UC San Diego

UC San Diego Electronic Theses and Dissertations

Title

Dissolution rates of biogenic carbonates in natural seawater at different pCO₂ conditions : :
A laboratory study

Permalink

<https://escholarship.org/uc/item/6n87h3pd>

Author

Pickett, Mallory

Publication Date

2014

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA, SAN DIEGO

Dissolution rates of biogenic carbonates in natural seawater at different $p\text{CO}_2$ conditions:
A laboratory study

A Thesis submitted in partial satisfaction of the requirements
for the degree Master of Science

in

Chemistry

by

Mallory Pickett

Committee in charge:

Andreas Andersson, Chair
Timothy Bertram
Stacey Brydges

2014

Copyright

Mallory Pickett, 2014

All rights reserved.

The Thesis of Mallory Pickett is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

The University of California, San Diego

2014

DEDICATION

I dedicate this thesis to my parents, Meghan and Toby Pickett, and to Oscar Beijbom. Thank you all for your love and support.

TABLE OF CONTENTS

Signature Page.....	iii
Dedication.....	iv
Table of Contents.....	v
List of Figures.....	vi
List of Tables.....	vii
Acknowledgements.....	viii
Abstract of the Thesis.....	ix
Introduction.....	1
Materials and Methods.....	5
Results.....	16
Discussion.....	19
Conclusion.....	30
References.....	42

LIST OF FIGURES

Figure 1 A schematic of the free-drift reactor used for all experiments.....	31
Figure 2 Results of control experiments.....	32
Figure 3 Weight-normalized dissolution rates.....	33
Figure 4 Surface area-normalized dissolution rates.....	34
Figure 5 Weight-normalized dissolution rates as a function of magnesium content.....	35
Figure 6 Surface area-normalized dissolution rates as a function of magnesium content	36
Figure 7 Results of previous work.....	37
Figure 8 Results of previous work extrapolated to relevant grain sizes.....	38

LIST OF TABLES

Table 1 The mineralogy and surface area of the substrates used in this study.....	39
Table 2 The average starting chemistry of the seawater used for all experiments.....	40
Table 3 Slope and fit data for the best-fit lines shown in Figure 3(a).....	41

ACKNOWLEDGEMENTS

I would like to acknowledge my adviser, Andreas Andersson, for his guidance, support, and patience. I would also like to thank all the members of the Andersson lab, who helped make this research possible in so many ways. Finally, I would like to acknowledge my committee members, Timothy Bertram and Stacey Brydges, for their helpful comments on this manuscript.

ABSTRACT OF THE THESIS

Dissolution rates of biogenic carbonates in natural seawater at different pCO₂ conditions:

A laboratory study

by

Mallory Pickett

Master of Science in Chemistry

University of California, San Diego, 2014

Andreas Andersson, Chair

The bulk dissolution rates of six biogenic carbonates (goose barnacle, benthic foraminifera, bryozoan, sea urchin, and two types of coralline algae) and a sample of mixed sediments from the Bermuda carbonate platform were measured in natural seawater at pCO₂ values ranging from approximately 3,000 to 5,500 μ atm. This range of pCO₂ values encompassed values regularly observed in pore waters at a depth of a few cm in carbonate sediments at shallow water depths (<15 m) on the Bermuda carbonate platform. The biogenic carbonates included calcites of varying Mg-content (2-17 mol%) and a range of specific surface areas (0.01-2.7 m² g⁻¹) as

determined by BET gas adsorption. Measured rates of dissolution increased with increasing pCO₂ treatment for all substrates and ranged from 2.5-18 μ mol g⁻¹ hr⁻¹. The highest rates of dissolution were observed for the bryozoans and the lowest rates for the goose barnacles. The relative ranking in dissolution rates between different substrates was consistent at all pCO₂ levels indicating that substrates dissolve sequentially and that some substrates will be more vulnerable than others to rising CO₂ and ocean acidification. Furthermore, dissolution rates were found to increase with increasing Mg-content, though the relative dissolution rates were observed to be a function of both Mg-content and microstructure (surface area).

