The changing carbonate chemistry of coral reefs: ocean acidification, submarine groundwater discharge, and calcium carbonate (CaCO3) sediment dissolution

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The changing carbonate chemistry of coral reefs: Ocean acidification, submarine groundwater discharge, and calcium carbonate (CaCO$_3$) sediment dissolution

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Submitted for the completion of a PhD

April, 2013
Declaration

I, Tyler Cyronak, certify that the work presented in this thesis is, to the best of my knowledge and belief, original, except as acknowledged in the text, and that the material has not been submitted, either in whole or in part, for a degree at this or any other university.

I acknowledge that I have read and understood the University's rules, requirements, procedures and policy relating to my higher degree research award and to my thesis. I certify that I have complied with the rules, requirements, procedures and policy of the University (as they may be from time to time).

Print Name:

Signature:

Date:
Preface

This thesis investigated two interrelated topics; (1) changing carbonate chemistry in coral reefs over short (tidal and diel) timescales, and (2) the impacts of ocean acidification on the dissolution of calcium carbonate (CaCO$_3$) sediments. The two topics are related because anthropogenic CO$_2$ inputs are raising the $p$CO$_2$ and lowering the pH of seawater at rates unprecedented in the past ~2 million years (Hönisch et al. 2012). In order to determine how rising atmospheric CO$_2$ will affect coral reef ecosystems it is necessary to understand the natural drivers of carbonate chemistry in these ecosystems. Therefore, the first portion of the introduction focuses on the natural drivers of carbonate chemistry in coral reefs. This leads into the first portion of my thesis (Chapters 1-3) that examines how sediment metabolism and groundwater inputs can influence diel and tidal cycles of water column carbonate chemistry. The second portion of the introduction reviews how the expected increase in seawater $p$CO$_2$ will affect the dissolution of CaCO$_3$ sediments. This was later examined in detail in chapter 5 by conducting in situ benthic incubations under current and elevated $p$CO$_2$ conditions. The two portions of the thesis are interconnected as changes to the natural variability in seawater carbonate chemistry will undoubtedly affect the dissolution of CaCO$_3$ sediments under future climate change scenarios.

This thesis is comprised of six chapters, some of which have been published or in the process of being published in scientific journals. Chapter 1 is an introduction that reviews our knowledge on the subjects outlined above. At the time of submitting this thesis, a portion of Chapter 1 (Appendix 1) is being prepared for publication with the title “Enhanced coral reef acidification driven by regional biogeochemical feedbacks.” This portion is included in the appendix because it contains a large portion (coral reef metabolism model) that was done by co-author Dr. Kai Schulz. Chapter 2 is a high resolution study of benthic CaCO$_3$ sediment metabolism over the course of a diel cycle. It
has been published in Limnology & Oceanography with the title “Carbon cycling hysteresis in permeable carbonate sands over a diel cycle: Implications for ocean acidification.” Chapter 3 examines the influence of CaCO$_3$ sediment metabolism and groundwater on the flux of alkalinity to a coral reef ecosystem (Rarotonga, Cook Islands). It has been published in Biogeosciences with the title “Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands).” Chapter 4 examines the influence of submarine groundwater discharge on the carbonate chemistry of two diverse coral reef ecosystems. This chapter is currently under the second round of revisions in the journal Global Biogeochemical Cycles with the title “Drivers of $p$CO$_2$ variability in two contrasting coral reef lagoons: The influence of submarine groundwater discharge.” Chapter 5 examines the influence of increasing $p$CO$_2$ on the dissolution of CaCO$_3$ sediments in situ. This chapter has been published in the journal Geophysical Research Letters with the title “Permeable coral reef sediment dissolution driven by elevated $p$CO$_2$ and pore water advection.” Chapter 5 was published with a supplemental section, which is presented as Appendix 2 in this thesis. Chapter 6 is a synthesis of the conclusions that can be drawn from the work done during this PhD thesis.

All previously published articles appear in their publication format at the end of this thesis in Appendix 3. Other articles that I was not first author on, but contributed extensively to, are also included in Appendix 3 (McMahon, 2013). The following are the citations for all articles currently under review or previously published relating to this thesis:


Statement of contribution


I performed field work, analysed the data, and wrote the original manuscript.


I performed field work, analysed the data, and wrote the original manuscript.


I performed field work, analysed the data, and wrote the original manuscript.


I performed field work, analysed the data, and wrote the original manuscript.


I performed field work, analysed the data, and wrote the original manuscript. K.G. Shulz developed and implemented the model.


I performed field work, analysed the data, and edited the original manuscript.
Acknowledgements

Firstly, I would like to thank my friends and family for supporting me on this journey. I couldn’t have done this without both of my parents convincing me this was a once in lifetime opportunity to move to the other side of the world and it couldn’t be passed on. I’d like to thank my Mom for supporting me in every way possible and my Dad who has instilled a love for science and critical thinking in me from an early age. My Aunt Mary and Uncle Tim helped make the decision to move overseas infinitely easier by agreeing to take my two black labs Kerouac and Ella into their home. I’d like to thank my friends in Australia who have made this place feel like a home for the past 3 years and the rest of my friends throughout the world for their support. I’d also like to thank my amazing partner, Ashley, for supporting me through the up and downs that come with doing a PhD thesis.

I thank my two advisors, Bradley Eyre and Isaac Santos, who provided invaluable support throughout the thesis and taught me to write publishable manuscripts. I couldn’t have completed my thesis without the support of the many postdocs and technicians in the Centre for Coastal Biogeochemistry. Iain Alexander helped to organize the logistics of my thesis and ran nutrient samples. Matheus Carvalho skilfully ran DIC concentration and isotope samples. Ashley McMahon, Kevin Befus, Alicia Hidden, and Douglas Tait provided invaluable help during field campaigns. I’d also like to acknowledge the staff of the Heron Island Research Station for their invaluable support during our investigations. This thesis was largely funded by the Australian Research Council grants (LP100200732 and DP110103638), the Australian Agency for International Development (AusAID), and the Cook Islands Ministry of Infrastructure and Planning.
Abstract

Physical uptake of anthropogenic CO$_2$ is the dominant driver of ocean acidification (OA) in the open ocean, which is lowering the pH of seawater at unprecedented rates. Coral reef ecosystems are thought to be highly susceptible to OA due to an expected decrease in calcification rates and increased dissolution of calcium carbonate (CaCO$_3$) framework. However, multiple processes can influence the $p$CO$_2$ and pH of coastal ecosystems on diel and seasonal timescales, potentially masking or intensifying any effects of increasing atmospheric CO$_2$. Therefore, it is important to quantify any biogeochemical drivers of carbonate chemistry variability in coral reef ecosystems that could act as positive or negative feedbacks to OA. This thesis focuses on the impacts of permeable sediment metabolism and submarine groundwater discharge on the carbonate system of coral reef ecosystems and, subsequently, the dissolution of CaCO$_3$ sediments.

To better predict how OA will affect coral reefs it is important to understand how biogeochemical cycles on reefs alter carbonate chemistry over various temporal and spatial scales. Submarine groundwater discharge (SGD) was a source of total alkalinity (TA) to the lagoon, with the highest fluxes measured at low tide, and an average daily TA flux of 1,080 mmol m$^{-2}$ d$^{-1}$ at the sampling site. The diel variability of $p$CO$_2$ in two distinct coral reef ecosystems was explained by a combination of biological drivers and SGD inputs. In Rarotonga, a South Pacific volcanic island, $^{222}$Rn-derived SGD was driven primarily by a steep terrestrial hydraulic gradient, and the water column was influenced by the high $p$CO$_2$ (5,501 µatm) of the fresh groundwater. In Heron Island, a Great Barrier Reef coral cay, SGD was dominated by seawater recirculation through sediments (i.e. tidal pumping) and $p$CO$_2$ was mainly impacted through the stimulation of biological processes.

Although permeable sediments represent the largest reservoir of CaCO$_3$ in coral reefs, the dissolution of shallow CaCO$_3$ sands under future $p$CO$_2$ levels has not been
measured under natural conditions. A complex hysteretic pattern between precipitation and dissolution of CaCO$_3$ sands and the aragonite saturation state (\(\Omega_{Ar}\)) of the overlying seawater was observed over the course of a diel cycle. The observed diel hysteresis seems to reflect a complex interaction between photosynthesis and respiration rather than \(\Omega_{Ar}\) as the main driver of carbonate precipitation and dissolution within permeable reef sediments. However, in situ, advective chamber incubations under elevated \(pCO_2\) (~800 \(\mu\)atm) shifted the sediments from net precipitating to net dissolving.
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Chapter 1

Introduction
1.1 Coral reef carbonate chemistry: Agents of change

The recent increase in atmospheric CO$_2$ has led to an increase in oceanic $p$CO$_2$ as roughly 30% of anthropogenically produced CO$_2$ has been absorbed by the oceans (Feely et al. 2004; Sabine et al. 2004; Orr et al. 2005; Doney et al. 2009). The accumulation of CO$_2$ in seawater changes the overall composition of dissolved inorganic carbon (DIC) species and lowers the pH (Zeebe and Wolf-Gladrow 2001; Morse and Arvidson 2002). Ocean acidification (OA) is the term given to this increase in oceanic $p$CO$_2$ and the associated changes in carbonate chemistry and reduction in pH (Feely et al. 2004; Doney et al. 2009; Bates and Dickson 2012). Ocean acidification can have drastic effects on biological processes and the biogeochemistry of marine ecosystems, with coral reefs thought to be some of the most susceptible ecosystems (Fabry et al. 2008; De’ath et al. 2009; Kleypas and Yates 2009). The biogeochemical processes occurring in coral reefs can modify the carbonate chemistry of the overlying seawater, leading to large diel and seasonal variations in $p$CO$_2$, pH, and dissolved oxygen (DO) (Bates 2002; Gray et al. 2012; Shaw et al. 2012; Silverman et al. 2012). In order to understand how OA will affect coral reefs, it is important to understand how natural processes, which can potentially buffer or intensify changes in $p$CO$_2$, alter the carbonate chemistry of seawater in coral reef ecosystems.

In coastal ecosystems multiple natural and anthropogenic factors can influence the seawater carbonate system on diel and seasonal time scales (Kayanne et al. 1995; Bates 2002; Kayanne et al. 2005; Blackford and Gilbert 2007). This variability represents a challenge to predicting how increasing atmospheric CO$_2$ concentrations will affect the carbonate system of coastal ecosystems such as coral reefs (Kleypas and Yates 2009; Andersson and Mackenzie 2012; Duarte et al. 2013). Due to their reliance on CaCO$_3$ framework to create habitat structure, coral reefs are some of the most susceptible
ecosystems to OA (Hoegh-Guldberg et al. 2007). However, the diel and seasonal variability of $pCO_2$ in coral reefs is among the largest for coastal ecosystems (Bates 2002; Silverman et al. 2007; Anthony et al. 2011; Andersson and Mackenzie 2012), and the influence of this variability on OA is just beginning to be explored. Models indicate that increases to the Revelle factor of the open ocean due to increasing $CO_2$ will amplify the diel variability of coral reef $pCO_2$ (Shaw et al. 2013, Jury et al. 2013). The models also show that a reduction in the seawater buffering capacity will cause pH to drop well below what is expected to occur in the open ocean by the year 2100 over the course of a day. Therefore, any drivers of carbonate system variability in coral reefs may be equally important as increasing atmospheric $CO_2$ in modulating the acidification of coral reefs.

Diel variation

The diel variability of coral reef $pCO_2$ is significant (~100-1500 µatm), with the majority this variation driven by benthic metabolism (i.e. production, respiration, and calcification). Numerous studies have examined rates of ecosystem production ($P$), respiration ($R$), and net calcification ($G$), which all affect $pCO_2$. Production decreases $pCO_2$ through the photosynthetic uptake of $CO_2$ while respiration releases $CO_2$ through the remineralisation of organic matter (OM). Calcification increases $CO_2$ through changes in carbonate chemistry, as ~0.6 moles of $CO_2$ are released for each mole of CaCO$_3$ formed (Frankignoulle et al. 1994). Calcification also influences the TA of seawater as TA is taken up in a 2:1 molar ratio when CaCO$_3$ is precipitated. Therefore, the rates of production, respiration, and calcification in benthic communities determine their influence on water column $pCO_2$. Community coral reef production ($P$) rates range from 216-1,600 mmol C m$^{-2}$ y$^{-1}$ and respiration ($R$) rates range from 208-1,474 mmol C m$^{-2}$ y$^{-1}$, resulting in net ecosystem production (NEP) rates (i.e. $P/R$) of close to 1 (Gattuso et al. 1998b; Gattuso
net et al. 1999). These changes result in large daytime uptake rates and night-time production rates of CO₂, while NEP rates on longer timescales have a near net zero effect on pCO₂. Net ecosystem calcification (NEC) rates of coral reefs range from -22 to 331 mmol CaCO₃ m⁻² d⁻¹ (see Table 2 in Andersson and Gledhill, 2013), with a global average of ~40 mmol CaCO₃ m⁻² d⁻¹ (Milliman and Dro xler, 1996). Therefore, calcification is thought to be a more significant source of CO₂ to coral reefs than NEP on longer timescales. Interestingly, any decrease in calcification due to OA will act to reduce the pCO₂ of coral reef ecosystems.

The benthos of coral reefs are a diverse assemblage of calcifying and non-calcifying algae, sediments, corals, and seagrasses, all of which have variable impacts on the carbonate system (Boucher et al. 1998). Specific communities modify the water column chemistry of coral reefs in complex ways. While coral communities are a net source of pCO₂, non-calcifying algae draw down pCO₂ (Anthony et al. 2011; Anthony et al. 2012). This difference is attributed to the high rates of coral calcification and imply that high macro-algal abundance may partially buffer downstream reef habitats against OA. Field data from Tiahura Reef, Moorea revealed that a reduction in % coral cover and increase in % algae cover increased pCO₂ uptake (Kleypas et al. 2011). However, this is based off of short term data and doesn’t reflect the capture and storage of OM by algae, which could later be remineralised into CO₂ over longer time scales.

Seasonal and latitudinal variation

A comprehensive seasonal study of pCO₂ at Hog Reef, Bermuda from 1994-1998 revealed a ~150 μatm variation in pCO₂ between winter and summer months (Bates, 2002). The reef was a net source of CO₂ to the atmosphere in the summer (~40-60 μatm above atmospheric) and a net sink in the winter (~40 μatm below atmospheric). This
seasonal trend of higher CO$_2$ in the summer compared to the winter agrees with other studies throughout the world and is related to changes in the $p$CO$_2$ of offshore water masses (i.e. temperature effects) and changes in community metabolism. Hog Reef was shown to be net productive in the summer and net heterotrophic in the winter, similar to other seasonal studies on reef metabolism (Langdon and Atkinson, 2005; Falter et al. 2012). The Hog Reef community production rates tracked changes in temperature corrected $p$CO$_2$ values, which were higher in the winter and lower in the summer. Community calcification has been shown to be relatively similar across seasons in Hog Reef (Bates, 2002) and along the GBR (Shaw et al. 2012). Therefore, any release of CO$_2$ due to calcification should not have any significant effect on the seasonal variation of $p$CO$_2$. However, a positive relationship between calcification and increasing temperature above 23°C and an increasing trend with decreasing temperature below 23°C was observed in Eilat Reef (Silverman et al. 2007). Observations of seasonal trends in $p$CO$_2$ and changes in reef metabolism indicate that increases in temperature drive the majority of the summertime increase in $p$CO$_2$, while seasonal changes in production have an opposing effect.

Since 1966 the average oceanic temperature has increased ~0.5°C (Grist et al. 2010; Bates and Dickson 2012) which would account for an increase in $p$CO$_2$ of ~10 µatm (Sweeney et al. 2002). Since $p$CO$_2$ increases ~150 µatm for an 8°C increase in temperature (Sweeney et al. 2002), diel variability is often well above any seasonal changes due to temperature in tropical regions. The trend of $p$CO$_2$ observed during diel cycles is consistent with this, as higher $p$CO$_2$ is observed at night when temperatures are lowest, overriding any physical effect of temperature on water column $p$CO$_2$ (Schmalz and Swanson, 1969; Kayanne et al. 1995). A cruise along the GBR in the winter of 1996 revealed that lagoon $p$CO$_2$ was significantly higher than that of offshore waters (Suzuki et
al. 2001). When normalized to temperature, the coral lagoons in the lower latitudes of the GBR had higher $p$CO$_2$. A large portion of this difference was attributed to latitudinal differences in terrestrial OM inputs along with the high calcification rate of lagoons (see Fig. 3 in Suzuki et al. 2001). About 80% of the higher $p$CO$_2$ in northern lagoons was estimated to be from terrestrial inputs, while 50% was due to terrestrial inputs in the southern lagoons.

**Watershed processes**

Watershed processes can influence the $p$CO$_2$ of coral reef ecosystems in various ways (Kawahata et al. 2000; Suzuki et al. 2001; Duarte et al. 2013). An increase in rainfall can influence the $p$CO$_2$ of coral reefs by increasing groundwater and river fluxes, or by dilution. Dilution is often limited to enclosed lagoons and river mouths and may increase $p$CO$_2$ by shifting speciation in the carbonate system. Increased watershed inputs would not only have a direct effect on $p$CO$_2$ through dilution or direct CO$_2$ delivery; but also through inputs of OM and nutrients (Suzuki et al. 2001). For instance, in Panama the average $p$CO$_2$ during the day was lower during the wet season due to the shoaling depth (Manzello, 2010). However, similar $p$CO$_2$ was observed at night between the wet and dry seasons indicating a stimulation of daytime production during the wet season, potentially through increased nutrient inputs. This also indicates that drier climates may result in elevated $p$CO$_2$ levels, although this is probably highly variable between coral reef ecosystems. In fact, observations in the GBR (Suzuki, 2001) and Ishigaki Island (Kawahata et al. 2000) demonstrated increased $p$CO$_2$ with terrestrial watershed inputs. This indicates that the influence of watershed inputs on $p$CO$_2$ is variable between ecosystems.
Chapter 1

Submarine groundwater discharge (SGD) has been shown to be an important component of freshwater delivery to coastal ecosystems, on the scale of 6% to 10% of surface water flow, which amounts to an estimated 10,000 L m$^{-1}$ d$^{-1}$ along the global coast (Burnett et al. 2003; Santos et al. 2012). Discharge rates of groundwater on coral reefs range from 52 to 4,732 L m$^{-1}$ h$^{-1}$ making SGD an important source of nitrogen to coral reef ecosystems (Lewis 1987; D'elia and Wiebe 1990; Paytan et al. 2006). There are multiple methods to estimate SGD into coastal ecosystems including seepage meters, piezometers, natural tracers, water balance approaches, and theoretical modelling (Burnett et al. 2006). Due to its naturally high concentrations in groundwater compared to surface waters and its unreactive nature, $^{222}$Rn has been used as a natural tracer for groundwater in aquatic systems (Cable et al. 1996a; Cable et al. 1996b; Burnett et al. 2006). Mixing models of $^{222}$Rn that take into account atmospheric evasion based on wind speeds have been developed that allow researchers to estimate groundwater fluxes into coastal ecosystems (Burnett and Dulaiova 2003).

Groundwater concentrations of TA can be higher than oceanic waters and encompasses a broad range from 90 to 23,300 µmol L$^{-1}$ (Mahlknecht et al. 2004; Rad et al. 2007; Moore et al. 2011; Schopka and Derry 2012). Moore et al. (2011) calculated radium based SGD fluxes of alkalinity to the water column in the Wadden Sea as high as 150 kmol per tidal cycle. Therefore, groundwater exchange processes have the potential to deliver TA to coral reef lagoons. In fact, Kleypas and Langdon (2006) postulated that ocean acidification may be buffered against in coral reef ecosystems through the exchange of groundwater. The ability of groundwater to act as a source of TA to coral reef lagoons is highly dependent on the exchange rates with the water column, which can have large temporal and spatial variation (Lewis 1987; Burnett et al. 2003; Santos et al. 2012). Dependent on the CO$_2$ concentration of the groundwater and groundwater flow, submarine
groundwater discharge (SGD) can directly influence the $pCO_2$ of coastal ecosystems (Atkins et al. 2013). Groundwater tends to have higher CO$_2$ concentrations than surface waters due to microbial decomposition and the subsequent build-up of CO$_2$, and therefore may be a source of CO$_2$ at the same time it is a source of TA. Determining how groundwater chemistry will affect the carbonate chemistry of coastal ecosystems is important in constraining whether any groundwater sources of TA can act as a positive or negative feedback to OA.

Coral reefs with the highest productivity are associated with higher nutrient inputs (Gattuso et al. 1998) and the loading of nutrients in groundwater has been shown to increase due to human activities, resulting in increased nutrient fluxes to coastal ecosystems (Hughes et al. 2003; Doney, 2010). The flux of nutrients into reefs and associated increase in production could act to paradoxically raise the $pCO_2$ of these ecosystems. Due to the Revelle factor, photosynthesis lowers $pCO_2$ less than respiration raises $pCO_2$ even though the same amount of DIC is consumed or produced (Egleston et al. 2010). Therefore, even though photosynthesis draws down CO$_2$, increases to general reef metabolism could act to raise the average $pCO_2$ of coral reefs. Also, the tight cycling of production and respiration in coral reefs (Gattuso et al. 1998) means that OM produced from photosynthesis is later remineralised. While $pCO_2$ is reduced by production on short timescales, the loading of OM could act to raise $pCO_2$ over longer timescales.

A direct of example of terrestrial inputs leading to increased $pCO_2$ may be evident in the high average $pCO_2$ values of Kaneohe Bay (Fig. 2), which is subject to large inputs of nutrients (Ringueut and Mackenzie, 2005; Drupp et al. 2011). CO$_2$ was drawn down during the rainy season when nutrients stimulate production (Drupp et al. 2011). However, Kaneohe Bay has some of the highest average $pCO_2$ values reported in worldwide coral reefs, which may be indicative of high rates of OM remineralisation.
Production driven OM remineralisation on coral reefs may be highly dependent on how OM is stored. For example, the input of nutrients from sewage discharge resulted in pelagic algal blooms in Kaneohe Bay in ~1960-1970 (Smith et al. 1981). The pelagic blooms subsided soon after the sewage discharge ceased, however, macro-algae abundance remained elevated due to nutrients stored in the sediments (Szmant, 2002). The eutrophication of Kaneohe Bay may offer insights into the storage of nutrients and OM in reef sediments and subsequent elevation of $pCO_2$.

In summary, the effects of watershed inputs on coral reef $pCO_2$ is highly variable and is most likely dependent on numerous factors including annual rainfall amounts, source water chemistry, elevation of the land mass associated with the reef, proximity to rivers, and anthropogenic impacts to the watersheds. Anthropogenic changes to watershed inputs could act to alter coral reef $pCO_2$ on the same magnitude as increased atmospheric $CO_2$ invasion.

*Episodic events*

Storm events can also have a significant influence on the $pCO_2$ of reef ecosystems. For example, an increase in average $pCO_2$ and reduction in variability was observed in a Caribbean reef during the passage of a tropical cyclone (Gray et al. 2012). Directly following the storm there was a reduction in $pCO_2$ coinciding with an algal bloom, potentially due to an increase in terrestrial nutrient inputs or resuspension of sediment porewaters. A similar pattern was observed at Cheeca Rocks, Florida with average $pCO_2$ increasing from 382 to 578 µatm directly following a tropical cyclone (Manzello et al. 2013). This increase was attributed to increased freshwater inputs, resuspension of sediments and increased porewater exchange, a reduction in PAR, and increase in upwelling of high $pCO_2$ water. Unlike Media Luna reef, there was no algae bloom
observed at Cheeca Rocks, which was attributed to increased stress on the benthic community. Therefore, any increases in tropical cyclone frequency and intensity (Knutson et al. 2010; Murakami et al. 2013) could act to raise the $pCO_2$ of coral reefs through increased runoff, reduction in PAR, and habitat destruction.

Coral bleaching can also increase coral reef $pCO_2$. During a bleaching event at Ishigaki Island average $pCO_2$, the range of $pCO_2$, P, and R were elevated while excess organic production (E), or P-R, decreased due to increased community respiration related to bleaching stress (Kayanne et al. 2005). A year following the bleaching, there was a decrease in $pCO_2$, P, R, and E. This supports the hypothesis that excess OM raises $pCO_2$ levels on reefs through C remineralisation. In fact, it was hypothesized that the ratio of excess organic production to calcification (E/G) may predict whether the reef will be a sink or source of CO$_2$ (Kayanne et al. 2005). This shows that degradation of coral communities increases the average $pCO_2$ of reefs, and questions whether algal dominance would enhance $pCO_2$ uptake as an increase in secondary consumers of algal biomass may act to raise $pCO_2$ (Kayanne et al. 2005). Therefore, elevated $pCO_2$ associated with the general degradation of reefs due to growing human populations (Hughes et al. 2013) represents an additional challenge to coral reefs.

**Summary**

In order to investigate whether coral reef $pCO_2$ has changed over the past ~50 years, $pCO_2$ data from the relevant literature was compiled (Table 1). In order to remove any effects of sampling time and diel variability, only average $pCO_2$ values measured over the course of at least one full diel cycle were used. Globally distributed observations show an increasing trend in the average $pCO_2$ of coral reefs since 1966 ($R = 0.64$, $p < 0.001$, $n = 51$) (Fig. 1A). The majority of values fall above the line of atmospheric CO$_2$, indicating
that increasing reef $pCO_2$ is not being driven solely by atmospheric forcing. In the past 20
years open ocean surface $pCO_2$ near both Hawaii and Bermuda has increased at a rate of
~1.9 $\mu$atm y$^{-1}$ (Doney et al. 2009; Bates and Dickson 2012). A linear regression of
average coral reef $pCO_2$ ($R = 0.58$, $p < 0.001$, $n = 47$) over the same time period indicates
that the $pCO_2$ of coral reefs has increased at a rate of $6.6 \pm 1.4$ $\mu$atm y$^{-1}$, ~3.5 times faster
than the open ocean ($p < 0.01$) (Fig. 1B). Between 1965-1975, average coral reef $pCO_2$
was ~30 $\mu$atm below the average atmospheric $CO_2$ level. In the ensuing decades, average
coral reef $pCO_2$ increased to 10 $\mu$atm (1990-1999), 66 $\mu$atm (2000-2009), and 73 $\mu$atm
(2010-2012) above average decadal atmospheric $CO_2$ concentrations (Fig. 1C). While we
still lack long-term uninterrupted observations in individual systems, the global coral reef
$pCO_2$ trends are consistent with observations showing a ~70% increase in $pCO_2$ at One
Tree Island, Great Barrier Reef (GBR) between 1968 and 2009 (Table 1).

In order to determine the causes behind this rapid increase in coral reef $pCO_2$
potential artefacts in the data due to seasonality, temperature, study length, and
methodology were first examined. The majority of seasonal coral reef $pCO_2$ variability is
due to temperature effects and changes in community metabolism (Bates 2002). Besides a
surplus of summer months during 2000-2010, seasons were well distributed throughout the
data set (Table 1). There was no significant difference in the slope of the linear regression
between $pCO_2$ and year since 1990 when all summer months were removed from the
analysis ($p > 0.3$) and when $pCO_2$ was normalized to a mean temperature (26.4°C) over the
past 50 years ($p > 0.1$). Over the past 50 years an increase (0.5°C) in the average oceanic
temperature would only account for an increase in $pCO_2$ of ~10 $\mu$atm $^{15}$, which is well
below the ~170 $\mu$atm increase observed in mean coral reef $pCO_2$ over the same time
period. Therefore, seasonal and long-term temperature variations alone cannot explain the
observed increase in coral reef $pCO_2$. There was no significant correlation ($p > 0.5$)
between study length and average $p$CO$_2$, indicating that the length of the studies had no effect on the observed long-term trend. Also, there was no significant difference between the regressions of $p$CO$_2$ versus year ($p > 0.3$) when only measured $p$CO$_2$ values were used, indicating that the method used to calculate $p$CO$_2$ from measurements of other carbonate chemistry parameters had no effect on the observed long-term trend.

Diel variability of carbonate chemistry in coral reefs (e.g. Schmalz and Swanson, 1969; Shaw et al., 2012) is the largest possible source of carbonate chemistry variation in reef ecosystems. Therefore, averaging carbonate chemistry parameters over at least one diel cycle acts to remove this high source of variability from the data set. The vigorous biogeochemical processes controlling carbonate chemistry in coral reefs can also be influenced by physical variables such as currents and light availability (e.g. Marubini et al., 2001; Suzuki and Kawahata, 2003) that vary over daily and seasonal time scales. However, any error introduced from variation in short-term physical drivers such as light availability due to changes in cloud cover would be random and non-systematic. Any short-term error of this sort would be expected to conceal or blur any long-term trends in $p$CO$_2$. Furthermore, using data from various systems, locations, and seasons would tend to create noise but no trend. Therefore, we consider the observed global trend to be robust in spite of any inherent short-term variation in coral reef carbonate chemistry.

To evaluate the potential causes behind this rapid increase in coral reef $p$CO$_2$, influences of seasonality, temperature, study length, methodology, and reef type were first examined. The majority of seasonal coral reef $p$CO$_2$ variability is due to temperature effects and changes in community metabolism (Bates, 2002). Besides a surplus of summer months during 2000-2010, seasons were well distributed throughout the data set (see Table 1). There was no significant difference in the slope of the linear regression between $p$CO$_2$ and year since 1990 when all summer months were removed from the analysis or when
only summer months were used in the analysis. Also, when $pCO_2$ was normalized to a mean temperature (26.4°C) over the past 50 years there was no significant difference between observed trends. Over the past 50 years an increase (0.5°C) in the average oceanic temperature would only account for an increase in $pCO_2$ of ~10 µatm (Sweeney et al., 2002), which is well below the ~170 µatm increase observed in mean coral reef $pCO_2$ over the same time period in our data set. Therefore, seasonal and long-term temperature variations alone cannot explain the observed increase in coral reef $pCO_2$. There was no significant correlation between study length and average $pCO_2$, indicating that the length of the studies had no effect on the observed long-term trend. Also, there was no significant difference between the regressions of increasing $pCO_2$ when only measured $pCO_2$ values were used, indicating that the method used to calculate $pCO_2$ from measurements of other carbonate chemistry parameters had no effect on the observed long-term trend.

An analysis of diverse coral reef types demonstrated that reef type can influence water column carbonate chemistry parameters (Suzuki and Kawahata, 2003). Some of the main factors influencing coral reef carbonate chemistry were determined to be proximity to land, terrestrial nutrient inputs, and residence time of reef water masses. However, the major determinant of whether or not a reef was a source or sink of CO$_2$ to the atmosphere was a system-level net organic-to-inorganic carbon production ratio ($R_{OI}$) (Suzuki and Kawahata, 2003). This agrees well with our model, which showed the largest metabolic influence on average diel coral reef $pCO_2$ to be changes in the ratio of photosynthesis to respiration. In order to examine any possible bias of reef type in our data set, the reefs were categorized as either fringing, atoll, or fringing-atoll (Table 1). These categories are largely representative of the proximity of each reef to a significant landmass, one of the more important factors shown to control carbonate chemistry by Suzuki and Kawahata
Chapter 1

(2003). The vast majority of reefs surveyed since 1992 were fringing reefs, and were therefore most likely to experience terrestrial influences (Table S1). The trend in mean $p$CO$_2$ changes slightly when only fringing reefs were included in the analysis, with the rate of change for $p$CO$_2$ increasing (6.58 $\mu$atm y$^{-1}$ vs. 8.38 $\mu$atm y$^{-1}$), although the difference is not significant. This increase may be indicative of land base inputs having a greater influence on fringing reefs and would be expected of reefs that are within closer to proximity to land.

In order to further investigate the increases in $p$CO$_2$ a model of coral reef metabolism was developed based off data in McMahon (2013). This model was developed by co-author Dr. K. G. Schulz, and therefore, a full description and analysis is included in Appendix 1. Overall, there is an overarching trend of increasing coral reef $p$CO$_2$ within the past 50 years, with an accelerated increase over the last 20 years. This accelerated increase could be explained by a combination of disturbances to the metabolic balance of reef ecosystems. These disturbances include anthropogenic perturbations to natural drivers of $p$CO$_2$ such as nutrient and OM loading, habitat degradation through storms, bleaching, and overfishing, and anthropogenic climate forcings (Table 2). In coastal ecosystems such as coral reefs, anthropogenic disturbances to regional drivers of seawater carbonate chemistry may be equally important as increasing atmospheric CO$_2$. Considering the difficulties associated with reducing global CO$_2$ emissions, any local controls may offer more approachable management options to combat the acidification of coral reefs.
Figure 1. (A) Average coral reef $pCO_2$ and pH values measured over at least one diel cycle. The studies ranged in length from 1 day to an entire year. Atmospheric $pCO_2$ from Mauna Loa, Hawaii is shown in black. The dashed line represents a quadratic regression of the data and the shaded region is the 95% confidence interval. (B) Linear regression of coral reef $pCO_2$ levels since 1990 compared to a regression of open ocean surface water $pCO_2$ (gold dashed line; Doney et al. 2009) over the same time period. (C) Box diagram of the data binned into decades.
Table 1. Average diel $p\text{CO}_2$ and pH values of coral reefs reported in the literature. Only averages over at least one diel cycle were used and any study indicating coral reefs as the study site were used. Method refers to the way $p\text{CO}_2$ values were obtained, by either calculation using specified carbonate chemistry parameters or by direct measurement (M). The season that the measurements were taken in are reported unless measurements were taken over all four seasons, in which case a yearly average is shown. When $\text{CO}_2$ levels were reported as $f\text{CO}_2$ in the original study, it was converted of $p\text{CO}_2$ by multiplying by 1.03, as this is the typical difference between fugacity and partial pressure of $\text{CO}_2$ at typical in situ temperatures. In order to normalize pH to the total scale, 0.13 was subtracted from all values on the NBS scale. The transformation of NBS to total scale is supported by the observed trend, which is consistent with changes in $p\text{CO}_2$ over the same time period.

<table>
<thead>
<tr>
<th>Avg. $p\text{CO}_2$ ($\mu\text{atm}$)</th>
<th>Range $p\text{CO}_2$ ($\mu\text{atm}$)</th>
<th>Avg. pH</th>
<th>Avg. Temp. ($^\circ\text{C}$)</th>
<th>Latitude</th>
<th>Location</th>
<th>Method</th>
<th>Season and Year Collected</th>
<th>Study</th>
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<td>Kayanne et al., 1995</td>
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Table 2. Summary of drivers of $p$CO$_2$ variability on coral reefs over short and long temporal scales.

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<th>Short (Diel/Seasonal) Timescales</th>
<th>Long (Decadal) Timescales</th>
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<td><strong>Atmospheric CO$_2$</strong></td>
<td>Winter: increase due to flux into seawater</td>
<td>Increase due to increasing atmospheric CO$_2$</td>
</tr>
<tr>
<td></td>
<td>Summer: decrease due to flux to atmosphere</td>
<td></td>
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<tr>
<td><strong>Temperature</strong></td>
<td>Winter: decrease</td>
<td>Increase with increase in average ocean temperature</td>
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<tr>
<td></td>
<td>Summer: increase</td>
<td></td>
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<td><strong>Nutrient Inputs</strong></td>
<td>Day: decrease due to production</td>
<td>Unknown, possible increase due to more OM storage and remineralisation.</td>
</tr>
<tr>
<td></td>
<td>Night: increase due to respiration</td>
<td></td>
</tr>
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<td><strong>Groundwater</strong></td>
<td>Increase from direct flux, however, can stimulate</td>
<td>Site specific</td>
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<tr>
<td></td>
<td>production as well</td>
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<td><strong>River Inputs</strong></td>
<td>Decrease in wet seasons</td>
<td>Increase</td>
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<td><strong>Storm Events</strong></td>
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<td>Likely increase as a result of more intense events</td>
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<td><strong>Reef Degradation</strong></td>
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1.2 Permeable calcium carbonate sediments: *In situ* drivers of dissolution and precipitation

The dissolution and precipitation of carbonate minerals, both biotic and abiotic, can alter the water column TA within coral reef lagoons (Andersson et al. 2007; Rao et al. 2012). These changes in TA are large enough that ecosystem calcification rates have historically been measured using the alkalinity anomaly technique (Chisholm and Gattuso 1991; Gattuso et al. 1996), which relies on the measuring changes in water column TA according to the following equation:
In order to associate changes in water column TA with community calcification it is important to constrain the sinks and sources of TA within a coral reef ecosystem.

Aragonite saturation state ($\Omega_{Ar}$) is an important term in ocean acidification research, and $\Omega_{Ar}$ of the water column has been shown to be correlated with coral and community calcification rates (De’ath et al. 2009; Shamberger et al. 2011). An increase in the pCO$_2$ of seawater lowers $\Omega_{Ar}$ through the subsequent decrease in concentrations of $HCO_3^-$ and $CO_3^{2-}$. This makes it more difficult for corals to create carbonate skeletons and is thought to be the driver behind reduced reef health in higher pCO$_2$ environments (Fabry et al. 2008; Andersson and Mackenzie 2011). However, recent research on carbonate dissolution in sediments has shown that diel variability of $\Omega_{Ar}$ in the water column is not a good predictor of precipitation and dissolution rates within permeable sands (Cyronak et al. 2013).

The precipitation and dissolution of carbonate minerals in marine sediments is thought to be determined by the saturation state ($\Omega$) of the porewater with respect to the metastable mineral (Ku et al. 1999; Yates and Halley 2006). Coral reef sediments are made up of a mixture of different carbonate mineral phases including low magnesium calcites (LMC), high magnesium calcites (HMC), and aragonite (Weber and Woodhead 1969). The threshold for HMC has historically been defined as any carbonates with Mg content $> 3\%$ (Reeder and Barber 1983; Morse et al. 2006). The mineralogy of carbonate sediments influences solubility such that calcites with higher magnesium content are more soluble than pure calcite and aragonite (Morse and Mackenzie 1990; Morse and Arvidson 2002; Andersson et al. 2007). Calcites that contain a magnesium content of 12% approach the solubility of pure aragonite, and solubility increases with magnesium content (Morse and Arvidson 2002; Morse et al. 2006). Carbonate sediments are composed of varying
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mineralogies, but in general the amount of HMC is higher in lower latitudes, with calcites approaching 20% Mg towards the equator (Chave 1954; Morse et al. 2006). As oceanic pH decreases due to ocean acidification the solubility of coral reef sediments could change based on the specific mineralogy of the sediments (Morse et al. 2006).

The dissolution kinetics of HMC is debated in the literature as there have been a few proposed methods to calculate the solubility of HMC with varying Mg concentrations (Morse and Arvidson 2002; Morse et al. 2006). An ion activity product (IAP) has been used in order to overcome the problem that as HMC dissolves, minerals with lower Mg content will precipitate out due to their lower solubilities (Plummer and Mackenzie 1974; Morse and Arvidson 2002; Morse et al. 2006). One interesting aspect of HMC solubility is that biogenic HMCs tend to have higher solubilities then synthetically derived minerals (Morse and Mackenzie 1990; Morse et al. 2006). Plummer and Mackenzie (1974) calculated solubilities of biogenic HMC about 5-times as high as aragonite in the Mg concentration range of 12% to 16%, while other data shows that biogenic HMCs within that range are only slightly more soluble then aragonite (Morse et al. 2006). Morse et al. (2006) attributed the differences in solubility of biogenic HMC to the different cleaning and preparation processes that the carbonates underwent. Biogenic carbonate grains have complex microstructure, which may add to their increased solubility (Walter and Morse 1984; Wild et al. 2006). Walter and Morse (1984) showed that microstructure and grain size were important in determining the solubility of biogenic carbonates, with grain size inversely correlated to dissolution rates. Henrich and Wefer (1986) found that pore size and the amount of organic matter had a larger effect on the dissolution of biogenic carbonates then did the mineral phase itself. Using scanning electron microscopy (SEM), Freiwald (1995) showed that bacterial growth on benthic foraminifera tests induced carbonate dissolution on micro scale levels in a broadly saturated environment. This may
be due to more pores and organic matter promoting bacterial growth and respiration which could enhance the dissolution of the biogenic carbonates in natural settings.

