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The interaction of ocean acidification and carbonate chemistry on coral reef calcification: evaluating the carbonate chemistry Coral Reef Ecosystem Feedback (CREF) hypothesis on the Bermuda coral reef

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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 carbonate chemistry. In this study, contemporaneous in situ datasets of 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 $p\mathrm{CO}_2$ 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 $[\mathrm{CO}_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$, rather than other environmental factors such as light and temperature. These field observations also 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 carbonate chemistry. In early summer, strong net autotrophy from benthic components of the reef system enhance $[\mathrm{CO}_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$ conditions, and rates of coral calcification due to the photosynthetic uptake of CO_2. In late summer, rates of coral calcification are suppressed by release of 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 $[\mathrm{CO}_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$ in Bermuda compared to tropical regions, we anticipate that Bermuda corals will experiences seasonal periods of zero net calcification within the next decade at $[\mathrm{CO}_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$ thresholds of $\sim$184 mmoles kg^{-1} and 2.65. 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, increasing sedimentation, eutrophication, sea level rise, cyclone damage, and natural climate variability such as El Niño Southern Oscillation (e.g. Hughes, 1994; Buddemeier, 1996; Wilkinson, 1998, 1999; Buddemeier and Smith, 1999; Buddemeier et al., 2004; Edmunds, 2007). In addition to these environmental pressures, the ability of coral reefs to calcify, produce calcium carbonate ($CaCO_3$) and provide framework structures as habitat may also be adversely affected by the oceanic uptake of anthropogenic CO_2 (Sabine et al., 2004) and gradual ocean acidification (Broecker et al., 1971; Bacastow and Keeling, 1973; Kleypas et al., 1999; Royal Society, 2005; Orr et al., 2005; Doney, 2006; Doney et al., 2009). For example, over the last few decades, dissolved inorganic carbon (DIC) and partial pressures of CO_2 (pCO$_2$) have increased while pH has decreased (Bates et al., 1996; Winn et al., 1998; Bates, 2007; Bates and Peters, 2007; Santana-Casiano et al., 2007). Given predicted atmospheric CO_2 stabilization scenarios of ~750 ppm or higher (IPCC, 1996, 2001, 2007; SAP 2.1, 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 ($[CO_3^{2-}]$) concentration and saturation states (Ω) with respect to carbonate minerals such as calcite ($\Omega_{calcite}$), and aragonite ($\Omega_{aragonite}$). In addition, it is also likely that the dissolution of carbonate sediments and structures will increase as W values decline in the future (Wollast et al., 1980; Andersson et al., 2003; Morse et al., 2006; Yates and Halley, 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 $[CO_3^{2-}]$ and Ω (e.g. Gattuso et al., 1998, 1999; Marubini and Atkinson, 1999; Marubini and Thake, 1999; Langdon et al., 2000; Langdon, 2001; Langdon and Atkinson, 2005).

Observations from coral colonies and coral reef community mesocosms exposed and equilibrated with high levels of atmospheric CO_2 (~500–700 ppm) and lowered $[CO_3^{2-}]$ concentration (with lower values of Ω with respect to aragonite) have generally shown reduction in the rates of coral calcification. However, a singular, predictable response of corals to changes in seawater 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 CO_2 conditions (typically $p\mathrm{CO_2}$ doubling to $700\pm100\,\mu$atm) has been observed in experiments studying "community" mesocosms (e.g. −19 to −58%; Leclercq et al., 1999; Langdon, 2001; Leclercq et al., 2002; Langdon et al., 2003; Jokiel et al., 2008) and individual coral species (e.g. Amat, 2000; Marubini et al., 2001, 2003; Renegear and Riegel, 2005; Schneider and Erez, 2005; Fine and Tchenov, 2007).

The widely ranging experimental response of scleractinian corals to elevated CO_2 conditions, decreasing seawater $[CO_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$, 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 $p\mathrm{CO_2}$ enhancing $CaCO_3$ saturation and precipitation of $CaCO_3$ at internal sites of coral calcification. Field studies have subsequently indicated that rates of calcification are 3–5 times greater in the light than in the dark (Gattuso et al., 1999; Schneider and Erez, 2006), with a coupling of photosynthesis and calcification. CO_2 uptake into zooxanthellae is thought to derive mainly from external inorganic carbon rather than internal consumption of respired CO_2 from the coral host (Allemand et al., 1998; Furla et al., 1998; Grottoli, 2002) with active transepithelial transport facilitated by carbonic anhydrase activity (Weis, 1991, 1993; Allemand et al., 1998; Weis et al., 1999). A "kinetic" model has been proposed in which Ca^{2+} ATPase enzyme activity, by removing H^+ ions from the calcification site, should also enhance $CaCO_3$ saturation states (McConnaughey, 1989a, b, 1997, 2004; McConnaughey and Whelan, 1997;

Cohen and McConnaughey, 2003). In addition, active uptake and transport of HCO_3^-, mediated by host-zooxanthellae energy exchanges, have also been proposed as important to calcification (e.g. Al-Moghrabi et al., 1996; Goiran et al., 1996; Lucas et al., 1997). However, it has also been shown that light and host-zooxanthellae activity might not necessarily be coupled to coral calcification (e.g. Marshall, 1996; Grottoli and Wellington, 1999; Grottoli, 2002; Reynaud et al., 2002; Marshall and Clode, 2004).

Field studies of coral reef ecosystems and carbonate chemistry have focused mainly on CO_2 variability and air-sea CO_2 gas exchange (e.g. Broecker and Takahashi, 1966; Gattuso et al., 1993, 1995, 1996, 1997; Kayanne et al., 1995, 1996; Kawahata et al., 1999, 2000; Bates et al., 2001; Bates, 2002; Kayanne et al., 2005), rather than relationships between coral calcification, $[CO_3^{2-}]$, $\Omega_{\text{aragonite}}$ and other environmental factors. In a few studies, decreased rates of calcification have been observed on coral reef ecosystems associated with decreases in seawater $[CO_3^{2-}]$ conditions (Yates and Halley, 2003, 2006; Silverman et al., 2007). With ocean acidification, it has been proposed that the combination of reduced rates of calcification and increased rates of $CaCO_3$ dissolution could result in coral reefs transitioning from net accumulation to a net loss in $CaCO_3$ material ("decalcification") during this century (Andersson et al., 2005, 2006, 2007; Hoegh-Guldberg et al., 2007; Manzello et al., 2008). The balance of $CaCO_3$ production and dissolution can be defined as net ecosystem calcification (NEC). It is generally considered that coral reef $CaCO_3$ production occurs at saturation state values >1, while dissolution of a particular carbonate mineral phase occurs when Ω 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 $p\text{CO}_2$, $[CO_3^{2-}]$ and $\Omega_{\text{aragonite}}$ when NEC=0. The transition is complicated due to the fact that coral species may have different "critical threshold values" whereas the "critical threshold values" of an entire coral reef ecosystem is influenced by a combination of hard coral and other calcifiers as well as bioerosion and sediment dissolution.