Introduction

Ocean acidification (OA) is predicted to cause a decrease in calcification rates (Andersson et al., 2011; Chan and Connolly, 2013; Pandolfi et al., 2011; Riebesell et al., 2000), and an increase in dissolution rates (Silverman, 2007; Silverman, 2009; Andersson et al., 2011; Andersson and Gledhill, 2013) for most marine calcifying communities. Such changes could eventually force a transition from a state of net calcification to one of net dissolution for these communities including coral reefs (Andersson et al., 2005; Hoegh-Guldberg et al., 2007; Silverman et al. 2009). However, the rate and the extent to which carbonate dissolution in the natural environment will be affected by OA is currently not well understood, making it difficult to predict when and under what conditions such a transition to net dissolution could occur. A large body of work has been dedicated to studying the effects of OA on calcification rates of marine organisms and communities (e.g., Erez et al., 2011; Hofmann et al., 2010; Langdon and Atkinson, 2005; Müller et al., 2010; Riebesell et al., 2000), but the effect of OA on dissolution of carbonate substrates and sediments in natural systems has so far received less attention (Andersson and Gledhill, 2013; Eyre et al., 2014).

Despite the disproportional efforts devoted to calcification and CaCO_3 dissolution in the context of anthropogenic OA, a significant amount of research has been dedicated to carbonate dissolution in the context of early sediment diagenesis, open ocean and deep-sea CaCO_3 deposition, paleo reconstruction and past climate change (e.g. Archer and Maier-Reimer, 1994; Archer et al., 1989; Broecker, 1974; Friedman, 1964; Jahnke and Jahnke, 2004). In particular the solubility, rate, and mechanisms of calcite dissolution have been extensively studied (e.g. Arakaki and Mucci, 1995; Hales and Emerson, 1997;

Plummer and Wigley, 1976; Plummer et al., 1978; Rickard and Sjöberg, 1983; Sjöberg, 1976). Fewer studies have attempted to investigate similar properties for biogenic carbonates, and only a fraction of these studies have attempted to characterize these properties in natural seawater and under conditions typically observed in the natural environment (e.g., Keir, 1980; Walter and Morse, 1984, 1985; Yamamoto 2011). Many experiments with biogenic carbonate substrates have been done in pure water (Chou et al., 1989; Svensson and Dreybrodt, 1991; Cubillas et al., 2005), with samples that have not been ultrasonically cleaned to remove submicron particles (Keir 1980), with calcite powders or very small grain sizes (Busenberg and Plummer, 1986; Sjöberg, 1976) and/or at seawater pH levels and saturation states much lower than those commonly observed in the shallow marine environment (Walter and Morse, 1985; Cubillas et al., 2005). These results have provided valuable mechanistic understanding and information of carbonate dissolution under those particular conditions, but are difficult to directly extend to natural systems where factors such as inhomogeneous mineral phases, inhibitors, and adsorbed organic material are known to affect dissolution rates (Morse and Arvidson, 2001; Morse, 2007). Despite the many laboratory studies of carbonate dissolution, a significant disparity currently exists between laboratory measurements and field observations, and reconciling this disparity remains one of the great challenges in the study of biogenic carbonate dissolution (Morse and Arvidson, 2002; Morse, 2007). In light of ongoing anthropogenic OA, bridging this gap has become increasingly important in order to predict future consequences to carbonate substrates, sediments, structures, and the marine communities dependent on the production and accumulation of CaCO_3 . Thus, it is critical to understand what biogenic calcareous substrates are most vulnerable to OA

(solubility), how fast do these substrates dissolve under different CO₂ conditions (kinetics), and how do mineral characteristics such as mineralogy (Mg content) and microstructure (surface area) control these properties.