Because sediments on coral reefs are highly permeable, the exchange of solutes with the water column is driven mainly by advective processes as opposed to diffusion (Eyre et al. 2008; Glud et al. 2008; Santos et al. 2012). Cycling of water through the sediments can alter the chemistry of the overlying water column, with influx and fluxes based on residence time, advection rate, sediment chemistry, biological processes, and the initial chemistry of the seawater (Eyre et al. 2008). Porewater advection can occur on various temporal and spatial scales resulting in numerous exchange rates over variable time scales (Santos et al. 2012). Flow and topography induced pore water exchange (see Fig 1(5) in Santos et al. 2012) is probably the dominant process driving porewater exchange within coral reef lagoons due to the formation of ripples and crests within permeable carbonate sediments (Precht and Huettel 2003). These processes act on short temporal and small spatial scales to induce the exchange of porewater solutes with the overlying water column (Precht and Huettel 2003).

The advection of overlying waters can replenish oxygen, organic compounds, and dissolved ions within the sediments causing them to act as biological catalysts, intensifying benthic processes such as respiration (Glud et al. 2008). In shallow carbonate sediments, photosynthesis and respiration modify the pH of porewaters (Yates and Halley 2006; Werner et al. 2008) which can potentially influence the precipitation and dissolution of carbonate minerals. Photosynthesis by benthic microalgae takes up CO$_2$ which leads to the over-saturation of porewaters and promotes the abiotic precipitation of carbonates as well as calcification by benthic microorganisms (Werner et al. 2008). The production of CO$_2$ during oxic respiration can drive the dissolution of carbonate sediments and release alkalinity into the porewaters (Ku et al. 1999; Yates and Halley 2006). The advection of
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seawater through permeable sediments has been shown to have a large effect on the rates of production and respiration in sediments (Janssen et al. 2005; Glud et al. 2008). Because pore water advection affects processes that influence the DIC chemistry of seawater, it should also influence the dynamics of carbonate precipitation and dissolution within permeable sediments.

Porewater advection been shown to have a stimulatory effect on TA fluxes, with increasing advection rates increasing net daily TA fluxes (Rao et al. 2012; Cyronak et al. 2013). However, most studies in carbonate sediments to date have focused on how advection affects photosynthesis and respiration (Rasheed et al. 2004; Clavier et al. 2008) or nutrient cycling (Eyre et al. 2008). The dynamics of carbonate precipitation and dissolution in permeable sediments is still poorly understood (Werner et al. 2008; Rao et al. 2012). When measured under diffusive conditions, carbonate dissolution rates range from 0.16 to 3.2 mmol CaCO$_3$ m$^{-2}$ h$^{-1}$ (Leclercq et al. 2000; Burdige and Zimmerman 2002; Yates and Halley 2003). These are much lower than dissolution rates reported under advective conditions which can be as high as 11.2 mmol CaCO$_3$ m$^{-2}$ h$^{-1}$ (Rao et al. 2012; Cyronak et al. 2013). Dissolution rates occurring on reefs are most likely heterogeneous across reef zones depending on numerous physical and biological factors. Rates of advection, availability of photosynthetically active radiation (PAR), and availability of labile organic material for respiration would be some of the factors which could affect carbonate dissolution rates in permeable sediments. It is important to determine how advection affects dissolution, which is probably a function of the residence time that porewaters come in contact with the minerals and the stimulation of biological processes occurring within and on the biogenic carbonate grains.

There are many processes besides the precipitation and dissolution of carbonates occurring within reef sediments that can affect the DIC cycling within coral reef
ecosystems (Wolf-Gladrow et al. 2007). In anoxic sediments, sulphate reduction can increase the carbonate alkalinity of porewaters (Ku et al. 1999) according to the following equation:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$$

The oxidation of sulphides associated with sulphate reduction lowers TA (Ku et al. 1999) according to the following equation:

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$$

Since advection stimulates the influx of oxygen into the sediments, it may inhibit sulphate reduction, thereby lowering the $\Omega_{AR}$ of porewater and increasing the dissolution of carbonates. However, coupled sulphate reduction and sulphide oxidation within porewaters has been shown to increase TA due to the production of $H^+$ and subsequent dissolution of carbonate minerals (Ku et al. 1999). Other processes occurring in anoxic sediments, nitrification and nitrogen fixation, can lower TA, while denitrification increases the carbonate alkalinity of porewaters (Wolf-Gladrow et al. 2007). All of these processes can affect the accumulation of TA in porewaters, which can then act as potential source of TA to the water column through the exchange of groundwater.

1.3 Aims and hypotheses

There are many knowledge gaps that exist regarding groundwater exchange mechanisms, calcium carbonate dissolution in permeable sands, and their influence on DIC and TA cycling in coral reefs. This thesis addresses the following aspects:

1. Does advection influence the dissolution and precipitation of CaCO$_3$ sediments over a diel cycle? Does advection influence DIC and TA cycling in the water column?
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2. What drives the dissolution and precipitation of CaCO$_3$ minerals in permeable sediments?

3. Can SGD act as a source of DIC and TA to coral reef ecosystems? How does SGD influence DIC and TA cycling in the water column on different coral reefs?

4. How do different groundwater exchange mechanisms (i.e. porewater advection and SGD) contribute to DIC and TA cycling on coral reefs?

5. How will lowering the pH of the water column due to ocean acidification affect sediment dissolution and precipitation?

6. Can groundwater sources of TA to coral reefs act in any buffering capacity against ocean acidification?

In order to investigate the above questions a combination of field based monitoring and *in situ* experiments was employed. Field work was conducted to determine how advection and SGD apply in natural ecosystems. Two field sites were chosen in order to investigate differences between coral reefs with high (Cook Islands) and low (Heron Island) SGD rates. Heron Island is an offshore coral cay located at the southern end of the Great Barrier Reef, 72 km off of the Australian mainland. Our study site in the Cook Islands is Muri Lagoon, a fringing, coral reef lagoon located along the south western coast of the island of Rarotonga. At each site, chamber incubations were performed in order to determine the role of small scale sediment advection at different advection rates. $^{222}\text{Rn}$, TA, pH, and $\rho$CO$_2$ were monitored in the water column in order to determine the influence of SGD on water column carbonate chemistry. A final experiment examined how ocean acidification will affect *in situ* CaCO$_3$ sediment dissolution at Heron Island.
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The following hypotheses were tested during this thesis:

1. Porewater advection stimulates the dissolution of CaCO$_3$ sands, thereby releasing TA into the water column.
2. SGD is a source of TA to coral reef lagoons.
3. SGD can alter the water column carbonate chemistry of coral reefs.
4. Alkalinity from groundwater sources can act to buffer coral reef ecosystems against future changes in pH due to ocean acidification.
5. Future projected levels of ocean acidification will stimulate the dissolution of carbonate sands.
Chapter 2

Carbon cycling hysteresis in permeable carbonate sands over a diel cycle: Implications for ocean acidification
Chapter 2

2.1 Abstract

Dissolved inorganic carbon (DIC), dissolved oxygen (DO), H⁺, and alkalinity fluxes from permeable carbonate sediments at Heron Island (Great Barrier Reef) were measured over one diel cycle using benthic chambers designed to induce advective porewater exchange. A complex hysteretic pattern between carbonate precipitation and dissolution in sands and the aragonite saturation state (ΩAr) of the overlying chamber water was observed throughout the incubations. During the day, precipitation followed a hysteretic pattern based on the incidence of photosynthetically active radiation (PAR) with lower precipitation rates in the morning than in the afternoon. The observed diel hysteresis seems to reflect a complex interaction between photosynthesis and respiration rather than ΩAr as the main driver of carbonate precipitation and dissolution within these permeable sediments. Changes in fluxes over a diel cycle demonstrates the importance of taking into account the short term variability of benthic metabolism when calculating net daily fluxes. Based on one diel cycle, the sediments were a net daily source of alkalinity to the water column (5.13 to 8.84 mmol m⁻² d⁻¹ depending on advection rates) and advection had a net stimulatory effect on carbonate dissolution. The enhanced alkalinity release associated with benthic metabolism and porewater advection may partially buffer shallow coral reef ecosystems against ocean acidification on a local scale.
2.2 Introduction

Rising atmospheric CO\textsubscript{2} concentrations have the potential to drastically alter biogeochemical cycles occurring in coastal ecosystems. The accumulation of CO\textsubscript{2} in seawater changes the overall composition of dissolved inorganic carbon (DIC) species and lowers the pH (Zeebe and Wolf-Gladrow 2001; Morse and Arvidson 2002). This can have inhibitory effects on numerous biological processes including marine calcification (Hoegh-Guldberg et al. 2007). Coral reefs are thought to be some of the most susceptible ecosystems to ocean acidification with future models indicating a complete ecosystem phase shift from corals to algae (De'ath et al. 2009; Veron 2011). In order to understand how ocean acidification will affect coral reef communities it is important to understand how the benthic communities contribute to ecosystem-level biogeochemical cycles.

The precipitation and dissolution of carbonate minerals in marine sediments is thought to be determined by the saturation state ($\Omega$) of the porewater with respect to the metastable mineral (Ku et al. 1999; Yates and Halley 2006). Most studies focusing on the effects of ocean acidification on coral reefs use the aragonite saturation state ($\Omega_{\text{Ar}}$) as an indicator of ecosystem health (De'ath et al. 2009; Veron 2011). However, coral reef sediments are made up of a mixture of different carbonate mineral phases including low magnesium calcites (LMC), high magnesium calcites (HMC), and aragonite (Weber and Woodhead 1969). The mineralogy of the carbonate sediments influences solubility such that calcites with higher magnesium content are more soluble than pure calcite and aragonite (Morse and Arvidson 2002; Andersson et al. 2007). As carbonate sediments dissolve they release alkalinity in the form of HCO\textsubscript{3} which can potentially buffer against decreases in pH due to ocean acidification (Andersson et al. 2005; Andersson et al. 2011).

In shallow carbonate sediments, photosynthesis and respiration modify the pH of porewaters (Yates and Halley 2006; Werner et al. 2008) which can potentially influence
the precipitation and dissolution of carbonate minerals. Photosynthesis by benthic microalgae takes up CO$_2$ which leads to the over-saturation of porewaters which would promote abiotic precipitation as well as calcification by benthic microorganisms (Werner et al. 2008). The release of CO$_2$ during oxic respiration can drive the dissolution of carbonate sediments and release alkalinity into the porewaters (Ku et al. 1999; Yates and Halley 2006). The advection of seawater through permeable sediments has been shown to have a large effect on the rates of production and respiration in sediments (Janssen et al. 2005; Glud et al. 2008). We suspect that advection also influences the dynamics of carbonate precipitation and dissolution.

Numerous mechanisms act on different temporal and spatial scales to transport seawater through permeable carbonate sediments within coastal ecosystems (Santos et al. 2012). Cycling of water through the sediments can alter the chemistry of the overlying water column, with influx and fluxes based on residence time, advection rate, sediment chemistry, biological processes, and the initial chemistry of the seawater (Eyre et al. 2008). The advection of overlying waters can replenish oxygen, organic compounds and dissolved ions within the sediments causing them to act as biological catalysts, intensifying benthic processes such as respiration (Glud et al. 2008). Most studies in carbonate sediments to date have focused on how advection affects photosynthesis and respiration (Rasheed et al. 2004; Clavier et al. 2008) or nutrient cycling (Eyre et al. 2008). The dynamics of carbonate precipitation and dissolution in permeable sediments are still poorly understood (Rao et al. 2012).

Because photosynthesis is affected by multiple processes such as the availability of photosynthetically active radiation (PAR), nutrients, and CO$_2$, photosynthetic rates are highly dependent on the time of day and have been shown to undergo hysteresis within corals and algae (Levy et al. 2004). Since benthic photosynthesis and respiration alter the
sea water chemistry in permeable carbonate sediments (Glud et al. 2008; Santos et al. 2011), carbonate precipitation and dissolution may therefore also undergo hysteresis over a diel cycle. It is expected that precipitation rates would be lower in the morning than in the afternoon due to a lowered saturation state caused by night time respiration. We hypothesize that carbonate precipitation and dissolution in permeable coral reef sediments will follow a diel hysteresis driven by benthic photosynthesis and respiration. To test this hypothesis we conducted high-resolution time-series observations of advective benthic chambers in permeable carbonate sediments at Heron Island. We also hypothesize that advection will stimulate the dissolution of carbonate sediments and release alkalinity into the water column that can buffer against ocean acidification on a local scale.

2.3 Methods

Study site

All sampling was performed from 09 - 10 October 2011 along the inner reef flat of Heron Island (23° 27’ S, 151° 55’ E) at a similar site to Glud et al. (2008) and Eyre et al. (2008). Heron Island is an offshore coral cay located at the southern end of the Great Barrier Reef, 72 km off of the Australian mainland. The reef flat covers an area of 26.4 Km² and roughly 85% is covered by carbonate sands (Glud et al. 2008), with an average depth of 1.7 m (Wild et al. 2004a). Our study site was a sand patch roughly 100 m offshore and east of the marine research station. Sediment grain size was mostly medium to very coarse sand (Wentworth scale) with 12.1% > 2 mm, 30.5% between 1–2 mm, 27.3% between 500 µm – 1 mm, 14.1% between 250 µm – 500 µm, 11.2% between 125 µm – 250 µm, 4.2% between 63 µm – 125 µm, and 0.6% < 63 µm. The sands were composed of 1% quartz, 33.1% calcite, and 65.4% aragonite as determined by X-ray diffraction (XRD). The calcite fraction was composed of 2% low magnesium calcite (2.3
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± 1 mol% MgCO$_3$) and 98% high magnesium calcite (15.2 ± 1 mol% MgCO$_3$). Carbonate sands from Heron Island were previously shown to be low in organic carbon content (0.24%) (Wild et al. 2004b).

Sampling

During sampling the wind and seas were calm with minimal cloud cover overhead. Advective chambers were deployed just before midday and sampled every two hours for 26 hours in order to capture an entire diel cycle. Discrete samples were taken from the chambers and water column along with the monitoring of the physico-chemical parameters of the water column every 20 minutes with an autonomous probe. A Hydrolab DS5X (Hach Environmental) was deployed 0.2 m from the bottom at the study site to monitor temperature (± 0.5%), PAR (± 5%), salinity (± 0.5%), and dissolved oxygen (DO) (± 1%) of the water column every 20 minutes. DO was calibrated to 100% saturated water based on the barometric pressure and all other sensors were factory calibrated. Discrete water samples were taken every hour from the water column using a 50 mL plastic syringe.

Chambers identical to those described in Glud et al. (2008) and Eyre et al. (2008) were used to measure in situ benthic solute fluxes at three different advection rates. The chamber bottoms extended 15 cm into the sediment and enclosed roughly 4 L of overlying seawater during the incubations. Advection was induced within the chambers based on the spinning rate, in rotations per minute (RPM), of the acrylic disk within each chamber (diffusive, 40 RPM, and 80 RPM). In order to maintain a homogenous distribution of solutes within the diffusive chamber it was operated with the disk slowly spinning clockwise for one rotation, then pausing and spinning counter clockwise for one rotation and repeating (Glud et al. 2008). The 40 RPM and 80 RPM settings resulted in advective rates of 43 and 213 L m$^{-2}$ d$^{-1}$ respectively (Glud et al. 2008). The permeability of the
sediment was between $6.0 \pm 0.7 \times 10^{-11} \text{ m}^2$ and $1.6 \pm 0.6 \times 10^{-11} \text{ m}^2$ depending on the depth, as measured by Glud et al. (2008). The chambers were deployed over carbonate sands with no visible macrophytes or macrofauna burrows with the lids open for one hour before being closed at the start of the incubation. Incubations started at 11:40 h on 09 October 2011 and lasted for 26 hours. Samples of 150 mL were drawn by syringe every 2 hours with ambient seawater allowed to replace the sample volume. As the seawater composition was similar to the chamber water composition (shown later), no corrections for seawater dilutions were made.

Sample preparation and analysis

Both water column and benthic chamber samples were immediately brought back into the laboratory. Dissolved oxygen ($\pm 1\%$) was measured directly following collection using a Hach Luminescent Dissolved Oxygen (LDO®) probe. Samples for nutrients were filtered with a 0.45 µm cellulose acetate filter and frozen at -20°C until analysed following the methods of Eyre and Ferguson (2005) using a Lachat Flow Injection Analysis (FIA) system. Samples for total alkalinity (TA) and pH were filtered through a 0.45 µm cellulose acetate filter and stored in an airtight container with no headspace until analysis within 4 hours of sampling. pH ($\pm 0.003$) was measured using a Metrohm Electrode Plus calibrated to Oakton National Bureau of Standards (NBS) standards of 4, 7, and 10. To determine TA, Gran titrations were performed using a Metrohm Titrando automatic titrator and pH electrode. Pre-standardized 0.01 mol L$^{-1}$ HCl was used as the titrant which was calibrated against Dickson Certified Reference Material (Batch 111). Alkalinity samples were run twice and the average of the two values was used. During the study the uncertainty of duplicate TA measurements was 0.19% $\pm 0.17$. 

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Samples for DIC concentrations (± 1.2%) were 0.7 µm filtered with a Whatman GF/F syringe filter, preserved using 50 µL of saturated HgCl with no head space, and stored at 4°C. For DIC measurements samples were acidified with 5% (v:v) phosphoric acid and the resulting CO₂ was analysed via continuous flow wet-oxidation isotope ratio mass spectrometry (CF-WO-IRMS) using an Aurora 1030W total organic carbon (TOC) analyzer coupled to a Thermo Delta V Plus IRMS (Oakes et al. 2010). DIC concentrations were also estimated with the Excel macro CO₂ System (CO2SYS) (Pierrot et al. 2006) using inputs of TA and pH and the constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987). CO2SYS also generated saturations states (Ω) for calcite and aragonite. A linear regression (y = 0.93x + 139.67; $R^2 = 0.974$) of measured and calculated DIC concentrations demonstrated an excellent agreement between the two methods over the concentration range measured during this study (Fig. 2). Measured DIC values were used for all further calculations.

Figure 2. A regression of measured DIC vs. calculated DIC concentration estimated using the Excel macro CO2SYS. The $R^2$ and equation for the regression are displayed as well as the 95% confidence intervals (dashed line).
Carbonate alkalinity ($T_{AC}$) for each sample was calculated by subtracting the alkalinity, as determined in CO2SYS using $TA$ and $pH$, contributed by $B(OH)_4^-$, $OH^-$ and total dissolved phosphorus (TDP) from $TA$. The contribution to $TA$ from each of the above ions was within the following ranges; $B(OH)_4^-$ contributed between 60 to 130 $\mu$mol Kg$^{-1}$, $OH^-$ 5 to 12 $\mu$mol Kg$^{-1}$, and TDP contributed around 1 $\mu$mol Kg$^{-1}$ for each sample. $T_{AC}$ was also corrected for $NH_4^+$ and $NO_3^-$ which represented a minor component to alkalinity ($\leq 1$ $\mu$mol Kg$^{-1}$).

**Calculation of rates**

Hourly fluxes of solutes from the sediment were calculated using the following equation,

$$r_x = \frac{\Delta s_x \times \Delta t}{h}$$

where $\Delta s_x$ is the change in solute concentration in $\mu$mol L$^{-1}$, $h$ is the average height of water enclosed within the chamber in meters, $\Delta t$ is the change in time in hours, and $r_x$ is the hourly flux of solute $x$ in mmol m$^{-2}$ h$^{-1}$.

The net daily flux of a solute from the sediment was calculated using three separate approaches. The first approach, as typically used by most investigators (Rasheed et al. 2004; Rao et al. 2012), relies on the linear slope of the solute concentration vs. time during both day time and night time hours. The slopes were then converted to mmol m$^{-2}$ h$^{-1}$, multiplied by either the amount of daylight (13 h) or darkness (11 h), and added together. The second approach used the concentrations at the start and end points of the light and dark periods over an entire diel cycle and calculated fluxes based on the sum of changes between those concentrations (Ferguson et al. 2003; Eyre et al. 2008).
The third approach involved plotting hourly rates against time and integrating the underlying area based on the equation for the area of a trapezoid,

\[ i_x = \frac{\Delta t \times (r_{x1} + r_{x2})}{2} \]  

(2)

where \( r_{x1} \) and \( r_{x2} \) are the hourly fluxes of solute \( x \) during the time interval \( \Delta t \), and \( i_x \) is the integrated flux of solute \( x \) in mmol m\(^{-2}\). The resulting fluxes can then be added up to represent a 24 hour time period and are presented as mmol m\(^{-2}\) d\(^{-1}\). By dividing \( i_x \) by its associated time interval, the integrated rates can be converted back to hourly integrated rates, which were used for all subsequent analyses. Negative rates designate a flux into the sediment from the water while a positive rate designates a flux out of the sediment.

Based on reaction stoichiometry, alkalinity can be used to determine the contribution of precipitation and dissolution to the DIC pool by dividing TA\(_C\) in half. The flux of DIC due to respiration and photosynthesis can then be calculated by subtracting half of the TA\(_C\) flux from the overall DIC flux, which we term DIC\(_{TA\_C}\). However, this assumes that no other reactions (e.g., sulphate reduction) are contributing or consuming alkalinity (see Discussion).

2.4 Results

Solute concentrations

PAR measured during the incubations is shown as Fig. 3. Both DO concentrations and pH increased during the day light hours and decreased at night with the greatest range in the 80 RPM chamber (Fig. 4). The concentrations of TA and DIC showed the same trend, increasing at night and decreasing in the day, with the greatest range in the 80 RPM chamber. Although both \( \Omega \) of calcite and aragonite varied during the course of the day, neither reached the theoretical dissolution threshold of 1. The range of solute
concentration within the chambers, particularly the 40 RPM chamber, was similar to the natural range measured in the water column (Fig. 4).

Figure 3. PAR levels measured over the course of the incubations.

Integrated fluxes

Integrated fluxes ($i_x$) of DO, $H^+$, TAC, and DIC$_{TAC}$ showed a distinct diel cycle (Fig. 4). Fluxes of DO and DIC$_{TAC}$ changed similarly between the three chambers during the day (Fig. 5A, C). However, during the night DO and DIC$_{TAC}$ showed differing trends. In the 80 RPM chamber, DO rates leveled off for most of the night, while in the diffusive and 40 RPM chamber they increased after two hours of darkness and moved towards more positive values throughout the night. DIC$_{TAC}$ fluxes had similar but opposite trends during the night (Fig. 5C). DIC$_{TAC}$ fluxes from both the 40 and 80 RPM chambers changed sharply from uptake to efflux during first 2 hours after sunset and then began to drop during the rest of the night and throughout the day. In the diffusive chamber, DIC$_{TAC}$ fluxes showed a pattern similar to TA$_C$ fluxes, increasing to a peak in the middle of the
night. H\textsuperscript+ fluxes showed the highest variation between the different advection rates and steadily increased during the night and decreased during the day (Fig. 5B).

![Graph showing DO, pH, TA\textsubscript{C}, DIC, and saturation state of calcite (Ω\textsubscript{Ca}) and aragonite (Ω\textsubscript{Ar}) in water column and three benthic chambers over the course of incubations. Dark grey bars indicate night time hours. Incubations started on 09 Oct 2011 at 11:40 h.](image)

**Figure 4.** (A) DO, (B) pH, (C) TA\textsubscript{C}, (D) DIC, and (E) saturation state of calcite (Ω\textsubscript{Ca}) (closed circles) and aragonite (Ω\textsubscript{Ar}) (open circles) in the water column and the three benthic chambers over the course of the incubations. The dark grey bars indicate night time hours. The incubations started on 09 October 2011 at 11:40 h.
Figure 5. Integrated fluxes of (A) DO, (B) H\textsuperscript{+}, (C) DIC\textsubscript{TAC}, and (D) TAC\textsubscript{C} from the diffusive, 40 RPM, and 80 RPM chambers plotted against the time since the start of the incubation. Dark grey bars indicate night time hours.

2.4 Discussion

Chamber artefacts and operation

A previous study from a similar study site using the same chambers and stirring rates showed much less variation between replicates for rates of productivity and respiration than between stirring rates (Glud et al. 2008). As such, we used a range of chamber stirring rates but did not perform replication. Although concentrations in the chambers changed dramatically over the diel cycle, which would influence the sediment biogeochemistry, the changes in the diffusive and 40 RPM chambers were similar to those in the water column (Fig. 4). For example, overnight the DO saturation in the water
column decreased to 70% while it decreased to 97%, 77%, and 33% in the diffusive, 40 RPM, and 80 RPM chambers, respectively. The similarity in concentration changes between the water column and the 40 RPM chamber suggests that the biogeochemical processes in the chambers reflect the natural sediments and that any major changes were unlikely due to incubation artifacts.

There are numerous mechanisms that induce the advection of overlying waters into sediments that acting on different spatial and temporal scales (Santos et al. 2012). The advective chambers used in this study are designed to induce advection that is similar to flow- and topography-induced advection (see Fig. 1(5) in Santos et al. 2012), but not necessarily designed to simulate in situ advective rates. The main advantage of using these chambers is that they allow for the manipulation of water filtration rates through the sediments in order to investigate the effects of advective rates on biogeochemical processes. However, the 40 and 80 RPM chambers induced filtration rates of 43 and 213 L m$^{-2}$ d$^{-1}$, respectively, in Heron Island sediments (Glud et al. 2008). These chamber-induced filtration rates are on the same order of magnitude as in situ filtration rates established from artificial (264 L m$^{-2}$ d$^{-1}$) (Wild et al. 2004a) and natural tracer observations (~150 L m$^{-2}$ d$^{-1}$) (Santos et al. 2010) at the same location in Heron Island.

Due to the above issues, and the fact that the sediment incubations were based on only one diel cycle, net daily fluxes from this study must be interpreted carefully.

Influence of calculation method on net daily benthic fluxes

The method used to calculate net daily solute fluxes can have a significant effect on both the magnitude and direction of the rate. The fluxes generated from the integration and endpoint methods were similar in both the magnitude and direction of the fluxes, while the rates generated from linear regressions tended to be overestimated and in the opposing
direction (Table 3). This is probably due to the regression based method overestimating photosynthesis in the daylight hours by not taking into account the changes in photosynthetic rates caused by fluctuations in PAR (discussed in further detail later). In addition, night time respiration rates calculated by integration varied considerably (Fig. 5). This variability in night time fluxes would have an effect on net daily rate calculations that would lead to the over or under estimation of night time rates depending, on how the incubations are performed.

Table 3. Net daily fluxes of $\text{TAC}$, $\text{DIC}_{\text{TAC}}$, DO, and $\text{H}^+$ calculated using the integral (Int), end point (EP), and regression (Reg) based approaches. All values are in mmol m$^{-2}$ d$^{-1}$ except $\text{H}^+$ fluxes which are in $\mu$mol m$^{-2}$ d$^{-1}$.

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</tr>
</thead>
<tbody>
<tr>
<td>Diffusive</td>
<td>5.13</td>
<td>5.58</td>
<td>-14.03</td>
<td>7.19</td>
<td>9.28</td>
<td>-9.67</td>
<td>-2.29</td>
<td>2.05</td>
<td>16.37</td>
<td>0.038</td>
<td>0.057</td>
<td>-0.200</td>
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<tr>
<td>40 RPM</td>
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<td>6.82</td>
<td>-17.37</td>
<td>18.34</td>
<td>18.80</td>
<td>-2.88</td>
<td>-5.24</td>
<td>-1.62</td>
<td>17.95</td>
<td>0.088</td>
<td>0.166</td>
<td>-0.293</td>
</tr>
<tr>
<td>80 RPM</td>
<td>8.78</td>
<td>14.66</td>
<td>-31.27</td>
<td>1.64</td>
<td>5.43</td>
<td>-2.31</td>
<td>-8.17</td>
<td>-6.59</td>
<td>24.59</td>
<td>-0.022</td>
<td>0.010</td>
<td>-0.486</td>
</tr>
</tbody>
</table>

Most previous studies in coral reef sands have carried out benthic flux incubations that last on time scales of 4 to 8 hours and measure dark respiration by blocking sunlight during the day (Rasheed et al. 2004; Rao et al. 2012) or during early dark hours (Boucher et al. 1998). Shorter incubations increase the potential to drastically under- or over-estimate benthic fluxes depending on the time of day the incubations are done (Fig. 5, Table 3). If incubations are performed during early evening hours they have the potential to overestimate night time respiration on a daily basis. If incubations are performed during daylight hours by covering the chamber with dark material, respiration rates may be underestimated as primary production may be inhibited, potentially reducing the amount of labile organic material available for respiration.

When the linear regression approach is used to calculate net daily fluxes the sediments are net autotrophic but when the integral based approach is used they are net
heterotrophic based both on DIC and DO concentrations (Table 3). Net daily TAC fluxes are also opposite depending on the calculation method employed. When the regression rate is used, alkalinity is taken up by the sediments, i.e., net precipitation is occurring. However, when the integral based approach is used net dissolution of the sediments is occurring. These results emphasize the importance of measuring fluxes over the course of an entire diel cycle. The complete reversal in the dynamics of benthic ecosystems can have a large influence on community level models and our understanding of their biogeochemistry. The diel variability of respiration, photosynthesis, and carbonate precipitation and dissolution needs to be taken into account when calculating net fluxes. However, if incubations are performed over the course of an entire diel cycle and the end point method (Ferguson et al. 2003; Glud et al. 2008) is used to calculate fluxes, there is good agreement with the integral based method (Table 3). Even though the end point method yielded net fluxes that were similar to the integral based method there were still discrepancies between some of the fluxes (Table 3). This may be due to the fact that the end point method does not take into account the small changes in hourly fluxes that occur over a diel cycle (Fig. 5). Due to the more detailed information provided by the integral based approach, net fluxes used in the discussion were calculated by integration.

Biological and geochemical carbon cycling based on DIC and TAC regressions

The proportion of DIC flux due to biological (respiration and photosynthesis, also referred to organic metabolism by others) and geochemical (carbonate precipitation and dissolution, also referred to inorganic metabolism by others) processes can be determined from the slope of DIC vs. TAC by accounting for the portion of DIC flux due to carbonate precipitation and dissolution (Gattuso et al. 1996). As the stirring rate increases, the ratio of DIC flux due to biological processes to that due to geochemical processes increases.
from 1.99 to 2.40 (Fig. 6, Table 4). These results are consistent with the stimulation of oxidative respiration by advection in carbonate sands (Glud et al. 2008). The average net DIC flux from the chambers was -12.5, 0.7, and -4.4 mmol m\(^{-2}\) d\(^{-1}\) in the 0, 40, and 60 RPM chambers, respectively. The average ratio of TA/DIC fluxes over the course of the day were 0.72, 0.60, and 0.67 in the 0, 40, and 60 RPM chambers respectively. This corresponds with the increase in respiration in the advective chambers, and a release of more CO\(_2\) per mole of TA fluxed into the water column under advective conditions. The increase in the biological component may be due to the stimulation of photosynthesis during the daylight hours at higher advection rates (see Fig. 5A) and subsequent release of more organic carbon that becomes available for respiration (Cook and Røy 2006). Whole community coral reef fluxes have been shown to have biological to geochemical ratios of DIC fluxes that range from 3 to 6 (Frankignoulle et al. 1996; Gattuso et al. 1996). The ratio of concentrations in the water column (2.83) was close to the bottom end of that range (Fig. 7, Table 4). Because carbonate sediments contain a large pool of inorganic carbon it is not surprising that the DIC fluxes from the sediments have a lower biological to geochemical ratio than whole reef communities, which are influenced by both benthic and pelagic processes.
Figure 6. Regressions of TA\text{C} vs. DIC and DO vs. DIC\text{TAC} fluxes from all three chambers.

Table 4. The $R^2$, y-intercept ($y_0$), and slope values from the regression analysis of DIC vs. TA\text{C} fluxes shown in Fig. 5. Percent precipitation was determined by dividing the slope by two and multiplying that value by 100. The ratios of biological (bio) to geochemical (geo) DIC fluxes were calculated from the slope and percent precipitation.

<table>
<thead>
<tr>
<th>Chamber</th>
<th>$r^2$</th>
<th>$y_0$</th>
<th>Slope Geochemical</th>
<th>% Precipitation</th>
<th>DIC \text{bio:geo}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusive</td>
<td>0.964</td>
<td>-0.040</td>
<td>0.669</td>
<td>33.5</td>
<td>1.99</td>
</tr>
<tr>
<td>40 RPM</td>
<td>0.942</td>
<td>-0.207</td>
<td>0.637</td>
<td>31.9</td>
<td>2.14</td>
</tr>
<tr>
<td>80 RPM</td>
<td>0.862</td>
<td>0.219</td>
<td>0.589</td>
<td>29.5</td>
<td>2.40</td>
</tr>
<tr>
<td>Water column</td>
<td>0.921</td>
<td>1175.4</td>
<td>0.522</td>
<td>26.1</td>
<td>2.83</td>
</tr>
</tbody>
</table>

Another process that could potentially affect sediment alkalinity fluxes is the uncoupling of sulphate reduction and sulphide oxidation (Ku et al. 1999). Regressions of DIC\text{TAC} vs. DO fluxes from the 40 RPM and 80 RPM chambers (i.e., when advection is induced) have slopes very close to one, indicating that once the DIC fluxes are corrected for the precipitation and dissolution of carbonates the two methods of measuring...
respiration and photosynthesis agree closely (Fig. 6). If there were an uncoupling of sulphate reduction and sulphide oxidation in anoxic zones (and subsequent increase in alkalinity), we would expect to see an increase in DIC unaccounted for by a decrease in DO (Eyre and Ferguson 2002), which is not observed in the advective chambers. This lends support not only to the validity of the two methods used to calculate photosynthesis and respiration rates, but also supports the majority of alkalinity changes being accounted for by the precipitation and dissolution of carbonate minerals. Also, sulphate concentrations have been shown to be conservative in carbonate sediments to depths where the advective cycling of porewaters is occurring, indicating no net flux of alkalinity due to these processes (Burdige and Zimmerman 2002).

**Effects of $\Omega_{Ar}$ on benthic fluxes of alkalinity**

When graphed against $\Omega_{Ar}$, the sediment flux of alkalinity follows a distinct diel hysteretic pattern (Fig. 8). Interestingly, $TAC$ flux does not follow a trend consistent with the

![Figure 7. Regression of $TAC$ vs. DIC concentrations from the water column.](image_url)
Chapter 2

\( \Omega_{\text{Ar}} \) of porewater being the main driver of carbonate precipitation and dissolution (Morse and Arvidson 2002). Instead, carbonate precipitation and dissolution are linearly correlated to photosynthesis and respiration fluxes occurring over the same time period (Fig. 9). It seems that even though respiration decreases \( \Omega_{\text{Ar}} \) consistently throughout the night (Fig. 4), dissolution is more closely linked to the amount of respiration occurring instead of the bulk \( \Omega_{\text{Ar}} \) of the porewater. This is consistent with the hypothesis that DIC within the microenvironments of carbonate sediment grains is intimately linked to the precipitation and dissolution of carbonate minerals (Henrich and Wefer 1986; Freiwald 1995).

These results have implications in using the \( \Omega_{\text{Ar}} \) of seawater as an overall indicator of carbonate precipitation and dissolution in sediments. Whole system calcification is often assumed to be linearly dependent on \( \Omega_{\text{Ar}} \) (see fig. 6 in Shamberger et al. 2011). However our results show that the processes occurring within the sediments make this interpretation much more complex (Fig. 8). Shamberger et al. (2011) used daily fluxes which would obscure any hysteretic pattern as evidenced by hourly fluxes. In large scale models (Morse et al. 2006), using the \( \Omega_{\text{Ar}} \) of overlying seawater to estimate the dynamics of carbonate dissolution in the sediments may misinterpret what is actually occurring. If respiration drives the dissolution of carbonates within microenvironments, porewaters, and especially the overlying waters, do not need to reach a \( \Omega < 1 \) of metastable minerals for dissolution to occur. In fact, Andersson et al. (2007) found that sediment dissolution rates in Devil’s Hole, Bermuda were similar to those reported throughout the literature despite the overlying water at their study sites having a much lower \( \Omega_{\text{Ar}} \). Even if porewaters have high \( \Omega_{\text{Ar}} \), microenvironments may promote the dissolution of carbonates and the export of
alkalinity into the water column, perhaps allowing coral reef ecosystems to self-buffer before large scale changes in $\Omega_{Ar}$ occur due to ocean acidification.

**Figure 8.** Carbonate alkalinity fluxes ($TA_C$) plotted against the saturation state of the overlying water during the incubations. The start and end points are shown and the fluxes are plotted from the beginning to the end of the incubations.
Integrated hourly fluxes of DO and DIC were clearly related to the average PAR measured during the same time interval (Fig. 10). By plotting DO and DIC fluxes against PAR, photosynthesis-irradiance (P-I) curves can be generated which allow for the modeling of production based on the amount of PAR received. The benthic DIC$_\text{TAC}$ and DO fluxes show trends consistent with P-I curves of whole ecosystem studies (Gattuso et al. 1996). The DO fluxes fit well to logarithmic curves with all of the $R^2$ values above 0.795 (Fig. 10). Based on the logarithmic fit, the maximal hourly fluxes of DO increased with advection rates from 3.13 to 4.85 to 6.19 mmol m$^{-2}$ h$^{-1}$ in the diffusive, 40 and 80 RPM chambers, respectively. This is consistent with other studies, which show the stimulation of benthic primary productivity with increased advection (Cook and Røy 2006;...
Glud et al. 2008). DIC fluxes were similarly stimulated by PAR, but in both the diffusive and 40 RPM chambers a maximum was not reached so linear regressions were used. At 80 RPM a logarithmic function fit the data with an $R^2$ of 0.848 and maximal day time flux of -5.39 mmol m$^{-2}$ h$^{-1}$ (Fig. 10).

Figure 10. DO and DIC fluxes plotted against the average PAR measurements made during the same time period the flux was measured. Regressions are displayed as explained in the text.

No distinct P-I like trend was observed for the TA$_C$ flux vs. PAR plot (Fig. 11). Instead the magnitude of the rates was highly influenced by the time of day, showing a hysteretic trend. The influx of alkalinity into the sediments (precipitation) increased with higher PAR, but the rates recorded in the morning were lower than those time intervals receiving similar PAR levels in the afternoon. This is most likely due to the lowering of the carbonate mineral saturation state overnight due to respiration (Fig. 4). As the saturation state increased during the day due to benthic photosynthesis, so too did the rates of precipitation. These observations are consistent with reports of photosynthesis having a stimulating effect on calcification in corals (Goreau 1959; Pearse and Muscatine 1971).

These results not only showed that solute fluxes over a 24 hour period were highly dependent on the amount PAR reaching the benthos, but also were highly variable throughout the night (Figs. 4, 7, 8). This observation supports our earlier suggestion that
shorter incubations (Rasheed et al. 2004; Rao et al. 2012) may not accurately reflect the changes in respiration occurring throughout the night. The results also imply (especially TA fluxes) that performing dark incubations during the day light hours and extrapolating those rates to night time hours can grossly over or underestimate rates based on the starting conditions within the incubation.

