UC San Diego

UC San Diego Electronic Theses and Dissertations

Title

Ocean acidification on coral reefs: the effects of community composition on benthic metabolism and seawater carbonate chemistry

Permalink

https://escholarship.org/uc/item/0mf7w1v9

Author

Page, Heather Nicole

Publication Date

2017

Peer reviewed|Thesis/dissertation

eScholarship.org Powered by the California Digital Library
University of California

UNIVERSITY OF CALIFORNIA, SAN DIEGO

Ocean acidification on coral reefs: the effects of community composition on benthic metabolism and seawater carbonate chemistry

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Oceanography

by

Heather N. Page

Committee in charge:

Professor Andreas Andersson, Chair
Professor Elsa Cleland
Professor Todd Martz
Professor Jennifer Smith
Professor Martin Tresguerres

2017

Copyright

Heather N. Page, 2017

All rights reserved.

The Dissertation of Heather N. Page is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

_____

_____

_____

_____

_____
Chair

University of California, San Diego

2017

DEDICATION

To my loving parents, Howard and Dawn Page, for standing up for my right to an education, teaching me to do the same, and always fostering a curiosity and love for the natural world

EPIGRAPH

"If there is magic on this planet, it is contained in water."

Loren Eiseley

"You are capable of more than you know.

Choose a goal that seems right for you and strive to be the best,

however hard the path. Aim high. Behave honorably.

Prepare to be alone at times, and to endure failure. Persist!

The world needs all you can give."

E.O. Wilson

TABLE OF CONTENTS

Signature Page……..… iii

Dedication……..iv

Epigraph……v

Table of Contents……...vi

List of Tables……..vii

List of Figures……viii

Acknowledgments……..….x

Vita……xiv

Abstract of the Dissertation……... xv

CHAPTER 1 Introduction: Ocean acidification on coral reefs…….… 1

CHAPTER 2 Differential modification of seawater carbonate chemistry by major coral reef benthic communities…….....21

CHAPTER 3 Net community metabolism and seawater carbonate chemistry scale non-intuitively with coral cover…….37

CHAPTER 4 Spatio-temporal variability in seawater carbon chemistry for a coral reef flat in Kaneohe Bay, Hawaii……55

CHAPTER 5 Conclusion……104

LIST OF TABLES

Chapter 2

Table 2.1 Statistical results from two-way ANOVA tests with benthic community and seasons as factors for average daytime and nighttime NCC and NCP……..28

Table 2.2 Average TA to DIC slopes……...…….33

Chapter 3

Table 3.1 Experimental design for mesocosm experiments in Bermuda and Hawaii……..…41

Table 3.2 Statistical comparison of NCC and NCP rates…….46

Chapter 4

Table 4.1 Instrument configuration for June and November……92

LIST OF FIGURES

Chapter 1

Figure 1.1 Deffeyes diagram showing effects of benthic metabolism on seawater TA, DIC, and pH……..……...7

Chapter 2

Figure 2.1 Seawater temperature and atmospheric PAR over a diel cycle…….26

Figure 2.2 Diel seawater pH, Ω_a, and pCO_2 …….……...…...27

Figure 2.3 Diel seawater salinity-normalized DIC and TA……... …28

Figure 2.4 Diel NCC and NCP rates for benthic communities……...29

Figure 2.5 Influence of benthic communities on seawater pH……...30

Figure 2.6 Influence of benthic communities on seawater Ω_a……32

Figure 2.7 TA to DIC slopes for each of the benthic communities……34

Chapter 3

Figure 3.1 Locations of coral reef buoys at reefs with contrasting coral cover in Bermuda and Hawaii…….43

Figure 3.2 Environmental conditions for mesocosm experiments……..44

Figure 3.3 NCC and NCP for Bermuda 2012 and Hawaii 2016…….45

Figure 3.4 Seawater carbonate chemistry …….……..…47

Figure 3.5 Scaled NCC and NCP rates vs. coral cover treatments for Hawaii 2016……..48

Figure 3.6 nTA:nDIC plots with pH and pCO_2 isolines ……49

Figure 3.7 Average nTA:nDIC slopes ……...50

Figure 3.8 *In situ* xCO_2 and environmental conditions including seawater temperature, tidal range, and wind speed and direction that may influence xCO_2 variability for different reefs in Bermuda and Hawiai …….51

Chapter 4

Figure 4.1 Study site in Kaneohe Bay, Hawaii showing sampling stations…….....93

Figure 4.2 Temporal variability in environmental conditions and seawater carbonate chemistry for June and November…….....94

Figure 4.3 Current data for June and November…….....95

Figure 4.4 Spatial variability in temperature, DO, DIC and TA for June……...96

Figure 4.5 Spatial variability in pCO_2, pH, and Ω_a for June……...97

Figure 4.6 Spatial variability in temperature, DO, DIC and TA for November…….....98

Figure 4.7 Spatial variability in pCO_2, pH, and Ω_a for November……..…99

Figure 4.8 Seawater DIC, TA, temperature, pH, and Ω_a as a function of depth……..…100

Figure 4.9 Seawater DIC, TA, temperature, pH, and Ω_a as a function of communities...…101

Figure 4.10 Seawater TA and DIC relative to offshore with regressions for June and Nov..102

Figure 4.11 Diel seawater pH and TA:DIC regressions compared to results from previous mesocosm experiments……103

ACKNOWLEDGMENTS

I would like to acknowledge my advisor, mentor, and committee chair, Dr. Andreas Andersson, for his guidance over the past five years. From our first meeting in Bermuda before I started the graduate program, we continuously have had engaging conversations about ocean acidification, coral reef science, and life in general. Thank you for playing an active role in my development as a scientist by leading, not just from in front, but also alongside me as we planned experiments, conducted research in Hawaii and Bermuda, analyzed data, and wrote manuscripts. I'm so appreciative for his support during the more challenging experiences of graduate school. Andreas fully supported my endeavors outside of scientific research which allowed me to explore and to develop my interests in science communication, education, and outreach. Finally, thank you so much for constantly reminding me to keep the "big picture" in mind – both in terms of research and life as a scientist. Thank you so much!!! Additionally, I would also like to thank other members of my PhD committee – Dr. Elsa Cleland, Dr. Todd Martz, Dr. Jen Smith, and Dr. Martin Tresguerres – for dedicating their time and providing feedback on my research.

I would like to acknowledge colleagues and peers at Scripps Institution of Oceanography (particularly the SCOOBY Lab), Hawaii Institute of Marine Biology, and UH Manoa, without whom my research would not have been possible. Thanks for helping me collect organisms from the field, staying up all night (multiple nights) to sample seawater chemistry, and assisting with field studies! I especially would like to mention my gratitude towards Dr. Paul Jokiel (1941-2016) who welcomed me into his laboratory on Coconut Island and served as a role model and mentor; I hope to foster curiosity about the natural world throughout my life and to leave an everlasting positive effect on the world as he did. In

addition, Dr. Ku'ulei Rodgers and Dr. Megan Donahue ensured that I felt included in the research community at Hawaii Institute of Marine Biology. Thank you to Dr. Eric De Carlo for contributing to a productive, fun collaboration.

There are far too many individuals within the SCOOBY Laboratory and Scripps Institution of Oceanography (SIO) communities to thank as well. I am incredibly grateful for such a supportive community of professors, staff, and peers that made the academic and research journeys more enjoyable. Dr. Cheryl Peach has continued to involve me in science education and outreach efforts within SIO and has provided invaluable advice and insight into this non-traditional career pathway. Thanks to the many professors at SIO for providing a solid foundation of oceanography knowledge through interesting courses and seminars. Although the members of the SCOOBY Laboratory changed throughout the years, it was always a great, supportive, and fun group of scientists. Thanks to my officemates, Dr. Lauren Linsmayer and Travis Courtney, for the countless discussions about science, data analysis, and life. I would like to acknowledge my friends Dr. Maggie Johnson and Dr. Levi Lewis for providing guidance as peer mentors. I would not have maintained my sanity while living on a small island for three months without Maggie's friendship. Levi, thank you for all of the writing dates, fun experiences, and accepting me into your tribe. I am grateful to have experienced the rollercoaster of graduate school with my fellow cohort and peers across disciplines at SIO. Finally, thank you to the graduate and Geosciences Research Division offices for facilitating academic and research endeavors of students and fostering a positive working environment.

I also like to acknowledge my friends and family outside of the Bermuda, Hawaii, and SIO communities. I'm so appreciative of the constant support from friends from all stages of

my life – childhood, college, and graduate school. I could not have mentally made it this far without your friendship. Words cannot express how much gratitude and love I have for my family – Howard, Dawn, Billy, and Maria Page – for supporting my childhood dream of studying the oceans, despite the obstacles faced due to my disability. I am so thankful that you allowed me to spread my wings while maintaining closeness and traveling this journey with me. I could not have asked for a better or more supportive family. THANK YOU!!!

I owe my thanks to several institutions and agencies for providing funding to support my academic career and research expenses. The UCSD Diversity Fellowship, NSF Graduate Research Fellowship, and NSF Graduate Teaching Fellowship in K-12 STEM Education provided significant financial support throughout the past five years. The Tegner Research Award provided funding for field research in Hawaii. Finally, thanks for additional financial support from Association of Women in Science, Foundation of Science and Disability, and Scripps Institution of Oceanography.

Chapter 2, in full, is a reprint of the material as it appears in **Page, HN**, Andersson, AJ, Jokiel, PL, Rodgers, KS, Lebrato, M, Yeakel, K, Davidson, C, D'Angelo, S, & Bahr, KD. (2016). Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral Reefs* 35(4): 1311-1325. The dissertation author was the primary investigator and author of this paper.

Chapter 3, in full, is a reprint of the material as it appears in **Page, HN**, Courtney, TA, Collins, A, De Carlo, EH, & Andersson, AJ. (2017). Net community metabolism and seawater carbonate chemistry scale non-intuitively with coral cover. *Frontiers in Marine Science* 4:161. doi: 10.3389/fmars.2017.00161. The dissertation author was the primary investigator and author of this paper.

Chapter 4, in full, is submitted for publication of the material as it may appear in **Page, HN**, Courtney, TA, Koester, I, Howins, N, De Carlo, EH & Andersson, AJ. (submitted). Spatio-temporal dynamics in seawater carbonate chemistry for a coral reef flat in Kaneohe Bay, Hawaii. *Limnology and Oceanography.* The dissertation author was the primary investigator and author of this paper.

VITA

2007 Bachelor of Science, University of North Carolina, Wilmington

2014 Master of Science, University of California, San Diego

2017 Doctor of Philosophy, University of California, San Diego

PUBLICATIONS

Courtney, TA, De Carlo, EH, **Page, HN**, Bahr, KD, Barro, A, Howins, N, Tabata, R, Terlouw, G, Rodgers, KS & Andersson, AJ. (in press). Recovery of reef-scale calcification following a bleaching event in Kāneʻohe Bay, Hawaiʻi. *Limnology and Oceanography Letters.*

Paulsen, M-L, Andersson, AJ, Aluwihare, L, Cyronak, T, D'Angelo, S, Davidson, C, Elwany, H, Giddings, S, Harvey, M, **Page, HN**, Porrachia, M, & Schroeter, S. (2017). Temporal changes in seawater carbonate chemistry and carbon export from a southern California estuary. *Estuaries and Coasts.* doi: https://doi.org/10.1007/s12237-017-0345-8.

Page, HN, Courtney, TA, Collins, A, De Carlo, EH, & Andersson, AJ. (2017). Net community metabolism and seawater carbonate chemistry scale non-intuitively with coral cover. *Frontiers in Marine Science* 4:161. doi: 10.3389/fmars.2017.00161.

Page, HN, Andersson, AJ, Jokiel, PL, Rodgers, KS, Lebrato, M, Yeakel, K, Davidson, C, D'Angelo, S, & Bahr, KD. (2016). Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral Reefs*. 35(4): 1311-1325.

Long, WC, Swiney, KM, Harris, C, **Page, HN**, & Foy, RJ. (2013). Effects of ocean acidification on juvenile red king crab and Tanner crab. *PloS one*. 8(4): e60959.

Hettinger, A, Sanford, E, Hill, TM, Russell, AD, Sato, KN, Hoey, J, Forsch, M, **Page, HN**, & Gaylord, B. (2012). Persistent carry-over effects of planktonic exposure to ocean acidification in the Olympia oyster. *Ecology*. 93(12): 2758-2768.

Page, HN. (2011). Biogeochemical effects on the adult oyster *Crassostrea virginica* feeding efficiency and condition. *University of North Carolina Wilmington Department of Biology and Marine Biology*, Thesis: 59 pp.

ABSTRACT OF THE DISSERTATION

Ocean acidification on coral reefs: the effects of community composition on benthic metabolism and seawater carbonate chemistry

by

Heather N. Page

Doctor of Philosophy in Oceanography

University of California, San Diego, 2017

Professor Andreas Andersson, Chair

The ability of many coral reefs to maintain community composition (i.e., high coral cover), ecosystem structure, and reef functions have diminished as they face regional perturbations and global climate change. Future anthropogenic ocean acidification (OA) from oceanic uptake of carbon dioxide (CO_2) may further contribute to declining global reef health.

However, the magnitude of OA on coral reefs will be compounded by natural temporal and spatial variability which is influenced by a suite of biological and physical oceanographic properties including benthic metabolism by reef communities. In mesocosm experiments, calcifying communities experienced relatively static seawater pH and saturation state with respect to aragonite (Ω_a) due to counteracting effects of net organic carbon production and net calcification on these parameters. In contrast, fleshy macroalgae elevated daytime seawater pH and Ω_a due to high rates of net organic carbon production; a mixed community also elevated seawater pH and Ω_a albeit to a lesser extent. Under short-term OA, daytime net organic carbon production by fleshy macroalgae and nighttime calcium carbonate dissolution buffered against acidification. In additional experiments, net community calcification and net respiration scaled proportionally to coral cover; however, daytime net organic carbon production did not. This differential scaling of benthic metabolism caused increasing acidification with increasing coral cover at night and similar seawater chemistry during the day. Thus, areas with higher coral cover experience larger diurnal seawater pH and CO_2 chemistry as observed in mesocosms and on reefs in Bermuda and Hawaii. Although community composition influences *in situ* temporal and spatial variability in seawater CO_2 chemistry on a reef flat in Kaneohe Bay, Hawaii, the strongest drivers relate to seawater depth, which reflects water volume to benthic biomass ratio, and circulation, which relates to the age of seawater that has been continuously modified by biogeochemical processes. Thus, to more accurately predict the magnitude and potential effects of future OA on coral reefs, experimental results should be bridged to natural settings which often are more complex and have co-varying biological (i.e., community composition and benthic metabolism) and

physical (i.e. seawater depth and circulation) properties that influence seawater CO_2 variability across space and time.

CHAPTER 1

Introduction: Ocean acidification on coral reefs

Heather N. Page

1.1 Background Information

Anthropogenic Carbon Dioxide and Ocean Acidification

Humans have caused dramatic changes in the global carbon cycle since the Industrial Revolution in the mid-1700s. This revolution resulted in an increase in burning of fossil fuels along with changes in land-use practices associated with industrialization and human population growth (Le Quéré et al. 2015). As a consequence, global average atmospheric carbon dioxide (CO_2) has increased at an unprecedented rate from a pre-Industrial concentration of 280 ppm to ~400 ppm today (Keeling et al. 2005; IPCC 2013; http://scrippsco2.ucsd.edu/data/ atmospheric_co2/primary_mlo_co2_record). This increase is projected to continue and atmospheric CO_2 concentration may reach over 1000 ppm by 2100 under the most extreme CO_2 emission scenario (Representative Concentration Pathway 8.5; IPCC 2013). The global change in atmospheric CO_2 owing to anthropogenic activities will most certainly have an impact on many terrestrial and marine ecosystems worldwide.

Approximately half of atmospheric CO_2 remains in the atmosphere with the remaining half distributed fairly equally between terrestrial and oceanic sinks (Le Quéré et al. 2015). Increased dissolution of CO_2 into surface seawater shifts carbonate chemistry equilibrium and decreases seawater pH (i.e., increases concentration of H^+ ions) through the following chemical equilibrium reactions (1):

$$CO_{2(atm)} \leftrightarrow CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (1)$$

The net effect of increasing CO_2 can somewhat simplified be illustrated by reaction (2):

$$CO_2 + H_2O + CO_3^{2-} \leftrightarrow 2HCO_3^- \quad (2)$$

Over the past few decades, surface seawater pH has decreased 0.001-0.003 annually in most oceanic regions (Bates et al. 2014; Lauvset et al. 2015; García-Ibáñez et al. 2016). The shift in

carbonate chemistry equilibrium associated with higher CO_2 causes increased bicarbonate (HCO_3^{2-}) ion concentration and less carbonate (CO_3^{2-}) ions (Zeebe and Wolf-Gladrow 2001). Additionally, lower carbonate ion concentration reduces seawater saturation state (Ω) with respect to calcium carbonate ($CaCO_3$) minerals, aragonite (Ω_a) and calcite (Ω_c):

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}^*}$$

where K_{sp}^* is the solubility product of calcite or aragonite at equilibrium. As Ω approaches values less than 1 (i.e. under-saturation), dissolution of $CaCO_3$ becomes thermodynamically favorable. Numerical models accounting for different CO_2 emission scenarios project continued decrease in open ocean Ω and seawater pH, effects collectively known as ocean acidification, through the next century (Hoegh-Guldberg et al. 2007; IPCC 2013; Gattuso et al. 2015). Under a business-as-usual CO_2 emission scenarios, seawater pH is projected to decrease 0.3-0.32 by the end of the 21st century (IPCC 2013) and seawater Ω_a would be greatly reduced, possibly reaching under-saturation in surface waters at high latitudes such as the Arctic and Southern Oceans (Feely et al. 2009).

The present and future changes in seawater carbonate chemistry have generated concerns about the fate of marine organisms and ecosystems, particularly those that depend on favorable chemical conditions to secrete their tests, shells, exoskeletons, and support structures made of $CaCO_3$ (Kleypas et al. 2005; Doney et al. 2009). Consequently, scientists have employed a variety of research approaches to study the potential consequences of OA across functional, spatial, and temporal scales (Andersson et al. 2015) with much of the focus on understanding direct effects of OA on calcifying individuals. In general, marine calcifiers tend to experience decreased growth and calcification rates when exposed to high pCO_2/low

pH seawater (Ries et al. 2009; Kroeker et al. 2010; Harvey et al. 2013; Kroeker et al. 2013a; Wittman and Pörtner 2013), although responses vary due to intra- and inter-specific variation and differences in experimental systems and design. The differential responses of marine organisms to OA may scale up to shift ecosystem structure and function (Guinotte and Fabry 2008; Sanford et al. 2014; Marshall et al. 2017; Vizzini et al. 2017), potentially having dramatic, negative socio-economic impacts (Cooley and Doney 2009; Narita et al. 2012; Barton et al. 2015).

However, the effects of OA on communities and ecosystems are still relatively uncertain due to experimental constraints and natural increases in complexity of communities and ecosystems relative to individuals. Marine organisms do not live in isolation in the natural world but interact with each other and the surrounding environment, and therefore the responses of individuals to OA may not directly reflect the responses at upper functional scales (Mumby and van Woesik 2014; Gaylord et al. 2015; Edmunds et al. 2016). In comparison to the number of studies conducted on individuals, there have been far fewer experiments examining the response of marine communities and ecosystems. Additionally, our understanding of the *in situ* response of marine organisms, communities, and ecosystems is limited to observations across natural pH gradients, typically located near CO_2 vents or seeps (Hall-Spencer et al. 2008; Fabricius et al. 2011; Kroeker et al. 2011). Thus, there is a gap in our understanding of how entire ecosystems may respond to changing seawater carbonate chemistry in natural settings and a need to integrate results across functional, spatial, and temporal scales (Andersson et al. 2015; Edmunds et al. 2016).

Ocean Acidification on Coral Reefs

Tropical coral reefs, which are highly valued ecosystems due to the number of tangible goods and services they provide (Spurgeon 1992; Moberg and Folke 1999; Costanza et al. 2004), have been identified as ecosystems that may be especially vulnerable to ongoing and future OA since they rely on a $CaCO_3$ foundation and have already been declining due to a variety of stressors (Hoegh-Guldberg et al. 2007; Kleypas and Yates 2009; Silverman et al. 2009). OA is predicted to decrease growth and calcification rates of corals and calcifying algae (Marubini et al. 2003; Ohde and Hossain 2004; Holcomb et al. 2010; Johnson and Carpenter 2012; Chan and Connolly 2013; Comeau et al. 2013; Johnson et al. 2014; Horvath et al. 2016) and lower net calcification of communities dominated by calcifiers (Leclercq et al. 2002; Langdon and Atkinson 2005; Andersson et al. 2009) while $CaCO_3$ dissolution, particularly of biogenic sediments, and bioerosion may increase (Andersson et al. 2007; Cyronak et al. 2013; Eyre et al. 2014; Pickett and Andersson 2015). These changes would influence the persistence of coral reefs which depend on the ability of reefs to maintain a positive carbonate budget where constructive processes (i.e. calcification and $CaCO_3$ accretion) are greater than or equal to destructive processes (i.e. $CaCO_3$ dissolution, bioerosion, and export) (Andersson and Gledhill 2013; Eyre et al. 2014). OA also may facilitate shifts from dominance by calcifiers to higher benthic coverage of non-calcifying algae (Kroeker et al. 2013b; Enochs et al. 2015). This belief is based on observations across natural acidification gradients around CO_2 vents and experimental evidence showing maintained or elevated growth (Koch et al. 2013; Johnson et al. 2014) as well as increased competitive strength via allelopathy (Diaz-Pulido et al. 2011) of non-calcifying autotrophs exposed to short-term acidification.

However, the effects of long-term anthropogenic OA on coral reefs will be compounded by the natural spatial and temporal variabilities in seawater carbonate chemistry and pH. Surface seawater CO_2 buoys and benthic instruments located on coral reefs around the world have recorded diurnal pH ranges of 0.1 to 0.4 and CO_2 ranging from 200 to >1000 μmol mol^{-1} with higher pH and lower CO_2 during the day relative to night (Kayanne et al. 1995; Dai et al. 2009; Manzello 2010; Hofmann et al. 2011; Andersson & Mackenzie 2012; Price et al. 2012; https://www.pmel.noaa.gov/co2/story/Coral+Reef+Moorings). These natural fluctuations on shallow, tropical coral reefs mainly are attributed to a combination of physical oceanographic setting (e.g. shallow water) and biogeochemical processes, including those involved in benthic metabolism, as shown by field observations (Smith 1973; Kawahata et al. 1997; Kayanne et al. 2005; Shaw et al. 2012; Kleypas et al. 2011; Falter et al. 2012; Albright et al. 2013; Teneva et al. 2013; Koweek et al. 2015a, b) and numerical models (Suzuki et al. 1995; Zhang et al. 2012; Falter et al. 2013).

Benthic metabolism refers to biogeochemical processes contributing to net community calcification (NCC = gross calcification – $CaCO_3$ dissolution) and net community production (NCP = gross organic carbon production – autotrophic and heterotrophic respiration). NCC and NCP directly influence seawater carbonate chemistry by producing and consuming total alkalinity (TA = $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] – [H^+]$ ± other minor constituents; the buffering capacity of seawater as determined by the excess of proton acceptors over proton donors) and dissolved inorganic carbon (DIC = $[CO_2] + [HCO_3^-] + [CO_3^{2-}]$). NCC always changes TA and DIC in a 2:1 ratio while NCP primarily influences DIC with comparatively minor changes in TA from nutrient uptake and release (Zeebe and Wolf-Gladrow 2001). These modifications in seawater TA and DIC promote either acidification or

alkalinization as visualized through TA-DIC regressions (Figure 1.1). Since both NCC and NCP occur simultaneously on coral reefs, both the absolute rates and relative balance of these processes determine the overall seawater carbonate chemistry average conditions and variability across space and time (Andersson and Gledhill 2013).

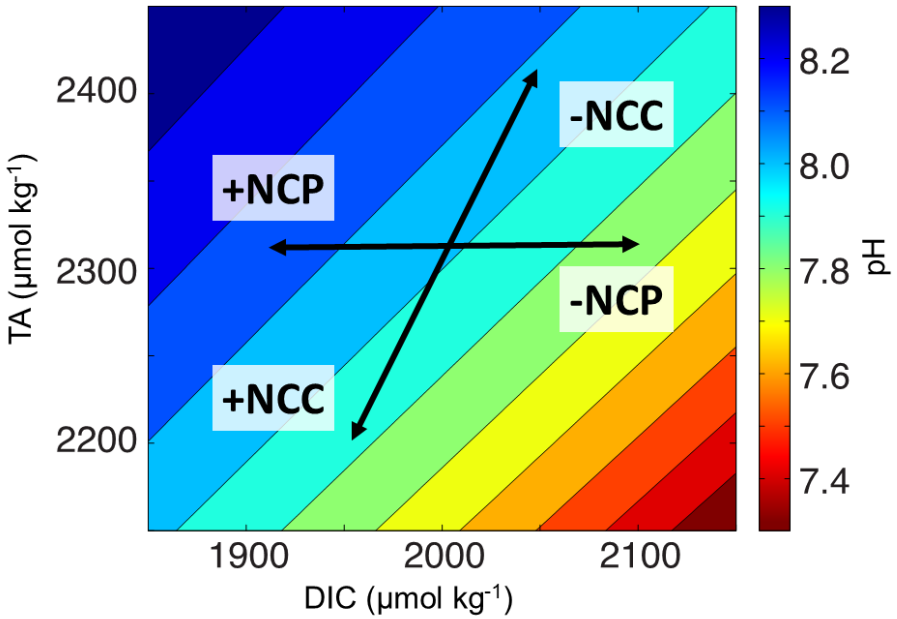


Figure 1.1 Deffeyes diagram showing effects of benthic metabolism on seawater TA, DIC, and pH. NCC alters TA and DIC in a 2:1 ratio such that net calcification (+NCC) acidifies seawater while net $CaCO_3$ dissolution (-NCC) alkalinizes seawater. Net organic carbon production (+NCP) consumes DIC and increases pH while net respiration (-NCP) produces DIC and decreases pH.

Benthic metabolism is related to community composition which has been undergoing dramatic changes during the past few decades as coral reefs respond to a variety of regional environmental disturbances and global climate changes (e.g. Hughes and Connell 1999). Coral reefs around the world have experienced decreased coral cover (Gardner et al. 2003; Bruno and Selig 2007; De'ath et al. 2012) and shifts towards higher relative abundance of non-calcifying organisms like algae, sponges, and cyanobacterial mats (Hughes 1994; Gardner et al. 2003; Pandolfi et al. 2005; de Bakker et al. 2017). These shifts in community

composition may alter benthic metabolism and natural seawater carbonate chemistry variability since observational data suggest that changing community composition from coral dominance to higher abundance of macroalgae results in lower NCC relative to NCP, causing an increase in average daytime pH and Ω_a (Anthony et al. 2011; Kleypas et al. 2011; Anthony et al. 2013; Jokiel et al. 2014) and a decrease in average night pH and Ω_a (Anthony et al. 2011). Thus, natural variabilities in seawater carbonate chemistry are likely to be modified as community composition of coral reefs continue to change in the future under changing environmental conditions.

However, we still do not understand how important changing community composition is to the seawater carbonate chemistry and pH on coral reefs. What are the contributions of different functional groups and densities to natural variabilities across time and space, and how are these contributions affected by physical and environmental properties such as depth, flow rates, and season? These questions need to be addressed before investigating the magnitude and effects of OA on reefs since communities may locally alleviate or exacerbate anthropogenic OA through benthic metabolism. Therefore, research aimed at understanding how much variability coastal ecosystems experience and the feedbacks between coral reef communities, benthic metabolism, and seawater carbonate chemistry is needed.

1.2 Outline of the Dissertation

In this dissertation, a combination of research approaches – mesocosm experiments and observational field studies – were used to address the broad objective of understanding the relationships between coral reef community composition, benthic metabolism, and seawater carbonate chemistry on diurnal time scales across seasons. First, mesocosm

experiments to study the influence of different reef communities (functional groups and coral cover) on diurnal (i.e., 24-hour) benthic metabolism and seawater carbonate chemistry were conducted. Then, temporal and spatial variabilities in seawater carbonate chemistry on a reef flat with varying community compositions in Kaneohe Bay, Hawaii were measured. Chapters 2-4 each were prepared as stand-alone studies (Page et al. 2016; Page et al. 2017; Page et al., *in prep*) and therefore similar introductory material and methodologies may be repeated throughout. A final chapter serves as a summary of key findings and conclusion to this dissertation.

Chapter 2 addresses several research objectives aimed at understanding how different coral reef benthic communities modify diurnal seawater carbonate chemistry. Specifically, the direct attributions of NCC and NCP to observed diurnal changes in seawater pH and Ω_a were compared across five reef communities (sand, crustose coralline algae, coral, fleshy macroalgae, and a mixed community) during two seasons and under two acidification scenarios (ambient and high pCO_2). An additional objective of this research was to evaluate whether observed TA-DIC regressions could be used as a potential tool for broad assessment of benthic reef metabolism and community composition. These objectives address the need to evaluate community-level metabolic responses of coral reefs to OA and to consider biogeochemical monitoring techniques for monitoring changes in ecosystem structure (i.e. community composition) and function (i.e. metabolism and carbon cycling) on coral reefs. Additionally, this is one of the first studies to quantify the direct attribution of NCC and NCP on seawater carbonate chemistry under a variety of environmental and chemical conditions. The research objectives were addressed by creating communities representing dominant functional groups on the reefs (carbonate sand, crustose coralline algae, corals, and fleshy

macroalgae) as well as a mixed community within flow-through mesocosms and then measuring seawater chemistry hourly over diurnal cycles. The results from this study highlights the ability of communities and biogeochemical processes, which are temporally and spatially variable in response to environmental changes, to possibly exacerbate or alleviate anthropogenic OA on reefs. Chapter 2 has been published, in full, as Page, HN, Andersson, AJ, Jokiel, PL, Rodgers, KS, Lebrato, M, Yeakel, K, Davidson, C, D'Angelo, S, & Bahr, KD. (2016). Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral Reefs*. 35(4): 1311-1325.

Chapter 3 focuses on coral communities in order to investigate the influence of coral cover on benthic metabolism (i.e. rates of NCC and NCP) and diurnal seawater carbonate chemistry in Bermuda and Hawaii. Coral cover has been decreasing on reefs worldwide in response to regional environmental perturbations and global climate change (e.g., Wilkinson 2008; Bruno and Valdivia 2016), but how does this influence natural variability of benthic metabolism and seawater carbonate chemistry on reefs? The first hypothesis tested in this study states that high coral cover has higher NCC and NCP rates compared to low coral and that these rates scale proportionally to coral cover. Due to this scaling, we also hypothesized that high coral cover results in greater diurnal variability of seawater carbonate chemistry (CO_2, pH, and Ω_a) due to the proportional scaling of benthic metabolism. These hypotheses initially were tested in Bermuda; however, an inability to precisely control seawater flow rates through mesocosms resulted in inconclusive results. Therefore, follow-up experiments were conducted in Hawaii since the mesocosm facility located there allows more uniform flow rates across mesocosms. In addition, comparison of *in situ* seawater CO_2 at three reef sites in Bermuda and Hawaii complemented the mesocosm results. This chapter highlights the need

to integrate metabolism of coral reefs across functional, spatial, and temporal scales in order to fully comprehend future responses to environmental changes. Chapter 3 has been published, in full, as Page, HN, Courtney, TA, Collins, A, De Carlo, EH, & Andersson, AJ. (2017). Net community metabolism and seawater carbonate chemistry scale non-intuitively with coral cover. *Front. Mar. Sci.* 4:161. doi: 10.3389/fmars.2017.00161.

The results presented in Chapters 2 and 3 primarily utilized flow-through mesocosm systems located at the Bermuda Institute of Ocean Sciences (BIOS) and Hawaii Institute of Marine Biology (HIMB). These experimental systems allowed reef communities created in mesocosms to experience natural diurnal fluctuations in environmental conditions (e.g. light, temperature) while giving us the ability to control seawater flow and community composition. Additionally, using these facilities allowed us to more easily sample seawater over diurnal time scales under environmentally relevant conditions compared to laboratory or *in situ* experiments. However, the ultimate goal is to understand the function and role of natural benthic communities on seawater CO_2 chemistry in their natural environment. Thus, Chapter 4 builds on the previous chapters by examining how *in situ* temporal and spatial variabilities in seawater chemistry relates to potential ecological (i.e. community composition), biogeochemical (i.e. benthic metabolism), and physical (i.e. seawater flow, residence time, and depth) drivers on a reef flat in Kaneohe Bay, Hawaii. Autonomous instruments sampled seawater conditions (e.g. pH, dissolved oxygen, temperature, and irradiance) along an offshore-inshore transect with three sites (coral-dominated, mixed, or rubble-dominated) on the reef flat during June and November of 2016. Additionally, spatial surveys of surface seawater carbonate chemistry were conducted at different times of the day within an area containing several contrasting habitats typical of backreef environments including a sand flat,

coral reef, and rubble field. This field study highlights the importance of considering the natural complexities of ecosystems where a combination of factors may influence chemical conditions of coral reefs. Chapter 4 is being prepared to be submitted, in full, as Page, HN, Courtney, TA, De Carlo, EH, Howins, N, Koester, I, and Andersson, AJ. (in prep). Spatio-temporal variability in seawater carbon chemistry for a coral reef flat in Kaneohe Bay, Hawaii. *Limnol. Oceanogr*.

Chapter 5 serves as a conclusion to this dissertation. Key findings from the previous chapters and implications for future OA on coral reefs are summarized here.

1.3 Research Significance

In order to understand the environmental impacts of anthropogenic OA, we first need to know what chemical conditions marine organisms and ecosystems experience presently and how this may change in the future. Current predictions of OA on coral reefs are based upon projected changes for open ocean surface seawater; however, reef seawater carbonate chemistry is much more variable than the open ocean. This natural variability may lead to localized regions on coral reefs that are more or less susceptible to OA depending on exacerbation or buffering of seawater pH by benthic metabolism. Therefore, there is a need to understand how biological and physical properties affects temporal and spatial variability in seawater chemistry. Furthermore, scientists have advocated using a combination of research and theoretical approaches in order to bridge experimental results to natural settings; integrating results across functional, spatial, and temporal scales will allow better predictions of how coral reefs may respond to changing environmental conditions in the future (Andersson et al. 2015; Gaylord et al. 2015; Edmunds et al. 2016). This dissertation addresses

these short-comings in OA research by first examining the influence of biological properties (community composition and benthic metabolism) on coral reefs to changes seawater carbonate chemistry through mesocosm experiments and then conducting an observational field study to examine the influence of different benthic communities in the context of natural flow and environmental gradients on a reef flat. The results from this study can be used to better inform policy and reef management through more accurate parameterization of numerical models projecting regional OA on coral reefs taking into account changes to community composition, benthic metabolism, and environmental conditions which influence natural variability in seawater carbonate chemistry and may compound the magnitude and effects of long-term anthropogenic OA on coral reefs in the future.

1.4 References Cited

Albright, R, Langdon, C, & Anthony, KRN. 2013. Dynamics of seawater carbonate chemistry, production, and calcification of a coral reef flat, central Great Barrier Reef. *Biogeosciences* 10: 6747.

Andersson, AJ, Bates, NR, & Mackenzie, FT. 2007. Dissolution of carbonate sediments under rising pCO_2 and ocean acidification: Observations from Devil's Hole, Bermuda. *Aquatic Geochemistry* 13: 237-264.

Andersson, AJ & Gledhill, D. 2013. Ocean acidification and coral reefs: Effects on breakdown, dissolution, and net ecosystem calcification. *Annual Review of Marine Science* 5:321-348.

Andersson, AJ, Kline, DI, Edmunds, PJ, Archer, SD, Bednaršek, N, Carpenter, RC, Chadsey, M, Goldstein, P, Grottoli, AG, Hurst, TP, King, AL, Kübler, JE, Kuffner, IB, Mackey, KRM, Menge, BA, Paytan, A, Riebesell, U, Schnetzer, A, Warner, ME, & Zimmerman, RC. (2015). Understanding ocean acidification impacts on organismal to ecological scales. *Oceanography* 28, 16–27. doi: 10.5670/oceanog.2015.27.

Andersson, AJ, Kuffner, IB, Mackenzie, FT, Jokiel, PL, Rodgers, KS, & Tan, A. 2009. Net loss of $CaCO_3$ from a subtropical calcifying community due to seawater acidification: mesocosm-scale experimental evidence. *Biogeosciences* 6:1811-1823.

Andersson, AJ & Mackenzie, FT. 2012. Revisiting four scientific debates in ocean acidification research. *Biogeosciences* 9:893-905.

Anthony, KRN, Kleypas, JA, & Gattuso, J-P. 2011. Coral reefs modify their seawater carbon chemistry – implications for impacts of ocean acidification. *Global Change Biology* 17:3655-3666.

Anthony, KRN, Diaz-Pulido, G, Verlinden, N, Tilbrook, B, & Andersson, AJ. 2013. Benthic buffers and boosters of ocean acidification on coral reefs. *Biogeosciences* 10: 4897-4909.

Barton, A, Waldbusser, GG, Feely, RA, Weisburg, SB, Newton, JA, Hales, B *et al.* 2015. Impacts of coastal acidification on the Pacific Northwest shellfish industry and adaptation strategies implemented in response. *Oceanography* 28: 146-159.

Bates, NR, Astor, YM, Church, MJ, Currie, K, Dore, JE, González-Dávila, M, Lorenzoni, L, Muller-Kargor, F, Olafsson, J, & Santana-Casiano, JM. 2014. A time-series view of changing surface ocean chemistry due to ocean uptake of anthropogenic CO_2 and ocean acidification. *Oceanography* 27: 126-141.

Bruno, JF & Selig, ER. 2007. Regional decline of coral cover in the Indo-Pacific: timing, extent, and subregional comparisons. *PLoS ONE* 2: e711. doi: 10.1371/journal.pone.0000711.

Chan, NCS & Connolly, SR. 2013. Sensitivity of coral calcification to ocean acidification: a meta-analysis. *Global Change Biology* 19: 282-290.

Comeau, S, Edmunds, PJ, Spindel, NB, & Carpenter, RC. 2013. The responses of eight coral reef calcifiers to increasing CO_2 do not exhibit a tipping point. *Limnology and Oceanography* 58: 388–398. doi: 10.4319/lo.2013.58.1.0388.

Cooley, SR & Doney, SC. 2009. Anticipating ocean acidification's economic consequences for commercial fisheries. *Environmental Research Letters* 4: 024007. doi: 10.1088/1748-9326/4/2/024007.

Costanza, R, de Groot, R, Sutton, P, van der Ploeg, S, Anderson, SJ, Kubiszewski, I, Farber, S, & Turner, RK. 2014. Changes in the global value of ecosystem services. *Global Environmental Change* 26, 152–158. doi: 10.1016/j.gloenvcha.2014.04.002.

Cyronak, T, Santos, IR, McMahon, A, & Eyre, BD. 2013. Carbon cycling hysteresis in permeable carbonate sands over a diel cycle: implications for ocean acidification. *Limnology and Oceanography* 58: 131-143.

Dai, M, Lu, Z, Zhai, W, Chen, B, Cao, Z, Zhou, K *et al.* 2009. Diurnal variations of surface seawater pCO_2 in contrasting environments. *Limnology and Oceanography* 54: 735-745.

De Bakker, DM, van Duyl, FC, Bak, RPM, Nugues, MM, Nieuwland, G, & Meesters, EH. 2017. 40 years of benthic community change on the Caribbean reefs of Curaçao and Bonaire: the rise of slimy cyanobacterial mats. *Coral Reefs* 36: 355-367.

De'ath, G, Fabricius, KE, Sweatman, H, & Puotinen, M. 2012. The 27-year decline of coral cover on the Great Barrier Reef and its causes. *Proceedings of the National Academy of Sciences of the United States of America* 109: 17995–17999. doi: 10.1073/pnas.1208909109.

Diaz-Pulido, G, Gouezo, M, Tilbrook, B, Dove, S, & Anthony, KRN. 2011. High CO_2 enhances the competitive strength of seaweeds over corals. *Ecology Letters* 14: 156-162.

Doney, SC, Fabry, VJ, Feely, RA, & Kleypas, JA. 2009. Ocean acidification: The other CO2 problem. *Annual Review of Marine Science* 1: 169-192.

Edmunds, PJ, Comeau, S, Lantz, C, Andersson, A, Briggs, C, Cohen, A, Gattuso, J-P, Grady, JM, Gross, K, Johnson, M, Muller, JEB, Ries, JB, Tambutté, S, Tambutté, E, Venn, A, & Carpenter, RC. 2016. Integrating the effects of ocean acidification across functional scales on tropical coral reefs. *Bioscience* 66, 350–362. doi: 10.1093/biosci/biw023.

Enochs, IC, Manzello, DP, Donham, EM, Kolodziej, G, Okano, R, Johnston, L, Young, C, Iguel, J, Edwards, CB, Fox, MD, Valentino, L, Johnson, S, Benavente, D, Clark, SJ, Carlton, R, Burton, T, Eynaud, Y, & Price, NN. 2015. Shift from coral to macroalgae dominance on a volcanically acidified reef. *Nature Climate Change* 5: 1083-1088.

Eyre, BD, Andersson, AJ, & Cyronak, T. 2014. Benthic coral reef calcium carbonate dissolution in an acidifying ocean. *Nature Climate Change* 4: 969–976.

Fabricius, KE, Langdon, C, Uthicke, S, Humphrey, C, Noonan, S, De-ath, G, Okazaki, R, Muehllehner, N, Glas, MS, & Lough, JM. 2011. Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations. *Nature Climate Change* 1: 165-169.

Falter, JL, Lowe, RJ, Atkinson, MJ, & Cuet, P. 2012. Seasonal coupling and de-coupling of net calcification rates from coral reef metabolism and carbonate chemistry at Ningaloo Reef, Western Australia. *Journal of Geophysical Research* 117: C05003. doi: 10.1029/2011JC007268.

Falter, JL, Lowe, RJ, Zhang, Z, & McCulloch, M. 2013. Physical and biological controls on the carbonate chemistry of coral reef waters: Effects of metabolism, wave forcing, sea level, and geomorphology. *PLoS ONE* 8: e53303.

Feely, RA, Doney, SC, & Cooley, SR. 2009. Ocean acidification: present conditions and future changes in a high-CO_2 world. *Oceanography* 22: 36-47.

García-Ibáñez, MI, Carracedo, LI, Ríos, AF, & Pérez, FF. 2016. Ocean acidification in the subpolar North Atlantic: rates and mechanisms controlling pH changes. *Biogeosciences* 13: 3701-3715.

Gardner, TA, Côté, IM, Gill, JA, Grant, A, & Watkinson, AR. 2003. Long-term region-wide declines in Caribbean corals. *Science* 301: 958–960.