Calcite containing inclusions of Mg greater than 8-12 mol% are in general more soluble than aragonite and their low-Mg counterparts (Plummer and Mackenzie, 1974; Busenberg and Plummer, 1989; Bischoff et al., 1993), though the solubility of biogenic Mg-calcites in seawater is the subject of significant controversy, as there are two widely used solubility curves. At this time, it is not known which of these curves is the best representation of biogenic Mg-calcite solubility in the natural environment, but it has been hypothesized that dissolution of Mg-calcites will be a “first responder” to OA (Morse et al., 2006; Andersson et al., 2008). However, because of the uncertainty surrounding Mg-calcite solubility and the relatively few experiments measuring biogenic Mg-calcite dissolution rates, predictions of the effect of OA on these mineral phases are currently associated with substantial uncertainty (Morse et al., 2006). Furthermore, it has been shown that under certain conditions microstructure and surface area are more important than the thermodynamic mineral stability in controlling relative rates of dissolution (Walter and Morse 1985). Walter and Morse (1985) measured the dissolution rates of shallow water marine carbonates of varying mineral composition (<1-18 mol% Mg-calcite, Iceland Spar, synthetic calcite, and biogenic aragonites) and microstructure (BET specific surface areas of 0.03-24m² g⁻¹) using a pH-stat reactor (Morse, 1979). These authors found that in seawater undersaturated with respect to aragonite, aragonitic samples with high specific surface areas dissolved faster than thermodynamically less stable high Mg-calcites (16-18% Mg).

This study builds on the results of Walter and Morse (1985), but CO₂ rather than HCl was used to manipulate the pH, and the dissolution experiments were conducted at higher seawater pH levels and larger grain sizes, to reflect the conditions observed in the Bermuda sediment. The goal of the present study was to determine empirical bulk reaction rates for a variety of shallow-water biogenic carbonate samples in natural seawater under environmental and chemical conditions commonly observed in sediments and pore waters on the Bermuda carbonate platform (i.e., pCO₂ 3,000-5,000 µatm and grain sizes 850-1,000 µm; Andersson et al., in prep.). We do not attempt to address mechanistic questions, but instead offer empirical dissolution rates of biogenic carbonates under close to natural conditions and evaluate the correlations between mineral composition, microstructure (surface area), and dissolution rates in seawater. The organisms studied here represent a range of mineral compositions (2-17 mol% Mg-calcite) and microstructures (BET surface areas 0.01-2.7 m² g⁻¹). The empirical rates presented provide valuable insight into the dissolution of these organisms and sediments in seawater under elevated pCO₂, and can help inform predictions of how these substrates will be affected by OA.

Materials and Methods

The Bermuda carbonate platform

The Bermuda sediment is composed almost entirely of carbonate minerals from marine calcifying organisms, and $p\text{CO}_2$ levels in the porewater are much higher (up to $7,500 \mu\text{atm}$) than is typically observed in surface seawater because organic matter settles and is remineralized in the sediment (Andersson et al., 2007). These conditions make the Bermuda sediment a suitable “natural laboratory” to study the dissolution of carbonate minerals under elevated $p\text{CO}_2$ (Andersson et al., 2007), and by creating similar conditions in the laboratory, the results of this study can be related to both the current natural environment and predicted future conditions. The $p\text{CO}_2$ levels employed in this study were based on samples collected monthly from porewater wells in Bermuda at five different sites over a one year period (Andersson et al., in prep). The porewater pH_{NBS} over this period ranged from 7.3-7.7, and the DIC varied between 3,000 and 5,000 $\mu\text{mol kg}^{-1}$ corresponding to $p\text{CO}_2$ values between $\sim 1,820$ and $7,500 \mu\text{atm}$. The $p\text{CO}_2$ values used in this study were intermediate of these values, at $\sim 3,000$ - $5,500 \mu\text{atm}$. The grain size used for these experiments was chosen to represent some of the most dominant grain sizes in the Bermuda sediment, based on sediment cores taken from the same five sites as the porewater wells. The coarse sand fraction (500-1,000 μm) dominated at all five sites, but because a 500 μm size range is broad enough that there could be significant differences in dissolution rates of grains between these sizes, the smaller fraction of 850-1,000 μm was used in these experiments.