Figure 11. TA fluxes plotted against the average PAR measurements made during the same time period the flux was measured. The start time for each flux measurement is written next to the data point with arrows showing the historical trends described in the text.

For example Rao et al. (2012) performed similar incubations to ours but covered the chambers with dark material and performed both light and dark incubations for 5 h starting at midday. Using the slope-based method to calculate net fluxes, combined with their experimental methodology, would result in artificially lowered dark alkalinity effluxes due to the time of day the incubations were performed (Fig. 5). In sediments similar to ours, Rao et al. (2012) generally found lower dark (1.0 to 2.1 mmol m$^{-2}$ h$^{-1}$) and net daily (-5.32 to 8.22 mmol m$^{-2}$ d$^{-1}$) fluxes of alkalinity than those described here. In addition, the net daily release of alkalinity decreased with increasing advection rate, with the sediments becoming net sinks at the highest advection rates. This supports the idea that diel variability should be taken into account when calculating net daily fluxes as there is a large potential for methodology to greatly influence the magnitude and direction of the
rate. Because the amount of PAR reaching the sediments greatly influenced their biogeochemistry, it may also be important to measure these cycles over daily and seasonal timescales that represent natural variability in PAR.

Interaction of advection and carbonate precipitation and dissolution

Porewater advection has been shown to have a large effect on the rates of photosynthesis and respiration occurring in permeable sediments (Janssen et al. 2005; Glud et al. 2008). Our experiment adds to previous work by demonstrating the advective stimulation of carbonate dissolution (Table 3, Fig. 5). Interestingly, the rates of photosynthesis and respiration are stimulated equally by advection. In the diffusive chamber the maximum rate of photosynthesis was 5.83 mmol C m\(^{-2}\) h\(^{-1}\) and the maximum rate of respiration was 4.63 mmol C m\(^{-2}\) h\(^{-1}\). The maximum hourly photosynthetic rate within the 80 RPM chamber was 7.64 mmol C m\(^{-2}\) h\(^{-1}\) while the maximum night time respiration rate was 6.69 mmol C m\(^{-2}\) h\(^{-1}\). Precipitation is stimulated by advection during the day, with maximum hourly TAC fluxes of -4.83, -5.65, and -7.36 mmol m\(^{-2}\) h\(^{-1}\) in the diffusive, 40 RPM, and 80 RPM chambers, respectively. Maximum fluxes of TAC during the night (dissolution) also increase with increasing stirring rates from 5.21 to 5.65 mmol m\(^{-2}\) h\(^{-1}\) between the diffusive and 80 RPM chambers, respectively. The maximum alkalinity fluxes from this study are roughly 5-times higher than previously reported, non-advective rates from similar carbonate environments (Table 5). On a daily basis alkalinity is fluxed out of the sediments and into the water column, with similar rates observed in the 40 RPM and 80 RPM chambers (Table 3).

There are a few potential reasons why advection stimulates the release of alkalinity from sediments. Firstly, advection stimulates respiration (Glud et al. 2008) which would induce TAC efflux due to the tight coupling of respiration and carbonate dissolution (Fig.
However, one interesting aspect of advective stimulation is that there is a balance between flux rates at the higher advection rates because counteracting processes (photosynthesis and respiration) may be stimulated in a similar manner. This can have a large effect on daily alkalinity fluxes which are highly dependent on those processes. The complex interaction between the advective stimulation of photosynthesis and respiration drives the advective stimulation of carbonate dissolution on a daily basis. Secondly, the water being advected into the sediments introduces oxygen to greater depths, which would reduce sulphate reduction and the associated production of alkalinity (Ku et al. 1999; Morse et al. 2006). This lessened production of alkalinity may decrease carbonate saturation and precipitation of CaCO$_3$. Fig. 9 implies that enhanced respiration is probably the main driver of increasing CaCO$_3$ dissolution with increasing advection of seawater into the sediments, although some of the scatter in Fig. 8 may be due to inhibited sulphate reduction. Further work is required to unravel the complex interactions between advection, benthic respiration and production, and CaCO$_3$ dissolution in permeable sediments.

Table 5. Hourly alkalinity fluxes from carbonate sands. Method refers to the method used to calculate alkalinity fluxes.

<table>
<thead>
<tr>
<th>Location</th>
<th>Bottom type</th>
<th>Alkalinity flux (mmol m$^{-2}$ h$^{-1}$)</th>
<th>Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bahamas oolithic</td>
<td>carbonatesands</td>
<td>0.008-0.08</td>
<td>Diffusive flux estimated from pore water</td>
<td>Burdige and Zimmerman 2002</td>
</tr>
<tr>
<td>Bermuda carbonate</td>
<td>sediments</td>
<td>0.4 - 1.6</td>
<td>Alkalinity excess and vertical eddy</td>
<td>Andersson 2007</td>
</tr>
<tr>
<td>Bermuda carbonate</td>
<td>sediments</td>
<td>0.6</td>
<td>Bell jar incubation</td>
<td>Balzer and Weller 1981</td>
</tr>
<tr>
<td>Biosphere 2</td>
<td>carbonate sediments</td>
<td>0.4</td>
<td>Mesocosm incubation</td>
<td>Langdon et al. 2000</td>
</tr>
<tr>
<td>Florida carbonate</td>
<td>sand bottom</td>
<td>0.06</td>
<td>Chamber incubation</td>
<td>Yates and Halley 2003</td>
</tr>
<tr>
<td>Hawaii carbonate</td>
<td>sand bottom</td>
<td>0.06</td>
<td>Chamber incubation</td>
<td>Yates and Halley 2003</td>
</tr>
<tr>
<td>Heron Island</td>
<td>carbonate sediments</td>
<td>0.5 - 5.6</td>
<td>Adveactive chamber incubation over complete</td>
<td>this study</td>
</tr>
<tr>
<td>Heron Island</td>
<td>carbonate sediments</td>
<td>1.0 - 2.1</td>
<td>Light and dark adveactive chamber</td>
<td>Rao et al. 2012</td>
</tr>
<tr>
<td>Mesoicosm</td>
<td>carbonate sand</td>
<td>1.6</td>
<td>Mesocosm incubation</td>
<td>Leclerc et al. 2002</td>
</tr>
<tr>
<td>Moorea carbonate</td>
<td>sand bottom</td>
<td>1.6</td>
<td>Chamber incubation</td>
<td>Boucher et al. 1998</td>
</tr>
</tbody>
</table>
Chapter 2

Contribution of sediments to community scale processes

Since low tides isolate the Heron Island lagoon from mixing with open ocean water, whole community fluxes for the lagoon can be estimated based on solute concentration changes during those times (Santos et al. 2011). Our community rates calculated during low tides agree well with other studies measuring community rates of photosynthesis and respiration on coral reefs, which report a range from 31 to 52 mmol C m\(^{-2}\) h\(^{-1}\) (Frankignoulle et al. 1996; Gattuso et al. 1996) (Table 4). Hourly fluxes from the sediments during the same time period of the low tides were compared to whole community fluxes obtained for the 3 low tides covered by our water column time series (Table 6). According to whole community estimates derived from our data, sediments contribute 3% to 14% of community photosynthesis and 3% to 9% of precipitation during the day. At night sediments contribute 9% to 19% of community respiration and 7% to 11% of community dissolution.

Table 6. Results of community fluxes calculated at low tides during the incubations. An average depth of 1.7 m was assumed for the lagoon. Fluxes 1 and 3 are during day light hours and flux 2 was at night. The fluxes from the chambers were calculated during the same time interval as the community fluxes. All rates are in mmol m\(^{-2}\) h\(^{-1}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>DO</th>
<th>TAC</th>
<th>DIC</th>
<th>DIC(_{TAC})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Community-1</td>
<td>45.20</td>
<td>-109.50</td>
<td>-60.76</td>
<td>-79.12</td>
</tr>
<tr>
<td>Diffusive-1</td>
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<tr>
<td>40 RPM-1</td>
<td>3.25</td>
<td>-3.82</td>
<td>-4.46</td>
<td>-2.55</td>
</tr>
<tr>
<td>80 RPM-1</td>
<td>3.14</td>
<td>-6.45</td>
<td>-8.28</td>
<td>-5.06</td>
</tr>
<tr>
<td>Community-2</td>
<td>-24.60</td>
<td>42.77</td>
<td>21.33</td>
<td>32.11</td>
</tr>
<tr>
<td>Diffusive-2</td>
<td>-2.52</td>
<td>3.25</td>
<td>5.82</td>
<td>4.63</td>
</tr>
<tr>
<td>40 RPM-2</td>
<td>-3.48</td>
<td>3.12</td>
<td>5.00</td>
<td>3.46</td>
</tr>
<tr>
<td>80 RPM-2</td>
<td>-4.76</td>
<td>4.71</td>
<td>6.19</td>
<td>2.79</td>
</tr>
<tr>
<td>Community-3</td>
<td>48.43</td>
<td>-80.03</td>
<td>-48.20</td>
<td>-55.93</td>
</tr>
<tr>
<td>Diffusive-3</td>
<td>2.42</td>
<td>-4.64</td>
<td>-8.15</td>
<td>-5.83</td>
</tr>
<tr>
<td>40 RPM-3</td>
<td>5.63</td>
<td>-5.18</td>
<td>-8.70</td>
<td>-6.11</td>
</tr>
</tbody>
</table>
Depending on the rate of advection, the dissolution of carbonate minerals fluxes 5.13 to 8.84 mmol m\(^{-2}\) d\(^{-1}\) of alkalinity into the water column from the sediments (Table 3). Because sediments make up roughly 85\% of the 26.4 Km\(^{2}\) reef flat (Glud et al. 2008), they contribute a total of 115 to 199 kmol d\(^{-1}\) of carbonate alkalinity into the system. If we assume the coral community calcification rate at Heron Island to be 100 mmol CaCO\(_3\) m\(^{-2}\) d\(^{-1}\) (Nakamura and Nakamori 2009) and the remaining 15\% of the reef flat to be covered by corals, then the uptake of carbonate alkalinity by corals is estimated as 792 kmol d\(^{-1}\). From a mass balance standpoint this means that on a daily basis the sediments can supply 14\% to 25\% of the carbonate alkalinity consumed by corals within the Heron Island reef flat. It is unresolved whether corals may grow at the expense of sediment dissolution, as opposed to the commonly believed notion that corals supply carbonate to the sediment pool, although there is probably a complex cycling that occurs between these two pools of carbonate minerals.

**Potential implications for ocean acidification**

By using a simple calculation similar to the one above we can estimate the addition of H\(^+\) ions into the system based on rates of ocean acidification. A high end estimate of pH change is -0.002 pH yr\(^{-1}\), or 0.0231 nmol H\(^+\) L\(^{-1}\) yr\(^{-1}\) (Gattuso et al. 2011). If we assume an average depth of 1.7 m, there is an increase in H\(^+\) concentration of 0.001 kmol yr\(^{-1}\) within the Heron Island reef flat due to ocean acidification. The amount of alkalinity put into the system on a yearly basis from the sediments is estimated as 41,975 to 72,635 kmol yr\(^{-1}\), orders of magnitude greater than a decrease caused by ocean acidification. While much of the alkalinity produced by sediments will likely be consumed by corals or exported offshore, this simple estimate illustrates the need to consider carbonate sands in ocean acidification models.

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Previous models relying on diffusive benthic fluxes suggest that sediments in shallow waters can buffer only a minor fraction of anthropogenic CO$_2$ inputs (Andersson et al. 2007). Our field observations demonstrate that porewater advection may enhance the buffering capacity of shallow water sediments against ocean acidification on a local scale, although local hydrodynamics and the ability of a system to accumulate alkalinity will also be important. The magnitude of this buffering capacity is probably highly dependent on the exact mineralogy, especially the amount of high magnesium calcites, of the sediments undergoing dissolution (Morse and Arvidson 2002). Most importantly, because much of the tropical continental shelf is covered by permeable carbonate sediments (Milliman and Droxler 1996) and permeable sands filter the entire ocean volume on a time scale of about 3000 years (Santos et al. 2012), and light reaches a large proportion of these shelves (Gattuso et al. 2006), our findings may be applicable to broader areas. Resolving the contribution of porewater advection in carbonate sands to the global alkalinity budget is important to refining ocean acidification models.
Chapter 3

Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon

(Muri Lagoon, Cook Islands)
3.1 Abstract

To better predict how ocean acidification will affect coral reefs, it is important to understand how biogeochemical cycles on reefs alter carbonate chemistry over various temporal and spatial scales. This study quantifies the contribution of fresh groundwater discharge (as traced by $^{222}\text{Rn}$) and shallow porewater exchange (as quantified from advective chamber incubations) to total alkalinity (TA) dynamics on a fringing coral reef lagoon along the southern Pacific island of Rarotonga over a tidal and diel cycle. Benthic alkalinity fluxes were affected by the advective circulation of water through permeable sediments, with net daily fluxes of carbonate alkalinity ranging from -1.55 to 7.76 mmol m$^{-2}$ d$^{-1}$, depending on the advection rate. Submarine groundwater discharge (SGD) was a source of TA to the lagoon, with the highest fluxes measured at low tide, and an average daily TA flux of 1,080 mmol m$^{-2}$ d$^{-1}$ at the sampling site. Both sources of TA were important on a reef wide basis, although SGD acted solely as a delivery mechanism of TA to the lagoon, while porewater advection was either a sink or source of TA dependent on the time of day. This study describes overlooked sources of TA to coral reef ecosystems that can potentially alter water column carbonate chemistry. We suggest that porewater and groundwater fluxes of TA should be taken into account in ocean acidification models in order to properly address changing carbonate chemistry within coral reef ecosystems.
Chapter 3

3.2 Introduction

The recent increase in atmospheric CO$_2$ has led to an increase in oceanic $p$CO$_2$ as roughly 30% of anthropogenic CO$_2$ has been absorbed by the oceans (Orr et al. 2005; Doney et al. 2009; Sabine et al. 2004; Feely et al. 2004). Ocean acidification is the term given to this increase in oceanic $p$CO$_2$, which alters the carbonate chemistry of seawater leading to a reduction in pH at a rate of roughly 0.002 y$^{-1}$ (Feely et al. 2004; Doney et al. 2009). Ocean acidification can have drastic effects on biological processes and the biogeochemistry of marine ecosystems, with coral reefs predicted to be some of the most susceptible ecosystems (De’ath et al. 2009; Fabry et al. 2008). The biogeochemical processes occurring on coral reefs can modify the carbonate chemistry of the overlying seawater, leading to large diel variations in alkalinity, $p$CO$_2$, pH, and dissolved oxygen (DO) (Shaw et al. 2012; Gray et al. 2012; Santos et al. 2011; Shamberger et al. 2011). In order to understand how ocean acidification will affect coral reefs, it is important to understand how natural processes, which can potentially buffer or intensify changes in seawater pH, alter the carbonate chemistry of seawater within coral reef ecosystems.

As CO$_2$ dissolves in water it is hydrolyzed to form carbonic acid in the following equilibrium reactions:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

(1)

Due to the production of $HCO_3^-$ and $CO_3^{2-}$, the increase in H$^+$ ions causes a reduction in seawater pH but does not change the total alkalinity (TA) (Millero, 1979; Zeebe and Wolf-Gladrow, 2001). The TA of a solution represents the ability of the solution to absorb H$^+$ ions without an associated reduction in the pH, and in seawater is equal to the following equation (Wolf-Gladrow et al. 2007):
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\[ TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-] - [H^+] - [H_2SO_4^-] - [HF] - [H_3PO_4] - [HNO_2] \]

(2)

Within the range of normal oceanic pH, and especially in oligotrophic waters, the majority of alkalinity in seawater is found in the form of dissolved inorganic carbon (DIC) as \( HCO_3^- \) and \( CO_3^{2-} \) (Wolf-Gladrow et al. 2007; Millero, 1979).

The dissolution and precipitation of carbonate minerals, both biotic and abiotic, can alter the water column TA within coral reef lagoons (Andersson et al. 2007; Rao et al. 2012). These changes in TA are large enough that ecosystem calcification rates have historically been measured using the alkalinity anomaly technique (Gattuso et al. 1996; Chisholm and Gattuso, 1991), which relies on the measuring the change in water column TA according to the following equation:

\[ CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \]

(3)

Because \( CO_3^{2-} \) is equal to 2 TA equivalents, calcification rates are equal to half the change of TA concentrations.

TA measurements are widely used in ocean acidification research to quantify community calcification rates (Shamberger et al. 2011; Silverman et al. 2012), measure sediment precipitation and dissolution rates (Andersson et al. 2007; Cyronak et al. 2013), correct net ecosystem production calculations for inorganic carbon contributions (Gattuso et al. 1996; Frankignouille et al. 1996; Suzuki and Kawahata, 2003), and to measure reef dissolution and bioerosion (Manzello et al. 2008; Lazar and Loya, 1991; Zundelevich et al. 2007). Also, it has been suggested that alkalinity generated from sediment dissolution may act as a partial buffer against any decrease in pH associated with ocean acidification, (Morse et al. 2006; Kleypas and Langdon, 2006), although this buffering capacity is still
being debated (see Andersson and Mackenzie, 2012). The importance of TA in ocean acidification research makes it important to constrain all sources and sinks of TA within coral reef ecosystems.

The exchange of solutes between the water column and permeable carbonate sediments is driven mainly by advective processes (Santos et al. 2012; Precht and Huettel, 2003). Flow and topography induced porewater exchange (see Fig 1(5) in Santos et al. 2012) is probably the dominant process driving porewater exchange within coral reef lagoons due to the formation of ripples and crests within permeable carbonate sediments (Precht and Huettel, 2003). This process acts on short temporal (minutes to hours) and small spatial (cm) scales to induce the exchange of porewater solutes with the overlying water column (Precht and Huettel, 2003). Porewater advection has a stimulatory effect on biological processes occurring within the sediments (Cook and Roy, 2006; Glud et al. 2008; Eyre et al. 2008) and has also been shown to have a stimulatory effect on TA fluxes, with increasing advection rates increasing net daily TA fluxes (Cyronak et al. 2013; Rao et al. 2012). However, while coral reef community calcification rates are positively correlated with the aragonite saturation state ($\Omega_{\text{Ar}}$) of the water column (see Fig. 6 in Shamberger et al. 2011), carbon cycling in permeable sediments cannot be easily predicted by the $\Omega_{\text{Ar}}$ of the overlying water (Cyronak et al. 2013).

Submarine groundwater discharge (SGD) has been shown to be an important component of freshwater delivery to coastal ecosystems, on the scale of 6% to 10% of surface water flow, which amounts to an estimated 10,000 L m$^{-1}$ d$^{-1}$ along the global coast (Burnett et al. 2003; Santos et al. 2012). The few studies assessing SGD rates on coral reefs describe a range from 52 to 4,732 L m$^{-1}$ h$^{-1}$, and suggest that SGD can be an important source of solutes to coral reef ecosystems (Paytan et al. 2006; D'Elia and Wiebe, 1990; Lewis, 1987; Blanco et al. 2011; Knee et al. 2010). There are multiple methods to
estimate SGD into coastal ecosystems including seepage meters, piezometers, natural tracers, water balance approaches, and theoretical modeling (Burnett et al. 2006). Due to its naturally high concentrations in groundwater compared to surface waters, and its unreactive nature, \(^{222}\text{Rn}\) has been used as a natural tracer for groundwater in aquatic systems for decades (Burnett et al. 2006; Cable et al. 1996). Mass balance models using \(^{222}\text{Rn}\) have been developed that estimate SGD fluxes into coastal ecosystems (Burnett and Dulaiova, 2003).

Groundwater concentrations of TA can be higher than oceanic waters and encompasses a broad range from 90 to 23,300 \(\mu\text{mol L}^{-1}\) (Rad et al. 2007; Schopka and Derry, 2012; Mahlknecht et al. 2004; Moore et al. 2011). Using radium based SGD effluxes, Moore et al. (2011) demonstrated that SGD is a source of alkalinity to the water column in the Wadden Sea. Therefore, groundwater exchange processes occurring on larger temporal and spatial scales than flow induced advective exchange also have the potential to deliver TA to coral reef lagoons. In fact, Kleypas and Langdon (2006) postulated that ocean acidification may be buffered against in coral reef ecosystems through the exchange of groundwater. The ability of groundwater to act as a source of TA to coral reef lagoons is highly dependent on the exchange rates with the water column, which can have large temporal and spatial variation (Santos et al. 2012; Lewis, 1987; Burnett et al. 2003). Determining the sources and sinks of alkalinity to coral reef ecosystems from groundwater and porewater exchange mechanisms is important in constraining how increasing \(p\text{CO}_2\) will impact seawater carbonate chemistry within coral reef ecosystems.

The hypothesis of this study is that two groundwater sources (porewater advection and fresh SGD) will contribute TA to Muri Lagoon, a fringing coral reef lagoon in the Cook Islands. To test this hypothesis, advective, benthic incubations were undertaken to
determine the influence of porewater advection on alkalinity fluxes from permeable sediments over short temporal and spatial scales (herein referred to as porewater fluxes). Measurements of $^{222}$Rn were also undertaken to determine the input of alkalinity from larger temporal and spatial scale groundwater exchange (herein referred to as SGD or groundwater). While “porewater” and “groundwater” are technically synonymous (i.e., any water in contact with geological materials), the hydrology and oceanography communities tend to refer to porewater as a shallow interstitial water and groundwater as deeper, fresher water (Burnett et al. 2003; Burnett et al. 2006).

### 3.3 Methods

**Study site**

Our study site was located on the island of Rarotonga, a South Pacific, volcanic island within the archipelago of the Cook Islands. Rarotonga is the largest island in the Cook Islands group (67 km$^2$) and made up of volcanic rocks that are comprised of 42% to 53% SiO$_2$ and 2% to 14% CaO (Waterhouse et al. 1986). Rarotonga has a rainy (November to April) and dry (May to October) season, with average annual rainfall of 1900 mm y$^{-1}$ (Thompson, 1986). Muri Lagoon is a fringing, coral reef lagoon located along the south western coast of Rarotonga (Fig. 12). The study site was divided into two locations within Muri Lagoon, one where the chamber incubations were performed and the second where the water column monitoring station was set up (Fig. 12). The chamber sampling site was located further (~75 m) from shore to minimize any SGD impact and because of the large area of carbonate sediments free from macrophytes. The monitoring station consisted of multiple probes and a bilge pump connected to a cinder block roughly 10 m offshore from the low tide mark. The lagoon extended roughly 750 m offshore to the reef crest from our monitoring station (Fig. 12). Muri Lagoon has an average depth of
about 1.4 m and covers an area of 1.75 km$^2$ (Holden, 1992). The flow in Muri Lagoon is dominated by wave setup and runs from the reef crest towards shore, and then northeast along the shore towards a channel which opens to the ocean (Holden, 1992). The tidal cycle in Muri Lagoon is semi-diurnal with an average range of 1 m. The tidal range during our sampling period was 0.4 m and was towards the beginning of the neap tide cycle.

![Map of Rarotonga showing the location of Muri Lagoon and the sampling site.](image)

Sediment in the lagoon has a hydraulic conductivity of $\sim 17.3$ m$^{-1}$ d$^{-1}$, which equates to a permeability of approximately $1.91 \times 10^{-11}$ m$^2$. Sediment grain size was 5.8$\% > 2$ mm, 16.5$\%$ between 1-2 mm, 19.4$\%$ between 500 $\mu$m–1 mm, 30.6$\%$ between 250 $\mu$m–500 $\mu$m, 25.0$\%$ between 125 $\mu$m–250 $\mu$m, 2.5$\%$ between 63 $\mu$m–125 $\mu$m, and 0.2$\% < 63$ $\mu$m. Bulk carbonate sediments were composed of 0.5$\%$ calcite, 0.7$\%$ quartz, 26.3$\%$ Mg-calcite (15.5$\%$ Mg content), and 71.9$\%$ aragonite as determined by XRD analysis. Visual
inspection of the sediments revealed black coloration a few cm below the surface, which is typical of high sulphide concentrations.

**Advective chamber sampling and porewater fluxes**

Chambers identical to those described in Glud et al. (2008) and Eyre et al. (2008) were used to measure in situ benthic solute fluxes at three different advection rates. Three chambers were inserted 15 cm into the sediment and enclosed roughly 4 L of overlying seawater during the incubations. Advection was induced within the chambers based on the spinning rate, in rotations per minute (RPM), of the acrylic disk within each chamber (diffusive, 40 RPM, and 60 RPM). Three stirring rates were chosen in order to investigate any effect of advection on alkalinity fluxes, similar to studies done in other coral lagoons (Cyronak et al. 2012; Glud et al. 2008). In order to maintain a homogenous distribution of solutes within the diffusive chamber it was operated with the disk slowly spinning clockwise for one rotation, then pausing and spinning counter clockwise for one rotation and repeating (Glud et al. 2008). Incubations were run concurrent with the water column sampling, starting at 07:00 h on 17 March 2012 and lasting for 28.5 hours. Samples of 150 mL were drawn by syringe with ambient seawater allowed to replace the sample volume. The sample volume removed represented a minor percentage of the volume within the chambers (< 4%) and therefore was unlikely to greatly influence chamber solute concentrations. Fluxes from the chambers were calculated using the integral-based technique as described in Cyronak et al. (2013). Negative numbers represent a flux into the sediments while positive numbers represent fluxes of solutes out of the sediments. In order to compare advective fluxes to $^{222}$Rn derived SGD fluxes, averages between the two advective stirring rates (40 and 60 RPM) were used (discussed in detail later).
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Water column sampling

Discrete samples were taken every 2 hours from the water column along with the monitoring of the physico-chemical parameters every 5 minutes using a multi-probe. A Hydrolab DS5X (Hach Environmental) was deployed 0.2 m from the bottom and 10 m offshore of the low tide mark to monitor temperature (± 0.5%), PAR (± 5%), and salinity (± 0.5%) every 5 min. Depth was measured using an In-Situ Inc. Aqua Troll 200. For the monitoring data, an average over one hour (30 min before and after) was taken over half hour intervals in order to smooth the data and better reveal any trends. Sampling of the water column started at 07:00 h on 17 March 2012 and lasted for 28.5 hours. Discrete water samples were taken using 150 mL plastic syringes and brought back to lab to measure salinity, DO, TA, δ¹³C DIC, and pH.

In order to measure ²²²Rn concentrations in the water column, a submersible bilge pump continuously pumped seawater to an onshore gas equilibration device (GED) at about 2 L min⁻¹. The GED equilibrates gas through a shower head exchanger similar to that described in Burnett et al. (2001). Air was recirculated through a closed loop from the GED into a RAD7 ²²²Rn detector in order to monitor ²²²Rn concentrations every 30 minutes (Burnett et al. 2001). In order to generate a groundwater end member for ²²²Rn derived flux calculations, a bore was dug 10 m onshore of the high tide mark and piezometers were inserted to depths of 1 m and 2.5 m. Discrete samples were taken from the 1 m piezometer at 3 separate times during a diel cycle and one sample was taken from the 2.5 m piezometer. To measure the ²²²Rn end member of groundwater, a peristaltic pump was used to pump water from the piezometers at 1 L min⁻¹ into the GED. Gas permeable silicone tubing was only used in the pump head in order to minimize any losses of ²²²Rn and CO₂. Laboratory experiments revealed no differences in concentrations when using a peristaltic pump and other pumps to feed the exchanger. The ²²²Rn concentrations
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were allowed to equilibrate then measured for 1 to 4 hours with the average concentration during that time used as the groundwater end member.

We used a non-steady state $^{222}$Rn mass balance model from Burnett and Dulaiova (2003) to determine groundwater advection rates in $\text{cm}^3 \text{m}^{-2} \text{d}^{-1}$. The model incorporated sources of $^{222}$Rn from groundwater balanced by losses due to atmospheric evasion as a function of wind speed, mixing, and radioactive decay. The alkalinity of the mixed end member (discussed in detail later) was multiplied by the fluxes generated by the model in order to get $^{222}$Rn derived fluxes of groundwater TA into the lagoon. Both the advective TA fluxes and $^{222}$Rn derived TA fluxes were calculated at the sampling locations and extrapolated along a 750m transect to the reef crest (discussed in detail later).

Sample analysis

Both water column and benthic chamber samples were immediately brought back into the laboratory. Dissolved oxygen (± 1%) was measured immediately following collection using a Hach Luminescent Dissolved Oxygen (LDO®) probe. Samples for nutrients were filtered with a 0.45 $\mu$m cellulose acetate filter and frozen at -20°C until analysed following the methods of Eyre and Ferguson (2005) using a Lachat Flow Injection Analysis (FIA) system. Samples for total alkalinity (TA) and pH were filtered through a 0.45 $\mu$m cellulose acetate filter and stored in an airtight container with no headspace until analysis within 4 hours of sampling. pH (±0.003) was measured using a Metrohm Electrode Plus calibrated to Oakton National Bureau of Standards (NBS) standards of 4, 7, and 10. To determine TA, Gran titrations were performed using a Metrohm Titrando automatic titrator and pH electrode. Pre-standardized 0.01 mol L$^{-1}$ HCl was used as the titrant which was calibrated against Dickson Certified Reference Material.
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(Batch 111). Alkalinity samples were run twice and the average of the two values was used. During the study the % CV of duplicate TA measurements was 0.15%.

Samples for $\delta^{13}$C DIC (analytical error of ± 0.1‰ ) were 0.7µm filtered with a Whatman GF/F syringe filter, preserved using 50 µL of saturated HgCl$_2$ with no head space, and stored at 4°C. $\delta^{13}$C DIC was measured in order to separate any sources of TA and DIC in the groundwater and water column. Samples were acidified with 5% (v:v) phosphoric acid and the resulting CO$_2$ was analysed via continuous flow wet-oxidation isotope ratio mass spectrometry (CF-WO-IRMS) using an Aurora 1030W total organic carbon (TOC) analyzer coupled to a Thermo Delta V Plus IRMS (Oakes et al. 2010). DIC concentrations were estimated with the Excel macro CO$_2$ System (CO2SYS) (Pierrot et al. 2006) using inputs of TA and pH and the constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987), CO2SYS also generated $\Omega_{Ar}$. Data from Cyronak et al. (2013) showed excellent agreement between measured and calculated DIC concentrations using the same inputs into CO2SYS as this study. Carbonate alkalinity ($TA_C$) for the chamber samples was calculated by subtracting the alkalinity, as determined in CO2SYS, contributed by B(OH)$_4^-$, OH$^-$ and total dissolved phosphorus (TDP) from TA.

3.4 Results

Advective chambers

The fluxes of $TA_C$, DIC, DO, and H$^+$ from the chambers are shown in Figure 2. All of the rates follow a distinct diel pattern that is consistent with biological activity acting as the driver of solute fluxes from permeable sediments. Fluxes of $TA_C$ decreased throughout the day and began to increase in the late afternoon (Fig. 13A). $TA_C$ fluxes became positive around sunset and increased until midnight, and then varied slightly for the rest of the night until becoming negative in the morning. DIC fluxes showed a similar
pattern to \( \text{TAC} \) (Fig. 13B). DO and \( \text{H}^+ \) fluxes followed the opposite pattern of DIC and TAC fluxes (Fig. 13). DO fluxes increased throughout the morning then decreased in the late afternoon, becoming negative around sunset and levelling off during the night (Fig. 13C). \( \text{H}^+ \) fluxes showed the same trend as DO fluxes with slight variation in the night (Fig. 13D). In all cases, the fluxes in the 40 RPM chamber exhibited the largest range over a diel cycle (Fig. 13). Figure 3 shows the hourly fluxes of \( \text{TAC} \), DIC, and DO plotted against the average photosynthetic active radiation (PAR) measured during the same time as the flux was calculated. All three solutes show a distinct hysteretic pattern, with lower rates of all fluxes in the morning at comparable PAR levels in the afternoon (Fig. 14). The fluxes of \( \text{TAC} \) in the 40 RPM chamber showed the largest variation between the morning and afternoon (Fig. 14).

Figure 13. Hourly, integral derived fluxes of \( \text{TAC} \), DIC, DO and \( \text{H}^+ \) from the advective chambers. The grey filled area in the background is PAR over the course of the incubations. All fluxes are in \( \text{mmol m}^{-2} \text{h}^{-1} \) besides \( \text{H}^+ \) which are in \( \text{µmol m}^{-2} \text{h}^{-1} \).
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**Water column time series**

The water column time series was conducted over two tidal cycles and one diel cycle (Fig. 15). Salinity fluctuated throughout the day and the lowest salinities occurred during the low tides (Fig. 15A, B). DO concentrations and Ω_Ar followed a trend that was consistent with diel variation driven by biological processes, and throughout the course of the day Ω_Ar varied from 2.3 to 4.4 (Fig. 15E, F.). In contrast, TA had complex dynamics that were related to both diel and tidal cycles, supported by the variation in TA concentrations measured over one diel cycle and two tidal cycles (Fig. 15C). DIC concentration showed a similar trend to TA while the δ^{13}C of DIC following the opposite trend, decreasing with any increase in [DIC] (Fig. 15D). During sampling, ^{222}Rn concentrations in the water column varied between 7,471 dpm m^{-3} to 16,040 dpm m^{-3}, and were highest during low tides (Fig. 16).
Figure 14. Fluxes of TA\(_{C}\), DIC, and DO plotted against the average PAR values measured during the same time period as the flux. Fluxes are in mmol m\(^{-2}\) h\(^{-1}\).
Figure 15. (A) Depth, (B) salinity, (C) TA, (D) DIC, (E) DO, and (F) $\Omega_{Ar}$ measured in the discrete water samples taken from the water column. The grey filled area in the background is PAR over the course of the study.
Groundwater end members

Groundwater measured from piezometers at 1 m and 2.5 m were both fresh but differed in solute composition (Table 7). The water chemistry in the three samples taken from the 1 m well did not vary much between the different sampling times, so we reported the average (see Table 7). The DIC concentrations were about twice as high in the shallower groundwater than in the deeper groundwater while $\delta^{13}$C DIC was more enriched in the deeper groundwater. TA was 7,134 μmol L$^{-1}$ in the shallow groundwater and 3,989 μmol L$^{-1}$ in the deeper groundwater. However, $^{222}$Rn concentrations showed the opposite trend of the solutes, with concentrations in the deeper groundwater roughly 6 times higher than in the shallow groundwater. The pH of the shallow groundwater was lower than the deeper groundwater. We suspect that the discharging groundwater represents a mixture of these two and potentially other groundwater end members.
Table 7. Measurements of solutes in the groundwater end members (EM), EM1 n=3, EM2 n=1. $\delta^{13}$C DIC of the mixed end member was estimated from the y-intercept of a Keeling plot. The 47% EM1 : 53% EM2 are concentrations calculated from the $\delta^{13}$C DIC estimated end member values.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>DIC (µmol L$^{-1}$)</th>
<th>$\delta^{13}$C DIC</th>
<th>TA (µmol L$^{-1}$)</th>
<th>$^{222}$Rn (dpm m$^{-3}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Water EM1</td>
<td>1</td>
<td>9,381 ± 354</td>
<td>-10.1 ± 1.0</td>
<td>7,134 ± 60</td>
<td>49,585 ± 1,743</td>
</tr>
<tr>
<td>Ground Water EM2</td>
<td>2.5</td>
<td>4,251</td>
<td>-6.3</td>
<td>3,989</td>
<td>294,146 ± 4,601</td>
</tr>
<tr>
<td>47% EM1 : 53% EM2</td>
<td>-</td>
<td>6,661</td>
<td>-8.10</td>
<td>5,467</td>
<td>179,202</td>
</tr>
</tbody>
</table>

3.5 Discussion

Diel cycling of TA in advective chambers

Hourly fluxes of TAC, DIC, DO, and H$^+$ followed trends that were consistent with biological activity driving the fluxes of those solutes over a diel cycle (Fig. 13). During the day, fluxes of all solutes were greatest, whether negative or positive, in the afternoon at the 3:30 h sampling point (Fig. 13). This is consistent with the availability of PAR driving rates of benthic photosynthesis. Photosynthesis would alter the chemistry of porewaters by taking up DIC and releasing DO into the porewaters, thereby affecting both fluxes of TAC (by promoting carbonate precipitation) and H$^+$ (Cook and Røy, 2006; Cyronak et al. 2013). Fluxes of TAC in the morning indicate that dissolution of carbonates is still occurring until the late morning when the sediments shifts to TAC uptake. During the night time, the fluxes of all solutes tended to level off after the transition between light and dark (Fig. 13). This is probably due to the shift in biological activity from production to respiration and the associated changes in porewater chemistry.

Maximum hourly TAC uptake and fluxes were highest in the 40 RPM chamber and similar in the diffusive and 60 RPM chambers (Table 8). When compared to fluxes obtained from identical chambers in Heron Island (Australia), fluxes from the Cook Islands were generally lower (Table 8). Uptake rates were stimulated by advection in
Heron Island, whereas \( \text{TAC} \) uptake rates in the Cook Islands decreased in the highest stirring rate. The exact mechanisms behind these differences are unknown, but visual inspection of the two sediments revealed less biota (e.g. calcareous algae and fauna) in the Cook Island sediments. Lower amounts of benthic fauna would decrease any biologically driven stimulatory effect of advection on benthic fluxes (Cook and Røy, 2006; Cyronak et al. 2013). In addition, the black reducing layer apparent in the Cook Island sediments was not present in Heron Island. As advection delivers oxygen to this layer it may lower the \( \text{TA} \) concentrations in the porewaters due to sulphide oxidation (Ku et al. 1999). This is consistent with reduced benthic fluxes in the 60 RPM chamber, which would deliver oxygen deepest into the sediments.

Grain size of the sediment was generally smaller in the Cook Islands, with the highest percentage between 250 \( \mu \text{m} \)-500 \( \mu \text{m} \) compared to Heron Island which was mostly in the 1-2 mm range. Even though permeability was similar (Glud et al. 2008), differences in grain size may affect the flow of water through the sediments and subsequent \( \text{TA} \) fluxes. Daily fluxes of \( \text{TA} \) from the sediments ranged from \(-1.55\) to \(7.76\) mmol m\(^{-2}\) d\(^{-1}\), with the highest rates in the 40 rpm chamber (Table 8). Although hourly rates between the three chambers were similar (Fig. 13), integrated daily rates in the 40 RPM chamber were higher than both the diffusive and 60 RPM chambers. Daily Cook Island \( \text{TAC} \) fluxes were lower than fluxes measured in Heron Island, although the daily \( \text{TAC} \) fluxes from the 40 RPM chambers were similar in magnitude.
The hysteretic pattern of solute fluxes in the advective chambers is indicative of processes in the sediments being influenced by the previous state of the system (Fig. 14). Lower fluxes in the morning than in the afternoon for TA, DIC, and DO may be due to the decrease in DO and $\Omega_{Ar}$ overnight and subsequent recovery of the system as photosynthesis increases DO in the porewaters (Cyronak et al. 2013). Similar patterns in coral photosynthesis and calcification have been shown over a diel cycle (Levy et al. 2004; Schneider et al. 2009). Levy et al. (2004) attributed the lower photosynthesis rates in the morning to a breakdown of photosynthetic machinery at night and subsequent build-up during the day, while the hysteresis in calcification rates were attributed to changes in respiration rates of corals at specific times during a diel cycle (Schneider et al. 2009). Similar processes may be occurring in the microbiota living in the sediments, which would contribute to the observed hysteresis. Also, because DO is consumed through sulphide oxidation (Ku et al. 1999), high sulphide production and the subsequent build-up in the porewaters overnight might also lead to the observed hysteresis in fluxes. If sulphide concentrations built up overnight, DO produced in the morning would be consumed in the sediments, potentially leading to the lower oxygen fluxes observed in the morning (Fig. 14).
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The slope of DIC vs. TA_C can be used to determine the amount of DIC that was produced due to organic or inorganic processes (Andersson and Gledhill, 2013; Gattuso et al. 1996). DIC and TA_C fluxes in the chambers were tightly correlated with an $R^2$ of 0.970 (Fig. 6A). The organic to inorganic ratio of the DIC flux was 2.13 as calculated from the slope in Figure 17A. This value is lower than those reported from water column measurements but typical of sediments, possibly due to sediment porewaters being in close contact to a non-organic source (i.e. carbonates) of DIC (Gattuso et al. 1996; Cyronak et al. 2013). TA flux rates were not as well correlated to DO fluxes (Fig. 6B) as DIC fluxes corrected for the contribution of TA due to carbonate precipitation and dissolution (Fig. 17C). This may be related to oxygen consumption by sulphides in the sediments (Ku et al. 1999). Additional investigations on the role sulphides play in alkalinity cycling in coral reef sediments are warranted.
Figure 17. Linear regressions of (A) TA\textsubscript{C} vs DIC, (B) TA\textsubscript{C} vs DO, and (C) TA\textsubscript{C} vs DIC corrected for CaCO\textsubscript{3} dissolution from all stirring rates of the advective chamber incubations. Equations and $R^2$ values are displayed for each regression.