As stated earlier, there is very limited field data on the relationships between calcification and carbonate chemistry (with the exception of Silverman et al., 2007), particularly over seasonal to annual timescales. and relevant reef spatial scales. The geographic distribution of coral reefs is generally dictated by light availability, sea surface temperature and by $[CO_3^{2-}]$ and $\Omega_{aragonite}$, 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, carbonate chemistry (i.e. $[CO_3^{2-}]$ and $\Omega_{aragonite}$ 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, ~80 km SE of Bermuda (Steinberg et al., 2001; Bates, 2007; Fig. 1) are used to contrain our estimates of net ecosystem calcification (NEC) and net ecosystem production (NEP) in a 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 $[CO_3^{2-}]$ and $\Omega_{aragonite}$ at which chemical conditions may no longer be favourable for calcification on the Bermuda coral reef and the timing of these theshoulds 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 feedback between the primary components of the reef ecosystem (i.e. scleractinian hard corals and macroalgae) and $CaCO_3$ saturation states that amplify and suppress calcification rates over seasonal timescales.

2 Methods and materials

2.1 Physiographic setting of the Bermuda coral reef

Bermuda has a geographically isolated subtropical coral reef ecosystem (~1000 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 (Morris et al., 1977; Dodge et al., 1982, 1984; Logan, 1988; Logan and Vaisnys, 1984) and the island of Bermuda (55 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 (~5–10 days) (R. J. Johnson, tide and wind mixing model, D. Kadko, unpublished ^{7}Be tracer data).

Hard coral cover on the Bermuda reef system typically ranges between 30 and 70% (CARICOMP, 1997a, b, 2002). The dominant coral reef taxa are the corals *D. labyrinthiformis* and *Porites astreoides*, with *D. strigosa, Montastrea franksii*, *M. cavernosa*, and *Madracis spp* being significant components of the reef. *D. labyrinthiformis* is arguably the dominant species and constitutes 25–35% of the reef hard coral cover.

2.2 Carbonate chemistry considerations

The complete seawater carbonic acid system (i.e. CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+) can be calculated from a combination of two carbonate system parameters DIC, TA, pCO$_2$ and pH, along with temperature and salinity. DIC is defined as (Dickson et al., 2007):

$$DIC=[CO_2*]+[HCO_3^-]+[CO_3^{2-}] \quad (1)$$

where [CO_2*] represents the concentration of all unionized carbon dioxide, whether present as H_2CO_3 or as CO_2. The total alkalinity of seawater (TA) is defined as:

$$\begin{aligned}\mathrm{TA} =& [\mathrm{HCO_3^-}]+2[\mathrm{CO_3^{2-}}]+[\mathrm{B(OH)_4^-}]+[\mathrm{OH^-}]+[\mathrm{HPO_4^{2-}}]+2[\mathrm{PO_4^{3-}}]+[\mathrm{SiO(OH)_3^-}] \\ &+[\mathrm{HS^-}]+[\mathrm{NH_3}]+\ldots-[\mathrm{H^+}]-[\mathrm{HSO_4^-}]-[\mathrm{HF}]-[\mathrm{H_3PO_4}]-\ldots \qquad (2)\end{aligned}$$

where [HCO_3^-] + 2[CO_3^{2-}]+ $B(OH)_4^-$ are the principal components of seawater TA. Here, pCO$_2$ is the partial pressure of CO_2 in equilibrium with seawater, while pH is expressed on the total seawater scale.

Calcium carbonate mineral production and dissolution is governed by the following chemical reaction:

$$\mathrm{CaCO_3}=[\mathrm{Ca^{2+}}]+[\mathrm{CO_3^{2-}}] \qquad (3)$$

$CaCO_3$ production and dissolution rates vary as a function of saturation state (Ω). For corals and other calcifying marine organisms whose carbonate mineralogy is aragonite, the saturation state is defined as the ion concentration product of calcium and carbonate ions, thus:

$$\Omega_{\mathrm{aragonite}}=[\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]/K^*_{\mathrm{sp(aragonite)}} \qquad (4)$$

where the solubility product, $K^*_{\mathrm{sp(aragonite)}}$, is a function of temperature, salinity and pressure (Mucci, 1983).

2.3 Seawater DIC, TA and pCO$_2$ observations

Surface samples at Hog Reef (~2 m deep) for DIC and TA were drawn from a Niskin sampler into clean 0.5 dm^3 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 μl of saturated $HgCl_2$ 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 CO_2 coulometer detector. The precision of DIC analyses of this system is typically better than 0.025% (~0.4 μmoles 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 μmoles 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 thermister (+0.05°) 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 μmoles kg^{-1}) of certified TA values reported by A. G. Dickson (http//www.dickson.ucsd.edu).

A time-series of seawater $p\mathrm{CO}_2$ 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 16th October 2002 (day 287 of the year) and recovered on the 20th of January 2003 (day 6 of the year) after breaking its mooring line. Instrument repair and calibration delayed the subsequent deployment and the CARIOCA buoy was deployed on the 26th of April 2003 (day 116 of the year). In anticipation of the passage of Hurricane Fabian over Bermuda (5th 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 28th August 2003 (day 239).

The CARIOCA buoy collected hourly measurements of seawater temperature, pCO_2 and fluorescence were sampled from an intake at 2 m depth. Seawater temperature data was measured using two Betatherm thermistors with an accuracy of 0.05°C. Tributyl 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 pCO_2 sensor. Seawater pCO_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 pCO_2 measurements were calibrated in the laboratory prior to deployment using a Licor infrared CO_2 analyzer (Model 6262) and 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 pCO_2 data were calculated and subsequently used to determine pCO_2 from spectrophotometric absorbance and temperature data.

