC (i.e.,  $\text{NEC}_{\text{reef}}$ ) is positive and NEP of the reef (i.e.,  $\text{NEP}_{\text{reef}}$ ) is zero, waters modified by net reef metabolism will gain  $\text{CO}_2$  (i.e., increase seawater  $p\text{CO}_2$ ) compared to offshore conditions due to the production of  $\text{CO}_2$  from calcification and formation of  $\text{CaCO}_3$  (DIC and TA will decrease). If  $\text{NEC}_{\text{reef}}$  is zero and  $\text{NEP}_{\text{reef}}$  negative (i.e., net autotrophic), waters modified by net reef metabolism will lose  $\text{CO}_2$  (i.e., decrease seawater  $p\text{CO}_2$ ) compared to offshore conditions due to uptake of  $\text{CO}_2$  from photosynthesis (i.e., photosynthesis > respiration; DIC will decrease while TA will increase marginally).

#### 4.4.1 Calculation of reef NEC and NEP rates

The calculation of rate of NEC (i.e.,  $\text{NEC}_{\text{reef}}$ ) is based on the alkalinity anomaly-water residence time technique (Smith and Key, 1975; Kinsey, 1978; Chisholm and Gattuso, 1991; Langdon et al., 2010) that has been used previously for estimating in situ rates of calcification for reef systems (Gattuso et al., 1996; Silverman et al., 2007). In the method, differences between offshore and onshore nTA are assumed to result from the balance of reef calcification and dissolution (i.e., NEC) that changes the TA content of waters overlying the reef (i.e.,  $\Delta\text{nTA}^{\text{NEC}}$ ). Thus, seasonal values for  $\Delta\text{nTA}^{\text{NEC}}$  are determined using the observed difference in salinity normalized TA (i.e., nTA) between offshore and onshore ( $\text{nTA}_{\text{offshore}} - \text{TA}_{\text{onshore}}$ ) using data from BATS and Hog Reef (Table 3). The  $\text{NEC}_{\text{reef}}$  rate is then calculated by scaling the values of  $\Delta\text{TA}^{\text{NEC}}$  to an appropriate water depth ( $Z$ ) and water residence time ( $\tau$ ) for the reef. Thus, following the method of Langdon et al. (2010):

$$\text{NEC}_{\text{reef}} = \Delta\text{nTA}^{\text{NEC}} = -0.5(\text{nTA}_{\text{offshore}} - \text{TA}_{\text{onshore}}) \cdot (\rho Z) / \tau \quad (9)$$

where  $\rho$  is the density of seawater. Here, an average water depth of 6 m and water residence time of 2 days is used in the calculations of  $\text{NEC}_{\text{reef}}$  and  $\text{NEP}_{\text{reef}}$  rates with scaling issues, caveats and uncertainties discussed further. Rates of  $\text{NEC}_{\text{reef}}$  are expressed in units of  $\text{mmoles CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$  (or expressed as  $\text{g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$  using a molecular weight of 100.09). Secondly, the change in DIC for waters overlying the reef due to NEC (i.e.,  $\Delta\text{nDIC}^{\text{NEC}}$ ) is calculated using a TA:DIC ratio of 2:1). Thus:

$$\Delta\text{nDIC}^{\text{NEC}} = \Delta\text{nTA}^{\text{NEC}} / 2 \quad (10)$$

The rate of NEP (i.e.,  $\text{NEP}_{\text{reef}}$ ) for the reef is calculated by mass balance given that NEP imparts a change in the DIC content of waters overlying the reef (with photosynthesis and respiration causing no change in TA). The rate of  $\text{NEP}_{\text{reef}}$  is thus calculated by mass balance using the observed differences in nDIC between onshore and offshore (i.e.,  $\Delta\text{nDIC}_{\text{offshore-onshore}}$ ; Table 3) and  $\Delta\text{nDIC}^{\text{NEC}}$ :

$$\text{NEP}_{\text{reef}} = \Delta\text{nDIC}^{\text{NEP}} = \Delta\text{nDIC}_{\text{offshore-onshore}} - \Delta\text{nDIC}^{\text{NEC}} \quad (11)$$

$\text{NEP}_{\text{reef}}$  is then expressed in units of  $\text{mmoles C m}^{-2} \text{ d}^{-1}$  (or expressed as  $\text{g C m}^{-2} \text{ d}^{-1}$  using a molecular weight of 12).