Estimating a mixed groundwater end member

There was no statistically significant relationship between $^{222}\text{Rn}$ and salinity in the water column, most likely because the range in salinity was low (~2) and because $^{222}\text{Rn}$ measurements represented an average over 30 minutes while salinity was discretely
measured every 5 minutes. However, when plotted against salinity, DIC concentrations in the water column showed a significant linear correlation consistent with conservative mixing between groundwater and the water column (Fig. 18). A Keeling plot, or the linear regression of $\delta^{13}$C DIC versus $1/[\text{DIC}]$, can be used to estimate the $\delta^{13}$C of DIC added to the system by calculating the y-intercept (Fig. 19) (Hu and Burdige, 2007; Köhler et al. 2006; Mortazavi and Chanton, 2004). The contribution of both groundwater end members (shallow and deep) to the water column can be estimated by using the $\delta^{13}$C of added DIC generated from the Keeling plot as the $\delta^{13}$C of the mixed end member. The estimated contribution of the shallow and deep end members to the water column was 47% and 53%, respectively (Table 7). The concentrations of DIC, TA, $^{222}$Rn, and pH calculated using the above percentages were used as the end member in subsequent mixing models, which matched well to the measured porewater values in the bores (Table 7). We recognize that since $^{222}$Rn concentrations were variable with depth the groundwater end members could be variable over larger spatial scales (Dulaiova et al. 2008; Santos et al. 2009). A larger number of groundwater samples could be important to decrease any potential uncertainties with the groundwater end member, and better elucidate fluxes over larger spatial scales.
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Figure 18. Regression of salinity vs concentrations of DIC in the water column measured over the course of the study. The regression equation and $R^2$ value are displayed.

\[ y = 18500x - 8.1 \]

$R^2 = 0.382$

Figure 19. Keeling plot of $\delta^{13}C$ DIC vs 1/[DIC] measured in the water column.

A two-source mixing model can be used to estimate the water column concentrations of TA based on $^{222}$Rn concentrations measured over the sampling period. $^{222}$Rn concentrations from the water column were divided by the mixed end member concentration (47% EM1 : 53% EM2), and a percent groundwater input was then multiplied by the end member of TA (Table 7). Gas exchange was not included in the model because wind speeds were relatively constant during the times that the model was developed. When a range of end members was used for the water column TA (2100 to 2400 $\mu$mol L$^{-1}$), which would change over the course of a day due to biological and geochemical activities (Gattuso et al. 1996; Shamberger et al. 2011), the measured concentration of TA fit within that range (Fig. 20A). A variable end member model was also calculated based on the change in TA over the course of a day estimated from Figure 21. During the day, $^{222}$Rn versus TA showed a different linear slope than during the night, which is consistent with carbonate precipitation being dominant during the day and dissolution during the night (Fig. 21). The initial concentration in the morning for the water column TA was estimated as the y-intercept from the night regression of TA vs
$^{222}\text{Rn} (2,327 \text{ mmol L}^{-1})$. Based on the difference between the y-intercepts for the night and day linear regressions (Fig. 21), an average rate in change of TA in the water column that excludes the effects of groundwater was estimated as -20 mmol m$^{-2}$ h$^{-1}$ during the day and 20 mmol m$^{-2}$ h$^{-1}$ at night. When the variable end member was applied to the water column portion of the $^{222}\text{Rn}$ mixing model, there was good agreement between the predicted and measured water column TA concentrations (Fig. 20B). Observed variability between the measured and predicted water column TA is probably due to diel variability in TA fluxes that are not accounted for in this model.
Figure 20. TA in the water column during the course of the study plotted along with the TA estimated from the $^{222}$Rn derived mixing model. (A) Four separate mixing models using a range of TA concentrations for the oceanic end member from 2100 – 2400 µmol L\(^{-1}\), (B) the variable oceanic end member model. All TA concentrations are in µmol L\(^{-1}\).

Figure 21. TA vs $^{222}$Rn concentrations in the water column, separate regressions were made for day time and night time hours. The three daylight time points taken during the second sampling day were removed from the regressions.

Because $\delta^{13}$C of DIC is depleted in the groundwater (-6‰ to -10‰) when compared to oceanic water (0‰ to 2‰) (Williams et al. 2011), and most of the TA in the groundwater is present as DIC, sources of TA to the groundwater can be inferred. The low $\delta^{13}$C values of DIC in the groundwater are indicative of an organic source of carbon, as carbonate minerals tend to have $\delta^{13}$C values from 0‰ to 2‰ (Weber and Woodhead, 1969; Eadie and Jeffrey, 1973; Ogrinc et al. 2003). Sulphate reduction is well known to increase TA concentrations (Wolf-Gladrow et al. 2007), and may account for a portion of the high TA concentrations in Rarotonga groundwater. The uncoupling of sulphate reduction from sulphide oxidation would generate carbonate alkalinity with a depleted $\delta^{13}$C value due to the organic C source, perhaps accounting for the depleted $\delta^{13}$C DIC values found in the
groundwater (Ku et al. 1999). Sulphate concentrations measured in the groundwater were two orders of magnitude lower than seawater (0.13 ± 0.11 mmol; see Table 4 in Waterhouse and Petty, 1986). However, these sulphate concentrations are 20-times what is necessary to produce the TA measured in the groundwater.

\textit{\textsuperscript{222}Rn derived groundwater fluxes of TA}

Advection rates of groundwater into the water column were estimated using a non-steady state \textit{\textsuperscript{222}Rn} mass balance model (Burnett and Dulaiova, 2003) and the concentration of \textit{\textsuperscript{222}Rn} estimated in the groundwater end member (179,202 dpm m\textsuperscript{-3}) (Table 7). Fluxes of groundwater ranged from 0 to 46 cm d\textsuperscript{-1} and were highest during low tides. This is consistent with steeper hydraulic gradients at low tide driving fresh groundwater flow into the lagoon (Kuan et al. 2012; Chanton et al. 2003). The groundwater fluxes can be converted to an hourly basis and multiplied by the groundwater end member concentration of TA (5,467 µmol L\textsuperscript{-1}) to estimate the fluxes of TA into the water column (Fig. 22). Fluxes ranged from 0 to 105 mmol m\textsuperscript{-2} h\textsuperscript{-1} during this study, with the highest fluxes observed during the lowest tides. The average daily \textit{\textsuperscript{222}Rn} derived TA flux measured during this study was 1,080 mmol m\textsuperscript{-2} d\textsuperscript{-1} at the sampling site. These fluxes are most likely spatially variable throughout the lagoon, with the highest fluxes found close to shore where SGD is most abundant.
Figure 22. Hourly SGD derived fluxes of TA into the water column plotted alongside depth over the course of the study.

The $^{222}$Rn derived TA fluxes are high when compared to other TA sources and sinks in coral reef environments (Shamberger et al. 2011; Gattuso et al. 1998). However, the hourly fluxes agree well with those needed to explain the observed changes in water column TA concentrations. The observed increase in TA was calculated as follows;

$$\Delta [TA] = \frac{(TA_{T2} - TA_{T1})}{(T2-T1)};$$

where $\Delta [TA]$ is the observed increase in TA in mmol m$^{-2}$ h$^{-1}$, T1 and T2 are time points T1 and T2 in hours, and TA$_{T1}$ and TA$_{T2}$ are TA concentrations at time points T1 and T2. Fluxes needed to account for the observed increases in TA concentrations during the day were as high as 103 mmol m$^{-2}$ hr$^{-1}$. These values are comparable to the SGD derived TA fluxes calculated from the $^{222}$Rn mass balance and groundwater alkalinity concentrations, which ranged from 0 to 105 mmol m$^{-2}$ hr$^{-1}$ (Fig. 22). The fact that these two calculations, which were derived from independent methods, agree well lends support to hourly and daily $^{222}$Rn derived SGD TA fluxes. Also, TA concentrations at our study site were elevated (up to 2608 μmol L$^{-1}$; Fig. 4) when compared to TA concentrations in
other coral reef lagoons (~2100 to 2400 µmol L\(^{-1}\)) (Shaw et al. 2012; Shamberger et al.
2011; Cyronak et al. 2013; Silverman et al. 2012) and the nearby Pacific Ocean (~2300
µmol L\(^{-1}\)) (Millero et al. 1998). This lends support to an external source of TA into Muri
Lagoon.

There are a number of factors that would influence the flux of TA from SGD into
doastal ecosystems, one of which is the concentration of TA in the groundwater. In
general TA concentrations of groundwater exhibit a large range, can be up to 6 times as
high as oceanic TA, and are probably highly dependent on local geology (Table 9). Also,
the amount of TA fluxed into the lagoon is dependent on how far the groundwater mixes
offshore and the location of point-sources of SGD within the lagoon (Schopka and Derry,
2012; Burnett et al. 2003; Burnett and Dulaiova, 2003). Based on radium isotope ratios in
Muri Lagoon, a conservative residence time of 6 days was estimated for water in the
lagoon (Tait et al. 2013). This long residence time means that TA derived from
groundwater can accumulate in the lagoon, raising the water column Ω_{Ar} above oceanic
levels and potentially buffer against ocean acidification. However, groundwater may also
act as a source of CO\(_2\), which would inhibit the buffering capacity of SGD derived TA
fluxes. Also, groundwater is a potential source of nutrients (Valiela et al. 1999; Burnett et
al. 2003; Paytan et al. 2006), contaminants (Cohen et al. 1984; Bedient et al. 1994), and
other solutes that could potentially degrade reef health.
Chapter 3

Table 9. Concentrations of TA (µmol L\(^{-1}\)) measured in groundwater throughout the world. *Designates concentrations measured as $\text{HCO}_3^-$.

<table>
<thead>
<tr>
<th>TA (µmol L(^{-1}))</th>
<th>System type</th>
<th>Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,150 - 2,949</td>
<td>Subtropical estuary</td>
<td>South Carolina, USA</td>
<td>Cai et al. 2003</td>
</tr>
<tr>
<td>90 - 8,920</td>
<td>Subtropical estuary</td>
<td>Kunsan, Korea</td>
<td>Kim et al. 2004</td>
</tr>
<tr>
<td>4,020</td>
<td>Subtropical estuary</td>
<td>Southern China</td>
<td>Liu et al. 2012</td>
</tr>
<tr>
<td>753 - 7,026*</td>
<td>Inland mountains</td>
<td>Central Mexico</td>
<td>Mahlknecht et al. 2004</td>
</tr>
<tr>
<td>2,550 - 23,300</td>
<td>Tidal flat</td>
<td>Wadden Sea, Germany</td>
<td>Moore 2011</td>
</tr>
<tr>
<td>95 - 2,000*</td>
<td>Tropical island</td>
<td>Guadeloupe</td>
<td>Rad et al. 2007</td>
</tr>
<tr>
<td>1,400 - 13,000*</td>
<td>Tropical island</td>
<td>Martinique</td>
<td>Rad et al. 2007</td>
</tr>
<tr>
<td>800 - 4,016*</td>
<td>Tropical island</td>
<td>Reunion</td>
<td>Rad et al. 2007</td>
</tr>
<tr>
<td>2,290*</td>
<td>Coastal lagoon</td>
<td>Brazil</td>
<td>Santos et al. 2008</td>
</tr>
<tr>
<td>1,328 - 2,162</td>
<td>Tropical island</td>
<td>Hawaii</td>
<td>Schopka and Derry 2012</td>
</tr>
<tr>
<td>3,989 - 7,134</td>
<td>Tropical island</td>
<td>Cook Islands</td>
<td>This study</td>
</tr>
</tbody>
</table>

There are not many studies assessing the influence of SGD on alkalinity fluxes to the water column, and none in coral reef ecosystems. Moore et al. (2011) used radium isotopes to trace the fluxes of groundwater to the Wadden Sea, showing that SGD acts as an important source of TA, Mn, dissolved organic carbon (DOC), and silicate to the ocean. Other studies have measured the concentration of TA in groundwater, but do not discuss SGD fluxes of TA to open water ecosystems (see Table 9). There are multiple groundwater exchange processes besides terrestrial hydraulic gradients that could alter TA cycling in coral lagoons (Santos et al. 2012; Burnett et al. 2003). For instance, the occurrence of tidal pumping and saltwater intrusion on a larger scale than advective processes may alter microbial reactions in the sediment, and subsequently the cycling of TA (Santos et al. 2012; Kuan et al. 2012). The impact of these processes on TA fluxes into coral reef lagoons merits further investigation. Also, any seasonal variability in rainfall is likely to influence SGD fluxes over larger temporal scales.

*Upscaling porewater and groundwater fluxes*
Because the fluxes due to benthic metabolic processes described above were variable temporally and spatially any extrapolation needs to be taken with care. In order to compare the influence of advective porewater circulation and fresh SGD on TA concentrations in the lagoon, a 750 m x 1 m box model was projected from the sampling site to the reef crest (Fig. 12). The flow of water in the lagoon is generally from the reef crest towards shore, therefore any changes in the water column chemistry due to metabolic processes would occur along this transect. Since chamber stirring rates did not show any major influence on hourly TA fluxes from the sediments, an average hourly flux from the two advective chambers (40 and 60 RPM) was used for this comparison. Since currents are the main driver of porewater advection, the different stirring rates used in this study are likely to be representative of any variability within the lagoon. SGD was conservatively assumed to occur within a horizontal seepage face of 50 m from the beach face, as suggested from resistivity transects (Tait et al. 2013).

The fluxes of TA associated with advective processes were both negative and positive while the groundwater fluxes were always positive (Fig. 23). Combined TA fluxes from both SGD and porewater advection along the 750 m transect were between 62.1 and 72.9 mmol m\(^{-2}\) d\(^{-1}\), which is greater than the TA uptake rates of coral lagoons (26 to 42 mmol m\(^{-2}\) d\(^{-1}\)) as measured by Kinsey (1983). These fluxes are consistent with the elevated TA concentrations measured at our sampling site. Across the 750 m transect, groundwater (from both porewater advection and SGD) contributed 46.3 to 52.8 mol TA d\(^{-1}\) to the water column. On a daily basis, porewater advection contributed from 1.6 to 3.5 mol TA d\(^{-1}\) into the lagoon, while SGD added 50 mol TA d\(^{-1}\) along the 750 m transect. SGD contributed 27\% to 97\% of the combined groundwater fluxes over a diel cycle, with the contribution dependent on both the time of day and the tidal cycle (Fig. 23). Since groundwater seepage is correlated to tidal range (Chanton et al. 2003), larger tides would
have more of an effect on groundwater flow, potentially fluxing more TA into the system during such tidal cycles. However, because advective processes follow a diel cycle and groundwater is driven by tidal cycles, longer term experiments may be needed to reveal which of the processes is more influential.

![Figure 23. Hourly fluxes of TA from advective sediments and SGD over a 750 m transect from the study site to reef crest. 100% cover was assumed for advective sediments and SGD was estimated as mixing 50 m offshore.](image)

Previous studies have estimated coral reef community calcification rates that range from 31.2 to 292.8 mmol CaCO3 m$^{-2}$ d$^{-1}$ (or -62.4 to -585.6 mmol TA m$^{-2}$ d$^{-1}$) (Shamberger et al. 2011). Using that range of community TA uptake rates along the 750 m transect reveals that porewater advection can account for up to 2% of community TA uptake, or add up to 12% of the TA taken out of the water column by coral communities. SGD derived TA fluxes can add from 12% to 115% of the TA taken up by coral communities. The community TA uptake rates of coral lagoons is generally low compared to other reef ecosystems (Kinsey, 1983), which means it is likely that SGD contributes towards the higher end of that range. This is consistent with the elevated TA concentrations at our study site. This previously unaccounted for source of TA is
important in controlling the carbon chemistry within Muri Lagoon over tidal and diel cycles.

Conclusions

Alkalinity concentrations in Muri Lagoon followed a pattern that is indicative of both biological and tidal drivers influencing the dynamics of water column TA over a diel cycle (Fig. 15). Different groundwater exchange mechanisms, acting on varying temporal and spatial scales can have different impacts on water column alkalinity. TA fluxes related to small scale porewater advection acted as both a source and sink of TA over the course of a day, with net daily fluxes ranging from -1.55 to 7.76 mmol m\(^{-2}\) d\(^{-1}\) depending on advection rates. Based on the average of the 40 and 60 RPM chambers, porewater advection was a net source of TA to the lagoon (2.1 to 4.7 mmol m\(^{-2}\) d\(^{-1}\)). SGD fluxes were driven by tidal processes and delivered 1,080 mmol TA m\(^{-2}\) d\(^{-1}\) to the water column over the course of this study. The daily SGD derived TA flux is high when compared to other sources and sinks of TA. However, it is site specific and groundwater is likely discharged only a discrete distance from shore. It is likely that similar advective exchanges of TA occur throughout different reef systems, while SGD is highly dependent on the specific geological, physical, and biological attributes of the land masses associated with coral reefs. It is important to constrain the variability of these fluxes over larger temporal and spatial scales by measuring \(^{222}\)Rn concentrations across broad areas of coral reef environments. Assessing groundwater exchange processes in coral reef ecosystems is necessary so that more detailed models can be developed to predict how ocean acidification will alter reef carbonate chemistry.
Chapter 4

Drivers of $p$CO$_2$ variability in two contrasting coral reef lagoons: The influence of submarine groundwater discharge
Chapter 4

4.1 Abstract

The impact of groundwater on $p\text{CO}_2$ variability was assessed in two coral reef lagoons with distinct drivers of submarine groundwater discharge (SGD). Diel variability of $p\text{CO}_2$ in the two ecosystems was explained by a combination of biological drivers and SGD inputs. In Rarotonga, a South Pacific volcanic island, $^{222}\text{Rn}$-derived SGD was driven primarily by a steep terrestrial hydraulic gradient, and the water column was influenced by the high $p\text{CO}_2$ (5,501 µatm) of the fresh groundwater. In Heron Island, a Great Barrier Reef coral cay, SGD was dominated by seawater recirculation through sediments (i.e. tidal pumping) and $p\text{CO}_2$ was mainly impacted through the stimulation of biological processes. The Rarotonga water column had a relatively higher average $p\text{CO}_2$ (549 µatm) than Heron Island (471 µatm). However, $p\text{CO}_2$ exhibited a greater diel range in Heron Island (778 µatm) than in Rarotonga (507 µatm). The Rarotonga water column received $29.0 \pm 8.2$ mmol free-$\text{CO}_2$ m$^{-2}$ d$^{-1}$ from SGD, while the Heron Island water column received $12.1 \pm 4.2$ mmol free-$\text{CO}_2$ m$^{-2}$ d$^{-1}$. Over the course of this study both systems were sources of $\text{CO}_2$ to the atmosphere (averaging $8.8 \pm 3.4$ and $2.5 \pm 2.1$ mmol $\text{CO}_2$ m$^{-2}$ d$^{-1}$ in Rarotonga and Heron Island, respectively), with SGD-derived free-$\text{CO}_2$ most likely contributing a large portion to the air-sea $\text{CO}_2$ flux. Studies measuring the carbon chemistry of coral reefs (e.g. community metabolism and calcification rates) may need to consider the effects of groundwater inputs on water column carbonate chemistry. Local drivers of coral reef carbonate chemistry such as SGD may offer more approachable management solutions to mitigating the effects of OA on coral reefs.
4.2 Introduction

Since the industrial revolution oceans have absorbed approximately 30% of anthropogenically produced CO$_2$ from the atmosphere, resulting in an increase in oceanic $p$CO$_2$ (Feely et al. 2004). This increase in $p$CO$_2$ changes the carbonate chemistry of seawater, reducing the pH in a process termed ocean acidification (OA) (Doney et al. 2009). This increase in $p$CO$_2$ has been apparent in the open ocean, but has been difficult to detect in coastal ecosystems which can experience large $p$CO$_2$ variability on diel and seasonal timescales (Duarte et al. 2013; Friedrich et al. 2012; Kayanne et al. 1995). High $p$CO$_2$ has been shown to have deleterious effects on coral health, through a reduction in calcification rates attributed to decreases in seawater pH and aragonite saturation state ($\Omega_{Ar}$) (Langdon et al. 2003; Leclercq et al. 2002; Leclercq et al. 2000). In order to properly address how OA is likely to affect coral reef ecosystems, a detailed understanding of $p$CO$_2$ variability and its associated drivers is needed.

Previous studies have generally assessed coral reef $p$CO$_2$ variability in terms of community metabolism (Frankignoulle et al. 1996; Gattuso et al. 1995; Gattuso et al. 1993), calcification (Shamberger et al. 2011; Shaw et al. 2012), and air-sea CO$_2$ fluxes (Bates 2002; Kayanne et al. 1995), and may have overlooked important drivers of CO$_2$ dynamics. In the early to mid-1990s there were a number of studies that measured $p$CO$_2$ variability in coral reefs, mainly attempting to assess whether reefs were a source or sink of CO$_2$ to the atmosphere (Buddemeier 1996; Kayanne et al. 1995; Ware et al. 1992). Recent interest in ocean acidification, however, has increased the demand for high-resolution $p$CO$_2$ data sets from coral reef ecosystems.

Diel variability of $p$CO$_2$ in coral reefs is often attributed to their high benthic metabolic rates (Kayanne et al. 1995). Along with photosynthesis and respiration, calcification has also been shown to alter the $p$CO$_2$ levels of coral reefs, as $\sim$0.6 moles of
CO$_2$ are released for each mole of CaCO$_3$ produced (Frankignoulle et al. 1994). In shallow coral reef lagoons and reef flats, pCO$_2$ can range from 77 to 1256 $\mu$atm over a diel cycle (Gray et al. 2012; Shaw et al. 2012). There is also variability in pCO$_2$ over seasonal timescales, with lower values and narrower diel ranges usually found in the winter due to temperature effects and reduced ecosystem metabolism (Bates 2002; Gray et al. 2012; Kayanne et al. 2005). Often, net ecosystem metabolism and calcification are calculated based on changes in carbonate system parameters, which can be reflected in pCO$_2$ values (Gattuso et al. 1993; Kinsey 1978; Shamberger et al. 2011). Therefore, any drivers that alter the carbonate chemistry of coral reefs that are not associated with metabolism and calcification could affect the measurements of net community metabolic and calcification rates.

Submarine groundwater discharge (SGD) has been shown to be an important source of freshwater and dissolved materials to coastal ecosystems (Burnett et al. 2003). There are varying mechanisms through which groundwater can be exchanged with coastal ecosystems (Santos et al. 2012a). SGD can refer to fresh groundwater delivered by terrestrial hydraulic gradients (Burnett et al. 2003), as well as to the tidally driven recirculation of seawater through sediments (Robinson et al. 2007; Santos et al. 2010). Radon ($^{222}$Rn) has been used as a tracer for groundwater in coastal systems due to its naturally high concentrations in groundwater compared to surface waters and its unreactive nature (Burnett et al. 2006; Cable et al. 1996). Because $^{222}$Rn is produced through contact with sediments, it can trace both fresh groundwater as well as tidally recirculated seawater (Santos et al. 2010). Studies assessing SGD input rates on coral reefs describe a broad range from 52 to 4,732 L m$^{-1}$ h$^{-1}$, and suggest that SGD can be an important source of nutrients to coral reef ecosystems (D'elia and Wiebe 1990; Lewis 1987; Paytan et al. 2006). Past studies have speculated that groundwater can influence the water column...
carbonate chemistry of coral reef ecosystems (Smith and Pesret 1974; Watanabe et al. 2013), but none have demonstrated a clear link between the two. It has been shown that point sources of SGD from geological features known as “ojos” can effect water column carbonate chemistry, however, these features are highly localized (Crook et al. 2012).

We hypothesize that SGD is a broadly occurring and overlooked driver of \( p\text{CO}_2 \) dynamics in the surface waters of coral reef ecosystems. We assessed this hypothesis in two contrasting coral reef lagoons: a Pacific Island lagoon (Rarotonga) subject to large fresh groundwater inputs, and a Great Barrier Reef system (Heron Island) with little to no fresh groundwater inputs. This study examined the variability of \( p\text{CO}_2 \) and \( ^{222}\text{Rn} \) over tidal and diel cycles within these two coral reef lagoons. We build on recent papers that examined net ecosystem calcification in Heron Island (Mcmahon et al. 2013) and assessed the influence of groundwater exchange on alkalinity in Rarotonga (Cyronak et al. 2013).

4.3 Methods

Study sites

Rarotonga (21° 14’ S, 159° 47’ W), the largest island in the South Pacific Cook Island archipelago, has an area of 67.19 km\(^2\) with ~36 km of shoreline (Fig. 24). The island is surrounded by a fringing coral reef lagoon which extends from 30 to 900 m to the reef crest. The Cook Island chain was formed through volcanic activity and is comprised of extinct volcanoes rising >5000m from the ocean floor (Thompson et al. 1998). Rarotonga has deeply dissected terrain, with steep ridges and deep valleys, and a maximum elevation of 650 m above sea level (Thompson et al. 1998). Rarotonga is characterized by a rainy (November to April) and dry (May to October) season, with average annual rainfall of 2,100 mm y\(^{-1}\). Our study site was located on the south-western side of the island in Muri Lagoon. Muri Lagoon has an average depth of about 1.4 m and
covers an area of 1.75 km$^2$ (Holden 1992). The flow in Muri Lagoon is dominated by wave setup and runs from the reef crest northwest towards shore, and then northeast along the shore towards a channel which opens to the ocean (Holden 1992). The tidal cycle in Muri Lagoon is semi-diurnal with a range of 0.56 m measured during this study. In order to avoid confusion, the sampling site is referred to as Rarotonga or Rarotonga lagoon throughout the rest of the paper.

![Figure 24. Map showing the location of Heron Island and Rarotonga. The dotted line around each island represents the boundary of the reef crest.](image)

Heron Island (23° 27′ S, 151° 55′ E) is a coral cay located along the southern portion of the Great Barrier Reef ~72 km east of mainland Australia (Fig. 24). The island itself is comprised mainly of course carbonate sands and has an area of 0.16 km$^2$, coastline of ~2.2km, and a maximum elevation of 3.6 m above sea level. The island is surrounded by a large coral lagoon (26.4 km$^2$) which has an average depth of 1.7 m (Wild et al. 2004). The benthic makeup of the lagoon is ~25% living coral cover, while the rest is predominately carbonate sands (Eyre et al. 2008; Glud et al. 2008; Wild et al. 2004). The permeability and porosity of the sands are high which allow seawater to easily flow through the sediments (Santos et al. 2010). Flow in the western half of the lagoon is influenced by a shipping channel which drains the lagoon at low tide. Our study site was on the southern side of the island, which receives a strong lagoonal signal due to tidally
influenced currents flowing east across the site. The tidal range measured during this study was 2.1 m.

Time series observations

The water column at Rarotonga was sampled from 15 to 19 March 2012. Comparable sampling at Heron Island was conducted from 17 to 26 April 2012. Due to limitations in gear, groundwater time series investigations were not run concurrently with water column time series. The beach groundwater time series on Rarotonga was performed on 21 March 2012 and lasted for 16 hours, while groundwater on Heron Island was monitored for 28 hours starting on 12 April 2012. In order to monitor fluctuations in groundwater chemistry a 0.5 m deep bore was dug at the high tide mark directly on shore from the sampling site at Rarotonga. Due to the coarse nature of the Heron Island sediments (i.e. large chunks of coral that prevented a bore from being installed onshore of the water column study site), a preinstalled bore 30 m landward of the low tide mark on the opposite side of the island was used. The bore on Heron Island was 7.5 m in depth.

During the water column time series at both study sites all instrumentation was deployed ~10 m offshore of the low tide mark and 0.2 m from the bottom. A Vantage Pro (Davis Instruments) weather station was used to measure atmospheric wind speed, temperature, and pressure directly onshore of each sampling site. Monitoring of physico-chemical parameters was done using a Hydrolab DS5X (Hach Environmental) and an Aqua Troll 200 (In-Situ Inc.). Data for depth, temperature (± 0.5%), and salinity (± 0.5%) were collected every 5 min. Dissolved oxygen (DO) (± 1%) was measured every 5 min using a Hach Luminescent Dissolved Oxygen (LDO®) probe connected to the Hydrolab. pH (±0.003) was measured every 5 min using a SAMI2-pH sensor, which determines pH spectrophotometrically using metacresol purple (mCP) as the indicator (Martz et al. 2003;
Seidel et al. 2008). The SAMI2 is factory calibrated to measure pH in the total hydrogen ion scale.

\[ pCO_2 \text{ and } ^{222}\text{Rn} \] were measured concurrently through a shower head type gas equilibration device (GED) (Santos et al. 2012b). Seawater was pumped from each sampling site into the GED at a rate of \( \sim 2 \text{ L min}^{-1} \) using a bilge pump. Air was recirculated through a closed loop from the GED through a Drierite\textsuperscript{TM} column and into a Licor 7000 CO\textsubscript{2} detector and a RAD7 \(^{222}\text{Rn}\) detector. The Licor 7000 is a differential non-dispersive infrared gas analyser that was set to measure \( pCO_2 \) (\( \pm 1\% \)) at 1 min intervals. Prior to each field campaign, the Licor was calibrated across a range of premixed CO\textsubscript{2} gasses (306, 502, and 2017 \( \mu \text{atm} \)). The RAD7 was factory calibrated and measures polonium daughters (\(^{218}\text{Po}^+ \) and \(^{214}\text{Po}^+ \)) which are converted into \(^{222}\text{Rn}\) concentrations using radioactive decay equations. Radon concentrations were integrated over 30 min intervals to ensure acceptable counting statistics (i.e. uncertainties lower than \( \sim 10\% \)). In order to compare all of the data on similar timescales an hourly average was taken from measurements a half hour before and after the RAD7 began each cycle.

In order to measure fluctuations in groundwater chemistry a peristaltic pump was used to pump water from the bores at \( \sim 1 \text{ L min}^{-1} \) into the GED. The lower flow rate used for groundwater could drive a lag in \(^{222}\text{Rn}\) response time of up to 1 hour, however, \(^{222}\text{Rn}\) values were used as measured because 1 hr running averages were used during all subsequent data analysis. The SAMI2-pH was connected in line with the peristaltic pump in order to measure pH in the groundwater bores. Total alkalinity (\( \text{TA}, \pm 0.1\% \)) was measured during the groundwater time series every two hours by Gran Titration using a Metrohm automatic titrator and 0.01 M HCl standardized to Dickson Certified Reference Material (Batch 111). Samples for NO\textsubscript{x} were also taken every two hours and were filtered with a 0.45 \( \mu \text{m} \) cellulose acetate filter and frozen at \(-20^\circ\text{C}\) until analysed following the
methods of Eyre and Ferguson (2005) using a Lachat FIA system. In Rarotonga, TA and NOx were also directly measured in the freshwater end member (Cyronak et al. 2013)

Data analysis

All pCO2 values were corrected according to the temperature and pressure measured in the GED using equations from Pierrot et al. (2009). ΩAr was estimated using the Excel macro CO2 System (CO2SYS) (Pierrot et al. 2006) with inputs of pCO2 and pH and the constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987). Estimates of ΩAr calculated using these two parameters of the carbonate system have been shown to be robust (Cullison Gray et al. 2011). Air-sea CO2 fluxes were calculated according to the following equation,

\[
Flux = k \cdot \alpha (pCO2_{water} - pCO2_{air})
\]

(1)

where k is gas transfer velocity for CO2, \(\alpha\) is the coefficient of chemical enhancement, \(pCO2_{water}\) is the partial pressure of CO2 in the water column, and \(pCO2_{air}\) is the partial pressure of CO2 in the air which was assumed to be constant at the Mauna Loa 2012 average of 393.8 ppm (Keeling et al. 1991). Due to the shallow depths and relatively strong currents at the study sites we used the wind speed-based \(k_{600}\) parameterization from Raymond and Cole (2001), which was derived from a compilation of estuarine and riverine studies. All \(k_{600}\) values were corrected for the Schmidt number of CO2 at in situ temperatures and salinities (Jahne et al. 1997; Wanninkhof 1992). Positive air-sea CO2 fluxes represent fluxes from the seawater into the atmosphere while negative fluxes represent fluxes into the seawater from the atmosphere. SGD fluxes were determined using a non-steady state \(^{222}\)Rn mass balance model described in detail in Burnett and Dulaiova (2003). The model has been successfully applied to both Heron Island (Santos et
al. 2010) and Rarotonga (Tait et al. 2013) in previous studies. The model estimates SGD fluxes based on the temporal change in $^{222}$Rn inventories in the water column (1 h time steps) after accounting for all known $^{222}$Rn sources and sinks (i.e. atmospheric evasion, mixing, $^{222}$Rn decay, and $^{226}$Ra). The missing $^{222}$Rn fluxes are then divided by the groundwater end member concentration to obtain SGD advection rates in units of cm d$^{-1}$.

### 4.4 Results

*Groundwater time series*

In Rarotonga groundwater, $pCO_2$ and $^{222}$Rn were 6 and 10 times higher than in the water column, respectively (Tables 10 and 11). $pCO_2$ ranged from 3,083 to 4,024 µatm, while $^{222}$Rn ranged from 80,111 to 159,937 dpm m$^{-3}$ over a tidal cycle and was highest during the ebb tide (Fig. 25). pH and salinity followed similar but opposite trends of $pCO_2$, with salinity ranging from 21.7 to 32.5 and pH ranging from 7.28 to 7.33 (Fig. 25). Both pH and salinity were lower in the groundwater than in the water column (Tables 10 and 11). Average TA was 3,339 µmol L$^{-1}$ during the bore time series and was ~5,500 µmol L$^{-1}$ in the freshwater end member. The average NO$_x$ concentration was 28.2 µmol L$^{-1}$ in the freshwater end member.
Table 10. The average (Avg), maximum (Max), minimum (Min), and range of parameters measured in the water column at Rarotonga and Heron Island during this study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rarotonga</th>
<th>Heron Island</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
<td>Min</td>
</tr>
<tr>
<td>Depth (m)</td>
<td>0.69</td>
<td>0.42</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>27.4</td>
<td>24.1</td>
</tr>
<tr>
<td>pH</td>
<td>7.96</td>
<td>7.76</td>
</tr>
<tr>
<td>Salinity</td>
<td>35.6</td>
<td>34.3</td>
</tr>
<tr>
<td>Wind speed (m s⁻¹)</td>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>DO (µmol L⁻¹)</td>
<td>204</td>
<td>118</td>
</tr>
<tr>
<td>p CO₂ (µatm)</td>
<td>549</td>
<td>327</td>
</tr>
<tr>
<td>^{222}Rn (dpm m⁻³)</td>
<td>12662</td>
<td>5638</td>
</tr>
<tr>
<td>Ω_Ar</td>
<td>3.5</td>
<td>1.7</td>
</tr>
<tr>
<td>SGD advection rate (cm d⁻¹)</td>
<td>16.7 ± 4.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Air-sea CO₂ flux (mmol m² d⁻¹)</td>
<td>8.8 ± 3.4</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

In Heron Island groundwater, pCO₂ and ^{222}Rn were approximately 3 times and 27 times higher than in the water column, respectively (Tables 10 and 11). The highest pCO₂ coincided with peaks in ^{222}Rn and the lowest salinities (Fig. 25). Salinity in the groundwater ranged from 32.7 to 33.5 and was lowest during the ebb tide with an average of 33.1 during the time series. pH followed a trend similar to salinity and varied between 7.49 and 7.69 during the time series. ^{222}Rn steadily increased during the low tide and was highest during the flood tide (Fig. 25). The temporal variability in the groundwater solutes indicates an active mixing of groundwater and seawater within the beach sands over tidal time scales. The average concentration of TA was 2243 µmol L⁻¹ and NOx was 76.5 µmol L⁻¹ during the Heron Island groundwater time series.
Table 11. Averages and standard deviations of parameters measured in the groundwater at Rarotonga and Heron Island. The NO\textsubscript{x} concentration from Rarotonga is the average of direct measurements (n = 4) from the freshwater end member, while the Heron Island NO\textsubscript{x} concentration is the average during the groundwater time series. \(p\text{CO}_2\)-EM, \(^{222}\text{Rn}\)-EM, and free-\(\text{CO}_2\)-EM are the groundwater end members calculated as described in the text.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rarotonga</th>
<th>Heron Island</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (m)</td>
<td>0.34 ± 0.12</td>
<td>4.63 ± 0.39</td>
</tr>
<tr>
<td>Temp ((^\circ)C)</td>
<td>25.4 ± 0.09</td>
<td>25.6 ± 0.03</td>
</tr>
<tr>
<td>pH</td>
<td>7.309 ± 0.01</td>
<td>7.602 ± 0.05</td>
</tr>
<tr>
<td>Salinity</td>
<td>28.3 ± 2.7</td>
<td>33.1 ± 0.2</td>
</tr>
<tr>
<td>TA ((\mu\text{mol L}^{-1}))</td>
<td>3339 ± 249</td>
<td>2243 ± 96</td>
</tr>
<tr>
<td>(p\text{CO}_2) ((\mu\text{atm}))</td>
<td>3515 ± 205</td>
<td>1397 ± 199</td>
</tr>
<tr>
<td>(\text{NO}_x) ((\mu\text{mol L}^{-1}))</td>
<td>28.2 ± 4.5</td>
<td>76.5 ± 27.6</td>
</tr>
<tr>
<td>(^{222}\text{Rn}) (dpm m(^{-3}))</td>
<td>130836 ± 16460</td>
<td>27204 ± 3231</td>
</tr>
<tr>
<td>(p\text{CO}_2)-EM ((\mu\text{atm}))</td>
<td>5501 ± 183</td>
<td>1397 ± 199</td>
</tr>
<tr>
<td>(^{222}\text{Rn})-EM (dpm m(^{-3}))</td>
<td>242836 ± 19561</td>
<td>27204 ± 3231</td>
</tr>
<tr>
<td>Free-(\text{CO}_2)-EM ((\mu\text{mol L}^{-1}))</td>
<td>173.9 ± 5.2</td>
<td>40.6 ± 5.1</td>
</tr>
</tbody>
</table>
Water column time series

The water column time series at Rarotonga covered 4 days and 7 tidal cycles (Fig. 26). Tidal range was highest in the beginning of the time series and decreased towards the end, with a range of 0.56 m over the course of the study. In the Rarotonga water column $p\text{CO}_2$ ranged from 327 to 833 µatm with an average of 549 µatm and followed a cycle that was indicative of both tidal and diel drivers (Fig. 26). This average $p\text{CO}_2$ was well in excess of the expected concentration if the water column was in equilibrium with the
atmosphere (~394 µatm), resulting in a relatively low average seawater pH (7.96). During
the first two days, there were two maximal peaks of $p$CO$_2$, one during the night, and one in
the early morning. These peaks of $p$CO$_2$ coincided with peaks in $^{222}$Rn concentrations at
low tides (Fig. 26). $p$CO$_2$ was generally lower during the final two diel cycles when the
tidal range was smaller. The trends in DO and pH were more consistent with biological
drivers, increasing and decreasing smoothly over a diel cycle (Fig. 26). The minimum and
maximum DO concentrations during the time series were 118 and 331 µmol L$^{-1}$ with an
average of 204 µmol L$^{-1}$. pH ranged 0.41 units over the course of the study, with a
minimum value of 7.76 and maximum of 8.17. $^{222}$Rn concentrations were highest during
ebb tides and the average $^{222}$Rn concentration in the water column was 12,662 dpm m$^{-3}$.
The highest $^{222}$Rn concentrations were measured on the first day during the tidal cycle with
the greatest range, and as the tidal ranges became smaller $^{222}$Rn concentrations decreased
(Fig. 26).