Reactor design

The reactor constructed for these experiments is shown in Fig.1. The reactor cells consisted of two 250mL jacketed Pyrex[®] beakers. The cells were temperature-controlled to $\pm 0.1^{\circ}\text{C}$ using an Isotemp[®] circulating water bath. Sierra Smartrak[®] S50 mass flow controllers were used to control the flow of nitrogen and carbon dioxide (± 0.01 slpm and ± 0.01 sccm, respectively). The nitrogen flow rate was maintained at 2.00 slpm, and the CO₂ flow rate was varied from 9.00-14.00 sccm to control the experimental seawater pCO₂. The CO₂ and N₂ were delivered from the mass flow controllers to a T-connection in the gas lines to be mixed, and then flowed into a gas humidifying chamber consisting of a 1L Pyrex[®] Erlenmeyer flask filled with approximately 100mL of seawater. The humidified gas was then split and delivered to both reactors through borosilicate glass Pasteur pipets. Fritted glass gas dispersion tubes were avoided as they can trap calcite within their frits even after thorough cleaning, contributing to the “memory” of the system (Morse 1974).

The pH and temperature were monitored using Metrohm Ecotrode Plus[®] electrodes in combination with the Orion Versastar[®] meter and automatic temperature compensation (ATC) probes. The pH measurements were recorded with a precision of ± 0.001 pH units (± 0.01 mV) (see Procedures for calibration details) and temperature was recorded to $\pm 0.1^{\circ}\text{C}$. The Orion meter was connected to a laptop computer, and temperature and pH data were recorded automatically using HyperTerminal[®].

The cells were fitted with identical custom-made rubber lids, with ports for the temperature, stirring, and pH probes, as well as an additional port for the gas pipette and an air vent. The lids were composed of two pieces stacked on top of one another, held together by screws with an O-ring in between. The screws could be tightened or loosened

to expand or contract the O-ring and adjust the lid's seal. The solution was stirred using Orion stir probes with propellers.

Materials used and their preparation:

Seawater

For each experiment, approximately 1L of natural seawater from the flow-through system at Scripps Institution of Oceanography (salinity ~33) was filtered using a vacuum filtration system and 0.47 μ m Millipore HVLP filters. The filtered seawater was exposed to UV light using a low-pressure mercury lamp (dominant wavelength 254nm, intensity: 6mW/cm² surface area: 15cm²) for two hours. After UV exposure the water was allowed to cool, and its salinity was measured using an YSI Pro-Plus meter equipped with a Quatro (ISE-DO-Cond-T) cable ($\pm$ 0.1 psu) and stored in a 1L Pyrex glass screw-top bottle. Each bottle provided enough seawater for one complete set of dissolution experiments at one pCO₂ level: 245 grams of seawater for each reactor cell, 100g of seawater for the gas humidifier, and 245g of seawater for the pre-dissolution gas equilibration tests conducted to characterize the seawater chemistry before dissolution.

One seawater sample was taken per batch of UV-treated seawater and analyzed for nitrate (NO₃⁻¹), nitrite (NO₂⁻¹), phosphate (PO₄³⁻), total reactive Si (Si, represents HSiO₄⁺ plus), and, when possible, ammonium (NH₄⁺).

Mineral samples

All biogenic samples used in this experiment were collected in Bermuda. Upon collection, the samples were soaked in bleach for twelve hours and then rinsed in deionized water and dried at 60°C for twelve hours. Iceland spar calcite obtained from

Fisher-Scientific was also used to provide a reference rate for a homogenous and well-characterized calcareous substrate.

Prior to dissolution, the mineral samples were crushed and ground with methanol in a glass mortar and pestle (excluding the mixed sediment, which was not ground prior to sieving). Grinding is known to strain the crystal structure (Chave and Schmalz, 1966; Walter and Morse, 1985), increasing surface dislocations and thus increasing the surface free energy of the crystal (Schott et al. 1989). Some experimenters (e.g. Walter and Morse 1984, 1985) have recommended that samples be annealed after grinding, to stabilize the crystal structure, but have observed that annealing the substrate reduces the observed dissolution rate by up to 80% (Walter and Morse, 1985). Thus, this step was not taken in these experiments. Instead, the samples were ground with methanol, which reduces the crystal strain of the grinding process. After grinding, the size fraction 850-1000 μm was selected by sieving using brass U.S. standard sieves (the mixed sediment was not ground prior to sieving). This grain size was chosen to represent the most dominant size fraction observed in the Bermuda sediment, as previously discussed. After grinding and sieving, the grains were ultrasonically cleaned in ethanol, decanting the ethanol solution and sonicating until the overlying ethanol remained clear after sonication. The sample was then oven-dried at 60°C for approximately 12 hours.