Gattuso, J-P, Magnan, A, Billé, R, Cheung, WWL, Howes, EL, Joos, F, Allemand, D, Bopp, L, Cooley, SR, Eakin, CM, Hoegh-Guldberg, O, Kelly, RP, Pörtner, H-O, Rogers, AD, Baxter, JM, Laffoley, D, Osborn, D, Rankovic, A, Rochette, J, Sumaila, UR, Treyer, S, & Turley, C. 2015. Contrasting futures for ocean and society from different anthropogenic CO_2 emissions scenarios. *Science* 349: aac4722. doi: 10.1126/science.aac4722.

Gaylord, B, Kroeker, KJ, Sunday, JM, Anderson, KM, Barry, JP, Brown, NE, Connell, SD, Dupont, S, Fabricius, KE, Hall-Spencer, JM, Klinger, T, Milazzo, M, Munday, PL, Russell, BD, Sanford, E, Schreiber, SJ, Thiyagarajan, V, Vaughan MLH, Widdicombe, S, & Harley, CDG. 2015. Ocean acidification through the lens of ecological theory. *Ecology* 96: 3-15.

Guinotte, JM & Fabry, VJ. 2008. Ocean acidification and its potential effects on marine ecosystems. *Annals of the New York Academy of Sciences* 1134: 320-342.

Hall-Spencer, JM, Rodolfo-Metalpa, R, Martin, S, Ransome, E, Fine, M, Turner, SM *et al.* 2008. Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* 454: 96-99.

Harvey, BP, Gwynn-Jones, D, & Moore, PJ. 2013. Meta-analysis reveals complex marine biological responses to the interactive effects of ocean acidification and warming. *Ecology and Evolution* 3: 1016-1030.

Hoegh-Guldberg, O, Mumby, PJ, Hooten, AJ, Steneck, RS, Greenfield, P, Gomez, E, Harvell, CD, Sale, PF, Edwards, AJ, Caldeira, K, Knowlton, N, Eakin, CM, Iglesias-Prieto, R, Muthiga, N, Bradbury, RH, Dubi, A, & Hatziolos, ME. 2007. Coral reefs under rapid climate change and ocean acidification. *Science* 318: 1737-1742.

Hofmann, GE, Smith, JE, Johnson, KS, Send, U, Levin, LA, Micheli, F, Paytan, A, Price, NN, Peterson, B, Takeshita, Y, Matson, PG, Crook, ED, Kroeker, KJ, Gambi, MC, Rivest, EB, Frieder, CA, Yu, PC, & Martz, TR. 2011. High-frequency dynamics of ocean pH: A multi-ecosystem comparison. *PLoS ONE* 6: e28983.

Holcomb, M, McCorkle, DC, & Cohen, AL. 2010. Long-term effects of nutrient and CO_2 enrichment on the temperate coral *Astrangia poculata* (Ellis and Solander, 1786). *Journal of Experimental Marine Biology and Ecology* 386: 27–33. doi: 10.1016/j.jembe.2010.02.007.

Horvath, KM, Castillo, KD, Armstrong, P, Westfield, IT, Courtney, T, & Ries, JB. 2016. Next-century ocean acidification and warming both reduce calcification rate, but only acidification alters skeletal morphology of reef-building coral *Siderastrea sidereal*. *Scientific Reports* 6: 29613. doi: 10.1038/srep29613.

Hughes, TP. 1994. Catastrophes, phase shifts, and large-scale degradation of a Caribbean coral reef. *Science* 265: 1547-1551.

Hughes, TP & Connell, JH. 1999. Multiple stressors on coral reefs: a long-term perspective. *Limnology and Oceanography* 44: 932-940.

IPCC. 2013. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

Johnson, MD & Carpenter, RC. 2012. Ocean acidification and warming decrease calcification in the crustose coralline alga *Hydrolithon onkodes* and increase susceptibility to grazing. *Journal of Experimental Marine Biology and Ecology* 434–435: 94-101.

Johnson, MD, Price, NN, & Smith, JE. 2014. Contrasting effects of ocean acidification on tropical fleshy and calcareous algae. *PeerJ* 2: e411.

Jokiel, PL, Jury, CP, & Rodgers, KS. 2014. Coral-algae metabolism and diurnal changes in the CO_2-carbonate system of bulk seawater. *PeerJ*. 2: e378.

Kawahata, H, Suzuki, A, & Goto, K. 1997. Coral reef ecosystems as a source of atmospheric CO_2: evidence from pCO_2 measurements of surface waters. *Coral Reefs* 16: 261-266.

Kayanne, H, Suzuki, A, & Saito, H. 1995. Diurnal changes in the partial pressure of carbon dioxide in coral reef water. *Science* 269: 214-216.

Kayanne, H, Hata, H, Kudo, S, Yamano, H, Watanabe, A, Ikeda, Y, Nozaki, K, Kato, K, Negishi, A, & Saito, H. 2005. Seasonal and bleaching-induced changes in coral reef metabolism and CO_2 flux. *Global Biogeochemical Cycles* 19: GB3015. doi: 10.1029/2004GB002400.

Keeling, CD, Piper, SC, Bacastow, RB, Wahlen, M, Whorf, TP, Heimann, M, & Meijer, HA. 2005. Atmospheric CO_2 and $^{13}CO_2$ exchange with the terrestrial biosphere and oceans from 1978 to 2000: observations and carbon cycle implications. *A History of Atmospheric CO_2 and its effects on Plants, Animals, and Ecosystems*, pp 83-113.

Kleypas, JA, Anthony, KRN, & Gattuso, J-P. 2011. Coral reefs modify their seawater carbon chemistry – case study from a barrier reef (Moorea, French Polynesia). *Global Change Biology* 17: 3667-3678.

Kleypas, JA, Feely, RA, Fabry, VJ, Langdon, C, Sabine, CL, & Robbins, LL. 2006. Impacts of Ocean Acidification on Coral Reefs and Other Marine Calcifiers: A Guide for Future Research, report of a workshop held 18–20 April 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the U.S. Geological Survey, 88 pp.

Kleypas, JA & Yates, KK. 2009. Coral reefs and ocean acidification. *Oceanography* 22: 108-117.

Koch, M, Bowes, G, Ross, C, & Zhang, X-H. 2013. Climate change and ocean acidification effects on seagrasses and marine macroalgae. *Global Change Biology* 19: 103-132.

Koweek, D, Dunbar, RB, Monismith, SG, Mucciarone, DA, Woodson, CB, & Samuel, L. 2015a. High-resolution physical and biogeochemical variability from a shallow back reef on Ofu, American Samoa: an end-member perspective. *Coral Reefs* 34: 979-991.

Koweek, D, Dunbar, R, Rogers, J, Williams, G, Price, N, Mucciarone, D, & Teneva, L. 2015b. Environmental and ecological controls of coral community metabolism on Palmyra Atoll. *Coral Reefs* 34: 339-351.

Kroeker, KJ, Kordas, RL, Crim, RN, Hendricks, IE, Ramajo, L, Singh, GS, Duarte, CM, & Gattuso, J-P. 2013. Impacts of ocean acidification on marine organisms: quantifying sensitivities and interaction with warming. *Global Change Biology* 19: 1884-1896.

Kroeker, KJ, Kordas, RL, Crim, RN, & Singh, GG. 2010. Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. *Ecology Letters* 13: 1419-1434.

Kroeker, KJ, Micheli, F, Gambi, MC, & Martz, TR. 2011. Divergent ecosystem responses within a benthic marine community to ocean acidification. *Proceedings of the National Academy of Sciences of the United States of America* 108: 14515-14520.

Kroeker, KJ, Micheli, F, & Gambi, MC. 2013b. Ocean acidification causes ecosystem shifts via altered competitive interactions. *Nature Climate Change* 3: 156-159.

Langdon, C & Atkinson, MJ. 2005. Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal changes in temperature/irradiance and nutrient enrichment. *Journal of Geophysical Research: Oceans* 110: C09S07.

Lauvset, SK, Gruber, N, Landschützer, P, Olsen, A, & Tjiputra, J. 2015. Trends and drivers in global surface ocean pH over the past 3 decades. *Biogeosciences* 12: 1285.

Le Quéré, C, Moriarty, R, Andrew, RM, Peters, GP, Ciais, R, Friedlingstein, P, Jones, SD, Sitch, S, Tans, P, Arneth, A, Boden, TA, Bopp, L, Bozec, Y, Canadell, JG, Chini, LP, Chevallier, F, Cosca, CE, Harris, I, Hoppema, M, Houghton, RA, House, JI, Jain, AK, Johannessen, T, Kato, E, Keeling, RF, Kitidis, V, Klein Goldewijk, K, Koven, C, Landa, CS, Landschützer, P, Lenton, A, Lima, ID, Marland, G, Mathis, JT, Metzl, N, Nojiri, Y, Olsen, A, Ono, T, Peng, S, Peters, W, Pfeil, B, Poulter, B, Raupach, MR,

Regnier, P, Rödenbeck, C, Saito, S, Salisbury, JE, Schuster, U, Schwinger, J, Séférian, R, Segschneider, J, Steinhoff, T, Stocker, BD, Sutton, AJ, Takahashi, T, Tilbrook, B, van der Werf, GR, Viovy, N, Wang, Y-P, Wanninkhof, R, Wiltshire, A, & Zeng, N. 2015. Global carbon budget 2014. *Earth System Science Data* 7: 47-85.

Leclercq, N, Gattuso, J-P, & Jaubert, J. 2002. Primary production, respiration, and calcification of a coral reef mesocosm under increased CO_2 partial pressure. *Limnology and Oceanography* 47: 558–564.

Manzello, DP. 2010. Ocean acidification hotspots: Spatiotemporal dynamics of the seawater CO_2 system of eastern Pacific coral reefs. *Limnology and Oceanography* 55: 239-248.

Marshall, KN, Kaplan, IC, Hodgson, EE, Hermann, A, Busch, DS, McElhany, P, Essington, TE, Harvey, CJ, & Fulton, EA. 2017. Risks of ocean acidification in the California Current food web and fisheries: ecosystem model projections. *Global Change Biology* 23: 1525-1539.

Marubini, F, Ferrier-Pagès, C, & Cuif, J-P. 2003. Suppression of skeletal growth in scleractinion corals by decreasing ambient carbonate-ion concentration: a cross-family comparison. *Proceedings of the Royal Society B* 270: 79–184. doi: 10.1098/rspb.2002.2212.

Moberg, F & Folke, C. 1999. Ecological goods and services of coral reef ecosystems. *Ecological Economics* 29: 215–233. doi: 10.1016/S0921-8009(99)00009-9.

Mumby, PJ & van Woesik, R. 2014. Consequences of ecological, evolutionary and biogeochemical uncertainty for coral reef responses to climatic stress. *Current Biology* 24: R413–R423. doi: 10.1016/j.cub.2014.04.029.

Narita, D, Rehdanz, K, & Tol, RSJ. 2012. Economic costs of ocean acidification: a look into the impacts on global shellfish production. *Climatic Change* 113: 1049-1063.

Ohde, S & Hossain, MMM. 2004. Effect of $CaCO_3$ (aragonite) saturation state of seawater on calcification of *Porites* coral. *Geochemical Journal* 38: 613–621. doi: 10.2343/geochemj.38.613.

Page, HN, Andersson, AJ, Jokiel, PL, Rodgers, KS, Lebrato, M, Yeakel, K, Davidson, C, D'Angelo, S, & Bahr, KD. 2016. Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral Reefs*. 35: 1311-1325.

Page, HN, Courtney, TA, Collins, A, De Carlo, EH, & Andersson, AJ. 2017. Net community metabolism and seawater carbonate chemistry scale non-intuitively with coral cover. *Frontiers in Marine Science* 4: 161. doi: 10.3389/fmars.2017.00161.

Pandolfi, JM, Jackson, JBC, Baron, N, Bradbury, RH, Guzman, HM, Hughes, TP, Kappel, CV, Micheli, F, Ogden, JC, Possingham, HP, & Sala, E. 2005. Are U.S. coral reefs on the slippery slope to slime? *Science* 307: 1725-1726.

Pickett, M & Andersson, AJ. 2015. Dissolution rates of biogenic carbonates in natural seawater of different pCO_2 conditions: a laboratory study. *Aquatic Geochemistry* 21: 459-485.

Ries, JB, Cohen, AL, & McCorkle, DC. 2009. Marine calcifiers exhibit mixed responses to CO_2-induced ocean acidification. *Geology* 37: 1131-1134.

Sanford, E, Gaylord, B, Hettinger, A, Lenz, EA, Meyer, K, & Hill, TM. 2014. Ocean acidification increases the vulnerability of native oysters to predation by invasive snails. *Proceedings of the Royal Society B* 281: 20132681.

Shaw, EC, McNeil, BI, & Tilbrook, B. 2012. Impacts of ocean acidification in naturally variable coral reef flat ecosystems. *Journal of Geophysical Research: Oceans* 117: C03038. doi: 10.1029/2011JC007655.

Silverman, J, Lazar, B, Cao, L, Caldeira, K, & Erez, J. 2009. Coral reefs may start dissolving when atmospheric CO_2 doubles. *Geophysical Research Letters* 36: L05606.

Smith, SV. 1973. Carbon dioxide dynamics: a record of organic carbon production, respiration, and calcification in the Eniwetok Reef flat community. *Limnology and Oceanography* 18: 106-120.

Spurgeon, JPG. 1992. The economic valuation of coral reefs. *Marine Pollution Bulletin* 24: 529-536.

Suzuki, A, Nakamori, T, & Kayanne, H. 1995. The mechanism of production enhancement in coral reef carbonate systems: model and empirical results. *Sedimentary Geology* 99: 259-280.

Teneva, L, Dunbar, RB, Mucciarone, DA, Dunckley, JF, & Koseff, JR. 2013. High-resolution carbon budgets on a Palau back-reef modulated by interactions between hydrodynamics and reef metabolism. *Limnology and Oceanography* 58: 1851-1870.

Vizzini, S, Martínez-Crego, B, Andolina, C, Massa-Gallucci, A, Connell, SD, & Gambi, MC. 2017. Ocean acidification as a driver of community simplification via the collapse of higher-order and rise of lower-order consumers. *Scientific Reports* 7: 4018. doi: 10.1038/s41598-017-03802-w.

Wittmann, AC & Pörtner, H-O. 2013. Sensitivities of extant animal taxa to ocean acidification. *Nature Climate Change* 3: 995-1001.

Zeebe, RE & Wolf-Gladrow, DA. 2001. CO_2 in seawater: equilibrium, kinetics, isotopes. Elsevier Oceanography Series 65, Elsevier Science, Amsterdam.

Zhang, Z, Falter, J, Lowe, R, & Ivey, G. 2012. The combined influence of hydrodynamic forcing and calcification on the spatial distribution of alkalinity in a coral reef system. *Journal of Geophysical Research: Oceans* 117: C04034. doi: 10.1029/2011JC007603.

CHAPTER 2

Differential modification of seawater carbonate chemistry by major coral reef benthic communities

Heather N. Page, Andreas J. Andersson, Paul L. Jokiel, Ku'ulei S. Rodgers, Mario Lebrato, Kiley Yeakel, Charlie Davidson, Sydney D'Angelo, and Keisha Bahr

Coral Reefs
DOI 10.1007/s00338-016-1490-4

REPORT

Differential modification of seawater carbonate chemistry by major coral reef benthic communities

Heather N. Page[1] · Andreas J. Andersson[1] · Paul L. Jokiel[2] · Ku'ulei S. Rodgers[2] · Mario Lebrato[1] · Kiley Yeakel[1] · Charlie Davidson[1] · Sydney D'Angelo[1] · Keisha D. Bahr[2]

Received: 14 December 2015 / Accepted: 3 August 2016
© Springer-Verlag Berlin Heidelberg 2016

Abstract Ocean acidification (OA) resulting from uptake of anthropogenic CO_2 may negatively affect coral reefs by causing decreased rates of biogenic calcification and increased rates of $CaCO_3$ dissolution and bioerosion. However, in addition to the gradual decrease in seawater pH and Ω_a resulting from anthropogenic activities, seawater carbonate chemistry in these coastal ecosystems is also strongly influenced by the benthic metabolism which can either exacerbate or alleviate OA through net community calcification (NCC = calcification – $CaCO_3$ dissolution) and net community organic carbon production (NCP = primary production − respiration). Therefore, to project OA on coral reefs, it is necessary to understand how different benthic communities modify the reef seawater carbonate chemistry. In this study, we used flow-through mesocosms to investigate the modification of seawater carbonate chemistry by benthic metabolism of five distinct reef communities [carbonate sand, crustose coralline algae (CCA), corals, fleshy algae, and a mixed community] under ambient and acidified conditions during summer and winter. The results showed that different communities had distinct influences on carbonate chemistry related to the relative importance of NCC and NCP. Sand, CCA, and corals exerted relatively small influences on seawater pH and Ω_a over diel cycles due to closely balanced NCC and NCP rates, whereas fleshy algae and mixed communities strongly elevated daytime pH and Ω_a due to high NCP rates. Interestingly, the influence on seawater pH at night was relatively small and quite similar across communities. NCC and NCP rates were not significantly affected by short-term acidification, but larger diel variability in pH was observed due to decreased seawater buffering capacity. Except for corals, increased net dissolution was observed at night for all communities under OA, partially buffering against nighttime acidification. Thus, algal-dominated areas of coral reefs and increased net $CaCO_3$ dissolution may partially counteract reductions in seawater pH associated with anthropogenic OA at the local scale.

Keywords Ocean acidification · Coral reef · Carbon chemistry · Ecosystem function · Biogeochemistry

Introduction

Global coral reef health has been declining over the past several decades with over half of the world's coral reefs experiencing loss of coral cover and/or regime shifts toward algal-dominated ecosystems (Bruno and Selig 2007; Wilkinson 2008). Consequently, there has been an increasing loss of the numerous ecosystem goods and services they provide, worth billions of dollars annually on a global scale (Pandolfi et al. 2005; Costanza et al. 2014). Primary causes of the global decline in coral reef health include disease outbreaks, overfishing, pollution, and climate change (Wilkinson 2008; Dubinsky and Stambler 2010). In addition, concerns have been raised as to how ocean acidification (OA), i.e., the decrease in seawater pH and saturation state with respect to aragonite [$\Omega_a = [Ca^{2+}][CO_3^{2-}]/K^*_{SP}$, where K^*_{SP} is the stoichiometric

Communicated by Biology Editor Mark R. Patterson

✉ Heather N. Page
hnpage@ucsd.edu

[1] Scripps Institution of Oceanography, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0244, USA

[2] Hawaii Institute of Marine Biology, University of Hawaii, 46-007 Lilipuna Road, Kaneohe, HI 96744, USA

solubility product] resulting from uptake of anthropogenic CO_2 will influence coral reefs (Kleypas et al. 1999; Hoegh-Guldberg et al. 2007) because these ecosystems may be particularly vulnerable to OA (Hoegh-Guldberg et al. 2007; Kleypas and Yates 2009; Silverman et al. 2009). Laboratory, mesocosm, and field experiments suggest that the calcification rates of corals and calcifying algae will decrease in response to OA (Anthony et al. 2008; Andersson et al. 2009; Erez et al. 2011; Johnson and Carpenter 2012; Cornwall et al. 2013), while rates of dissolution and bioerosion of $CaCO_3$ substrates are likely to increase (Andersson et al. 2009; Wisshak et al. 2012; Eyre et al. 2014). Decreased calcification concomitant with increased bioerosion and dissolution may potentially drive reefs from a state of net accretion to a state of net dissolution and erosion (Kleypas et al. 1999; Silverman et al. 2009), but the timing of when, how fast, and what the imminent consequences of such a transition exactly means are currently unknown. Furthermore, fleshy macroalgae tend to have increased primary productivity and growth when exposed to CO_2-enriched seawater (Johnson et al. 2014), which further could favor shifts toward algal-dominated reefs (Hoegh-Guldberg et al. 2007; Enochs et al. 2015).

Predicting the future effects of OA on coral reefs and their inhabitants first requires an understanding of how the seawater carbonate chemistry on coral reefs will change, which can then be used to evaluate potential responses by organisms. Open ocean surface seawater carbonate chemistry can be relatively well constrained based on fundamental chemical principles for any given atmospheric CO_2 scenario. In contrast, predicting the surface seawater carbonate chemistry of coral reefs is more challenging because these shallow inshore areas are strongly controlled by the benthic net metabolism and physical oceanographic conditions such as water flow, residence time, and in some cases also by mixing with groundwater or riverine runoff (Suzuki and Kawahata 1999; Falter et al. 2013; Cyronak et al. 2014). Benthic net metabolism refers to the sum of the biogeochemical processes of calcification, $CaCO_3$ dissolution, primary production, and total respiration that influence seawater-dissolved inorganic carbon (DIC) and total alkalinity (TA), the ratio of which combined with temperature, salinity, and pressure determines seawater pH, pCO_2, and Ω_a (Zeebe and Wolf-Gladrow 2001). Net community calcification (NCC) is the balance between gross calcification and $CaCO_3$ dissolution and changes DIC and TA in a ratio of 1:2. Consequently, net calcification (positive NCC) results in a reduction in seawater pH and Ω_a, while net dissolution (negative NCC) results in an increase in seawater pH and Ω_a. Net community production (NCP) is the difference between gross primary production and total respiration, and this process primarily changes DIC, while TA stays relatively constant. A community with positive NCP is identified as net autotrophic and acts to elevate seawater pH and Ω_a through net drawdown of DIC, while net heterotrophic communities (negative NCP) decrease seawater pH and Ω_a. Due to these relationships, scientists have utilized linear regressions of seawater DIC and TA to characterize the relative importance of NCC and NCP in reef environments (Suzuki and Kawahata 2003; Watanabe et al. 2006; Andersson et al. 2014). It has also been proposed that this method could be used as a chemical tool to evaluate changes in community composition, biogeochemical properties, and performance of coral reefs in the context of climate change and OA (Andersson and Gledhill 2013; Lantz et al. 2014).

Because coral reefs are comprised of organisms and communities with different capacities for calcification, primary production, and respiration, community composition is strongly linked to benthic net metabolism and the resulting modifications of seawater carbonate chemistry. Model simulations parameterized with field data from Moorea (French Polynesia) and flume studies conducted at Heron Island (Great Barrier Reef, Australia) showed increased average seawater Ω_a as community composition changed from coral dominance to higher abundance of macroalgae during the day (Anthony et al. 2011; Kleypas et al. 2011). At night, benthic communities decreased seawater Ω_a, with increasingly lower values resulting as a function of increasing relative abundance of corals (Anthony et al. 2011). Modifications of seawater carbonate chemistry from benthic metabolism, which could either increase or decrease seawater pH and Ω_a, may in turn influence rates of NCC and NCP, potentially creating intrinsic feedback loops between different benthic communities, metabolic activity, and seawater carbonate chemistry (Suzuki et al. 1995; Bates et al. 2010). For example, seawater pH and calcification rates of red and green calcareous algae were observed to be higher in the presence of seagrass and lower in areas where seagrass had been removed (Semesi et al. 2009). On the Bermuda reef platform, coral skeletal growth and estimated reef NEC rates were highest during a seasonal period of net autotrophy (early summer) when $[CO_3^{2-}]$ and consequently Ω_a were temporally elevated. In contrast, net heterotrophic conditions hypothesized to result from a die-off of macroalgae corresponded to lower $[CO_3^{2-}]$ and Ω_a at the end of summer and resulted in suppressed coral calcification and skeletal growth rates (Bates et al. 2010).

In order to develop the ability to predict future changes in seawater carbonate chemistry for different coral reef communities, it is necessary to understand how these benthic communities modify seawater carbonate chemistry and how they might change in response to future environmental perturbations including warming and OA. Changes in coral reef community composition and/or

biogeochemical processes will alter the influence of reef communities on seawater carbonate chemistry, which could alleviate or exacerbate acidification in local or downstream environments (Anthony et al. 2011; Kleypas et al. 2011; Andersson et al. 2014) with potential consequences for marine organisms. In the present study, we investigated the relative influence of five distinct benthic coral reef communities (carbonate sand, coral, crustose coralline algae, fleshy algae, and a mixed community) on seawater carbonate chemistry in carefully controlled mesocosm experiments. While the mesocosms do represent a simplification of the natural world, they allow benthic communities to experience natural fluctuations of environmental conditions and provide a method to control seawater flow rates and manipulation of seawater carbonate chemistry (Jokiel et al. 2008, 2014; Andersson et al. 2009). The main objectives of the study were to identify the relative influence on seawater carbonate chemistry by different benthic communities and to quantify the direct attribution of NCC and NCP to observed changes in pH and Ω_a. To broaden the scope of the study, we also evaluated the attribution of these processes under short-term OA conditions during both summer and winter. Finally, we aimed to establish whether observed TA–DIC relationships can be used as a potential tool to characterize benthic reef metabolism and composition.

Methods

Study site and experimental design

To determine the influence of different reef benthic communities on seawater carbonate chemistry under ambient and acidified conditions during summer and winter, short-term (26-h) mesocosm experiments were conducted at the Hawaii Institute of Marine Biology (HIMB; Moku o Loe, Kaneohe Bay, HI). Kaneohe Bay, which extends along 30 km of the northeastern (windward) coast of Oahu, is surrounded by a barrier reef and contains over 60 patch reefs scattered throughout the lagoon as well as fringing reefs along the shoreline (Hunter and Evans 1995). Although coral cover in the past has been quite low (<15%) due to a variety of stressors including sewage and freshwater inputs, reefs in the bay now contain higher coral cover (40–60%) comparable to other reefs in Hawaii (Jokiel et al. 2004; Bahr et al. 2015).

Benthic communities representing assemblages of taxa common to reefs in Kaneohe Bay were created within outdoor, flow-through mesocosms ($n = 2$ mesocosms per community) that experience natural fluctuations in environmental conditions including irradiance and temperature. Seawater was pumped from the bay into a main header tank. This header tank supplied seawater to smaller header tanks, which fed experimental mesocosms with a planar area of 1.369 m^2 and water depth of approximately 0.35 m. Seawater flowed up from the bottom at the center of each mesocosm, creating a well-mixed system with an average residence time of 0.72 ± 0.05 h (mean $\pm$ 1 SD). To examine the effects of individual functional groups, four mono-specific benthic communities were used: carbonate sand (volume 40 L), crustose coralline algae (CCA, *Lithophyllum kotschyanum*, 5040 ± 14 g buoyant weight), coral (*Montipora capitata*, 4767 ± 356 g buoyant weight), and fleshy algae (*Gracilaria salicornia*, 4413 ± 3 g wet weight). Mixed communities using half the amounts of sand, CCA, corals, and fleshy algae were also created to more closely represent reefs in the field. All specimens were collected from the reef flat surrounding Moku o Loe and HIMB and covered nearly 100% of the bottom of each mesocosm. Mesocosms with flowing seawater and no benthic communities served as controls.

Four diel experiments using the same benthic communities were conducted during August 2013 and January 2014. These months were chosen because they have different environmental conditions (e.g., light, temperature) representative of summer and winter. During each season, the first experiment used ambient seawater carbonate chemistry conditions. Communities were then exposed to acidified conditions created by the bubbling of carbon dioxide gas into the main header tank leading to treatment mesocosms following the protocol outlined in Jokiel et al. (2014). The mesocosm communities were exposed to acidified conditions 24 h prior to the start of the experiments. Briefly, a peristaltic pump controlled the flow of CO_2 gas into a fountain pump that dispersed the gas as small bubbles into the header tank. The rate of carbon dioxide addition was controlled to reach target pH 0.4 units below ambient seawater pH, the decrease predicted by 2100 under a business-as-usual CO_2 emission scenario (IPCC 2014). However, it is important to note that these experiments only tested short-term, direct effects of OA on community metabolism. They did not account for any long-term effects that may arise from chronic exposure to low seawater pH.

Experimental procedure and seawater analysis

Sampling protocol over 26 h was the same for all four experiments conducted. A weather monitoring station continuously measured wind and irradiance during the course of the experiments. Seawater salinity and temperature were measured every hour using a handheld YSI 556 multiprobe sensor, which was calibrated prior to each experiment. Every 2 h, seawater samples were collected in 250-ml glass Pyrex borosilicate glass bottles for DIC and TA and poisoned with a saturated solution of $HgCl_2$ to kill

any biological organisms in the samples that may alter seawater DIC and TA. These seawater samples were shipped to Scripps Institution of Oceanography (SIO) where they were analyzed for DIC and TA using an automated infrared inorganic carbon analyzer (Marianda, Kiel, Germany) and an open-cell potentiometric titration system developed by the Dickson Laboratory (SIO, La Jolla, CA) and equipped with a Metrohm 876 Dosimat Plus automated titrator and a Metrohm Ecotrode Plus pH electrode (Herisau, Switzerland), respectively. Both sampling and analytical protocols followed the standard procedures outlined in Dickson et al. (2007). Accuracy of the instruments, calculated as the mean offsets (±1 SD) from certified reference material, was -1.05 ± 2.35 ($n = 374$) and -0.20 ± 3.29 ($n = 277$) μmol kg^{-1} for DIC and TA, respectively. The seawater carbonate chemistry in the mesocosms was calculated based on DIC and TA data at in situ temperature and salinity using CO2SYS (Lewis and Wallace 1998). K1 and K2 constants were adopted from Mehrbach et al. (1973) refitted by Dickson and Millero (1987), and the total pH scale was used.

Calculations of NCC and NCP

NCC and NCP were calculated from observed changes in seawater TA and DIC according to the assumptions that NCC modifies TA and DIC in a ratio of 2:1 and NCP modifies DIC only (Langdon et al. 2010). The incoming seawater in the mesocosms is pumped directly from offshore of the coral reefs surrounding Moku o Loe so TA and DIC show a diurnal signature along with variations resulting from changes in tide and current. Thus, the observed DIC and TA in mesocosms represent changes occurring in the incoming source seawater and changes from planktonic communities within the water as well as modifications due to metabolism of the contained benthic communities. Therefore, the measured average value from the control tanks were subtracted from the treatment values to calculate rates of NCC and NCP owing to benthic metabolism only:

$$\mathrm{NCC} = \left[\frac{\mathrm{nTA_{Treatm}} - \mathrm{nTA_{Ctrl}}}{\tau_{\mathrm{Treatm}}} \times \rho_{\mathrm{SW}} \times h \times 0.5\right] \quad \mathrm{mmol\ m^{-2}\ h^{-1}} \tag{1}$$

$$\mathrm{NCP} = \left[\left(\frac{\mathrm{nDIC_{Treatm}} - \mathrm{nDIC_{Ctrl}}}{\tau_{\mathrm{Treatm}}} \times \rho_{\mathrm{SW}} \times h\right) - \mathrm{NCC}\right] \quad \mathrm{mmol\ m^{-2}\ h^{-1}} \tag{2}$$

where nTA and nDIC are salinity-normalized values [e.g., nTA = TA/S(in situ) × S(normalized), where S is salinity] of measured TA and DIC in treatment (Treatm) and control (Ctrl) mesocosms, τ is the residence time of the treatment mesocosms (0.67–0.72 h), ρ_{sw} is seawater density (kg m^{-3}), and h is the seawater depth of the mesocosms (0.34–0.37 m). CO_2 gas exchange with the atmosphere also influenced seawater DIC in the mesocosms, but calculations based on the average wind speed (6 m s^{-1}) and the maximum ΔpCO_2 (−99.04 μatm) conditions indicate that this influence was less than 1 μmol kg^{-1} during the average residence time of the water (0.67–0.72 h). Thus, we consider gas exchange negligible in the present evaluation. Similarly, the associated uptake and release of nutrients during photosynthesis and respiration may have influenced TA, but observed changes in inorganic nutrients $[PO_4^{3-}, NO_3^-, NO_2^-, Si(OH)_4]$ were always <0.003 ± 0.004 μmol kg^{-1}, and thus, negligible in terms of the influence on TA.

Average daytime and nighttime NCC and NCP rates of the communities were statistically compared using analysis of variance (ANOVA) in R Studio. First, a within-subjects ANOVA was performed to test for differences between ambient and acidified experiments during each season. Since no significance was detected ($p > 0.05$), the ambient and acidified experiments were combined. Then, two-way ANOVA tests were performed to test for significant differences between benthic communities and seasons. When significance was detected, a post hoc Tukey's test with a confidence level of 95% was performed to determine which communities were different from one another during each season and which communities had different rates in summer and winter, with $p < 0.05$ indicating statistical significance.

Calculations of attribution of NCC and NCP to changes in pH and Ω_a

The direct attribution of benthic community NCC and NCP to changes in seawater pH and Ω_a was calculated based on the same assumptions described above. To eliminate any influence of temperature and salinity variability on pH and Ω_a, all calculations were conducted based on nTA and nDIC at one temperature (28 °C) and salinity (35.5 g kg^{-1}). For this case at any given time point, pH in treatment and control mesocosms were related by the following expression:

$$\mathrm{pH_{Treatm}} = \mathrm{pH_{Ctrl}} + \Delta\mathrm{pH_{NCC\text{-}Treatm}} + \Delta\mathrm{pH_{NCP\text{-}Treatm}}, \tag{3}$$

where $\Delta\mathrm{pH_{NCC\text{-}Treatm}}$ and $\Delta\mathrm{pH_{NCP\text{-}Treatm}}$ refer to the modification in pH owing to NCC and NCP in the treatment mesocosms, respectively. These two terms were calculated according to the following equations:

$$\Delta\mathrm{pH_{NCC\text{-}Treatm}} = \mathrm{pH_{Ctrl}} - \mathrm{pH}(\mathrm{nTA_{Ctrl}} + \Delta\mathrm{nTA_{NCC\text{-}Treatm}}, \mathrm{nDIC_{Ctrl}} + \Delta\mathrm{nDIC_{NCC\text{-}Treatm}}) \tag{4}$$

where $\Delta nTA_{NCC\text{-}Treatm} = nTA_{Treatm} - nTA_{Ctrl}$ and $\Delta nDIC_{NCC\text{-}Treatm} = 0.5 \times (nTA_{Treatm} - nTA_{Ctrl})$, and finally,

$$\Delta pH_{NCP\text{-}Treatm} = pH_{Treatm} - pH_{Ctrl} - \Delta pH_{NCC\text{-}Treatm} \quad (5)$$

The same calculations were conducted with respect to Ω_a to evaluate the attribution of NCC and NCP to this parameter.

Assessment of community TA–DIC relationships

Deffeyes (1965) originally proposed graphical analysis of TA and DIC vectors as a technique to simplify the use of complex equations to solve for seawater carbonate chemistry equilibrium. It has since been used as a tool for assessing coral reef ecosystem function in carbon cycling as the slopes of the vectors (i.e., reaction paths) indicate the relative balance between NCC and NCP (Suzuki and Kawahata 2003; Watanabe et al. 2006; Andersson and Gledhill 2013; Lantz et al. 2014). In the present analyses, we plotted and evaluated the difference in nTA and nDIC between treatment and control mesocosms (i.e., $\Delta nTA = nTA_{Treatm} - nTA_{Ctrl}$, and $\Delta nDIC = nDIC_{Treatm} - nDIC_{Ctrl}$) because the goal was to explicitly evaluate the influence of each benthic community. The slopes and correlation coefficients were calculated by fitting a type II linear regression to the data using R version 3.2.0.

Results

Physical and chemical properties

During each of the four experiments, seawater physical and chemical properties varied naturally with changes in light and biogeochemical processes. The mean summer temperature was 27.8 ± 0.9 °C, while winter temperature averaged 23.1 ± 0.6 °C. Peak levels of PAR reached 1758 μE m^{-2} s^{-1} in the summer and 1271 μE m^{-2} s^{-1} during the winter (Fig. 1). Salinity remained relatively constant throughout each experiment but was slightly lower during winter compared to summer (34.30 ± 0.43 g kg^{-1} vs. 35.50 ± 0.05 g kg^{-1}).

Benthic communities modified seawater carbonate chemistry through NCC and NCP, resulting in distinct diel trends. In general, seawater pH and Ω_a were elevated during the day and lower at night for all mesocosms, but of varying amplitude, whereas seawater pCO_2 was lower during the day and elevated at night. Across all four experiments, fleshy algae and mixed communities experienced the highest seawater pH and Ω_a, and the lowest pCO_2 during the day. Seawater carbonate chemistry at night was relatively similar between all benthic communities (Fig. 2).

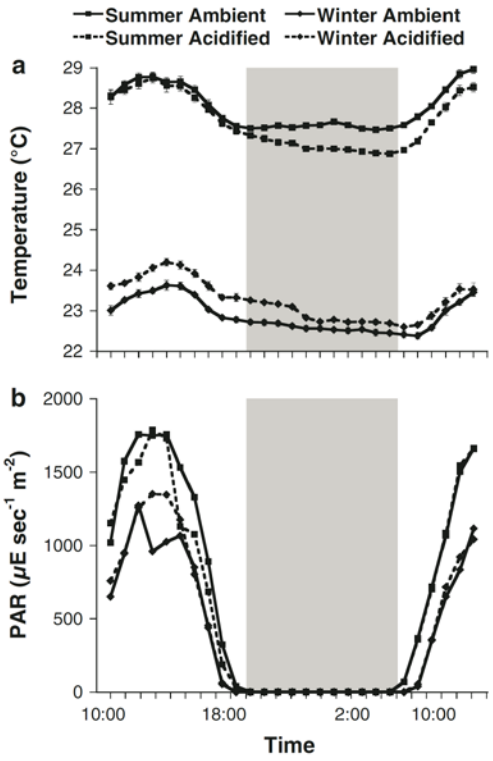


Fig. 1 Seawater temperature (**a**) and atmospheric photosynthetically active radiation (PAR) (**b**) over a diel cycle during each of the four experiments conducted during summer and winter. Data represent mean ± 1 SD and the *shaded area* shows night

Although the overall trends and differences in seawater carbonate chemistry between benthic communities were consistent across experiments, the average conditions varied across seasons and pCO_2–pH treatments. In general, the ambient DIC and TA were slightly higher during winter compared to summer, and bubbling of CO_2 gas elevated seawater DIC by approximately 200 μmol kg^{-1} (Fig. 3), resulting in a significant reduction in pH and Ω_a. Seawater pH and Ω_a ranged from 7.80 to 8.00 and 2.25 to 3.50, respectively, during ambient conditions in the summer, and 7.95 to 8.05 and 2.25 to 3.25, respectively, during ambient conditions in the winter. Under acidified conditions in the summer, pH and Ω_a ranged from 7.40 to 7.80 and 1.00 to 2.25, respectively, and in the winter from 7.20 to 7.70 and 0.50 to 1.50, respectively. During the acidification experiment in winter, all communities experienced seawater undersaturation with respect to aragonite ($\Omega_a < 1$) at night (Fig. 2).

NCC and NCP rates

Different benthic communities had statistically different NCC and NCP rates (Table 1) during the day and night

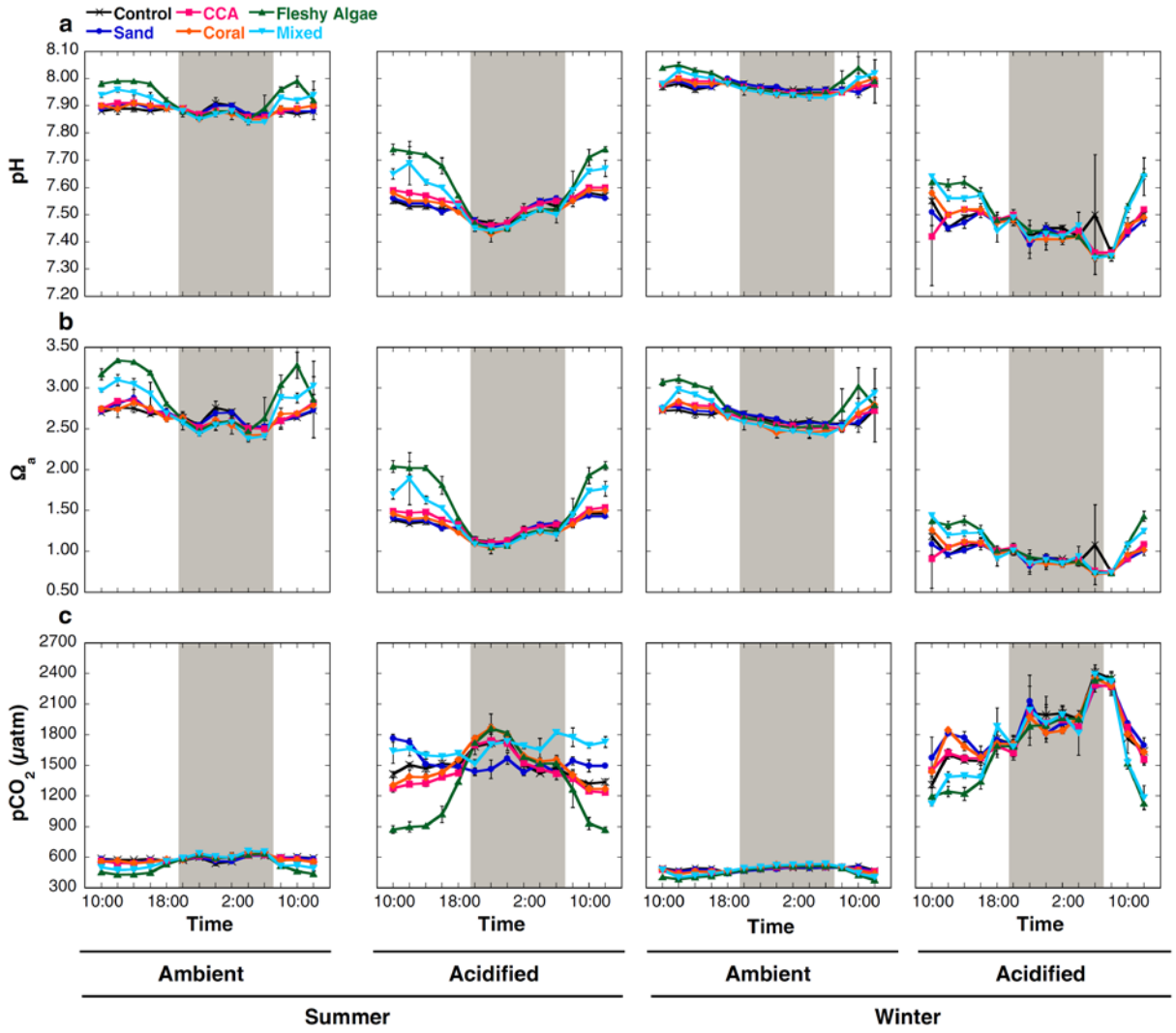


Fig. 2 Diel seawater pH (**a**), saturation state with respect to aragonite (Ω_a) (**b**), and pCO_2 (**c**) during each of the four experiments conducted in summer and winter. Data represent mean ± 1 SD and the *shaded area* shows night. Seawater pH and Ω_a were calculated from nDIC and nTA using the program CO2SYS on the total pH scale and using K1 and K2 constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987)

with similar diel trends across all experiments. In general, NCC and NCP rates were highest during the day and decreased sharply as light levels decreased. Throughout the night, NCC and NCP rates were fairly constant until light levels increased at which time NCC and NCP rates also increased (Fig. 4). Interestingly, community rates were relatively similar to one another at night compared to the larger differences observed during the day. All communities experienced net calcification during the day with NCC rates decreasing according to the following order: Coral = mixed > CCA > Sand = fleshy algae communities (Table 1). At night, corals had significantly higher NCC rates than the other benthic communities, which experienced net dissolution during portions or most of the night for each experiment. NCP rates were positive during the day and negative at night for all benthic communities and experiments with fleshy algae and mixed communities having the highest positive NCP rates during the day (Fig. 4).