The water column time series at Heron Island covered 10 days and 19 tidal cycles.
Tidal range was greatest during the first half of the time series (Fig. 27). All parameters
exhibited variations indicative of biological drivers, with $p$CO$_2$ decreasing until the late
afternoon and then increasing throughout the night (Fig. 27). Average $p$CO$_2$ over the
course of the study was 471 µatm in the Heron Island water column, which was lower than
in Rarotonga (549 µatm). However, $p$CO$_2$ in the Heron Island water column exhibited a
larger range (178 to 956 µatm) than in Rarotonga (327 to 833 µatm). Heron Island $p$CO$_2$
showed small but detectable variations unrelated to biological drivers, some of which
coincided with peaks in $^{222}$Rn concentrations and shifted with the tidal cycle (Fig. 27). DO
and pH variability were opposite of $p$CO$_2$, and average pH was higher in the Heron Island
water column (8.04) than in the Rarotonga water column (7.96) (Table 10). The average
$^{222}$Rn concentration was 1,003 dpm m$^{-3}$ with minimum and maximum concentrations of
255 and 2,360 dpm m\(^{-3}\). \(^{222}\text{Rn}\) concentrations were highest at the beginning of the flood tide and lowest during high tides (Fig. 27).

Figure 26. \(pCO_2\), DO, pH, \(^{222}\text{Rn}\) (red), salinity, and depth measured in the water column at Rarotonga over the course of this study. All time is in local time and grey bars represent night time hours. The arrows indicate times when \(pCO_2\) and \(^{222}\text{Rn}\) vary concurrently. The line-graphs represent data points every half-hour, which are averages for 30 min before and after each respective time point (see methods for more detail).
Chapter 4

4.5 Discussion

Drivers of SGD exchange

SGD exchange processes in both Rarotonga and Heron Island were clearly influenced by tides (Figs. 25, 26, and 27). Tidal pumping can refer to multiple, but...
fundamentally distinct processes (Santos et al. 2012a). Both seawater recirculation and terrestrial hydraulic gradient driven SGD can fall under the more general term of tidal pumping due to the influence of tides on both processes (Santos et al. 2009). Tides affect seawater recirculation as seawater infiltrates the beach face during high tides and is discharged at low tides. Likewise, steeper hydraulic gradients at low tide cause greater amounts of fresh groundwater to be discharged than during high tides. $^{222}$Rn concentrations during the groundwater time series at Rarotonga were highest during the ebb tide (Fig. 25), which is indicative of positively pressured fresh groundwater being held off by sea level at high tides. Heron Island groundwater showed a different trend, with $^{222}$Rn concentrations highest during the flood tide (Fig. 25). This is indicative of a slow release of high $^{222}$Rn groundwater, and seawater recirculation being the exchange mechanism for SGD at Heron Island.

When plotted against salinity, $^{222}$Rn exhibited a significant negative linear trend in the groundwater (Fig. 28). End members can be extrapolated from the y-intercept (i.e. when salinity equals 0). In Rarotonga, estimates of a $^{222}$Rn groundwater end member (242,836 ± 19,561 dpm m$^{-3}$) using this method agree well those measured in fresh groundwater (179,202 to 294,146 dpm m$^{-3}$) (Cyronak et al. 2013), which is consistent with previous studies using a similar approach in systems where fresh SGD is the main source of $^{222}$Rn (Peterson et al. 2009). This is further evidence of fresh groundwater and a terrestrial hydraulic gradient driving SGD at Rarotonga (see Fig. 1 in Santos et al. 2012a).

When $^{222}$Rn is plotted against salinity in Heron Island groundwater, there is a disagreement with expected end member concentrations. The concentration of the $^{222}$Rn end member extrapolated to zero salinity is 3-fold higher than the highest measured groundwater $^{222}$Rn concentration, and is ~7.5-fold higher than the average groundwater $^{222}$Rn concentration (Santos et al. 2010). This is further evidence of seawater recirculation being the driver of
SGD because there would be no freshwater end member to extrapolate $^{222}$Rn values back to in Heron Island. These observations are consistent with the isolated, narrow freshwater lens observed in Heron Island (Santos et al. 2010). Therefore the end members for Rarotonga groundwater were calculated from the y-intercept of each parameter versus salinity, while the end members for Heron Island were calculated as the average concentrations measured over the groundwater time series (Table 11).

Figure 28. Linear regressions of $^{222}$Rn, $p$CO$_2$ and pH versus salinity in the groundwater time series on Rarotonga and Heron Island.
Linear regressions between $^{222}\text{Rn}$ and salinity in the Rarotonga ($R^2 = 0.008$, data not shown) and Heron Island ($R^2 = 0.016$, data not shown) water columns showed no significant correlation between $^{222}\text{Rn}$ and salinity, possibly due to the small range of salinity in both water columns (Table 10). However, temporal variations of $^{222}\text{Rn}$ concentrations in the water column revealed that the highest $^{222}\text{Rn}$ concentrations in Rarotonga coincided with ebb tides and the highest $^{222}\text{Rn}$ concentrations in Heron Island coincided with the beginning of flood tides (Figs. 26 and 27). Also, salinity was generally lower (35.6) with a greater range in the Rarotonga water column (2.4) when compared to the Heron Island water column (avg. = 38.7, range = 1.1) (Table 10). This also indicates that a terrestrial hydraulic gradient driving fresh groundwater exchange is the main driver of SGD in Rarotonga, while seawater recirculation is dominant in Heron Island. In support of this, using a combination of $^{223}\text{Ra}$ and $^{224}\text{Ra}$ isotopes, $^{222}\text{Rn}$ concentrations, and electrical resistivity mapping Tait et al. (2013) estimated that fresh groundwater was a significant source of SGD to the Rarotonga lagoon. Tait et al. (2013) also found that average $^{222}\text{Rn}$ concentrations in shallow saline groundwater were lower than the highest surface water concentrations, implying that recirculated seawater cannot possibly explain the radon enrichments observed in the Rarotonga water column.

**Contrasting $\text{pCO}_2$ dynamics in Rarotonga and Heron Island**

$p\text{CO}_2$ in the Rarotonga water column was positively correlated with $^{222}\text{Rn}$ concentrations (Fig. 29). Since the highest $^{222}\text{Rn}$ concentrations were associated with larger tidal ranges, which would influence SGD inputs, there are probably different correlations between $p\text{CO}_2$ and $^{222}\text{Rn}$ based on tidal height. However, over the course of the entire study there was a statistically significant correlation ($R^2 = 0.301$, $p < 0.01$), indicating that SGD is a source of free-$\text{CO}_2$ to the Rarotonga water column (Fig. 29).
Over the course of the time series, $p$CO$_2$ in the water column was negatively correlated with salinity ($R^2 = 0.402$, $p < 0.01$, data not shown), indicating that fresh groundwater is a source of free-CO$_2$. The significant correlations between $p$CO$_2$ and both $^{222}$Rn and salinity despite multiple other drivers of $p$CO$_2$ dynamics over the course of a diel cycle (i.e. reef metabolism), indicate that SGD is an important source of free-CO$_2$. It seems that due to the high $p$CO$_2$ in the fresh groundwater (~5,500 µatm), SGD on Rarotonga can act as a delivery mechanism of free-CO$_2$ to the water column.

![Figure 29. Regressions of $p$CO$_2$, DO, $\Omega_{Ar}$, and pH versus $^{222}$Rn in the water column on Rarotonga.](image)

The dynamics of $p$CO$_2$ and $^{222}$Rn in the Heron Island water column were more complex than in Rarotonga (Fig. 30). There were distinct correlations of $p$CO$_2$ with $^{222}$Rn depending on the time of day. $p$CO$_2$ was positively correlated with $^{222}$Rn concentrations when the afternoon time points (time of highest primary production) were removed (Fig.
Salinity and $pCO_2$ were not well correlated in the water column ($R^2 = 0.07$, data not shown), indicating that fresh SGD does not play a role in driving the $pCO_2$ dynamics of the Heron Island water column. During the afternoon there was no statistically significant correlation between $^{222}$Rn and $pCO_2$ ($R^2 = 0.01$). DO concentrations were negatively correlated with $^{222}$Rn during the night and morning, and positively correlated in the afternoon and evening (Fig. 30). The high $pCO_2$/low DO and low $pCO_2$/high DO concentrations associated with high $^{222}$Rn in the Heron Island water column indicate that SGD may stimulate coral reef metabolism. Figure 8 illustrates how $pCO_2$ and DO concentrations in the water column are related to $^{222}$Rn concentrations (and thus SGD) over the course of a day. High nutrient and organic loads from SGD could stimulate photosynthesis during the day and respiration at night, which would influence $pCO_2$ and DO correlations with $^{222}$Rn differently over a diel cycle (see next paragraph, Figs. 30 and 31).

![Figure 30. Regressions of $pCO_2$, DO, $\Omega_{Ar}$, and pH versus $^{222}$Rn in the water column on Heron Island. Regression equations displayed for $pCO_2$, $\Omega_{Ar}$, and pH are shown with values in the afternoon removed. Measurements are divided into night (22:00 to 05:00), morning, afternoon, and evening.](image-url)
06:00), morning (06:00 to 12:20), afternoon (12:20 to 17:20), and evening (17:20 to 22:00). Regressions for the DO versus $^{222}\text{Rn}$ correlations are as follows; night (DO = $-0.07(\text{^{222}Rn}) + 218$, $R^2 = 0.55$), morning (DO = $-0.1(\text{^{222}Rn}) + 279$, $R^2 = 0.35$), afternoon (DO = $-0.03(\text{^{222}Rn}) + 272$, $R^2 = 0.21$), and evening (DO = $-0.03(\text{^{222}Rn}) + 199$, $R^2 = 0.06$).

**Figure 31.** Diagram showing the relationship between $p\text{CO}_2$, DO and $^{222}\text{Rn}$ over different times of the day in the Heron Island water column.

Average concentrations from the groundwater time series at both Rarotonga and Heron Island are reported in Table 11. Salinity and pH were both lower in the Rarotonga groundwater than in Heron Island groundwater. The groundwater in Rarotonga had ~3 times the average $p\text{CO}_2$ and ~5 times the $^{222}\text{Rn}$ concentrations as in Heron Island. The $p\text{CO}_2$ end member in Rarotonga was almost 5 times the end member of that in Heron Island, perhaps influencing the higher average $p\text{CO}_2$ observed in the Rarotonga water column (Tables 10 and 11). In general, the Heron Island water column exhibited a larger
range of $p$CO$_2$ than in Rarotonga. However, the Rarotonga water column had higher average $p$CO$_2$ over the course of the study, which is indicative of the different drivers of SGD. A constant input of high $p$CO$_2$ groundwater from SGD in Rarotonga would result in the higher average $p$CO$_2$ in the water column, while potentially reducing the range. Conversely, because biological activity drives the majority of $p$CO$_2$ variability in the Heron Island water column, the range of $p$CO$_2$ is higher while the average is lower, in part due to the lower $p$CO$_2$ of Heron Island groundwater. Interestingly, SGD stimulates the uptake and release of CO$_2$ through controls on biological processes in the Heron Island water column (Figs. 30 and 31). We hypothesize that the differences between the influence of SGD on $p$CO$_2$ in Rarotonga and Heron Island were related to the different NO$_x$ concentrations in the groundwater at both locations (Table 11). Fluxes of NO$_x$ from Heron Island groundwater were calculated to be some of the highest in undisturbed ecosystems due to large local bird populations (Santos et al. 2010), although these loads are not reflected in water column NO$_x$ concentrations (0.8 µmol L$^{-1}$) due to rapid biological assimilation and high rates of NO$_x$ loss via denitrification (Eyre et al. 2008; Eyre et al. 2013). Based on $^{222}$Rn and NO$_x$ end members in the groundwater (Tables 1 and 2), average SGD-derived fluxes of NO$_x$ were $4.7 \pm 1.3$ mmol m$^{-2}$ d$^{-1}$ to the Rarotonga water column and $22.7 \pm 7.9$ mmol m$^{-2}$ d$^{-1}$ to the Heron Island water column. Therefore, the delivery of large amounts of NO$_x$ from SGD to the Heron Island water column may stimulate both heterotrophic and autotrophic activity, while lower fluxes of NO$_x$ to the Rarotonga water column have less of an effect on primary productivity.

The frequency distributions of $p$CO$_2$ offer another way to examine the differences between the influence of SGD on water column carbonate chemistry at Rarotonga and Heron Island. The $p$CO$_2$ distribution in the Rarotonga water column was bimodal, with peaks between 300-400 µatm and 600-700 µatm (Fig. 32). This implies that two distinct
phases occur in Rarotonga, one with high SGD inputs and high $p$CO$_2$ values and another with low SGD inputs and low $p$CO$_2$ values. This supports the hypothesis that steep hydraulic gradients of groundwater act as a source of free-CO$_2$ to the Rarotonga water column at low tide. Heron Island, however, follows a smoother, Gaussian distribution, with the frequency of higher concentrations trailing off after 400 µatm (Fig. 9). This supports the hypothesis that diel $p$CO$_2$ variability in the Heron Island water column is predominantly influenced by biological activity.

![Figure 32. Percent frequency distributions of $p$CO$_2$ values at the two study sites in the water column. Each value represents $p$CO$_2$ measurements that had same value in the hundreds place (i.e. 100 represents values between 100 to 199).](image)

The two distinct ways in which SGD can influence $p$CO$_2$ variability in coral reefs has implications for how OA will impact each ecosystem over the long term. Rarotonga has a consistently higher $p$CO$_2$ that may reduce community calcification, while $p$CO$_2$ in Heron Island is highly dependent on biological activity, which could both raise and lower community calcification rates at different times of day. Systems like Rarotonga, with elevated $p$CO$_2$, may offer sites analogous to volcanic vents used to predict in-situ effects of
OA (Fabricius et al. 2011; Hall-Spencer et al. 2008). In fact, systems throughout the world with differing SGD inputs may offer natural gradients of average $p\text{CO}_2$ while still maintaining the diel variability observed on most reef flats. This would offer novel ways to study the impact of OA because, unlike volcanic vents and “ojos” (Crook et al. 2012; Hall-Spencer et al. 2008), calcification rates of entire coral reef lagoons could be compared against a natural range of average $p\text{CO}_2$ and pH values. However, SGD would also flux fresh water and other solutes such as nutrients into the lagoons, which could confound any comparisons between different ecosystems.

**Influences of groundwater chemistry**

The influence of groundwater on the $p\text{CO}_2$ dynamics of coral reef water columns is not only highly dependent on the groundwater chemistry, but can also be influenced by freshwater dilution and changes in seawater buffering capacity. Calculations were performed in CO2SYS in order to assess the influence of pure dilution and a reduction in buffering capacity on $p\text{CO}_2$. A seawater end member with starting TA (2,300 $\mu$mol L$^{-1}$), dissolved inorganic carbon (DIC; 1,950 $\mu$mol L$^{-1}$), salinity (38), and temperature (25°C) was diluted to a range of salinities (34-38) assuming dilution by a freshwater end member with no TA and DIC. The linear regression between salinity and $p\text{CO}_2$ indicates that between salinities of 34 to 38, a decrease in salinity of one results in a decrease in $p\text{CO}_2$ of $\sim$13 $\mu$atm, the opposite of what was observed (Fig. 33A). However, if a freshwater end member with chemistry similar to Rarotonga groundwater (TA = 5,500 $\mu$mol, DIC = 5,617 $\mu$mol) is used, a decrease in salinity of one results in an increase in $p\text{CO}_2$ of $\sim$42 $\mu$atm, similar to the results from the Rarotonga groundwater time series (Figs. 27 and 33A). Therefore, any changes to water column carbonate chemistry due SGD is highly dependent on the specific groundwater chemistry including salinity, DIC, and TA concentrations.
Because $^{222}\text{Rn}$ is a conservative, unambiguous tracer of SGD inputs, correlations between $^{222}\text{Rn}$ and carbonate system parameters represent bulk changes in carbonate chemistry due to both dilution and groundwater chemistry.

![Diagram of carbonate chemistry](image)

**Figure 33.** (A.) Modelled effect of freshwater dilution on $p\text{CO}_2$ using CO2SYS and two freshwater end members. An end member with both DIC and TA set to zero (circles) and an end member with chemistry similar to Rarotonga groundwater (triangles; $\text{TA} = 5,500 \mu\text{mol}$, $\text{DIC} = 5,617 \mu\text{mol}$) were used. (B.) TA versus DIC concentrations in both the Rarotonga and Heron Island lagoons. Data is from discrete samples taken during the same time series as presented in this study but previously published in Cyronak et al. (2013) and McMahon et al. (2013).

Plots of TA versus DIC offer a way to separate out the effects of biological (i.e. photosynthesis and respiration) from geochemical (i.e. $\text{CaCO}_3$ precipitation and
dissolution) processes on the carbonate system (Andersson and Gledhill 2013; Suzuki and Kawahata 2003). Because geochemical processes affect both TA and DIC concentrations ($\Delta\text{DIC} = \Delta\text{TA}/2$) and biological processes affect only DIC, the slope of the TA versus DIC relationship can offer insights into changes in the water column carbonate chemistry. As presented in other studies, discrete samples for TA and DIC were taken from both Rarotonga (Cyronak et al. 2013) and Heron Island (Mcmahon et al. 2013) water columns during the respective time series presented here (Fig. 33B). The relationship in Rarotonga ($\text{TA} = 0.68(\text{DIC}) + 947$, $R^2 = 0.926$) indicates that the carbonate system is influenced 66% by biological processes while the relationship in Heron Island ($\text{TA} = 0.32(\text{DIC}) + 1,635$, $R^2 = 0.842$) indicates an 84% biological influence. This further supports the hypothesis that biological processes are more of a dominant driver of carbonate system variability in the Heron Island water column than in Rarotonga. However, the more apparent influence of “geochemical” processes in Rarotonga is most likely due to differences in groundwater chemistry and the large amount of TA fluxed from SGD into the water column (Cyronak et al. 2013) and not necessarily increases in $\text{CaCO}_3$ precipitation and dissolution. The TA versus DIC plots further demonstrate the diverse influences of SGD on water column carbonate chemistry. Also, this indicates that care must be taking when using the TA versus DIC relationship to determine biological versus geochemical influences on the carbonate system of whole ecosystems.

Groundwater in Rarotonga is high in TA (~5,500 $\mu$mol L$^{-1}$) and SGD has been shown to increase the TA of the lagoon water column (Fig. 33) (Cyronak et al. 2013). It has been hypothesized that any source of TA to a coral reef lagoon may be able to buffer coral ecosystems against decreases in pH due to OA (Andersson et al. 2007; Kleypas and Langdon 2006). This is due to increases in $\text{HCO}_3^-$ and $\text{CO}_2^{3-}$ ions and their ability to absorb $\text{H}^+$ ions as CO$_2$ is added to seawater. However, both pH and $\Omega_{\text{Ar}}$ of the water
column exhibited negative, though not significant trends with $^{222}$Rn concentrations (Fig 29). The impact of SGD on pH and $\Omega_{Ar}$ may be explained by the concurrent flux of CO$_2$ with TA. Even though there are many drivers influencing pH and $\Omega_{Ar}$ over a diel cycle (Gray et al. 2012; Shaw et al. 2012), this suggests that SGD lowers the buffering capacity of the water column and may represent a positive feedback to OA in Rarotonga. There are other aspects that need to be taken into account in order to properly address any buffering capacity (Andersson and Mackenzie 2012). For instance, excess CO$_2$ would be released to the atmosphere while TA would remain in the water column. Both lagoonal circulation patterns and residence time also play large roles in any buffering capacity (Andersson and Mackenzie 2012).

In contrast to Rarotonga, the average TA in the groundwater of Heron Island was only 2,243 µmol L$^{-1}$, which is very similar to the TA of the water column (2,185 to 2,323 µmol L$^{-1}$) (Fig. 10, Table 2) (Mcmahon et al. 2013). Therefore, SGD is unlikely to be a significant source of TA to the Heron Island water column. In the water column, pH ($R^2 = 0.145$, $p < 0.01$) and $\Omega_{Ar}$ ($R^2 = 0.113$, $p < 0.01$) were both negatively correlated with $^{222}$Rn when the afternoon time points (i.e. most productive time of day) were removed, indicating that SGD also acts as a positive feedback to OA in Heron Island. In the afternoon, a stimulation of production could increase the pH and $\Omega_{Ar}$, however, there is no statistically significant correlation between pH or $\Omega_{Ar}$ and $^{222}$Rn in the afternoon (Fig. 30). This may be because SGD is also source of free-CO$_2$ to the water column, due to the high $pCO_2$ of the groundwater (1,397 µatm), at the same time that it stimulates production.

*SGD and air-sea CO$_2$ fluxes*

Average air-sea CO$_2$ fluxes over the course of this study indicate that both lagoons were a source of CO$_2$ to the atmosphere (Fig. 34). Rarotonga (8.8 ± 3.4 mmol m$^{-2}$ d$^{-1}$) had
a ~3-fold higher average air-sea flux of CO$_2$ than Heron Island (2.5 ± 2.1 mmol m$^{-2}$ d$^{-1}$).

Air-sea CO$_2$ fluxes in other reefs have been shown to vary over a diel cycle, ranging from -2.1 to 6.5 mmol m$^{-2}$ d$^{-1}$, and are thought to be predominantly biologically controlled (Bates 2002; Frankignoulle et al. 1996; Gattuso et al. 1995; Gattuso et al. 1993). Air-sea CO$_2$ fluxes at both Rarotonga and Heron Island varied over diel cycles, with higher fluxes observed at night (Fig. 11). However, the majority of these fluxes were positive over the entire diel cycle, even when photosynthesis was occurring. Coral reef ecosystems have also been shown to switch between sources and sinks of CO$_2$ dependant on the time of year (Bates 2002). However, it was not within the scope of this study to assess the seasonal variability of air-sea CO$_2$ fluxes at Rarotonga and Heron Island.
Figure 34. SGD advection rates derived from the steady state model in Burnett and Dulaiova (2003) and air-sea CO$_2$ fluxes derived from Raymond and Cole (2001) with the atmospheric CO$_2$ concentration assumed to be constant at 393.8 ppm in (A.) the Rarotonga water column, and (B.) the Heron Island water column. Only a portion of the Heron Island time series is shown in order to better reveal the diel trends. Error bars on the SGD advection rates represent uncertainty derived from the model.

A non-steady state $^{222}$Rn mass balance (Burnett and Dulaiova 2003) estimated average SGD advection rates to be 16.7 ± 4.7 cm d$^{-1}$ at Rarotonga and 29.7 ± 10.3 cm d$^{-1}$ at Heron Island. Using the end member concentrations of free-CO$_2$ in the groundwater (Table 11), SGD released an average of 29.0 ± 8.2 mmol free-CO$_2$ m$^{-2}$ d$^{-1}$ to the Rarotonga water column and an average of 12.1 ± 4.2 mmol free-CO$_2$ m$^{-2}$ d$^{-1}$ to the Heron Island.
water column. In support of these SGD-derived free-CO$_2$ fluxes is a TA mass balance that was done over one day at the same sampling site during this study (Cyronak et al. 2013). The mass balance agreed well with SGD-derived TA fluxes calculated from $^{222}$Rn inputs, indicating that the $^{222}$Rn fluxes derived from the freshwater end member are reliable. Even though average $^{222}$Rn-derived SGD fluxes in Rarotonga (mostly fresh SGD) were roughly half of those in Heron Island (saline SGD), the ~3-fold higher SGD-derived CO$_2$ fluxes were consistent with the ~3-fold higher average air-sea CO$_2$ fluxes in Rarotonga. Since net ecosystem production of coral reefs is close to zero, the main reason reefs are thought to be sources of CO$_2$ to the atmosphere is due to CO$_2$ released during calcification (Frankignoulle et al. 1994; Gattuso et al. 1999). Our results demonstrate that SGD can also contribute to the air-sea flux of CO$_2$ from coral reefs. Interestingly, any reduction in calcification due to a lower pH and $\Omega_{Ar}$ from SGD could reduce $p$CO$_2$ levels in the water column. More studies to assess the impact of SGD on air-sea CO$_2$ fluxes in coral reef ecosystems over broader time scales are needed.

Implications of SGD to community level metabolism measurements

These results have implications to studies that calculate community level metabolic and calcification rates in coral reefs. There are generally two methods, besides incubations, used to calculate coral reef community metabolic and calcification rates. The Lagrangian, or flow respirometry method refers to measuring changes in solute concentrations as seawater flows across reef habitats (Barnes and Devereux 1984; Gattuso et al. 1996). This is usually done by measuring changes in seawater chemistry as an instrument package is floated across the reef (Chisholm and Barnes 1998; Gattuso et al. 1996), or as seawater flows between two stations (Shamberger et al. 2011; Yates and Halley 2006). SGD could easily impact Lagrangian studies if there were significant
groundwater inputs as the water mass flowed across the reef. The slack, or low tide method refers to measuring changes in carbonate chemistry over time during low tides when coral communities are isolated from mixing with the open ocean (Kinsey 1978; Ohde 1995; Silverman et al. 2012). Selection of the sampling site in studies using the slack tide approach is critical as SGD fluxes tend to be highest at low tides (Burnett et al. 2003).

A possible example of discrepancies in coral reef calcification rates, possibly due to SGD inputs, can be found in the literature. To determine community metabolic rates, Chisholm and Barnes (1998) floated an instrument package across Lizard Island lagoon in the northern Great Barrier Reef. There were large discrepancies in rates of calcification determined by two separate techniques, a combined DO/pH technique and via changes in alkalinity. The rates of organic matter decomposition and nitrification evoked to explain these discrepancies were determined to be unrealistic (Gattuso et al. 1999), but no alternative explanations were suggested. Due to the relatively high rainfall preceding the study, proximity of the instruments to land, and the relatively high elevation of Lizard Island (360m, somewhat similar to Rarotonga), it is reasonable to assume that there were some SGD inputs during their study. If SGD impacts the seawater chemistry of Lizard Island lagoon similarly to the locations investigated here, any changes in DO/pH would be less affected by SGD than changes in $pCO_2$ and TA (Figs. 3 and 4). If the package was floated across an area of high SGD inputs it could account for the anomalies observed by Chisholm and Barnes (1998).

Conclusions

In summary, the distinct ways that SGD can influence water column $pCO_2$ are highly dependent on groundwater chemistry, SGD fluxes, and the driving forces of
groundwater exchange, which are variable across different coral reef ecosystems (Fig. 35). Anomalies of $pCO_2$ in both systems were indicative of broadly occurring SGD inputs as supported by: (1) temporal variations of $^{222}$Rn and CO$_2$, (2) correlations between $^{222}$Rn, salinity, and $pCO_2$, (3) $pCO_2$ dynamics in the groundwater, (4) frequency distributions of $pCO_2$ values in the water column, (5) TA versus DIC plots, and (6) air-sea CO$_2$ fluxes compared to SGD-derived free-CO$_2$ fluxes. The exchange mechanisms of SGD can impact $pCO_2$ variability through both the direct delivery of free-CO$_2$ and the stimulation of biological processes over broad spatial scales across coral reefs.

The high SGD-derived fluxes of free-CO$_2$ into the two coral reef ecosystems may represent a positive feedback to OA (i.e. decreases local pH and $\Omega_{Ar}$) on a local scale. Carbonate system variability caused by SGD may also influence ecosystem level calculations of metabolism and calcification. This has important implications for OA research, as measuring net ecosystem calcification (NEC) rates is critical to understanding how OA will impact coral reefs. In fact, systems with variable SGD inputs may have naturally variable $pCO_2$ levels, potentially allowing for in-situ studies on the impact of OA on coral reefs over ecosystem wide scales. Finally, local drivers of coral reef carbonate chemistry may offer more approachable management solutions to mitigating the effects of OA on coral reefs (Kelly et al. 2011). In conclusion, this overlooked driver of carbonate system dynamics has important implications to studies examining the impact that OA will have on coral reefs.
Figure 35. Conceptual models showing how SGD influences $pCO_2$ dynamics in the water column on Rarotonga and Heron Island.
Chapter 5

Permeable coral reef sediment dissolution driven by elevated $\rho$CO$_2$ and porewater advection
5.1 Abstract

Ocean acidification (OA) is expected to drive the transition of coral reef ecosystems from net calcium carbonate (CaCO$_3$) precipitating to net dissolving within the next century. Although permeable sediments represent the largest reservoir of CaCO$_3$ in coral reefs, the dissolution of shallow CaCO$_3$ sands under future $p$CO$_2$ levels has not been measured under natural conditions. In situ, advective chamber incubations under elevated $p$CO$_2$ (~800 µatm) shifted the sediments from net precipitating to net dissolving. Porewater advection more than doubled dissolution rates (1.10 g CaCO$_3$ m$^{-2}$ d$^{-1}$) when compared to diffusive conditions (0.42 g CaCO$_3$ m$^{-2}$ d$^{-1}$). Sediment dissolution could reduce net ecosystem calcification (NEC) rates of the Heron Island lagoon by 8% within the next century, which is equivalent to a 25% reduction in the global average calcification rate of coral lagoons. The dissolution of CaCO$_3$ sediments needs to be taken into account in order to address how OA will impact the net accretion of coral reefs under future predicted increases in CO$_2$. 
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5.2 Introduction

The atmospheric CO$_2$ concentration is expected to stabilize between 660 to 790 µatm by the year 2100, an increase of ~400 µatm from the present day concentration (Pachauri and Reisinger 2007). This increase in CO$_2$ is predicted to decrease oceanic pH by ~0.3 units by the end of the century, a phenomenon termed ocean acidification (OA) (Feely et al. 2004). Multiple studies have demonstrated a reduction in the net ecosystem calcification (NEC) rates of coral reefs due to increasing oceanic pCO$_2$ (Andersson et al. 2009; Shamberger et al. 2011). However, most studies to date have not separated the effects of OA on calcium carbonate (CaCO$_3$) dissolution and coral calcification, despite dissolution being potentially more sensitive to OA than calcification (Andersson et al. 2009).

Calcium carbonate found within coral reefs exists in two main pools; reef framework and CaCO$_3$ sediments. Sediments often exceed the areal coverage of living coral and framework by up to one order of magnitude (Gattuso et al. 1998). While reef framework is the main site of CaCO$_3$ production due to the presence of living coral and other calcifying organisms, sediments represent the accumulation of reef generated CaCO$_3$ over thousands of years (Smith et al. 2009). Porewater advection refers to the bulk exchange of sediment porewater with the overlying water column and is largely driven by tides, wave action, sediment topography, sediment permeability, and currents (Precht and Huettel 2003). In contrast, exchange by diffusion results from a concentration gradient between the water column and porewater. Advection can enhance biological and geochemical processes occurring within the porewaters and fluxes of solutes into the water column (Cyronak et al. 2013a; Eyre et al. 2008; Wild et al. 2004). To date, most studies have examined the dissolution kinetics of shallow CaCO$_3$ sediments in the laboratory or under diffusive conditions (Tynan and Opdyke 2011;
Yamamoto et al. 2012), making it difficult to predict dissolution kinetics in the environment. The few field investigations done that incorporate advective conditions and diel cycles have demonstrated that advection influences benthic alkalinity fluxes (i.e. CaCO₃ precipitation and dissolution) (Cyronak et al. 2013a; Cyronak et al. 2013b; Rao et al. 2012). However, none of the studies have manipulated the $pCO_2$ of seawater to simulate predicted future OA conditions. In order to understand how OA will impact the accumulation of CaCO₃ in coral reefs it is necessary to determine the rates at which CaCO₃ sediments will dissolve *in situ* under porewater advection, diel cycles, and predicted increases in $pCO_2$. Herein, we performed *in situ*, diffusive and advective chamber incubations on Heron Island under current and increased $pCO_2$ scenarios.

5.3 Methods

Heron Island is a coral cay in the Great Barrier Reef surrounded by a large (26.4 km$^2$) and shallow (1.7m) coral lagoon covered mostly (~75-85%) by CaCO₃ sands (Eyre et al. 2008; Wild et al. 2004). The high permeability and porosity of the sands allow seawater to easily flow in and out of the sediments. Our incubations were conducted in an area dominated by CaCO₃ sands free from macrophytes and macrofauna burrows. Sediments from this site are comprised mostly of aragonite (65%) and high Mg$^{2+}$ calcite (HMC, 32%) with a Mg$^{2+}$ content of 15.2% (Cyronak et al. 2013a).

A total of 23, 24h-long incubations were conducted on three separate days (the 28 and 30 April 2013 and the 02 May 2013). On each day duplicate incubations for each treatment were run, with one advective high $pCO_2$ incubation lost on 28 April 2013. The incubations on 28 April 2013 started at sunset (~18:00), while the other two incubations started at sunrise (~06:00). Benthic chambers as detailed in Eyre et al. (2008) were used to measure benthic fluxes under diffusive and advective conditions (S1). The chambers were
placed in the sediments without lids and left open to the overlying water for at least 1 h. Advective chambers were run at 80 RPM during the first incubation, and 40 RPM thereafter. Previous studies have shown that these stirring rates induce porewater advection rates similar to those measured \textit{in situ} at Heron Island (Glud et al. 2008; Wild et al. 2004). The six replicates of each treatment were averaged for further analysis. Prior to the first sample being taken, chambers were closed to the overlying water and CO$_2$ additions began. The $p$CO$_2$ of the chambers was raised by pressurizing a closed loop of silicone tubing (Tygone 3350, 0.48 cm i.d.) at 2 bar with 99.9% pure CO$_2$ gas (S1). pH was monitored until the desired offset (~0.2) was reached, and the chambers were allowed to equilibrate for 30 min before the first samples were taken.

Chambers were sampled (120 mL) every 12 hours (on 02 May 2013 sampling was conducted every 6 h) via syringe and water was brought into the laboratory for analysis. DO (± 1%) was measured immediately in unfiltered samples using a Hach LDO probe. Samples for pH (± 0.008) and total alkalinity (TA) (± 0.1%) were 0.45 μm filtered and kept in an airtight container with no bubbles until analysis within 4 hours using a Metrohm Titrando automated titrator with a Metrohm Electrode Plus pH probe. The pH probe was calibrated to pH NBS buffers (4, 7, 10) and TA was corrected against Dickson reference material (Batch 122). pH was also monitored every 0.5 h in selected chambers using a SAMI-pH unit, which measures pH in the total scale using metacresol purple (mCP) as an indicator dye. pH in the total scale is ~0.13 lower than the NBS scale, however the exact magnitude is dependent on temperature, salinity, and individual pH electrode, therefore pH between the two scales is presented as measured in both NBS and total scales. pH and PAR were monitored in the water column every 15 min at the study site using a Hydrolab DS5X. pH from the Hydrolab was corrected to standards and seawater samples measured using the Metrohm electrode (NBS scale). $p$CO$_2$ and $\Omega_{Ar}$ were calculated using CO2SYS.
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with pH, TA, and laboratory temperature measured during the TA titrations and a constant salinity of 35 as the input parameters. CO2SYS was set to the parameters as described in McMahon et al. (2013).

CaCO₃ dissolution rates were calculated from TA fluxes assuming that half of the molar TA flux is equivalent to the molar CaCO₃ flux. Other benthic fluxes that could contribute to TA fluxes within the chambers (i.e. nutrient fluxes and sulphate reduction) were shown to be minimal at the same study site, implying that TA fluxes represent CaCO₃ precipitation and dissolution (Cyronak et al. 2013a; Rao et al. 2012). The molar weight of CaCO₃ (100.1 g mol⁻¹) was used to convert fluxes to g m⁻². Student’s t-tests were performed to compare means between treatments while linear regression analysis was performed on any regressions.

5.4 Results

During the incubation on 02 May 2013, all carbonate parameters (pH, TA, pCO₂, and ΩAr) varied over a diel cycle (Fig. 36). The average pCO₂ (n=6) of the control incubations was 418 ± 48 and 427 ± 20 µatm in the diffusive and advective chambers, respectively. The high pCO₂ treatments had significantly higher (p < 0.05, n=6) averages of pCO₂ (803 ± 98 and 839 ± 90 µatm) (Fig. 36, S2). This resulted in a ΔpCO₂ between the treatments and controls of 385 and 412 µatm in the diffusive and advective chambers, respectively, close to predicted changes for the end of the century (Pachauri and Reisinger 2007). Average pH was 0.24 units lower (p < 0.05, n=6) between the control and high pCO₂ treatments under both diffusive and advective conditions, while ΩAr was reduced by an average of 1 unit (p < 0.05, p=6) (Fig 36, S2). The offset of pH between low and high pCO₂ treatments was relatively stable throughout the day long incubations (Fig. 36). Average pH in the water column of the Heron Island lagoon where the incubations took
place was 8.12 with a minimum of 7.90 and maximum of 8.41. Therefore, the variability in the chamber incubations was similar to the natural variability of the lagoon water column. This variability was maintained at an offset in the high \( pCO_2 \) treatments, in contrast to most previous \( CO_2 \) manipulations in which \( pCO_2 \) was kept constant over a diel cycle (Fig. 36).

Figure 36. Average \( \Omega_{Ar} \) (triangles) and \( pCO_2 \) (circles) over the course of the third incubation. \( pH \) was measured every 30 minutes in an advective chamber on 2/5/2013 and an advective chamber with elevated \( pCO_2 \) on 30/4/2013 using a SAMI \( pH \) spectrophotometer. Diamonds are \( pH \) measurements from grab samples and the
black line is pH of the water column where the incubations were performed. The yellow star represents the time when CO$_2$ was added to the incubation chamber. The grey filled area in the background is PAR and all error bars represent SE.