Analytical Procedures:

pH electrode calibration

Before a series of experiments, electrode slopes were calibrated using NBS buffers 4.00, 7.00, and 10.00. Before each experiment, the electrodes were calibrated to the seawater scale using tris buffer (pH 8.11 at 25°C, prepared in 0.04M HCl and

adjusted with NaCl to S=35) prepared by the Martz laboratory at SIO. The electrodes were reevaluated in the same tris buffer after each experiment to characterize the electrode drift, which was found to be less than ± 0.003 pH units, and considered negligible, in all experiments.

Solid sample characterization

The mineral composition of the samples were determined by x-ray diffraction (XRD), using the calculated offset of the calcite peak to determine the Mg-content using the data of Goldsmith et al. (1961). Calcium fluoride was used as an internal standard in all samples. This analysis was performed by the Crystallography Laboratory at UC San Diego using a Bruker Powder Diffractometer with a Cu radiation source. The scanning speed used for all samples was 0.1 degrees/min and the scan window used was 27-32 degrees. The reproducibility of the analysis was found to be ± 0.4 mol% Mg based on repeated analysis of the Iceland spar, and the accuracy of the calculations based on the Goldsmith et al. (1961) calibration curve are likely within ± 1 mol % (Nash et al., 2013).

The surface area of the experimental substrates were determined at 80°C using a 4-point Krypton gas adsorption and application of Bernard-Emmet-Teller (BET) theory. This analysis was performed by Particle Technology Labs in Chicago, IL, using a Quantachrome Autosorb 3B.

Control experiments:

A series of control experiments were conducted to evaluate the reproducibility of reactor conditions between experiments, and to ensure that the chemistry in the two cells was as close to identical as possible (Fig. 2a-c). These experiments consisted of equilibrating UV-treated seawater to a set CO₂ level and allowing the gas to bubble for

approximately the length of time of one dissolution experiment, and for a range of times from 0.5-8 hours to examine the effect of evaporation on the seawater chemistry over time. After equilibration, the seawater was collected and stored in 200ml Kimax[®] bottles, and dissolved inorganic carbon (DIC) and total alkalinity (TA) were analyzed for comparison to seawater from the same UV “batch” that had not been equilibrated. These experiments were repeated a total of 16 times, over several CO₂ levels ranging from the highest and lowest levels used in the dissolution experiments. The average Δ TA (TA reactor 1-TA reactor 2) after equilibration between the two reactor cells was found to be 1.93 ± 1.24 (n=8) (Fig. 2b), and the average Δ DIC was 2.83 ± 2.29 (n=8) (Fig. 2a). The precision of both the TA and DIC measurements were $\pm 1-3 \mu\text{mol kg}^{-1}$, so this level of precision between the two cells was considered satisfactory.

Evaporation corrections

The gas equilibration experiments procedures outlined above were extended to several experiments to quantify the rate of evaporation in the reactor cells. While every effort was made to minimize evaporation, the system was not sealed and closed to the atmosphere, so some evaporation was unavoidable. The average rate of increase in TA due to evaporation was found to equal $3.41 \pm 1.67 \mu\text{mol kg}^{-1} \text{ hr}^{-1}$ (n=32) (Fig. 2e). This amounts to an average increase in TA of $6.81 \pm 3.34 \mu\text{mol kg}^{-1}$ over the course of one two hour dissolution experiment, which was corrected for in the dissolution rate calculations (Eq. 1).

Dissolution Experiments:

Gas equilibration/starting conditions

For each experiment, 245 grams from the designated batch of UV-treated seawater were equilibrated to a target $p\text{CO}_2$ level, controlled by the flow rate of the CO_2 gas. During the equilibration, both electrodes and ATC probes were in the same cell and the pH measured by both electrodes was recorded. After forty minutes, the equilibrated seawater was collected by siphoning (see *Section 2.4.3 Sample collection*) and bottled in 200mL screw-top Kimax[®] bottles. This sample represented the seawater conditions before carbonate substrate dissolution was initiated. The DIC and TA of this sample were analyzed to characterize the complete carbonic system of the seawater before the mineral sample was added.