Although there were no significant differences in NCC and NCP between ambient and acidification experiments, there were slight seasonal differences. Daytime NCP rates were significantly higher in the summer compared to winter (Table 1), and this was driven by fleshy algae which was the only significant interaction between benthic community and season. At night, average NCP rates were

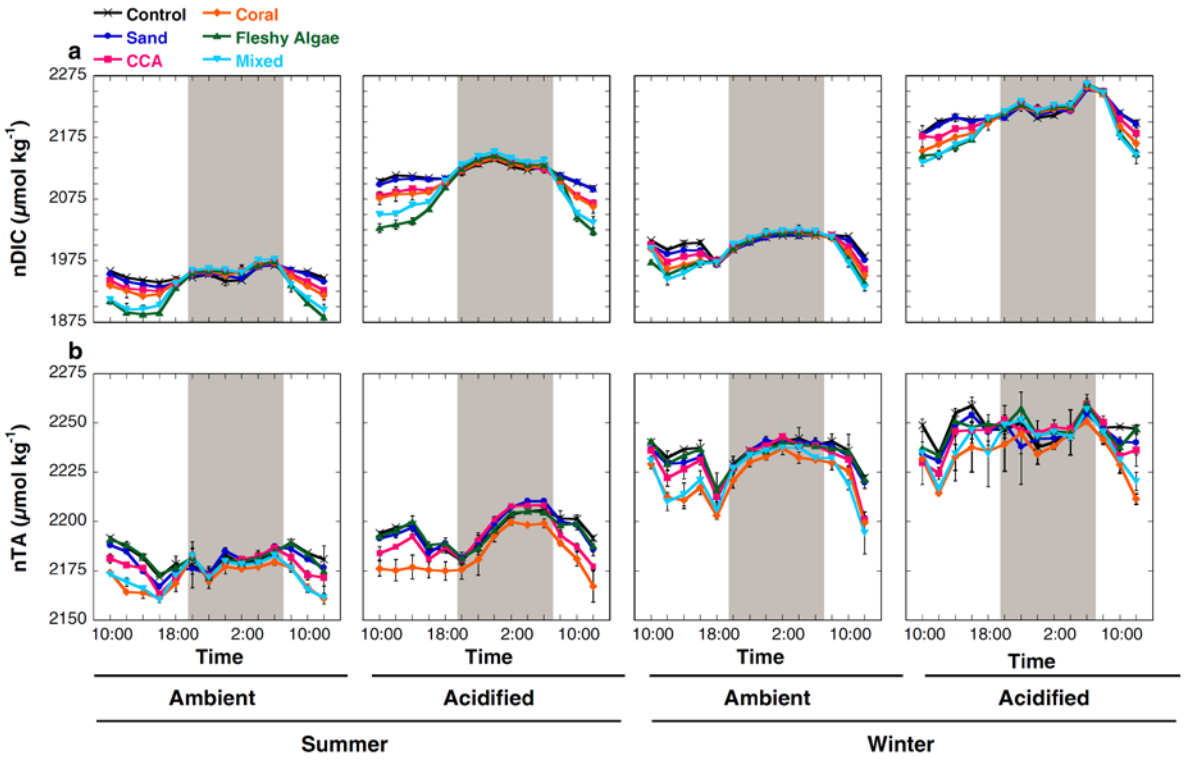


Fig. 3 Diel seawater salinity-normalized DIC (**a**) and TA (**b**) during each of the four experiments conducted in summer and winter. Data represent mean ± 1 SD and the *shaded area* shows night

Table 1 Statistical results from two-way ANOVA tests with benthic community and seasons as factors for average daytime (a) and nighttime (b) NCC and NCP rates

	df	*F* statistic	*p* value	Significant groupings
(a) Daytime average rates				
NCC (mmol m^{-2} h^{-1})				
Benthic community	4	65.995	<0.001*	C = M>CCA > S=FA
Season	1	1.165	0.289	
Benthic community × season	1	0.771	0.553	
NCP (mmol m^{-2} h^{-1})				
Benthic community	4	73.228	<0.001*	FA = M>C > CCA > S
Season	1	14.830	0.001*	Summer > winter
Benthic community × season	1	5.068	0.003*	
(b) Nighttime average rates				
NCC (mmol m^{-2} h^{-1})				
Benthic community	4	8.996	<0.001*	C > FA = M=S = CCA
Season	1	1.761	0.194	
Benthic community × season	1	0.627	0.647	
NCP (mmol m^{-2} h^{-1})				
Benthic community	4	8.195	<0.001*	C = S=CCA ≥ FA = M
Season	1	8.120	0.008*	Winter > summer
Benthic community × season	1	0.424	0.790	

df degrees of freedom, *C* coral, *FA* fleshy algae, *M* mixed, *S* sand

Data were considered significant when $p < 0.05$

* Statistical significance

significantly less negative (i.e., less respiration) in the winter compared to the summer.

Influences of benthic communities on seawater carbonate chemistry and attribution of NCC and NCP to changes in pH and Ω_a

The biogeochemical processes of the different communities directly attributed to observed trends of elevated seawater pH and Ω_a during the day and lower values at night (Fig. 2). However, differences in NCC and NCP rates between benthic communities consequently modified seawater pH and Ω_a differently (Figs. 5, 6). Fleshy algae elevated seawater pH and Ω_a the most during the day due to low NCC rates and high NCP rates. In contrast, sand, CCA, and corals had very little overall influence on daytime seawater pH and Ω_a due to the counteracting effects of positive NCC and NCP rates. The influence of the mixed community on seawater pH and Ω_a fell between fleshy algae and calcifying communities, slightly elevating both parameters during the day. Notably, nighttime acidification from benthic community metabolism was similar for all treatments with seawater pH and Ω_a decreasing slightly.

Fig. 5 Influence of benthic communities on seawater pH. The total Δ▶ pH (*black line*) shows the observed difference (mean ± 1 SD) between treatment and average control seawater pH, while the *bars* show the direct attribution of NCC (*light gray*) and NCP (*dark gray*) to those observed changes in seawater pH, calculated as $pH_{Treatm} = pH_{Ctrl} + \Delta pH_{NCC} + \Delta pH_{NCP}$. **a** Sand, **b** CCA, **c** coral, **d** fleshy algae, and **e** mixed community

Modest differential influences of benthic communities on seawater pH and Ω_a were observed between the four different experiments. All of the benthic communities elevated daytime seawater pH more relative to nighttime pH under acidified conditions during both summer and winter. In contrast, the influence of benthic communities on daytime seawater Ω_a was typically unchanged or slightly smaller during acidified experiments. There were no obvious differences for sand, CCA, or coral communities between winter and summer experiments, but fleshy algae and mixed communities elevated seawater pH and Ω_a less during the day in the winter compared to summer. Nighttime acidification was similar across all four experiments.

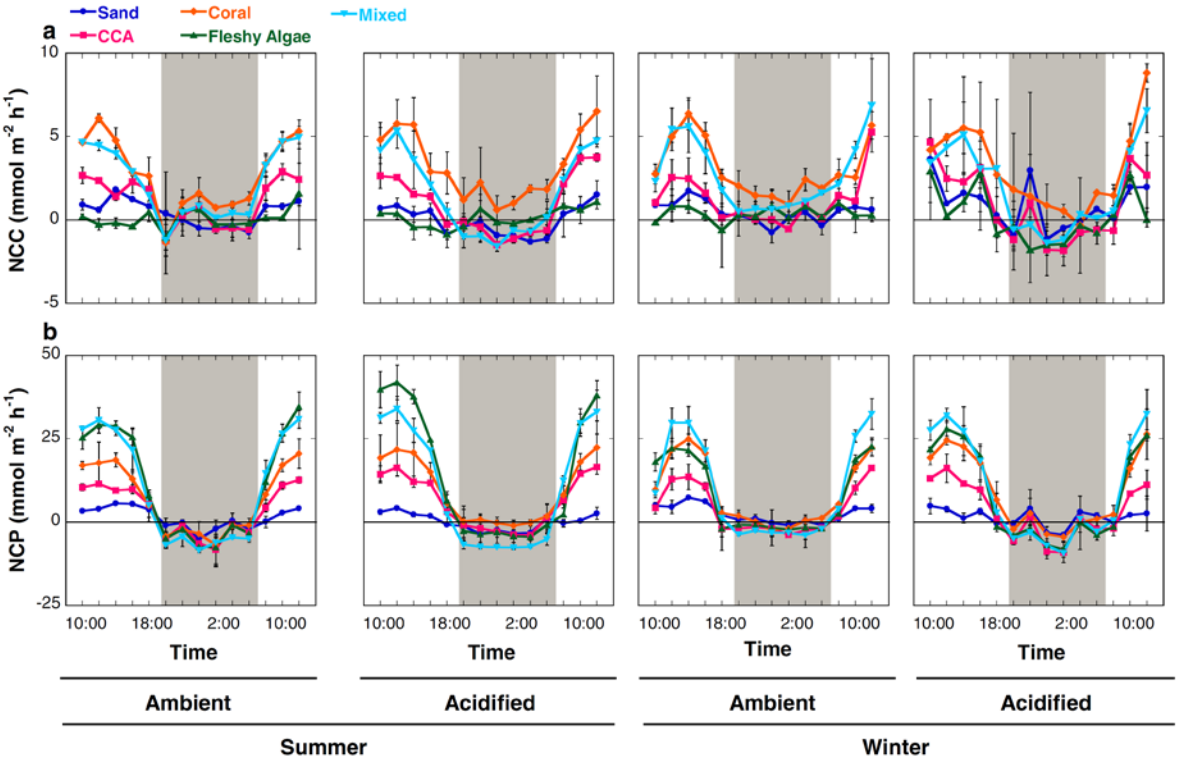
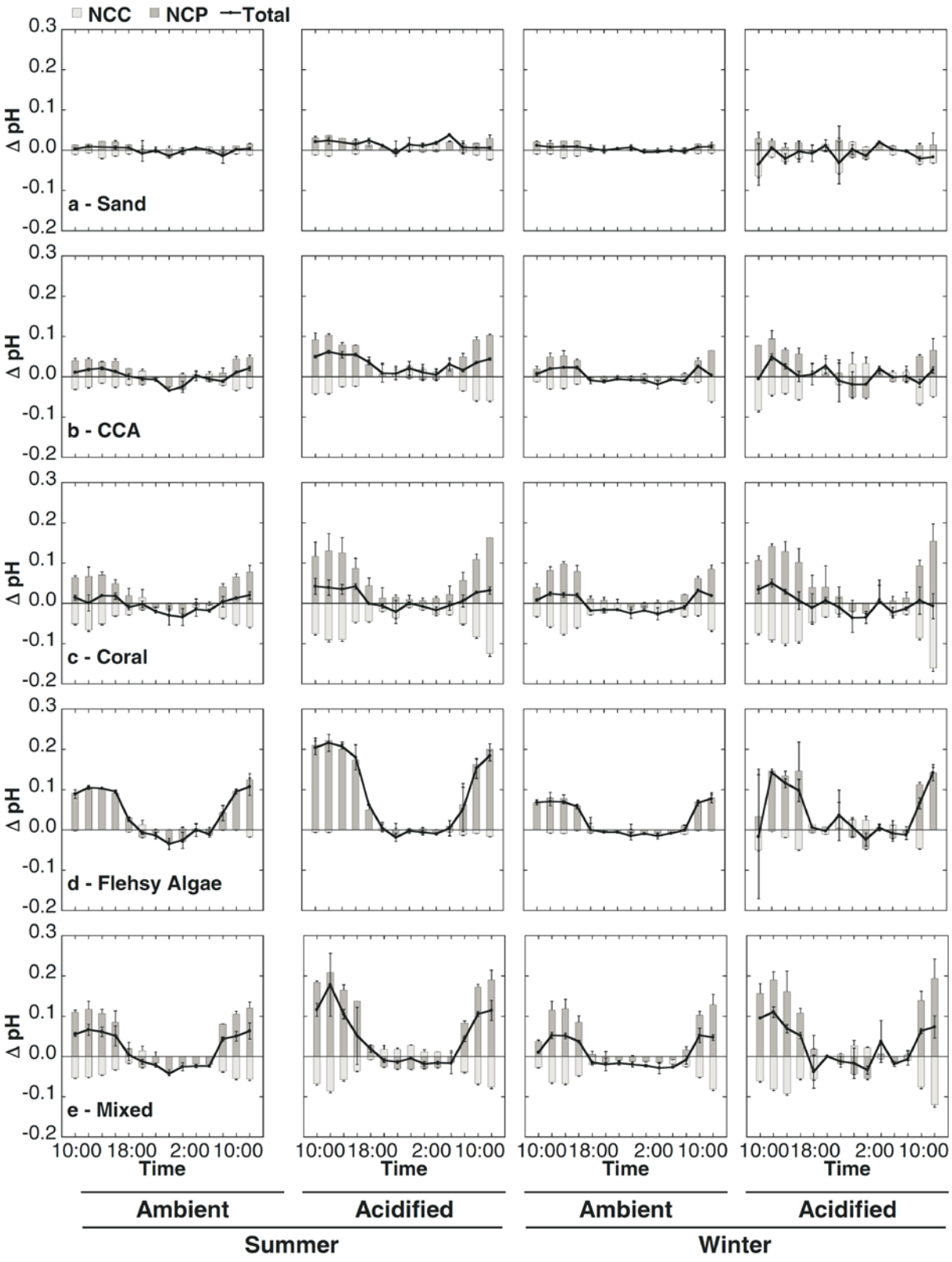


Fig. 4 Diel NCC (**a**) and NCP (**b**) rates for benthic communities during each of the four experiments conducted during summer and winter. Data represent mean ± 1 SD and the *shaded area* shows night. The *rows* represent seasons, while the *columns* show ambient and acidified conditions


NCC
NCP
Total
Δ pH
a - Sand
b - CCA
c - Coral
d - Flehsy Algae
e - Mixed
0.3
0.2
0.1
0.0
-0.1
-0.2
10:00 18:00 2:00 10:00
Time
Ambient
Acidified
Ambient
Acidified
Summer
Winter

Community TA–DIC relationships

The TA to DIC slopes varied distinctly among different benthic communities and experiments (Table 2; Fig. 7). In general, fleshy algae always had the lowest slopes (0.01–0.16), while sand (0.54 to 1.60), CCA (0.40–0.68), and corals (0.41–0.57) had the highest slopes. The mixed community had slopes that fell between fleshy algae and calcifying communities (0.28–0.38). Since most of the slopes were <1, the approximate slope anticipated if NCP and NCC were balanced, these communities were dominated by organic carbon cycling over inorganic carbon cycling. There was generally very little to no seasonal difference between TA to DIC slopes, but slight increases were observed for all benthic communities when exposed to short-term OA (Table 2).

Discussion

Results of this study show the ability of benthic communities to modify their chemical environment through biogeochemical processes of calcification, dissolution, photosynthesis, and respiration. The modulation of seawater carbonate chemistry differed between major coral reef communities due to differences in their NCC and NCP rates (Anthony et al. 2013; Figs. 5, 6). Sand, CCA, and coral communities had relatively static seawater pH and Ω_a that were similar to control conditions throughout the day due to the counteracting effects of net calcification (positive NCC) and net autotrophy (positive NCP) on these parameters (Andersson and Gledhill 2013). Fleshy algae and mixed communities, on the other hand, boosted seawater pH and Ω_a during the day due to the effects of positive NCP outweighing the effects of NCC. These results agree with previous findings by Murillo et al. (2014) who also observed the highest daytime pH and Ω_a in fleshy algae and mixed communities during a series of flume studies conducted at HIMB. Although benthic communities clearly had different influences on daytime seawater carbonate chemistry, their effects at night were much more similar with relatively minor decreases in pH and Ω_a occurring across all communities.

Benthic communities had a slightly smaller influence on seawater pH and Ω_a during winter compared to summer due to seasonal differences in NCP rates during day and night. NCC rates remained fairly constant between seasons as previously shown for reefs in Kaneohe Bay and coral communities in experimental systems at HIMB (Langdon and Atkinson 2005; Jokiel et al. 2008; Shamberger et al. 2011). Lower daytime NCP rates in the winter conditions were most likely due to lower light since photosynthetic rates have a well-established relationship with irradiance (Chalker et al. 1988; Martin et al. 2013), but were certainly also influenced by temperature and possibly nutrient availability, both of which were lower during the winter experiments. During summer, slightly more negative NCP rates were observed at night compared to winter under ambient conditions, possibly indicating enhanced metabolic rates induced by the warmer temperatures (Gillooly et al. 2001).

Fig. 6 Influence of benthic communities on seawater Ω_a. The total $\Delta\Omega_a$ (*black line*) shows the observed difference (mean ± 1 SD) between treatment and average control seawater pH, while the bars show the direct attribution of NCC (*light gray*) and NCP (*dark gray*) to those observed changes in seawater Ω_a, calculated as described for pH. **a** Sand, **b** CCA, **c** coral, **d** fleshy algae, and **e** mixed community

OA did not affect NCC or NCP rates during these short-term experiments, but it is possible that the effect was too small to detect and could manifest itself if communities were exposed to OA over longer time periods (i.e., weeks, months, or years). In addition, some coral and calcified algal species have been observed to maintain calcification rates under high pCO_2 and low pH conditions in laboratory experiments (Reynaud et al. 2003; Comeau et al. 2013; Schoepf et al. 2013), but it is likely that this comes at an increased energetic cost (Wood et al. 2010). It is also possible that coral reef organisms and communities show variable sensitivities to acidification under natural conditions of light, flow, food, and temperature compared to controlled laboratory levels. Despite the fact that NCC and NCP rates were maintained under OA conditions, the net metabolism resulted in larger variability in seawater pH and smaller changes in seawater Ω_a compared to ambient conditions. This could be explained by the chemical properties of seawater and decreasing buffering capacity under OA, for which diel changes in NCC and NCP will result in greater variability in seawater pH (Shaw et al. 2012; Jury et al. 2013). In contrast, smaller variations in seawater Ω_a are expected due to the nonlinear behavior of Ω_a as a function of CO_2, with decreasing changes in Ω_a for a given change in CO_2 as Ω_a approaches equilibrium (i.e., $\Omega_a = 1$). These chemical properties of seawater can account for the observed differences of daytime seawater pH and Ω_a under OA treatments since NCC and NCP rates were similar to ambient conditions, but fail to explain that there were no observed differences of nighttime seawater pH and Ω_a. Instead, we hypothesize nighttime acidification was partially offset by $CaCO_3$ dissolution (Andersson et al. 2014), which was slightly higher under OA during the winter. Hence, ecosystem and biogeochemical feedbacks as well as changes in the seawater buffering capacity interact, making predictions of future OA on coral reefs, and the resulting effects on marine organisms, complex.

In general, it is anticipated that the community structure of coral reefs will change in response to multiple ongoing

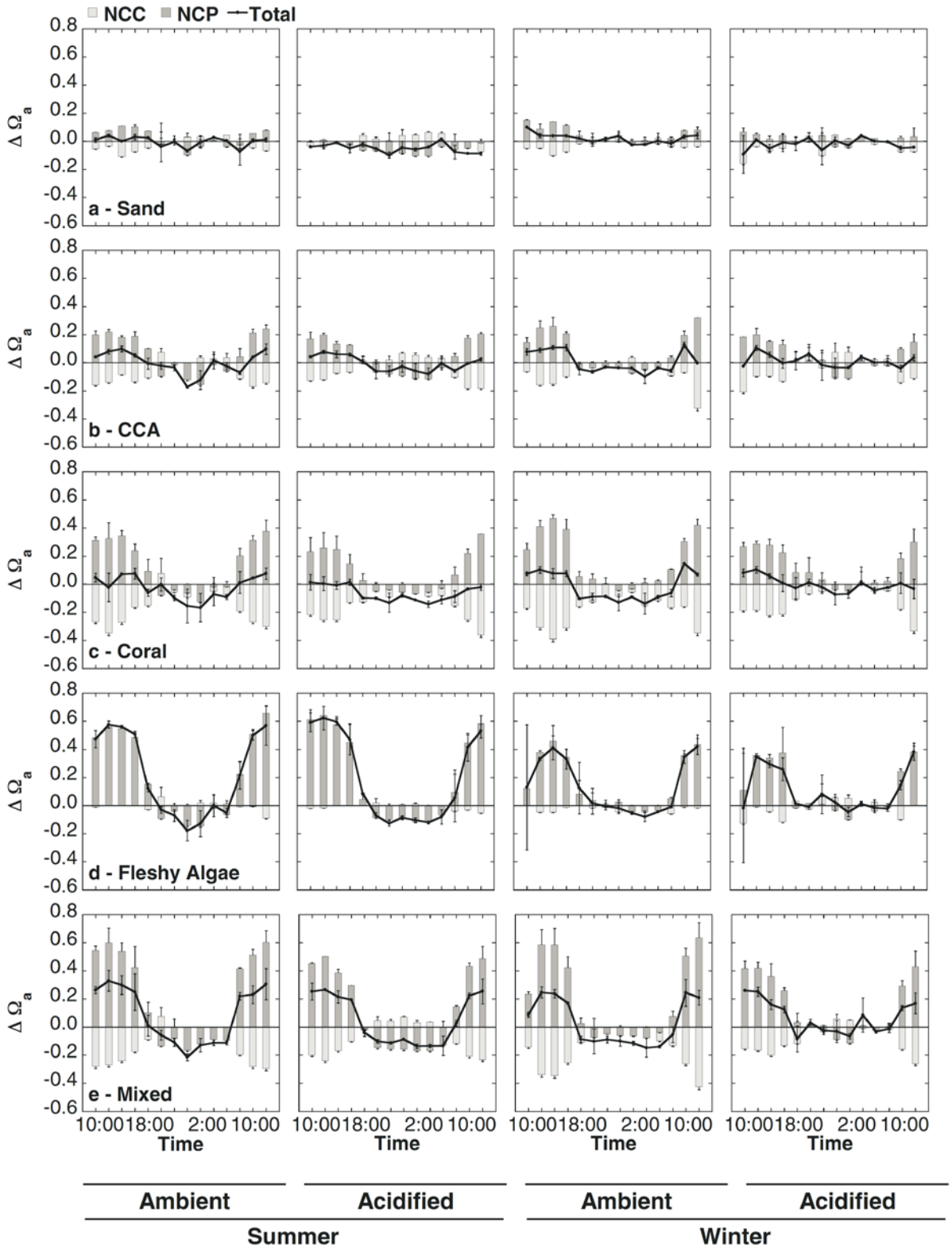

NCC
NCP
Total
Δ Ω a
a - Sand
b - CCA
c - Coral
d - Fleshy Algae
e - Mixed
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
10:00 18:00 2:00 10:00
Time
Ambient
Acidified
Ambient
Acidified
Summer
Winter

Table 2 Average TA to DIC slopes with confidence intervals (C.I.) for benthic communities during each of the four experiments (a–d)

Benthic community	ΔnTA:ΔnDIC slope	2.5% CI	97.5% CI	R^2	p value
(a) Summer ambient					
Sand	0.54	0.26	0.90	0.35	0.001*
CCA	0.40	0.28	0.53	0.64	<0.001*
Coral	0.48	0.36	0.60	0.72	<0.001*
Fleshy algae	0.02	−0.03	0.07	0.02	0.465
Mixed	0.28	0.23	0.32	0.86	<0.001*
(b) Summer acidified					
Sand	0.89	0.27	2.47	0.17	0.030*
CCA	0.51	0.41	0.63	0.77	<0.001*
Coral	0.51	0.41	0.61	0.82	<0.001*
Fleshy algae	0.01	−0.01	0.04	0.04	0.304
Mixed	0.31	0.27	0.35	0.91	<0.001*
(c) Winter ambient					
Sand	0.55	0.37	0.76	0.58	<0.001*
CCA	0.40	0.28	0.54	0.62	<0.001*
Coral	0.41	0.32	0.50	0.78	<0.001*
Fleshy algae	0.02	−0.03	0.07	0.02	0.491
Mixed	0.35	0.29	0.41	0.85	<0.001*
(d) Winter acidified					
Sand	1.60	0.43	−24.30	0.10	0.113
CCA	0.68	0.45	0.96	0.56	<0.001*
Coral	0.57	0.41	0.77	0.63	<0.001*
Fleshy algae	0.16	0.06	0.27	0.30	0.003*
Mixed	0.38	0.28	0.48	0.73	<0.001*

Slopes were calculated by fitting a Type II linear regression to ΔnTA and ΔnDIC data where ΔnTA and ΔnDIC were calculated as the treatment difference from average control conditions

* Statistical significance

environmental perturbations (e.g., overfishing, warming, nutrient pollution) (McCook et al. 2007; Dubinsky and Stambler 2010), which may act additively or synergistically to reduce reef health, often observed as decreased coral cover and regime shifts from coral-dominated reefs to fleshy algal species (Gardner et al. 2003; Pandolfi et al. 2005; Bruno and Selig 2007). Based on the present results, such regime shifts from calcifying communities to non-calcifying algal communities would alter the reef seawater carbonate chemistry. Short-term changes are likely to result in higher daytime seawater pH and Ω_a with little to no additional acidification at night, but unless significant amounts of organic matter are permanently stored in biomass, buried in the sediments, or exported to the open ocean, lower pH and Ω_a are likely to eventually occur as a result of decomposition of the "new" organic matter. However, this decomposition may be separated in time and/or space (Bates et al. 2010) and thus may have differential effects on different parts of the reef. Thus, algal-dominated areas of coral reefs may at times partially buffer against the effects of OA, which could enhance calcification via intrinsic feedback loops (Bates et al. 2010; Kleypas et al. 2011), but could also exacerbate the effect of OA depending on when and where the organic matter is reoxidized. Experimental incubations have shown that *Acropora* and *Montipora* corals calcified faster when they were incubated with fleshy algae in short-term microcosm experiments (Adey and Small 2000). However, in addition to the temporal and spatial limitations of these results, there are other caveats that need to be considered since fleshy algae can reduce coral recruitment and growth via biologically and physically mediated competitive interactions (Hughes 1994; McCook et al. 2001). Therefore, local chemical facilitation by fleshy algae on coral reefs may be outweighed by its deleterious effects on corals and CCA, but careful evaluations in the natural environment over larger spatial and longer temporal scales are required to further understand these intrinsic relationships and feedbacks.

The anticipated regime shift toward non-calcifying algal-dominated ecosystems implies that the organic carbon cycle will become increasingly important relative to

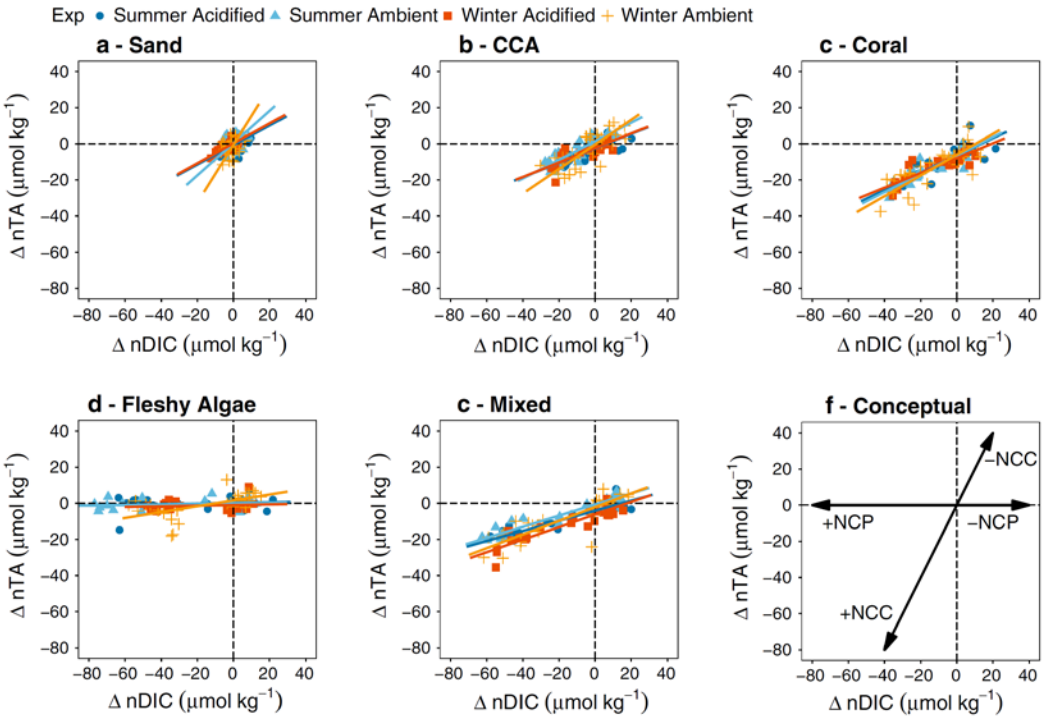


Fig. 7 TA to DIC slopes for each of the benthic communities. Linear (type II) regressions were fitted to the ΔnTA and ΔnDIC data for each experiment (Exp. 1: *dark blue*, Exp. 2: *light blue*, Exp. 3: *red*, Exp. 4: *orange*) to examine only the influence of benthic community metabolism on the TA to DIC slopes. Outliers were excluded from linear regression analyses ($n = 2$ for Sand). The conceptual plot (**f**) shows TA to DIC slopes expected from NCC and NCP. **a** Sand, **b** CCA, **c** coral, **d** fleshy algae, and **e** mixed community

the inorganic carbon cycle on reef systems. Such changes, which ultimately are driven by the ecological changes in community composition, should be reflected in coral reef system's influence on seawater carbonate chemistry (as demonstrated by the present results). Consequently, it has been proposed that TA–DIC relationships can be used as a tool to characterize benthic reef community composition and biogeochemical function of coral reefs in the context of climate change and OA (Andersson and Gledhill 2013; Lantz et al. 2014). This approach has previously been successfully used to characterize reefs as a net source or sink of CO_2 to the atmosphere (Suzuki and Kawahata 2003) as well as the influence of extensive coral bleaching on relative NCC rates (Watanabe et al. 2006). However, at present time, it is somewhat uncertain exactly how measured TA–DIC relationships relate to benthic community composition in natural environments, and we know even less of how it relates to coral reef health, resistance, and resilience. Based on the present results for well-constrained benthic communities in mesocosms, this method appears promising as a tool to broadly assess the functional community composition and function since each community was associated with a relatively distinct TA–DIC relationship and the mixed community had a relationship represented by the combined effect of the individual communities. In addition, comparing reef TA with source water, TA provides a relative estimate of NCC, which is an important indicator of reef $CaCO_3$ deposition and dissolution. The next natural step is to verify these types of relationships for a range of well defined but different benthic communities in the natural environment, including pristine reef systems as well as systems heavily influenced by human perturbations. Based on the projected changes from previous studies toward algae-dominated reefs and decreasing NCC (Hoegh-Guldberg et al. 2007; Silverman et al. 2014; Enochs et al. 2015), it is anticipated that the slope of TA–DIC relationships will gradually decrease and reef TA anomalies will become smaller and even negative if a reef undergoes net $CaCO_3$ dissolution. However, slight increases in the slopes of TA–DIC relationships under OA for all benthic communities were consistently observed, and this most likely can be attributed to the increased dissolution at night. Regardless, additional research combining ecological benthic assessments and reef health with quantitative physical and biogeochemical measurements is required before TA–DIC relationships can be used as a potential tool to assess coral reef health and resilience in the context of climate change and OA.

Acknowledgments The authors are grateful for support from NSF GRFP (HP) and NSF OCE 12-55042 (AJA). We also appreciate the constructive comments by three anonymous reviewers which significantly improved an earlier draft of this manuscript.

References

Adey WH, Small AM (2000) Community and environmental influences on reef coral calcification. Limnol Oceanogr 45:1667–1671

Andersson AJ, Gledhill D (2013) Ocean acidification and coral reefs: Effects on breakdown, dissolution, and net ecosystem calcification. Ann Rev Mar Sci 5:321–348

Andersson AJ, Yeakel KL, Bates NR, de Putron SJ (2014) Partial offsets in ocean acidification from changing coral reef biogeochemistry. Nat Clim Chang 4:56–61

Andersson AJ, Kuffner IB, Mackenzie FT, Jokiel PL, Rodgers KS, Tan A (2009) Net loss of $CaCO_3$ from a subtropical calcifying community due to seawater acidification: mesocosm-scale experimental evidence. Biogeosciences 6:1811–1823

Anthony KRN, Kleypas JA, Gattuso J-P (2011) Coral reefs modify their seawater carbon chemistry – implications for impacts of ocean acidification. Glob Chang Biol 17:3655–3666

Anthony KRN, Kline DI, Diaz-Pulido G, Dove S, Hoegh-Guldberg O (2008) Ocean acidification causes bleaching and productivity loss in coral reef builders. Proc Natl Acad Sci USA 105:17442–17446

Anthony KRN, Diaz-Pulido G, Verlinden N, Tilbrook B, Andersson AJ (2013) Benthic buffers and boosters of ocean acidification on coral reefs. Biogeosciences 10:4897–4909

Bahr KD, Jokiel PL, Toonen RJ (2015) The unnatural history of Kāne'ohe Bay: coral reef resilience in the face of centuries of anthropogenic impacts. PeerJ 3:e950

Bates NR, Amat A, Andersson AJ (2010) Feedbacks and responses of coral calcification on the Bermuda reef system to seasonal changes in biological processes and ocean acidification. Biogeosciences 7:2509–2530

Bruno JF, Selig ER (2007) Regional decline of coral cover in the Indo-Pacific: timing, extent, and subregional comparisons. PLoS One 2:e711

Chalker BE, Barnes DJ, Dunlap WC, Jokiel PL (1988) Light and reef-building corals. Interdiscip Sci Rev 13:222–237

Comeau S, Edmunds PJ, Spindel NB, Carpenter RC (2013) The responses of eight coral reef calcifiers to increasing partial pressure of CO_2 do not exhibit a tipping point. Limnol Oceanogr 58:388–398

Cornwall CE, Hepburn CD, McGraw CM, Currie KI, Pilditch CA, Hunter KA, Boyd PW, Hurd CL (2013) Diurnal fluctuations in seawater pH influence the response of a calcifing macroalga to ocean acidification. Proc R Soc Lond B Biol Sci 280:20122201

Costanza R, de Groot R, Sutton P, van der Ploeg S, Anderson SJ, Kubiszewski I, Farber S, Turner RK (2014) Changes in the global value of ecosystem services. Glob Environ Change 26:152–158

Cyronak T, Santos IR, Erler DV, Maher DT, Eyre BD (2014) Drivers of pCO_2 variability in two contrasting coral reef lagoons: The influence of submarine groundwater discharge. Global Biogeochem Cycles 28:2013GB0024598

Deffeyes KS (1965) Carbonate equilibria: a graphic and algebraic approach. Limnol Oceanogr 10:412–426

Dickson AG, Millero FJ (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. Deep Sea Res Part I Oceanogr Res Pap 34:1733–1743

Dickson AG, Sabine CL, Christian JR (2007) Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, 191 pp

Dubinsky Z, Stambler N (2010) Coral reefs: An ecosystem in transition. Springer, Netherlands

Enochs IC, Manzello DP, Donham EM, Kolodziej G, Okano R, Johnston L, Young C, Iguel J, Edwards CB, Fox MD, Valentino L, Johnson S, Benavente D, Clark SJ, Carlton R, Burton T, Eynaud Y, Price NN (2015) Shift from coral to macroalgae dominance on a volcanically acidified reef. Nat Clim Chang 5:1083–1088

Erez J, Reynaud S, Silverman J, Schneider K, Allemand D (2011) Coral calcification under ocean acidification and global change. In: Dubinsky Z, Stambler N (eds) Coral reefs: An ecosystem in transition. Springer, Netherlands, pp 151–176

Eyre BD, Andersson AJ, Cyronak T (2014) Benthic coral reef calcium carbonate dissolution in an acidifying ocean. Nat Clim Chang 4:969–976

Falter JL, Lowe RJ, Zhang Z, McCulloch M (2013) Physical and biological controls on the carbonate chemistry of coral reef waters: effects of metabolism, wave forcing, sea level, and geomorphology. PLoS One 8:e53303

Gardner TA, Côté IM, Gill JA, Grant A, Watkinson AR (2003) Long-term region-wide declines in Caribbean corals. Science 301:958–960

Gillooly JF, Brown JH, West GB, Savage VM, Charnov EL (2001) Effects of size and temperature on metabolic rate. Science 293:2248–2251

Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS, Greenfield P, Gomez E, Harvell CD, Sale PF, Edwards AJ, Caldeira K, Knowlton N, Eakin CM, Iglesias-Prieto R, Muthiga N, Bradbury RH, Dubi A, Hatziolos ME (2007) Coral reefs under rapid climate change and ocean acidification. Science 318:1737–1742

Hughes TP (1994) Catastrophes, phase shifts, and large-scale degradation of a Caribbean coral reef. Science 265:1547–1551

Hunter CL, Evans CW (1995) Coral reefs in Kaneohe Bay, Hawaii: two centuries of western influence and two decades of data. Bull Mar Sci 57:501–515

IPCC (2014) Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Core Writing Team, R.K. Pachauri and L.A. Meyer (eds) Geneva, Switzerland, 151 pp

Johnson MD, Carpenter RC (2012) Ocean acidification and warming decrease calcification in the crustose coralline alga *Hydrolithon onkodes* and increase susceptibility to grazing. J Exp Mar Bio Ecol 434–435:94–101

Johnson MD, Price NN, Smith JE (2014) Contrasting effects of ocean acidification on tropical fleshy and calcareous algae. PeerJ 2:e411

Jokiel PL, Bahr KD, Rodgers KS (2014) Low-cost, high-flow mesocosm system for simulating ocean acidification with CO_2 gas. Limnol Oceanogr Methods 12:313–322

Jokiel PL, Brown EK, Friedlander A, Rodgers KS (2004) Hawai'i coral reef assessment and monitoring program: Spatial patterns and temporal dynamics in reef coral communities. Pac Sci 58:159–174

Jokiel PL, Rodgers KS, Kuffner IB, Andersson AJ, Cox EF, Mackenzie FT (2008) Ocean acidification and calcifying reef organisms: a mesocosm investigation. Coral Reefs 27:473–483

Jury CP, Thomas FIM, Atkinson MJ, Toonen RJ (2013) Buffer capacity, ecosystem feedbacks, and seawater chemistry under global change. Water 5:1303–1325

Kleypas JA, Yates KK (2009) Coral reefs and ocean acidification. Oceanography 22:108–117

Kleypas JA, McManus JW, Meñez LAB (1999) Environmental limits to coral reef development: Where do we draw the line? Am Zool 39:146–159

Kleypas JA, Anthony KRN, Gattuso J-P (2011) Coral reefs modify their seawater carbon chemistry – case study from a barrier reef (Moorea, French Polynesia). Glob Chang Biol 17:3667–3678

Langdon C, Atkinson MJ (2005) Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal changes in temperature/irradiance and nutrient enrichment. J Geophys Res Oceans 110:C09S07

Langdon C, Gattuso J, Andersson A (2010) Measurements of calcification and dissolution of benthic organisms and communities. Guide to best practices for ocean acidification research and data reporting Luxembourg: Office for Official Publications of the European Union pp. 213-234

Lantz CA, Atkinson MJ, Winn CW, Kahng SE (2014) Dissolved inorganic carbon and total alkalinity of a Hawaiian fringing reef: chemical techniques for monitoring the effects of ocean acidification on coral reefs. Coral Reefs 33:105–115

Lewis E, Wallace D (1998) CO2SYS—program developed for the CO_2 system calculations. Carbon Dioxide Inf. Anal. Center. Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, TN, USA

Martin S, Charnoz A, Gattuso J-P (2013) Photosynthesis, respiration and calcification in the Mediterranean crustose coralline alga *Lithophyllum cabiochae* (Corallinales, Rhodophyta). Eur J Phycol 48:163–172

McCook L, Jompa J, Diaz-Pulido G (2001) Competition between corals and algae on coral reefs: a review of evidence and mechanisms. Coral Reefs 19:400–417

McCook LJ, Folke C, Hughes TP, McCook LJ, Nyström M, Obura D, Salm R, Great barrier Reef Marine Park A (2007) Ecological resilience, climate change and the Great Barrier Reef. In: Johnson JE, Marshall PA (eds) Climate change and the Great Barrier Reef: a vulnerability assessment. The Great barrier Reef Marine Park Authority, Townsville, pp 79–96

Mehrbach C, Culberson CH, Hawley JE, Pytkowicx RM (1973) Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnol Oceanogr 18:897–907

Murillo LJA, Jokiel PL, Atkinson MJ (2014) Alkalinity to calcium flux ratios for corals and coral reef communities: variances between isolated and community conditions. PeerJ 2:e249

Pandolfi JM, Jackson JBC, Baron N, Bradbury RH, Guzman HM, Hughes TP, Kappel CV, Micheli F, Ogden JC, Possingham HP, Sala E (2005) Are U.S. coral reefs on the slippery slope to slime? Science 307:1725–1726

Reynaud S, Leclercq N, Romaine-Lioud S, Ferrier-Pagés C, Jaubert J, Gattuso J-P (2003) Interacting effects of CO_2 partial pressure and temperature on photosynthesis and calcification in a scleractinian coral. Glob Chang Biol 9:1660–1668

Schoepf V, Grottoli AG, Warner ME, Cai W-J, Melman TF, Hoadley KD, Pettay DT, Hu X, Li Q, Xu H, Wang Y, Matsui Y, Baumann JH (2013) Coral energy reserves and calcification in a high-CO_2 world at two temperatures. PLoS One 8:e75049

Semesi IS, Kangwe J, Björk M (2009) Alterations in seawater pH and CO_2 affect calcification and photosynthesis in the tropical coralline algae *Hydrolithon* sp. (Rhodophyta). Estuar Coast Shelf Sci 84:337–341

Shamberger KEF, Feely RA, Sabine CL, Atkinson MJ, DeCarlo EH, Mackenzie FT, Drupp PS, Butterfield DA (2011) Calcification and organic production on a Hawaiian coral reef. Mar Chem 127:64–75

Shaw EC, McNeil BI, Tilbrook B (2012) Impacts of ocean acidification in naturally variable coral reef flat ecosystems. J Geophys Res Oceans 117:C03038

Silverman J, Lazar B, Cao L, Caldeira K, Erez J (2009) Coral reefs may start dissolving when atmospheric CO_2 doubles. Geophys Res Lett 36:L05606

Silverman J, Schneider K, Kline DI, Rivlin T, Rivlin A, Hamylton S, Lazar B, Erez J, Caldeira K (2014) Community calcification in Lizard Island, Great Barrier Reef: a 33 year perspective. Geochim Cosmochim Acta 144:72–81

Suzuki A, Kawahata H (1999) Partial pressure of carbon dioxide in coral reef lagoon waters: comparative study of atolls and barrier reefs in the Indo-Pacific oceans. J Oceanogr 55:731–745

Suzuki A, Kawahata H (2003) Carbon budget of coral reef systems: an overview of observations in fringing reefs, barrier reefs and atolls in the Indo-Pacific regions. Tellus B 55:428–444

Suzuki A, Nakamori T, Kayanne H (1995) The mechanism of production enhancement in coral reef carbonate systems: model and empirical results. Sed Geol 99:259–280

Watanabe A, Kayanne H, Hata H, Kudo S, Nozaki K, Kato K, Negishi A, Ikeda Y, Yamano H (2006) Analysis of the seawater CO_2 system in the barrier reef-lagoon system of Palau using total alkalinity-dissolved inorganic carbon diagrams. Limnol Oceanogr 51:1614–1628

Wilkinson C (2008) Status of coral reefs of the world: 2008. Global Coral Reef Monitoring Network and Reef and Rainforest Research Centre, Townsville, Australia, 296 p

Wisshak M, Schönberg CHL, Form A, Freiwald A (2012) Ocean acidification accelerates reef bioerosion. PLoS One 7:e45124

Wood HL, Spicer JI, Widdicombe S (2010) Ocean acidification may increase calcification rates, but at a cost. Proc R Soc Lond B Biol Sci 275:1767–1773

Zeebe RE, Wolf-Gladrow DA (2001) CO_2 in seawater: equilibrium, kinetics, isotopes. Elsevier Oceanography Series 65, Elsevier Science, Amsterdam

Acknowledgments

Chapter 2, in full, is a reprint of the material as it appears in **Page, HN**, Andersson, AJ, Jokiel, PL, Rodgers, KS, Lebrato, M, Yeakel, K, Davidson, C, D'Angelo, S, & Bahr, KD. (2016). Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral Reefs* 35(4): 1311-1325. The dissertation author was the primary investigator and author of this paper.