#### 4.4.2 Scaling of NEC and NEP rates

In the above method, the rates of  $\text{NEC}_{\text{reef}}$  and  $\text{NEP}_{\text{reef}}$  are scaled from observed seasonal changes in  $\Delta\text{nTA}_{\text{offshore-onshore}}$  and  $\Delta\text{nDIC}_{\text{offshore-onshore}}$  as a function of water depth and water residence time. Based on observations/models (Johnson, 2003; R. J. Johnson tide/wind mixing model of the Bermuda reef), an average water depth

**Table 3.** Hog Reef TA and DIC data compiled into a composite year. Julian day of sampling is shown along with original sampling date, sea surface temperature (SST), salinity (S), DIC and TA data (both  $\mu\text{moles kg}^{-1}$ ). These data are used in Sect. 4.4 to calculate rates of  $\text{NEP}_{\text{reef}}$  and  $\text{NEC}_{\text{reef}}$  using  $\Delta n\text{TA}_{\text{offshore-onshore}}$  and  $\Delta n\text{DIC}_{\text{offshore-onshore}}$  values.  $\Delta n\text{TA}_{\text{offshore-onshore}}$  and  $\Delta n\text{DIC}_{\text{offshore-onshore}}$  are calculated from  $n\text{TA}$  and  $n\text{DIC}$  (adjusted to a salinity of 36.6) using contemporaneous Hog Reef (onshore) and BATS data (offshore).

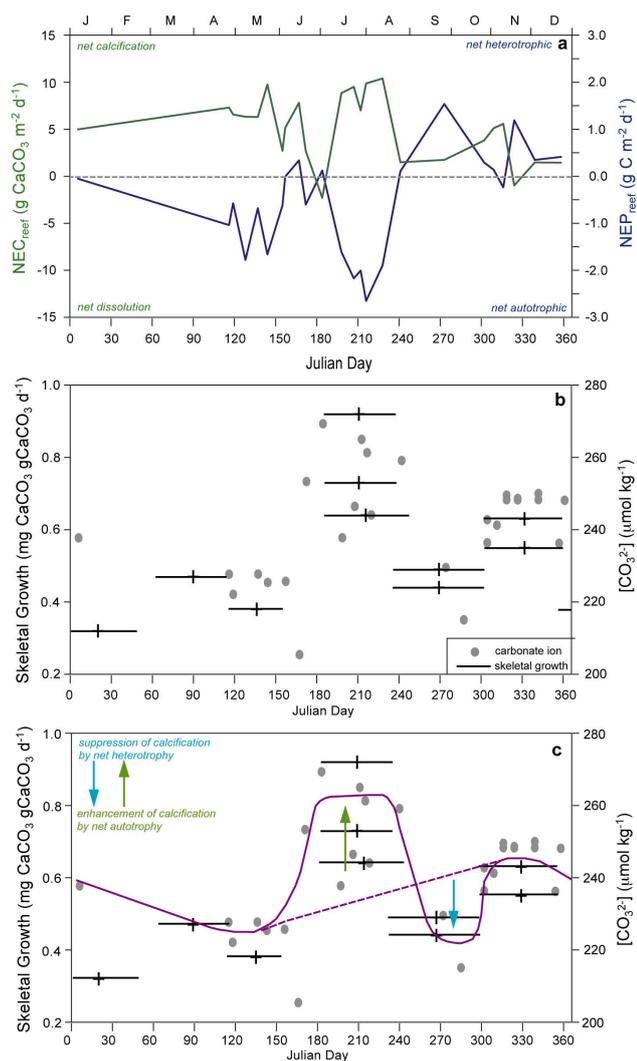
Julian Day	Original Sampling Date	SST	S	TA	DIC	$\Delta n\text{TA}_{\text{offshore-onshore}}$	$\Delta n\text{DIC}_{\text{offshore-onshore}}$
6	6 Jan 2003	20.71	36.815	2372.3	2053.8	33.3	-6.8
116	25 Apr 2003	20.79	36.815	2353.4	2048.8	48.7	16.7
119	28 Apr 2003	20.97	36.627	2346.3	2050.1	43.7	5.0
128	7 May 2003	22.13	36.677	2353.0	2020.1	42.2	38.8
137	16 May 2003	22.19	36.712	2355.4	2052.6	42.0	8.4
144	23 May 2003	22.50	36.616	2326.2	2025.7	65.0	29.9
155	3 Jun 2003	23.55	36.564	2363.0	2027.5	18.1	12.7
157	5 Jun 2003	24.03	36.564	2346.7	2048.6	34.4	-8.4
167	15 Jun 2003	25.80	36.642	2333.9	2067.0	52.1	-22.4
172	20 Jun 2003	25.63	36.619	2366.7	2030.9	17.8	12.3
184	2 Jul 2003	26.49	36.589	2400.3	2044.2	-15.2	0.4
198	16 Jul 2003	28.36	36.671	2331.3	2019.0	59.0	30.1
207	25 Jul 2003	28.76	36.899	2341.4	2017.1	63.4	44.5
212	30 Jul 2003	28.96	36.516	2330.3	1979.4	46.7	44.0
216	3 Aug 2003	29.42	36.608	2317.1	1971.2	65.8	57.2
228	15 Aug 2003	30.00	36.614	2314.0	1993.4	69.3	35.3
241	28 Aug 2003	28.31	36.161	2351.9	2010.6	9.9	-5.5
273	29 Sep 2003	26.50	36.135	2346.0	2045.5	11.6	-45.6
302	29 Oct 2002	25.42	36.524	2359.6	2038.7	25.4	-14.5
309	5 Nov 2002	24.27	36.591	2353.5	2033.1	34.0	-2.0
316	12 Nov 2002	22.82	36.760	2361.2	2027.2	37.2	13.3
324	20 Nov 2002	23.60	36.253	2371.9	2042.2	-6.5	-30.0
339	5 Dec 2002	22.38	36.506	2378.8	2045.3	9.8	-12.1
358	24 Dec 2002	21.44	36.515	2379.5	2047.5	9.6	-13.9