In this study, pCO_2, $[CO_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$ 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 pCO_2 and other carbonate parameters, using the equations of Zeebe and Wolf-Gladrow (2001). In addition, the CO_2 solubility equations of Weiss (1974), and dissociation constants for borate (Dickson, 1990), and phosphate (Dickson and Goyet, 1994) were used. DIC data was also recalculated as salinity normalized DIC (nDIC) using a salinity of 36.6. This correction accounts for the DIC changes imparted by precipitation and evaporation (Bates et al., 1996).

Meteorological data was collected each hour from the island of Bermuda by the Bermuda Weather Service. Wind speed data was corrected to 10 m using the equations of Smith (1988). Net shortwave radiation, Q_{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):

$$Q_{\mathrm{sw}} = T_{\mathrm{r}} E_{\mathrm{t}} a C_{\mathrm{f}} \tag{5}$$

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 ephemera 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 ~45% of estimated total insolation or Q_{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-Gottlib 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 using the buoyant weight technique. 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. Skeletal growth is expressed as weight increase per g weight ($CaCO_3$ plus very minor contributions from tissue) for each coral colony and expressed as $\mathrm{mg\,CaCO_3\,g^{-1}\,d^{-1}}$ (Table 1). Skeletal growth rate per unit area was also calculated from weight changes and determination of individual coral colony surface area (determined at end of deployment) expressed as $\mathrm{mg\,CaCO_3\,cm^{-2}\,d^{-1}}$ (Table 1).

3 Results

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

Surface temperatures decreased from mid-summer maxima of ~27°C in 2002 to a winter minima of ~20°C in the January to March 2003 period (Fig. 2a). Subsequently, a mid-summer maxima of ~30°C was observed in August 2003. For context, winter temperatures on the Bermuda coral reef are typically 1–2°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 μmoles kg^{-1} (MEP, 2006, (http://www.bios-mep.info/)) 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). Salinity typically has a range of ~36.0 to 36.8, with slightly fresher conditions during summertime (MEP, 2006).

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 ~120 mph (~200 kph) during the passage of Hurricane Fabian over the island of Bermuda on the 5th of September 2003 (JD 247; Fig. 2b).

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 $p\mathrm{CO}_2$ ranged from low wintertime values (∼300–360 µatm) to summertime values exceeding 550 µatm (Fig. 2b). In comparison, seawater $p\mathrm{CO}_2$ values at the BATS site had a seasonal range of ∼300–420 µatm (Bates, 2007), with the major difference observed during the summertime, when seawater $p\mathrm{CO}_2$ was significantly higher on the Bermuda coral reef. The continuous observations of seawater at Hog Reef also showed considerable diurnal variability of ∼20–100 µatm. In contrast, diurnal variability at the BATS site is significantly attenuated (∼5–25 µatm; Bates et al., 2000, 2001). In other coral reef systems, diurnal to seasonal seawater $p\mathrm{CO}_2$ ranged from as low as ∼100 µatm to as high as 1000 µatm, the largest amplitude in seawater $p\mathrm{CO}_2$ typically observed in the shallower reefs. These previous studies have typically observed seawater CO_2 and associated variables over a few days only or with transects across reef systems (e.g. Smith, 1973; Gattuso et al., 1993; Kayanne et al., 1995, 1996; Frankignoulle et al., 1996; Kawahata et al., 1997; Ohde and van Woesik, 1999; Kawahata et al., 2000; Suzuki and Kawahata, 2003).

Surface DIC at Hog Reef had a seasonal variability of ∼100 µmoles kg^{-1}, with a maxima of ∼2070 µmoles kg^{-1} and minima of ∼1970 µmoles 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 ∼20 µmoles 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 30–40 µmoles kg^{-1} relative to DIC at the BATS site.

Total alkalinity at Hog Reef varied seasonally by ∼100 µmoles kg^{-1} (Fig. 2c), with considerable differences observed between Hog Reef and offshore at BATS. For example, Hog Reef TA was generally lower by ∼20–40 µmoles 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 ~60–80 μmoles kg^{-1} and 30–40 μmoles kg^{-1}, respectively, compared to offshore concentrations at BATS (Fig. 2c). The depletion of Hog Reef TA and DIC had an approximate ratio of ~2:1, similar to theoretical predictions that the formation of $CaCO_3$ decreases TA and DIC in a ratio of 2:1 due to the uptake of [Ca^{2+}] and [CO_3^{2-}] (Eqs. 1–3).

The seasonal range of [CO_3^{2-}] observed at Hog Reef ranged from 190 to 250 μmoles kg^{-1}, a smaller range than changes observed on other reefs (Table 1; Fig. 2d). Hog Reef [CO_3^{2-}] and $\Omega_{aragonite}$ were generally lower by ~30–70 μmoles kg^{-1} and ~0.3 (not shown) relative to offshore [CO_3^{2-}] and $\Omega_{aragonite}$ values at BATS, with the exception of a few occurences during early summer 2003 (JD~180–210) (Fig. 2d).

The annual range of skeletal growth rates was ~0.28–0.65 mg $CaCO_3$ g^{-1} d^{-1} for *D. labyrinthiformis* colonies (Table 1). Skeletal growth rates per unit area ranged from 0.40–0.96 mg $CaCO_3$ cm^{-2} d^{-1} for the same *D. labyrinthiformis* colonies (Table 1). 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 [CO_3^{2-}] (Fig. 2e) and $\Omega_{aragonite}$ (not shown).