CHAPTER 3

Net community metabolism and seawater carbonate chemistry scale non-intuitively with coral cover

Heather N. Page, Travis A. Courtney, Andrew Collins, Eric H. De Carlo, and Andreas J. Andersson

frontiers in Marine Science

ORIGINAL RESEARCH
published: 30 May 2017
doi: 10.3389/fmars.2017.00161

Net Community Metabolism and Seawater Carbonate Chemistry Scale Non-intuitively with Coral Cover

Heather N. Page[1], Travis A. Courtney[1], Andrew Collins[2], Eric H. De Carlo[3] and Andreas J. Andersson[1]*

[1] Scripps Institution of Oceanography, University of California, San Diego, San Diego, CA, United States, [2] Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, Seattle, WA, United States, [3] Department of Oceanography, University of Hawaii at Manoa, Honolulu, HI, United States

Coral cover and reef health have been declining globally as reefs face local and global stressors including higher temperature and ocean acidification (OA). Ocean warming and acidification will alter rates of benthic reef metabolism (i.e., primary production, respiration, calcification, and $CaCO_3$ dissolution), but our understanding of community and ecosystem level responses is limited in terms of functional, spatial, and temporal scales. Furthermore, dramatic changes in coral cover and benthic metabolism could alter seawater carbonate chemistry on coral reefs, locally alleviating or exacerbating OA. This study examines how benthic metabolic rates scale with changing coral cover (0–100%), and the subsequent influence of these coral communities on seawater carbonate chemistry based on mesocosm experiments in Bermuda and Hawaii. In Bermuda, no significant differences in benthic metabolism or seawater carbonate chemistry were observed for low (40%) and high (80%) coral cover due to large variability within treatments. In contrast, significant differences were detected between treatments in Hawaii with benthic metabolic rates increasing with increasing coral cover. Observed increases in daily net community calcification and nighttime net respiration scaled proportionally with coral cover. This was not true for daytime net community organic carbon production rates, which increased the most between 0 and 20% coral cover and then less so between 20 and 100%. Consequently, diel variability in seawater carbonate chemistry increased with increasing coral cover, but absolute values of pH, Ω_a, and pCO_2 were not significantly different during daytime. To place the results of the mesocosm experiments into a broader context, *in situ* seawater carbon dioxide (CO_2) at three reef sites in Bermuda and Hawaii were also evaluated; reefs with higher coral cover experienced a greater range of diel CO_2 levels, complementing the mesocosm results. The results from this study highlight the need to consider the natural complexity of reefs and additional biological and physical factors that influence seawater carbonate chemistry on larger spatial and longer temporal scales. Coordinated efforts combining various research approaches (e.g., experiments, field studies, and models) will be required to better understand how benthic metabolism integrates across functional, spatial, and temporal scales, and for making predictions on how coral reefs will respond to climate change.

Keywords: coral reef, metabolism, carbon chemistry, ocean acidification, coral cover

OPEN ACCESS

Edited by:
Hajime Kayanne, University of Tokyo, Japan

Reviewed by:
Atsushi Watanabe, Tokyo Institute of Technology, Japan
Emma Camp, University of Technology, Sydney, Australia

****Correspondence:***
Heather N. Page
hnpage@ucsd.edu

Specialty section:
This article was submitted to Coral Reef Research, a section of the journal Frontiers in Marine Science

Received: *15 January 2017*
Accepted: *12 May 2017*
Published: *30 May 2017*

Citation:
Page HN, Courtney TA, Collins A, De Carlo EH and Andersson AJ (2017) Net Community Metabolism and Seawater Carbonate Chemistry Scale Non-intuitively with Coral Cover. Front. Mar. Sci. 4:161. doi: 10.3389/fmars.2017.00161

INTRODUCTION

Coral reefs are one of the most diverse ecosystems in the world and provide numerous ecosystem goods and services including habitat provision, shoreline protection, nutrition, medicinal compounds, and monetary revenue from fisheries and tourism (Moberg and Folke, 1999; Costanza et al., 2014). The total economic valuation of the services provided by coral reefs has been estimated at several billions of U.S. dollars per year (de Groot et al., 2012; Costanza et al., 2014). In recent decades, the function of worldwide coral reefs has changed drastically owing to shifts in community structure with declines in coral cover and increases in turf and fleshy macroalgae (Wilkinson, 2008; Costanza et al., 2014; Chen et al., 2015; Bruno and Valdivia, 2016). In the Indo-Pacific region during 1980-1983, the majority of surveyed coral reefs had 20–50% coral cover with some reefs having up to 100% coral cover. In contrast, in 2003, the highest coral cover reported for this region was 70% with most reefs having less than 30% coral cover (Bruno and Selig, 2007). Similarly, reefs in the Caribbean have experienced massive declines in coral cover from an average of 50% in the mid-1970s to 10% now (Gardner et al., 2003).

The global trend of decreasing coral cover has been attributed to both local and global factors including disease outbreaks (Harvell et al., 1999), overfishing (Hughes et al., 2007), nutrient and sediment pollution (Koop et al., 2001; Szmant, 2002), storm damage, and climate change (Hoegh-Guldberg et al., 2007; Buddemeier et al., 2008; De'ath et al., 2012; Bruno and Valdivia, 2016). The major climate change concerns are prolonged periods of elevated seawater temperature, which can lead to mass coral bleaching events (Glynn, 1993; Brown, 1997; Hoegh-Guldberg, 1999; Baker et al., 2008; Rodgers et al., 2015), and ocean acidification (OA), i.e., a reduction in seawater pH and saturation state with respect to the calcium carbonate mineral aragonite (Ω_a) resulting from oceanic uptake of anthropogenic CO_2. It has been hypothesized that OA could cause reefs to shift from states of net accretion to states of net calcium carbonate ($CaCO_3$) dissolution and erosion (Kleypas and Yates, 2009; Silverman et al., 2009; Eyre et al., 2014; Enochs et al., 2016).

The potential response of corals and coral reef community metabolism (i.e., primary production, respiration, calcification, and $CaCO_3$ dissolution) to ocean warming and acidification has been studied extensively in laboratory and mesocosm experiments. Coral calcification rates are typically reduced when exposed to low seawater pH and Ω_a (Marubini et al., 2003; Ohde and Hossain, 2004; Anthony et al., 2008; Holcomb et al., 2010; Comeau et al., 2013; Horvath et al., 2016), which also has been observed for coral communities and rates of net community calcification (NCC = gross calcification – gross $CaCO_3$ dissolution) (e.g., Langdon et al., 2000; Leclerq et al., 2000; Andersson et al., 2009; Anthony et al., 2013). Similarly, relatively modest warming above summer maximum temperatures has been shown to affect coral skeletal growth and calcification negatively, although small increases in seawater temperature have been observed to increase coral calcification rates (Jokiel and Coles, 1990; Marshall and Clode, 2004; Bahr et al., 2016). In general, coral primary production and net community organic carbon production (NCP = primary production – autotrophic and heterotrophic respiration) decrease under elevated seawater temperatures (Coles and Jokiel, 1977; Brown, 1997) due to increasing rates of respiration, but the response of these processes to OA is less clear (Andersson et al., 2011). Langdon and Atkinson (2005) observed increased NCP for coral communities exposed to high pCO_2 and low pH seawater in flume experiments, but other experiments have reported a decrease or no effect on NCP under similar conditions (e.g., Anthony et al., 2013; Page et al., 2016). However, temperature and/or OA induced coral bleaching generally results in a reduction in NCP owing to decreased photosynthesis and increased respiration (Anthony et al., 2008; Crawley et al., 2010). Concurrent with the effects of warming and OA on coral reef metabolic processes, decreasing coral cover will also affect these processes. To date, this has received relatively little attention. As a result of decreasing coral cover, metabolic rates could change in non-intuitive ways because of changing resource availability, flow regime, boundary layer thickness, and intra- and inter specific competition (Lesser et al., 1994; Tanner, 1995; Ferrier-Pagès et al., 2003; Evensen and Edmunds, 2016).

Understanding how coral reef metabolism will change in response to decreasing coral cover and ocean warming and acidification is critical because it relates to a reef's ability to accrete $CaCO_3$ and its ability to locally alleviate or exacerbate OA (Anthony et al., 2011; Kleypas et al., 2011; Jury et al., 2013; Andersson et al., 2014; Page et al., 2016). Coral reef metabolism can have a significant influence on the local seawater carbonate chemistry (Bates, 2002; Bates et al., 2010; Hofmann et al., 2011; Andersson and Mackenzie, 2012; Shaw et al., 2012; Drupp et al., 2013), and diel and seasonal variations in coral reef CO_2 parameters (e.g., pCO_2, pH, and Ω_a) are much greater than in the open ocean. Many reefs may periodically already experience seawater pCO_2, pH, and Ω_a levels predicted to occur in the open ocean by the end of the century (Andersson and Mackenzie, 2012; Shaw et al., 2012; Drupp et al., 2013; Manzello et al., 2014; Albright et al., 2015) owing to strongly positive NCC, close to balanced trophic status, and negative NCP occurring at night. Positive NCC decreases dissolved inorganic carbon (DIC) and total alkalinity (TA) in a ratio of 1:2 resulting in a reduction of pH and Ω_a while negative NCP decrease pH and Ω_a owing to increased DIC. Furthermore, variations in metabolic rates and ratios of NCC to NCP between benthic functional groups (e.g., coral, turf and fleshy algae, coralline algae, sand, etc.) lead to different influences on seawater carbonate chemistry depending on community composition and structure (Anthony et al., 2013; Jokiel et al., 2014; Page et al., 2016), and these effects could either alleviate or enhance local seawater acidification or alkalinization. Based on mainly mesocosm and modeling experiments, changing community composition in favor of increasing coral cover has resulted in higher rates of NCC relative to NCP, causing a decrease in average seawater pH and Ω_a, while the opposite has been true for a decrease in coral cover in favor of macroalgae (Kleypas et al., 2011; Page et al., 2016).

The current understanding of the potential impacts of environmental perturbations to coral community metabolism and the effect of changing community structure on seawater

carbonate chemistry is limited with respect to the functional, spatial, and temporal scales of these impacts. To date, researchers have been constrained to extrapolating short term individual or community level responses observed in aquaria or mesocosm experiments to larger functional (e.g., ecosystems), spatial (e.g., regions or world), and/or temporal (e.g., years) scales. This approach often assumes that the whole response of coral reefs is equal to the sum of their individual components and frequently lacks consideration for the natural complexity of coral reefs, where organisms do not exist in isolation, but rather interact with other organisms and their physical environment (Mumby and van Woesik, 2014; Andersson et al., 2015; Edmunds et al., 2016). Being able to integrate effects of environmental perturbations on metabolic rates across functional scales, from organisms to reefs, however, is critical to better understand the fate of coral reefs in a future warmer and less alkaline ocean. Edmunds et al. (2016) proposed that existing ecological theories, namely metabolic theory of ecology (MTE; Brown et al., 2004), could provide the framework for this integration of metabolic rates. MTE states that allometric scaling between body size and metabolic rates governs ecological principles at higher functional scales (Brown et al., 2004). For example, net coral community calcification can be estimated as long as one knows (1) the functional relationship between coral colony size and calcification rate and (2) the abundance of different colony sizes within a reef (Edmunds et al., 2016). One of the first steps to develop a MTE for coral reefs is to better understand how colony sizes and coral densities relate to physiological rates in controlled, experimental settings, and then gradually evaluate these relationships for increasingly complex natural settings.

In this study, the main objectives were to examine the influence of different coral densities on rates of NCC and NCP (here referred to as "benthic metabolism") as well as their influence on the overlying seawater carbonate chemistry in two different locations, Bermuda and Hawaii. Through two sets of mesocosm experiments, we tested two hypotheses: (1) High coral cover has higher NCC and NCP rates compared to low coral cover, and rates scale proportionally to the percent coral cover, and (2) As a consequence of higher NCC and NCP rates, high coral cover results in greater diel variability of seawater pH, pCO_2, and Ω_a compared to low coral cover. As a complement to the mesocosm experiments, we also evaluated *in situ* seawater CO_2 measurements from three contrasting reef locations with different coral cover in Bermuda and Hawaii. It is not our intention to quantitatively link and connect the mesocosm results with these field observations, as this would require a range of additional data, but simply to provide a broader context in which to place the results of the mesocosm experiments. We also hope that these data will stimulate additional research aimed at quantitatively connecting experimental and field results which, combined, will strengthen our understanding of the links between coral communities, benthic metabolism, and seawater carbonate chemistry.

MATERIALS AND METHODS

Two mesocosm experiments were conducted to examine the relationships between coral cover, benthic metabolism, and diel seawater carbonate chemistry. An initial experiment was conducted at the Bermuda Institute of Ocean Sciences (BIOS) in 2012 to examine the effects of two treatments (40 and 80% coral cover) on daytime (06:00–00:00) seawater carbonate chemistry. This initial study was followed up by an experiment at the Hawaii Institute of Marine Biology (HIMB) in 2016 to include more coral cover treatments (20–100% coral cover) as well as a complete diel cycle (**Table 1**). These two sites (BIOS and HIMB) were primarily chosen because they contain outdoor, flow-through mesocosm facilities that experience natural fluctuations in environmental conditions representative of conditions experienced on a coral reef and allow control of flow rates. They also represent contrasting coral reef characteristics (e.g., different latitudes, high terrestrial vs. low terrestrial material inputs, and Atlantic vs. Pacific Oceans) and different dominant coral species.

Experiment 1: Bermuda 2012

Experimental Design

The experimental system at BIOS pumped filtered seawater from Ferry Reach, Bermuda into carboys which had gravity-fed flow into nine flow-through mesocosms with the dimensions 53 × 39 × 30.5 cm and flow rates (±1 std) averaging 1.67 ± 0.12 L min^{-1} (residence time, $\tau = 0.64 \pm 0.28$ h). Additionally, two fountain pumps circulated water within each mesocosm, ensuring that the seawater was well-mixed and corals were provided with extensive water flow. To prevent extreme temperature and light stress to the corals, shades were kept over the mesocosms throughout the experiment.

The coral communities in the mesocosms were made up of the scleractinian corals *Diploria labyrinthiformis*, *Porites astreoides*, and *Madracis aurentenra*, which are common to reefs in Bermuda (Bates et al., 2010; Courtney et al., 2016). Most of the corals had been previously collected from the Bermuda reef platform and acclimated to mesocosm conditions for over a year. However, to obtain higher coral cover in the mesocosms, additional *M. aurentenra* corals were collected from a shallow patch reef and acclimated for 1 week. Two coral cover treatments (40 and 80%) and controls (0% coral cover) were replicated in three mesocosms each ($n = 3$ per treatment). The 40% coral cover treatment contained five medium-sized colonies (<25 cm diameter) of *D. labyrinthiformis* and *P. astreoides* whereas 10 colonies total (five of each species) were used in the 80% coral cover treatment; *M. aurentenra* were filled in around these colonies to obtain the desired coral cover percentages.

Sampling Protocol

Seawater chemistry was monitored every 1–3 h from 06:00 to 00:00 (18 h total) on 29 August 2012 in order to encompass the full daylight period. Relative light intensity was measured using HOBO Pendant® temperature/light data loggers (Onset Computer Corporation) set to record light every 10 min. Seawater temperature (±0.15°C) and salinity (±1.0% of reading) were measured hourly using a YSI 556 multiprobe sensor, which was calibrated immediately prior to the experiment. Every 3 h, seawater samples were collected in 200 mL glass Kimax bottles for dissolved inorganic carbon (DIC) and total alkalinity (TA) analyses. These samples were immediately poisoned with a

TABLE 1 | Experimental design for mesocosm experiments in Bermuda and Hawaii.

Experiment	Day(s)	Hours sampled	Treatments (% Coral Cover)	Replication unit
Bermuda 2012	August 29	6:00–0:00	0, 40, 80	Mesocosm ($n = 3$)
Hawaii 2016	June 13–14, June 15–16	18:00–18:00	0, 20, 40, 60, 80, 100	Days ($n = 2$)

saturated solution of mercuric chloride to halt any biological activity in the samples.

Sample Analyses

Seawater samples were shipped to Scripps Institution of Oceanography (SIO) where they were analyzed for DIC and TA. DIC was measured using an Automated Infra-Red Inorganic Carbon Analyzer (AIRICA, Marianda Inc.) equipped with an infrared LI-COR 7000 CO_2/H_2O differential, non-dispersive infrared (NDIR) gas analyzer while TA was measured using an open-cell potentiometric acid-titration procedure outlined in Best Practices for Seawater CO_2 Measurements (Dickson et al., 2007). Precision for both instruments was typically within ±3 μmol kg^{-1} while the accuracies, calculated as the average (±1 std) offset from certified reference material (CRM) values, were 1.45 ± 2.62 ($n = 45$) and −0.85 ± 1.51 ($n = 24$) μmol kg^{-1} for DIC and TA, respectively.

Experiment 2: Hawaii 2016

Experimental Design

The mesocosm facility at HIMB (Smith et al., 1977; Andersson et al., 2009; Page et al., 2016) pumps water from Kaneohe Bay into a main header tank. This header tank flows into smaller header tanks that feed flow-through mesocosms with the dimensions 117 × 117 × 50 cm. Water flows up into the mesocosm from the center of the bottom, causing seawater to be well-mixed and providing plenty of flow for corals. Flow rates for the mesocosms averaged 10.81 ± 0.14 L min^{-1} ($\tau = 0.74 \pm 0.01$ h) while water depth was ∼0.35 m. Mesocosms were kept exposed to full sunlight since the reef from which corals were collected was approximately the same depth as the mesocosms.

Two of the dominant coral species, *Montipora capitata* and *Porites compressa*, were collected from the patch reef along the north side of Coconut Island. These are among the five dominant coral species in the state of Hawaii (Rodgers et al., 2015). Five coral cover treatments in addition to a control (0% coral cover) were set up in the mesocosms: 20, 40, 60, 80, and 100%. These percentages were composed of approximately half *M. capitata* and half *P. compressa* (Supplementary Figure 1). These coral communities were acclimated to mesocosm conditions for 36 h before beginning sampling on the first day.

Sampling Protocol

Seawater chemistry was sampled every 1–3 h for two diel (24 h) cycles (18:00–18:00) during June of 2016, following a similar protocol described for Experiment 1. HOBO loggers recorded relative light levels every 5 min. Seawater temperature (± 0.2°C) and salinity (± 1.0% of reading) were measured hourly using a handheld YSI Professional Plus multi-probe sensor which was calibrated to the certified salinity value (psu) for a CRM (Dickson Laboratory, SIO) immediately prior to each diel cycle. Every 3 h, seawater samples were collected in 250 mL glass Pyrex borosilicate bottles for DIC and TA analyses; these samples were immediately poisoned with a saturated solution of mercuric chloride.

Sample Analyses

Seawater samples were shipped to SIO where they were analyzed for DIC and TA using the same protocol as Experiment 1. Once again, the precision of the instruments was ±3 μmol kg^{-1}. The instrument accuracies were −1.31 ± 2.98 ($n = 62$) and 0.33 ± 2.21 ($n = 23$) μmol kg^{-1} for DIC and TA, respectively.

Data Analysis and Calculations of Mesocosm Experiments

The HOBO loggers recorded relative light levels as lux. However, photosynthesis only utilizes specific wavelengths of light, and thus, photosynthetically available radiation (PAR) provides more insight into the light levels that can drive autotrophic carbon fixation. We converted lux to PAR by using the following equation: PAR (μmol photons m^{-2} s^{-1}) = LUX ÷ 51.2 (Valiela, 1984; Smith et al., 2013).

Because the source water at each location passes through several ecosystems that modify carbon chemistry over diel cycles (Andersson and Mackenzie, 2012), variability in seawater carbonate chemistry of treatment mesocosms was due to changes both in the source water and modifications by the coral communities in the mesocosms. Additionally, plankton in the seawater may have modified seawater DIC and TA. To eliminate the influences of source water variability and plankton on seawater DIC and TA, and simply evaluate the influence of the benthic community in each mesocosm, the average control values were subtracted from treatment values. Thus, the resulting residual of DIC and TA of the treatment tanks represent modifications owing solely to the specific benthic community within each tank. Values of DIC and TA can be used to calculate NCC and NCP rates by modifying standard equations (Langdon et al., 2010) to:

$$NCC = -\left[\frac{TA_{Treatment} - TA_{Average\ Control}}{\tau_{Treatment}} \times \rho \times H \times 0.5\right] \text{mmol m}^{-2}\ \text{h}^{-1}$$

$$NCP = -\left[\frac{DIC_{Treatment} - DIC_{Average\ Control}}{\tau_{Treatment}} \times \rho \times H\right] - NCC\ \text{mmol m}^{-2}\ \text{h}^{-1}$$

where control values are averages for a specific sampling time, τ is the average residence time of seawater in the mesocosm (h), ρ is the seawater density (kg m^{-3}), and H is the height of the water column (m). The effect of gas exchange on the DIC in the treatment tanks is partly taken into account by subtracting the DIC from the control tanks, but fails to account for additional CO_2 flux as a result of biological modification of the seawater pCO_2. However, calculations of this flux (<0.2 mmol m^{-2} h^{-1}) show that it is small relative to the observed changes and residence time of the water.

Statistical analysis was performed using R v3.3.1 software (R Development Core Team, 2008) to test for differences in NCC and NCP rates between coral cover treatments. For Experiment 1, only rates occurring during daylight hours were used for this analysis; NCC and NCP rates were split into day and night for Experiment 2 since full diel cycles were measured. Data were first visually compared for no differences between replication units (mesocosm for Experiment 1 and day for Experiment 2). Since there were no differences between the replication units for either experiment, they were then combined for a one-way ANCOVA to determine statistically significant differences between coral cover treatments on NCC and NCP rates, controlling for time. When significance for treatment was detected, a *post-hoc* Tukey's HSD Test with a confidence level of 0.95 was used to examine which treatments were statistically different from one another.

In order to determine how NCC and NCP rates scaled to coral cover (Hypothesis 1), rates measured in Experiment 2 were scaled relative to the observed NCC and NCP rates for the 100% coral cover treatment on each day for each time point. For NCC, the following equation was used:

$$\text{Scaled NCC} = \frac{\text{NCC}_{\text{Treatment}}}{\text{NCC}_{\text{100\% Coral Cover}}} \times 100\%$$

Since NCP rates are in general positive during the day (primary production > respiration) and negative at night (respiration > primary production), day and night rates were evaluated separately. NCP rates measured at 18:00 were not used for this analysis since the rates at this time transitioned between net primary production and net respiration, and thus, caused misrepresentative scaling values. Therefore, daytime rates were scaled from 0 to 100% and nighttime rates from 0 to – 100%:

$$\text{Scaled NCP}_{\text{Day}} = \frac{\text{NCP}_{\text{Treatment}}}{\text{NCP}_{\text{100\% Coral Cover}}} \times 100\%$$

$$\text{Scaled NCP}_{\text{Night}} = \frac{\text{NCP}_{\text{Treatment}}}{\text{NCP}_{\text{100\% Coral Cover}}} \times -100\%$$

Using R v3.3.1 software (R Development Core Team, 2008), linear regression models (lm) were used to describe the relationships between coral cover and scaled rates.

Seawater pH, pCO_2, and Ω_a were calculated from measured temperature, salinity, DIC and TA using CO2SYS (Lewis and Wallace, 1998). K1 and K2 constants from Mehrbach et al. (1973), refitted by Dickson and Millero (1987) were selected for calculations on the total pH scale.

To further examine the relationships between coral cover, benthic metabolism, and seawater carbonate chemistry, a graphical analysis of TA and DIC vectors was performed (Deffeyes, 1965). Type II Linear Regressions were fit to TA and DIC data for each treatment from Experiment 2 using the lmodel2 package within R v3.3.1 software (R Development Core Team, 2008). The slopes provided by the major axis method, which assumes error in both the x and y axes, are reported and subsequently compared using an ANOVA after ensuring data meet assumptions for this statistical test. This analysis was not completed for Experiment 1 because the linear regressions were not significant ($p > 0.05$).

In situ Surface Seawater CO_2 Measurements in Bermuda and Hawaii

To put the mesocosm results into a broader context we evaluated the diel CO_2 variability and environmental conditions at three reef sites equipped with autonomous CO_2 sensors and contrasting coral cover for a period of 12 days coincident with the mesocosm experiments (**Figure 1**). In Bermuda, Crescent Reef is a patch reef located within a sandy bottom lagoon with water depth ranging from ~2 to 7 m at the reef site. Coral cover is ~15% (Jones, 2006). In contrast, Hog Reef is located on the rim reef with depth ranging from ~6 to 11 m. The benthic community at Hog Reef is comprised of close to 30% hard (Scleractinian) corals with almost 70% of the community consisting of macroalgae, turf algae, and soft corals (Courtney et al., 2016). *D. labyrinthiformis* and *P. astreoides* constitute ~10 and 1.5% of the benthic cover, respectively (Jones, 2006; Bates et al., 2010; Courtney et al., 2016). The seawater residence time on the rim reef is relatively short (1–4 days) while the lagoon experiences longer seawater residence times ranging from 5 to 12 days (Bates et al., 2010; Venti et al., 2012). In Hawaii, the monitoring site is a back reef environment located within Kaneohe Bay right at the shallow (~2 m) transition zone between the barrier reef with ~65% coral cover (Jokiel et al., 2015) and the inside deep (~12 m) lagoon (**Figure 1**). The seawater residence time on the barrier reef of Kaneohe Bay, based on numerical simulations forced by historical wave, wind and tidal data is on the order of a day (Lowe et al., 2009), but can be much shorter depending on the wind strength and wave height conditions.

At each reef site, the mole fraction of CO_2 (xCO_2) in seawater and in air was measured every 3 h by NOAA PMEL $MAPCO_2$ systems (Sutton et al., 2014). The $MAPCO_2$ moorings utilize a Battelle Memorial Institute CO_2 system equipped with a LI-COR LI-820 infrared CO_2 gas analyzer and SHT71 relative humidity and temperature sensor (Sutton et al., 2014). The system calculates xCO_2 in air that has been equilibrated with seawater. The system is calibrated with a zero and a non-zero CO_2 reference gas provided by NOAA Earth System Research Laboratory (ESRL) and traceable to World Meteorological Organization (WMO) standards. The accuracy and precision of both air and seawater xCO_2 measurements are typically better than 2 μmol mol^{-1} (Sutton et al., 2014). At each of these sites, seawater temperature (°C) is also measured every 3 h by a Seabird 16plus V2 Seacat CTD. Tide and wind measurements were retrieved from nearby monitoring stations. Hourly mean lower low water (MLLW, m) data

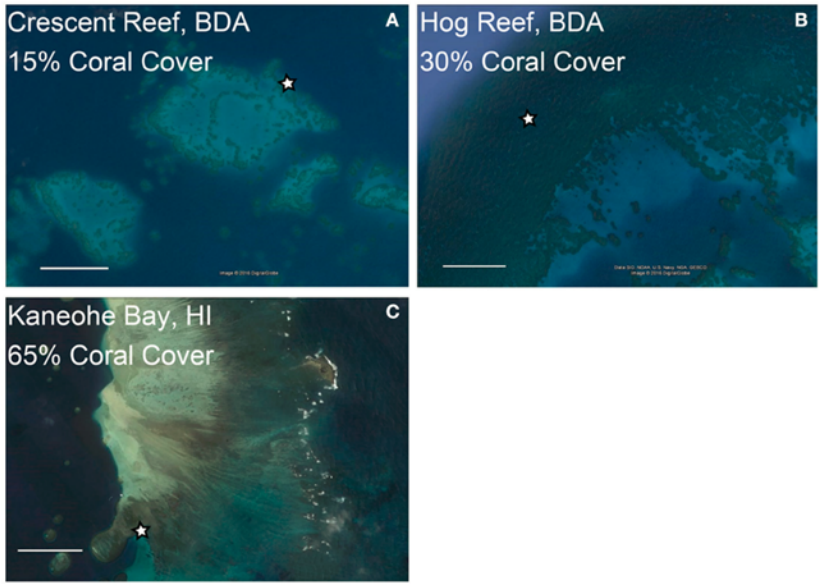


FIGURE 1 | Locations of coral reef buoys at reefs with contrasting coral cover in Bermuda (BDA, **A,B**) and Hawaii (HI, **C**). The stars indicate locations of coral reef CO_2 buoys and coral cover estimates are for the area surrounding these buoys. The scale bars represent 0.50 km in each image. Images were obtained from Google Earth.

were obtained for St. George's Island, Bermuda and Coconut Island (Mokuoloe), Kaneohe, Hawaii from NOAA/National Ocean Service (NOS) Center for Operational Oceanographic Products and Services (https://tidesandcurrents.noaa.gov). Wind data from Bermuda were taken from International Civil Aviation Organization (ICAO) standard observations at the LF Wade International Airport, Bermuda. The NOAA/NOS Data Buoy Center (www.ndbc.noaa.gov) provided hourly wind speed and direction for Coconut Island (Mokuoloe), Kaneohe, Hawaii.

RESULTS

All values are reported as the mean ±1 standard deviation, unless otherwise noted. The term "benthic metabolism" refers to the NCC and NCP rates for the communities containing different densities of coral within the mesocosms.

Experiment 1: Bermuda 2012

Environmental Conditions

The mesocosms experienced natural variations in seawater temperature, salinity, and light (**Figure 2**). From the beginning of the experiment, seawater temperature increased to a maximum of 30.37 ± 0.19°C at 15:00. Temperatures then decreased to 29.53 ± 0.07°C and remained fairly stable until the last sampling at midnight. Salinity fluctuated slightly around 36.67 psu for most of the experiment. There was a decline to 36.30 ± 0.15 psu at 21:00 due to a rain shower but salinity quickly recovered due to the short residence times of the mesocosms. Light started increasing slightly just before sunrise, which was at 6:52. Light levels reached a maximum (~325 μmol photons m^{-2} s^{-1}) around 15:00 and then decreased to zero just prior to sunset (19:46).

Benthic Metabolism

NCC rates remained fairly stable throughout the experiment while NCP rates followed temperature and light closely, with the significantly highest rates occurring during the middle of the day (**Figure 3**). Coral communities maintained positive net calcification and organic carbon production throughout the day. Despite slightly higher rates for 80% coral cover throughout most of the day, there were no statistically significant differences in average daytime NCC or NCP between the two coral cover treatments (**Table 2**). The 40% coral cover treatment had an average daytime NCC rate of 3.37 ± 2.94 mmol m^{-2} h^{-1} while the 80% coral cover had a slightly higher average daytime NCC rate of 3.93 ± 2.55 mmol m^{-2} h^{-1}. NCP rates reached peak organic production at 15:00 when irradiance was highest and rates were ~35% higher for high coral cover than for 40% coral cover (7.94 ± 3.82 vs. 5.93 ± 3.00 mmol m^{-2} h^{-1}).

Seawater Carbonate Chemistry

The net effect of NCC and NCP in the treatment mesocosms modified the seawater carbonate chemistry relative to the control, with positive NCC promoting acidification and positive NCP promoting alkalinization (**Figure 4**). Seawater pH and Ω_a increased throughout the morning until 15:00 after which they slightly decreased. In contrast, seawater pCO_2 started at maximum values and decreased until 15:00. At the start of the experiment, before sunrise, seawater pH was lowest for both coral cover treatments (7.85 ± 0.07 and 7.86 ± 0.02 for 40 and

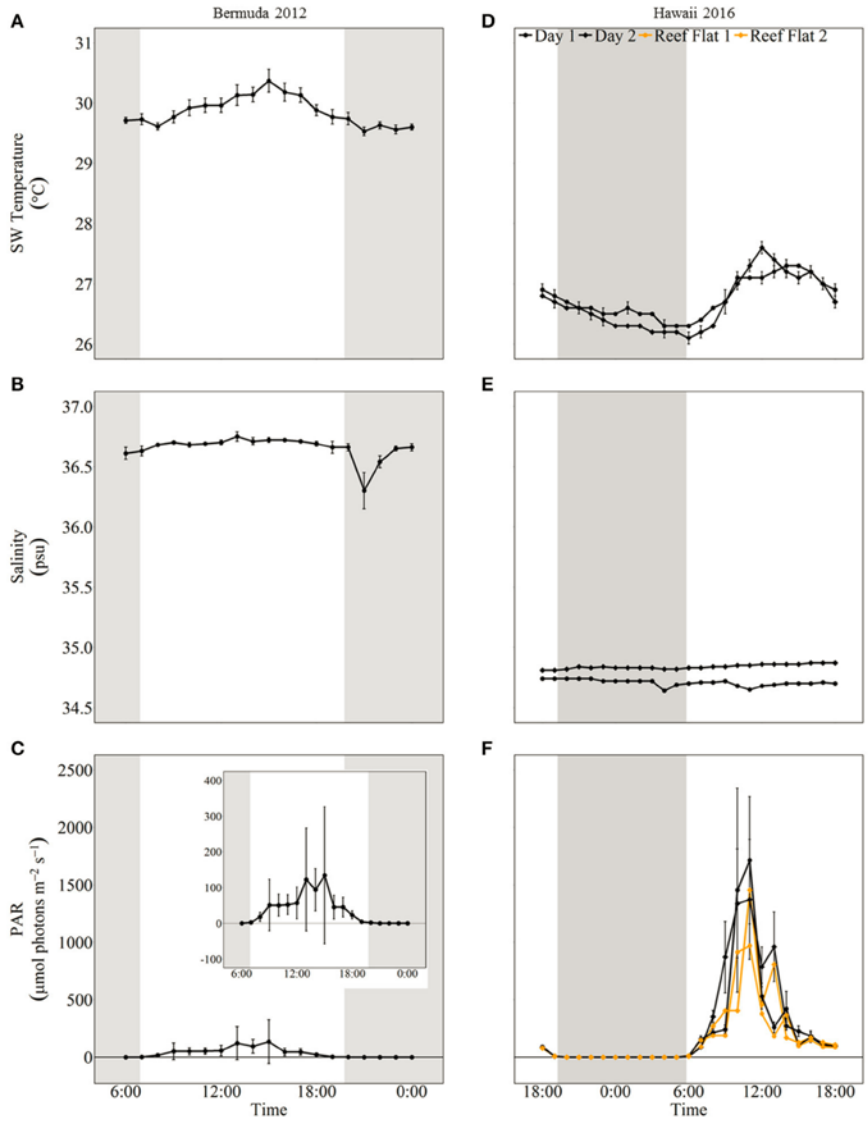


FIGURE 2 | Environmental conditions (mean ± 1 std) for mesocosm experiments in Bermuda 2012 (left panel, **A–C**) and Hawaii 2016 (right panel, **D–F**). The shaded areas show night as defined by sunset and sunrise times. In Hawaii, a light sensor was also placed on the reef flat where specimen were collected and these data are shown in orange.

80% coral cover, respectively) and lower than the control pH. Maximum pH for both treatments was 7.94 ± 0.01 which was 0.01 ± 0.01 higher than the control pH. Therefore, the pH range was 0.09 and 0.08 for 40 and 80% coral cover, respectively, which were twice the variability of seawater pH in the control (0.04). Seawater pCO_2 was highest in the morning and then decreased to 519.1 ± 10.3 µatm in 40% coral cover and 517.5 ± 11.4 µatm in 80% coral cover. The pCO_2 variability for 40 and 80% coral cover was 148.1 µatm and 122.9 µatm, respectively. Seawater Ω_a followed the same trend as seawater pH. The minimum values were 2.77 ± 0.40 for 40% coral cover and 2.83 ± 0.13 for 80% coral cover. The Ω_a rose to approximately maximum values of 3.33 for both coral cover treatments, which was 0.09 higher than the control (3.24 ± 0.04). The ranges of variability were 0.56 and 0.49 for 40 and 80% coral cover, respectively.

Experiment 2: Hawaii 2016

Environmental Conditions

Seawater temperature and light had strong diel variations while salinity remained stable throughout both days of sampling. The

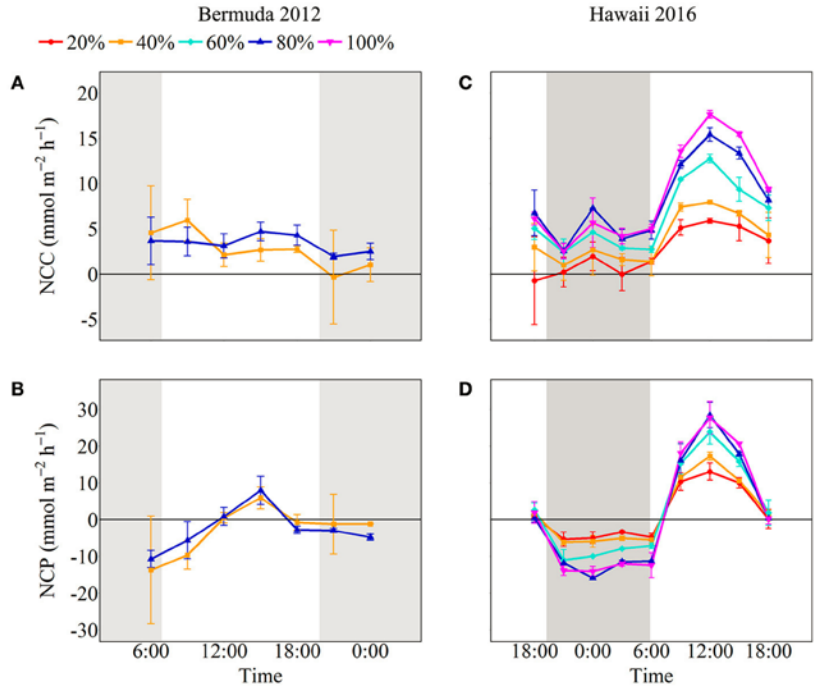


FIGURE 3 | NCC and NCP for Bermuda 2012 (left panels, **A,B**) and Hawaii 2016 (right panels, **C,D**) with colors and symbols representing coral cover treatments (red circle: 20%, orange square: 40%, aqua diamond: 60%, blue triangle: 80% and pink inverted triangle: 100%). The shaded areas show night as defined by sunset and sunrise times.

minimum and maximum seawater temperatures were similar for both days; the minimum temperature was around 26°C at night and then increased to ~27.5°C during midday. On the first day of sampling, salinity averaged 34.71 ± 0.03 psu and was slightly higher on the second day, averaging 34.84 ± 0.03 psu. Light levels reached zero around 19:00 and started increasing when sunrise occurred just before 6:00. Maximum light levels (PAR) were ~1,700 μmol photons m^{-2} s^{-1} during both days of sampling. These light levels were almost twice as high as measurements taken on the reef flat where corals were collected (**Figure 2**).

Benthic Metabolism

Both NCC and NCP followed similar diel trends to seawater temperature and irradiance; rates were low at night and then steadily increased to maximum rates during midday after which they decreased (**Figure 3**). Although all coral communities maintained net calcification most of the time, there were statistically significant differences between average night [ANCOVA, $F_{(4, 13)} = 5.048$, $p = 0.011$] and day [ANCOVA, $F_{(4, 35)} = 42.947$, $p < 0.001$] NCC rates (**Table 2**). The lowest rates of NCC were observed during night and the lowest coral cover had the lowest average NCC rate of 0.73 ± 1.6 mmol m^{-2} h^{-1}. This rate differed significantly from the highest nighttime NCC rates for 80% (4.0 ± 2.0 mmol m^{-2} h^{-1}) and 100% (4.1 ± 1.9 mmol m^{-2} h^{-1}) coral cover, which were not significantly different from one another. These differences between coral cover continued during the day as NCC rates followed the irradiance and temperature increase. The lowest coral cover (20%) had an average daytime NCC rate of 3.4 ± 3.0 mmol m^{-2} h^{-1} while the highest coral cover (100%) had an average daytime NCC rate of 11.2 ± 4.9 mmol m^{-2} h^{-1}.

All of the coral communities experienced net respiration at night and net organic production during the day. As observed for average NCC rates at night, there were also significant differences between treatment average NCP rates at night [ANCOVA, $F_{(4, 13)} = 53.43$, $p < 0.001$; **Table 2**]. The most negative average NCP rates were observed for 80% (−12.5 ± 1.9 mmol m^{-2} h^{-1}) and 100% (−13.3 ± 1.3 mmol m^{-2} h^{-1}) coral cover treatments. The 20 and 40% coral cover treatments had the least negative average night NCP rates at −4.5 ± 1.5 and −5.7 ± 0.97 mmol m^{-2} h^{-1}, respectively, and did not differ significantly from one another. The only significant interaction between coral cover treatment and time occurred for average daytime NCP rates [ANCOVA, $F_{(16, 35)} = 7.695$, $p < 0.001$] such that there were only differences between treatments at noon and 15:00 when maximum NCP rates were observed. At noon, 20% coral cover had the lowest positive NCP rate of 13.1 ± 2.3 mmol m^{-2} h^{-1} while the maximum NCP rate for the 100% coral cover treatment was approximately doubled at 27.7 ± 4.4 mmol m^{-2} h^{-1}.