Both dissolved oxygen (DO) and TA fluxes followed trends that were indicative of biological drivers (Fig. 37A). DO fluxes were positive during the day (net benthic production; NPP) and negative during the night (respiration), while alkalinity fluxes revealed the sediments to be net precipitating in the day and net dissolving at night (S2). Net precipitation rates in the day were similar between all treatments except the advective low pH treatment, which was 30% lower than the control. Since NPP and TA fluxes are correlated (S3), a 15% reduction in daytime production rates may partially explain the 30% decrease in daytime precipitation rates in the advective chambers. At night, elevated $p$CO$_2$ resulted in a 35% and 68% increase in CaCO$_3$ dissolution rates ($p < 0.05$, n=6) in the diffusive and advective treatments, respectively.
Figure 37. (A) Box diagrams of TA and DO fluxes from all chambers during the three sample periods under diffusive (D), diffusive plus CO\textsubscript{2} (D CO\textsubscript{2}), advective (A), and advective plus CO\textsubscript{2} (A CO\textsubscript{2}) treatments. (B) The difference in dissolution rates between the control and high CO\textsubscript{2} treatments under advective and diffusive conditions (average of all chambers from the three sample periods). (C) Average $p$CO\textsubscript{2} and CaCO\textsubscript{3} dissolution rates in the individual diffusive and advective chambers. The dotted lines are the 95% confidence interval for the advective regression. All error bars represent SE.
The amount of photosynthetically active radiation (PAR) varied between the days that incubations were performed, with daytime averages of 455, 272, and 521 µmol quanta m⁻² s⁻¹ during the first, second, and third day, respectively. Despite this variability in PAR, all of the chambers were net productive on a daily basis, while they varied between net CaCO₃ precipitating and dissolving dependent on the treatment (Fig. 37A). Both the diffusive and advective high pCO₂ treatments were net dissolving while the controls were net precipitating (p < 0.05, n=6). Advection interacted with high pCO₂ to stimulate the night, day, and net dissolution rates of CaCO₃ sediments above diffusive rates by 12%, 26%, and 150% (p < 0.05, n=6), respectively (Fig. 37A, S2). The net difference between control and high pCO₂ conditions was 0.42 ± 0.22 g CaCO₃ m⁻² d⁻¹ under diffusive conditions and 1.10 ± 0.22 g CaCO₃ m⁻² d⁻¹ under advective conditions. This equates to a 162% increase in dissolution rates between diffusive and advective chambers (Fig. 37B). This is consistent with increased flow of low pH surface waters into the interstitial porewaters under advective conditions. A significant positive linear trend was observed between net dissolution rates and the average chamber pCO₂ under advective conditions (r² = 0.660, p < 0.005, n = 11), while under diffusive conditions the regression was not significant (r² = 0.333, p = 0.05, n = 12) (Fig. 37C).

5.5 Discussion

The goal of this study was to assess in situ CaCO₃ dissolution rates in permeable sediments over a natural diel cycle under OA conditions and their influence on coral reef NEC rates. Previous observations in the Heron Island lagoon resulted in an average community NEC rate of 6.15 g CaCO₃ m⁻² d⁻¹ (2,246 g m⁻² y⁻¹) (McMahon et al. 2013). Using this estimate of NEC, CaCO₃ sands currently contribute from 1.0% to 3.7% of community CaCO₃ precipitation under diffusive and advective conditions, respectively. In
the elevated $p$CO$_2$ treatments, CaCO$_3$ sands dissolved at rates equivalent to 5.9% of the daily NEC rate under diffusive conditions and 14.6% under advective conditions. The net differences between control and high $p$CO$_2$ treatments equate to 6.8% and 17.9% of the NEC rate (Fig. 37B). Because solute transport in permeable sands is often dominated by advective exchange (Santos et al. 2012), and sands make up at least 80% (Eyre et al. 2008; Wild et al. 2004) of the benthos of Heron Island lagoon, a 400 µatm increase in the average $p$CO$_2$ could result in a reduction of current Heron Island NEC rates by ~14%.

The relationship between TA and dissolved inorganic carbon (DIC) offers insights into changes in the carbonate system (Andersson and Gledhill 2013). Under OA conditions, elevated $p$CO$_2$ increased DIC concentrations while TA remained constant (Fig. 38). Advection in both the low and high $p$CO$_2$ treatments shifted the slope of the TA vs. DIC relationship by ~13% towards a more biological dominated system (i.e. more influence from photosynthesis/respiration than CaCO$_3$ precipitation/dissolution) (Fig. 38, S2). This increase in the influence of organic processes under advective flow is consistent with other permeable sand studies (Cyronak et al. 2013a; Rao et al. 2012). More biological control on the carbonate system would result in a larger range of $\Omega_{Ar}$ values in the overlying water column over a diel cycle (Andersson and Gledhill 2013). This also indicates that more CO$_2$ per unit of TA would be fluxed out of the sediments under advective conditions, partially inhibiting the buffering effect (see Andersson and Mackenzie 2012) that sediment derived TA may have in the water column. This is also supported by the lower net production rates measured in the high CO$_2$ and advective incubations, indicating less of a net uptake of CO$_2$ from the water column under future conditions (Fig. 37A).
Figure 38. (A) Linear regression of TA vs. DIC concentrations combined from the incubations done on 30/4/2013 and 02/5/2013. (B) Conceptual model showing the effects of OA and advection on the carbonate system. The arrows in the background refer to biological (i.e. photosynthesis and respiration) and geochemical (i.e. carbonate precipitation and dissolution) effects on the carbonate system. OA drives the linear regressions towards the right of the graph as CO$_2$ is added and TA stays constant, while advection pushes the relationship towards more biological control. A constant salinity of 35 and temperature of 25°C were used to calculate the $\Omega_{Ar}$ values at each TA and DIC concentration.

Considering advection dominates solute exchange in coral reef permeable sands (Wild et al. 2004), and flushing rates in our advective chambers are comparable to in situ rates (Glud et al. 2008), we used the advective regression in order to model how the dissolution of CaCO$_3$ sands will effect community NEC rates as a function of average water column $p$CO$_2$. Assuming 80% coverage of CaCO$_3$ sands, an increase in average $p$CO$_2$ to 800 µatm in the overlying water (predicted by the year 2100) will result in a 8% decrease in the NEC rate of the Heron Island lagoon (Fig. 39A). If our results are compared to the global average NEC rate of coral lagoons (Milliman 1993) (800 g CaCO$_3$ m$^{-2}$ y$^{-1}$), the dissolution of CaCO$_3$ sediments alone could reduce the annual NEC of coral lagoons 25% by 2100 (Fig 39A). Other models predict a 42% decrease in the CaCO$_3$
production of the global coastal ocean by 2100 due to reductions in calcification rates alone (Andersson et al. 2005; Andersson et al. 2006). Therefore, increases in sediment dissolution could decrease CaCO$_3$ production an additional 25% above calcification-based model predictions. Also, the same models predicted an increase in CaCO$_3$ sediment dissolution of only 20% by the year 2100 (Andersson et al. 2005; Andersson et al. 2006), while our model indicates that the dissolution of shallow CaCO$_3$ sediments could increase 380% by the year 2100. Porewater advection at rates similar to those induced in our study have been calculated to occur at water column depths of up to ~50m, and may occur deeper depending on the physical characteristics of the sediments and surface gravity waves (Precht and Huettel 2003). Therefore, our results may be applicable to large areas of the coastal ocean and demonstrate the necessity of further elucidating other drivers of sediment dissolution in order to adequately predict changes to the global CaCO$_3$ budget under future CO$_2$ levels.

Applying our model to the global estimate of coral NEC rates assumes that CaCO$_3$ dissolution will be similar across coral reef ecosystems. However, there are multiple variables that could affect the dissolution rates of CaCO$_3$ sediments. For instance, the % Mg content, structural disorder, presence of impurities, porosity of sediments, and biological activity can all influence dissolution (Cyronak et al. 2013a; Morse et al. 2006). The exact influence of % Mg on dissolution rates of biogenic CaCO$_3$ has yet to be fully elucidated, and has been further complicated by the recent discovery of dolomite producing coralline algae (Nash et al. 2013). However, the mineralogical makeup of Heron Island sediments (15 mol% Mg$^{2+}$) put it within the greatest frequency of occurrences for mid-depth bank CaCO$_3$ sands (Morse et al. 2006). This implies that the dissolution rates measured in the Heron Island sediments may be a reasonable first order
estimate of future dissolution rates throughout different ecosystems with similar sediment mineralogy and porewater advection rates.

Figure 39. (A) Model showing the impact of sediment dissolution rates on coral NEC rates. The lower limit represents the % of the Heron Island NEC rate (2246 g CaCO$_3$ m$^{-2}$ y$^{-1}$), while the upper limit represents the % of the global average NEC rate of coral lagoons (Milliman 1993) (800 g CaCO$_3$ m$^{-2}$ y$^{-1}$). The dashed line was calculated using the global average NEC rate of all coral reef ecosystems (Milliman 1993) (1500 g CaCO$_3$ m$^{-2}$ y$^{-1}$). (B) Model showing the effect of depth on net daily dissolution rates in the sediments. The global average NEC rate of coral lagoons is represented by the dashed, red line. The lower limit was calculated from advective treatments under current $p$CO$_2$ levels (427 µatm) while the upper limit was calculated from advective treatments under elevated $p$CO$_2$ levels (839 µatm). Depth “x” represents when there is no production occurring.
Correlations between benthic NPP and average water column depth in Heron Island ($r^2 = 0.77$, $p < 0.05$, $n = 26$) (Eyre et al. 2013) offer insights into how net dissolution rates may vary with depth (S4). Because NPP is significantly correlated to fluxes of alkalinity ($\text{CaCO}_3$ dissolution) (S3), any reduction in NPP would also result in an increase in net daily $\text{CaCO}_3$ dissolution (Fig. 39B). By the year 2100, sediment at an average water column depth of 3 m could undergo dissolution rates equal to the global average NEC rate of coral lagoons. If there is no photosynthesis in the sands, sediment dissolution rates approach the global average NEC rate under current $\text{CO}_2$ levels. This suggests that the average depth of coral lagoons is critical in determining how shallow water systems will respond to future $p\text{CO}_2$ levels. While our calculations illustrate the potential impact of water column depth on sediment dissolution in coral lagoons, additional studies may be needed to better understand permeable $\text{CaCO}_3$ sediment dissolution in deeper environments such as continental shelves.

In summary, considering that up to 90% of the $\text{CaCO}_3$ in coral reefs is contained within the sediments, measuring their dissolution rates in situ provides insights into how OA will affect the net accretion of coral reefs. Our results demonstrate that elevated $p\text{CO}_2$ (~400 µatm above current) and advection act in synergy to increase dissolution ~5-times above the current precipitation rates of shallow $\text{CaCO}_3$ sediments. Also, porewater advection may more than double any rates previously estimated under diffusive conditions. Other studies have estimated $\text{CaCO}_3$ sedimentation rates of ~0.5 kg m$^{-2}$ y$^{-1}$ in sandy reef environments (Harney and Fletcher 2003; Ryan et al. 2001). Comparing this sedimentation rate to dissolution rates estimated in this study demonstrates that by the year 2100 dissolution of $\text{CaCO}_3$ sediments could reduce sedimentation rates by up to 80% of current values. This has drastic implications to the formation of valuable reef habitat, especially under rising sea levels.
Chapter 6

Conclusions
To provide a synthesis of the conclusions derived from this thesis, I will discuss each goal and hypothesis in detail below:

1. *Does advection influence the dissolution and precipitation of CaCO$_3$ sediments over a diel cycle? Does advection influence DIC and TA cycling in the water column?*

Chapter 1 showed how rates of benthic processes (photosynthesis, respiration, and CaCO$_3$ precipitation and dissolution) in permeable CaCO$_3$ sediments can vary greatly over a diel cycle. This can have consequences when measuring net daily fluxes, especially CaCO$_3$ precipitation and dissolution. Benthic photosynthesis and respiration seemed to be the dominant drivers of CaCO$_3$ precipitation and dissolution, with the highest precipitation rates in the middle of the day and dissolution occurring throughout the night. Therefore, the most accurate incubations are those done over a full diel cycle that capture all changes in the rates of benthic metabolism. Also, because the carbonate chemistry of seawater varies over a diel cycle, performing dark incubations by covering chambers in the day could underestimate CaCO$_3$ dissolution rates. Since rates of production and respiration drive the majority of CaCO$_3$ dynamics there is a hysteresis between the $\Omega_{Ar}$ of the water column and CaCO$_3$ precipitation and dissolution. This hysteresis makes predicting future CaCO$_3$ dissolution rates from trends between water column $\Omega_{Ar}$ over naturally variable diel cycles tenuous. The same hysteretic pattern was observed between NEC rates and average $\Omega_{Ar}$ of the Heron Island water column, with NEP being the dominant driver of NEC on an ecosystem level as well (McMahon 2013). Therefore, using natural variation in seawater chemistry to predict the effects of OA on calcification and CaCO$_3$ dissolution may be unrealistic, especially when NEC rates are highly correlated with other processes (photosynthesis and respiration) and physical variables (temperature). Disentangling the
effects of physical and biological variables on NEC rates in coral reefs remains an important topic in OA research.

Advection shifted the carbonate system of benthic sediment incubations towards more biological control on water column carbonate chemistry. Therefore, the release of more free-CO$_2$ with any alkalinity at higher advection rates may inhibit the buffering capacity of any TA inputs into the water column. Sediments can play an important role in modifying the carbonate chemistry of a coral reef when compared to other drivers (see Chapter 3). Higher flow rates and advection through the sediments could lead to more diel variation in the Ω$_{Ar}$ of the water column. Advection can also stimulate the precipitation and dissolution of CaCO$_3$ sediments under current conditions, most likely by increasing rates of respiration and photosynthesis. Overall, advection can play an important role in the biogeochemical cycling of permeable sediments, including the dissolution and precipitation of CaCO$_3$ minerals. Therefore, any studies looking at the effects of OA on coral reef sediment dissolution need to take advective flow into consideration. Also, enhanced dissolution of CaCO3 sediments could lead to the loss of valuable reef habitat. Sediments create the base of shallow coral reef environments such as coral cays, reef flats, and shallow lagoons. If the rate of sediment dissolution surpasses the sedimentation rate of these sediments, this effect combined with predicted sea level rise could lead to the accelerated loss of invaluable coral reef habitat.

2. What drives the dissolution and precipitation of CaCO$_3$ minerals in permeable sediments?

*How will lowering the pH of the water column due to ocean acidification affect sediment dissolution and precipitation?*
As discussed above, the dynamics of CaCO$_3$ dissolution and precipitation over the course of a diel cycle are highly correlated to benthic photosynthesis and respiration. However, under elevated $p$CO$_2$ conditions advection can stimulate the dissolution of CaCO$_3$ sands, most likely by increasing the exchange of high $p$CO$_2$ water in the water column with the porewaters (see Chapter 5). This means that interpolating dissolution rates based on natural diel variability may not accurately predict how OA will affect CaCO$_3$ sediment dissolution. Even though CaCO$_3$ dissolution and precipitation are related to photosynthesis and respiration in the sediments, lowering the water column pH through $p$CO$_2$ intrusion acts to increase CaCO$_3$ dissolution rates. Future research is needed to assess how changes to drivers of photosynthesis and respiration (i.e. inputs of organic matter and nutrients) act in synergy with increasing $p$CO$_2$ to drive CaCO$_3$ precipitation and dissolution dynamics in permeable CaCO$_3$ sediments.

3. Can SGD act as a source of DIC and TA to coral reef ecosystems? How does SGD influence DIC and TA cycling in the water column on different coral reefs?

How do different groundwater exchange mechanisms (i.e. porewater advection and SGD) contribute to DIC and TA cycling on coral reefs?

Can groundwater sources of TA to coral reefs act in any buffering capacity against ocean acidification?

Previous studies have shown that isolated inputs of groundwater through ‘ojos’ can influence carbonate chemistry. Chapters 3 and 4 demonstrate that ecosystem scale SGD inputs can have an important influence on the carbonate chemistry of coral reef systems. This impact can be direct (i.e. through inputs of TA, DIC, and CO$_2$) or indirect (i.e. through inputs of nutrients). The effect of groundwater on surface water carbonate chemistry is highly dependent on the chemistry of the groundwater. Groundwater high in TA may act to buffer coral reef ecosystems. However, this is highly dependent on the
concentration of free-CO$_2$ as any inputs of CO$_2$ will act to acidify the water column. Nutrients can stimulate production which draws down CO$_2$, but that may be counter balanced by inputs of free- CO$_2$ as well. Therefore, anthropogenic impacts on groundwater chemistry and exchange mechanisms may be important in predicting the changing carbonate chemistry of coral reefs.

Across an ecosystem scale, groundwater inputs and sediment porewater exchange can affect water column carbonate chemistry to a similar extent. However, CaCO$_3$ sediment dissolution also acts to remove valuable reef substrate that has accumulated over thousands of years.

Overall, the carbonate chemistry of coral reef water columns can be influenced by local groundwater inputs and sediment biogeochemistry. These controls may be equally important to increasing atmospheric CO$_2$ and may offer regional solutions to the acidification of coral reefs. Independent of the agent of change, increasing the average $p$CO$_2$ of coral reefs will lead to increased dissolution of CaCO$_3$ sediments. This could have important implications in the formation and accretion of coral reefs under future climate change.

Hypotheses

1. *Porewater advection stimulates the dissolution of CaCO$_3$ sands, thereby releasing TA into the water column.*

Porewater advection does stimulate the dissolution of CaCO$_3$ sands, most likely by stimulating respiration. Therefore, even though TA is released to the water column, the sediments are also a source of CO$_2$.

2. *SGD is a source of TA to coral reef lagoons.*

Groundwater can be a source of TA dependent on the groundwater chemistry and groundwater fluxes.

3. *SGD can alter the water column carbonate chemistry of coral reefs.*
SGD can change both the DIC and TA of the water column, with variable effects on water column carbonate chemistry dependent on the chemistry of the source groundwater.

4. Alkalinity from groundwater sources can act to buffer coral reef ecosystems against future changes in pH due to ocean acidification.

TA from groundwater could potentially buffer coral reefs, however, the extent of buffering will be dependent on numerous factors including groundwater CO$_2$ concentration and water column residence time.

5. Future projected levels of ocean acidification will stimulate the dissolution of CaCO$_3$ sands.

Increasing the $p$CO$_2$ of the water column will likely increase the dissolution rates of permeable CaCO$_3$ sediments and this effect is strongly stimulated by advective flow.


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Literature Cited


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Literature Cited


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Appendix 1

Enhanced coral reef acidification driven by regional biogeochemical feedbacks

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Appendix 1

Enhanced coral reef acidification driven by regional biogeochemical feedbacks

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Keywords: ocean acidification, $p$CO$_2$, coral reefs
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Abstract

Physical uptake of anthropogenic CO$_2$ is the dominant driver of ocean acidification (OA) in the open ocean. Due to expected decreases in calcification and increased dissolution of calcium carbonate (CaCO$_3$) framework, coral reefs are thought to be highly susceptible to OA. However, biogeochemical processes can influence the $p$CO$_2$ and pH of coastal ecosystems on diel and seasonal timescales, potentially modifying the long-term effects of increasing atmospheric CO$_2$. By compiling data from the literature and removing the effects of short-term variability, we show that the global average $p$CO$_2$ of coral reefs has increased ~3.5-fold faster than in open ocean surface waters within the past 20 years. This rapid increase in $p$CO$_2$ has the potential to enhance the predicted effects of OA on coral reef ecosystems. A simple model of coral reef metabolism illustrates that relatively small changes to the balance between primary production and respiration could be responsible for the observed trend. Potential drivers include additional anthropogenic disturbances beyond increasing atmospheric CO$_2$ such as enhanced nutrient and organic matter inputs. Therefore, regional scale management may be equally important as reducing global CO$_2$ emissions in mitigating the effects of OA on coral reefs.

Significance Statement

Coral reefs are thought to be highly susceptible to the increasing acidity of seawater driven by atmospheric CO$_2$ inputs. However, biogeochemical cycles occurring within coral reef ecosystems can change $p$CO$_2$ drastically over the course of daily and seasonal cycles. Therefore, it is important to understand how potential changes to these biogeochemical cycles might influence the acidification of coral reef waters. We demonstrate that coral reef $p$CO$_2$ has been increasing faster than expected when compared to the open ocean, most likely driven by anthropogenic changes to the biogeochemical
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cycles occurring within coral reefs. This means that regional anthropogenic impacts on coral reefs could be equally important as increasing atmospheric CO$_2$ in acidifying these important ecosystems.
The conventional view of ocean acidification (OA) is based on the oceanic uptake of anthropogenic CO\textsubscript{2} emissions and subsequent reduction in seawater pH (1, 2). However, considering atmospheric CO\textsubscript{2} as the sole driver may only apply to the open ocean as a number of additional anthropogenic perturbations can influence carbonate chemistry in coastal ecosystems (3, 4). Coral reefs exhibit some of the largest diel and seasonal seawater pCO\textsubscript{2} and pH variability, with pCO\textsubscript{2} levels occasionally well above what is projected by the turn of the century due to anthropogenic CO\textsubscript{2} emissions (5-8). Multiple drivers are known to contribute to this variability including watershed inputs of nutrients and organic matter and community metabolism (3, 7, 9). Unfortunately, no long-term monitoring stations analogous to those in open ocean surface waters (2, 10) exist in coral reefs which would allow for integration beyond diel and seasonal variability.

It is estimated that over 50% of coral reefs across the globe experience medium-high to very-high human related impacts from a combination of overfishing, nutrient inputs, pollutants, and other drivers (11). These anthropogenic impacts are known to effect community level metabolic processes and could play an important and synergistic role in the acidification of coral reefs. Models indicate that the natural variability of coral reef seawater carbonate chemistry will be amplified by increasing atmospheric CO\textsubscript{2} due to a decrease in seawater buffering capacity (12, 13) Therefore, any anthropogenic perturbations to ecosystem level drivers of coral reef seawater carbonate chemistry could be equally important as increasing atmospheric CO\textsubscript{2} in raising the pCO\textsubscript{2} of these ecosystems. It was projected that, based on a seasonal dataset in a Bermuda coral reef system, OA could be partially buffered by changes to coral reef metabolism (4). Here we use global observations integrated over at least one diel cycle and a simple model of reef metabolism to show that average coral reef pCO\textsubscript{2} has increased faster than open ocean pCO\textsubscript{2}, mostly likely due to local anthropogenic disturbances to the metabolic balance of
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reef ecosystems. This rapid increase in $pCO_2$ has the potential to enhance the predicted effects of OA on coral reef ecosystems.

Results and Discussion

Globally distributed observations show an increasing trend in the diel averages of $pCO_2$ in coral reefs since 1966 ($R = 0.64$, $p < 0.001$, $n = 51$) (Fig. 1A, Table S1). The majority of values fall above the line of atmospheric CO$_2$ indicating that increasing reef $pCO_2$ is not being driven solely by atmospheric forcing. In the past 20 years open ocean, surface $pCO_2$ near both Hawaii and Bermuda has increased at a rate of ~1.9 µatm y$^{-1}$ (1, 2). A linear regression of average coral reef $pCO_2$ ($R = 0.58$, $p < 0.001$, $n = 48$) over the same time period indicates that the $pCO_2$ of coral reefs has increased at a rate of $6.6 \pm 1.4$ µatm y$^{-1}$, ~3.5 times faster than in the open ocean ($p < 0.01$) (Fig. 1B). Between 1965-1975, average coral reef $pCO_2$ was ~30 µatm below the average atmospheric CO$_2$ level. In the ensuing decades, average coral reef $pCO_2$ increased to 10 µatm (1990-1999), 66 µatm (2000-2009), and 73 µatm (2010-2012) above average decadal atmospheric CO$_2$ concentrations (Fig. 1C). While we lack long-term uninterrupted observations in individual systems, the global coral reef $pCO_2$ trend is consistent with observations at One Tree Island, Great Barrier Reef (GBR) between 1968 and 2009, showing a ~70% increase in $pCO_2$ (Table S1).

In order to evaluate potential causes behind this rapid increase in coral reef $pCO_2$, influences of seasonality, temperature, study length, and methodology were first examined. The majority of seasonal coral reef $pCO_2$ variability is due to temperature effects and changes in community metabolism (6). Besides a surplus of summer months during 2000-2010, seasons were well distributed throughout the data set (see Table S1). There was no significant difference in the slope of the linear regression between $pCO_2$ and year since
1990 when all summer months were removed from the analysis (p > 0.3) and when $pCO_2$ was normalized to a mean temperature (26.4°C) over the past 50 years (p > 0.1). Over the past 50 years an increase (0.5°C) in the average oceanic temperature would only account for an increase in $pCO_2$ of ~10 µatm (14), which is well below the ~170 µatm increase observed in mean coral reef $pCO_2$ over the same time period. Therefore, seasonal and long-term temperature variations alone cannot explain the observed increase in coral reef $pCO_2$. There was no significant correlation (p > 0.5) between study length and average $pCO_2$, indicating that the length of the studies had no effect on the observed long-term trend. Also, there was no significant difference between the regressions of increasing $pCO_2$ (p > 0.3) when only measured $pCO_2$ values were used, indicating that the method used to calculate $pCO_2$ from measurements of other carbonate chemistry parameters had no effect on the observed long-term trend.

Next, it was examined whether changes in coral reef metabolism could explain the observed trend in $pCO_2$. Diel variability in coral reef $pCO_2$ is mainly driven by benthic metabolic processes (i.e. respiration, photosynthesis, calcification, and CaCO$_3$ dissolution) and the diel amplitude is often well above that of seasonal changes. Coral calcification rates in the GBR have been shown to decrease ~10-14% in the past 50 years (15). Since calcification shifts the carbonate system towards CO$_2$ any reduction in calcification would reduce $pCO_2$ levels, opposite to our observations (Fig. 1). Primary production and respiration can exert strong control seawater carbonate chemistry and are thought to be near balanced in coral reef systems due to the rapid turnover and cycling of nutrients and organic matter (OM) (16). Therefore, any changes in the ratio of production to respiration (P/R) or overall increases in community metabolism could lead to changes in the average $pCO_2$ of coral reefs.
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In order to test these hypotheses we adopted a simple model based on one month of high frequency carbonate chemistry observations at Heron Island (GBR). As photosynthesis and respiration change dissolved inorganic carbon (DIC) concentrations over the course of a day, increases in $pCO_2$ are greater than decreases due to changes in the Revelle factor (Fig. 2) (12, 13). Therefore, the tight coupling of respiration and photosynthesis in coral reefs means that a bulk increase in reef metabolism could lead to a higher average $pCO_2$ and lower average pH. In fact, our model indicates that increasing photosynthesis and respiration equally by 50% above current values leads to an increase in average $pCO_2$ of $\sim$54 $\mu$atm (Fig. 2A). Interestingly, increases in global ocean temperatures could preferentially stimulate respiration over photosynthesis (17, 18). If this occurs in coral reefs, it would act to raise the mean $pCO_2$ even quicker than stimulating both photosynthesis and respiration equally. A decrease in the photosynthesis to respiration (P/R) ratio by 10% results in an increase of average reef $pCO_2$ by $\sim$130 $\mu$atm (Fig. 2C). Changing the calcification rate has only a minor effect on $pCO_2$, with an increase in calcification of 10% leading to a decrease in the average $pCO_2$ of $\sim$12 $\mu$atm (Fig. 2B). According to our model, realistic changes to bulk ecosystem metabolism and P/R can have significant effects on the average $pCO_2$ of coral reefs, equal or greater in magnitude to changes due to increasing atmospheric CO$_2$.

Our model demonstrates that relatively modest changes in reef metabolism could account for the rapid increase in average coral reef $pCO_2$, but are there anthropogenic drivers of sufficient magnitude to cause changes in community metabolism over the past 50 years? Terrestrial derived sediment, nutrient, and OM inputs represent some of the major anthropogenic pressures on coral reef ecosystems (19, 20). Significant human alteration of the global nitrogen and phosphorus cycles (21) now deliver excess nutrients to coral reefs via surface runoff, submarine groundwater discharge, and atmospheric
due to the tight coupling of photosynthesis and respiration, increased nutrient loading to coral reefs could lead to higher average $pCO_2$ levels by stimulating overall reef metabolism. Also, increased OM inputs in the form of particulate and dissolved organic carbon could lower the P/R ratio of reefs and increase the average $pCO_2$ more dramatically than changing bulk metabolism. In fact, the input of terrestrial derived OM was associated with elevated $pCO_2$ within the GBR (9). Therefore, it is possible that anthropogenic inputs of nutrients and OM along with impacts to watershed processes (i.e. increased runoff) could drive changes in reef metabolism leading to increases in average coral reef $pCO_2$.

An example of high $pCO_2$ associated with high terrestrial inputs of nutrients and OM is evident in Kaneohe Bay, Hawaii (23, 24). Kaneohe Bay has some of the highest average $pCO_2$ values reported in worldwide coral reefs (*see Table S1*), which may be indicative of high rates of OM remineralisation and the intimate connection between reef primary productivity and respiration. Reef metabolism at Kaneohe bay has also been shown to be net heterotrophic, which corresponds to a P/R ratio below one (25). The P/R of coral reefs may be highly dependent on the production and storage of OM. For example, the input of nutrients from sewage discharge resulted in pelagic algal blooms in Kaneohe Bay between ~1960-1970 (26). The pelagic blooms subsided soon after the sewage discharge ceased, however, macro-algae abundance remained elevated due to nutrients stored in sediments. The eutrophication of Kaneohe Bay may offer insights into the long term storage of OM in the sediments of reef habitats, and subsequent remineralisation and export of CO$_2$ to the water column.

Episodic events such as bleaching and storms can also have a significant influence on the $pCO_2$ of reef ecosystems by disturbing the reef’s metabolic balance. Bleaching induced stress and respiration were associated with a ~50 µatm increase in the average
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$pCO_2$ of a coral reef, most likely due to the release of high amounts of OM (27). Tropical cyclones have also been shown to increase reef $pCO_2$ over short timescales through increased terrestrial runoff, increases in respiration, and habitat destruction (28, 29). Therefore, increases in bleaching (30) and tropical cyclones (31) over the last 50 years could have also contributed to the increasing average $pCO_2$ of coral reefs. In addition, the historical overfishing of coral reefs is thought to have shifted community structure through the loss of herbivores and the proliferation of crown of thorns starfish, which may impact the inorganic carbon biogeochemistry of reef ecosystems (32).

In summary there is an overarching trend of increasing coral reef $pCO_2$ within the past 50 years, with an accelerated increase over the last 20 years. This accelerated increase is most likely explained by a combination of disturbances to the metabolic balance of reef ecosystems. These disturbances include anthropogenic perturbations to natural drivers of $pCO_2$ such as nutrient and OM loading, habitat degradation through storms, bleaching, and overfishing, and anthropogenic climate forcings (Table 1). In coastal ecosystems such as coral reefs, regional disturbances to drivers of seawater carbonate chemistry may be equally important as increasing atmospheric CO$_2$. Therefore, combating the acidification of coral reefs may require not only reducing global CO$_2$ emissions, but also managing the regional biogeochemical controls of carbon chemistry in individual coral reef systems.

**Materials and Methods**

*Data compilation*

Average diel $pCO_2$ and pH values of coral reefs were compiled from the literature (Table S1). Any study indicating coral reefs as the field site were used when measurements were taken over at least one diel cycle. In the cases that seasonal measurements were taken, a yearly average is shown. When CO$_2$ levels were reported as
Appendix 1

$\text{jCO}_2$ in the original study, it was converted to $p\text{CO}_2$ by multiplying by 1.03, as this is the typical difference between fugacity and partial pressure of CO$_2$ at typical in situ temperatures. In order to normalize pH to the total scale, 0.13 was subtracted from all values on the NBS scale. The transformation of NBS to total scale is supported by the observed trend, which is consistent with changes in $p\text{CO}_2$ over the same time period. When averages were not available explicitly in the text, the graph digitation program GetData (v. 2.25) was used to extract data.

Model description

The model considers changes in dissolved inorganic carbon (DIC) and total alkalinity (TA) measured at Heron Island (33), driven by processes of photosynthesis (light and autotrophic biomass dependent), respiration (biomass dependent), calcification (light and coral biomass dependent), calcium carbonate dissolution (coral biomass dependent), and mixing of lagoon seawater with an open ocean end-member as:

\[
\begin{align*}
\frac{d\text{DIC}}{dt} &= -Bk_p\sin

- Cp\sin(\pi t^4 + Ck_d) - k_m(TA - TA_{oceanic})S - 2

\frac{dT_A}{dt} &= 2
\end{align*}
\]

with $B$ denoting autotrophic biomass (expressed in $\mu$mol kg$^{-1}$), $C$ denoting coral biomass (expressed in $\mu$mol kg$^{-1}$), $\sin(\pi t)^4$ simulating diurnal changes in light availability, $k_p$, $k_r$, $k_c$, $k_m$, $S$, $TA_{oceanic}$, and $T_A$.
Appendix 1

$k_d$ and $k_m$ being rate constants (d$^{-1}$) for photosynthesis, respiration, calcification, calcium carbonate dissolution and mixing, respectively, and $\text{DIC}_{\text{oceanic}}$ and $\text{TA}_{\text{oceanic}}$ representing typical open ocean end-members for DIC and TA, set to 2000 and 2300 $\mu$mol kg$^{-1}$, respectively. The latter value combination has been chosen to result in modern oligotrophic open ocean $p\text{CO}_2$ levels of about 400 µatm at an observed salinity of 34 and a temperature of 26 degrees Celsius. Autotrophic and coral biomass was set to identical levels and then $k_p$, $k_r$, $k_c$, $k_d$ and $k_m$ were tuned to fit observations of diurnal variability in DIC, TA and $p\text{CO}_2$, and corresponding mean levels (Fig. S1). Note that initial biomass settings do not influence model results as the tuned rate constants scale accordingly. This also applies to the respiration term (Eq. 1) which actually includes both autotrophic and heterotrophic components. Final parameter settings for modern Heron island conditions were 400 $\mu$mol kg$^{-1}$ for B and C, and 3, 1.15, 0.5, 0.15 and 1 d$^{-1}$ for $k_p$, $k_r$, $k_c$, $k_d$ and $k_m$, resulting in a ratio of photosynthesis to respiration of 0.98, of calcification to calcium carbonate dissolution of 1.25 and of photosynthesis to calcification of 6. The differential equations (Eq. 1 and 2) were solved numerically with the MATLAB 'ode45’ solver (34) until reaching steady-state conditions. Carbonate chemistry speciation such as pH and $p\text{CO}_2$ was calculated from modelled DIC and TA using the temperature and salinity dependent stoichiometric equilibrium constants for carbonic acid determined by Mehrbach et al. (35) as refitted by Lueker et al. (36).
Appendix 1

Literature Cited


Appendix 1


Appendix 1


Figure 1. (A) Average coral reef $p$CO$_2$ and pH values measured over at least one diel cycle. The studies ranged in length from 1 day to multiple years. Atmospheric $p$CO$_2$ from Mauna Loa, Hawaii is shown in black. The dashed line represents a quadratic regression of the data and the shaded region is the 95% confidence interval. (B) Linear regression of coral reef $p$CO$_2$ levels since 1990 compared to a regression of open ocean surface water $p$CO$_2$ (gold dashed line) (2) over the same time period. (C) Box diagram of the data binned into decades.

Figure 2. Impact of potential changes in various reef processes on diel variability of seawater $p$CO$_2$ at Heron Island. Intermediate red lines represent model runs fitting present day observations (compare Fig. S1) while light and dark red lines depict model runs with certain process rates decreased or increased, respectively. (A) Changes in overall reef metabolism, with a 50% decrease or increase in both photosynthesis and respiration rates, (B) changes in calcification rate, with a 10% decrease or increase, and (C) changes in the balance between photosynthesis (P) and respiration (R), with a decrease or increase in P/R by 10% in comparison to modern day conditions. Numbers denote mean $p$CO$_2$ levels over the entire diel cycle in the different model runs.
Figure 1.
Figure 2.
Table 1. Summary of drivers of $pCO_2$ variability on coral reefs over short and long temporal scales.

<table>
<thead>
<tr>
<th></th>
<th>Short (Diel/Seasonal) Timescales</th>
<th>Long (Decadal) Timescales</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric CO$_2$</td>
<td>Winter: increase due to flux into seawater</td>
<td>Increase due to increasing atmospheric CO$_2$</td>
</tr>
<tr>
<td></td>
<td>Summer: decrease due to flux to atmosphere</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Winter: decrease</td>
<td>Increase with increase in average ocean temperature</td>
</tr>
<tr>
<td></td>
<td>Summer: increase</td>
<td></td>
</tr>
<tr>
<td>Nutrient Inputs</td>
<td>Day: decrease due to production</td>
<td>Unknown, possible increase due to more OM storage and remineralisation.</td>
</tr>
<tr>
<td></td>
<td>Night: increase due to respiration</td>
<td></td>
</tr>
<tr>
<td>Groundwater</td>
<td>Increase from direct flux, however, can stimulate production as well</td>
<td>Site specific</td>
</tr>
<tr>
<td>River Inputs</td>
<td>Decrease in wet seasons</td>
<td>Increase</td>
</tr>
<tr>
<td>Storm Events</td>
<td>Increase</td>
<td>Likely increase as a result of more intense events</td>
</tr>
<tr>
<td>Bleaching</td>
<td>Increase</td>
<td>Increase</td>
</tr>
<tr>
<td>Reef Degradation</td>
<td>Increase</td>
<td>Increase</td>
</tr>
</tbody>
</table>
Appendix 2

Supplementary material for Chapter 5
Appendix 2

Methods for model calculations

The % reduction in NEC rates ($D_{\%NEC}$) due to sediment dissolution were calculated based off the regression of CaCO$_3$ dissolution rates vs. average $p$CO$_2$ using the following equation,

$$D_{\%NEC} = \frac{(pCO_2 \times 0.0023 - 1.1614)}{NEC} \times 0.8 \times 100$$

(1)

where pH is the average $p$CO$_2$, NEC is the NEC rate in g CaCO$_3$ m$^{-2}$ d$^{-1}$, and 0.8 is the fraction of sediment making up the benthos.