of 6 m and water residence time of 2 days (i.e.,  $Z$  and  $\tau$  in Eq. 9) were used in the calculations of  $\text{NEC}_{\text{reef}}$  and  $\text{NEP}_{\text{reef}}$  rates (Fig. 5). It is important to recognize that this mass balance approach does not provide absolute values for  $\text{NEC}_{\text{reef}}$  and  $\text{NEP}_{\text{reef}}$ , but rather, provides a seasonal view of changes in the balance of calcification/dissolution, and net heterotrophy/net autotrophy. As a sensitivity test, the annual rates of  $\text{NEC}_{\text{reef}}$  and  $\text{NEP}_{\text{reef}}$  were plotted in Fig. 6 for a range of  $Z$  and  $\tau$  values that are within observed ranges for the Bermuda rim reef (e.g., 4–8 m water depth and 1–4 day water residence time). If the  $Z$  term (i.e., water depth) in Eq. (9) is increased, rates of  $\text{NEC}_{\text{reef}}$  and  $\text{NEP}_{\text{reef}}$  also increase (Fig. 6) since reef rate processes (e.g., calcification) have to be higher for equivalency to observed  $\Delta n\text{TA}_{\text{offshore-onshore}}$  and  $\Delta n\text{DIC}_{\text{offshore-onshore}}$  data. In contrast, longer water residence times (i.e.,  $\tau$  in Eq. 9) reduce  $\text{NEC}_{\text{reef}}$  and  $\text{NEP}_{\text{reef}}$  rates (Fig. 6). The strong summertime net autotrophy and late summertime net heterotrophy shown in Fig. 5 and discussed later occurs for all proscribed values of  $Z$  and  $\tau$  values shown in Fig. 6.

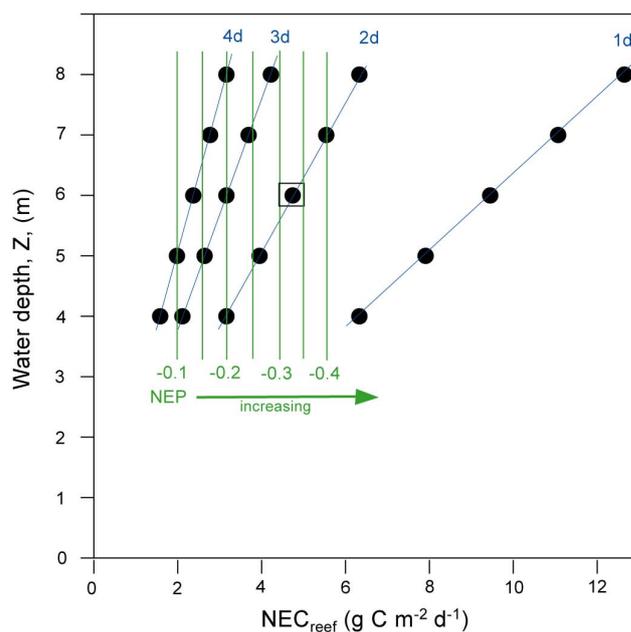
#### 4.4.3 Further caveats and uncertainties for estimating rates of $\text{NEC}_{\text{reef}}$ and $\text{NEP}_{\text{reef}}$

There are further caveats and uncertainties using the alkalinity anomaly-water residence time technique. Firstly, it should be noted that onshore and offshore seawater carbonate chemistry were not typically sampled on the same day, but, we have chosen data sampled as closely in time to estimate onshore-offshore differences. Secondly, seawater carbonate chemistry data were not corrected for long-term changes observed at the BATS due to the oceanic uptake of anthropogenic  $\text{CO}_2$  (Bates, 2007; Bates and Peters, 2007) since the observations occurred over a 16 month period. These long-term changes are very minor compared to the observed changes in seawater carbonate chemistry over the timeframe of the study. It is also assumed that the uptake of nitrate by coral photosynthesis does not contribute significantly to changes in  $n\text{TA}$ .