Although there was quite a bit of variance in scaled NCC and NCP rates, linear regressions of scaled rates vs. coral cover

TABLE 2 | Statistical comparison of NCC and NCP rates for Bermuda 2012 and Hawaii 2016.

Experiment	Day/ night	Response	Factor	*df*	*F*-Statistic	*p*-value
Bermuda 2012	Day	NCC	Treatment	1	0.974	0.338
			Time	3	2.462	0.100
			Treatment*Time	3	3.114	0.056
		NCP	Treatment	1	2.715	0.120
			Time	3	15.72	<0.001*
			Treatment*Time	3	0.638	0.602
Hawaii 2016	Day	NCC	*Treatment*	4	42.95	<0.001*
			Time	4	50.30	<0.001*
			Treatment*Time	16	1.402	0.197
		NCP	*Treatment*	4	9.843	<0.001*
			Time	4	362.2	<0.001*
			*Treatment*Time*	16	7.695	<0.001*
	Night	NCC	*Treatment*	4	5.048	0.011*
			Time	2	5.891	0.015*
			Treatment*Time	8	0.302	0.952
		NCP	*Treatment*	4	53.43	<0.001*
			Time	2	6.425	0.012*
			Treatment*Time	8	1.021	0.467

For each analysis, an ANCOVA was used to compare the effect of coral cover on NCC and NCP rates while accounting for time. Results were considered significant when $p < 0.05$ and these significant results are italicized and indicated by asterisks.
**Indicates statistical significance.*

explained over 95% of this variance and thus were statistically significant for NCC ($R^2 = 0.98$, $p = 0.001$), NCP_{Day} ($R^2 = 0.96$, $p = 0.003$), and NCP_{Night} ($R^2 = 0.95$, $p = 0.003$). NCC rates scaled proportionally to coral cover with the linear regression having a slope of 0.99. (A linear regression with a slope of 1 would indicate increases in metabolic rates proportional to increases in coral cover.) The scaled NCC rates increased from 25 ± 33% to 89 ± 28% for 20% and 80% coral cover, respectively. NCP_{Night} also scaled relatively proportionally to coral cover with the linear regression having a slope of −0.90. The lowest coral cover (20%) had scaled NCP_{Night} rates of −35 ± 9% while 80% coral cover had scaled NCP_{Night} rates of −93 ± 12%. Unlike NCC and NCP_{Night}, scaled rates for NCP_{Day} did not scale proportionally to coral cover; the slope of the linear regression was only 0.66. The 20% coral cover treatment had scaled NCP_{Day} of 51 ± 6% and this scaled rate increased to 93 ± 9% for 80% coral cover (**Figure 5**). Comparison of rates of nighttime net respiration to daytime net production revealed that the balance between net respiration and net production shifts toward the former as coral cover increases (inset on **Figure 5**). Consequently, daily positive net community production remained relatively similar between treatments.

Seawater Carbonate Chemistry

Net calcification and net respiration at night resulted in low seawater pH and Ω_a and high pCO_2 while net organic carbon production during the day elevated seawater pH and Ω_a, and decreased pCO_2 (**Figure 4**). Interestingly, there were noticeable differences in seawater carbonate chemistry between different coral cover treatments at night but not during the day. Seawater pH for coral cover treatments was lower than control at night and had minimum pH ranging from 7.89 ± 0.00 (20% coral cover) to 7.84 ± 0.01 (80 and 100% coral cover). During the day, control pH reached a maximum of 7.96 ± 0.01 while the coral cover treatments had pH values 0.01–0.03 higher than the control. The diel variability of seawater pH was lowest for the control (0.04) and increased with increasing coral cover (0.08 for 20% coral cover to 0.14 for 100% coral cover). Maximum seawater pCO_2 occurred at the end of the night, just before sunrise. The control reached a maximum pCO_2 of 539.0 ± 3.5 μatm while coral cover treatment maxima ranged from 577.0 ± 4.2 (20% coral cover) to 662.0 ± 14.4 μatm (100% coral cover). Minimum seawater pCO_2 was observed at midday with coral cover treatments having lower pCO_2 relative to the control. As with seawater pH, these diel trends led to increasing variability of pCO_2 with increasing coral cover. Coral cover treatments had the lowest Ω_a during the night with minimum values of 2.48 ± 0.02 (20% coral cover) to 2.23 ± 0.04 (100% coral cover) and these were lower than the minimum value for the control (2.62 ± 0.01). During the day, coral cover treatments had slightly higher seawater Ω_a relative to control values. The diel variability of seawater Ω_a was lowest for the control (0.27) and increased with increasing coral cover (0.49–0.71 for 20 and 100% coral cover, respectively). Although the magnitude of changes observed in seawater TA and DIC differed between treatments (**Figure 6**), there were no differences between the slopes of TA:DIC ratios [ANOVA, $F_{(4, 5)} = 0.271$, $p = 0.885$; **Figure 7**]. These slopes ranged from 0.43 ± 0.10 for 40% coral cover to 0.54 ± 0.24 for 80% coral cover. This resulted in a pH range of 7.8–8.0 and pCO_2 range of 400–800 μatm for all coral densities.

In Situ Surface Seawater CO_2 Measurements in Bermuda and Hawaii

In general, *in situ* observations showed that reefs with higher coral cover experienced greater diel variability in seawater CO_2 than reefs with lower coral cover (**Figure 8**). Crescent Reef, which had the lowest coral cover, experienced a mean xCO_2 of 483.6 μmol mol^{-1} and a range of 455.2–521.8 μmol mol^{-1}. Hog Reef had slightly higher mean xCO_2 (501.5 μmol mol^{-1}) and range (444.9–574.8 μmol mol^{-1}) compared to Crescent Reef. The larger range of CO_2 at Hog Reef can be attributed to nighttime maxima always being greater than Crescent Reef whereas daytime minima were similar to or slightly lower than Crescent Reef. However, both reefs always had higher xCO_2 than the atmosphere, which averaged 385 μmol mol^{-1}. The reef in Kaneohe Bay experienced a much greater range of xCO_2 compared to the reefs in Bermuda with both nighttime maxima and daytime minima higher and lower, respectively. The minimum value during the study period was 306.0 μmol mol^{-1} while the maximum was 691.0 μmol mol^{-1} with a mean of 473.5 μmol mol^{-1}. The average seawater temperature in Bermuda was 29.3°C with a 1.5°C range while Hawaii was slightly

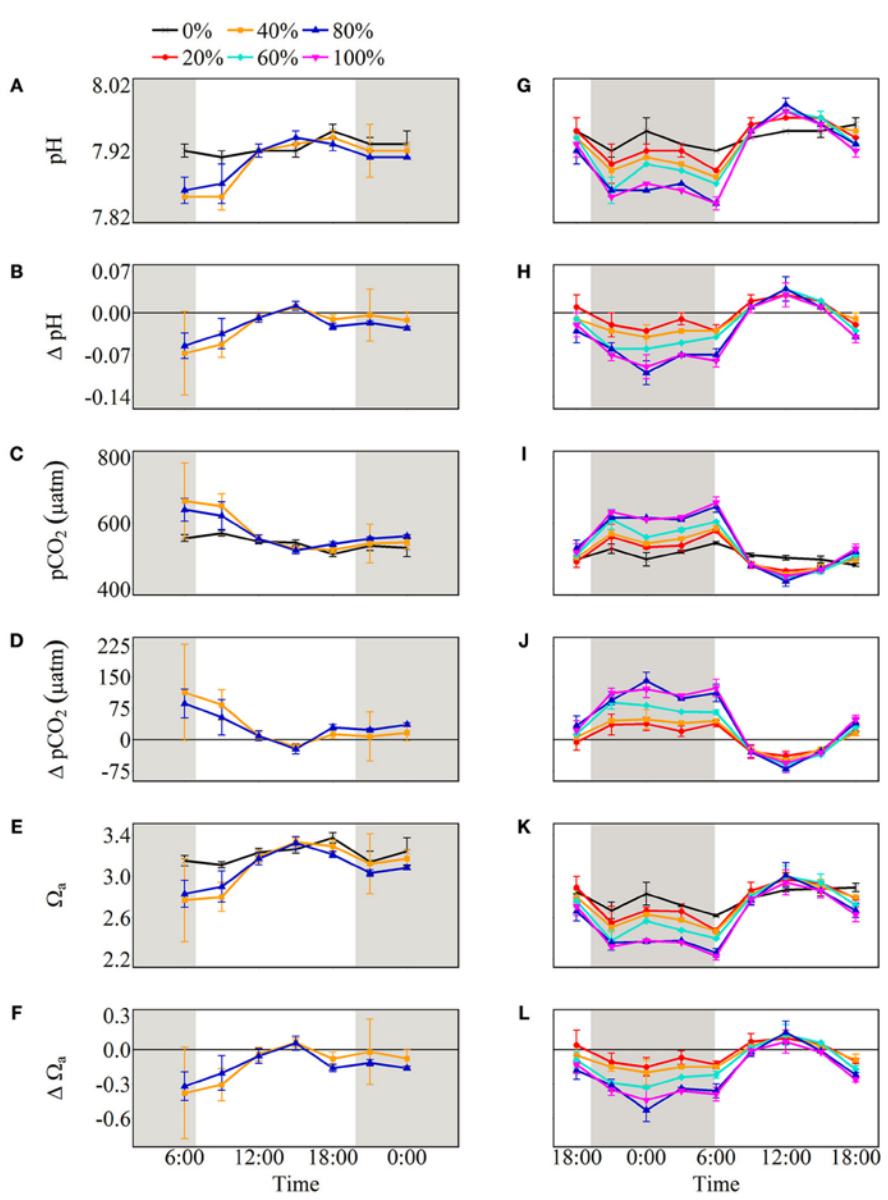


FIGURE 4 | Seawater carbonate chemistry shown as absolute values (pH, pCO_2, and Ω_a) and the difference from control (0%) values (Δ pH, Δ pCO_2, and Δ Ω_a) for Bermuda 2012 (left panel, **A–F**) and Hawaii 2016 (right panel, **G–L**). The shaded areas show night as defined by sunset and sunrise times while the colors and symbols represent coral cover treatments (black cross: 0%, red circle: 20%, orange square: 40%, aqua diamond: 60%, blue triangle: 80% and pink inverted triangle: 100%).

cooler (mean = 26.4°C) and experienced a larger range of 4°C. Both regions had semidiurnal tides with a tidal range less than or equal to 1 m. Wind speed and direction were variable in Bermuda while east to northeasterly trade winds dominated in Hawaii during the time frames examined (**Figure 8**).

DISCUSSION

This study was designed to test hypotheses relevant for the scaling of NCC and NCP rates and their influence on seawater carbonate chemistry for different coral densities. Higher coral density

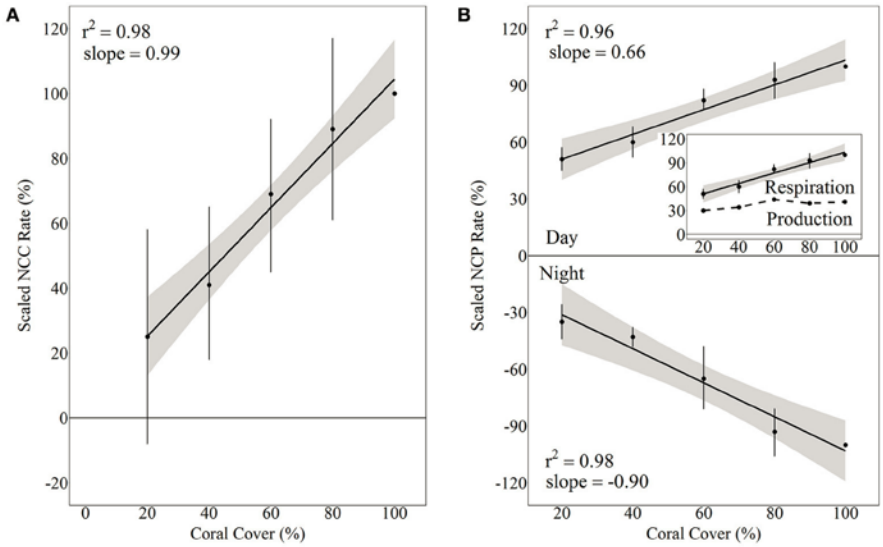


FIGURE 5 | Scaled NCC **(A)** and NCP **(B)** rates vs. coral cover treatments for Hawaii 2016 with linear regressions and shaded 95% confidence intervals during day and night. Separate linear regressions were performed for NCP day and night to show scaled rates for NCP_{Night} (net respiration, **B**, bottom panel) and NCP_{Day} (net organic carbon production, (**B**, top panel). The inset shows the daytime NCP rates as well as the difference between day and night NCP rates (dashed line), which essentially is a relative estimate of the integrated daily net production rate relative to daytime NCP in the 100% coral cover treatment.

sometimes, but not always led to higher NCC and NCP rates that scaled with increases in coral cover. In Bermuda, the higher coral density treatment (80%) did not have statistically significantly higher average daytime NCC or NCP rates (H1) compared to the low coral density (40%) treatment. Consequently, no significantly different influences on seawater carbonate chemistry were observed between low and high coral cover for this experiment (H2). In contrast, higher coral cover did lead to statistically higher average NCC and NCP rates in Hawaii (H1). Furthermore, these increases were roughly linearly proportional to the increases in coral cover for NCC and NCP_{Night}. That is, a doubling in coral cover doubled the rate of NCC and the rate of nighttime net respiration (-NCP) (H1). NCP_{Day} also increased with increasing coral cover, but was not directly proportional to the percent increase in cover. Notably, the observed increases in metabolic rates led to increases in diel variability of seawater pH, pCO_2, and Ω_a (H2). Likewise, field measurements of seawater xCO_2 in Bermuda and Hawaii showed greater diel ranges for reef areas with higher coral cover. We discuss these results further in the subsequent sections.

Coral Density and Benthic Metabolic Rates

The first experiment conducted in Bermuda during 2012 showed no significant difference between daytime NCC and NCP rates between two coral cover treatments. In addition, NCC rates remained relatively low and did not follow a clear diurnal cycle (average of 2.68 and 3.40 mmol m^{-2} h^{-1} for 40 and 80% coral cover, respectively), while NCP rates tracked light and temperature closely with the highest rates occurring in the late afternoon. These results were unexpected as we had anticipated high coral cover to have significantly higher metabolic rates than low coral cover (Kleypas et al., 2011). We had also expected NCC rates to track variations in light intensity and NCP due to light and/or production enhanced calcification (e.g., Vandermeulen et al., 1972; Gattuso et al., 1999; Albright et al., 2015; Cohen et al., 2016). However, the observed variability in NCC and NCP rates between treatments was high, masking any potential systematic differences (**Figure 3**). It is likely this variability was partly related to insufficient control and characterization of flow rates, and therefore residence time within the mesocosms, which has a large influence on calculations of NCC and NCP. Furthermore, shading cloth intended to moderate temperatures in the mesocosms resulted in low light intensities that only reached a maximum of 325 μmol photons m^{-2} h^{-1}. This may have resulted in metabolic rates that were insufficient to distinguish differences between the two treatments. In addition, limited light conditions may also explain the low and temporally flat NCC rates despite a distinct temporal trend in NCP, since photosynthesis and light enhanced calcification could respond differently to different wavelengths and intensity of light (Cohen et al., 2016). However, additional studies would be required to evaluate whether this could have been the case. Compared to the Hawaii experiments conducted under higher light conditions (max ~1,700 μmol photons m^{-2} h^{-1}), NCP rates for the Bermuda experiment were much lower although the qualitative trend and difference between treatments were similar to the Hawaii experiments (**Figure 2**). Regardless of the shortcomings of this experiment, the results represent metabolic rates of two coral density treatments and their influence on seawater carbonate chemistry under the reported conditions, which could

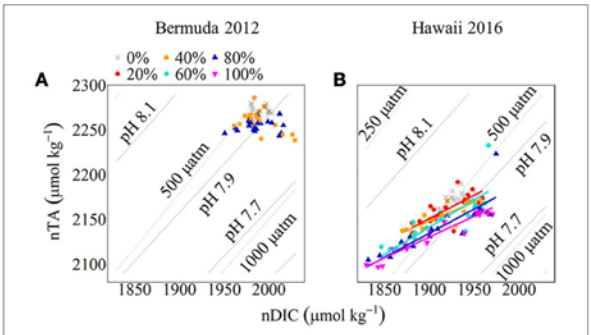


FIGURE 6 | nTA:nDIC plots with pH and pCO_2 isolines for Bermuda 2012 **(A)** and Hawaii 2016 **(B)**. Seawater pH and pCO_2 was calculated using nDIC, nTA, and average temperature and salinity for each site. The colored symbols show coral cover treatments (black cross: 0%, red circle: 20%, orange square: 40%, aqua diamond: 60%, blue triangle: 80% and pink inverted triangle: 100%) for both experiments. The colored lines show Type II Linear Regressions for each coral community.

naturally be experienced *in situ* on cloudy days or at deeper depths. The results also provide important information to be considered in the interpretation of other studies as well as in the design of future experiments.

Because of the somewhat inconclusive results achieved in Bermuda, the follow-up study in Hawaii was designed using the mesocosm facility at HIMB, which experiences full exposure to sunlight and has a proven ability to control seawater flow rates (Andersson et al., 2009; Page et al., 2016). Using more different coral cover treatments and full diel cycles also allowed a more incisive investigation into the effects of coral densities on benthic metabolism and seawater carbonate chemistry. In contrast to the Bermuda experiments, these experiments showed statistically significant increasing rates of NCC and NCP as a function of increasing coral cover. In addition, both NCC and NCP followed the light cycle with lower rates at night and higher rates during the day as expected based on previous mesocosm experiments at HIMB (Jokiel et al., 2014; Page et al., 2016). Coral communities typically maintained net calcification (positive NCC) throughout the experiments with a few instances of net $CaCO_3$ dissolution for the lower coral cover communities (20 and 40%) during the night. Interestingly, rates of NCC and NCP_{night} scaled directly to coral cover while NCP_{day} did not (**Figure 5**). Because rates of respiration are linked to body size and metabolic demand, the proportional link between coral cover and NCP_{night} seems reasonable. The same might be true for NCC assuming that this rate is directly linked to the energetic expenditure of the colonies within a community. However, this relationship between body size and metabolic demand for NCC would imply that communities with low coral cover require more energy to calcify or can store more energy for other processes than high coral cover since NCP_{day} rates were proportionally higher for low coral cover compared to high coral cover communities. For example, the 20% coral cover treatment had NCP_{day} rates on average approximately half of the rates for the 100% coral cover treatment, but maintained NCC rates at ~20% of the rates observed in the 100% treatment. One possibility is that higher coral cover may have depleted the availability of resources (e.g, inorganic macro-nutrients) necessary for primary production, thus leading to proportionally lower NCP in these treatments. Mesocosms with higher coral cover also contained more complex topography, which could result in shading of some coral colonies and/or different boundary layer thicknesses (Shashar et al., 1996; Hearn et al., 2001), which could affect rates of primary production (Dennison and Barnes, 1988). Furthermore, intra- and inter-specific interactions in high coral density could reduce rates of physiological processes as organisms cope with stress and/or divert energy resources toward defense mechanisms against competitors (Rinkevich and Loya, 1985; Tanner, 1997). Regardless of the various factors that may have influenced the metabolic rates, it is unclear why NCC scaled proportionally with coral cover while NCP_{day} did not. Time may also be a factor with potential lag in responses that are not detected over the diel timescale of the current experiments. Experiments of longer duration could potentially reveal different relationships and scaling of metabolic rates in response to variations in environmental parameters. Our initial results indicate that additional studies are warranted to better understand how different environmental and physical properties interact and influence benthic metabolic rates.

Coral Density and Seawater Carbonate Chemistry

In general, positive NCC and negative NCP at night led to seawater acidification while positive NCP exceeding NCC during the day promoted alkalinization for most treatments (**Figure 4**). Intuitively, one might anticipate that higher coral cover and higher rates of NCC and NCP would lead to significantly different seawater pH, pCO_2, and Ω_a as well as different diel amplitude and variability, but this was not always the case. Naturally, for the Bermuda experiments, no differences in seawater pH, pCO_2, and Ω_a were observed between coral densities because NCC and NCP rates were not significantly different. However, even for the Hawaii experiments, no significant differences were observed in these parameters between coral density treatments during the day despite significantly different NCC and NCP rates. In contrast, seawater pH and Ω_a were progressively lower and pCO_2 higher with increasing coral cover at night, which resulted from increased net respiration and positive NCC as a function of higher coral cover. As a result of the differential influence by communities with different coral densities on seawater chemistry at night, the daily average pH and Ω_a, and the diel variability of these parameters decreased and increased slightly, respectively, with increasing coral cover.

Deffeyes diagrams (Deffeyes, 1965) provide a useful tool to understand the observed trends in carbonate chemistry and illuminate differences in diel variability of seawater pH, pCO_2, and Ω_a between coral cover treatments. These diagrams graphically depict seawater carbonate chemistry parameters (i.e., pH, Ω_a, and pCO_2) as a function of variations in TA and DIC owing to modification by biogeochemical processes such as NCC and NCP (Watanabe et al., 2006; Andersson and Gledhill, 2013).

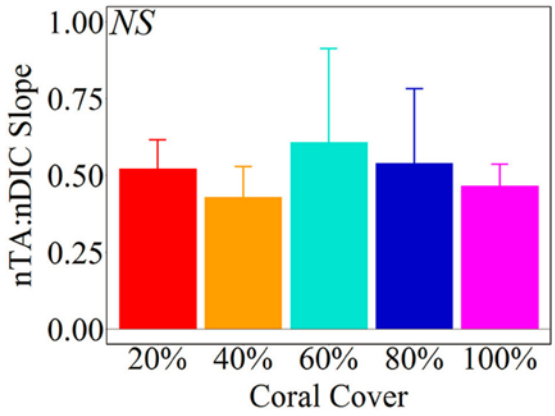


FIGURE 7 | Average (± 1 std) nTA:nDIC slopes from Type II Linear Regressions of the Hawaii mesocosm data. There were no statistical significant differences between coral cover treatments [ANOVA, $F_{(4, 5)} = 0.271$, $p = 0.885$].

Depending on the slope of the TA-DIC relationship, one can infer the relative importance of organic to inorganic carbon cycling (i.e., NCP vs. NCC) with slopes less than ~1 indicating higher dominance by organic carbon cycling. In this study, the overall slopes of the vectors were always less than 1 for the duration of the experiments. Some of the observed variability in TA-DIC slopes could be accounted for by changes in the source water, but in general this was small compared to the changes due to metabolic processes within the mesocosms (**Figure 6**). Although TA-DIC slopes were similar across treatments, there was consistently lower TA with increasing coral cover owing to higher NCC rates, which combined with more negative NCP rates during night, led to differences in the daily mean and the range of variability of seawater pH, pCO_2, and Ω_a between treatments. At night, positive NCC and negative NCP acted additively in modifying seawater carbonate chemistry parameters while during the day, positive NCC and positive NCP counteracted the influence on these parameters (Page et al., 2016). Consequently, both the absolute NCC and NCP rates and the relative balance between these processes, which combined modify the seawater TA and DIC balance, are important to consider in evaluating the influence of biogeochemical processes on seawater pH, pCO_2, and Ω_a (Andersson and Gledhill, 2013).

Similar to the mesocosm results, natural coral reefs with higher coral cover experienced greater diel ranges of seawater CO_2 concentrations relative to reefs with lower coral cover. In Bermuda, observations of seawater CO_2 from Crescent and Hog Reefs qualitatively agreed with the mesocosm results with large differences at night, but similar conditions during the day between the two reef sites. At this time, it is not our intention to fully assess the *in situ* variability and quantitatively compare it to the mesocosm results, as additional data are required (see for example, Kayanne et al., 2005); however, initial assessments show that the range of *in situ* CO_2 and temperatures are comparable to values measured in the mesocosm experiments. Compared to the mesocosms, additional biological and physical factors influence seawater carbonate chemistry on natural coral reefs. Even though coral cover is the only biological metric reported here, additional functional groups (e.g., calcifying algae, fleshy macroalgae, and sand) differed between each reef site, but were not included in the mesocosms. The magnitude of the influence by benthic metabolism on seawater carbonate chemistry is likely to depend on benthic community composition. Previous mesocosm and flume studies have shown differential modification of seawater pCO_2, pH, and Ω_a(Anthony et al., 2011, 2013; Page et al., 2016) between fleshy algae, crustose coralline algae, coral, and sand communities due to differences in benthic metabolic rates. Although benthic metabolism typically has a large influence on the magnitude of CO_2 changes on a reef, physical drivers such as water depth, residence time, tidal flow, wind speed, and wave forcing strongly influence this variability as well (Suzuki and Kawahata, 2003; Drupp et al., 2013; Falter et al., 2013). Furthermore, air-sea gas exchange (Bates et al., 2001; Fagan and Mackenzie, 2007) and terrestrial influences (Kawahata et al., 2000; Suzuki and Kawahata, 2003; Drupp et al., 2011; Massaro et al., 2012; Cyronak et al., 2013) must also be considered as they may differ greatly between Bermuda and Hawaii (particularly terrestrial inputs). The Kaneohe Bay reef system is more strongly dominated by organic carbon cycling than inorganic carbon cycling (Massaro et al., 2012) while the opposite is true for the Bermuda reefs (Andersson et al., 2014). Consequently, additional studies would be required to tease apart the exact drivers of seawater CO_2 variability on these reefs and to determine the *in situ* relative importance of coral cover and other benthic components to this variability.

Integrating Effects across Scales to Predict Coral Reef Response to Environmental Changes

The results from this study highlight the need to develop a more comprehensive understanding of how metabolic processes and the subsequent effects on seawater carbonate chemistry integrate across functional, spatial, and temporal scales. Community scale mesocosm experiments provide an intermediate step between experiments with individual coral colonies and natural reef communities, and provide valuable insight into drivers of benthic community metabolism (e.g., coral cover, community composition, flow rates, and resource availability) (Anthony et al., 2013; Page et al., 2016). However, the question remains: how do these results translate to an entire reef system across different temporal and spatial scales? In this study, altering coral cover alone in mesocosms did not always change the influence on the magnitude of the variability of diel seawater pCO_2, pH, and Ω_a, but natural reefs with variable coral cover exhibited significantly different diel variability in seawater CO_2. It is clear from the current results that additional processes need to be considered to account for the *in situ* observations, which may include water depth, water flow, and the major functional groups' relative composition and metabolism. Nonetheless, the process of comparing results from controlled laboratory experiments with *in situ* observations is a necessary first step of developing a more sophisticated model that is able to account for the observed variability in the natural

field observations and numerical modeling, but these efforts will be essential to advance our understanding regarding the future impacts of climate change and OA on these important systems (Andersson et al., 2015). One of the main challenges is related to the fact that different processes and drivers of net reef metabolism operate on different temporal and spatial scales, and perhaps this can only fully be accounted for by a well-defined numerical model integrating physical, ecological and biogeochemical processes.

AUTHOR CONTRIBUTIONS

HP and AA designed the study, analyzed the results, and wrote the initial draft of the manuscript. HP, TC, and AC conducted the experiments. ED contributed data. All authors contributed to writing of the revised manuscript.

FUNDING

NSF GRFP (HP, TC); NSF OCE 09-28406; NSF OCE 12-55042 (AA), NOAA: NA14OAR4170071, Project R/IR-27, University of Hawaii Sea Grant College Program (ED).

ACKNOWLEDGMENTS

We would like to thank Melissa Wartman and Noah Howins for assistance with preparing and conducting these mesocosm experiments in Bermuda and Hawaii as well as Kyra Freeman for help with analyzing seawater samples. We would also like to thank the reviewers for their comments which greatly improved the original version of this paper. This paper is funded in part by a grant/cooperative agreement from the National Oceanic and Atmospheric Administration, Project R/IR-27, which is sponsored by the University of Hawaii Sea Grant College Program, SOEST, under Institutional Grant No. NA14OAR4170071 from NOAA Office of Sea Grant, Department of Commerce. The views expressed herein are those of the author(s) and do not necessarily reflect the views of NOAA or any of its subagencies. UNIHI-SEAGRANT-JC-17-01.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: http://journal.frontiersin.org/article/10.3389/fmars.2017.00161/full#supplementary-material

REFERENCES

Albright, R., Benthuysen, J., Cantin, N., Caldeira, K., and Anthony, K. (2015). Coral reef metabolism and carbon chemistry dynamics of a coral reef flat. *Geophys. Res. Lett.* 42, 3980–3988. doi: 10.1002/2015GL063488

Andersson, A. J., and Gledhill, D. (2013). Ocean acidification and coral reefs: effects on breakdown, dissolution, and net ecosystem calcification. *Ann. Rev. Mar. Sci.* 5, 321–348. doi: 10.1146/annurev-marine-121211-172241

Andersson, A. J., Kline, D. I., Edmunds, P. J., Archer, S. D., Bednaršek, N., Carpenter, R. C., et al. (2015). Understanding ocean acidification impacts on organismal to ecological scales. *Oceanography* 28, 16–27. doi: 10.5670/oceanog.2015.27

Andersson, A. J., Kuffner, I. B., Mackenzie, F. T., Jokiel, P. L., Rodgers, K. S., and Tan, A. (2009). Net loss of $CaCO_3$ from a subtropical calcifying community due to seawater acidification: mesocosm-scale experimental evidence. *Biogeosciences* 6, 1811–1823. doi: 10.5194/bg-6-1811-2009

Andersson, A. J., and Mackenzie, F. T. (2012). Revisiting four scientific debates in ocean acidification research. *Biogeosciences* 9, 893–905. doi: 10.5194/bg-9-893-2012

Andersson, A. J., Mackenzie, F. T., and Gattuso, J.-P. (2011). "Effects of ocean acidification on benthic processes, organisms, and ecosystems" in *Ocean Acidification*, eds. J.-P. Gattuso and L. Hansson (New York, NY: Oxford University Press), 122–153.

Andersson, A. J., Yeakel, K. L., Bates, N. R., and de Putron, S. J. (2014). Partial offsets in ocean acidification from changing coral reef biogeochemistry. *Nat. Clim. Chang.* 4, 56–61. doi: 10.1038/nclimate2050

Anthony, K. R. N., Diaz-Pulido, G., Verlinden, N., Tilbrook, B., and Andersson, A. J. (2013). Benthic buffers and boosters of ocean acidification on coral reefs. *Biogeosciences* 10, 4897–4909. doi: 10.5194/bg-10-4897-2013

Anthony, K. R. N., Kleypas, J., and Gattuso, J.-P. (2011). Coral reefs modify their seawater carbon chemistry – implications for impacts of ocean acidification. *Glob. Chang. Biol.* 17, 3655–3666. doi: 10.1111/j.1365-2486.2011.02510.x

Anthony, K. R. N., Kline, D. I., Diaz-Pulido, G., Dove, S., and Hoegh-Guldberg, O. (2008). Ocean acidification causes bleaching and productivity loss in coral reef builders. *Proc. Natl. Acad. Sci. U.A.S.* 105, 17442–17446. doi: 10.1073/pnas.0804478105

Bahr, K. D., Jokiel, P. L., and Rodgers, K. S. (2016). Relative sensitivity of five Hawaiian coral species to high temperature under high-pCO_2 conditions. *Coral Reefs.* 35, 729–738. doi: 10.1007/s00338-016-1405-4

Baker, A. C., Glynn, P. W., and Riegl, B. (2008). Climate change and coral reef bleaching: an ecological assessment of long-term impacts, recovery trends and future outlook. *Estuar. Coas. Shelf Sci.* 80, 435–471. doi: 10.1016/j.ecss.2008.09.003

Bates, N. R. (2002). Seasonal variability of the effect of coral reefs on seawater CO_2 and air-sea CO_2 exchange. *Limnol. Oceanogr.* 47, 43–52. doi: 10.4319/lo.2002.47.1.0043

Bates, N. R., Amat, A., and Andersson, A. J. (2010). Feedbacks and responses of coral calcification on the Bermuda reef system to seasonal changes in biological processes and ocean acidification. *Biogeosciences* 7, 2509–2530. doi: 10.5194/bg-7-2509-2010

Bates, N. R., Smauels, L., and Merlivat, L. (2001). Biogeochemical and physical factors influencing seawater fCO_2 and air-sea CO_2 exchange on the Bermuda coral reef. *Limnol. Oceanogr.* 46, 833–846. doi: 10.4319/lo.2001.46.4.0833

Brown, B. E. (1997). Coral bleaching: causes and consequences. *Coral Reefs.* 16(Suppl.), S129–S138. doi: 10.1007/s003380050249

Brown, J. H., Gillooly, J. F., Allen, A. P., Savage, V. M., and West, G. B. (2004). Toward a metabolic theory of ecology. *Ecology* 85, 1771–1789. doi: 10.1890/03-9000

Bruno, J. F., and Selig, E. R. (2007). Regional decline of coral cover in the Indo-Pacific: timing, extent, and subregional comparisons. *PLoS ONE* 2:e711. doi: 10.1371/journal.pone.0000711

Bruno, J. F., and Valdivia, A. (2016). Coral reef degradation is not correlated with local human population density. *Sci. Rep.* 6:29778. doi: 10.1038/srep29778

Buddemeier, R. W., Jokiel, P. L., Zimmerman, K. M., Lane, D. R., Carey, J. M., Bohling, G. C., et al. (2008). A modeling tool to evaluate regional coral reef responses to changes in climate and ocean chemistry. *Limnol. Oceanogr. Methods.* 6, 395–411. doi: 10.4319/lom.2008.6.395

Chen, P. Y., Chen, C.-C., Chu, L., and McCarl, B. (2015). Evaluating the economic damage of climate change on global coral reefs. *Global Environ. Change.* 30, 12–20. doi: 10.1016/j.gloenvcha.2014.10.011

Cohen, I., Dubinsky, Z., and Erez, J. (2016). Light enhanced calcification in hermatypic corals: new insights from light spectral responses. *Front. Mar. Sci.* 2:122. doi: 10.3389/fmars.2015.00122

Coles, S. L., and Jokiel, P. L. (1977). Effects of temperature on photosynthesis and respiration in hermatypic corals. *Mar. Biol.* 43, 209–216. doi: 10.1007/BF00402313

Comeau, S., Edmunds, P. J., Spindel, N. B., and Carpenter, R. C. (2013). The responses of eight coral reef calcifiers to increasing CO_2 do no exhibit a tipping point. *Limnol. Oceanogr.* 58, 388–398. doi: 10.4319/lo.2013.58.1.0388

Costanza, R., de Groot, R., Sutton, P., van der Ploeg, S., Anderson, S. J., Kubiszewski, I., et al. (2014). Changes in the global value of ecosystem services. *Glob. Environ. Change* 26, 152–158. doi: 10.1016/j.gloenvcha.2014.04.002

Courtney, T. A., Andersson, A. J., Bates, N. R., Collins, A., Cyronak, T., de Putron, S. J., et al. (2016). Comparing chemistry and census-based estimates of net ecosystem calcification on a rim reef in Bermuda. *Front. Mar. Sci.* 3:181. doi: 10.3389/fmars.2016.00181

Crawley, A., Kline, D. I., Dunn, S., Anthony, K. R. N., and Dove, S. (2010). The effect of ocean acidification on symbiont photorespiration and productivity in *Acropora formosa*. *Glob. Chang. Biol.* 16, 851–863. doi: 10.1111/j.1365-2486.2009.01943.x

Cyronak, T., Santos, I. R., Erler, D. V., and Eyre, B. D. (2013). Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands). *Biogeosciences* 10, 2467–2480. doi: 10.5194/bg-10-2467-2013

De'ath, G., Fabricius, K. E., Sweatman, H., and Puotinen, M. (2012). The 27-year decline of coral cover on the Great Barrier Reef and its causes. *Proc. Natl. Acad. Sci. U.S.A.* 109, 17995–17999. doi: 10.1073/pnas.1208909109

Deffeyes, K. S. (1965). Carbonate equilibria: a graphic and algebraic approach. *Limnol. Oceanogr.* 10, 412–426. doi: 10.4319/lo.1965.10.3.0412

de Groot, R., Brander, L., van der Ploeg, S., Costanza, R., Bernard, F., Braat, L., et al. (2012). Global estimates of the value of ecosystems and their services in monetary units. *Ecosyst. Serv.* 1, 50–61. doi: 10.1016/j.ecoser.2012.07.005

Dennison, W. C., and Barnes, D. J. (1988). Effect of water motion on coral photosynthesis and calcification. *J. Exp. Mar. Biol. Ecol.* 115, 67–77. doi: 10.1016/0022-0981(88)90190-6

Dickson, A. G., and Millero, F. J. (1987). A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep Sea Res. Part I Oceanogr. Res Pap.* 34, 1733–1743. doi: 10.1016/0198-0149(87)90021-5

Dickson, A. G., Sabine, C. L., and Christian, J. R. (2007). Guide to best practices for ocean CO_2 measurements. *PICES Special Publication* 3, 191.

Drupp, P., De Carlo, E. H., Mackenzie, F. T., Bienfang, P., and Sabine, C. (2011). Nutrient inputs, phytoplankton response and CO_2 variations in a semi-enclosed subtropical embayment, Kaneohe Bay, Hawaii. *Aquatic Geochem.* 17, 473–498. doi: 10.1007/s10498-010-9115-y

Drupp, P. S., De Carlo, E. H., Mackenzie, F. T., and Sabine, C. L. (2013). A comparison of CO_2 dynamics and air-sea exchange in differing tropical reef environments. *Aquatic Geochem.* 19, 371–397. doi: 10.1007/s10498-013-9214-7

Edmunds, P. J., Comeau, S., Lantz, C., Andersson, A., Briggs, C., Cohen, A., et al. (2016). Integrating the effects of ocean acidification across functional scales on tropical coral reefs. *Bioscience.* 66, 350–362. doi: 10.1093/biosci/biw023

Enochs, I. C., Manzello, D. P., Kolodziej, G., Noonan, S. H. C., Vlentino, L., and Fabricius, K. E. (2016). Enhanced macroboring and depressed calcification drive net dissolution at high-CO_2 coral reefs. *Proc Royal Soc B.* 283:20161742. doi: 10.1098/rspb.2016.1742

Evensen, N. R., and Edmunds, P. J. (2016). Interactive effects of ocean acidification and neighboring corals on the growth of *Pocillopora verrucosa*. *Mar. Biol.* 163:148. doi: 10.1007/s00227-016-2921-z

Eyre, B. D., Andersson, A. J., and Cyronak, T. (2014). Benthic coral reef calcium carbonate dissolution in an acidifying ocean. *Nat. Clim. Chang.* 4, 969–976. doi: 10.1038/nclimate2380

Fagan, K. E., and Mackenzie, F. T. (2007). Air-sea CO_2 exchange in a subtropical estuarine-coral reef ecosystem, Kaneohe Bay, Oahu, Hawaii. *Mar. Chem.* 106, 174–191. doi: 10.1016/j.marchem.2007.01.016

Falter, J. L., Lowe, R. J., Zhang, Z., and McCulloch, M. (2013). Physical and biological controls on the carbonate chemistry of coral reef waters: effects of metabolism, wave forcing, sea level, and geomorphology. *PLoS ONE* 8:e53303. doi: 10.1371/journal.pone.0053303

Ferrier-Pagès, C., Witting, J., Tambutté, E., and Sebens, K. P. (2003). Effect of natural zooplankton feeding on the tissue and skeletal growth of the scleractinian coral *Stylophora pistillata*. *Coral Reefs.* 22, 229–240. doi: 10.1007/s00338-003-0312-7

Gardner, T. A., Côté, I. M., Gill, J. A., Grant, A., and Watkinson, A. R. (2003). Long-term region-wide declines in Caribbean corals. *Science* 301, 958–960. doi: 10.1126/science.1086050

Gattuso, J.-P., Frankignoulle, M., and Smith, S. V. (1999). Measurement of community metabolism and significance in the coral reef CO_2 source-sink debate. *Proc. Natl. Acad. Sci. U.S.A.* 96, 13017–13022. doi: 10.1073/pnas.96.23.13017

Glynn, P. W. (1993). Coral reef bleaching: ecological perspectives. *Coral Reefs.* 12, 1–17. doi: 10.1007/BF00303779

Harvell, D. D., Kim, K., Burkholder, J. M., Colwell, R. R., Epstein, P. R., Grimes, D. J., et al. (1999). Emerging marine diseases – climate links and anthropogenic factors. *Science* 285, 1505–1510. doi: 10.1126/science.285.5433.1505

Hearn, C., Atkinson, M., and Falter, J. (2001). A physical derivation of nutrient-uptake rates in coral reefs: effects of roughness and waves. *Coral Reefs.* 20, 347–356. doi: 10.1007/s00338-001-0185-6

Hoegh-Guldberg, O. (1999). Climate change, coral bleaching and the future of the world's coral reefs. *Mar. Freshwater Res.* 50, 839–866. doi: 10.1071/MF99078

Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., et al. (2007). Coral reefs under rapid climate change and ocean acidification. *Science* 318, 1737–1742. doi: 10.1126/science.1152509

Hofmann, G. E., Smith, J. E., Johnson, K. S., Send, U., Levin, L. A., Micheli, F., et al. (2011). High-frequency dynamics of ocean pH: a multi-ecosystem comparison. *PLoS ONE* 6:e28983. doi: 10.1371/journal.pone.0028983

Holcomb, M., McCorkle, D. C., and Cohen, A. L. (2010). Long-term effects of nutrient and CO_2 enrichment on the temperate coral *Astrangia poculata* (Ellis and Solander, 1786). *J. Exp. Mar. Biol. Ecol.* 386, 27–33. doi: 10.1016/j.jembe.2010.02.007

Horvath, K. M., Castillo, K. D., Armstrong, P., Westfield, I. T., Courtney, T., and Ries, J. B. (2016). Next-century ocean acidification and warming both reduce calcification rate, but only acidification alters skeletal morphology of reef-building coral *Siderastrea sidereal*. *Sci. Rep.* 6:29613. doi: 10.1038/srep29613

Hughes, T. P., Rodrigues, M. J., Bellwood, D. R., Ceccarelli, D., Hoegh-Guldberg, O., McCook, L., et al. (2007). Phase shifts, herbivory, and the resilience of coral reefs to climate change. *Curr. Biol.* 17, 360–365. doi: 10.1016/j.cub.2006.12.049

Jokiel, P. L., and Coles, S. L. (1990). Response of Hawaiian and other Indo-Pacific reef corals to elevated temperature. *Coral Reefs.* 8, 155–162. doi: 10.1007/BF00265006

Jokiel, P. L., Jury, C. P., and Rodgers, K. S. (2014). Coral-algae metabolism and diurnal changes in the CO_2-carbonate system of bulk seawater. *PeerJ.* 2:e378. doi: 10.7717/peerj.378

Jokiel, P. L., Rodgers, K. S., Brown, E. K., Kenyon, J. C., Aeby, G., Smith, W. R., et al. (2015). Comparison of methods used to estimate coral cover in the Hawaiian Islands. *PeerJ.* 3:e954. doi: 10.7717/peerj.954

Jones, R. J. (2006). "Bermuda Institute of Ocean Sciences (BIOS)," in *Marine Environmental Program (MEP) Annual report (2006–2007), submitted to the Bermuda Government Department of Environmental Protection, Ministry of the Environment* (Hamilton), 79.