Daytime TA fluxes at different depths were estimated based off of the regressions in S3 and S4 using the following equation,

$$TA_D = -0.48 \times (-4.47 \times d + 11.87) + 0.15$$

(2)

where d is depth in meters and TA$_D$ is in mmol m$^{-2}$ h$^{-1}$. Net daily CaCO$_3$ dissolution rates in Figure 4B were calculated using the following equation,

$$D_{CaCO_3} = (TA_N \times t) + (TA_D \times t) \times 0.5 \times 0.1001$$

(3)

where TA$_N$ is the average night time flux of TA measured in the advective chambers under either the low or high $p$CO$_2$ treatments, TA$_D$ is the daytime TA flux calculated from Eq. 2, t is time (t = 12 h), 0.5 is the molar conversion for TA to CaCO$_3$ fluxes, and 0.1001 is the molecular weight of CaCO$_3$ in g mmol$^{-1}$. Daytime TA fluxes in the high $p$CO$_2$ treatment were multiplied by 0.7 due to a 30% reduction in the average between the two treatments (S2).
S1. Picture showing the (A) advective chambers used during this study and the (B) silicone tubing loop used to raise $p\text{CO}_2$ during the incubation. The spinning disc in the middle of the chamber is rotated at different rates in order to induce advection into the sediments. The loop was used instead of bubbling in order to raise $p\text{CO}_2$ levels without introducing bubbles into the chambers. Once the desired pH levels were reached (see manuscript), the loops were depressurized and closed off to the external environment.
Table S2. Average parameters between all chambers (n=6) for the three sample periods in each treatment.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>pH</th>
<th>$pCO_2$</th>
<th>$\Omega_{ar}$</th>
<th>Dissolution Rate (g CaCO$_3$ m$^{-2}$ d$^{-1}$)</th>
<th>TA vs. DIC Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Night</td>
<td>Day</td>
<td>Net</td>
<td>$r^2$</td>
<td>$y_0$</td>
</tr>
<tr>
<td>Difffuse</td>
<td>8.18 ± 0.02</td>
<td>418 ± 48</td>
<td>3.20 ± 0.25</td>
<td>1.19 ± 0.08</td>
<td>-1.34 ± 0.05</td>
</tr>
<tr>
<td>Difffuse pH</td>
<td>7.94 ± 0.06</td>
<td>803 ± 98</td>
<td>2.16 ± 0.23</td>
<td>1.61 ± 0.08</td>
<td>-1.35 ± 0.13</td>
</tr>
<tr>
<td>Advective</td>
<td>8.18 ± 0.05</td>
<td>427 ± 20</td>
<td>3.23 ± 0.10</td>
<td>1.08 ± 0.12</td>
<td>-1.42 ± 0.15</td>
</tr>
<tr>
<td>Advective pH</td>
<td>7.95 ± 0.05</td>
<td>839 ± 90</td>
<td>2.18 ± 0.21</td>
<td>1.81 ± 0.14</td>
<td>-1.00 ± 0.11</td>
</tr>
</tbody>
</table>
TA Flux = -0.4847*NPP + 0.1474
\( r^2 = 0.53, p < 0.05, n = 11 \)

S3. Graph showing the relationship between daytime TA fluxes and NPP rates in the advective chambers during this study. Additional scatter may be apparent from combining the high and low \( p\text{CO}_2 \) treatments. Dashed lines represent 95% confidence intervals.
S4. Relationship of NPP vs. daytime average depth from Eyre et al. 2013. The same chambers as this experiment were run at the same study site under advective conditions (40 RPM) for 12 consecutive days in December 2009 (summer). Daytime NPP rates were similar in magnitude to those measured during this study (4.11-4.86 mmol O\textsubscript{2} m\textsuperscript{-2} h\textsuperscript{-1}). However, rates from this study were low when compared to the average depth measured during this study (1.3 m), possibly due to seasonal differences in NPP rates. Therefore, dissolution rates in the depth model (Fig. 4B) may be underestimated due to the higher amounts of NPP per depth found in Eyre et al. 2013. Dashed lines represent 95% confidence intervals.
Appendix 3

Articles as published
Carbon cycling hysteresis in permeable carbonate sands over a diel cycle: Implications for ocean acidification

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Abstract

Dissolved inorganic carbon, dissolved oxygen, H\(^+\), and alkalinity fluxes from permeable carbonate sediments at Heron Island (Great Barrier Reef) were measured over one diel cycle using benthic chambers designed to induce advective pore-water exchange. A complex hysteretic pattern between carbonate precipitation and dissolution in sands and the aragonite saturation state (\(\Omega_{\text{Ar}}\)) of the overlying chamber water was observed throughout the incubations. During the day, precipitation followed a hysteretic pattern based on the incidence of photosynthetically active radiation with lower precipitation rates in the morning than in the afternoon. The observed diel hysteresis seems to reflect a complex interaction between photosynthesis and respiration rather than \(\Omega_{\text{Ar}}\) of the overlying water as the main driver of carbonate precipitation and dissolution within these permeable sediments. Changes in flux rates over a diel cycle demonstrate the importance of taking into account the short-term variability of benthic metabolism when calculating net daily flux rates. Based on one diel cycle, the sediments were a net daily source of alkalinity to the water column (5.13 to 8.84 mmol m\(^{-2}\) d\(^{-1}\), depending on advection rates), and advection had a net stimulatory effect on carbonate dissolution. The enhanced alkalinity release associated with benthic metabolism and pore-water advection may partially buffer shallow coral reef ecosystems against ocean acidification on a local scale.

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Carbon cycling in permeable sand
Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands)

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Abstract. To better predict how ocean acidification will affect coral reefs, it is important to understand how biogeochemical cycles on reefs alter carbonate chemistry over various temporal and spatial scales. This study quantifies the contribution of shallow porewater exchange (as quantified from advective chamber incubations) and fresh groundwater discharge (as traced by $^{222}$Rn) to total alkalinity (TA) dynamics on a fringing coral reef lagoon along the southern Pacific Island of Rarotonga over a tidal and diel cycle. Benthic alkalinity fluxes were affected by the advective circulation of water through permeable sediments, with net daily flux rates of carbonate alkalinity ranging from $-1.55$ to $7.76$ mmol m$^{-2}$ d$^{-1}$, depending on the advection rate. Submarine groundwater discharge (SGD) was a source of TA to the lagoon, with the highest flux rates measured at low tide, and an average daily TA flux of $1080$ mmol m$^{-2}$ d$^{-1}$ at the sampling site. Both sources of TA were important on a reef-wide basis, although SGD acted solely as a delivery mechanism of TA to the lagoon, while porewater advection was either a sink or source of TA dependent on the time of day. This study describes overlooked sources of TA to coral reef ecosystems that can potentially alter water column carbonate chemistry. We suggest that porewater and groundwater fluxes of TA should be taken into account in ocean acidification models in order to properly address changing carbonate chemistry within coral reef ecosystems.

1 Introduction

The recent increase in atmospheric CO$_2$ has led to an increase in oceanic pCO$_2$ as roughly 30% of anthropogenic CO$_2$ has been absorbed by the oceans (Feely et al., 2004; Sabine et al., 2004; Orr et al., 2005; Doney et al., 2009). Ocean acidification is the term given to this increase in oceanic pCO$_2$, which alters the carbonate chemistry of seawater leading to a reduction in pH at a rate of roughly 0.002 pH yr$^{-1}$ (Feely et al., 2004; Doney et al., 2009). Ocean acidification can have drastic effects on biological processes and the biogeochemistry of marine ecosystems, with coral reefs being some of the most susceptible ecosystems (Fabry et al., 2008; De’ath et al., 2009). The biogeochemical processes occurring in coral reefs can modify the carbonate chemistry of the overlying seawater, leading to large diel variations in alkalinity, pCO$_2$, pH, and dissolved oxygen (DO) (Santos et al., 2011; Shamberger et al., 2011; Gray et al., 2012; Shaw et al., 2012). In order to understand how ocean acidification will affect coral reefs, it is important to understand how natural processes, which can potentially buffer or intensify changes in seawater pH, alter the carbonate chemistry of seawater within coral reef ecosystems.

As CO$_2$ dissolves in water, it is hydrolyzed to form carbonic acid in the following equilibrium reactions:

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}. \quad (1)$$

Due to the production of HCO$_3^-$ and CO$_3^{2-}$, the increase in H$^+$ ions causes a reduction in seawater pH but does not change the total alkalinity (TA) (Millero, 1979; Zeebe and Wolf-Gladrow, 2001). The TA of a solution represents the ability of the solution to absorb H$^+$ ions without an
associated reduction in the pH, and in seawater is equal to the following equation (Wolf-Gladrow et al., 2007):

\[
TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)^+] + [OH^-] 
+ [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3]
+ [HS^-] - [H^+] - [HSO_4^-] - [HF] 
- [H_3PO_4] - [HNO_2].
\] (2)

Within the range of normal oceanic pH, and especially in oligotrophic waters, the majority of alkalinity in seawater is found in the form of dissolved inorganic carbon (DIC) as \(HCO_3^-\) and \(CO_3^{2-}\) (Millero, 1979; Wolf-Gladrow et al., 2007).

The dissolution and precipitation of carbonate minerals, both biotic and abiotic, can alter the water column TA within coral reef lagoons (Andersson et al., 2007; Rao et al., 2012). These changes in TA are large enough that ecosystem calcification rates have historically been measured using the alkalinity anomaly technique (Chisholm and Gattuso, 1991; Gattuso et al., 1996), which relies on measuring the change in water column TA according to the following equation:

\[
CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}. \] (3)

Because \(CO_3^{2-}\) is equal to 2 TA equivalents, calcification rates are equal to half the change of TA concentrations.

TA measurements are widely used in ocean acidification research to quantify community calcification rates (Shamberger et al., 2011; Silverman et al., 2012), measure sediment precipitation and dissolution rates (Andersson et al., 2007; Cyronak et al., 2013), correct net ecosystem production calculations for inorganic carbon contributions (Frankignoule et al., 1996; Gattuso et al., 1996; Suzuki and Kawahata, 2003), and to measure reef dissolution and bioerosion (Lazar and Loya, 1991; Zundelevich et al., 2007; Manzello et al., 2008). Also, it has been suggested that alkalinity generated from sediment dissolution may act as a partial buffer against any decrease in pH associated with ocean acidification, (Kleypas and Langdon, 2006; Morse et al., 2006), although this buffering capacity is still being debated (see Andersson and Mackenzie, 2012). The importance of TA in ocean acidification research makes it important to constrain all sources and sinks of TA within coral reef ecosystems.

The exchange of solutes between the water column and permeable carbonate sediments is driven mainly by advective processes (Precht and Huettel, 2003; Santos et al., 2012). Flow- and topography-induced porewater exchange (see Fig. 1 in Santos et al., 2012) is probably the dominant process driving porewater exchange within coral reef lagoons due to the formation of ripples and crests within permeable carbonate sediments (Precht and Huettel, 2003). This process acts on short temporal (minutes to hours) and small spatial scales (cm) to induce the exchange of porewater solutes with the overlying water column (Precht and Huettel, 2003). Porewater advection has a stimulatory effect on biological processes occurring within the sediments (Cook and Rey, 2006; Eyre et al., 2008; Glud et al., 2008) and has also been shown to have a stimulatory effect on TA fluxes, with increasing advection rates increasing net daily TA fluxes (Rao et al., 2012; Cyronak et al., 2013). However, while coral reef community calcification rates are negatively correlated with the aragonite saturation state (\(\Omega_{AIP}\)) of the water column (see Fig. 6 in Shamberger et al., 2011), carbon cycling in permeable sediments cannot be easily predicted by the \(\Omega_{AIP}\) of the overlying water (Cyronak et al., 2013).

Submarine groundwater discharge (SGD) has been shown to be an important component of freshwater delivery to coastal ecosystems, on the scale of 6% to 10% of surface water flow, which amounts to an estimated 10,000 L m\(^{-1}\) d\(^{-1}\) along the global coast (Burnett et al., 2003; Santos et al., 2012). The few studies assessing SGD rates on coral reefs describe a range from 52 to 4732 L m\(^{-1}\) h\(^{-1}\), and suggest that SGD can be an important source of solutes to coastal reef ecosystems (Lewis, 1987; D’Elia and Wiebe, 1990; Paytan et al., 2006; Knee et al., 2010; Blanco et al., 2011). There are multiple methods to estimate SGD into coastal ecosystems including seepage meters, piezometers, natural tracers, water balance approaches, and theoretical modeling (Burnett et al., 2006). Due to its naturally high concentrations in groundwater compared to surface waters, and its unreactive nature, \(^{222}\)Rn has been used as a natural tracer for groundwater in aquatic systems for decades (Cable et al., 1996; Burnett et al., 2006). Mass balance models using \(^{222}\)Rn have been developed that estimate SGD fluxes into coastal ecosystems (Burnett and Dulaiova, 2003).

Groundwater concentrations of TA can be higher than oceanic waters and encompass a broad range from 90 to 23 300 µmol L\(^{-1}\) (Mahlknecht et al., 2004; Rad et al., 2007;
Moore et al., 2011; Schopka and Derry, 2012). Using radium-based SGD efflux rates, Moore et al. (2011) demonstrated that SGD is a source of alkalinity to the water column in the Wadden Sea. Therefore, groundwater exchange processes occurring on larger temporal and spatial scales than flow-induced advective exchange also have the potential to deliver TA to coral reef lagoons. In fact, Kleypas and Langdon (2006) postulated that ocean acidification may be buffered against in coral reef ecosystems through the exchange of groundwater. The ability of groundwater to act as a source of TA to coral reef lagoons is highly dependent on the exchange rates with the water column, which can have large temporal and spatial variation (Lewis, 1987; Burnett et al., 2003; Santos et al., 2012). Determining the sources and sinks of alkalinity to coral reef ecosystems from groundwater and porewater exchange mechanisms is important in constraining how increasing $pCO_2$ will impact seawater carbonate chemistry within coral reef ecosystems.

The hypothesis of this study is that two groundwater sources will contribute TA to Muri Lagoon, a fringing coral reef lagoon in the Cook Islands. To test this hypothesis, advective, benthic incubations were used to determine the influence of porewater advection on alkalinity fluxes from permeable sediments over short temporal and spatial scales (herein referred to as porewater fluxes). Measurements of $^{222}$Rn were also undertaken to determine the input of alkalinity from larger temporal and spatial scale groundwater exchange (herein referred to as SGD or groundwater). While “porewater” and “groundwater” are technically synonymous (i.e., any water in contact with geological materials), the hydrology and oceanography communities tend to refer to porewater as a shallow interstitial water and groundwater as deeper, fresher water (Burnett et al., 2003, 2006).

2 Materials and methods

2.1 Study site

Our study site was located on the island of Rarotonga, a South Pacific, volcanic island within the archipelago of the Cook Islands. Rarotonga is the largest island in the Cook Islands group (67 km$^2$) and made up of volcanic rocks that are comprised of 42 % to 53 % SiO$_2$ and 2 % to 14 % CaO (Waterhouse et al., 1986). Rarotonga has a rainy (November to April) and dry (May to October) season, with average annual rainfall of 1900 mm yr$^{-1}$ (Thompson, 1986). Muri Lagoon is a fringing, coral reef lagoon located along the southwestern coast of Rarotonga (Fig. 1). The study site was divided into two locations within Muri Lagoon: one where the chamber incubations were performed and the second where the water column monitoring station was set up (Fig. 1). The chamber sampling site was located further (~75 m) from shore to minimize any SGD impact and because of the large area of carbonate sediments free from macrophytes. The monitoring station consisted of multiple probes and a bilge pump connected to a cinder block roughly 10 m offshore from the low tide mark. The lagoon extended ~750 m offshore to the reef crest from our monitoring station (Fig. 1). Muri Lagoon has an average depth of about 1.4 m and covers an area of 1.75 km$^2$ (Holden, 1992). The flow in Muri Lagoon is dominated by wave setup and runs from the reef crest towards shore, and then northeast along the shore towards a channel that opens to the ocean (Holden, 1992). The tidal cycle in Muri Lagoon is semi-diurnal with an average range of 1 m. The tidal range during our sampling period was 0.4 m and was towards the end of a spring tide cycle.

Sediment in the lagoon has a hydraulic conductivity of $\sim$ 17.3 m$^{-1}$ d$^{-1}$, which equates to a permeability of approximately $1.91 \times 10^{-11}$ m$^2$. Sediment grain size was 5.8 % >2 mm, 16.5 % between 1–2 mm, 19.4 % between 500 µm–1 mm, 30.6 % between 250 µm–500 µm, 25.0 % between 125 µm–250 µm, 2.5 % between 63 µm–125 µm, and 0.2 % < 63 µm. Bulk carbonate sediments were composed of 0.5 % calcite, 0.7 % quartz, 26.3 % Mg calcite (15.5 % Mg content), and 71.9 % aragonite as determined by X-ray diffraction analysis. Visual inspection of the sediments revealed black coloration a few cm below the surface, which is typical of high sulfide concentrations.

2.2 Advective chamber sampling and porewater fluxes

Chambers identical to those described in Glud et al. (2008) and Eyre et al. (2008) were used to measure in situ benthic solute fluxes at three different advection rates. Three chambers were inserted 15 cm into the sediment and enclosed roughly 4 L of overlying seawater during the incubations. Advection was induced within the chambers based on the spinning rate, in rotations per minute (RPM), of the acrylic disk within each chamber (diffusive, 40 RPM, and 60 RPM). Three stirring rates were chosen in order to investigate any effect of advection on alkalinity flux rates, similar to studies done in other coral lagoons (Glud et al., 2008; Cyronak et al., 2013). In order to maintain a homogenous distribution of solutes within the diffusive chamber, it was operated with the disk slowly spinning clockwise for one rotation, then pausing and spinning counter clockwise for one rotation and repeating (Glud et al., 2008). Incubations were run concurrently with the water column sampling, starting at 07:00 LT on 17 March 2012 and lasting for 28.5 h. Samples of 150 mL were drawn by syringe with ambient seawater allowed to replace the sample volume. The sample volume removed represented a minor percentage of the volume within the chambers (< 4 %) and therefore was unlikely to greatly influence chamber solute concentrations. Flux rates from the chambers were calculated using the integral-based technique as described in Cyronak et al. (2013). Negative numbers represent a flux into the sediments, while positive numbers represent fluxes of solutes out of the sediments. In order to compare advective flux rates to $^{222}$Rn-derived SGD
flux rates, averages between the two advective stirring rates (40 and 60 RPM) were used (discussed in detail later).

2.3 Water column sampling

Discrete samples were taken every 2 h from the water column along with the monitoring of physico-chemical parameters every 5 min using a multi-probe. A Hydrolab DSSX (Hach Environmental) was deployed 0.2 m from the bottom and 10 m offshore of the low tide mark to monitor temperature (±0.5 °C), PAR (±5%), and salinity (±0.5%) every 5 min. Depth was measured using an In-Situ Inc. Aqua Troll 200. For the monitoring data, an average over 1 h (30 min before and after) was taken over half-hour intervals in order to smooth the data and better reveal any trends. Sampling of the water column started at 7:00 LT on 17 March 2012 and lasted for 28.5 h. Discrete water samples were taken using 150 mL plastic syringes and brought back to lab to measure salinity, DO, TA, δ13C DIC, and pH.

In order to measure 222Rn concentrations in the water column, a submersible bilge pump continuously pumped seawater to an onshore gas equilibration device (GED) at about 2 L min⁻¹. The GED equilibrates gas through a shower head exchanger similar to that described in Burnett et al. (2001). Air was recirculated through a closed loop from the GED into a RAD7 222Rn detector in order to monitor 222Rn concentrations every 30 min (Burnett et al., 2001). In order to generate a groundwater endmember for 222Rn-derived flux calculations, a bore was dug 10 m onshore of the high tide mark and piezometers were inserted to depths of 1 m and 2.5 m. Discrete samples were taken from the 1 m piezometer at 3 separate times during the study, and one sample was taken from the 2.5 m piezometer. To measure the 222Rn endmember of groundwater, a peristaltic pump was used to pump water from the piezometers at 1 L min⁻¹ into the GED. The 222Rn concentrations were allowed to equilibrate and then measured for 1 to 4 h with the average concentration during that time used as the groundwater endmember. Gas permeable silicone tubing was only used in the pump head in order to minimize any losses of 222Rn. Laboratory experiments revealed no differences in concentrations when using a peristaltic pump and other pumps to feed the exchanger.

We used a non-steady-state 222Rn mass balance model from Burnett and Dulaiova (2003) to determine groundwater flux rates in cm³ m⁻² d⁻¹. The model incorporated sources of 222Rn from groundwater balanced by losses due to atmospheric evasion as a function of wind speed, mixing, and radioactive decay. The alkalinity of the mixed endmember (discussed in detail later) was multiplied by the flux rates generated by the model in order to get 222Rn-derived fluxes of groundwater TA into the lagoon. Both the advective TA fluxes and 222Rn-derived TA fluxes were calculated at the sampling locations and extrapolated along a 750 m transect to the reef crest (discussed in detail later).

2.4 Sample analysis

Both water column and benthic chamber samples were immediately brought back into the laboratory. Dissolved oxygen (±1%) was measured directly following collection using a Hach Luminescent Dissolved Oxygen (LDO®) probe. Samples for nutrients were filtered with a 0.45 µm cellulose acetate filter and frozen at −20 °C until analyzed following the methods of Eyre and Ferguson (2005) using a Lachat flow injection analysis (FIA) system. Samples for TA and pH were filtered through a 0.45 µm cellulose acetate filter and stored in an airtight container with no headspace until analysis within 4 h of sampling. pH (±0.003) was measured using a Metrohm Electrode Plus calibrated to Oakton National Bureau of Standards (NBS) standards of 4, 7, and 10. To determine TA, Gran titrations were performed using a Metrolm Titrando automatic titrator and pH electrode. Prestandardized 0.01 mol L⁻¹ HCl was used as the titrant, which was calibrated against Dickson certified reference material (Batch 111). Alkalinity samples were run twice, and the average of the two values was used. During the study the % CV of duplicate TA measurements was 0.15%.

Samples for δ13C DIC (analytical error of ±0.1 ‰) were 0.7 µm filtered with a Whatman GF/F syringe filter, preserved using 50 mL of saturated HgCl with no head space, and stored at 4 °C. δ13C DIC was measured in order to separate any sources of TA and DIC in the groundwater and water column. Samples were acidified with 5% (v/v) phosphoric acid, and the resulting CO₂ was analyzed via continuous flow wet-oxidation isotope ratio mass spectrometry (CF-WO-IRMS) using an Aurora 1030W total organic carbon (TOC) analyzer coupled to a Thermo Delta V Plus IRMS (Oakes et al., 2010). DIC concentrations and W_AT were estimated with the Excel macro CO₂ System (CO2SYS) (Pierrot et al., 2006) using inputs of TA and pH and the constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987) and W_AT. Data from Cyronak et al. (2013) showed excellent agreement between measured and calculated DIC concentrations using the same inputs into CO2SYS as this study. Carbonate alkalinity (TAₐ) for the chamber samples was calculated by subtracting the alkalinity, as determined in CO2SYS, contributed by B(OH)₄⁻, OH⁻ and total dissolved phosphorus (TDP) from TA.

3 Results

3.1 Advective chambers

The flux rates of TAₐ, DIC, DO, and H⁺ from the chambers are shown in Fig. 2. All of the rates follow a distinct diel pattern that is consistent with biological activity acting as the driver of solute fluxes from permeable sediments. Flux rates of TAₐ decreased throughout the day and began to increase in the late afternoon (Fig. 2a). TAₐ flux rates became
positive around sunset and increased until midnight, and then varied slightly for the rest of the night until becoming negative in the morning. DIC flux rates showed a similar pattern to $\text{TA}_C$ (Fig. 2b). DO and $\text{H}^+$ flux rates followed the opposite pattern of DIC and $\text{TA}_C$ fluxes (Fig. 2). DO fluxes increased throughout the morning then decreased in the late afternoon, becoming negative around sunset and levelling off during the night (Fig. 2c). $\text{H}^+$ fluxes showed the same trend as DO fluxes with slight variation in the night (Fig. 2d). Figure 3 shows the hourly flux rates of $\text{TA}_C$, DIC, and DO plotted against the average PAR values measured during the same time period as the flux. Flux rates are in mmol m$^{-2}$ h$^{-1}$.

### 3.2 Water column time series

The water column time series was conducted over two tidal cycles and one diel cycle (Fig. 4). Salinity fluctuated throughout the day, and the lowest salinities occurred during the low tides (Fig. 4a and b). DO concentrations and $\Omega_{\text{Ar}}$ followed a trend that was consistent with diel variation driven by biological processes, and throughout the course of the day $\Omega_{\text{Ar}}$ varied from 2.3 to 4.4 (Fig. 4e and f). In contrast, TA had a complex dynamics that was related to both diel and tidal cycles, supported by the variation in TA concentrations measured over one diel cycle and two tidal cycles (Fig. 4c). DIC concentration showed a similar trend to TA while the $\delta^{13}\text{C}$ of DIC followed the opposite trend, decreasing with any increase in [DIC] (Fig. 4d). During sampling, $^{222}\text{Rn}$ concentrations showed the opposite trend of the solutes, with concentrations in the deeper groundwater roughly 6 times higher than in the shallow groundwater. The pH of the shallow groundwater was lower than the deeper groundwater. We suspect that the discharging groundwater represents a mixture of these two and potentially other groundwater endmembers.

### 3.3 Groundwater endmembers

Groundwater measured from piezometers at 1 m and 2.5 m was fresh but differed in solute composition (Table 1). The water chemistry in the three samples taken from the 1 m well did not vary much between the different sampling times, so we reported the average (see Table 1). The DIC concentrations were about twice as high in the shallower groundwater than in the deeper groundwater while $\delta^{13}\text{C}$ DIC was more enriched in the deeper groundwater. TA was 7134 µmol L$^{-1}$ in the shallow groundwater and 3989 µmol L$^{-1}$ in the deeper groundwater. However, $^{222}\text{Rn}$ concentrations showed the opposite trend of the solutes, with concentrations in the deeper groundwater roughly 6 times higher than in the shallow groundwater. The pH of the shallow groundwater was lower than the deeper groundwater. We suspect that the discharging groundwater represents a mixture of these two and potentially other groundwater endmembers.

### 4 Discussion

#### 4.1 Diel cycling of TA in advective chambers

Hourly flux rates of $\text{TA}_C$, DIC, DO, and $\text{H}^+$ followed trends that were consistent with biological activity driving the fluxes of those solutes over a diel cycle (Fig. 2). During the day, flux rates of all solutes were greatest, whether negative or positive, in the afternoon at the 15:30 LT sampling point (Fig. 2). This is consistent with the availability of PAR driving rates...
of benthic photosynthesis. Photosynthesis would alter the chemistry of porewaters by taking up DIC and releasing DO into the porewaters, thereby affecting both flux rates of TA\(_C\) (by promoting carbonate precipitation) and H\(^+\), while respiration would have the opposite effect (Cook and Røy, 2006; Cyronak et al., 2013). Efflux rates of TA\(_C\) in the morning indicate that dissolution of carbonates is still occurring until the late morning when the sediments shift to TA\(_C\) uptake. During the nighttime, the flux rates of all solutes tended to level off after the transition between light and dark (Fig. 2). This is probably due to the shift in biological activity from production to respiration and the associated changes in porewater chemistry.

Maximum hourly TA\(_C\) uptake and efflux rates were similar between all three chambers (Table 2). When compared to flux rates obtained from identical chambers in Heron Island (Australia), fluxes from the Cook Islands were generally lower (Table 2). Also uptake rates were stimulated by advection in Heron Island, whereas TA\(_C\) uptake rates in the Cook Islands were similar between the stirring rates. The exact mechanisms behind these differences are unknown, but visual inspection of the two sediments revealed less biota (e.g., calcareous algae and fauna) in the Cook Island sediments. Lower amounts of benthic fauna would decrease any biologically driven stimulatory effect of advection on benthic fluxes (Cook and Røy, 2006; Cyronak et al., 2013). In addition, the black reducing layer apparent in the Cook Island sediments was not present in Heron Island. As advection delivers oxygen to this layer, it may lower the TA concentrations in the porewaters due to sulfide oxidation (Ku et al., 1999). This is consistent with reduced benthic fluxes in the

<table>
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<th>Location</th>
<th>Chamber</th>
<th>TA(_C) Efflux (mmol m(^{-2}) h(^{-1}))</th>
<th>TA(_C) Uptake (mmol m(^{-2}) h(^{-1}))</th>
<th>Daily TA(_C) Flux (mmol m(^{-2}) d(^{-1}))</th>
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<td>3.17</td>
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<tr>
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<td>Cyronak et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>80 RPM</td>
<td>5.61</td>
<td>-7.36</td>
<td>8.78</td>
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</tbody>
</table>

Grain size of the sediment was generally smaller in the Cook Islands, with the highest percentage between 250–500 µm compared to Heron Island, which was mostly in the 1–2 mm range. Even though permeability was similar (Glud et al., 2008), differences in grain size may affect the flow of water through the sediments and subsequent TA fluxes. Daily fluxes of TA from the sediments ranged from -1.55 to 7.76 mmol m\(^{-2}\) d\(^{-1}\), with the highest rates in the 40 RPM chamber (Table 2). Although hourly rates between the three chambers were similar (Fig. 2), integrated daily rates in the 40 RPM chamber were higher than both the diffusive and 60 RPM chambers. Daily Cook Island TA\(_C\) fluxes were lower than flux rates measured in Heron Island, although the daily TA\(_C\) flux rates from the 40 RPM chambers were similar in magnitude.

The hysteretic pattern of solute fluxes in the advective chambers is indicative of processes in the sediments being influenced by the previous state of the system (Fig. 3). Lower fluxes in the morning than in the afternoon for TA\(_C\), DIC, and DO may be due to the decrease in DO and \(\Omega_{Ar}\) overnight and subsequent change in the system as photosynthesis increases DO in the porewaters (Cyronak et al., 2013). Similar patterns in coral photosynthesis and calcification have been shown over a diel cycle (Levy et al., 2004; Schneider et al., 2009). Levy et al. (2004) attributed the lower photosynthesis rates in the morning to a breakdown of photosynthetic machinery at night and subsequent buildup during the day, while the hysteresis in calcification rates was attributed to changes in respiration rates of corals at specific times during
a diel cycle (Schneider et al., 2009). Similar processes may be occurring in the microbiota living in the sediments, which would contribute to the observed hysteresis. Also, because DO is consumed through sulfide oxidation (Ku et al., 1999), high sulfide production and the subsequent buildup in the porewaters overnight might also lead to the observed hysteresis in flux rates. If sulfide concentrations built up overnight, DO produced in the morning would be consumed in the sediments, potentially leading to the lower oxygen efflux rates observed in the morning than the afternoon (Fig. 3).

The slope of DIC vs. TA\textsubscript{C} can be used to determine the amount of DIC that was produced due to organic or inorganic processes (Gattuso et al., 1996; Andersson and Gledhill, 2013). DIC and TA\textsubscript{C} fluxes in the chambers were tightly correlated with an \textit{R\textsuperscript{2}} of 0.970 (Fig. 6a). The organic to inorganic ratio of the DIC flux was 2.13 as calculated from the slope in Fig. 6a. This value is lower than those reported from water column measurements but typical of sediments, possibly due to sediment porewaters being in close contact to a non-organic source (i.e., carbonates) of DIC (Gattuso et al., 1996; Cyronak et al., 2013). TA\textsubscript{C} flux rates were well correlated with DO and DIC fluxes in the sediments (Fig. 6b and c), indicating that photosynthesis and respiration drive carbonate precipitation and dissolution. However, TA\textsubscript{C} flux rates were not as well correlated with DO fluxes (Fig. 6b) as DIC fluxes corrected for the contribution of TA due to carbonate precipitation and dissolution (Fig. 6c). This may be related to oxygen consumption by sulfides in the sediments (Ku et al., 1999). Additional investigations on the role sulfides play in alkalinity cycling in coral reef sediments are warranted.

### 4.2 Estimating a mixed groundwater endmember

When plotted against salinity, DIC concentrations in the water column showed a significant linear correlation consistent with conservative mixing between groundwater and the water column (Fig. 7). A Keeling plot, or the linear regression of \(\delta^{13}\text{C}\) DIC versus 1/[DIC], can be used to estimate the \(\delta^{13}\text{C}\) of DIC added to the system by calculating the y-intercept (Fig. 8) (Mortazavi and Chanton, 2004; Köhler et al., 2006; Hu and Burdige, 2007). The contribution of both groundwater endmembers (shallow and deep) to the water column can be estimated by using the \(\delta^{13}\text{C}\) of added DIC generated from the Keeling plot as the \(\delta^{13}\text{C}\) of the mixed endmember. The estimated contribution of the shallow and deep endmembers to the water column was 47\% and 53\%, respectively (Table 1). The concentrations of DIC, TA, \(^{222}\text{Rn}\), and pH calculated using the above percentages were used as the endmember in subsequent mixing models, which matched well to the measured groundwater values in the bores (Table 1). We recognize that since \(^{222}\text{Rn}\) concentrations were variable with depth, the groundwater endmembers could be variable over larger spatial scales (Dulaiova et al., 2008; Santos et al., 2009). A larger number of groundwater samples could be important to decrease any potential uncertainties with the groundwater endmember and better elucidate fluxes over larger spatial scales.

A two-source mixing model can be used to estimate the water column concentrations of TA based on \(^{222}\text{Rn}\) concentrations measured during the sampling period. \(^{222}\text{Rn}\) concentrations from the water column were divided by the mixed
endmember concentration (47% EM1 : 53% EM2), and a percent groundwater input was then multiplied by the endmember of TA (Table 1). When a range of endmembers was used for water column TA concentrations (2100 to 2400 µmol L$^{-1}$), which would change over the course of a day due to biological and geochemical activities (Gattuso et al., 1996; Shamberger et al., 2011), the measured concentration of TA fit within the model (Fig. 9a). A variable endmember model was also calculated based on the change in lagoonal TA concentrations over the course of a day estimated from Fig. 10. During the day, $^{222}$Rn versus TA showed a different linear slope than during the night, which is consistent with carbonate precipitation being dominant during the day and dissolution during the night (Fig. 10). The initial concentration of water column TA (i.e., in the morning) was estimated as the y-intercept from the night regression of TA vs. $^{222}$Rn (2327 mmol L$^{-1}$). Based on the difference between the y-intercepts for the night and day linear regressions (Fig. 10), an average rate of change for TA in the water column that excludes the effects of groundwater was estimated as $-20$ mmol m$^{-2}$ h$^{-1}$ during the day and $20$ mmol m$^{-2}$ h$^{-1}$ at night. When the variable endmember was applied to the water column portion of the $^{222}$Rn mixing model, there was good agreement between the predicted and measured water column TA concentrations (Fig. 9b). Observed variability between the measured and predicted water column TA is probably due to diel variability in TA fluxes that are not accounted for in this model.

Because $\delta^{13}$C of DIC is depleted in the groundwater ($-6\%e$ to $-10\%e$) when compared to oceanic water ($0\%e$ to $2\%e$) (Williams et al., 2011), and most of the TA in the groundwater is present as DIC, sources of TA to the groundwater can be inferred. The low $\delta^{13}$C values of DIC in the groundwater are indicative of an organic source of carbon, as carbonate minerals tend to have $\delta^{13}$C values from $0\%e$ to $2\%e$ (Weber and Woodhead, 1969; Eadie and Jeffrey, 1973; Ogrinc et al., 2003). Sulfate reduction is well known to increase TA concentrations (Wolf-Gladrow et al., 2007), and may account for a portion of the high TA concentrations in Rarotonga groundwater. The uncoupling of sulfate reduction from sulfide oxidation would generate carbonate alkalinity with a depleted $\delta^{13}$C value due to the organic C source, perhaps accounting for the depleted $\delta^{13}$C DIC values found in the groundwater (Ku et al., 1999).
4.3 $^{222}$Rn-derived TA groundwater fluxes

Advection rates of groundwater into the water column were estimated using a non-steady-state $^{222}$Rn mass balance model (Burnett and Dulaiova, 2003) and the concentration of $^{222}$Rn estimated in the groundwater endmember (179 202 dpm m$^{-3}$) (Table 1). Fluxes of groundwater ranged from 0 to 46 cm d$^{-1}$ and were highest during low tides. This is consistent with steep hydraulic gradients at low tide driving fresh groundwater flow into the lagoon (Chanton et al., 2003; Kuan et al., 2012). The groundwater flux rates can be converted to an hourly basis and multiplied by the groundwater endmember concentration of TA (5467 µmol L$^{-1}$) to estimate the fluxes of TA into the water column (Fig. 11). Fluxes ranged from 0 to 105 mmol m$^{-2}$ h$^{-1}$ during this study, with the highest fluxes observed during the lowest tides. The average daily $^{222}$Rn-derived TA flux measured during this study was 1080 mmol m$^{-2}$ d$^{-1}$ at the sampling site. These flux rates are most likely spatially variable throughout the lagoon, with the highest flux rates found close to shore where SGD is most influential.

The $^{222}$Rn-derived TA fluxes are high when compared to other TA sources and sinks in coral reef environments (Gatuesto et al., 1998; Shamberger et al., 2011). However, the hourly flux rates agree well with flux rates that are needed to explain the observed changes in water column TA concentrations. Flux rates needed to account for the observed increases in TA concentrations during the day were as high as 103 mmol m$^{-2}$ h$^{-1}$. These values are comparable to the SGD-derived TA fluxes calculated from the $^{222}$Rn mass balance and groundwater TA concentrations, which ranged from 0 to 105 mmol m$^{-2}$ h$^{-1}$ (Fig. 11). The fact that these two independent calculations, agree well lends support to hourly and daily $^{222}$Rn-derived SGD TA fluxes. Also, TA concentrations at our study site were elevated (up to 2608 µmol L$^{-1}$);
Fig. 10. TA vs. $^{222}$Rn concentrations in the water column: separate regressions were made for daytime and nighttime hours. The three daylight time points taken during the second sampling day were removed from the regressions.

Fig. 11. Hourly SGD-derived flux rates of TA into the water column plotted alongside depth over the course of the study.

Fig. 12. Hourly flux rates of TA from advective sediment incubations and SGD along a 750 m transect from the study site to reef crest. 100% cover was assumed for advective sediments, and SGD was estimated as mixing 50 m offshore.

There are a number of factors that would influence the flux of TA from SGD into coastal ecosystems, one of which is the concentration of TA in the groundwater. In general TA concentrations of groundwater exhibit a large range and are probably highly dependent on local geology, but can be up to 6 times as high as oceanic TA (Table 3). Also, the amount of TA fluxed into the lagoon is dependent on how far the groundwater mixes offshore and the location of point sources of SGD within the lagoon (Burnett et al., 2003; Burnett and Dulaiova, 2003; Schopka and Derry, 2012). Based on radium isotope ratios in Muri Lagoon, a conservative residence time of 6 days was estimated for water in the lagoon. This long residence time means TA derived from groundwater can accumulate in the lagoon, raising the water column $\Omega_{Ar}$ above oceanic levels and potentially buffer against ocean acidification. However, groundwater may also act as a source of CO$_2$, which would inhibit the buffering capacity of SGD-derived TA fluxes. Also, groundwater is a potential source of nutrients (Valiela et al., 1999; Burnett et al., 2003; Paytan et al., 2006), contaminants (Cohen et al., 1984; Bedient et al., 1994), and other solutes that could degrade reef health.

There are not many studies assessing the influence of SGD on alkalinity fluxes to the water column, and none in coral reef ecosystems. Moore et al. (2011) used radium isotopes to trace the fluxes of groundwater to the Wadden Sea, showing that SGD acts as an important source of TA, Mn, dissolved organic carbon (DOC), and silicate to the ocean. Other studies have measured the concentration of TA in groundwater, but do not discuss SGD fluxes of TA to open water ecosystems (see Table 3). There are multiple groundwater exchange processes besides terrestrial hydraulic gradients that could alter TA cycling in coral lagoons (Burnett et al., 2003; Santos et al., 2012). For instance, tidal pumping and saltwater intrusion occurring on a larger scale than advective process may alter microbial processes in the sediment, and subsequently the cycling of TA (Kuan et al., 2012; Santos et al., 2012). The impact of these processes on TA fluxes into coral reef lagoons merits further investigation. Also, any seasonal variability in rainfall may influence SGD flux rates over larger temporal and spatial scales.
Table 3. Concentrations of TA (µmol L⁻¹) measured in groundwater throughout the world. * Designates concentrations measured as HCO₃⁻.