In addition, as argued previously by Bates (2002), benthic coral calcification/dissolution, and coral/macroalgae photosynthesis/respiration are the dominant processes influencing NEM for the Bermuda reef, with air-sea  $\text{CO}_2$  gas exchange, pelagic phytoplankton primary production



**Fig. 5.** (a) Annual composite of rates of  $NEC_{reef}$  ( $g\ CaCO_3\ m^{-2}\ d^{-1}$ ; green line) and  $NEP_{reef}$  ( $g\ C\ m^{-2}\ d^{-1}$ ; blue line) for the Bermuda reef using seawater TA and DIC data from Hog Reef and BATS, and the alkalinity anomaly-water mass residence technique. Positive  $NEC_{reef}$  values represent net calcification, and negative values represent net dissolution, with the zero line denote by grey dashed line. Positive  $NEP_{reef}$  values represent net heterotrophy, and negative values represent net autotrophy, with the zero line denote by grey dashed line. (b) Annual composite and comparison of surface seawater  $[CO_3^{2-}]$  data ( $\mu\text{moles}\ kg^{-1}$ ; gray circles) and skeletal growth rates (i.e.,  $G_{diploria}$ ;  $mg\ CaCO_3\ g^{-1}\ d^{-1}$ ). (c) Repeat of panel b showing the CREF hypothesis superimposed on Hog Reef data. In early summer, enhancement of  $[CO_3^{2-}]$  and calcification during June and July [green arrow] occurs due to negative NEP. In late summer, suppression during September and October on the Bermuda reef due to positive NEP [blue arrow]. The dashed line illustrates the hypothesized  $[CO_3^{2-}]$  in absence of the feedback on carbonate chemistry due to seasonal changes in NEP. (d) Seasonal composite of alkalinity difference (i.e.,  $\Delta nTA_{offshore-onshore}$ ) between Hog Reef and the BATS site for the periods 2002–2003 (square symbol) and 2005–2006 (circle symbol).

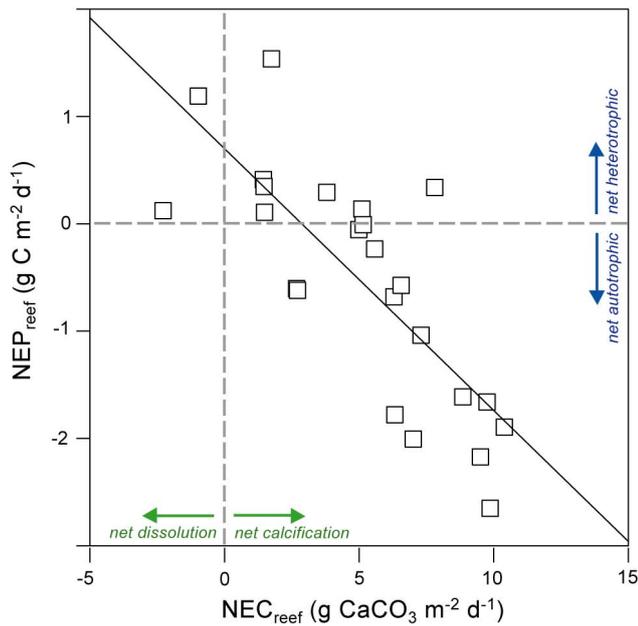


**Fig. 6.** Annual rates of  $NEC_{reef}$  ( $g\ CaCO_3\ m^{-2}\ d^{-1}$ ) plotted against water depth (m) using the alkalinity anomaly-water mass residence technique, and mass balance. Different water residence times ( $\tau$ ) of 1 to 4 days are plotted with isolines in blue.  $NEP_{reef}$  ( $g\ C\ m^{-2}\ d^{-1}$ ; green lines) are superimposed as isolines in green with negative values indicating net autotrophy. The most appropriate water depth of 6 m and residence time of 2 days for the Bermuda reef is shown by the square.

and vertical mixing processes having minor impact on the carbonate chemistry of waters resident for a short time ( $<2$  days) on the rim reefs of Bermuda (Bates, 2002). The NEC for the reef (i.e.,  $NEC_{reef}$ ) includes contributions from other calcifiers such as coralline red algae, green algae, echinoderms, bryozoans, foraminifera and bivalves. In the absence of data for other calcifiers, we assume that their contribution is minor and that corals are the dominant calcifier on the Bermuda coral reef with  $NEC_{reef} \approx NEC_{coral}$ .