Jury, C. P., Thomas, F. I. M., Atkinson, M. J., and Toonen, R. J. (2013). Buffer capacity, ecosystem feedbacks, and seawater chemistry under global change. *Water* 5, 1303–1325. doi: 10.3390/w5031303

Kawahata, H., Yukino, I., and Suzuki, A. (2000). Terrestrial influences on the Shiraho fringing reef, Ishigaki Island, Japan: high carbon input relative to phosphate. *Coral Reefs* 19, 172–178. doi: 10.1007/s003380000093

Kayanne, H., Hata, H., Kudo, S., Yamano, H., Watanabe, A., Ikeda, Y., et al. (2005). Seasonal and bleaching-induced changes in coral reef metabolism and CO_2 flux. *Glob. Biogeochem. Cycles.* 19:GB3015. doi: 10.1029/2004GB002400

Kleypas, J. A., Anthony, K. R. N., and Gattuso, J.-P. (2011). Coral reefs modify their seawater carbon chemistry – case study from a barrier reef (Moorea, French Polynesia). *Glob. Chang. Biol.* 17, 3667–3678. doi: 10.1111/j.1365-2486.2011.02530.x

Kleypas, J. A., and Yates, K. K. (2009). Coral reefs and ocean acidification. *Oceanography* 22, 108–117. doi: 10.5670/oceanog.2009.101

Koop, K., Booth, D., Broadbent, A., Brodie, J., Bucher, D., Capone, D., et al. (2001). ENCORE: the effect of nutrient enrichment on coral reefs: synthesis of results and conclusions. *Mar. Pollut. Bull.* 42, 91–120. doi: 10.1016/S0025-326X(00)00181-8

Langdon, C., and Atkinson, M. J. (2005). Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal changes in

temperature/irradiance and nutrient enrichment. *J. Geophys. Res. Oceans.* 110:C09S07. doi: 10.1029/2004JC002576

Langdon, C., Gattuso, J.-P., and Andersson, A. (2010). "Measurements of calcification and dissolution of benthic organisms and communities," in *Guide to Best Practices for Ocean Acidification Research and Data Reporting. Luxembourg: Office for Official Publications of the European Union* (Luxembourg), 213–234.

Langdon, C., Takahashi, T., Sweeney, C., Chpman, D., Goddard, J., Marubini, F., et al. (2000). Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Global Biogeochem. Cycles.* 14, 639–654. doi: 10.1029/1999GB001195

Leclerq, N., Gattuso, J.-P., and Jaubert, J. (2000). CO_2 partial pressure controls the calcification rate of a coral reef community. *Glob. Chang. Biol.* 6, 329–334. doi: 10.1046/j.1365-2486.2000.00315.x

Lesser, M. P., Weis, V. M., Patterson, M. R., and Jokiel, P. L. (1994). Effects of morphology and water motion on carbon delivery and productivity in the reef coral, *Pocillopora demicornis* (Linnaeus): diffusion barriers, inorganic carbon limitation, and biochemical plasticity. *J. Exp. Mar. Biol. Ecol.* 178, 153–179. doi: 10.1016/0022-0981(94)90034-5

Lewis, E., and Wallace, D. (1998). *CO2SYS—Program Developed for the CO_2 System Calculations*. Oak Ridge: Carbon Dioxide Information and Analysis Center, Oak Ridge National Laboratory, US Department of Energy.

Lowe, R. J., Falter, J. L., Monismith, S. G., and Atkinson, M. J. (2009). A numerical study of circulation in a coastal reef-lagoon system. *J. Geophys. Res.* 114:C06022. doi: 10.1029/2008JC005081

Manzello, D. P., Enochs, I. C., Bruckner, A., Renaud, P., Kolodziej, G., Budd, D. A., et al. (2014). Galápagos coral reef persistence after ENSO warming across an acidification gradient. *Geophys. Res. Lett.* 41, 9001–9008. doi: 10.1002/2014GL062501

Marshall, A. T., and Clode, P. (2004). Calcification rate and the effect of temperature in a zooxanthellate and an azooxanthellate scleractinian reef coral. *Coral Reefs.* 23, 218–224. doi: 10.1007/s00338-004-0369-y

Marubini, F., Ferrier-Pagès, C., and Cuif, J.-P. (2003). Suppression of skeletal growth in scleractinion corals by decreasing ambient carbonate-ion concentration: a cross-family comparison. *Proc. Soc. R. B.* 270, 79–184. doi: 10.1098/rspb.2002.2212

Massaro, R. F. S., De Carlo, E. H., Drupp, P., Mackenzie, F. T., Maenner-Jones, S., Fagan, K. E., et al. (2012). Multiple factors driving variability in the exchange of CO_2 between the ocean and atmosphere in a tropical coral reef environment. *Aquatic Geochem.* 18, 357–386. doi: 10.1007/s10498-012-9170-7

Mehrbach, C., Culberson, C. H., Hawley, J. E., and Pytkowicx, R. M. (1973). Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* 18, 897–907. doi: 10.4319/lo.1973.18.6.0897

Moberg, F., and Folke, C. (1999). Ecological goods and services of coral reef ecosystems. *Ecol. Econ.* 29, 215–233. doi: 10.1016/S0921-8009(99)00009-9

Mumby, P. J., and van Woesik, R. (2014). Consequences of ecological, evolutionary and biogeochemical uncertainty for coral reef responses to climatic stress. *Curr. Biol.* 24, R413–R423. doi: 10.1016/j.cub.2014.04.029

Ohde, S., and Hossain, M. M. M. (2004). Effect of $CaCO_3$ (aragonite) saturation state of seawater on calcification of *Porites* coral. *Geochem. J.* 38, 613–621. doi: 10.2343/geochemj.38.613

Page, H. N., Andersson, A. J., Jokiel, P. L., Rodgers, K. S., Lebrato, M., Yeakel, K., et al. (2016). Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral Reefs.* 35, 1311–1325. doi: 10.1007/s00338-016-1490-4

R Development Core Team (2008). R: *A Language and Environment for Statistical Computing*. Vienna: R Foundation for Statistical Computing. Available online at: http://www.R-project.org

Rinkevich, B., and Loya, Y. (1985). Intraspecific competition in a reef coral: effects on growth and reproduction. *Oecologia* 66, 100–105. doi: 10.1007/BF00378559

Rodgers, K. S., Jokiel, P. L., Brown, E. K., Hau, S., and Sparks, R. (2015). Over a decade of change in spatial and temporal dynamics of Hawaiian coral reef communities. *Pac. Sci.* 69, 1–13. doi: 10.2984/69.1.1

Shashar, N., Kinane, S., Jokiel, P. L., and Patterson, M. R. (1996). Hydromechanical boundary layers over a coral reef. *J. Exp. Mar. Biol. Ecol.* 199, 17–28. doi: 10.1016/0022-0981(95)00156-5

Shaw, E. C., Hamylton, S. M., and Phinn, S. R. (2016). Incorporating benthic community changes into hydrochemical-based projections of coral reef calcium carbonate production under ocean acidification. *Coral Reefs.* 35, 739–750. doi: 10.1007/s00338-016-1407-2

Shaw, E. C., McNeil, B. I., and Tilbrook, B. (2012). Impacts of ocean acidification in naturally variable coral reef flat ecosystems. *J. Geophys. Res. Oceans.* 117:C03038. doi: 10.1029/2011JC007655

Silverman, J., Lazar, B., Cao, L., Caldeira, K., and Erez, J. (2009). Coral reefs may start dissolving when atmospheric CO_2 doubles. *Geophys. Res. Lett.* 36:L05606. doi: 10.1029/2008GL036282

Smith, J. E., Price, N. N., Nelson, C. E., and Haas, A. F. (2013). Coupled changes in oxygen concentration and pH caused by metabolism of benthic coral reef organisms. *Mar Biol.* 160, 2437–2447. doi: 10.1007/s00227-013-2239-z

Smith, S. V., Jokiel, P. L., Key, G. S., and Guinther, E. B. (1977). *Metablic Responses of Shallow Tropical Benthic Microcosm Communities to Perturbation*. Environmental Protection Agency, Narragansett, Rhode Island. Final report of contract R800906. 110 pp.

Sutton, A. J., Sabine, C. L., Maenner-Jones, S., Lawrence-Slavas, N., Meinig, C., Feely, R. A., et al. (2014). A high-frequency atmospheric and seawater pCO_2 data set from 14 open-ocean sites using a moored autonomous system. *Earth Syst. Sci. Data* 6, 353–366. doi: 10.5194/essd-6-353-2014

Suzuki, A., and Kawahata, H. (2003). Carbon budget of coral reef systems: an overview of observations in fringing reefs, barrier reefs and atolls in the Indo-Pacific regions. *Tellus B.* 55, 428–444. doi: 10.1034/j.1600-0889.2003.01442.x

Szmant, A. M. (2002). Nutrient enrichment on coral reefs: is it a major cause of coral reef decline? *Estuaries* 25, 743–766. doi: 10.1007/bf02804903

Tanner, J. E. (1995). Competition between scleractinian corals and macroalgae: an experimental investigation of coral growth, survival and reproduction. *J. Exp. Mar. Biol. Ecol.* 190, 151–168. doi: 10.1016/0022-0981(95)00027-O

Tanner, J. E. (1997). Intraspecific competition reduces fitness in scleractinian corals. *J. Exp. Mar. Biol. Ecol.* 214, 19–34. doi: 10.1016/S0022-0981(97)00024-5

Valiela, I. (1984). *Marine Ecological Processes*. New York, NY: Springer.

Vandermeulen, J. H., Davis, N. D., and Muscatine, L. (1972). The effect of inhibitors of photosynthesis on zooxanthellae in corals and other marine invertebrates. *Mar Biol.* 16, 185–191.

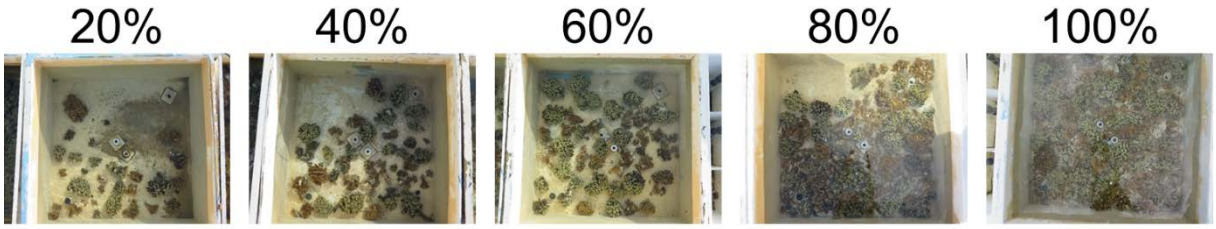
Venti, A., Kadko, D., Andersson, A. J., Langdon, C., and Bates, N. R. (2012). A multi-tracer model approach to estimate reef water residence times. *Limnol. Oceanogr. Methods.* 10, 1078–1095. doi: 10.4319/lom.2012.10.1078

Watanabe, A., Kayanne, H., Hata, H., Kudo, S., Nozaki, K., Kato, K., et al. (2006). Analysis of the seawater CO_2 system of Palau using total alkalinity-dissolved inorganic carbon diagrams. *Limnol. Oceanogr.* 51, 1614–1628. doi: 10.4319/lo.2006.51.4.1614

Wilkinson, C. (ed.). (2008). "Status of coral reefs of the world: 2008," in *Global Coral Reef Monitoring Network and Reef and Rainforest Research Centre* (Townsville: Global Coral Reef Monitoring Network and Reef and Rainforest Research Centre), 296.

Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2017 Page, Courtney, Collins, De Carlo and Andersson. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) or licensor are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.



Supplementary Material. The coral communities in the mesocosms during Hawaii 2016 experiments. The treatments represent a range of coral densities presented as coral cover.

Acknowledgments

Chapter 3, in full, is a reprint of the material as it appears in **Page, HN**, Courtney, TA, Collins, A, De Carlo, EH, & Andersson, AJ. (2017). Net community metabolism and seawater carbonate chemistry scale non-intuitively with coral cover. *Frontiers in Marine Science* 4:161. doi: 10.3389/fmars.2017.00161. The dissertation author was the primary investigator and author of this paper.

CHAPTER 4

Spatio-temporal variability in seawater carbon chemistry for a coral reef flat in Kaneohe Bay, Hawaii

Heather N. Page, Travis A. Courtney, Eric H. De Carlo, Noah Howins, Irina Koester, and Andreas J. Andersson

Abstract

The persistence of coral reef community composition and ecosystem function may be threatened by anthropogenic ocean acidification. However, the magnitude of effects of ocean acidification on coral reefs will be compounded by natural spatial and temporal variability in seawater CO_2 chemistry. The ecological, biogeochemical, and physical drivers of this natural variability must be understood before predicting how reefs may fare in a changing ocean. We measured temporal and spatial variability on a reef flat in Kaneohe Bay, Oahu, Hawaii by placing autonomous instruments recording high-frequency temporal variability at site with contrasting benthic communities on the reef flat and sampling surface seawater chemistry across a large area of the reef flat at different times of the day during two seasons. Mean and diurnal variability of seawater chemistry most closely follows depth gradients on the reef with shallower sites typically experiencing the highest variability and mean temperature, pH, and Ω_a during the day. This result highlights the relative importance of seawater volume to benthic biomass ratio for controlling seawater conditions on the reef. Community composition, particularly coral cover, and hydrodynamics, seawater circulation and residence time, also influences the spatial and temporal variability on this reef flat. Therefore, comprehending ecosystem responses to future anthropogenic changes in seawater CO_2 chemistry requires consideration of the natural complexity of ecosystems where a combination of factors that often co-vary may influence chemical conditions and biogeochemistry of coral reefs.

Introduction

The increase in anthropogenic carbon dioxide (CO_2) in the atmosphere since pre-Industrial time has resulted in a range of environmental changes including warming of the

troposphere and the upper ocean and increasing concentrations of dissolved CO_2 and hydrogen ions [H^+] (i.e., lower pH) in the surface ocean (Soloman et al. 2009; IPCC 2013; Bates et al. 2014). These changes in seawater CO_2-chemistry result in a decrease in carbonate ions [CO_3^{2-}] and the saturation state (Ω) with respect to calcium carbonate ($CaCO_3$) minerals (e.g., aragonite and calcite; $\Omega=[Ca^{2+}][CO_3^{2-}]/K_{sp}^*$ where K_{sp}^* is the ion concentration solubility product at equilibrium). Collectively these changes have been referred to as ocean acidification (OA). Ongoing OA has raised concerns about the potential impacts on marine calcifiers because their ability to secrete calcareous shells or skeletons partly depends on seawater pH and Ω (Kleypas et al. 2006; Doney et al. 2009). Coral reefs are thought to be particularly vulnerable to OA because of experimental results under high CO_2 conditions showing: 1) decreased rates of calcification of corals and calcifying algae (Chan and Connolly 2012; Comeau et al. 2013; Johnson et al. 2014), 2) increased rates of carbonate dissolution and bioerosion (Andersson et al., 2009; Wisshak et al., 2012; Eyre et al. 2014), and 3) increased growth and competitive strength of fleshy macroalgae (McCook et al. 2001; Diaz-Pulido et al. 2011; Johnson et al. 2014). Combined with the effects of other environmental perturbations (e.g., warming, eutrophication, sedimentation, overfishing), these changes may scale up to ecosystem-wide impacts on coral reefs, resulting in shifts from net calcification and accretion towards net $CaCO_3$ dissolution and erosion (Silverman et al. 2009; Andersson and Gledhill 2013; Eyre et al. 2014), and shifts towards reefs dominated by fleshy macroalgae (Jokiel et al. 2008; Kroeker et al. 2013). However, the magnitude and timing of these shifts are currently uncertain and vary between different reefs.

To understand future impacts of OA on coral reefs, it is necessary to understand how reef seawater CO_2-chemistry will change. Many predictions of coral reef response to OA are

based on projected acidification in the open ocean rather than on the actual reefs (Silverman et al. 2009; Hoegh-Guldberg et al. 2007; Ricke et al. 2013). However, because of large natural variability owing to high biological activity and high biomass to water volume ratio (i.e., shallow depth), as well as variable flow rates, seawater CO_2-chemistry on coral reefs can be substantially different compared to the open ocean (Hofmann et al. 2011; Andersson and Mackenzie 2012; Drupp et al. 2013; Andersson et al. 2014). Consequently, this large variability may confound the magnitude (Jury et al. 2013; Shaw et al. 2013) and effects of OA on reef organisms and ecosystems (Dufault et al. 2012; Cornwall et al. 2013), and both the mean and/or extreme pH and Ω values may be important in determining these effects (Boyd et al. 2016). Hence, there is a need to understand when and where seawater pH and Ω will reach certain conditions within different coral reef habitats, as well as the specific set of properties and mechanisms leading to these conditions (Falter et al. 2013).

The variability of seawater CO_2-chemistry on coral reefs is influenced by a combination of ecological, biogeochemical, and physical properties and processes (e.g., Bates et al. 2010; Kleypas et al. 2011; Shaw et al. 2012; Falter et al. 2012; Albright et al. 2013; Teneva et al. 2013; Falter et al. 2013; Koweek et al. 2015a, b; Lowe and Falter 2015). The major biogeochemical processes to consider include net community production (NCP=primary production – autotrophic and heterotrophic respiration) and net community calcification (NCC=calcification – $CaCO_3$ dissolution), which affect the seawater dissolved inorganic carbon (DIC) and total alkalinity (TA) balance. NCP mainly affects DIC with positive NCP reducing DIC and increasing pH and Ω while positive NCC results in a reduction of TA and DIC in a ratio of 2:1 leading to a decrease in pH and Ω (Zeebe and Wolf-Gladrow 2001; Andersson and Gledhill 2013). The balance of NCP and NCC contributes to

the overall reef metabolism, which is strongly linked to diurnal and seasonal cycles in light and temperature, but also external input of organic material and nutrients via advection, upwelling, river and runoff, as well as internal waves (Kawahata et al. 2000; Bates et al. 2010; Jantzen et al. 2013; Eidens et al. 2014; van Hoytema et al. 2016). Air-sea CO_2 exchange also influence the reef seawater CO_2-chemistry, but for reefs with seawater residence times of a few hours to several days, this flux is typically minor relative to the influence of NCP and NCC (Frankignoulle et al. 1996; Yeakel et al. 2015).

The degree of influence exerted by different biogeochemical processes on seawater CO_2-chemistry is directly related to the benthic community composition including coral cover and the relative dominance of calcifiers to non-calcifiers (Kleypas et al. 2011; Anthony et al. 2011; Page et al. 2016). Early studies of reef productivity at Eniwetok Atoll noted differences in seawater pH and oxygen depending on the relative abundance of algal turfs (Johannes et al. 1972; Smith 1973), and more recently, flume and mesocosm experiments have quantified how different key benthic functional groups on reefs (e.g., corals, calcifying algae, carbonate sand, macroalgae, and mixed communities) modify seawater CO_2-chemistry differently (Anthony et al. 2011; Anthony et al. 2013; Jokiel et al. 2014; Page et al. 2016). Because of the differential influence of different benthic communities on seawater pH and Ω, it has been proposed that some habitats may be able to alleviate OA while others may exacerbate it (Semesi et al. 2009; Manzello et al. 2012; Kleypas et al. 2011; Anthony et al. 2011; Anthony et al. 2013; Hendricks et al. 2014; Camp et al. 2016; Kwiatkowski et al. 2016).

In addition to the benthic community composition, the geomorphology, depth, ratio of biomass to water volume, flow rates and residence time are important factors that influence the variability of seawater CO_2-chemistry (Falter et al. 2013; Lowe and Falter 2015). Longer

residence time, shallower depth, and higher biomass allow biological processes to modify seawater CO_2-chemistry to a greater extent compared to shorter residence time, deeper depth and lower biomass. However, the absolute changes in pH and Ω are dependent on the relative modification of DIC and TA as the influence of NCP and NCC on these parameters can counteract each other (Andersson and Gledhill 2013; Page et al. 2016, 2017). Previous studies based on coupled hydrodynamic-biogeochemical models parameterized with field data have emphasized the importance of both benthic metabolism and residence time in controlling the temporal and spatial variability in seawater CO_2-chemistry (Zhang et al. 2012; Falter et al. 2013).

Previously, we have conducted a number of mesocosm experiments at the Hawaii Institute of Marine Biology (HIMB) to elucidate how OA may affect coral reef community metabolism and how different benthic communities modify the overlying seawater CO_2-chemistry (Andersson et al. 2009; Jokiel et al. 2014; Page et al. 2016, 2017). Some of our findings suggested that algal dominated areas and nighttime $CaCO_3$ dissolution could partially counteract reductions in pH at the local scale (Page et al. 2016) whereas communities with high coral cover experienced the lowest daily seawater pH, which was exacerbated at night due to the combined influence of negative NCP and positive NCC (Page et al. 2017). Although these mesocosm studies identify key relationships between community composition, benthic metabolism, and seawater CO_2-chemistry under controlled laboratory conditions, there is a need to bridge these results across natural functional, spatial, and temporal scales (Andersson et al. 2015; Edmunds et al. 2016). This requires comparison of experimental results with observations from the field to ascertain whether observed relationships hold true and can be extrapolated to the natural environment.

In this study, we built on the previous mesocosm experiments conducted at HIMB (Andersson et al. 2009; Page et al. 2016, 2017) to evaluate the spatio-temporal variations in seawater CO_2-chemistry for a reef flat in Kaneohe Bay, Oahu, Hawaii (Fagan and Mackenzie 2007; Shamberger et al. 2011; Massaro et al. 2012; Drupp et al. 2013; Courtney et al. 2017). Our overarching research objectives were to better understand the natural temporal and spatial variabilities in seawater CO_2-chemistry for this reef flat, how these variabilities relate to ecological (e.g., community composition), biogeochemical (NCP vs. NCC), and physical (e.g., depth and flow rates) properties, and relative importance of these drivers. Resolving these relationships will allow for a better understanding of natural variability of CO_2-chemistry on coral reefs, identification of reef areas that are more or less vulnerable to OA, and better parameterization of regional models aimed at forecasting local and regional coral reef seawater CO_2-chemistry under changing ecological (Gardner et al. 2003; Wilkinson et al. 2008; Bruno and Valvidia 2016), and biogeochemical conditions.

Methods

Temporal and spatial variability in seawater carbon biogeochemistry was sampled over a barrier reef in Kaneohe Bay, Hawaii (Figure 4.1) during June and November. Kaneohe Bay, which is located on the northeastern (windward) coast of Oahu, encompasses an area of 13 km (alongshore) by 4 km (cross-shore). The bay contains a characteristic reef crest, reef flat, sand flat, and lagoon that includes more than 60 patch reefs scattered throughout. The shallow reef platform contains a variety of benthic communities that are dominated by rubble, coral, or sand; much of the reef flat is classified as a “mixed community” with two or more of these functional groups equally present. The rubble community mainly consists of coral

skeletons overgrown by a variety of benthic algae (CCA, *Halimeda* spp., and turf algae) with few coral colonies scattered throughout.

Temporal variability was measured by deploying autonomous instruments on the benthos while surface seawater chemistry was sampled via spatial surveys. In June, one transect of instruments across the reef platform (Figure 4.1; Stations 1-3) measured seawater conditions for 15 days. The spatial surveys (n=4) covered the southeastern portion of the reef flat and included the reef crest and sand flat as well. In November, instruments were deployed along an additional transect that was perpendicular to the original transect (Figure 4.1; Stations 4-5) in order to capture any spatial gradients along the reef flat. The instruments were deployed for a shorter period of time (9 days) but more spatial surveys of surface seawater chemistry were conducted (n=6). See Table 4.1 for a summary of the sampling effort for each month.

Autonomous sampling of seawater carbon biogeochemistry

Instruments were deployed at five stations on the reef flat to measure short-term variability in seawater temperature, salinity, pH, dissolved oxygen (DO), and light. Each of the stations consisted of different benthic community compositions and seawater depths (Table 4.1). In June, Stations 1-3 were sampled every 30 min for ~15 days. Station 1, which was located over rubble closest to the reef crest, contained a SeapHOx (Bresnahan et al. 2014) that measured seawater pH, DO, temperature, and salinity. Station 2, located at the midpoint of the transect which had a mixed community of rubble and coral, had a Seafet (pH) and Aquadopp High Resolution Current Profiler (Nortek Instruments). Three instruments were deployed between large coral colonies at Station 3: SeapHOx, Aquadopp Low Resolution

Current Profiler (Nortek Instruments), and an ECO-PAR (photosynthetically active radiation) sensor (Wetlabs, Seabird Scientific).

During November, temporal variability was measured at five stations that formed two transects that were intended to capture gradients across and along the reef flat. Station 1 contained a SeapHOx and Aquadopp Low Resolution Current Profiler. A seafet and Aquadopp High Resolution Current Profiler were deployed at Station 2. Station 2 also had a Seabird SBE 16plus V2 SeaCAT recorder (temperature and salinity) equipped with an oxygen optode (Aandera Oxygen Sensor 3835). Station 3 consisted of a SeapHOx and ECO-PAR sensor. At Station 4, the benthic community contained mostly coral and sand. We deployed a Seabird SBE 16plus V2 SeaCAT recorder equipped with a second oxygen optode (Aandera Oxygen Sensor 3835) at this station. Station 5 was also a mixed community of rubble and sand; a third Seabird SBE 16plus V2 SeaCAT recorder was deployed here.

Data from the instruments deployed on the reef were calibrated to *in situ* conditions measured after a two-day acclimation period during one of the autonomous sampling times. Temperature was calibrated to measurements taken using a YSI Professional Plus multi-meter probe (Texas Instruments, Inc.) when the offset (Instrument Value – YSI Value) was greater than the error of the YSI measurement (±0.2°C), assuming a constant offset through time; this calibration was applied to temperature measured at Station 5. The DO values are reported relative to mean conditions at each station (ΔDO) since no calibration samples were available. Seawater samples were taken near the intake valve of the SeapHOxes and Seafets for later analysis of DIC and TA (see below for sampling protocol). Seawater pH was calculated from *in situ* temperature, salinity, pressure, DIC, and TA using CO2sys (Lewis and Wallace 1998). The total pH scale (pH_T) was used as well as K1 and K2 dissociation constants from

Mehrbach et al. (1973) as refit by Dickson and Millero (1987). Additional calibration samples taken throughout the sampling periods confirmed that there was no drift in the instruments over time.

Temporal variations in additional environmental conditions were assessed from publically available data from NOAA. Water level (Mean Lower Low Water, MLLW) was measured at Mokuoloe, HI by the NOAA Tides and Currents program. Hourly wind speed and direction data for Station MOKH1 (Mokuoloe, HI) were downloaded from the NOAA National Buoy Data Center (http://www.ndbc.noaa.gov/station_history.php?station=mokh1).

Spatial sampling of surface seawater carbon chemistry

Seawater chemistry was measured via boat over a spatial grid covering ~1.45 km by ~1.25 km area of the reef in Kaneohe Bay (Figure 4.1) during different times of the day (divided into morning and afternoon) to capture spatial variability throughout the diurnal period. This spatial area was selected to encompass a variety of benthic habitats including the reef crest, reef flat (mostly rubble), backreef, and carbonate sand flat. Each spatial survey took approximately 60-90 min which is smaller than the residence time that ranges of the order of <1 day to a few days (Lowe et al. 2009).

At each sampling location, *in situ* temperature (±0.2°C), salinity (±1%), and DO (±0.2 mg L^{-1}) approximately 0.25 m below the sea surface were measured using an YSI Professional Plus multi-parameter probe (Texas Instruments, Inc.). Once again, ΔDO is reported relative to mean conditions for each spatial survey in order to assess the relative changes over space. In addition, seawater from each site was collected into 250 mL Pyrex glass bottles and immediately poisoned with a saturated solution of mercuric chloride ($HgCl_2$)

to halt any biological activity in the sample. These samples were shipped to Scripps Institution of Oceanography where they were analyzed for DIC and TA using an Automated Infrared Inorganic Carbon Analyzer (AIRICA, Marianda Inc.) equipped with a Li-cor 7000 CO_2/H_2O gas analyzer and open-cell potentiometric acid titrations, respectively, according to standard protocols for seawater CO_2 measurements (Dickson et al. 2007).

The accuracy and precision of the DIC and TA instruments were checked periodically using certified reference material from the Dickson Laboratory (Scripps Institution of Oceanography). Accuracy was calculated as the average (±1 std) offset from certified values of DIC and TA. During June, DIC had an accuracy (n=25) of -0.55±2.05 μmol kg^{-1} and TA had an accuracy (n=10) of -1.77±1.45 μmol kg^{-1}. During November, the accuracy of DIC (n=72) and TA (n=24) were -1.84±1.73 and -0.35±2.41 μmol kg^{-1}, respectively. Data were adjusted for instrument drift when the precision was greater than 3 μmol kg^{-1} by assuming a consistent drift between CRM samples.

Once again, seawater pCO_2, pH, and Ω_a were calculated from *in situ* temperature, salinity, pressure, DIC, and TA using CO2sys (Lewis and Wallace 1998). The total pH scale (pH_T) was used as well as K1 and K2 dissociation constants from Mehrbach et al. (1973) as refit by Dickson and Millero (1987).

In order to visualize spatial variability in measured and calculated parameters of seawater chemistry, data were interpolated between sampling sites using a triangulation-based cubic interpolation in Matlab. A graphical analysis of TA and DIC vectors (Deffeyes, 1965; Andersson and Gledhill, 2013) was also performed as an additional method for visualizing seawater chemistry changes on the reef flat due to benthic metabolism (NCC and NCP). Mean DIC and TA (mean ± 1 sd) measured at Station ALOHA as part of the ongoing Hawaii Ocean

Time Series (Karl and Lukas 1996) were included as an "offshore" reference (http://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html). For comparison of regression slopes from Page et al. (2016) which were calculated as the change in TA (ΔTA) and DIC (ΔDIC) relative to control conditions to examine the influence from the benthic communities only, we calculated the ΔTA and ΔDIC relative to the average TA and DIC for the "outer reef" sites which represents the source water for the reef flat. Type II linear regressions, which assume error for both the y and x axes, were fit to TA and DIC data for June and November using the 'lmodel2' package within R v3.3.1 software (R Development Core Team, 2008). The slopes produced by the major axis method are reported.

Results

Temporal variability across space based on autonomous sensors

Seasonal differences in environmental properties such as light and temperature were observed in Kaneohe Bay between June and November, but some other properties appeared similar. During both months, the bay experienced dominant northeasterly trade winds and the amplitude of the mixed semi-diurnal tides was less than 1.00 m (Figure 4.2). Salinity fluctuated between 34.7 and 35.1, but was typically similar between stations (data not shown). Current speeds under 0.3 m/s were recorded during both months (Figure 4.3). In June, seawater dominantly flowed towards the southwest at Stations 2 and 3, with slightly higher flow rates at Station 2 which is deeper. During November, currents at Station 1 were recorded flowing to the southeast. Drifters that were tracked over the reef (see Figure 4.1) also turned towards the southeast around this site, owing to shoaling. At Station 2, currents mostly flowed southwest as measured in June.

During both June and November, seawater temperature, pH, and DO closely followed light levels with higher values during the day and lower values at night (Figure 4.2). On June 24, the concrete block that held the PAR sensor tipped over, but it was placed upright again on June 29. Excluding these data because the sensor did not receive full light due to its displacement, maximum light levels reached 1600 μmol photons m^{-2} s^{-1} in June. In contrast, maximum PAR levels reached 400-1200 μmol photons m^{-2} s^{-1} in November with higher irradiance during the last few days of sampling. Mean seawater temperature was slightly higher in June compared to November (26.5±0.6 vs. 26.0±0.5 °C). In June, Station 3, which was the innermost station, had higher maximum and lower minimum temperatures during 6 out of the 12 days sampled compared to Station 2. This was also observed during November, but most noticeable was the higher daytime temperatures observed at Station 5, which was the shallowest station (not sampled in June).

Each station experienced higher seawater pH during the day and lower pH at night. In June, Station 1 had seawater pH of 8.01 ± 0.04 (mean ± sd) over the 12-day time period. This station was located closest to the outer reef and had a benthic community dominated by rubble. Station 2, which was also covered in rubble with few scattered coral colonies (mixed community), experienced similar mean pH but higher variability (8.01 ± 0.06). Finally, the innermost station located in an active coral reef community (Station 3) had the lowest mean and highest variability in seawater pH of 7.98 ± 0.07. The lower overall mean can be attributed to this station typically having the lowest seawater pH during night. During November, mean seawater pH was similar across all stations, but Station 1 experienced lower variability compared to the mixed community (Station 2) and the coral community sites (Station 3); Station 1 had seawater pH of 8.02 ± 0.04 while Stations 2 and 3 had seawater pH

of 8.01 ± 0.07. During the last three days of sampling, daytime maximum seawater pH increased as water flowed from the outermost station (Station 1) to the innermost coral-dominated station (Station 3).

Dissolved oxygen also was higher during the day and lower at night as observed for seawater pH. In June, one of the oxygen sensors on a SeapHOx failed, so only data for the coral community at Station 3 are reported; this station experienced relatively consistent variability throughout the study period. Dissolved oxygen was as low as 100 μmol kg^{-1} below mean conditions at night and then increased to ~150 μmol kg^{-1} above mean conditions by midday when light levels were the highest. During November, the diel variability was smaller with lower daytime elevation of DO and higher nighttime depression of DO. In general, less variability in DO between stations was observed at night compared to day.

Spatial variability across time based on surveys and sampling by boat

There were distinct spatial gradients in measured (T, ΔDO, DIC, TA) and calculated (pCO_2, pH, Ω_a) parameters of seawater chemistry across the reef flat (Figures 4.4-4.7) although the magnitude of spatial gradients varied between surveys. In general, these gradients appeared to reflect a combination of depth (Figure 4.8) and the integrated influence of biogeochemical processes on seawater properties.

a. June

In general, seawater temperature was lower in the morning relative to the afternoon. The shallower sandy stations to the west were warmer than the other stations in the sampling area. Dissolved oxygen generally followed the same pattern as temperature while DIC mirrored the oxygen distribution. DIC was ~30 μmol kg^{-1} lower in the afternoon compared to

the morning surveys. TA was relatively similar across surveys regardless of the time of day, but there was always a drawdown of TA from the outermost to the innermost stations with the lowest TA observed at the coral community station (Station 3) (Figure 4.9). Seawater pCO_2 was higher in the morning compared to the afternoon while pH and Ω_a had the opposite trends. There was a pattern of increasing pCO_2 and decreasing pH and Ω_a from northwest to southeast during most of the surveys, particularly in the afternoon (Figure 4.5).

b. November

Similar to June, seawater temperature was generally higher in the afternoon compared to the morning. The shallowest stations over the sand flat experienced the coolest temperatures during the morning and warmest temperatures in the afternoon, leading to a spatial gradient from southwest to northeast. DO had smaller spatial gradients in November compared to June. The highest DIC values were observed during the November morning surveys, which were conducted just after sunrise. DIC was lower in the afternoon and comparable to June concentrations. During the afternoon, the lowest DIC values were observed over the shallow sand flat, creating a spatial gradient of increasing DIC from southwest to northeast. TA was slightly higher, albeit with smaller gradients in November compared to June with the largest TA drawdown over the coral community station during the afternoon (Figure 4.6). As observed in June, seawater pCO_2 was higher in the morning compared to the afternoon while pH and Ω_a had the opposite pattern. The sand flat had the lowest pCO_2 and highest pH and Ω_a during the afternoon (Figure 4.7).

TA-DIC relationships

There was mostly a drawdown of TA and DIC across the reef flat compared to offshore waters measured at Station ALOHA (Figure 4.10), indicating +NCC (net calcification) and +NCP (net organic carbon production). The observed drawdown was greater in June compared to November (Figure 4.10). In general, the lowest TA and DIC values were measured over the coral communities within the study area. The slopes of the TA-DIC regressions were less than 1 for each season indicating that carbon cycling across the reef flat was dominated by organic carbon cycling (NCP) versus inorganic carbon cycling (NCC). Furthermore, the regression slopes differed between seasons with June having a greater slope (0.85) compared to November (0.24), indicating a seasonal shift in net reef metabolism.

Discussion

This study used a combination of field research approaches to better understand temporal and spatial variabilities in seawater CO_2-chemistry for a coral reef flat in Kaneohe Bay, Hawaii. Seasonal differences in light intensity (PAR) and seawater temperature were associated with lower mean and diel variability in DO, higher mean DIC and TA, and higher daytime spatial variability in seawater pH and Ω_a across the reef flat in November compared to June. These differences were most likely due to overall lower rates of NCP and NCC, and a relative shift in favor of organic carbon cycling over inorganic carbon cycling during November (Figure 4.10). In this month, lower PAR most likely depressed photosynthesis of marine autotrophs (Chalker 1981; Comeau et al. 2017) while lower temperatures suppressed metabolic respiration rates (Coles and Jokiel 1977; Gillooly et al. 2001), which is consistent with observations of lower diel variability in DO. In contrast, the shift towards organic carbon

cycling (i.e., lower TA-DIC slope) in November resulted in increasing variability in seawater pH and Ω_a across the reef whereas lower variability in these parameters in June was due to more closely balanced organic and inorganic carbon cycling changing pH and Ω_a along isolines of equal value (Figure 4.10; Andersson and Gledhill 2013). A greater drawdown and lower mean TA during June was consistent with higher rates of NCC owing to higher energy availability fueling calcification from primary production (Muscatine 1990; Davies 1984; Rinkevich 1989; Marubini et al. 2001; LaVelle 1979; de Beer and Larkum 2001), higher temperature increasing metabolic rates (Gillooly et al. 2001; Courtney et al., 2017), and higher light intensity possibly stimulating light sensitive ion pumps involved in the process of calcification (Al-Horani et al. 2003; Cohen et al. 2016). However, these findings contrast previous studies reporting relatively consistent rates of NCC across seasons in mesocosms (Langdon and Atkinson 2005; Page et al. 2016) and field studies in Kaneohe Bay (Shamberger et al. 2011). This discrepancy may partly be due to differences in the scale of studies or the prevalent environmental conditions. The previous studies focused on single communities in mesocosms or a restricted area of the reef while the present study covered a large area with multiple benthic communities. However, it is important to recognize that day-to-day variability can be large in response to environmental conditions and quantifying rates of NCC is associated with large uncertainty, which could mask nuanced differences. From the present study, it was evident that the temporal and spatial variabilities in seawater CO_2-chemistry across the reef flat were due to a combination of factors ranging from environmental conditions (e.g., light and temperature), physical properties (geomorphology and depth), benthic community composition (e.g., coral vs. rubble vs. sand communities), reef metabolism (NCP vs NCC), and seawater hydrodynamics (e.g., seawater flow rates, flow

trajectory, and residence time) as previously highlighted by Falter, Lowe and colleagues (e.g., Falter et al. 2012, 2013; Lowe and Falter 2015 and references therein).

Drivers of temporal and spatial variability across the reef

The daily light cycle was clearly the dominant driver of diel variability of seawater temperature and biogeochemical properties with minor influences from semi-diurnal tidal flow (Figure 4.2), which is consistent with observations from many other shallow coral reef environments (e.g., Hofmann et al. 2011; Guadayol et al. 2014; Koweek et al. 2015a, b; Takeshita et al. 2016). In the present study, day-to-day variations for a given location were likely due to variations in solar irradiance, tidal cycles, wind speed as well as swell size and direction, properties that influence the rates of reef metabolism (i.e., NCC and NCP), the timing of low and high tides, and/or the water circulation on the reef (Falter et al. 2013; Lowe and Falter 2015). The circulation of the reef flat in Kaneohe Bay is mainly driven by breaking waves and the associated wave setup at the reef crest, which drives shoreward water flow over the reef flat with modifications from geomorphology and depth gradients (Lowe et al. 2009; Falter et al. 2013; Lowe and Falter 2015). Some general trends emerged from the different measurement approaches that provide insight to the influence of different factors such as community composition, depth gradients, and hydrodynamics on the Kaneohe Bay reef flat CO_2-chemistry.

Benthic community composition

Based on the spatial measurements in June, there appeared to be qualitatively small differences in mean DIC and TA between the outer reef, rubble and mixed communities whereas the coral community had qualitatively lower mean DIC and TA, and also exhibited

greater variability (Figure 4.9). During June, mean TA at the sand community was also slightly lower whereas mean DIC was similar to the mixed community. A slightly different pattern was observed in November with respect to both DIC and TA. Mean DIC exhibited a gradual decrease from the outer reef, rubble, mixed community, coral and the sand community. Mean TA was lower for the coral community but similar between the other communities. Based on these observations, it can be concluded that only the coral community had sufficiently large influence on seawater TA and DIC to distinguish it from the influence of the other communities under the current environmental and physical conditions. However, despite these differences, pH and Ω_a were relatively similar in June across different communities, which is attributed to the close balance between organic and inorganic carbon metabolism (see previous section; Figure 4.10). In contrast mean pH and Ω_a and their variability gradually increased moving from the outer reef towards the rubble, mixed and the sand community owing to higher dominance by organic carbon cycling (Figure 4.10). pH measurements from autonomous sensors also showed increasing variability associated with the coral and mixed communities compared to the rubble community, but no clear differences in mean pH were observed for neither June nor November. Differences between spatial and autonomous measurements result from the fact that spatial measurements were only conducted during the day at multiple locations while sensors measured continuously throughout both day and night, but at single locations. Although it was only the coral dominated community's influence on seawater CO_2-chemistry that clearly stood out among the different communities, all communities may have exerted different influence on seawater chemistry (Page et al. 2016), but the influence from other factors such as depth, flow rates and

flow trajectory may have been more important and masking the community-specific influence on seawater chemistry.

Physical properties: water depth, flow rates and distance from the reef edge

The highest mean seawater temperature, the lowest mean DIC minima, the highest mean pH and Ω_a maximums, as well as the largest range of variability were all associated with the shallowest depths of the reef flat, which for depth less than 2 m qualitatively changed non-linearly with decreasing depth (Figure 4.8). The only exceptions were TA and observations associated with the coral dominated community. No clear trends were apparent with respect to seawater TA as a function of depth, but TA was always lower at the coral community compared to the other communities (Figure 4.9), which can be attributed to higher rates of calcification within this community (Anthony et al. 2013; Page et al. 2016). Also, the depth for the coral reef community is somewhat misrepresented as the immediate area surrounding the sample location is extremely shallow with depths < 1 m (Figure 4.1). The explanation for the observed trends as a function of depth was twofold; first, shallower depth likely resulted in increasing biomass to water volume ratio, and thus, greater modification of seawater chemistry by volume owing to biogeochemical processes (i.e., NCP and NCC). Similarly, shallow depths have higher heat gain or loss per volume of water compared to deeper parts of the reef, and consequently, experienced greater temperature extremes and variability. Second, the frictional resistance of the benthos increases non-linearly at depths <1 m leading to reduced flow rates and increased contact time between the water and the benthos, and thus, greater modification of physical and chemical properties (Falter et al. 2013). Based on water flow measurements from drifters and current profilers, it was evident that flow rates were on average higher on the outer part compared to the inner part of the reef

flat, and deflected southward due to the shoaling of the seafloor in an east to west direction of the study area (Figures 4.1 and 4.3). Consequently, in addition to higher biomass to water volume ratio, slower flow rates on the inner part of the reef flat allowed reef metabolism to have a larger influence on seawater chemistry also leading to greater variability (Zhang et al. 2012; Falter et al. 2013; Mongin and Baird 2014; Koweek et al. 2015a, b). The proposed underlying mechanism of depth is strongly supported by the present observations, although the bulk of observations were biased towards daytime observations.