4 Discussion

4.1 Estimates of annual rates of in situ calcification

Previous studies of Bermuda corals such as *D. labyrinthiformis* and *Porites astreoides*, have been shown to accrete narrow, high density bands of $CaCO_3$ during the summer, and wider low-density bands during the fall to spring (Logan and Tomascik, 1991; Cohen et al., 2001). 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 reef ranged from ∼1.9 to 13.1 g $CaCO_3$ m^{-2} d^{-1}, assuming a range of coral cover from 30–70%. 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 substantively to this estimate of calcification rate. Calcification rates on other reefs can vary by a couple of orders of magnitude but the calcification rate estimate for the Bermuda coral reef is within the typical observed range for other reefs (∼ <2–40 g $CaCO_3$ m^{-2} d^{-1}; e.g. 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 3.5 kg $CaCO_3$ m^{-2} $year^{-1}$, slightly lower than the average calcification rate of 4±0.7 kg $CaCO_3$ m^{-2} $year^{-1}$ 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. 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 $[CO_3^{2-}]$ and $\Omega_{aragonite}$. Mean in situ skeletal growth rates had a range of 0.3 mg $CaCO_3$ g^{-1} d^{-1} while $[CO_3^{2-}]$ and $\Omega_{aragonite}$ varied by ~40 μmoles kg^{-1} 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 $[CO_3^{2-}]$ and $\Omega_{aragonite}$ (Fig. 3a, b), with r^2 of ~0.68. Similar findings have been shown in the natural environment (Silverman et al., 2007) and other 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 poorly correlated with rates of in situ skeletal growth (Fig. 3c). This is perhaps not surprising, since the highest seasonal rates of calcification have been observed a few degrees below the seasonal temperature maximum [e.g. Abramovitch-Gottlib et al., 2003; Marshall and Clode, 2004]. There was a poor correlation between in situ skeletal growth of *D. labyrinthiformis* and mean Q_{sw} (Fig. 3c). This is perhaps surprising since other studies have shown a strong coupling between light and calcification (e.g. 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^{-2} s^{-1}) and zooxanthellae photosynthesis and respiration rates (as expressed as oxygen production or consumption) in short-term (<2 h) chamber experiments (Amat and Bates, 2004). If Q_{sw} is an appropriate proxy for coral photosynthesis, our in situ observations would suggest a poor coupling between coral photosynthesis and calcification. However, while Q_{sw} is a good proxy for the seasonally integrated mean light conditions at Hog Reef, Q_{sw} may not accurately reflect variability 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.

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 $[CO_3^{2-}]$ in the external reef environment was at seasonally high concentrations (while $[HCO_3^-]$ 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.

Recent experimental studies have indicated that corals have a very active internal control of carbonate chemistry (Al-Horani et al., 2003a, b). In these studies, Ca^{2+} uptake from seawater for example appears to be regulated by light (de Beer et al., 2000; Al Horani et al., 2003a, b; Marshall and Clode, 2003), consistent with light enhanced calcification (e.g. Goreau, 1959; McConnaughey and Whelan, 1997; Gattuso et al., 1999; McConnaughey and Cohen, 2004). Al-Horani et al. (2003a, b) observed that Ca^{2+} and *p*H increased in the coelenteron during the light and decreased in the dark and that *p*H increased from the polyp surface to the calcifying fluid indicating increased alkalinization and enhanced saturation state with respect to aragonite within the calcifying fluids of the coral system. In explanation, they proposed an enzyme mediated transfer by Ca^{2+} ATPase with active transport of Ca^{2+} into the calcifying fluid in exchange for H^+. In a "kinetic" model, removal of H^+ ions from the calcification site by Ca^{2+} ATPase enzyme activity, was proposed as a mechanism for enhancing Ω in the calcifying fluids (e.g. McConnaughey, 1989a, b, 1997, 2004; McConnaughey and Whelan, 1997). Without removal of H^+ ions from the calcification site, active uptake of HCO_3^- from the coelenteron into the calicoblastic layer and its subsequent dissociation to CO_3^{2-} and

H^+ could result in the progressive acidification of the calcifying fluids rather than an alkalinization and enhancement of Ω in the calcifying fluids. In lower external *p*H and $[CO_3^{2-}]$ conditions, Ca^{2+} ATPase enzyme mediated exchanges of Ca^{2+} and H^+, uptake of HCO_3^- and calcification might have to be suppressed in order to prevent low *p*H (high H^+) conditions in the coral coelenteron and aboral/oral endoderm/ectoderm tissue.

The above models suggest that HCO_3^- in external seawater is the only source of inorganic carbon for coral calcification. If coral uptake of HCO_3^- is directly proportional to external seawater $[HCO_3^-]$, then it might be expected that calcification rates should be correlated to $[HCO_3^-]$. However, field data from Hog Reef indicates that calcification rates are strongly correlated with and proportional to $[CO_3^{2-}]$, and inversely correlated with $[HCO_3^-]$ (i.e. decreasing calcification rate with increasing $[HCO_3^-]$). As a potential solution to this conundrum, Marubini et al. (2001) suggested uptake of CO_3^{2-} in addition to HCO_3^- and, that the *p*H of the calcifying fluid (calicoblastic layer) would have to be proportionate to external seawater *p*H. In this scenario, if uptake of CO_3^{2-} and HCO_3^- occurs in proportion to external conditions, external seawater carbonate chemistry can enhance or suppress calcification. For example, at higher external *p*H conditions (i.e. higher $[CO_3^{2-}]$ and $\Omega_{aragonite}$, and lower $[HCO_3^-]$), the alkalinization of the calcifying fluids would be enhanced by reduced needs to actively remove H^+ from the calicoblastic layer produced by dissociation of HCO_3^-.

Does this solution agree with field data from Bermuda? At Hog Reef, $[CO_3^{2-}]$ has a seasonal range of ~190–250 μmoles kg^{-1} (Fig. 2d), while $[HCO_3^-]$ has a range of ~1720–1870 μmoles kg^{-1} (not shown). In summertime, during the highest observed rates of coral calcification, when $[CO_3^{2-}]$ is at a seasonal maxima and $[HCO_3^-]$ at a seasonal minima, the ratio of $[HCO_3^-]$:$[CO_3^{2-}]$ is ~6.8:1. In contrast, in wintertime, during the lowest observed rates of coral calcification, when $[CO_3^{2-}]$ is at a seasonal minima and $[HCO_3^-]$ at a seasonal maxima, the ratio of $[HCO_3^-]$:$[CO_3^{2-}]$ is ~9.8:1. Thus the ratio of $[HCO_3^-]$ to $[CO_3^{2-}]$ changes by almost 40% in the natural environment at Hog Reef. In the summertime, the low ratio of $[HCO_3^-]$ to $[CO_3^{2-}]$ may lessen the need for corals to actively remove H^+ from the calicoblastic layer (from the dissociation of HCO_3^-), thereby facilitating alkalinization of the calicoblastic fluids and calcification. In contrast, during winter, the higher seawater proportion of $[HCO_3^-]$ relative to $[CO_3^{2-}]$, may mean that there is a greater demand for active removal of H^+ from the calicoblastic layer. Higher energetic demands to remove H^+ combined with lower energetic supply resulting from reduction of solar input, may make it more difficult to alkalinize calicoblastic fluids with lower calcification rates as a result.