#### 4.4.4 Seasonal rates of $NEC_{reef}$ and $NEP_{reef}$

The alkalinity anomaly-water residence time technique used here indicates that  $NEC_{reef}$  seasonally ranged between  $-2.2$  to  $10.4\ g\ CaCO_3\ m^{-2}\ d^{-1}$  (Fig. 5a) with highest net calcification in winter (January–April) and mid-summer (July–August) and lower net calcification in late-summer to fall (September–December). For comparison, as shown in section 4.1, NEC rates scaled up to the Bermuda reef using observed skeletal growth rates for *D. labyrinthiformis* (i.e.,  $G_{diploria}$ ) and a 50% coral cover would be in the range of  $4.5$  to  $11.1\ g\ CaCO_3\ m^{-2}\ d^{-1}$ . In addition, in situ observations ( $G_{diploria}$ ) and mass balance approaches (i.e.,  $NEC_{reef}$ ), both determined independently of each other, show similar seasonal patterns (compare Fig. 5a and b). For most of the



**Fig. 7.** Rates of  $NEC_{\text{reef}}$  ( $\text{g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$ ) against  $NEP_{\text{reef}}$  ( $\text{g C m}^{-2} \text{ d}^{-1}$ ) using onshore and offshore seawater TA and DIC data from Hog Reef and BATS.  $NEC_{\text{reef}}$  and  $NEP_{\text{reef}}$  data are shown in Fig. 5a using seawater TA and DIC data, and  $\Delta nTA_{\text{offshore-onshore}}$  and  $\Delta nDIC_{\text{offshore-onshore}}$  data shown in Table 3. The regression statistics for the line are:  $-0.244x + 0.700$ ,  $r^2 = 0.607$ . Arrows indicates direction of net autotrophy (i.e.,  $-NEP_{\text{reef}}$ ), net heterotrophy ( $+NEP_{\text{reef}}$ ), net calcification (i.e.,  $+NEC_{\text{reef}}$ ) and net dissolution (i.e.,  $-NEC_{\text{reef}}$ ). For example, the upper left quadrant denotes conditions on the reef with net heterotrophy and net dissolution.

year,  $NEC_{\text{reef}}$  rates are generally positive (i.e., calcification > dissolution) with rates of net calcification similar to other reefs (e.g., Kinsey, 1985; Pichon 1997; Gattuso et al., 1993, 1996, 1999; Barnes and Lazar, 1993; Yates and Halley, 2006; Silverman et al., 2007). However, negative  $NEC_{\text{reef}}$  values were occasionally observed suggesting that the reef may experience brief periods of net dissolution.

The alkalinity anomaly-water residence time technique also reveals seasonal changes in net reef metabolism and shifts between net autotrophy and heterotrophy for the Bermuda coral reef ecosystem (Fig. 5a). Rates of  $NEP_{\text{reef}}$  seasonally ranged between  $\sim -2.8$  to  $+1.5 \text{ g C m}^{-2} \text{ d}^{-1}$ . This compares to early estimates for NEP of other reefs that ranged from  $\sim -0.6$  to  $+0.6 \text{ g C m}^{-2} \text{ d}^{-1}$  (Kinsey, 1985; Andersson et al., 2005). Over relatively short-timescales, Gattuso et al. (1996) showed that the Moorea and Yonge reefs were net autotrophic with ranges of  $-0.4$  to  $-5.8 \text{ g C m}^{-2} \text{ d}^{-1}$ . More recently, Silverman et al., 2007 showed that the Eilat reef was predominantly net autotrophic (up to  $-2.2 \text{ g C m}^{-2} \text{ d}^{-1}$ ) over the 1997–2002 period, but also occasionally net heterotrophic ( $+0.5 \text{ g C m}^{-2} \text{ d}^{-1}$ ).

In general,  $NEP_{\text{reef}}$  rates were negative over most of the

year indicating net autotrophic status of the reef, with rates of photosynthesis greater than respiration. In the summer (July/August) and fall (November–January) periods,  $NEP_{\text{reef}}$  rates were negative indicative of net autotrophy. However, in late summer (September/October),  $NEP_{\text{reef}}$  rates were strongly positive, indicative of net heterotrophic conditions that generate  $\text{CO}_2$ , similar to previous findings of Bates (2002). These seasonal patterns suggest that  $\text{CO}_2$  is taken up by the reef system in early summer and fall periods, while  $\text{CO}_2$  is released from net reef metabolism to waters overlying the reef during the late summer.