Although it is evident that depth, flow rates and biomass to water volume ratio played important roles on seawater CO_2-chemistry of the Kaneohe Bay reef flat, superimposed on the observed trends were the effects of distance from the reef edge and the seawater flow trajectory, i.e., the chemical memory of the water as it transited the reef. As water transited the reef during the day, the cumulative influence of reef metabolism contributed to a sequential drawdown of DIC in both summer and winter, and TA in the summer. That partly explains the observed spatial trends in mean pH and Ω_a (Figures 4.4-4.7). The combined influences of depth, flow rates and flow trajectory were likely responsible for the two-directional-gradients in the spatial distribution of chemical properties tracking both depth gradients and distance from the reef edge (Figures 4.4 and 4.6). Although the present spatial dataset lacks adequate representation of nighttime conditions, we would expect the opposite trends compared to daytime. This is partly corroborated by the November morning datasets (Figures 4.6-4.7) and also illustrated in numerical simulations for an idealized reef flat by Falter et al. (2013).

Comparing experimental mesocosm results with in situ field observations

Direct comparison between mesocosm and field observations needs to be viewed with caution due to inherent differences in the two approaches; yet, this comparison is critical to better interpret results from both the field and mesocosm experiments. While mesocosm results represent the influence of distinct benthic communities on seawater chemistry under roughly identical conditions, all field communities essentially represent the influence of mixed communities that are potentially affected by different depth, biomass to water volume ratio, flow rates, residence times and chemical memory. Mean seawater pH in the field were elevated relative to mesocosms in both summer and winter (Figure 4.11), which may be attributed to differences between the locations (central vs. south bay), timing of the studies, and/or the deeper (~3 m) water intake for the mesocosms in the southern part of Kaneohe Bay. Furthermore, diel seawater pH extremes (maxima and minima) in the field appeared slightly delayed and had similar or greater ranges relative to the mesocosms. These differences were likely due to the larger spatial scale (100s of m to km), longer residence time (hours to days; Lowe et al. 2009), and cumulative influence from multiple communities for the field observations compared to a residence time of < 1 hour for the 1 m × 1 m flow-through mesocosms (Page et al. 2016, 2017). The influence of residence time was also apparent in TA-DIC analyses for which the total ranges of changes in TA and DIC were much smaller in mesocosm compared to field observations due to the shorter duration for interaction between the benthos and the seawater (Figure 4.11).

The strong differential influences on seawater chemistry by different communities observed in mesocosms were not apparent in field observations except for the coral and sand dominated communities. This was likely due to the more homogenous composition of field communities compared to mesocosm communities, and stronger influence by depth, flow

rates, and cumulative changes in chemistry across communities (Falter et al. 2013). However, observed changes in the balance between inorganic and organic carbon cycling in the field reaffirmed results from the mesocosms that communities with balanced NCP and NCC had dampened influence on seawater pH and communities dominated by organic carbon cycling experienced greater overall variability and more extreme pH values (Andersson and Gledhill 2013; Falter et al. 2013; Page et al. 2016; Cyronak et al. in review). In general, most areas on the reef appeared similarly influenced by organic carbon cycling, but unfortunately, there were no distinct areas that were markedly dominated by autotrophs such as turf and/or macroalgae in order to assess their stronger potential to elevate daily mean pH as inferred from mesocosm results (Figure 4.11). In the mesocosms, these results were partly due to the fact that nighttime influence on pH from respiration was similar across different communities so that the strong positive influence of daytime NCP in algal communities resulted in overall higher daily mean pH. However, in the field, all areas experiencing elevated daytime pH owing to positive NCP appeared to experience a comparable suppression in pH at night owing to negative NCP of similar magnitude (Figure 4.11). This reaffirms the strong control by depth, flow rates, and the cumulative modification of seawater chemistry from reef metabolism as water flows across the Kaneohe Bay reef flat. This influence was especially pronounced in the November spatial surveys where a gradual decrease in mean DIC and increase in variability were observed across the outer reef, rubble, mixed, and sand communities (Figure 4.9).

Whether $CaCO_3$ dissolution played a role in buffering nighttime seawater pH or not across the reef flat as indicated in acidified mesocosm experiments (Page et al. 2016) was not clear from the present study due to a lack of nighttime observations. Also, seawater pH and

Ω_a remained well above the treatment levels of the mesocosm experiment where net dissolution was observed. Similarly, Shamberger et al. (2011) did not observe any alkalinity repletion and net dissolution at night in approximately the same area during winter or summer. In contrast, benthic chamber incubations conducted in the sediments of Kaneohe Bay have reported some of the highest net $CaCO_3$ dissolution rates among a range of reef locations in the Atlantic and Pacific Oceans (Eyre et al. in review), but are obviously limited to this specific benthic community. However, ΔTA-ΔDIC analyses based on spatial samples calculated relative to mean offshore DIC and TA, calculated for the "outer reef" sites (n=4) for each survey (n=10), indicated occasional TA repletion across the reef flat indicative of net dissolution (Figure 4.11).

Comparison of the overall net reef metabolism in the field and mesocosms revealed ΔTA-ΔDIC slopes of 0.23 for the reef flat compared to 0.35 for a mixed mesocosm community in winter, with slopes ranging from 0.02 to 0.55 for individual communities of macroalgae (0.02), crustose coralline algae (0.40), corals (0.41) and carbonate sand (0.55). Although no statistically significant differences were observed in net metabolism between summer and winter for mesocosm communities (Page et al. 2016), the ΔTA-ΔDIC slope for the reef flat in June exceeded 1, indicating relative increasing importance by inorganic carbon cycling and net calcification compared to organic carbon cycling (Figure 4.11). Environmental conditions during June were certainly more favorable for calcification, contributing to the more balanced inorganic to organic carbon cycling. However, it has been clearly demonstrated that studies conducted on larger spatial scales tend to have higher TA-DIC or ΔTA-ΔDIC slopes due to integration of processes across multiple habitats and longer

timescales where NCP tends to approach 0, i.e., primary production is roughly balanced by total respiration (Falter et al. 2013; Cyronak et al. in review).

Seawater CO_2-chemistry and carbon cycling on coral reefs under climate change

Based on the results of this study and others (e.g., Falter et al. 2013), it is evident that different areas and habitats on coral reef flats experience different means and variabilities of CO_2-chemistry linked to a range of factors. Although these properties are partly related to the benthic community composition, in Kaneohe Bay, shallow depths appeared to be the most influential factor of CO_2-chemistry extreme values and variability due to the associated increase in biomass to water volume ratio and reduction in flow rate with seafloor shoaling (Falter et al. 2013). Consequently, the shallowest parts of the reef were the areas with the strongest potential for exacerbating and/or alleviating OA. However, areas with the most elevated pH conditions during the day also experienced the most suppressed pH conditions at night, which put doubts on the effectiveness of localized seawater buffering over complete diel cycles in these habitats. In a future high-CO_2 world, the daily range between extreme pH values will increase due to reduced buffering capacity (Shaw et al. 2011), further exacerbating these extremes. It is unknown whether marine organism sensitive to seawater-CO_2 chemistry has differential susceptibility between day and night, but if so, the range of variability and extreme values may play a role in their overall fitness and response to OA (Rivest et al. 2017). On diel timescales and for individual habitats, organic carbon cycling has the largest influence on seawater CO_2-chemistry, but on longer temporal and larger spatial scales NCP is close to balanced (i.e., +NCP and –NCP are close to balanced) on coral reefs. The mean and median production to respiration ratio (P:R) for a range of coral reef environments (n=20) are

1.24±0.38 and 1.09, respectively (Falter et al., 2013). Consequently, on longer temporal and larger spatial scales, the influence of inorganic carbon cycling on CO_2-chemistry becomes increasingly important, and the ecosystem scale balance of NCP and NCC ultimately control the offset between mean reef and open ocean TA and DIC, (Figure 4.11; Cyronak et al. in review). Hence, ecosystem scale changes in benthic community composition in response to long-term environmental forcings and/or short-term disturbances will influence the local seawater CO_2-chemistry properties (for example, compare June to November in Figure 4.10; see also Andersson et al. 2014 and Cyronak et al. in review).

Kaneohe Bay has a documented history of both short-term and long-term disturbances affecting reef metabolism and benthic community composition in response to both natural and human activities (Banner and Bailey 1970; Hunter and Evans 1995; Bahr et al. 2015). For example, storm events and the associated input of terrestrially derived nutrients have been observed to initially reduce seawater pCO_2 across the bay due to phytoplankton blooms, followed by a gradual increase in pCO_2 as the organic detritus is decomposed and the bay returns to baseline conditions (Fagan and Mackenzie 2007). In 2014, abnormally warm seawater temperatures led to widespread coral bleaching and mortality across the bay (Bahr et al. 2015, 2017). During this event, a transition towards net heterotrophy and net $CaCO_3$ dissolution was recorded at the reef scale, which consequently modulated net changes in seawater pH (Courtney et al. in press). Due to limited coral mortality and rapid recovery of symbiotic algae, the reef recovered to pre-bleaching rates of NEC in less than 1 year. Similar modulation in seawater pH was reported by Andersson et al. (2014) under a range of modeling scenarios for the Bermuda carbonate platform in response to a decrease in NCC and

increase in NCP, which was most effective in areas of long residence time reflecting the integrated chemical memory of the reef water.

The largest and most significant perturbation of Kaneohe Bay to this date includes sewage input to the bay which began in the 1950s (Banner and Bailey 1970; Smith et al. 1981). This caused increased sedimentation and nutrients, supporting higher abundance of filter and suspension feeders and the green bubble algae *Dictyosphaeria cavernosa* at the expense of coral cover, which decreased during this time period (Banner and Bailey 1970; Hunter and Evans 1995; Bahr et al. 2016). Once sewage was diverted away from the bay in 1978, coral populations recovered and the abundance of *D. cavernosa* decreased (Smith et al. 1981; Hunter and Evans 1995). In addition to the changes in benthic community composition, benthic metabolism of reefs, particularly those located closest to sewage effluent, shifted towards net heterotrophy through increasing respiration and net $CaCO_3$ dissolution through lower calcification and higher bioerosion (Smith et al. 1981).

As coral reefs respond to future warmer temperatures, OA, sea level rise, and local perturbations such as eutrophication, sewage input, and overfishing, the net metabolism and the benthic community composition will continue to change with subsequent changes in seawater CO_2-chemistry. The present study highlights that results derived under controlled experimental conditions need to be carefully examined in the light of the dominant properties and processes in the natural environment. Although experimental results reveal the operational function of different properties (e.g., community composition), the relative importance of these properties in a natural setting may be easily overlooked unless they are specifically evaluated. In the case of coral reefs, this study reiterates the statements previously expressed by Falter, Lowe and colleagues (Falter et al. 2012, 2013; Zhang et al. 2012; Lowe

and Falter 2015) that geomorphology and hydrodynamics need equal attention as the biological fluxes in characterizing and interpreting the controls of reef seawater CO_2-chemistry. Resolving the quantitative relationships between these factors, as well as their controls (e.g., wave height and depth control on flow rates; light, temperature and community composition on biological fluxes) will allow for improved predictions of seawater CO_2-chemistry conditions and variability at 1) present reef habitats with limited CO_2 measurements, and 2), global reef locations undergoing changing ecological (Gardner et al. 2003; Wilkinson et al. 2008; Bruno and Valvidia 2016) and biogeochemical conditions in response to OA, climate change, and other potential disturbances.

Acknowledgments

We would like to acknowledge the following funding sources: NSF GRFP (HNP, TAC) and NSF OCE 12-55042 (AJA).

References Cited

Albright, R, Langdon, C, & Anthony, KRN. 2013. Dynamics of seawater carbonate chemistry, production, and calcification of a coral reef flat, central Great Barrier Reef. *Biogeosciences* 10: 6747.

Al-Horani, FA, Al-Moghrabi, SM, & de Beer, D. 2003. The mechanism of calcification and its relation to photosynthesis and respiration in the scleractinian coral *Glaxea fascicularis. Marine Biology* 142: 419-426.

Andersson, AJ & Gledhill, D. 2013. Ocean acidification and coral reefs: Effects on breakdown, dissolution, and net ecosystem calcification. *Annual Review of Marine Science* 5:321-348.

Andersson, AJ, Kline, DI, Edmunds, PJ, Archer, SD, Bednaršek, N, Carpenter, RC, Chadsey, M, Goldstein, P, Grottoli, AG, Hurst, TP, King, AL, Kübler, JE, Kuffner, IB, Mackey, KRM, Menge, BA, Paytan, A, Riebesell, U, Schnetzer, A, Warner, ME, &

Zimmerman, RC. (2015). Understanding ocean acidification impacts on organismal to ecological scales. *Oceanography* 28, 16–27. doi: 10.5670/oceanog.2015.27.

Andersson, AJ, Kuffner, IB, Mackenzie, FT, Jokiel, PL, Rodgers, KS, & Tan, A. 2009. Net loss of $CaCO_3$ from a subtropical calcifying community due to seawater acidification: mesocosm-scale experimental evidence. *Biogeosciences* 6:1811-1823.

Andersson, AJ & Mackenzie, FT. 2012. Revisiting four scientific debates in ocean acidification research. *Biogeosciences* 9:893-905.

Andersson, AJ, Yeakel, KL, Bates, NR, & De Putron, SJ. 2014. Partial offsets in ocean acidification from changing coral reef biogeochemistry. *Nature Climate Change* 4: 56-61.

Anthony, KRN, Kleypas, JA, & Gattuso, J-P. 2011. Coral reefs modify their seawater carbon chemistry – implications for impacts of ocean acidification. *Global Change Biology* 17:3655-3666.

Anthony, KRN, Diaz-Pulido, G, Verlinden, N, Tilbrook, B, & Andersson, AJ. 2013. Benthic buffers and boosters of ocean acidification on coral reefs. *Biogeosciences* 10:4897-4909.

Bahr, KD, Jokiel, PL, & Toonen, RJ. 2015. The unnatural history of Kāneʻohe Bay: coral reef resilience in the face of centuries of anthropogenic impacts. *PeerJ* 3:e950.

Bahr, KD, Jokiel, PL, & Rodgers, KS. 2015. The 2014 coral bleaching and freshwater flood events in Kāneʻohe Bay, Hawaiʻi. *PeerJ* 3: e1136.

Bahr, KD, Rodgers, KS, & Jokiel, PL. 2017. Impact of three bleaching events on the resiliency of Kāneʻohe Bay, Hawaiʻi. *Frontiers in Marine Science* 4: 398.

Banner, AH & Bailey, JH. 1970. The effects of urban pollution upon a coral reef system: a preliminary report. Honolulu (HI): Hawaiʻi Institute of Marine Biology, University of Hawaiʻi. Report No.: 25.

Barbier, EB, Hacker, SD, Kennedy, C, Koch, EW, Stier, AC, & Silliman, BR. 2011. The value of estuarine and coastal ecosystem services. *Ecological Monographs* 81: 169-193.

Bates, NR, Amat, A, & Andersson, AJ. 2010. Feedbacks and responses of coral calcification on the Bermuda reef system to seasonal changes in biological processes and ocean acidification. *Biogeosciences* 7:2509-2530.

Bates, NR, Astor, YM, Church, MJ, Currie, K, Dore, JE, González-Dávila, M, Lorenzoni, L, Muller-Kargor, F, Olafsson, J, & Santana-Casiano, JM. 2014. A time-series view of changing surface ocean chemistry due to ocean uptake of anthropogenic CO_2 and ocean acidification. *Oceanography* 27: 126-141.

Boyd, PW, Cornwall, CE, Davison, A, Doney, SC, Fourquez, M, Hurd, CL, Lima, ID, & McMinn, A. 2016. Biological responses to environmental heterogeneity under future ocean conditions. *Global Change Biology* 22: 2633-2650.

Bresnahan, PJ, Martz, TR, Takeshita, Y, Johnson, KS, & LaShomb, M. 2014. Best practices for autonomous measurement of seawater pH with the Honeywell Durafet. *Methods in Oceanography* 9: 44-60.

Bruno, JF & Valdivia, A. 2016. Coral reef degradation is not correlated with local human population density. *Scientific Reports*. doi: 10.1038/srep29778.

Camp, EF, Suggett, DJ, Gendron, G, Jompa, J, Manfrino, C, & Smith, DJ. 2016. Mangrove and seagrass beds provide different biogeochemical services for corals threatened by climate change. *Frontiers in Marine Science* 3: 52.

Chalker, BE. 1981. Simulating light-saturation curves for photosynthesis and calcification by reef-building corals. *Marine Biology* 63: 135-141.

Chan, NCS & Connolly, SR. 2013. Sensitivity of coral calcification to ocean acidification: a meta-analysis. *Global Change Biology* 19: 282-290.

Cohen, I, Dubinsky, Z, & Erez, J. 2016. Light enhanced calcification in hermatypic corals: new insights from light spectral responses. *Frontiers in Marine Science* 2: 122. doi: 10.3389/fmars.2015.00122.

Coles, SL & Jokiel, PL. 1977. Effects of temperature on photosynthesis and respiration in hermatypic corals. *Marine Biology* 43: 209-216.

Comeau, S, Edmunds, PJ, Spindel, NB, & Carpenter, RC. 2013. The responses of eight coral reef calcifiers to increasing CO_2 do not exhibit a tipping point. *Limnology and Oceanography* 58, 388–398. doi: 10.4319/lo.2013.58.1.0388.

Comeau, S, Edmunds, PJ, Lantz, CA, & Carpenter, RC. 2017. Daily variation in net primary production and net calcification in coral reef communities exposed to elevated pCO_2. *Biogeosciences* 14: 3549.

Cornwall, CE, Hepburn, CD, McGraw, CM, Currie, KI, Pilditch, CA, Hunter, KA, Boyd, PW, & Hurd, CL. 2013. Diurnal fluctuations in seawater pH influence the response of a calcifing macroalga to ocean acidification. *Proceedings of the Royal Society B* 280:20122201.

Courtney, TA, Lebrato, M, Bates, NR, Collins, A, de Putron, SJ, Garley, R, Johnson, R, Molinero, J-C, Noyes, TJ, Sabine, CL, & Andersson, AJ. 2017. Environmental controls on modern scleractinian coral and reef-scale calcification. *Science Advances* 3: e1701356.

Davies, PS. 1984. The role of zooxanthellae in the nutritional energy requirements of *Pocillopora eydouxi*. *Coral Reefs* 2: 181-186.

de Beer, D & Larkum, AWD. 2001. Photosynthesis and calcification in the calcifying algae *Halimeda discoidea* studied with microsensors. *Plant, Cell, & Environment* 24: 1209-1217.

Deffeyes, KS. 1965. Carbonate equilibria: A graphic and algebraic approach. *Limnology and Oceanography* 10: 412-426.

Diaz-Pulido, G, Gouezo, M, Tilbrook, B, Dove, S, & Anthony, KRN. 2011. High CO_2 enhances the competitive strength of seaweeds over corals. *Ecology Letters* 14: 156-162.

Dickson, AG & Millero, FJ. 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep Sea Research Part A Oceanographic Research Papers* 34:1733-1743.

Dickson, AG, Sabine, CL, & Christian, JR. (Eds.) 2007. Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, 191 pp.

Doney, SC, Fabry, VJ, Feely, RA, & Kleypas, JA. 2009. Ocean acidification: The other CO2 problem. *Annual Review of Marine Science* 1: 169-192.

Drupp, PS, De Carlo, EH, Mackenzie, FT, & Sabine, CL. 2013. A comparison of CO_2 dynamics and air-sea exchange in differing tropical reef environments. *Aquatic Geochemistry.* 19: 371-397. doi: 10.1007/s10498-013-9214-7.

Dufault, AM, Cumbo, VR, Fan, TY, & Edmunds, PJ. 2012. Effects of diurnally oscillating pCO_2 on the calcification and survival of coral recruits. *Proceedings of the Royal Society of London B: Biological Sciences* doi: 10.1098/rspb2011.2545.

Edmunds, PJ, Comeau, S, Lantz, C, Andersson, A, Briggs, C, Cohen, A, Gattuso, J-P, Grady, JM, Gross, K, Johnson, M, Muller, JEB, Ries, JB, Tambutté, S, Tambutté, E, Venn, A, & Carpenter, RC. 2016. Integrating the effects of ocean acidification across functional scales on tropical coral reefs. *Bioscience* 66, 350–362. doi: 10.1093/biosci/biw023.

Eidens, C, Bayraktarov, E, Hauffe, T, Pizarro, V, Wilke, T, & Wild, C. 2014. Benthic primary production in an upwelling-influenced coral reef, Colombian Caribbean. *PeerJ* 2: e554.

Eyre, BD, Andersson, AJ, & Cyronak, T. 2014. Benthic coral reef calcium carbonate dissolution in an acidifying ocean. *Nature Climate Change* 4: 969–976.

Fagan, KE & Mackenzie, FT. 2007. Air-sea CO_2 exchange in a subtropical estuarine-coral reef system, Kaneohe Bay, Oahu, Hawaii. *Marine Chemistry* 106: 174-191.

Falter, JL, Lowe, RJ, Atkinson, MJ, & Cuet, P. 2012. Seasonal coupling and de-coupling of net calcification rates from coral reef metabolism and carbonate chemistry at Ningaloo Reef, Western Australia. *Journal of Geophysical Research* 117: C05003. doi: 10.1029/2011JC007268.

Falter, JL, Lowe, RJ, Zhang, Z, & McCulloch, M. 2013. Physical and biological controls on the carbonate chemistry of coral reef waters: Effects of metabolism, wave forcing, sea level, and geomorphology. *PLoS ONE* 8:e53303.

Frankignoulle, M, Gattuso, J-P, Biondo, R, Bourge, I, Copin-Montégut, G, & Pichon, M. 1996. Carbon fluxes in coral reefs. II. Eulerian study of inorganic carbon dynamics and measurement of air-sea CO_2 exchanges. *Marine Ecology Progress Series* 145: 123-132.

Gardner, TA, Côté, IM, Gill, JA, Grant, A, & Watkinson, AR. 2003. Long-term region-wide declines in Caribbean corals. *Science* 301, 958–960.

Gillooly, JF, Brown, JH, West, GB, Savage, VM, & Charnov, EL. 2001. Effects of size and temperature on metabolic rate. *Science* 293:2248-2251.

Guadayol, Ò, Silbiger, NJ, Donahue, MJ, & Thomas, FI. 2014. Patterns in temporal variability of temperature, oxygen and pH along an environmental gradient in a coral reef. *PloS ONE* 9: e85213.

Hendriks, IE, Olsen, YS, Ramajo, L, Basso, L, Steckbauer, A, Moore, TS, Howard, J, & Duarte, CM. 2014. Photosynthetic activity buffers ocean acidification in seagrass meadows. *Biogeosciences* 11: 333.

Hoegh-Guldberg, O, Mumby, PJ, Hooten, AJ, Steneck, RS, Greenfield, P, Gomez, E, Harvell, CD, Sale, PF, Edwards, AJ, Caldeira, K, Knowlton, N, Eakin, CM, Iglesias-Prieto, R, Muthiga, N, Bradbury, RH, Dubi, A, & Hatziolos, ME. 2007. Coral reefs under rapid climate change and ocean acidification. *Science* 318: 1737-1742.

Hofmann, GE, Smith, JE, Johnson, KS, Send, U, Levin, LA, Micheli, F, Paytan, A, Price, NN, Peterson, B, Takeshita, Y, Matson, PG, Crook, ED, Kroeker, KJ, Gambi, MC, Rivest, EB, Frieder, CA, Yu, PC, & Martz, TR. 2011. High-frequency dynamics of ocean pH: A multi-ecosystem comparison. *PLoS ONE* 6: e28983.

Hofmann, LC, Koch, M, & de Beer, D. 2016. Biotic control of surface pH and evidence of light-induced H^+ pumping and Ca^{2+}-H^+ exchange in a tropical crustose coralline alga. *PloS ONE* 11: e0159057.

Hunter, CL & Evans, CW. 1995. Coral reefs in Kaneohe Bay, Hawaii: Two centuries of Western influence and two decades of data. *Bulletin of Marine Science* 57:501-515.

IPCC. 2013. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate

Change [Stocker, TF, D Qin, G-K Plattner, M Tignor, SK Allen, J Boschung, A Nauels, Y Xia, V Bex and PM Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

Islam, MN, Casareto, BE, Higuchi, T, Niraula, MP, & Suzuki, Y. 2012. Contribution of coral rubble associated microbial community to the dissolution of calcium carbonate under high pCO_2. *Galaxea, Journal of Coral Reef Studies 14*: 119-131.

Jantzen, C, Schmidt, GM, Wild, C, Roder, C, Khokiattiwong, S, & Richter, C. 2013. Benthic reef primary production in response to large amplitude internal waves at the Similan Islands (Andaman Sea, Thailand). *PloS ONE* 8: e81834.

Johannes, RE, Alberts, J, D'elia, C, Kinzie, RA, Pomeroy, LR, Sottile, W, Wiebe, W, Marsh, JA, Helfrich Jr, P, Maragos, J, Meyer, J, Smith, S, Crabtree, D, Roth, A, McCloskey, LR, Betzer, S, Marshall, N, Pilson, MEQ, Telek, G, Clutter, RI, DuPaul, WD, Webb, KL, & Wells Jr, JM. 1972. The metabolism of some coral reef communities: a team study of nutrient and energy flux at Eniwetok. *Bioscience* 22: 541-543.

Johnson, MD, Price, NN, & Smith, JE. 2014. Contrasting effects of ocean acidification on tropical fleshy and calcareous algae. *PeerJ* 2: e411.

Jokiel, PL, Jury, CP, & Rodgers, KS. 2014. Coral-algae metabolism and diurnal changes in the CO_2-carbonate system of bulk seawater. *PeerJ*. 2: e378. doi: 10.7717/peerj.378.

Jokiel, PL, Rodgers, KS, Kuffner, IB, Andersson, AJ, Cox, EF, & Mackenzie, FT. 2008. Ocean acidification and calcifying reef organisms: a mesocosm investigation. *Coral Reefs* 27: 473-483.

Jury, CP, Thomas, FIM, Atkinson, MJ, & Toonen, RJ. 2013. Buffer capacity, ecosystem feedbacks, and seawater chemistry under global change. *Water* 5: 1303-1325.

Karl, DM & Lukas, R. 1996. The Hawaii Ocean Time-series (HOT) program: Background, rationale and field implementation. *Deep Sea Research Part II: Topical Studies in Oceanography* 43: 129-156.

Kawahata, H, Yukino, I, & Suzuki, A. 2000. Terrestrial influences on the Shiraho fringing reef, Ishigaki Island, Japan: high carbon input relative to phosphate. *Coral Reefs* 19: 172-178.

Kleypas, JA, Anthony, KRN, & Gattuso, J-P. 2011. Coral reefs modify their seawater carbon chemistry – case study from a barrier reef (Moorea, French Polynesia). *Global Change Biology* 17: 3667-3678.

Kleypas, JA, Feely, RA, Fabry, VJ, Langdon, C, Sabine, CL, & Robbins, LL. 2006. Impacts of Ocean Acidification on Coral Reefs and Other Marine Calcifiers: A Guide for Future Research, report of a workshop held 18–20 April 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the U.S. Geological Survey, 88 pp.

Koweek, D, Dunbar, RB, Monismith, SG, Mucciarone, DA, Woodson, CB, & Samuel, L. 2015a. high-resolution physical and biogeochemical variability from a shallow back reef on Ofu, American Samoa: an end-member perspective. *Coral Reefs* 34: 979-991.

Koweek, D, Dunbar, R, Rogers, J, Williams, G, Price, N, Mucciarone, D, & Teneva, L. 2015b. Environmental and ecological controls of coral community metabolism on Palmyra Atoll. *Coral Reefs* 34: 339-351.

Kroeker, KJ, Micheli, F, & Gambi, MC. 2013. Ocean acidification causes ecosystem shifts via altered competitive interactions. *Nature Climate Change* 3: 156-159.

Kwiatkowski, L, Gaylord, B, Hill, T, Hosfelt, J, Kroeker, KJ, Nebuchina, Y, Ninokawa, A, Russell, AD, Rivest, EB, Sesboüé, M, & Caldeira, K. 2016. Nighttime dissolution in a temperate coastal ocean ecosystem increases under acidification. *Scientific Reports* 6: 22984.

Langdon, C & Atkinson, MJ. 2005. Effect of elevated pCO2 on photosynthesis and calcification of corals and interactions with seasonal changes in temperature/irradiance and nutrient enrichment. *Journal of Geophysical Research: Oceans* 110:C09S07.

Lantz, CA, Atkinson, MJ, Winn, CW, & Kahng, SE. 2014. Dissolved inorganic carbon and total alkalinity of a Hawaiian fringing reef: chemical techniques for monitoring the effects of ocean acidification on coral reefs. *Coral Reefs* 33: 105-115.

LaVelle, JM. 1979. Translocation in *Calliarthron tuberculosum* and its role in the light-enhancement of calcification. *Marine Biology* 55: 37-44.

Lewis, E & Wallace, D. 1998. CO2SYS—program developed for the CO_2 system calculations. Carbon Dioxide Inf. Anal. Center. Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, TN, USA.

Lowe, RJ & Falter, JL. 2015. Oceanic forcing of coral reefs. *Annual Review of Marine Science* 7: 43-66.

Lowe, RJ, Falter, JL, Monismith, SG, & Atkinson, MJ. 2009. A numerical study of circulation in a coastal reef-lagoon system. *Journal of Geophysical Research* 114: C06022. doi: 10.1029/2008JC005081.

Manzello, DP, Enochs, IC, Melo, N, Gledhill, DK, & Johns, EM. 2012. Ocean acidification refugia of the Florida Reef Tract. *PloS ONE* 7: e41715.

Marubini, F, Barnett, H, Langdon, C, & Atkinson, MJ. 2001. Dependence of calcification on light and carbonate ion concentration for the hermatypic coral *Porites compressa*. *Marine Ecology Progress Series* 220: 153-162.

Massaro, RFS, De Carlo, EH, Drupp, PS, Mackenzie, FT, Jones, SM, Shamberger, KE, Sabine, CL, & Feely, RA. 2012. Multiple factors driving variability of CO_2 exchange

between the ocean and atmosphere in a tropical coral reef environment. *Aquatic Geochemistry* 18: 357-386.

McCook, L, Jompa, J, & Diaz-Pulido, G. 2001. Competition between corals and algae on coral reefs: a review of evidence and mechanisms. *Coral Reefs* 19: 400-417.

Mehrbach, C, Culberson, CH, Hawley, JE, & Pytkowicx, RM. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography* 18: 897-907.

Moberg, F & Folke, C. 1999. Ecological goods and services of coral reef ecosystems. Ecological Economics 29: 215–233. doi: 10.1016/S0921-8009(99)00009-9.

Muscatine, L. 1990. The role of symbiotic algae in carbon and energy flux in coral reefs. pp 75–87 In: Dubinsky Z (ed) Coral reefs. Elsevier Science Publishers BV, Amsterdam.

Page, HN, Andersson, AJ, Jokiel, PL, Rodgers, KS, Lebrato, M, Yeakel, K, Davidson, C, D'Angelo, S, & Bahr, KD. 2016. Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral Reefs*. 35: 1311-1325.

Page, HN, Courtney, TA, Collins, A, De Carlo, EH, & Andersson, AJ. 2017. Net community metabolism and seawater carbonate chemistry scale non-intuitively with coral cover. *Frontiers in Marine Science* 4:161. doi: 10.3389/fmars.2017.00161.

R Development Core Team. 2008. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL http://www.R-project.org.

Rao, AM, Polerecky, L, Ionescu, D, Meysman, FJ, & De Beer, D. 2012. The influence of pore-water advection, benthic photosynthesis, and respiration on calcium carbonate dynamics in reef sands. *Limnology and Oceanography* 57: 809-825.

Reaka-Kudla, ML. 2001. Known and unknown biodiversity, risk of extinction and conservation strategy in the sea. *Waters in Peril* 19: 33.

Ricke, KL, Orr, JC, Schneider, K, & Caldeira, K. 2013. Risks to coral reefs from ocean carbonate chemistry changes in recent earth system model projections. *Environmental Research Letters* 8: 034003.

Rinkevich, B. 1989. The contribution of photosynthetic products to coral reproduction. *Marine Biology* 101: 259-263.

Rivest, EB, Comeau, S, & Cornwall, CE. 2017. The role of natural variability in shaping the response of coral reef organisms to climate change. *Current Climate Change Reports* 3: 271-281.

Semesi, IS, Kangwe, J, & Björk, M. 2009. Alterations in seawater pH and CO_2 affect calcification and photosynthesis in the tropical coralline algae *Hydrolithon* sp. (Rhodophyta). *Estuarine Coastal and Shelf Science* 84: 337-341.

Shamberger, KEF, Feely, RA, Sabine, CL, Atkinson, MJ, DeCarlo, EH, Mackenzie, FT, Drupp, PS, & Butterfield, DA. 2011. Calcification and organic production on a Hawaiian coral reef. *Marine Chemistry* 127: 64-75.

Shaw, EC, McNeil, BI, & Tilbrook, B. 2012. Impacts of ocean acidification in naturally variable coral reef flat ecosystems. *Journal of Geophysical Research: Oceans* 117: C03038. doi: 10.1029/2011JC007655.

Shaw, EC, McNeil, BI, Tilbrook, B, Matear, R, & Bates, ML. 2013. Anthropogenic changes to seawater buffer capacity combined with natural reef metabolism induce extreme future coral reef CO_2 conditions. *Global Change Biology* 19: 1632-1641.

Silverman, J, Lazar, B, Cao, L, Caldeira, K, & Erez, J. 2009. Coral reefs may start dissolving when atmospheric CO_2 doubles. *Geophysical Research Letters* 36: L05606.

Smith, SV, Kimmerer, WJ, Laws, EA, Brock, RE, & Walsh, TW. 1981. Kaneohe Bay sewage diversion experiment: perspectives on ecosystem responses to nutritional perturbation. *Pacific Science* 35: 279-395.

Solomon, S, Plattner, GK, Knutti, R, & Friedlingstein, P. 2009. Irreversible climate change due to carbon dioxide emissions. *Proceedings of the National Academy of Sciences* 106: 1704-1709.

Takeshita, Y, McGillis, W, Briggs, EM, Carter, AL, Donham, EM, Martz, TR, Price, NN, & Smith, JE. 2016. Assessment of net community production and calcification of a coral reef using a boundary layer approach. *Journal of Geophysical Research: Oceans* 121: 5655-5671.

Teneva, L, Dunbar, RB, Mucciarone, DA, Dunckley, JF, & Koseff, JR. 2013. High-resolution carbon budgets on a Palau back-reef modulated by interactions between hydrodynamics and reef metabolism. *Limnology and Oceanography* 58: 1851-1870.

van Hoytema, N, Bednarz, VN, Cardini, U, Naumann, MS, Al-Horani, FA, & Wild, C. 2016. The influence of seasonality on benthic primary production in a Red Sea coral reef. *Marine Biology* 163: 52.

Watanabe, A, Kayanne, H, Hata, H, Kudo, S, Nozaki, K, Kato, K, Negishi, A, Ikeda, Y, & Yamano, H. 2006. Analysis of the seawater CO_2 system in the barrier reef-lagoon system of Palau using total alkalinity-dissolved inorganic carbon diagrams. *Limnology and Oceanography* 51: 1614-1628.

Werner, U, Blazejak, A, Bird, P, Eickert, G, Schoon, R, Abed, RM, Bissett, A, & de Beer, D. 2008. Microbial photosynthesis in coral reef sediments (Heron Reef, Australia). *Estuarine, Coastal and Shelf Science* 76: 876-888.

Wilkinson, C. 2008. Status of coral reefs of the world: 2008. Global Coral Reef Monitoring Network and Reef and Rainforest Research Centre, Townsville, Australia, 296 p.

Wisshak, M, Schönberg, CHL, Form, A, & Freiwald, A. 2012. Ocean acidification accelerates reef bioerosion. *PLoS ONE* 7: e45124.

Yates, KK & Halley, RB. 2006. CO_3^{2-} concentration and pCO_2 thresholds for calcification and dissolution on the Molokai reef flat, Hawaii. *Biogeosciences Discussions* 3: 123-154.

Yeakel, KL, Andersson, AJ, Bates, NR, Noyes, TJ, Collins, A, & Garley, R. 2015. Shifts in coral reef biogeochemistry and resulting acidification linked to offshore productivity. *Proceedings of the National Academy of Sciences* 112: 14512-14517.

Zeebe, RE & Wolf-Gladrow, DA. 2001. CO2 in seawater: equilibrium, kinetics, isotopes. Elsevier Oceanography Series 65, Elsevier Science, Amsterdam.

Zhang, Z, Falter, J, Lowe, R, & Ivey, G. 2012. The combined influence of hydrodynamic forcing and calcification on the spatial distribution of alkalinity in a coral reef system. *Journal of Geophysical Research: Oceans* 117: C04034. doi: 10.1029/2011JC007603.

Tables

Table 4.1. Instrument configuration for June and November. Three stations were used in June, and this array was expanded in November for a total of five stations. HR ADCP = High Resolution Acoustic Doppler Current Profiler. LR = Low Resolution Acoustic Doppler Current Profiler. ECO-PAR = ECO Photosynthetically Active Radiation sensor. T = temperature. S = salinity. DO = dissolved oxygen.

Month	Station	Water Depth (m)	Instruments	Variable(s) Measured	Description of Benthic Community
June	1	2.5	SeapHOx	T, S, DO, pH	Mixed community dominated by rubble with *Halimeda* and scattered corals
	2	1.9	Seafet Aquadopp HR ADCP	pH Current Velocity	Mixed community dominated by rubble with scattered corals
	3	1.8	SeapHOx Aquadopp LR ADCP ECO-PAR	T, S, DO, pH Currents PAR	Coral community
Nov.	1	2.5	SeapHOx Aquadopp LR ADCP	T, S, DO, pH Current Velocity	Mixed community dominated by rubble with *Halimeda* and scattered corals
	2	1.9	Seafet Aquadopp HR ADCP Seabird SBE 16plus V2 SeaCAT Aandera Oxygen sensor	pH Currents T, S DO	Mixed community dominated by rubble with scattered corals
	3		SeapHOx ECO-PAR	T, S, DO, pH PAR	Coral community
	4	1.0	Seabird SBE 16plus V2 SeaCAT Aandera Oxygen sensor	T, S DO	Mixed community with mostly coral and sand
	5	0.4	Seabird SBE 16plus V2 SeaCAT	T, S	Mixed community with mostly rubble and sand

Figures

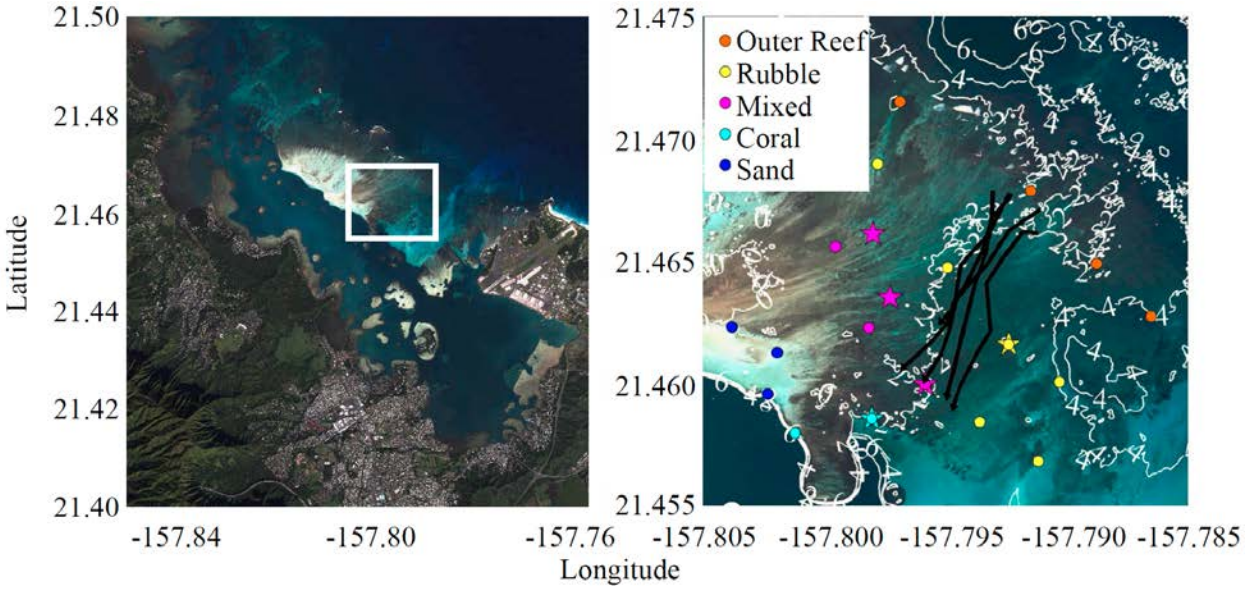


Figure 4.1. Study site in Kaneohe Bay, Hawaii (left) showing each of the sampling stations on the reef flat. The stars indicate locations of the instruments on the benthos while the circles show sites where seawater surface chemistry was measured. The survey area encompassed a variety of benthic habitats (reef break: orange; rubble: yellow; mixed community: magenta; coral: cyan; sand: blue) and depths ranging from 0 to 8 m (contour intervals of 2 m). The black arrows show the dominant direction of water flow as measured using drifters.