If corals do actively take up both HCO_3^- and CO_3^{2-}, changes in zooxanthellae photosynthesis could also enhance or suppress calcification. Since HCO_3^- (internally converted to CO_2 by CA) is the source of inorganic carbon for photosynthesis, increased demand for HCO_3^- by increased zooxanthellae photosynthesis (in response to enhanced light conditions) should shift the ratio of $[HCO_3^-]$:$[CO_3^{2-}]$ to lower values. This should further elevate *p*H, enhance alkalinization, and the $\Omega_{aragonite}$ in the calicoblastic 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

A composite of data from the Bermuda coral reef can be compiled to demonstrate seasonal changes over a “idealized” annual cycle (Fig. 5). In this analysis, carbonate chemistry and in situ skeletal growth rate data were not corrected for long-term changes observed at the BATS due to the oceanic uptake of anthropogenic 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 carbonate chemistry and in situ skeletal growth rates over the timeframe of the study.

The deviation of Hog Reef seawater pCO_2 from offshore values and other datasets (e.g. in situ skeletal growth rates) can be used to evaluate the seasonal changes in net coral reef metabolism and the impact of benthic processes on water overlying the reef system (Bates, 2002). Two processes dominate the net ecosystem metabolism (NEM) of the reef, each with different influence on seawater pCO_2 and other components of the 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 CO_2 to the surrounding environment per mole of $CaCO_3$ precipitated in coral reef systems (Kinsey, 1985; Frankignoulle et al., 1994; Lerman and Mackenzie, 2006). When rates of calcification exceed dissolution (i.e. NEC is positive), the uptake of inorganic carbon into the coral skeleton as $CaCO_3$ decreases DIC and TA in a ratio of 1:2, with the net result of CO_2 production and increase in seawater pCO_2. Thus, NEC on most coral reefs results in net production of CO_2 (Gattuso et al., 1999). In many coral reef systems, higher reef seawater pCO_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 pCO_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).

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 positive and the uptake of CO_2 decreases DIC only (and seawater pCO_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 negative, CO_2 is produced and DIC and seawater pCO_2 increase over time. In many reef systems, net

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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 $p\mathrm{CO_2}$ 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 over the year (i.e. net productivity rates were positive) while net heterotrophic conditions occurred in August and September (i.e. net productivity rates were negative; Fig. 3 in Bates, 2002).

In this study, we estimated the NEP rates over the annual cycle using seawater $p\mathrm{CO_2}$ differences between the Bermuda coral reef at Hog Reef and offshore values at BATS, and contemporaneous in situ skeletal growth data for *D. labyrinthiformis* collected at Hog Reef. In this method, the difference in seawater $p\mathrm{CO_2}$ observed at Hog Reef compared to offshore observations at the BATS site (i.e. $\Delta p\mathrm{CO}_2^{\mathrm{HogReef-BATS}}$), reflect the modification by net reef metabolism of offshore source water mixed onto the Bermuda coral reef. As argued previously by Bates (2002), coral NEC (i.e. $\mathrm{NEC_{coral}}$), and coral/macroalgal NEP (i.e. $\mathrm{NEP_{coral/macroalgae}}$) are the dominant processes influencing net reef metabolism, with air-sea $\mathrm{CO_2}$ gas exchange, pelagic primary production 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. $\mathrm{NEC_{reef}}$) includes contributions from other calcifiers such as coralline algae and bivalves (Andersson et al., 2009). 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 $\mathrm{NEC_{coral}} \simeq \mathrm{NEC_{reef}}$.

In a mass balance sense, if $\mathrm{NEC_{coral}}$ and $\mathrm{NEP_{coral/macroalgae}}$ are in balance and equal, there is no loss or gain of $\mathrm{CO_2}$ for waters that become resident on the reef from offshore. If $\mathrm{NEC_{coral}}$ is positive and $\mathrm{NEP_{coral/macroalgae}}$ zero, waters modified by net reef metabolism will gain CO_2 (i.e. increase seawater pCO_2) compared to offshore conditions due to the production of CO_2 from calcification and formation of $CaCO_3$. If NEC_{coral} is zero and $NEP_{coral/macroalgae}$ positive (i.e. net autotrophic), waters modified by net reef metabolism will lose CO_2 (i.e. decrease seawater pCO_2) compared to offshore conditions due to uptake of CO_2 from photosynthesis.

In calculating NEC_{coral}, we assume that rates of in situ skeletal growth or calcification rate determined for *D. labyrinthiformis* at Hog Reef (using skeletal growth rates per mean colony area section 4.1) are representative of other coral species on the Bermuda reef. The calcification rate data are then scaled up to coral cover percentages of 30%, 50% and 70% (i.e. typical range for Bermuda reef cover) to estimate NEC_{coral} rates in $\mathrm{g\,CaCO_3\,m^{-2}\,d^{-1}}$. Assuming an average water depth of 2 m and residence time of water on the reef at 2 days, changes in seawater pCO_2 due to coral NEC (i.e. $\Delta pCO_2\mathrm{coral}^{NEC}$) were computed from NEC_{coral} rates.

Since the mean difference in seawater pCO_2 observed between Hog Reef and the BATS site offshore ($\Delta pCO_2^{HogReef-BATS}$) is the sum of seawater pCO_2 changes imparted by NEC_{coral} (i.e. $\Delta pCO_2^{NECcoral}$) and $NEP_{coral/macroalgae}$ (i.e. $\Delta pCO_2\mathrm{coral/macroalgae}^{NEP}$), the following applies:

$$\Delta pCO_2{}^{HogReef-BATS} = \Delta pCO_2{}^{NEC}_{coral} + \Delta pCO_2{}^{NEP}_{coral/macroalgae} \qquad (6)$$

With a prerequisite of maintaining mass balance, rates of $NEP_{coral/macroalgae}$ can then be computed from $\Delta pCO_2\mathrm{coral/macroalgae}^{NEP}$ that was determined from seasonal residual differences between $\Delta pCO_2^{HogReef-BATS}$ and $\Delta pCO_2\mathrm{coral}^{NEC}$. Thus, given coral cover percentages of 30% to 70%, $NEP_{coral/macroalgae}$ was determined over the annual cycle when contemporaneous in situ skeletal growth rate data (scaled to $\mathrm{g\,m^{-2}\,d^{-1}}$) was available (Fig. 5a).