Dissolution

The remaining seawater from each UV-treated “batch” was used for the dissolution experiments. Approximately 245g of seawater was weighed exactly and quantitatively transferred to each cell. The rubber lid was fitted to the cell, and the electrodes, gas dispersion pipette, and ATC probes were positioned. The seawater was allowed to equilibrate to the given $p\text{CO}_2$ level for forty minutes, at which point the pH was stable within ± 0.002 . Once the seawater had equilibrated, equal amounts of carbonate substrate were added to each cell. In the majority of experiments, approximately 1.5 grams of substrate were added to each cell, resulting in a solid to solution ratio of 6×10^{-3} . However, due to limited amounts of the coralline algae and bryozoan substrates, solid to solution ratios of 2.3×10^{-3} and 3.4×10^{-3} were used in the coralline algae and bryozoan dissolution experiments, respectively. (Table 4). The substrate was introduced by pouring it through the air vent, which also served as a sample

introduction port. The pH and temperature of the solution as the calcite dissolved were continuously recorded for two hours.

Sample collection

After two hours of dissolution, the seawater and solid sample were recovered. The gas pipette and the stir probe were removed from the first cell before sample collection, and the mineral grains were allowed to settle to the bottom, which usually took about 5 seconds. A siphoning tube, consisting of 15cm plastic PPE tubing was inserted through the air vent/sample port, and filled once with seawater to rinse. The siphon was then used to transfer the seawater from the cell to a 200mL Kimax[®] screw-top bottle with a cone-lid and Teflon-taped threads. Extreme care was taken to stop the siphon before any of the grains on the bottom of the cell were siphoned into the bottle. This was repeated to collect the sample from the second cell.

Total alkalinity and dissolved inorganic carbon analysis

DIC was characterized using an AIRICA (Automated Infra Red Inorganic Carbon Analyzer; <http://www.marianda.com>) system equipped with a Li-Cor 7000. Replicate injections of 2 ml of sample were used to estimate the DIC relative to certified reference material (CRM) prepared by A. Dickson at Scripps Institution of Oceanography. CRMs were analyzed every 5-7 samples to ensure the accuracy and performance of the system. The typical precision of replicate CRMs was $\pm 2.65 \mu\text{mol kg}^{-1}$ (1s, n=4). TA was determined via potentiometric acid titrations of 90 g sample using an open titration-cell system developed by A. Dickson at Scripps Institution of Oceanography (Dickson *et al.*, 2007). The typical precision of replicate CRMs was $\pm 0.48 \mu\text{mol kg}^{-1}$ (1s, n=3).

Calculations and data treatment:

Seawater carbon chemistry calculations

The complete carbonic system was calculated using CO2SYS (Lewis and Wallace, 1998) based on constants defined by Mehrbach et al. (1973).

Rate calculations

For each experiment, the substrate was allowed to dissolve for two hours, at which point the pH was still increasing by a slow but constant rate. The rate was calculated from the total change in TA over the 2 hour dissolution period according to:

$$R = 0.5W_{SW} \left(\frac{\Delta TA - TA_e}{tW_c} \right) \quad (1)$$

where W_{SW} designates the weight of the seawater (kg), ΔTA represents the final-initial total alkalinity ($\mu\text{mol kg}^{-1}$), TA_e represents the correction for the increase in TA due to evaporation ($6.81 \mu\text{mol kg}^{-1}$), t is the length of the experiment (hr), and W_c is the weight of the carbonate substrate (g). The total value is multiplied by 0.5 because the dissolution of one mol of CaCO_3 results in a two mole increase in TA.

The results of these experiments represent average dissolution rates under certain average conditions for specific organisms. Because there is no reliable measurement of reactive surface area for biogenic carbonates (see Discussion Section 5.4), and dissolution rates are known to depend on both reactive surface area as well as mineralogy, no attempt was made to extrapolate the results of specific organisms to general rate laws for Mg-calcites of the same mol% Mg.