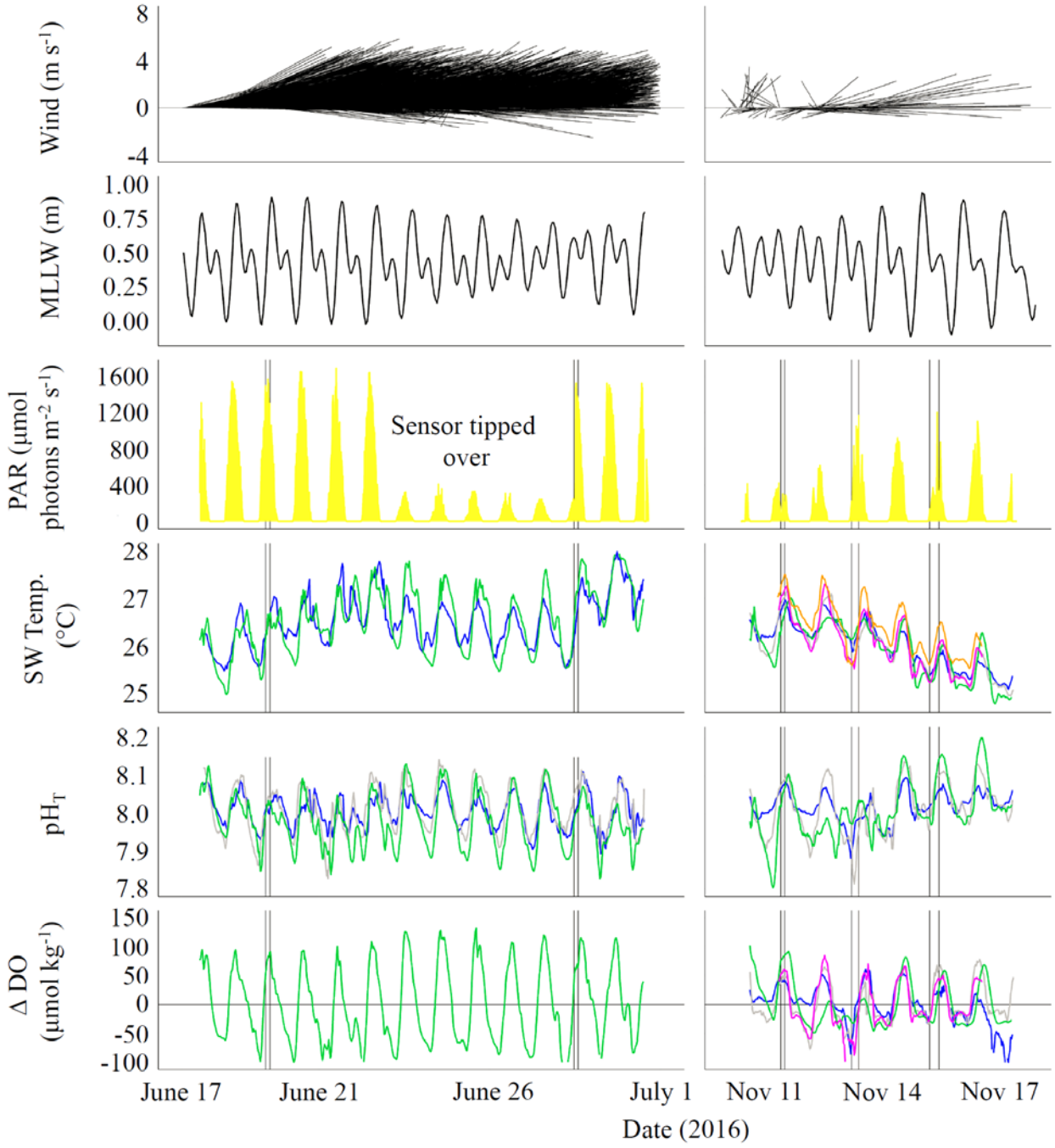


Figure 4.2. Temporal variability in environmental conditions and seawater chemistry for June (left panel) and November (right panel) with vertical black lines indicating the times of the spatial surveys. Wind and tide data were obtained from the NOAA NDBC website while PAR, temperature, pH, and DO were measured by sensors on the reef flat. DO is reported as the offset from the mean DO at each station.

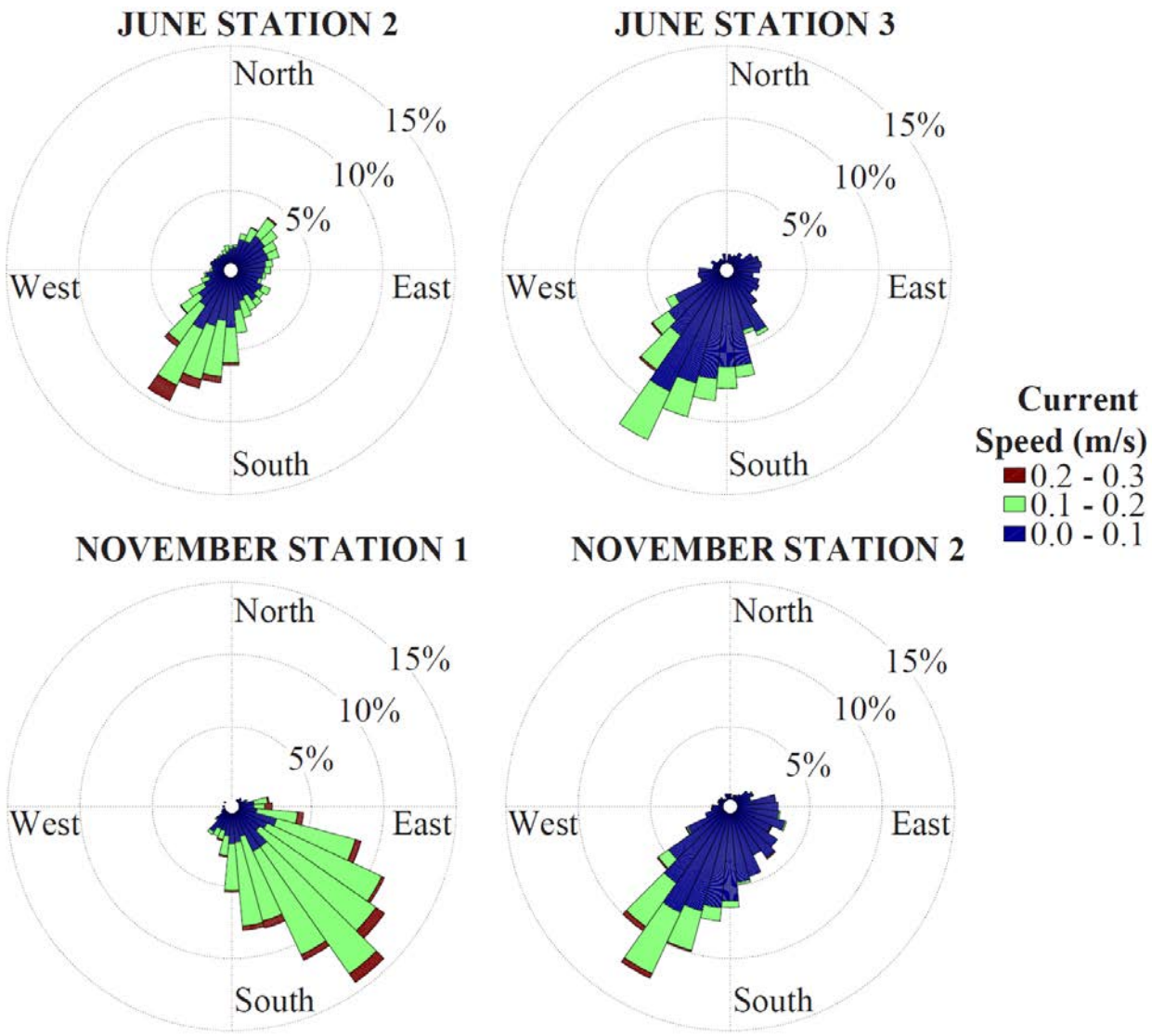


Figure 4.3. Current data integrated across depth for June and November. Current speeds ranged from 0 to 0.3 m s^{-1} with dominant directions being variable by station and season.

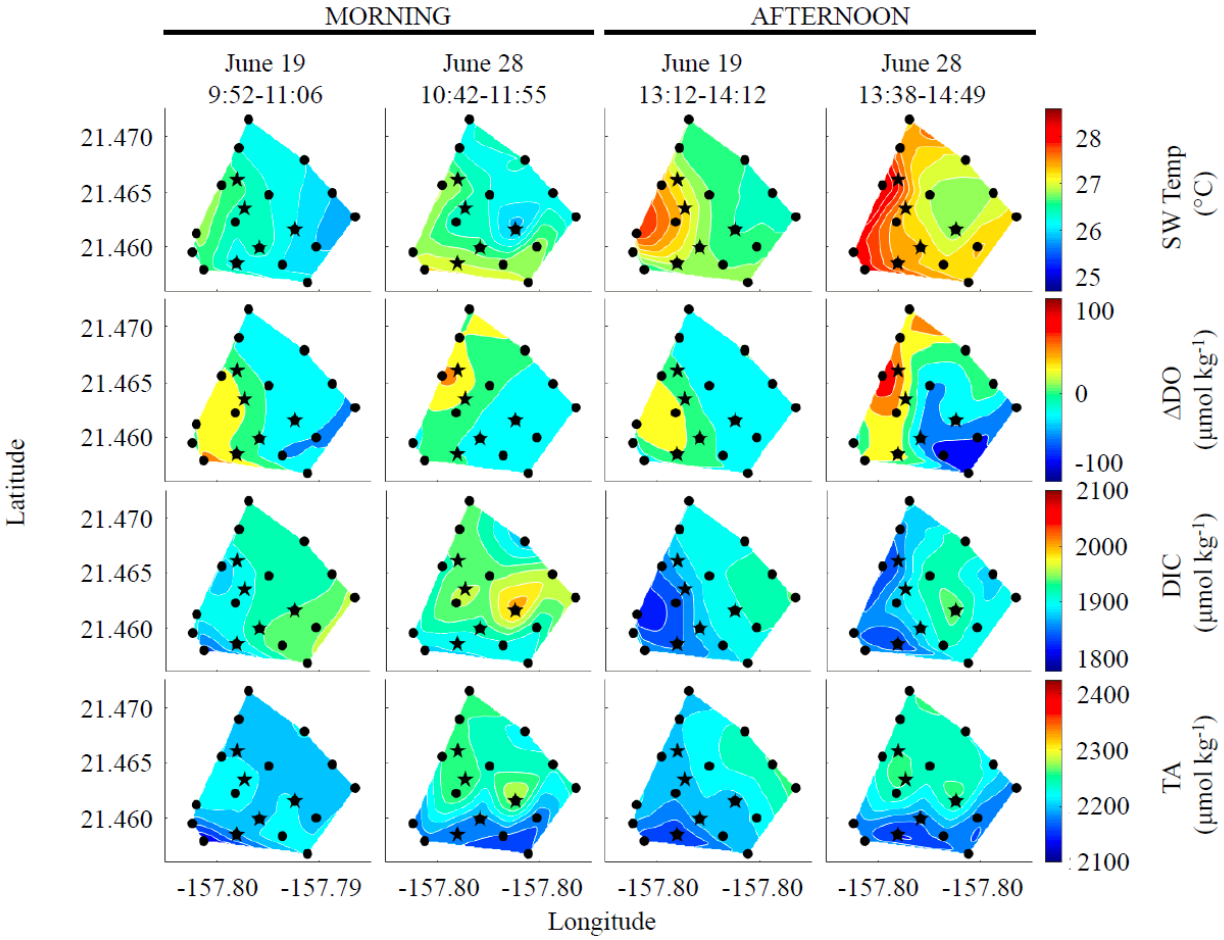


Figure 4.4. Spatial variability in seawater T, ΔDO, DIC, and TA for June morning and afternoon with color gradients representing the range of values. Contour intervals (white lines) show 0.2°C or 25 µmol kg^{-1} for ΔDO, DIC, and TA.

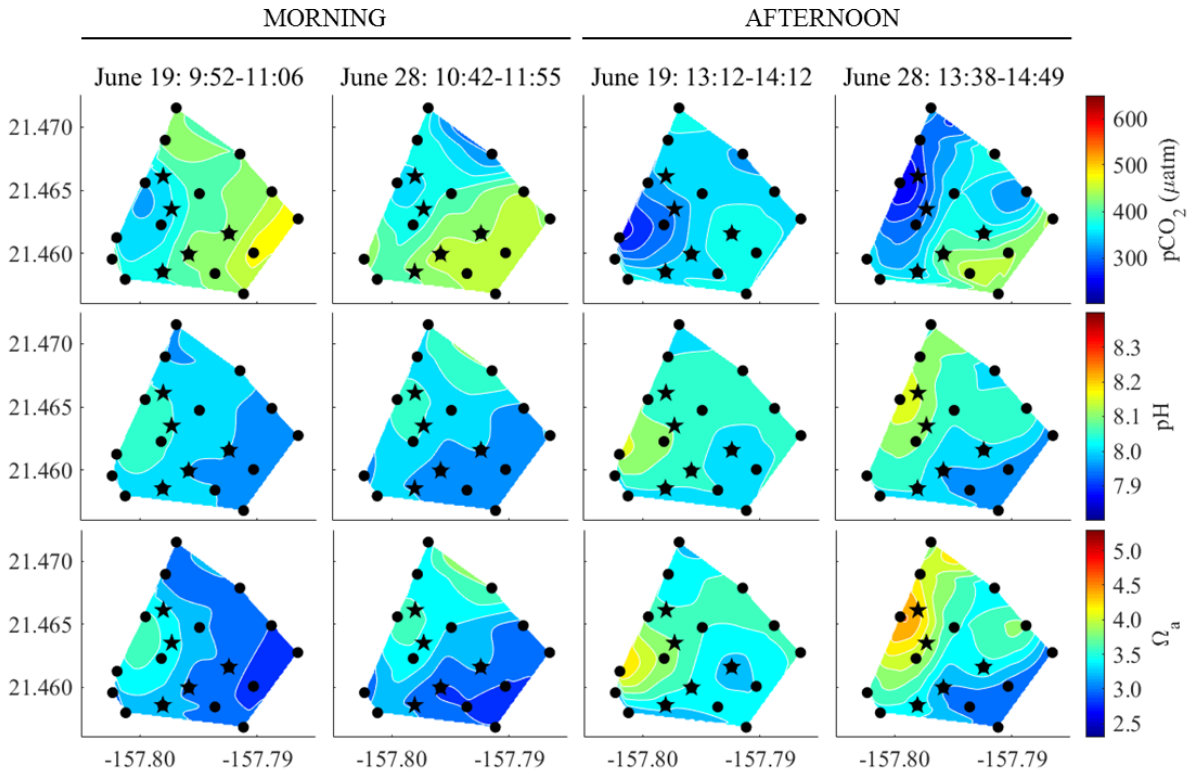


Figure 4.5. Spatial variability in pCO_2, pH, and Ω_a for June morning and afternoon with color gradients representing the range of values. Contour intervals (white lines) show 25 µatm pCO_2, 0.05 pH, or 0.2 Ω_a.

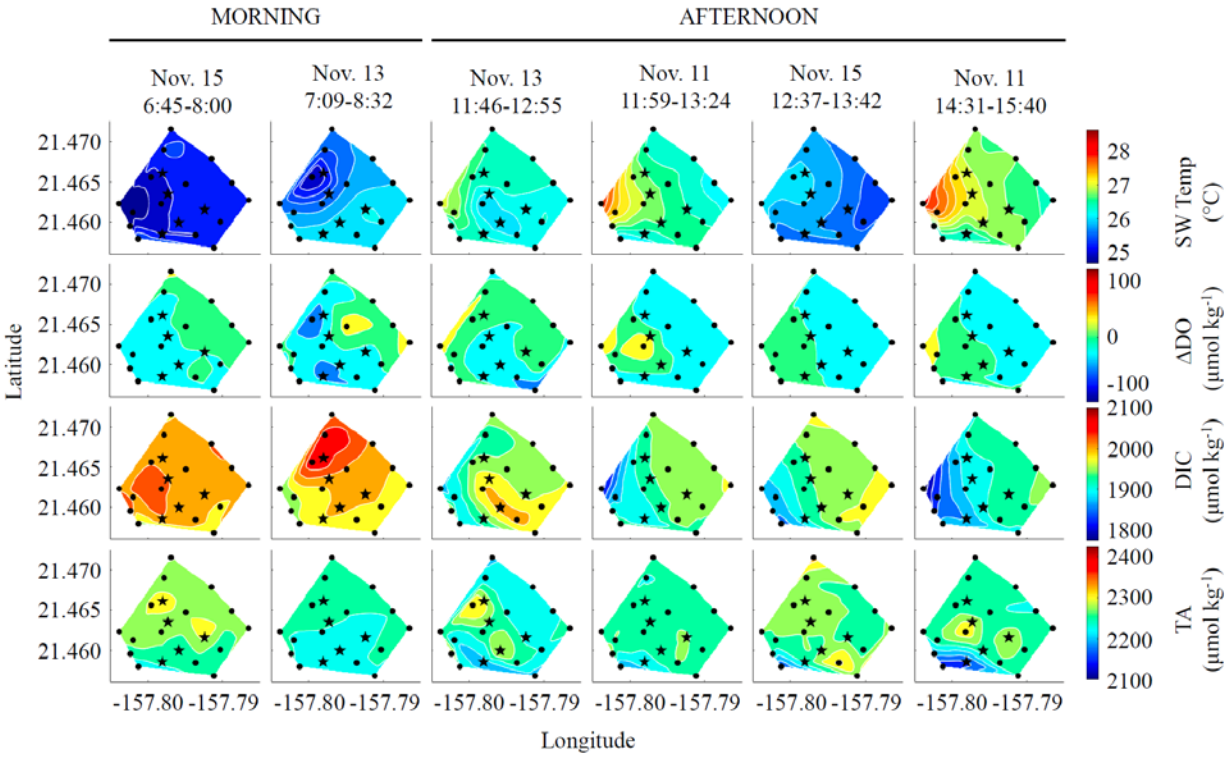


Figure 4.6. Spatial variability in seawater T, ΔDO, DIC, and TA for November morning and afternoon with color gradients representing the range of values. Contour intervals (white lines) show 0.2°C or 25 µmol kg^{-1} for ΔDO, DIC, and TA.

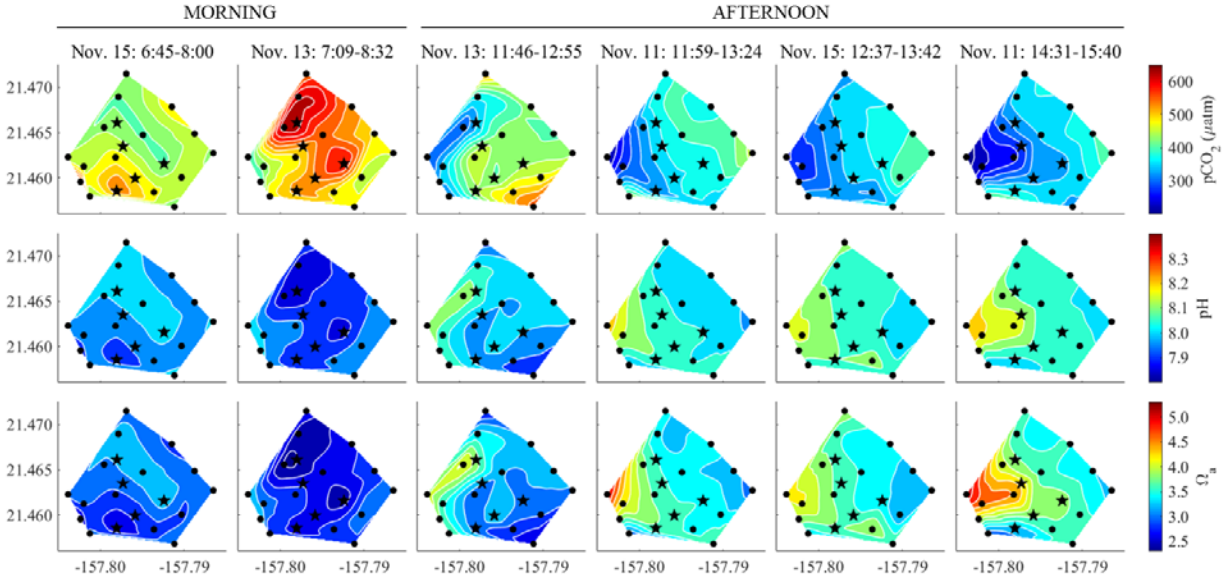


Figure 4.7. Spatial variability in pCO_2, pH, and Ω_a for November morning and afternoon with color gradients representing the range of values. Contour intervals (white lines) show 25 µatm pCO_2, 0.05 pH, or 0.2 Ω_a.

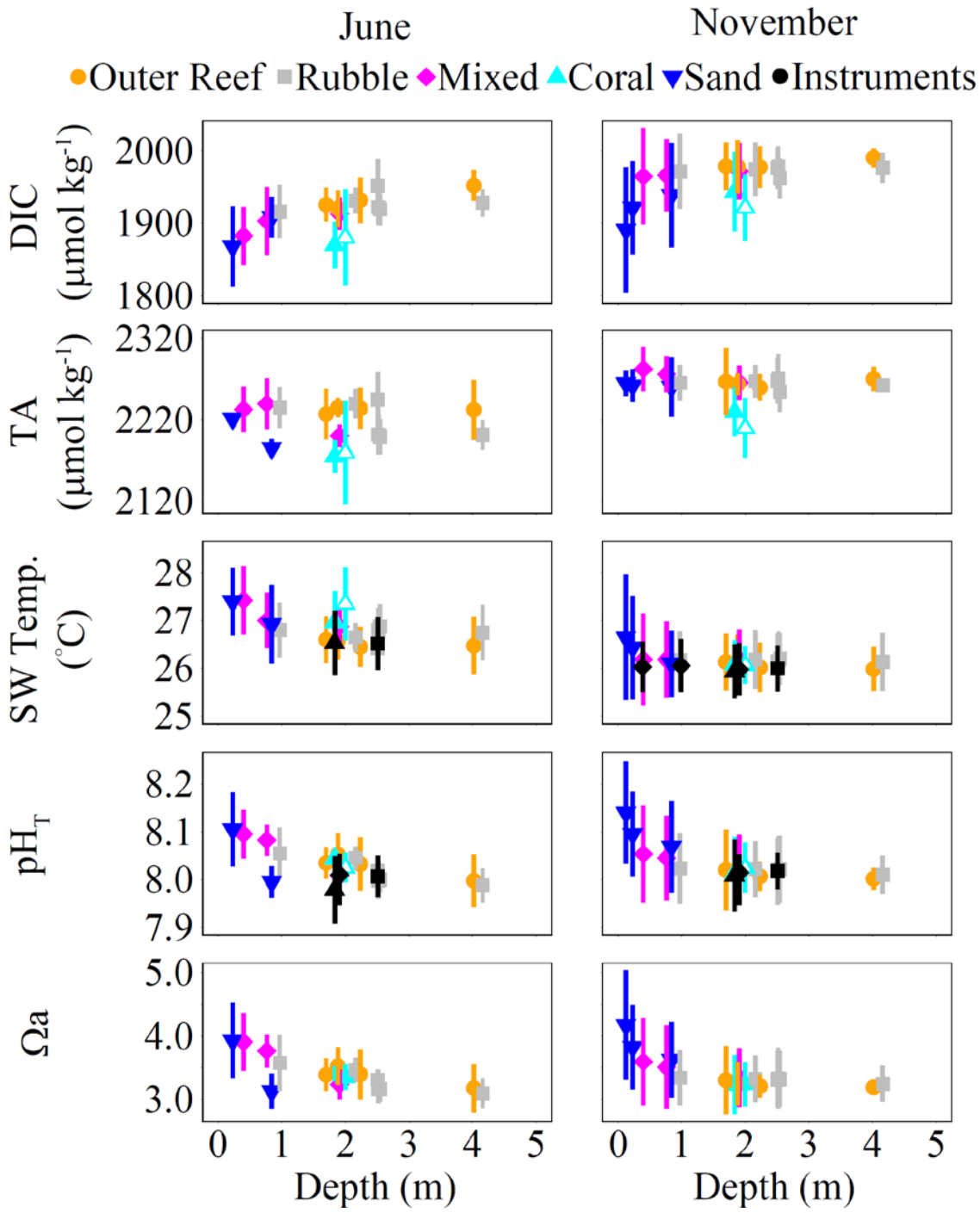


Figure 4.8. Seawater chemistry as a function of depth with shapes and colors representing the benthic communities (reef break: orange circle; rubble: yellow square; mixed community: magenta diamond; coral: cyan triangle; sand: blue inverse triangle) and instrument measurements (black). The open cyan triangle represents an estimated depth since this site is located on a slope. In general, seawater flowed from the outer reef (deeper sites) over rubble and mixed communities before reach coral and sand.

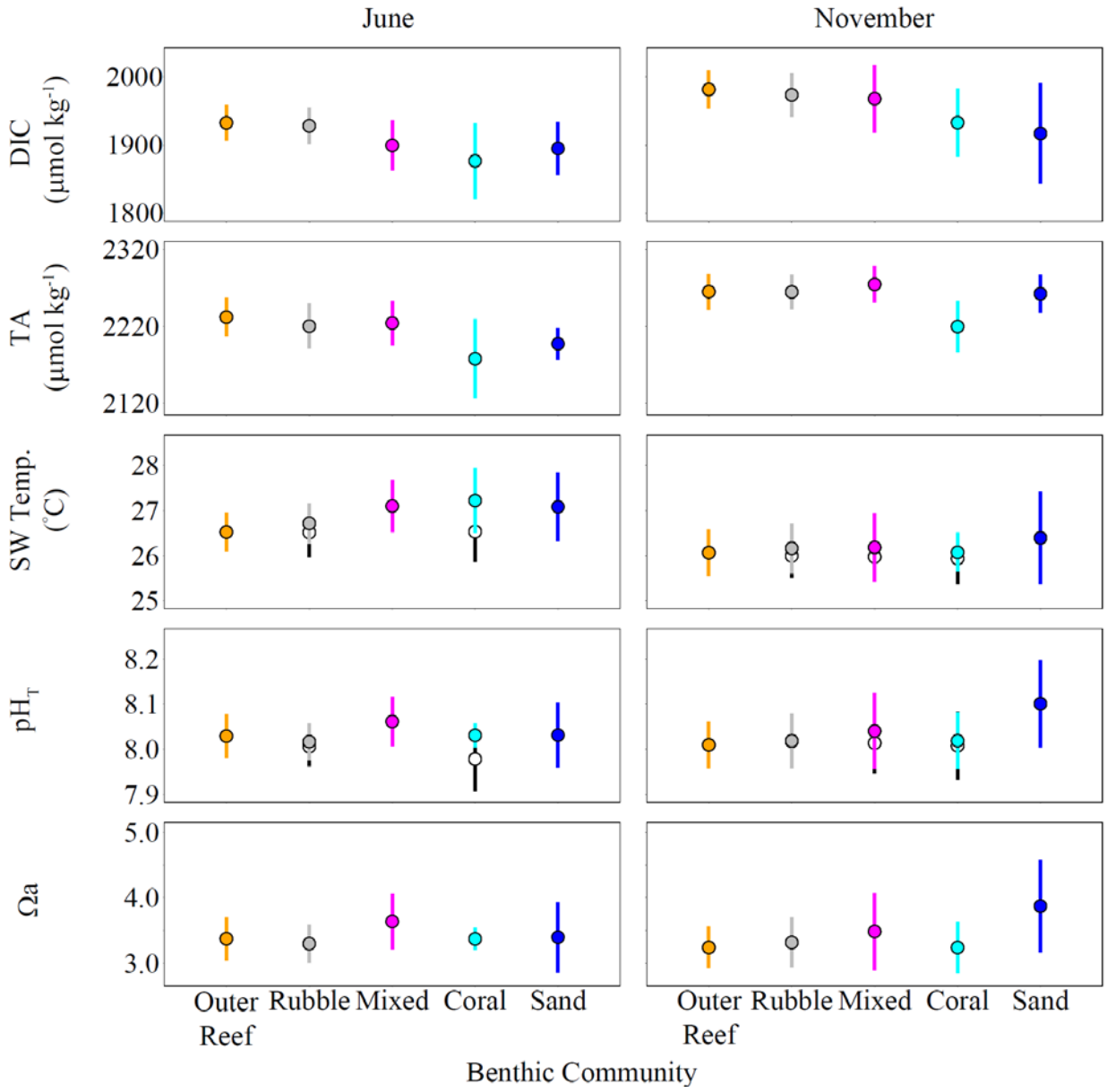


Figure 4.9. Seawater chemistry (mean ± 1 sd) as a function of benthic community with colors representing data collected from the spatial surveys and open black symbols showing data from the instruments on the benthos.

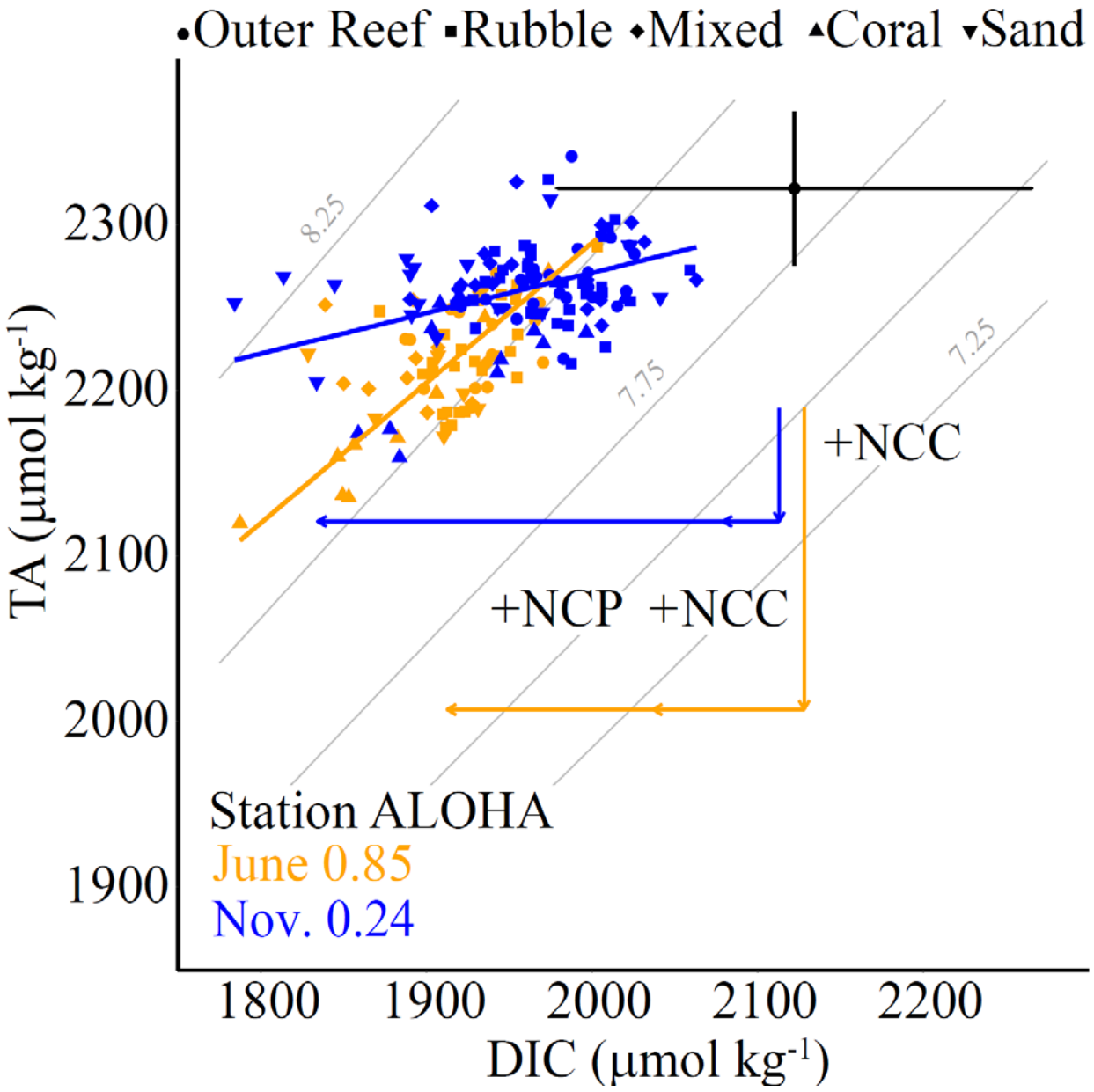


Figure 4.10. Seawater TA and DIC of the reef relative to offshore waters at Station ALOHA (mean ± 1 sd) with Type II linear regressions for June (blue) and November (orange). The larger regression during June (0.85) reflects nearly balanced NCC and NCP while NCP was dominant during November (0.24). The shapes represent different benthic communities and show the biggest TA and DIC drawdown for coral communities. pH isolines are shown as the grey lines.

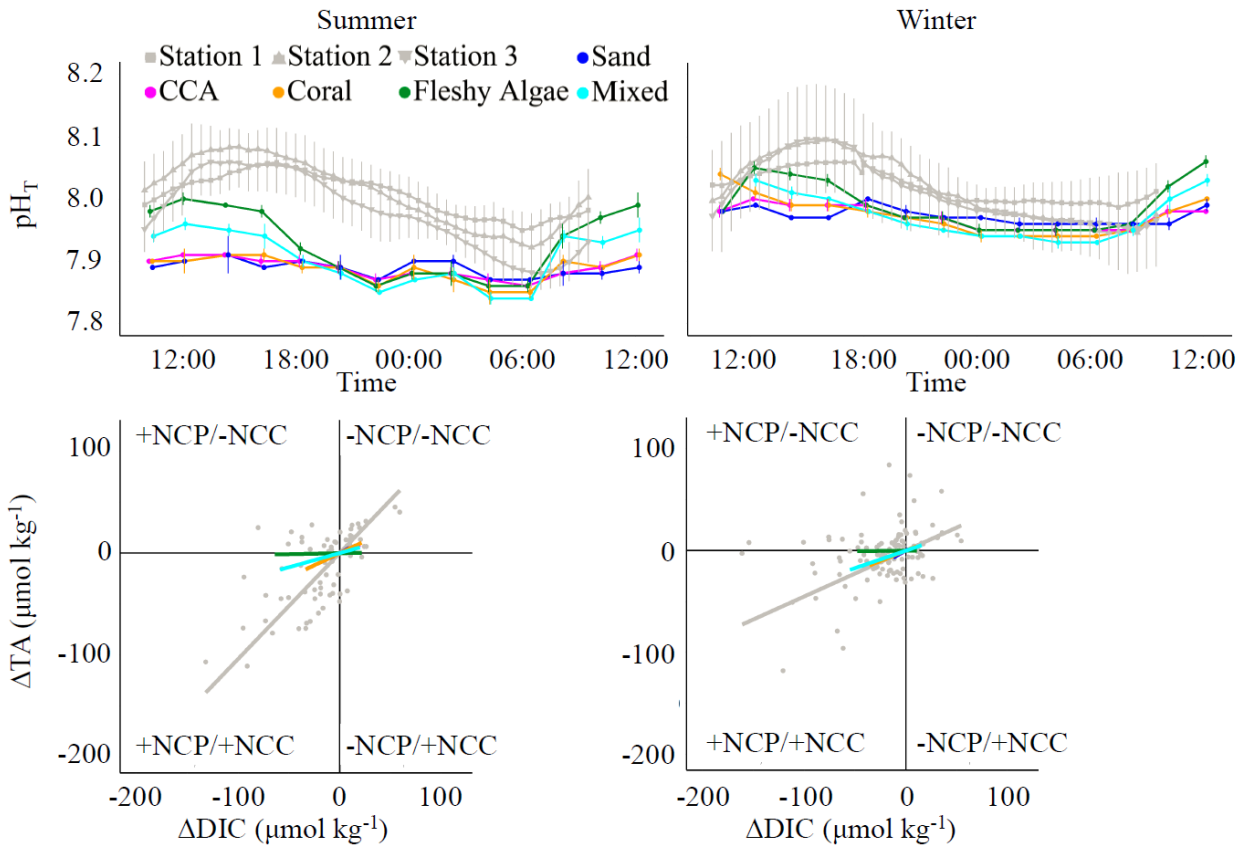


Figure 4.11. Comparison to previous mesocosm experiments (Page et al. 2016) showing seawater pH (mean ± 1 sd) over 24 hours (top) and seawater ΔTA:ΔDIC regressions (bottom). The ΔTA and ΔDIC values for the present study were calculated as the offset from mean values at Station ALOHA.

CHAPTER 5

Summary of Key Findings

Heather N. Page

5.1 Key findings of the dissertation

In order to predict how coral reefs may fare under long-term changes in seawater CO_2 chemistry and pH, we must first understand what chemical conditions reefs experience presently and how these conditions may change in the future. This requires taking into account natural variability in seawater chemistry and potential responses of the factors (e.g. community composition, NCC, NCP, seawater flow) that drive this natural variability to various co-occurring regional disturbances and global climate change. This dissertation contributes to this field by demonstrating the importance of coral reef community composition to benthic metabolism (NCC and NCP) and seawater carbonate chemistry variability.

Mesocosm experiments showed that observed diurnal changes in seawater pH and Ω_a and differences between benthic communities are directly attributed to NCC and NCP (Page et al. 2016). During the day, calcifying communities (sand, CCA, and corals) did not modify seawater pH and Ω_a due to counter-balancing influence of net calcification (+NCC) and net organic carbon production (+NCP) on seawater TA and DIC. Fleshy macroalgae, however, elevated seawater pH and Ω_a by 0.1 and 0.6, respectively, owing to high net organic carbon production (+NCP) with insignificant NCC. A mixed community containing calcifiers and fleshy macroalgae also elevated daytime seawater pH and Ω_a albeit to a lesser extent since net organic carbon production (+NCP) outweighed acidification owing to net calcification (+NCC). At night, all communities slightly acidified seawater as net calcification (+NCC) and net respiration (-NCP) occurred. Seasonal differences in NCP rates led to smaller diurnal changes in seawater pH and Ω_a owing to the benthic communities during winter compared to summer.

Communities maintained NCC and NCP rates during both seasons when exposed to short-term OA simulating conditions expected by 2100 (IPCC 2013). However, changes to seawater buffering capacity under OA would be expected to cause larger influence of benthic metabolism on pH (i.e., higher elevation of pH during the day and additional acidification at night). Indeed, fleshy macroalgae and mixed communities boosted seawater pH more during the day. However, the anticipated additional acidification by net calcification (+NCC) and net respiration (-NCP) at night did not occur, possibly due to increased calcium carbonate dissolution. Thus, net organic carbon production (+NCP) by fleshy macroalgae and mixed communities as well as calcium carbonate dissolution of communities, which are spatially and temporally variable on reefs in response to environmental changes, may partly locally offset long-term anthropogenic OA.

Additionally, mesocosm experimental results revealed that TA-DIC regression analysis may be useful for assessment of the functional community composition and ecosystem function of reefs since each benthic community had a different TA-DIC regression slope. The TA-DIC regression slope reflects the relative balance of NCC and NCP. Thus, the calcifying communities had the highest slopes ranging 0.40-1.60 while the fleshy macroalgae had the lowest slopes (0.01-0.16). The mixed community represented each functional community since the slopes were intermediate (0.28-0.38) relative to the calcifying and fleshy macroalgae communities.

In mesocosm experiments, NCC and –NCP (i.e., net respiration at night) scaled proportionally to coral cover while +NCP (i.e., net organic carbon production during the day) did not. Therefore, while NCC may be scaled across communities and reefs with different coral cover, NCP cannot simply be scaled the same way. The observed scaling of metabolic

rates in the mesocosm experiment caused increasing diurnal variability of seawater pH, Ω_a, and pCO_2 with increasing coral cover. Specifically, coral communities experienced similar chemistry during the day when there were smaller differences in NCP between communities and increasing acidification with increasing coral cover at night owing to combined effects of net calcification (+NCC) and net respiration (-NCP). Similarly, field measurements showed greater diurnal ranges of seawater CO_2 for coral reefs in Bermuda and Hawaii with higher coral cover.

Field observations on a reef flat in Kaneohe Bay built on the previous mesocosm experiments by demonstrating that seawater carbonate chemistry variability across space and time depends on a combination of ecological, biogeochemical, and hydrodynamic properties of the reef. Mean conditions and spatial variability in seawater chemistry most closely followed depth gradients which reflects the importance of seawater volume (i.e., shallow or deep water) to benthic biomass ratio for controlling seawater conditions on the reef. Shallower areas typically experienced the highest variability and mean temperature, pH and Ω_a during the day. Seawater circulation, which generally flows from the outer reef over the rubble and mixed communities before reaching coral and sand communities, also influences temporal and spatial variabilities since it relates to the history of modification to seawater chemical properties. While these physical drivers are dominant on this reef flat, variations in community composition, particularly coral cover, also played a role in modifying local seawater conditions. Areas with dominated by corals experiencing lower TA and DIC, primarily owing to high net calcification rates (+NCC) and net organic carbon production (+NCP) during the day. During June, pH minima were increasingly lower as coral cover increased, confirming mesocosm observations. During November, pH maxima were higher

over coral and algae dominated communities when light was higher. However, the coral community was located inshore relative to other communities, and thus seawater pH also represents previous modifications that were accumulated over time. These results highlighting the combined influence of multiple drivers that often are co-varying generally agree with coupled hydrodynamic-biogeochemical models suggesting the importance of benthic metabolism, seawater residence time, and reef topography (i.e. seawater depth) to seawater carbonate chemistry on reefs in Australia (Zhang et al. 2012; Falter et al. 2013). In general, the reef flat in Kaneohe Bay was net calcifying and net autotrophic with higher +NCC and TA-DIC regression slope during June compared to November. Thus, this reef flat experiences diurnal, seasonal, and spatial variations in seawater chemistry owing to a combination of ecological (i.e., community composition), biogeochemical (i.e., NCC and NCP), and physical oceanographic (i.e., seawater depth and flow) processes. This field study highlights the natural complexity of coral reef ecosystems which needs to be considered when predicting *in situ* responses of reefs to future OA.

In conclusion, community composition of a coral reef influences diurnal and spatial seawater CO_2 chemistry through effects on the relative balance of NCC and NCP. However, bridging these experimental results to natural settings requires consideration of environmental conditions (e.g. light and temperature) and physical oceanographic properties of the reef (e.g. seawater depth and flow), which also exert strong influences on *in situ* temporal and spatial variabilities. Therefore, projections of future regional OA on coral reefs should carefully consider the feedbacks between biological and physical properties of the reef and seawater CO_2 chemistry in order to more accurately identify reefs that will experience exacerbated or alleviated acidification from combined anthropogenic OA and natural variability.

5.2 References Cited

Falter, JL, Lowe, RJ, Zhang, Z, & McCulloch, M. 2013. Physical and biological controls on the carbonate chemistry of coral reef waters: Effects of metabolism, wave forcing, sea level, and geomorphology. *PLoS ONE* 8:e53303.

IPCC. 2013. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

Page, HN, Andersson, AJ, Jokiel, PL, Rodgers, KS, Lebrato, M, Yeakel, K, Davidson, C, D'Angelo, S, & Bahr, KD. 2016. Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral Reefs*. 35: 1311-1325.

Page, HN, Courtney, TA, Collins, A, De Carlo, EH, & Andersson, AJ. 2017. Net community metabolism and seawater carbonate chemistry scale non-intuitively with coral cover. *Frontiers in Marine Science* 4:161. doi: 10.3389/fmars.2017.00161.

Zhang, Z, Falter, J, Lowe, R, & Ivey, G. 2012. The combined influence of hydrodynamic forcing and calcification on the spatial distribution of alkalinity in a coral reef system. *Journal of Geophysical Research: Oceans* 117: C04034. doi: 10.1029/2011JC007603.