This mass balance method reveals seasonal changes in net reef metabolism for the Bermuda coral reef ecosystem (Fig. 5a). In general, NEP rates were positive over most of the year indicating a net autotrophic status of the reef, with rates of photosynthesis greater than respiration. In the summer (July/August) and fall (November–January) periods, NEP rates were strongly positive. However, in late summer (September/October), NEP rates were strongly negative, indicative of net heterotrophic conditions that generate CO_2, similar to previous findings of Bates (2002). These seasonal patterns suggest that CO_2 is taken up by the reef system in early summer and fall periods, while CO_2 is released from net reef metabolism to waters overlying the reef during the late summer.

We describe the seasonal changes in carbonate chemistry, NEC, and NEP as a case of a seasonal *carbonate chemistry coral reef ecosystem feedback* (CREF), with a feedback between carbonate chemistry and reef metabolism that enhances or suppresses coral calcification. In this scenario, in early summer, when macroalgal biomass is at its maxima on the Bermuda reef, strongly positive NEP indicates net uptake of CO_2 into the benthic biomass (i.e. macroalgae and coral zooxanthellae), which in turn increases the $[CO_3^{2-}]$ and $\Omega_{aragonite}$ 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). Similar seasonal enhancement of surface layer $[CO_3^{2-}]$ and $\Omega_{aragonite}$ 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 contrast, in late summer, NEP rates change to negative values indicating a change to net heterotrophic conditions. Release of CO_2 in late summer suppresses $[CO_3^{2-}]$ and $\Omega_{aragonite}$ which in turn appears to suppress coral calcification rates (Fig. 5b, 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 CO_2 appears to depress carbonate chemistry conditions favourable for calcification (evidenced by low rates in situ skeletal growth) (Fig. 5c). It may also be that late summer macroalgal respiration and entrainment of respiratory 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 $p\mathrm{CO}_2$ and decrease $[CO_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$. The subsequent seasonal rebound in $[CO_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$ 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 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 $[CO_3^{2-}]$, $\Omega_{\mathrm{aragonite}}$ 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 $[CO_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$ thresholds of the Bermuda coral reef

There is growing evidence from experimental and modeling studies that ocean acidification and decreasing $[CO_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$ 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 $[CO_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$. Ocean acidification and the gradual decline of $[CO_3^{2-}]$ and $\Omega_{\mathrm{aragonite}}$ 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, unpublished data; Cohen et al., 2004). Such historical records show that skeletal density for *D. labyrinthiformis* has declined from a high of 4.5 g cm^{-3} yr^{-1} in 1959 to a low of 3 g cm^{-3} yr^{-1} in 1999, a change of 1.5 g cm^{-3} yr^{-1}, or decrease of ∼33%. At the BATS site offshore from the island of Bermuda, over the last 25 years, the observed annual rate of [CO_3^{2-}] decrease due to the oceanic uptake of anthropogenic CO_2 was 0.50±0.03 μmoles kg^{-1} year^{-1} (Bates, 2007; Bates and Peters, 2007). If the rate of [CO_3^{2-}] decrease is applied to the observed in situ correlation between skeletal growth of *D. labyrinthiformis* and [CO_3^{2-}] at Hog Reef (Fig. 3a), a ∼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 [CO_3^{2-}] decrease of 0.50±0.03 μmoles kg^{-1} year^{-1} is accompanied by an observed increase in salinity normalized DIC of 0.80±0.06 μmoles kg^{-1} year^{-1} (Bates, 2007; his Table 2). In the subtropical gyre of the North Atlantic, the increase in DIC due to uptake of anthropogenic CO_2 is estimated at ∼60 μmoles kg^{-1} (Sabine et al., 2004). Given the ratios of observed DIC/[CO_3^{2-}] change, we estimate that the mean [CO_3^{2-}] was ∼37.5 μmoles 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 mg $CaCO_3$ g^{-1} d^{-1}, the application of the skeletal growth/[CO_3^{2-}] correlation shown in Fig. 3 gives a hindcast estimate of mean annual skeletal growth of 0.97 mg $CaCO_3$ g^{-1} d^{-1} in the pre-industrial period. 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.

The future impact of ocean acidification on coral calcification on the Bermuda reef also appears to be negative. Our in situ data suggests that the calcification rate of *D. labyrinthiformis* would reach zero at [CO_3^{2-}] and $\Omega_{aragonite}$ thresholds of ~184 μmoles kg^{-1} and 2.65, respectively (for both skeletal growth nomalized to colony weight or colony surface area; Fig. 3). Due to lower annual mean surface seawater [CO_3^{2-}] and $\Omega_{aragonite}$ 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 [CO_3^{2-}] on the Bermuda coral reef in 2002–2003 was ~190 μmoles kg^{-1} during winter, and assuming that the rate of [CO_3^{2-}] decrease (i.e. 0.50±0.03 μmoles kg^{-1} year^{-1}) continues linearly in the near-future (Solomons et al., 2007), we anticipate that the Bermuda coral reef should experience seasonal periods of zero calcification rates (i.e. NEC_{coral}=0) within the next decade. In our analysis we have assumed that NEC_{coral}=NEC_{reef}. Recent data from the Bermuda coral reef collected during the winter of 2009 showed no difference between offshore and onshore alkalinity. This indicates that the threshold for when NEC_{reef} equals zero may have already been reached. 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).

In the near-future, the Bermuda coral reef will experience seasonal decalcification for increasing periods of the year. Given that the Bermuda coral reef experiences a maximum [CO_3^{2-}] seasonality of ~60 μmoles 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 [CO_3^{2-}] reduction continues under IPPC assessments of future anthopogenic CO_2 release. During this period, we anticipate that suitable conditions for corals and other organisms to calcify will decrease progessively 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 CO_2 emissions continue to accelarate, 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 *extended* 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 carbonate chemistry $[CO_3^{2-}]$ 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 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 $[CO_3^{2-}]$ and $\Omega_{\text{aragonite}}$ in Bermuda compared to more tropical regions, Bermuda coral 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 occuring many decades before summertime decalcification. 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 in tropical coral reef counterparts.

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Table 1. Natural seawater [CO_3^{2-}] variability observed at coral reef sites.