The seasonal changes in carbonate chemistry,  $NEC_{\text{reef}}$ , and  $NEP_{\text{reef}}$  are evidence for a feedback between seawater carbonate chemistry and reef metabolism that enhances or suppresses coral calcification. As shown in Fig. 5, the highest rates of net calcification (i.e.,  $+NEC_{\text{reef}}$  values) generally occur during periods when rates of net autotrophy are at their highest (i.e.,  $-NEP_{\text{reef}}$ ). We term this feedback as a seasonal carbonate chemistry coral reef ecosystem feedback (CREF). In this scenario, in early summer, when macroalgal biomass is at its maxima on the Bermuda reef, strongly negative  $NEP_{\text{reef}}$  indicates net uptake of  $\text{CO}_2$  into the benthic biomass (i.e., macroalgae and coral zooxanthellae), which in turn increases the  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  of waters resident on the reef. Thus, early summer net autotrophy enhances carbonate chemistry conditions favourable for calcification (evidenced by high rates in situ skeletal growth; Fig. 5c and high rates of net calcification,  $NEC_{\text{reef}}$ , Fig. 5a). Similar seasonal enhancement of surface layer  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  have been observed elsewhere as response to pelagic phytoplankton primary production and strongly net autotrophic conditions (Feely et al., 1988; Bates et al., 2009). In addition, a diurnal model of the enhancement and suppression of  $[\text{CO}_3^{2-}]$  and coral calcification by photosynthesis and respiration, respectively, has been shown for the Shiraho Reef by Suzuki et al. (1995) using one daytime and one nighttime set of in situ observations for validation of the model. In our study, although there are caveats and uncertainties in using mass balance models, the  $NEP_{\text{reef}}$  values for spring-summer net autotrophy suggest that in addition to coral metabolism, other components of the reef system (i.e., macroalgae photosynthesis) contributed to net autotrophy and enhancement of  $[\text{CO}_3^{2-}]$ ,  $\Omega_{\text{aragonite}}$ , and  $NEC_{\text{reef}}$ .

In contrast to the early summer condition,  $NEP$  rates shift in late summer to positive values indicating a change from net autotrophy to net heterotrophic conditions. Release of  $\text{CO}_2$  in late summer suppresses  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  which in turn appears to suppress coral calcification rates (Fig. 5b and c). During this period, benthic macroalgal biomass typically decreases from a seasonal maxima in early summer (S. R. Smith, unpublished data). Net heterotrophic conditions in late summer likely result from a combination of factors, such as reduction in zooxanthellae photosynthesis rates, and remineralization of organic matter produced from the earlier benthic macroalgal production in early summer. Thus,

late summer net heterotrophy and release of  $\text{CO}_2$  appears to depress carbonate chemistry conditions favourable for calcification (evidenced by low rates in situ skeletal growth; Fig. 5c and low rates of net calcification,  $\text{NEC}_{\text{reef}}$ , Fig. 5a). It is likely that other components of the reef system (i.e., macroalgae respiration) contributed to net heterotrophy and suppression of  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$ . It may also be that late summer macroalgal respiration and entrainment of respiratory  $\text{CO}_2$  from below the mixed layer due to the breakdown of the warm, shallow thermocline through mixing induced by cooling and storms act to increase seawater  $p\text{CO}_2$  and decrease  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$ . The subsequent seasonal rebound in  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  conditions and in situ skeletal growth rates during the fall is associated with a return to net autotrophic conditions. This perhaps reflects a combination of exhaustion of benthic macroalgal organic matter as a fuel for remineralization to  $\text{CO}_2$  and dilution effects as mixing of reef and offshore waters become more vigorous in the fall due to higher windspeeds and weather frontal passages as observed at the BATS site (Bates, 2007). Since the Bermuda coral reef is a high-latitude reef that experiences strong seasonality in  $[\text{CO}_3^{2-}]$ ,  $\Omega_{\text{aragonite}}$  and other environmental conditions (e.g., light, temperature) compared to tropical reef counterparts, we expect that the CREF mechanism would be attenuated in tropical reefs, and not as strongly manifested as shown for the Bermuda reef.

#### 4.5 Ocean acidification, future seasonal decalcification and critical $[\text{CO}_3^{2-}]$ and $\Omega_{\text{aragonite}}$ thresholds of the Bermuda coral reef

There is growing evidence from experimental and modeling studies that ocean acidification and decreasing  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  will negatively affect marine calcifiers and ecosystems, but relatively little evidence exists from studies of the natural environment. For the Bermuda reef, we show that rates of calcification for *D. labyrinthiformis* were strongly correlated with  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$ . Ocean acidification and the gradual decline of  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  should have impacted coral calcification in the past. Historical records of coral calcification on tropical reefs show a decline over the recent past (e.g., Wilkinson, 2000; Edmunds, 2007; Edmunds and Elahi, 2007; Cooper et al., 2008; De'ath et al., 2009). In Bermuda, calcification rates of mature colonies of *D. labyrinthiformis* sampled at Hog Reef have also been reconstructed using coral skeletal density analyses (A. Cohen and N. Jacowski, unpub. data; Cohen et al., 2004). Such historical records show that skeletal density for *D. labyrinthiformis* has declined from a high of  $4.5 \text{ g cm}^{-3} \text{ year}^{-1}$  in 1959 to a low of  $3 \text{ g cm}^{-3} \text{ year}^{-1}$  in 1999, a change of  $1.5 \text{ g cm}^{-3} \text{ year}^{-1}$ , or decrease of  $\sim 33\%$ . At the BATS site offshore from the island of Bermuda, over the last 25 years, the observed annual rate of  $[\text{CO}_3^{2-}]$  decrease due to the oceanic uptake of anthropogenic  $\text{CO}_2$  was  $0.50 \pm 0.03 \mu\text{moles kg}^{-1} \text{ year}^{-1}$  (Bates, 2007; Bates and Pe-