Experimental Uncertainties

The experimental error corresponding to the rate measurements was calculated according to the standard rules of error propagation, by first calculating the error in the numerator term of the rate (see Eq. 1) according to:

$$U_{RN} = 0.5 * \sqrt{[(U_{Wsw})^2 + (U_{TAi})^2 + (U_{TAf})^2 + (U_{TAE})^2 + (U_E)^2]} \quad (2)$$

where U_{RN} is the uncertainty in the numerator of the rate, U_{Wsw} is the precision in the measurement of the weight of the seawater ($\pm 0.0001\text{g}$), U_{TAi} , U_{TAf} , are the precision in the initial and final TA values ($\pm 3\mu\text{mol kg}^{-1}$), and a U_{TAE} is the precision in the TA values used to calculate the evaporation correction ($\pm 3\mu\text{mol kg}^{-1}$), and U_E is the variability ($\pm 3.4\mu\text{mol kg}^{-1}$ standard deviation, $n=32$) in the evaporation rate values averaged to obtain the evaporation correction used. Then the error in the rate numerator term was calculated according to :

$$U_{RD} = \sqrt{[(U_{Wc})^2 + (U_t)]} \quad (3)$$

where U_{Wc} represents the uncertainty in the measurements of the weight of the carbonate sample ($\pm 0.0001\text{g}$), and U_t is the uncertainty in the time measured ($\pm 1\text{min}$).

Then the uncertainty in the rate measured by each reactor was calculated according to

$$U_R = R * \frac{U_R}{R} = \sqrt{\left[\left(\frac{U_{RN}}{R_N}\right)^2 + \left(\frac{U_{RD}}{R_{DN}}\right)^2\right]} \quad (4)$$

where U_R is the uncertainty in the rate, R is the rate, R_n and R_D represent the rate numerator and denominator, respectively.

The rate for each experiment was calculated by averaging the rate obtained by each reactor, so the overall error was calculated according to

$$U_T = \sqrt{[(U_{R1})^2 + (U_{R2})^2]} \quad (5)$$

with U_T representing the total uncertainty. In all experiments, U_T was found to be significantly smaller than the variation in the rates determined by each reactor, which may be due to inhomogeneity in the biogenic samples. In all figures, the error bars in the rates represent the range of rates determined for each experiment

Results

Seawater chemistry: starting conditions

For the four treatment levels of each dissolution experiment, a “batch” of seawater was prepared consisting of 4 1L bottles of UV-treated and filtered seawater (See Methods *Section X*). Within each batch, the average variability of the measured salinity was ± 0.05 (Table 2). The average salinity of the seawater used in all experiments was 33.64 ± 0.07 . The average variability of the total alkalinity within each batch was $\pm 2.57 \mu\text{mol kg}^{-1}$, and the average pre-dissolution total alkalinity for all experiments was $2243.09 \pm 5.43 \mu\text{mol kg}^{-1}$ (Table 2).

The nutrient values for each batch of seawater and the average nutrient values are shown in Table 2. The concentrations of ammonium showed the highest variability, ranging from $0.74\text{--}2.76 \mu\text{mol kg}^{-1}$, and the concentrations of phosphate were the most constant, varying from $0.30\text{--}0.73 \mu\text{mol kg}^{-1}$.

Mg content and specific surface areas

The mol % Mg in each substrate as determined via X-ray diffraction, and the specific surface area determined using BET gas adsorption is shown in Table 1. The Mg-content of the Iceland spar was found to be 1.3 mol % with an uncertainty of 0.3 mol% based on repeated analyses. The Mg-content of the biogenic substrates ranged from 2.4 (*Pedunculata*) to 17.4 (*Porolithon*). The BET surface area of the Iceland spar was $0.01 \text{ m}^2 \text{ g}^{-1}$ and the BET surface areas of the biogenic substrates ranged from 0.15 (*Lytechinus variegatus*) to 2.70 (*Porolithon*).