Date	Timescale	Diurnal [CO_3^{2-}] range & amplitude (μmoles kg^{-1})	Seasonal [CO_3^{2-}] range & amplitude (μmoles kg^{-1})	Source
Okinawa, site 1 (Japan)	1 d	~144–350 (~200)	NA	Ohde and Woesik, 1999
Hog Reef (Bermuda)	38 d	~200–270 (~10–30)	NA	Bates et al., 2001
Ferry Reach (Bermuda)	1 d	~180–260 (80)	~200-280 (70)	Bates (unpublished data)
North Lagoon	1994–1998	NA	~220–280 (60)	Bates, 2002

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

Date	Day of year	n	Skeletal Growth $(\mathrm{mg\,CaCO_3\,g^{-2}\,d^{-1}})$	Skeletal Growth $(\mathrm{mg\,CaCO_3\,cm^{-2}\,d^{-1}})$	SST (°C)	Q_{sw} $\mathrm{W\,m^{-2}\,d^{-1}}$
1st Jul 2002–21st Aug 2002	181–237	8	0.73+0.09	0.87+0.20		6773±1209
21st Aug 2002–19th Oct 2002	233–301	7	0.44+0.08	0.74+0.18	26.0±0.7[*]	5217±1328
29th Oct 2002–22nd Dec 2002	301–356	8	0.55+0.15	0.92+0.21	23.1±0.9	3138±701
22nd Dec 2002–17th Feb 2003	356–48	8	0.32+0.08	0.46+0.15	20.2±0.6	3014±542
4th Mar 2003–22nd Apr 2003	63–115	8	0.47+0.08	0.72+0.07	20.0±0.5	4985±999
22nd Apr 2003–4th Jun 2003	116–154	8	0.43+0.11	0.59+0.09	22.2±0.8	5890±1800
1st Jul 2003–5th Sep 2003	181–247	8	0.64+0.05[**]	0.96+0.15	28.4±0.9	7368±963
5th Sep 2003–6th Nov 2003	247–314	8	0.79+0.11[***]	0.69+0.18	26.3±1.1	4485±1082

[*] surface temperatures only available for day of year 288–301.

[**] several of the coral specimens had moderate signs of bleaching potentially suppressing coral skeletal growth.

[***] in situ during Hurricane Fabian.

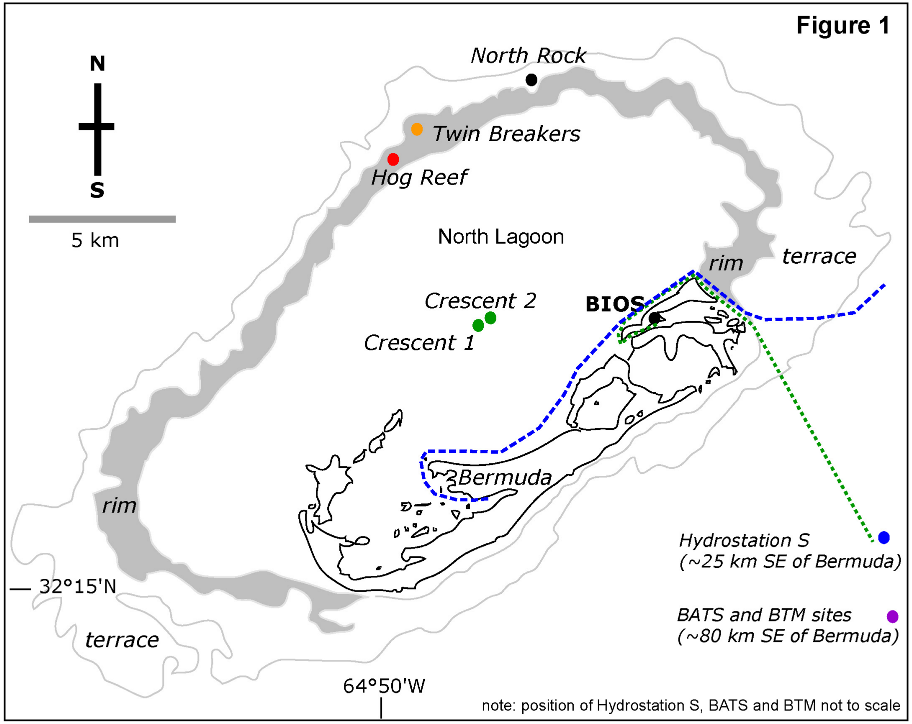

Fig. 1. Location of rim and terrace reefs of Bermuda, the North Lagoon and island of Bermuda. Two reef sites, Hog Reef (red symbol) and Twin Breakers (orange symbol), were chosen as representative of the broad rim reefs that enclose lagoonal waters of the North Lagoon. The North Lagoon contains patch coral reefs and extensive sand area, with two sites (Crescent 1 and 2; gree symbol) representative of patch reefs. The track of weekly underway, shipboard sampling from the R/V *Atlantic Explorer* (greee 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).

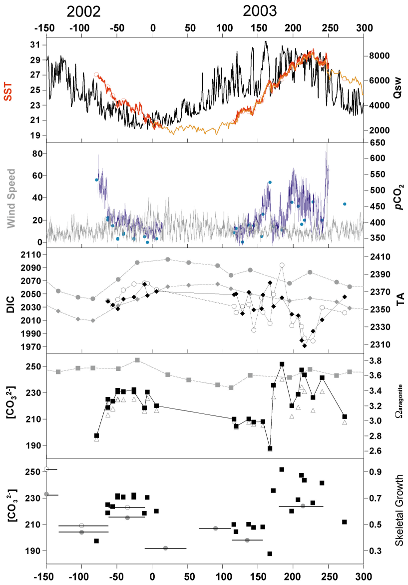

Fig. 2. Time-series of physical, chemical and biological variables from the coral reefs of Bermuda from August 2002 to October 2003. **(a)** surface temperature (°C) and short wave radiation (Q_{SW}; W m^{-2}) from the coral reefs of Bermuda. Surface temperature was collected hourly at Hog Reef (~15 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_{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 $p\text{CO}_2$(μatm; 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; μmoles kg^{-1}) and alkalinity (open circle; μmoles 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; μmoles 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; μmoles kg^{-1}) and in situ skeletal growth (grey circle; Hog Reef and open diamond, Twin Breakers; mg CaCO_3 g^{-1} 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.