ters, 2007). If the rate of  $[\text{CO}_3^{2-}]$  decrease is applied to the observed in situ correlation between skeletal growth of *D. labyrinthiformis* and  $[\text{CO}_3^{2-}]$  at Hog Reef (Fig. 3a), a  $\sim 37\%$  decrease in calcification would be predicted for the 1959–1999 period. Since these assessments are based on the same coral species, but using very different approaches, there seems to be strong evidence that ocean acidification has significantly decreased calcification rates on the Bermuda coral reef over the recent past.

We can also estimate the decrease in coral calcification due to ocean acidification from the pre-industrial period to present. At the BATS site, the observed  $[\text{CO}_3^{2-}]$  decrease of  $0.50 \pm 0.03 \mu\text{moles kg}^{-1} \text{ year}^{-1}$  is accompanied by an observed increase in salinity normalized DIC of  $0.80 \pm 0.06 \mu\text{moles kg}^{-1} \text{ year}^{-1}$  (Bates, 2007; see his Table 2). In the subtropical gyre of the North Atlantic, the increase in DIC due to uptake of anthropogenic  $\text{CO}_2$  is estimated at  $\sim 60 \mu\text{moles kg}^{-1}$  (Sabine et al., 2004). Given the ratios of observed  $\text{DIC}/[\text{CO}_3^{2-}]$  change, we estimate that the mean  $[\text{CO}_3^{2-}]$  was  $\sim 37.5 \mu\text{moles kg}^{-1}$  higher in pre-industrial times compared to the 2002–2003 period of observations at Hog Reef. Since the mean annual skeletal growth of *D. labyrinthiformis* observed at Hog Reef was  $0.47 \text{ mg CaCO}_3 \text{ g}^{-1} \text{ d}^{-1}$ , the application of the skeletal growth/ $[\text{CO}_3^{2-}]$  correlation shown in Fig. 3 gives a hindcast estimate of mean annual skeletal growth of  $0.97 \text{ mg CaCO}_3 \text{ g}^{-1} \text{ d}^{-1}$  in the pre-industrial period (with a range of  $0.78\text{--}1.15 \text{ mg CaCO}_3 \text{ g}^{-1} \text{ d}^{-1}$ ). Thus, our results suggest that coral calcification rates (for *D. labyrinthiformis* at least) at Hog Reef have declined by 52% compared to the pre-industrial period as a result of changes in seawater carbonate chemistry.

The future impact of ocean acidification on coral calcification on the Bermuda reef also appears to be negative. Based on a linear extrapolation, our in situ data suggests that the calcification rate of *D. labyrinthiformis* would reach zero at  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  thresholds of  $\sim 184 \mu\text{moles kg}^{-1}$  and 2.65, respectively (for both skeletal growth normalized to colony weight or colony surface area; Fig. 3). The  $\Omega_{\text{aragonite}}$  threshold has a range of 2.22–3.08 at the 95% confidence level so some caution should be advised proscribing definitive thresholds. Furthermore, the dependence of community calcification on  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  may not be linear, but rather based on a second or higher order relationship resulting in a weaker dependence closer to the critical threshold (Andersson et al., 2009). Nonetheless, with these caveats in mind, due to lower annual mean surface seawater  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  in Bermuda compared to more tropical regions, the Bermuda reef should experience critical threshold values earlier than its tropical reef ecosystem counterparts in response to future acidification of the oceans. Given that the lowest observed  $[\text{CO}_3^{2-}]$  on the Bermuda coral reef in 2002–2003 was  $\sim 190 \mu\text{moles kg}^{-1}$  during winter, and assuming that the rate of  $[\text{CO}_3^{2-}]$  decrease