<table>
<thead>
<tr>
<th>TA (µmol L⁻¹)</th>
<th>System type</th>
<th>Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2150–2949</td>
<td>Subtropical estuary</td>
<td>South Carolina, USA</td>
<td>Cai et al. (2003)</td>
</tr>
<tr>
<td>90–8920</td>
<td>Subtropical estuary</td>
<td>Kunsan, South Korea</td>
<td>Kim et al. (2004)</td>
</tr>
<tr>
<td>4020</td>
<td>Subtropical estuary</td>
<td>Southern China</td>
<td>Liu et al. (2012)</td>
</tr>
<tr>
<td>753–7026*</td>
<td>Inland mountains</td>
<td>Central Mexico</td>
<td>Mahlknecht et al. (2004)</td>
</tr>
<tr>
<td>2550–23 300</td>
<td>Tidal flat</td>
<td>Wadden Sea, Germany</td>
<td>Moore (2011)</td>
</tr>
<tr>
<td>95–2000*</td>
<td>Tropical island</td>
<td>Guadeloupe</td>
<td>Rad et al. (2007)</td>
</tr>
<tr>
<td>1400–13 000*</td>
<td>Tropical island</td>
<td>Martinique</td>
<td>Rad et al. (2007)</td>
</tr>
<tr>
<td>800–4016*</td>
<td>Tropical island</td>
<td>Réunion</td>
<td>Rad et al. (2007)</td>
</tr>
<tr>
<td>2290*</td>
<td>Coastal lagoon</td>
<td>Brazil</td>
<td>Santos et al. (2008)</td>
</tr>
<tr>
<td>1328–2162</td>
<td>Tropical island</td>
<td>Hawaiian Islands</td>
<td>Schopka and Derry (2012)</td>
</tr>
<tr>
<td>3989–7134</td>
<td>Tropical island</td>
<td>Cook Islands</td>
<td>This study</td>
</tr>
</tbody>
</table>

4.4 Upscaling porewater and groundwater fluxes

Because the flux rates of these benthic processes are variable temporally and spatially, any extrapolation needs to be taken with care. In order to compare the two sources of groundwater and their influence on TA concentrations in the lagoon, a 750 m × 41 m transect was projected from the sampling site to the reef crest (Fig. 1). The flow of water in the lagoon is generally from the reef crest towards shore; therefore, any changes in the water column chemistry would occur along this transect. Since chamber stirring rates did not show any major influence on hourly TA fluxes from the sediments, an average hourly flux rate from the two advective chambers (40 and 60 RPM) was used for this comparison. Since currents are the main driver of porewater advection, the different stirring rates would likely reflect any variability within the lagoon. SGD was conservatively assumed to occur within a horizontal seepage face of 50 m from the beach face, as suggested from resistivity transects.

The fluxes of TA associated with advective processes were both negative and positive while the groundwater fluxes were always positive (Fig. 12). Combined TA flux rates from both SGD and porewater advection along the 750 m transect were between 62.1 and 72.9 mmol m⁻² d⁻¹, which is above the TA uptake rates of coral lagoons (26 to 42 mmol m⁻² d⁻¹) as measured by Kinsey (1983). These flux rates are consistent with the elevated TA concentrations measured at the sampling site. On a daily basis, porewater advection fluxed from 2.1 to 4.7 mmol TA m⁻² d⁻¹ into the lagoon, while SGD fluxed 60 to 67 mmol TA m⁻² d⁻¹ along the 750 m transect. SGD contributed 7% to 97% of the combined groundwater fluxes over a diel cycle, with the percent contribution dependent on both the time of day and the tidal cycle (Fig. 12). Since groundwater seepage is correlated with tidal height (Chanton et al., 2003), larger tides would have more of an effect on groundwater flow, potentially fluxing more TA into the system during those tidal cycles. However, because advective processes follow a diel cycle and groundwater is driven by tidal cycles, longer term experiments may be needed to reveal which of the processes is more influential.

Previous studies have estimated coral reef community calcification rates that range from 31.2 to 292.8 mmol CaCO₃ m⁻² d⁻¹ (or –62.4 to –585.6 mmol TA m⁻² d⁻¹) (Shamberger et al., 2011). Using that range of community TA uptake rates along the 750 m transect reveals that porewater advection can add from 0.4 to 7.5% of the TA taken out of the water column by coral communities. SGD-derived TA fluxes can add from 10% to 107% of the TA taken up by coral communities. The community TA uptake rates of coral lagoons are generally low compared to other reef ecosystems (Kinsey, 1983), which means it is likely that groundwater processes contribute towards the higher end of that range in Muri Lagoon. This is consistent with the elevated TA concentrations at the study site. This previously unaccounted for source of TA is important in changing the carbonate chemistry within Muri Lagoon over tidal and diel cycles.

5 Conclusions

Alkalinity concentrations in Muri Lagoon followed a pattern that is indicative of both biological and tidal drivers influencing the dynamics of water column TA over a diel cycle (Fig. 4). Different groundwater exchange mechanisms, acting on varying temporal and spatial scales, can have different influences on water column alkalinity. Small-scale porewater advection acted as both a source and sink of TA over the course of a day, with net daily fluxes ranging from –1.55 to 7.76 mmol m⁻² d⁻¹ depending on advection rates. Based on the average of the 40 and 60 RPM chambers along the 750 m transect, porewater advection was a net source of TA to the lagoon (2.1 to 4.7 mmol m⁻² d⁻¹). SGD fluxes were driven by tidal processes and delivered 1080 mmol TA m⁻² d⁻¹ to the water column at the study site. The daily SGD-derived TA flux is high when compared to other sources and sinks of TA. However, it is site-specific and groundwater is likely discharged only a discrete distance from shore. Along the
750 m transect, SGD fluxed from 60 to 67 mmol TA m\(^{-2}\) d\(^{-1}\) to the water column. It is likely that similar advective exchanges of TA occur throughout different reef systems, while SGD is highly dependent on the specific geological, physical, and biological attributes of the land masses associated with coral reefs. It is important to constrain the variability of SGD-derived fluxes over larger temporal and spatial scales by measuring \(^{222}\)Rn concentrations across broad areas of coral reef environments. Assessing groundwater exchange processes occurring in coral reef ecosystems is necessary so that more detailed models predicting how ocean acidification will alter reef carbonate chemistry can be developed.

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2480 T. Cyronak et al.: Groundwater and porewater as major sources of alkalinity

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Permeable coral reef sediment dissolution driven by elevated pCO2 and pore water advection

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[1] Ocean acidification (OA) is expected to drive the transition of coral reef ecosystems from net calcium carbonate (CaCO3) precipitating to net dissolving within the next century. Although permeable sediments represent the largest reservoir of CaCO3 in coral reefs, the dissolution of shallow CaCO3 sands under future pCO2 levels has not been measured under natural conditions. In situ, advective chamber incubations under elevated pCO2 (~800 µatm) shifted the sediments from net precipitating to net dissolving. Pore water advection more than doubled dissolution rates (1.10 g CaCO3 m⁻² d⁻¹) when compared to diffusive conditions (0.42 g CaCO3 m⁻² d⁻¹). Sediment dissolution could reduce net ecosystem calcification rates of the Heron Island lagoon by 8% within the next century, which is equivalent to a 25% reduction in the global average calcification rate of coral lagoons. The dissolution of CaCO3 sediments needs to be taken into account in order to address how OA will impact the net accretion of coral reefs under future predicted increases in CO2. Citation: Cyronak, T., I. R. Santos, and B. D. Eyre (2013), Permeable coral reef sediment dissolution driven by elevated pCO2 and pore water advection, Geophys. Res. Lett., 40, doi:10.1002/grl.50948.

1. Introduction

[2] The atmospheric CO2 concentration is expected to stabilize between 660 and 790 µatm by the year 2100, an increase of ~400 µatm from the present day concentration [Pachauri and Reisinger, 2007]. This increase in CO2 is predicted to decrease oceanic pH by ~0.3 units by the end of the century, a phenomenon termed ocean acidification (OA) [Feely et al., 2004]. Multiple studies have demonstrated a reduction in the net ecosystem calcification (NEC) rates of coral reefs due to increasing oceanic pCO2 [Andersson et al., 2009; Shamberger et al., 2011]. However, most studies to date have not separated the effects of OA on calcium carbonate (CaCO3) dissolution and coral calcification, despite dissolution being potentially more sensitive to OA than calcification [Andersson et al., 2009].

[3] Calcium carbonate found within coral reefs exists in two main pools; reef framework and CaCO3 sediments. Sediments often exceed the areal coverage of living coral and framework by up to one order of magnitude [Gattuso et al., 1998]. While reef framework is the main site of CaCO3 production due to the presence of living coral and other calcifying organisms, sediments represent the accumulation of reef generated CaCO3 over thousands of years [Smith et al., 2009]. Pore water advection refers to the bulk exchange of sediment pore water with the overlying water column and is largely driven by tides, wave action, sediment topography, sediment permeability, and currents [Precht and Huettel, 2003]. In contrast, exchange by diffusion results from a concentration gradient between the water column and pore water. Advection can enhance biological and geochemical processes occurring within the pore waters and fluxes of solutes into the water column [Wild et al., 2004; Eyre et al., 2008; Cyronak et al., 2013a].

[4] To date, most studies have examined the dissolution kinetics of shallow CaCO3 sediments in the laboratory or under diffusive conditions [Tynan and Opdyke, 2011; Yamamoto et al., 2012], making it difficult to predict dissolution kinetics in the environment. The few field investigations done that incorporate advective conditions and diel cycles have demonstrated that advection influences benthic alkalinity fluxes (i.e., CaCO3 precipitation and dissolution) [Rao et al., 2012; Cyronak et al., 2013a; Cyronak et al., 2013b]. However, none of the studies manipulated pCO2 to simulate predicted future OA conditions. In order to understand how OA will impact the accumulation of CaCO3 in coral reefs, it is necessary to determine the rates at which CaCO3 sediments will dissolve in situ under pore water advection, diel cycles, and predicted increases in pCO2. Herein, we performed in situ diffusive and advective chamber incubations on Heron Island under current and increased pCO2 scenarios.

2. Methods

[5] Heron Island is a coral cay in the Great Barrier Reef surrounded by a large (26.4 km²) and shallow (1.7m) coral lagoon covered mostly (~75%–85%) by CaCO3 sands [Wild et al., 2004; Eyre et al., 2008]. The high permeability and porosity of the sands allow seawater to easily flow in and out of the sediments. It is estimated that ~15% of the Heron Island lagoon seawater volume is filtered through permeable sands every day [Wild et al., 2004]. Our incubations were conducted in an area dominated by CaCO3 sands free from macrophytes and macrofauna burrows. Sediments from this site are comprised mostly of aragonite (65%) and high Mg2+ calcite (32%) with a Mg2+ content of 15.2% [Cyronak et al., 2013a]. A total of 23, 24 h long incubations were conducted on three separate days (28 and 30 April 2013 and 2 May 2013). On each day, duplicate incubations for each treatment were run, with one advective high pCO2 incubation lost on 28 April 2013. The incubations on 28 April 2013 started at sunset (~18:00), while the other two incubations started at sunrise...
Benthic chambers as detailed in Eyre et al. [2008] were used to measure benthic fluxes under diffusive and advective conditions (see supporting information Figure S1). The chambers were placed in the sediments without lids and left open to the overlying water for at least 1 h. Advective chambers were run at 80 RPM during the first incubation and 40 RPM thereafter. Previous studies have shown that these stirring rates induce pore water advection rates similar to those measured in situ at Heron Island [Wild et al., 2004; Glud et al., 2008]. The six replicates of each treatment were averaged for further analysis. Prior to the first sample being taken, chambers were closed to the overlying water and CO2 additions began. The pH of the chambers was raised by pressurizing a closed loop of silicone tubing (Tygone 3350, Cole-Palmer, Vernon Hills, IL, USA, 0.48 cm i.d.) at 2 bar with 99.9% pure CO2 gas (Figure S1). The pH was monitored until the desired offset (~0.2) was reached, and the chambers were allowed to equilibrate for 30 min before the first samples were taken.

Chambers were sampled (120 mL) every 12 h via syringe, and water was brought into the laboratory within 15 minutes for analysis. Dissolved oxygen (DO) (± 1%) was measured immediately in unfiltered samples using a Hach LDO probe (Hach Co., Loveland, CO, USA). Samples for pH (± 0.008) and total alkalinity (TA) (± 0.1%) were 0.45 μm filtered and kept in an airtight container with no bubbles until analysis within 4 h using a Metrohm Titrando automated titrator with a Metrohm Electrode Plus pH probe (Metrohm, Herisau, Switzerland). The pH probe was calibrated to pH NBS buffers (4, 7, 10), and TA was corrected against Dickson reference material (Batch 122). The pH was also monitored every 0.5 h in selected chambers using a SAMI2-pH (Sunburst Sensors, Missoula, MT, USA) unit, which measures pH in the total scale using metacresol purple as an indicator dye. The pH in the total scale is ~0.13 lower than the NBS scale; however, the exact magnitude is dependent on temperature, salinity, and individual pH electrode, therefore pH between the two scales is presented as measured. The pH and photosynthetically active radiation (PAR) were monitored in the water column every 15 min at the study site using a Hydrolab DS5X (Hach Co., Loveland, CO, USA). The pH from the Hydrolab was corrected to standards and seawater samples measured using the Metrohm electrode (Metrohm, Herisau, Switzerland) (NBS scale).

$\mathrm{pCO}_2$ and $\Omega_{\text{Ar}}$ were calculated using CO2SYS with pH, TA, and laboratory temperature measured during the TA titrations and a constant salinity of 35 as the input parameters. CO2SYS was set to the parameters as described in McMahon et al. [2013].

CaCO3 dissolution rates were calculated from TA fluxes assuming that half of the molar TA flux is equivalent to the molar CaCO3 flux. Other benthic fluxes that could contribute to TA fluxes within the chambers (i.e., nutrients) were shown to be minimal at the same study site, implying that TA fluxes represent CaCO3 precipitation and dissolution [Rao et al., 2012; Cyronak et al., 2013a]. The molar concentration of CaCO3 (100.1 g mol$^{-1}$) was used to convert fluxes to g m$^{-2}$. Student’s t tests were performed to compare means between treatments while linear regression analysis was performed on any regressions.

3. Results

During the incubation on 2 May 2013, all carbonate parameters (pH, TA, $p\mathrm{CO}_2$, and $\Omega_{\text{Ar}}$) varied over a diel cycle (Figure 1). The average $p\mathrm{CO}_2$ ($n=6$) of the control incubations was 418 ± 48 and 427 ± 20 μatm in the diffusive and advective chambers, respectively. The high $p\mathrm{CO}_2$
All error bars represent SE.

between low and high 

CaCO3 dissolution rates in the individual diffusive and advective 

treatments were net dissolving while the controls 

were net precipitating (p < 0.05, n = 6). Advection interacted 

with high pCO2 to stimulate the night, day, and net dissolution 

rates of CaCO3 sediments above diffusive rates by 12%, 26%, and 

150% (p < 0.05, n = 6), respectively (Figure 2a and Table S2). The net difference between control 

and high pCO2 conditions was 0.42 ± 0.22 g CaCO3 m⁻² d⁻¹ 

under diffusive conditions and 1.10 ± 0.22 g CaCO3 m⁻² d⁻¹ 

under advective conditions. This equates to a 162% increase 

in dissolution rates between diffusive and advective 

chambers. This is consistent with increased flow 

of low pH surface waters into the interstitial pore waters 

under advective conditions. A significant positive linear 

trend was observed between net dissolution rates and 

the average chamber pCO2 under advective conditions 
(r² = 0.660, p < 0.005, n = 11), while under diffusive conditions the regression was not significant (r² = 0.333, p = 0.05, n = 12) (Figure 2c).

4. Discussion

The goal of this study was to assess in situ CaCO3 

dissolution rates in permeable sediments over a natural 

diel cycle under OA conditions, and their influence on 
coral reef NEC rates. Previous observations in the Heron Island lagoon 
estimated an average community NEC rate of 6.15 g CaCO3 m⁻² d⁻¹ (2,246 g m⁻² yr⁻¹) 

[McMahon et al., 2013]. Using this estimate of NEC, 

CaCO3 sands currently contribute from 1.0% to 3.7% of 

community CaCO3 precipitation under diffusive and advective 

conditions, respectively. In the elevated pCO2 

treatments, CaCO3 sands dissolved at rates equivalent to 

5.9% of the daily NEC rate under diffusive conditions 

and 14.6% under advective conditions. The net differences 
between control and high pCO2 treatments equate to 6.8% 

and 17.9% of the NEC rate (Figure 2b). Because solute transport in permeable sands is often dominated by advective 

exchange [Santos et al., 2012] and sands make up at 

least 80% [Wild et al., 2004; Eyre et al., 2008] of the benthos of Heron Island lagoon, a 400 µatm increase in the
average $p$CO$_2$ could result in a reduction of current Heron Island NEC rates by $\sim$14%.

[13] The relationship between TA and dissolved inorganic carbon (DIC) offers insights into changes in the carbonate system [Andersson and Gledhill, 2013]. Under OA conditions, elevated $p$CO$_2$ increased DIC concentrations while TA remained constant (Figure 3). Advection in both the low and high $p$CO$_2$ treatments shifted the slope of the TA versus DIC relationship by $\sim$13% toward a more biological dominated system (i.e., more influence from photosynthesis/respiration than CaCO$_3$ precipitation/dissolution) (Figure 3 and Table S2). This increase in the influence of organic processes under advective flow is consistent with other permeable sand studies [Rao et al., 2012; Cyronak et al., 2013a]. More biological control on the carbonate system would result in a larger range of $\Omega_{Ar}$ values in the overlying water column over a diel cycle [Andersson and Gledhill, 2013]. This also indicates that more CO$_2$ per unit of TA would be fluxed out of the sediments under advective flow, partially inhibiting any buffering effect [see Andersson and Mackenzie, 2012] that sediment-derived TA may have in the water column. This is also supported by the lower net production rates measured in the high CO$_2$ and advective incubations, indicating less of a net uptake of CO$_2$ from the water column under future conditions (Figure 2a).

[14] Considering advection dominates solute exchange in coral reef permeable sands [Wild et al., 2004] and flushing rates in our advective chambers are comparable to in situ rates [Glud et al., 2008], we used the advective regression in order to model how the dissolution of CaCO$_3$ sands could affect community NEC rates as a function of average water column $p$CO$_2$. Assuming 80% coverage of CaCO$_3$ sands, an increase in average $p$CO$_2$ to 800 μatm in the overlying water (predicted by the year 2100) would result in an 8% decrease in the NEC rate of the Heron Island lagoon (Figure 4a). If our results are compared to the global average NEC rate of coral lagoons [Milliman, 1993] (800 g CaCO$_3$ m$^{-2}$ yr$^{-1}$), the dissolution of CaCO$_3$ sediments alone could reduce the annual NEC of coral lagoons 25% by 2100 (Figure 4a). Other models...
predict a 42% decrease in the CaCO₃ production of the global coastal ocean by 2100 due to reductions in calcification rates alone [Andersson et al., 2005; Andersson et al., 2006]. Therefore, increases in sediment dissolution could decrease CaCO₃ production an additional 25% above calcification-based model predictions. Also, the same models predicted an increase in CaCO₃ sediment dissolution of only 20% by the year 2100 [Andersson et al., 2005; Andersson et al., 2006], while our model indicates that the dissolution of shallow CaCO₃ sediments could increase 380% by the year 2100. Pore water advection at rates similar to those induced in our study have been calculated to occur at depths of up to ~50m and may occur deeper, depending on the physical characteristics of the sediments and surface gravity waves [Precht and Huettel, 2003]. Therefore, our results may be applicable to large areas of the coastal ocean and demonstrate the necessity of further elucidating other drivers of sediment dissolution in order to adequately predict changes to the global CaCO₃ budget under future CO₂ levels.

[15] Applying our model to the global estimate of coral NEC rates assumes that CaCO₃ dissolution will be similar across coral reef ecosystems. However, there are multiple variables that could affect the dissolution rates of CaCO₃ sediments. For instance, the % Mg content, structural disorder, presence of impurities, porosity of sediments, and biological activity can all influence dissolution [Morse et al., 2006; Cyronak et al., 2013a]. The exact influence of % Mg on dissolution rates of biogenic CaCO₃ has yet to be fully elucidated and has been further complicated by the recent discovery of dolomite producing coralline algae [Nash et al., 2013]. However, the mineralogical makeup of Heron Island sediments (15 mol% Mg₂⁺) puts it within the greatest frequency of occurrences for middepth bank CaCO₃ sands [Morse et al., 2006]. This implies that the dissolution rates measured in the Heron Island sediments may be a reasonable first-order estimate of future dissolution rates throughout different ecosystems with similar sediment mineralogy and pore water advection rates.

[16] Correlations between benthic NPP and average water column depth in Heron Island (r² = 0.77, p < 0.05, n = 26) [Eyre et al., 2013] offer insights into how net dissolution rates may vary with depth (Figure S4). Because NPP is significantly correlated to fluxes of alkalinity (CaCO₃ dissolution) (Figure S3), any reduction in NPP would also result in an increase in net daily CaCO₃ dissolution (Figure 4b). By the year 2100, sediment at an average depth of 3 m could undergo dissolution rates equal to the global average NEC rate of coral lagoons. If there is no photosynthesis in the sands, sediment dissolution rates approach the global average NEC rate under current CO₂ levels. This suggests that the average depth of coral lagoons is critical in determining how shallow water systems will respond to future pCO₂ levels. While our calculations illustrate the potential impact of depth on sediment dissolution in coral lagoons, additional studies may be needed to better understand permeable CaCO₃ sediment dissolution in deeper environments such as continental shelves.

[17] In summary, considering that up to 90% of CaCO₃ in coral reefs is contained within the sediments, measuring their dissolution rates in situ provides insights into how OA will affect the net accretion of coral reefs. Our results demonstrate that elevated pCO₂ (~400 µatm above current) and advection act in synergy to increase dissolution ~5 times above the current precipitation rates of shallow CaCO₃ sediments. Also, pore water advection may more than double any rates previously estimated under diffusive conditions. Other studies have estimated CaCO₃ sedimentation rates of ~0.5 kg m⁻² yr⁻¹ in sandy reef environments [Ryan et al., 2001; Harley and Fletcher, 2003]. Comparing this sedimentation rate to the dissolution rates measured in this study demonstrates that by the year 2100 dissolution of CaCO₃ sediments could reduce sedimentation rates by up to 80% of current values. Assuming our short term observations persist in the long term, this has drastic implications to the formation of valuable reef habitat, especially under rising sea levels.

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[19] The Editor thanks Merinda Nash and an anonymous reviewer for their assistance in evaluating this paper.

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Hysteresis between coral reef calcification and the seawater aragonite saturation state

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[1] Some predictions of how ocean acidification (OA) will affect coral reefs assume a linear functional relationship between the ambient seawater aragonite saturation state (Ωa) and net ecosystem calcification (NEC). We quantified NEC in a healthy coral reef lagoon in the Great Barrier Reef during different times of the day. Our observations revealed a diel hysteresis pattern in the NEC versus Ωa relationship, with peak NEC rates occurring before the Ωa peak and relatively steady nighttime NEC in spite of variable Ωa. Net ecosystem production had stronger correlations with NEC than light, temperature, nutrients, pH, and Ωa. The observed hysteresis may represent an overlooked challenge for predicting the effects of OA on coral reefs. If widespread, the hysteresis could prevent the use of a linear extrapolation to determine critical Ωa threshold levels required to shift coral reefs from a net calcifying to a net dissolving state. Citation: McMahon, A., I. R. Santos, T. Cyronak, and B. D. Eyre (2013), Hysteresis between coral reef calcification and the seawater aragonite saturation state, Geophys. Res. Lett., 40, doi:10.1002/grl.50802.

1. Introduction

[2] The global seawater pH is predicted to drop ~0.3 units by 2100, and the associated drop in aragonite saturation state (Ωa) is expected to result in lower coral calcification [Doney et al., 2009]. For example, a 14% reduction in calcification has been detected over a 40 year time period in a system on the Great Barrier Reef [Silverman et al., 2012]. A major implication of ocean acidification (OA) is that coral reefs may experience a transition from net CaCO3 production to net dissolution [Andersson and Gledhill, 2013]. An understanding of the chemical thresholds required to shift coral reefs to a net erosive state is fundamental for developing predictions of how OA will impact reef survival. The carbonate chemistry of coral reefs is highly dynamic, and multiple biogeochemical interactions within coral reefs may drive feedbacks to OA on a local scale [Shaw et al., 2012]. For example, primary production can shift Ωa over the short and long terms, potentially masking the local impacts of OA [Anthony et al., 2011].

[3] A number of mesocosm [Andersson et al., 2009; Langdon and Atkinson, 2005; Langdon et al., 2003] and field studies [Ohde and van Woesik, 1999; Shamberger et al., 2011; Shaw et al., 2012] have found decreasing net ecosystem calcification (NEC) rates in coral reefs as Ωa decreases. A recent review relied on theoretical considerations and hypothetical reactions to highlight that the Ωa versus NEC relationship may not represent a functional relationship [Andersson and Gledhill, 2013]. Here, we further develop this hypothesis by describing detailed NEC observations in a healthy coral reef lagoon during different times of the day.

2. Material and Methods

[4] This study was performed at Heron Island in the Great Barrier Reef, Australia (23°27′S, 151°55′E). The reef covers 26.2 km² and has an average depth of 1.7 m. The lagoon benthos is approximately 85% CaCO3 sand with scattered coral clusters [Santos et al., 2010, and references therein]. The lagoon is at a higher level than the open ocean during low tide periods. Tidal isolation is a convenient feature widespread in reef lagoons that allows for flux rates to be calculated during times when mixing with offshore waters is negligible. Here, samples were taken at a designated site 10 m off the beach at low tide in the lagoon adjacent to the Heron Island Research Station. All samples were taken approximately 1–2 h each side of the low tide. Three to five samples were collected per low tide (every 30–40 min) dependent on the length of the tide. We report the results of a total of 47 tides sampled in the autumn (April 2012).

[5] Water analysis was carried out within 20 min of sampling. Total alkalinity (TA) and pH were measured using a high-precision titration unit (Metrohm Titrando). TA was estimated by Gran Titration using 0.01 M prestandardized HCl and certified against Dickson’s reference material (Batch 111). Calibration of the pH probe (Metrohm Electrode Plus) was done using Oaktion National Bureau of Standards (buffers pH 4, 7, and 10). Alkalinity replicates were obtained for each sample and an average of replicates was used (<0.2%). A Hydrolab DSX5 data logger was used to monitor photosynthetically active radiation (PAR) (+5%), salinity (+0.5%), dissolved oxygen (DO) (+1%), and temperature (+0.5%) every 15 min. Samples for dissolved ammonium, nitrate, and nitrite (NO3−) and orthophosphate were filtered through a 0.45 μm cellulose acetate syringe filter before the sample was frozen for later analysis by a Lachat Flow Injection Analysis Unit (+5%) [Eyre and Ferguson, 2005]. Dissolved inorganic carbon (DIC) concentrations were estimated using the Excel macro CO2SYS [Lewis et al., 1998]
with temperature, pH, and TA inputs measured during the titrations and a constant salinity of 35 g kg⁻¹. Settings in CO2SYS were set to the NBS pH scale and the constants from Dickson and Millero [1987] as cited in Lewis et al. [1998].

Net ecosystem calcification (NEC) rates were determined by the alkalinity anomaly technique [Chisholm and Gattuso, 1991] using the average depth of the lagoon (1.7 m). This technique captures only net calcification or dissolution (NEC or Gnet) and does not separate the relative contribution of gross calcification and dissolution to each individual NEC rate. Net ecosystem production (NEP) was calculated from the change in DIC corrected for changes in alkalinity [Silverman et al., 2012]. Wind speed measurements were taken using a Davis Vantage Pro2 weather station. Calculations of fCO2 and Ωa were done with the CO2SYS program, using inputs of temperature, salinity, alkalinity, and pH (constants from Dickson and Millero [1987] and piston velocities from Wanninkhof [1992] as cited in Lewis et al. [1998]).

3. Results and Discussion

3.1. Diel Trends

There were clear diel trends in DO, pH, TA, and DIC, as expected for coral reefs (Figure 1). For example, DO increased from a minimum of 68% saturation just before sunrise to a maximum of 190% saturation towards late afternoon. Alkalinity increased during the night and was consumed during the day (range from 2185 to 2322 μmol L⁻¹). Metabolic rates (NEC and NEP) steadily increased from sunrise to a peak in the mid-afternoon (15:00), about 3 h after the peak in PAR (Figure 2). The 15:00 peak was followed by a sharp decline in both NEC and NEP. NEP was lowest just before sunset and was less variable at night than during the day. On a few occasions, net calcification was observed during the night, even at low Ωa and pH. Integrating the hourly rates over a full diel cycle yielded an overall NEC rate of 2.4 mmol CaCO₃ m⁻² h⁻¹. The overall NEC daytime rate was 8.5 mmol CaCO₃ m⁻² h⁻¹, and the nighttime rate was −3.7 mmol CaCO₃ m⁻² h⁻¹. NEP rates revealed a nighttime respiration rate of −27.4 mmol C m⁻² h⁻¹ and daytime production of 38.4 mmol C m⁻² h⁻¹. Overall, the system was net productive at a rate of 5.5 mmol C m⁻² h⁻¹, which was about threefold higher than NEC rates. The dynamic NEC and NEP rates demonstrate the need for intensive sampling during all times of the day to characterize coral reef metabolic rates.

3.2. The Ωa and NEC Relationship

At first glance, our observations revealed a significant positive linear relationship between Ωa and NEC in spite of some scatter (Figure 3 and Table 1). In most similar studies (Table 1), a linear relationship was used to predict the Ωa value required for corals to shift from a net calcifying to a net erosive state (i.e., Ωa for NEC = 0). Interestingly, mesocosm experiments found a lower threshold value for Ωa than in situ studies. Controlled experiments showed that the bulk of reef carbonates may dissolve at a Ωa of 3.5–3.8, while high Mg calcites dissolve at 3.0 to 3.2 [Yamamoto et al., 2012], though it is unclear how these Ωa thresholds relate to sediments subjected to metabolic dissolution and pore water flow [Cyronak et al., 2013]. In Heron Island, using a linear relationship leads to the interpretation that at Ωa = 2.64, the reef lagoon would shift from net calcifying to net dissolving. Calculations of Ωa at pCO2 levels predicted for the year 2100 (660–790 μatm) show that 100% of coral reefs will have a Ωa < 3.25 [Cao and Caldeira, 2008]. Therefore, it would be reasonable to expect that many reefs will shift to net dissolution by the end of this century.

However, we cannot make this prediction using this approach if the assumption that there is a linear functional relationship between NEC and Ωa is not valid. When grouping our data by night, morning, and afternoon time periods, the linear correlation becomes much less apparent and a diel hysteresis emerges in the Ωa versus NEC relationship (Figure 3). We suggest that this hysteresis may invalidate the application of a simple linear correlation to predict coral reef dissolution threshold levels using field data obtained...
over diel time scales. This is consistent with recent theoretical predictions demonstrating that a correlation between \( \Omega_a \) and NEC may not necessarily be interpreted as a functional relationship [Andersson and Gledhill, 2013]. It is also in line with the self-regulation hypothesis suggesting that corals can alter the carbonate chemistry within microenvironments and calcify at suboptimal seawater pH conditions [McCulloch et al., 2012]. We speculate that similar hysteresis patterns may be hidden in other coral reef NEC data sets. Several previous studies relied on a small number of samples (Table 1) or seasonal sampling (not necessarily at the same time of the day), perhaps preventing complex relationships from emerging.

[10] Some pioneering controlled mesocosm studies were based on weekly NEC which may remove the short-term effect of light availability and thus better isolate the influence of \( \Omega_a \) on NEC rates [Langdon et al., 2000, 2003; Marubini et al., 2001]. However, it is very difficult to perform such experiments in field conditions. As a result, recent field investigations attempting to replicate these earlier mesocosm observations are more likely to reflect a combination of multiple processes driving NEC rates. To better understand the influence of \( \Omega_a \) on NEC, it may be necessary to separate out the processes of calcification and dissolution which is not possible using our data set. Other studies have shown that dissolution may be more sensitive to OA [Andersson et al., 2009]. However, we observed stable net dissolution throughout the night despite a \( \Omega_a \) drop. Long-term, high-resolution NEC, calcification, and dissolution observations in reefs with contrasting \( pCO_2 \) levels may help to improve predictions of how OA will impact NEC.

3.3. Other Drivers of NEC

[11] Uncoupling the multiple drivers of NEC is difficult in field experiments. Coral calcification may be controlled by a complex combination of drivers that include light, nutrients, temperature, pH, and \( \Omega_a \). A linear relationship was apparent between light intensity and NEC in spite of the 2–3 h lag in the NEC peak relative to the PAR peak (Figure 4). Temperature and nitrate had weaker, but still significant, linear correlations with NEC. NEC had the strongest correlation with NEC indicating that NEC (not \( \Omega_a \)) may be the strongest control over NEC. The relationship between NEC and NEC may be associated with photosynthesis creating microenvironments at coral calcification sites that are conducive to calcification. It is interesting that nighttime NEC rates were relatively constant in spite of an overall decrease in \( \Omega_a \) during the night (Figure 1). This supports our suggestion that NEC is more closely related to NEC over a diel cycle than to the bulk \( \Omega_a \) of the overlying seawater, similar to results from sediment chamber incubations at Heron Island [Cyronak et al., 2013]. Therefore, the effect of OA on coral reef NEC rates could be masked by other processes that influence NEC (i.e., the input of nutrients, light, and temperature) [Shaw et al., 2012].

[12] Several studies have demonstrated that light exerts a strong control on NEC rates [Marubini et al., 2001]. The availability of PAR is potentially one of the main drivers of the observed hysteresis in the in situ NEC versus \( \Omega_a \) relationship from Heron Island. To remove any effects of PAR on the \( \Omega_a \) versus NEC relationship, we performed a linear regression using only the hours when PAR is saturating (10:00 to 14:00), similar to Langdon et al. [2003]. This approach revealed a significant linear trend (\( p < 0.05, \)

Figure 2. NEC and NEP rates during different times of the day. The small black dots represent rates estimated from two consecutive samples, while the large black squares represent rates estimated from the slope of all of the three to five samples taken at each low tide. The use of several samples from each low tide smoothed the data and revealed a peak in NEC and NEP at about 3:00 P.M.

Figure 3. Net ecosystem calcification (NEC) rates as a function of \( \Omega_a \). The grey circles represent NEC rates estimated from every two consecutive samples, while the colored triangles represent NEC rates estimated from three to five samples taken at each low tide. The red triangles (06:00–15:00), green triangles (15:00–18:00), and black triangles (18:00–06:00) represent groups of samples taken during different time intervals. A clockwise diel hysteresis pattern emerged from the observations, as indicated by arrows.
between Ωₐ and NEC, with a similar x intercept (Ωₐ = 2.62 at NEC = 0) to that calculated when using all of the data (Table 1). A previous study demonstrated a hysteretic pattern in coral photosynthesis, with higher production rates observed in the afternoon than during the morning though the corals received similar levels of PAR [Levy et al., 2004]. Therefore, any hysteresis in coral NEP could drive the observed hysteresis in NEC rates. Interestingly, net dissolution was relatively stable during the evening and nighttime periods even though Ωₐ decreased throughout the night due to respiration (Figure 3). At Heron Island, a DIC versus alkalinity plot (Figure 5) highlights that NEP is the major control on seawater Ωₐ. While a linear relationship can be observed between DIC and TA (R² = 0.73), a closer inspection of the plot reveals a hysteresis pattern over a diel cycle as also observed for the NEC versus Ωₐ plot. The current ratio of NEP to NEC in Heron Island is about 3. While NEC can account for changes in both the TA and DIC concentrations, net ecosystem production (NEP) only changes DIC concentrations [Langdon and Atkinson, 2005]. Therefore, Ωₐ is a function of the changes in carbonate chemistry due to both NEP and NEC, and any changes in DIC concentration relative to alkalinity will result in different influences on Ωₐ. For example, in systems with high organic production relative to calcification (i.e., high DIC to TA consumption), Ωₐ will increase due to a low uptake of TA and high uptake of CO₂. Conversely, in systems with low organic production relative to calcification, Ωₐ will decrease due to the uptake of TA [Andersson and Gledhill, 2013]. The reaction pathways shown in Figure 5 indicate that a decrease in calcification associated with an increase in organic production would increase Ωₐ and potentially change the way NEC responds to OA. Therefore, any prediction of NEC based on ambient seawater Ωₐ also needs to take into account the influence of NEP on both NEC and Ωₐ.

Table 1. Summary of NEC Versus Ωₐ Relationships in Different Coral Reef Communities Assuming a Linear Correlation to Predict Critical Ωₐ Values Required to Shift a Coral Reef from a Net Calcifying to a Net Dissolving System (i.e., NEC = 0)

<table>
<thead>
<tr>
<th>Location</th>
<th>Approach</th>
<th>Slope</th>
<th>Ωₐ for NEC = 0</th>
<th>p Value</th>
<th>n</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaneohe Bay</td>
<td>Mesocosm</td>
<td>187 ± 41</td>
<td>0.93 ± 0.61</td>
<td>0.0195</td>
<td>5</td>
<td>Langdon and Atkinson [2005]</td>
</tr>
<tr>
<td>Biosphere-2</td>
<td>Mesocosm</td>
<td>28 ± 3</td>
<td>1.50 ± 0.30</td>
<td>&lt;0.0001</td>
<td>12</td>
<td>Langdon et al. [2003]</td>
</tr>
<tr>
<td>Kaneohe Bay</td>
<td>Mesocosm</td>
<td>78 ± 14</td>
<td>1.57 ± 0.32</td>
<td>0.0002</td>
<td>14</td>
<td>Andersson et al. [2009]</td>
</tr>
<tr>
<td>Hawaii</td>
<td>Flow respirometry</td>
<td>210 ± 98</td>
<td>1.65 ± 0.92</td>
<td>0.0841</td>
<td>7</td>
<td>Shamberger et al. [2011]</td>
</tr>
<tr>
<td>Lady Elliot Island</td>
<td>Slack water</td>
<td>85 ± 17</td>
<td>1.78 ± 0.41</td>
<td>&lt;0.0001</td>
<td>56</td>
<td>Shaw et al. [2012]</td>
</tr>
<tr>
<td>Red Sea</td>
<td>Flow respirometry</td>
<td>80 ± 12</td>
<td>3.25 ± 0.24</td>
<td>&lt;0.0001</td>
<td>14</td>
<td>Silverman [2007]</td>
</tr>
<tr>
<td>Ryukyu Islands</td>
<td>Slack water</td>
<td>190 ± 63</td>
<td>4.72 ± 0.52</td>
<td>0.0357</td>
<td>5</td>
<td>Ohde and van Woesik [1999]</td>
</tr>
<tr>
<td>Heron Island</td>
<td>Slack water</td>
<td>240 ± 26</td>
<td>2.64 ± 0.21</td>
<td>&lt;0.0001</td>
<td>47</td>
<td>This study</td>
</tr>
</tbody>
</table>

*Our observations revealed that a linear correlation assumption may not be valid because of a hysteretic behavior (Figure 3).

![Figure 4](image1.png)

**Figure 4.** Correlations between NEC and some potential drivers. The open circles represent daytime observations, while the closed circles represent nighttime observations. The correlation coefficients for the daytime observations are also shown.
4. Summary and Conclusions

[14] The ambient seawater $\Omega_a$ versus NEC relationship in coral reefs may be more complex than a simple linear trend. The observed hysteresis pattern demonstrates that we should exert caution when using the $\Omega_a$ versus NEC relationship from short-term observations over natural variations in carbonate chemistry to predict tipping points in coral reef calcification. Our field observations thus support theoretical considerations that question the use of $\Omega_a$ to predict NEC using short-term experimental observations [Andersson and Gledhill, 2013]. We hypothesize that the observed $\Omega_a$ versus NEC relationship in Heron Island and elsewhere are not necessarily functional. In fact, these correlations may be a casual effect of the way organic metabolism (i.e., photosynthesis and respiration) drives both $\Omega_a$ and calcification.

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