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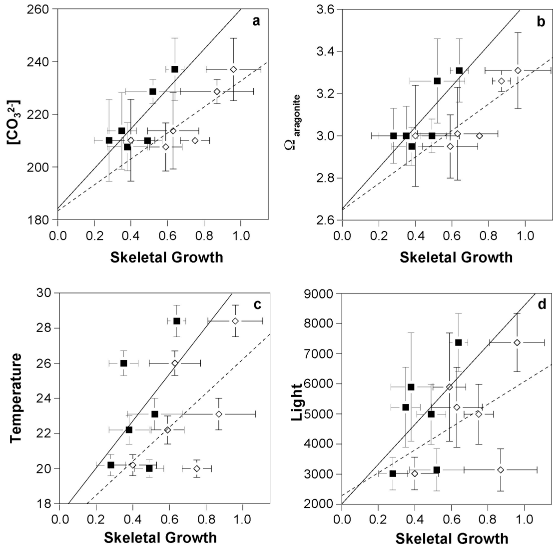

Fig. 3. Relationship between in situ skeletal growth of *D. labyrinthiformis* at Hog Reef against mean [CO_3^{2-}], $\Omega_{\text{aragonite}}$, temperature and light conditions observed at Hog Reef. Skeletal growth rates are expressed either as mg $CaCO_3$ g^{-1} d^{-1} (black square) or as skeletal growth rate per unit surface area (mg $CaCO_3$ cm^{-2} d^{-1}; open diamond) **(a)** relationship between in situ skeletal growth of *D. labyrinthiformis* and average [CO_3^{2-}] (observed at Hog Reef during the concurrent skeletal growth 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 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). **(c)** relationship between in situ skeletal growth of *D. labyrinthiformis* and temperature (°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 (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 3791.8+2281.1, r^2=0.21 (skeletal growth rate per unit surface area).

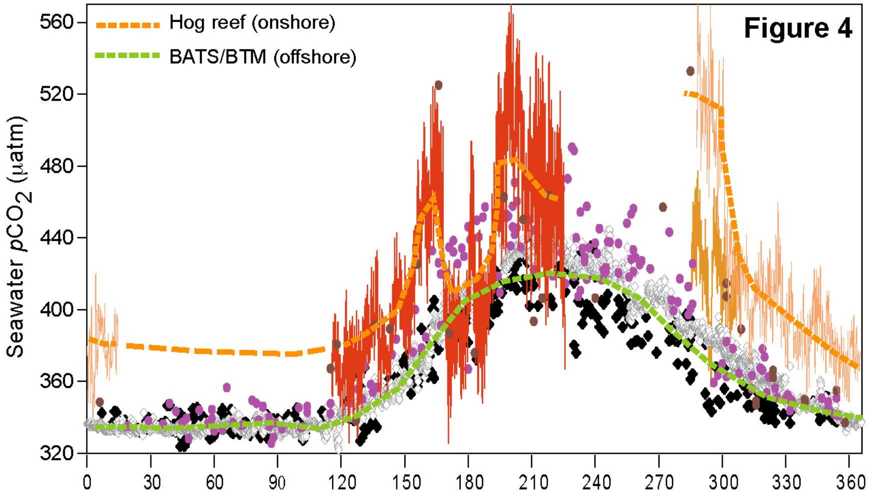

Fig. 4. Annual composite and comparison of surface seawater pCO_2 data (μatm) collected over the last twelve years from the coral reef of Bermuda and offshore in the North Atlantic Ocean at BATS and the Bermuda Testbed Mooring (BTM). All seawaterpCO_2 datasets have been adjusted to the year 2006 using the long-term trend of $+1.7\,\mu$atm year^{-1} observed at the BATS site in the North Atlantic Ocean from 1983–2006 (Bates, 2007). *Coral reef* seawater pCO_2 datasets include: (1) surface seawater pCO_2 from October 2002 to January 2003 collected hourly at Hog Reef using a CARIOCA buoy (red line); (2) surface seawater pCO_2 from April 2002 to September 2003 hourly at Hog Reef using a CARIOCA buoy (peach line); (3) surface seawater pCO_2 from October 1998 to Novenber 1998 hourly at Hog Reef using a CARIOCA buoy (orange line) (Bates et al., 2001). (4) surface seawater pCO_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 pCO_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 ∼150 cruises between 1994 and 1998. *Offshore* seawater pCO_2 datasets include: (6) surface seawater pCO_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 pCO_2 (black closed diamond) collected every 2 min at the BATS site from the R/V *Weatherbird II* during ∼150 cruises between 1994 and 1998 (Bates, 2007).

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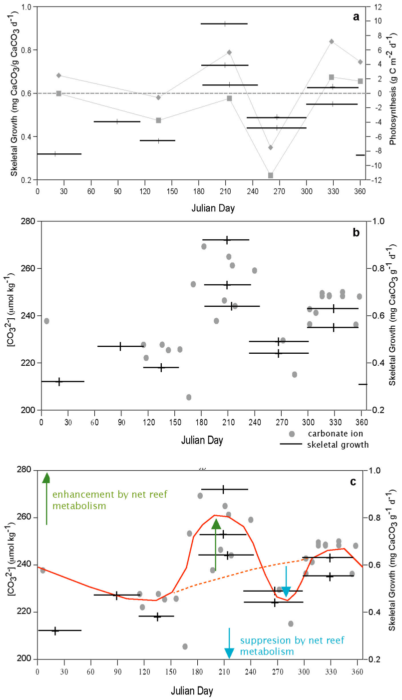

Fig. 5. Annual composite of skeletal growth rates ($\mathrm{mg\,CaCO_3\,g^{-1}\,d^{-1}}$; black lines; the length of the horizontal line represents the duration of the in situ incubation) of *D. labyrinthiformis* at Hog Reef from July 2002 to November 2003, and modeled rates of NEP ($\mathrm{g\,C\,m^{-2}\,d^{-1}}$). Positive values represent net autotrophy, and negative values represent net heterotrophy, with the zero line denote by grey dashed line. Rates of NEP are computed with 30% coral reef cover (grey diamonds), 50% coral reef cover (bold line) and 70% coral reef cover (grey squares) to bound the typical range of coral cover found on the Bermuda coral reef. **(b)**. Annual composite and comparison of surface seawater $[\mathrm{CO_3^{2-}}]$ data ($\mu\mathrm{moles\,kg^{-1}}$; gray circles) and skeletal growth rates ($\mathrm{mg\,CaCO_3\,g^{-1}\,d^{-1}}$). **(c)** Repeat of panel b showing the CREF hypothesis superimposed on Hog Reef data. In early summer, enhancement of $[\mathrm{CO_3^{2-}}]$ and calcification during June and July [green arrow] occurs due to positive NEP. In late summer, suppression during September and October on the Bermuda reef due to negative NEP (blue arrow). The dashed line illustrates the hypothesized $[\mathrm{CO_3^{2-}}]$ in absence of the feedback on carbonate chemistry due to seasonal changes in NEP.