(i.e.,  $0.50 \pm 0.03 \mu\text{moles kg}^{-1} \text{ year}^{-1}$ ) continues linearly in the near-future (Bindoff et al., 2007), we anticipate that the Bermuda coral reef should experience seasonal periods of zero calcification rates (i.e.,  $\text{NEC}_{\text{reef}} = 0$ ) within the next decade. Silverman et al. (2007) suggest that decalcification of coral reefs occurs when the gross calcification rate is equal to or less than 20% of the pre-industrial calcification rate. Given our observations of skeletal growth rates of  $\sim 0.28\text{--}0.65 \text{ mg CaCO}_3 \text{ g}^{-1} \text{ d}^{-1}$  for *D. labyrinthiformis* colonies, the Bermuda reef is currently about 30% of the mean pre-industrial calcification rate (i.e.,  $0.97 \text{ mg CaCO}_3 \text{ g}^{-1} \text{ d}^{-1}$ ). During wintertime, NEC is close to zero, a condition where dissolution and calcification are nearly in balance. Salinity normalized alkalinity data from Hog Reef (2002–2003) also exhibits close to zero difference between onshore and offshore values in the wintertime and during the late summer when net heterotrophy on the reef suppresses  $\Omega$  and calcification. This suggests that the threshold for when  $\text{NEC}_{\text{reef}}$  equals zero may already be occurring seasonally (2005–2006 data from Hog Reef also shows  $\text{NEC}_{\text{reef}}$  values close to zero or negative values indicating net dissolution; N. R. Bates and A. J. Andersson, unpublished data). Thus for the Bermuda coral reef, there are periods when the balance of calcification (from corals and other calcifiers such as coralline algae) and dissolution are equal, with the likelihood of net decalcification going forward in time as shown experimentally for reef mesocosms (Andersson et al., 2009). A potentially ameliorating process, as discussed earlier in Sect. 4.4, may be that net autotrophy of the reef during winter and spring (as part of the carbonate chemistry coral reef ecosystem feedback) which enhances  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  may delay the onset of zero NEC or decalcification going forward.

In the near-future, the above scenarios predict that the Bermuda coral reef will experience seasonal decalcification for increasing periods of the year. Given that the Bermuda coral reef experiences a maximum  $[\text{CO}_3^{2-}]$  seasonality of  $\sim 60 \mu\text{moles kg}^{-1}$ , we might expect that the reef system will experience seasonal decalcification for a further 100–140 years, if the long-term trend of  $[\text{CO}_3^{2-}]$  reduction continues under IPCC assessments of future anthropogenic  $\text{CO}_2$  release. During this period, we anticipate that suitable conditions for corals and other organisms to calcify will decrease progressively going forward in time. In addition, seasonal decalcification will impact such processes as dissolution of the framework structure of the reef and settlement of juvenile corals. This impact is difficult to predict, but most likely negative. In the next century, carbonate saturation states will transition into conditions that no longer facilitate coral reef calcification. As discussed earlier, if anthropogenic  $\text{CO}_2$  emissions continue to accelerate, this transition will occur earlier in time. Due to the seasonality of carbonate chemistry on the Bermuda coral reef, the critical thresholds for initiation of coral decalcification are not *sharp* transitions as suggested by Silverman et al. (2009), but relatively *ex-*

*tended* transitions that potentially extend over a period of many years. Since, the Bermuda coral reef is a high-latitude reef that experience strong seasonality, we expect that the tropical reef counterparts (with reduced seasonality of temperature, light, NEP, and NEC) will have attenuated seasonality of carbonate chemistry. Thus, we anticipate that the period of seasonal decalcification on tropical reefs will be shorter compared to higher latitude reefs.

## 5 Conclusions

In our study, we show that rates of coral calcification were closely coupled with seawater carbonate chemistry  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$ , in the natural environment, rather than other environmental factors such as light and temperature. Our field observations provide sufficient data to hypothesize that there is a seasonal carbonate chemistry coral reef ecosystem feedback (i.e., CREF hypothesis) between the primary components of the reef ecosystem (scleractinian hard corals and macroalgae) and seawater carbonate chemistry. It is also likely that this seasonal phenomenon is present in other tropical reefs although attenuated compared to high-latitude reefs such as Bermuda. Furthermore, due to lower annual mean surface seawater  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{aragonite}}$  in Bermuda compared to more tropical regions, the Bermuda coral reef will likely experience seasonal periods of zero NEC within a decade in response to future acidification of the oceans. It appears that the entire reef may already be experiencing periods of zero NEC during the wintertime, resulting in a transition to net decalcification (i.e., net dissolution over calcification). As such, the Bermuda coral reef appears to be one of the first responders to the negative impacts of ocean acidification among tropical and subtropical reefs. Furthermore, we anticipate that the Bermuda coral reef (as well as other high latitude reefs) will likely be subjected to “seasonal decalcification” with wintertime decalcification occurring many decades before summertime decalcification. However, net autotrophy of the reef during winter and spring, as part of the CREF feedback process may delay the onset of zero NEC or decalcification going forward. Thus, on societally relevant time-scales, we expect that the Bermuda reef will endure an *extended* transition to decalcified conditions over a period of decades rather than a short transition at *sharply-defined* critical thresholds expected for tropical coral reef counterparts.

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