Relative dissolution rates

The dissolution rates for Iceland Spar calcite ranged from 0.3-1.7 $\mu\text{mol g}^{-1} \text{hr}^{-1}$ whereas rates for biogenic substrates ranged from 2.5-18.7 $\mu\text{mol g}^{-1} \text{hr}^{-1}$, (Fig.3 a-c) at average seawater $[\text{CO}_3^{2-}]$ ranging from 23-47 $\mu\text{mol kg}^{-1}$, and average pH and pCO_2 values from 6.95-7.24 and 3,053-5,560 μatm , respectively. The dissolution rates of all substrates increased with decreasing average seawater $[\text{CO}_3^{2-}]$ and pH, and increasing average pCO_2 . For all of the substrates the relationships between dissolution rate and inorganic seawater carbon chemistry were linear, with correlation coefficients for the biogenic substrates (from a linear least-squares fit) ranging from 0.90-0.99 (Table 3). The observed dependences of the dissolution rates of each substrate on the $[\text{CO}_3^{2-}]$ varied from a minimum of 0.085 $\mu\text{mol g}^{-1} \text{hr}^{-1} / \mu\text{mol kg}^{-1} [\text{CO}_3^{2-}]$ for the Iceland Spar calcite to a maximum of 0.701 $\mu\text{mol g}^{-1} \text{hr}^{-1} / \mu\text{mol kg}^{-1} [\text{CO}_3^{2-}]$ for the coralline algae, based on the slope of the linear least squares fit (Fig. 3; Table 3). For the biogenic substrates, the dissolution rates of the coralline algae *Porolithon* showed the least dependence on the seawater chemistry (0.136 $\mu\text{mol g}^{-1} \text{hr}^{-1} / \mu\text{mol kg}^{-1} [\text{CO}_3^{2-}]$) based on the slope of the linear least squares fit to the rate versus $[\text{CO}_3^{2-}]$ data. The relative ranking of the measured dissolution rates of different substrates remained the same at each pCO_2 level, with the exception of some overlap between the bryozoan and *Porolithon* at the lowest pCO_2 /highest pH and $[\text{CO}_3^{2-}]$ (Fig. 3).

Specific surface area normalized dissolution rates

Normalizing observed dissolution rates to substrate specific surface areas as determined via BET gas adsorption with Krypton resulted in a large change to the relative magnitude of the dissolution rates and most of the dependences on the seawater chemistry, though the linearity of the relationship of the rates to $[\text{CO}_3^{2-}]$ remained

unchanged (Fig.4). The surface area-normalized rates for Iceland Spar calcite ranged from 33-165 $\mu\text{mol m}^{-2} \text{hr}^{-1}$ whereas the surface area-normalized rates for biogenic substrates ranged from 1-43 $\mu\text{mol m}^{-2} \text{hr}^{-1}$ at average $[\text{CO}_3^{2-}]$ ranging from 23-47 $\mu\text{mol kg}^{-1}$, and average pH and pCO_2 values from 6.95-7.24 and 3,053-5,560 μatm , respectively. Iceland Spar calcite had the highest surface area-normalized dissolution rates, and the highest dependence on the seawater inorganic carbon chemistry (8.52 $\mu\text{mol m}^{-2} \text{hr}^{-1} / \mu\text{mol kg}^{-1} [\text{CO}_3^{2-}]$). Among the biogenic substrates the urchin had the highest surface area-normalized rates, ranging from 24-43 $\mu\text{mol m}^{-2} \text{hr}^{-1}$, and the highest dependence on the seawater inorganic carbon chemistry (1.6 $\mu\text{mol m}^{-2} \text{hr}^{-1} / \mu\text{mol kg}^{-1} [\text{CO}_3^{2-}]$). The remainder of the biogenic substrates had surface area-normalized rates ranging from 1.3 (gooseneck barnacle) to 34 (benthic foraminifera) $\mu\text{mol m}^{-2} \text{hr}^{-1}$, and rate dependencies on the $[\text{CO}_3^{2-}]$ between 0.05 (coralline algae *Porolithon*) to 1.18 $\mu\text{mol m}^{-2} \text{hr}^{-1} / \mu\text{mol kg}^{-1} [\text{CO}_3^{2-}]$, (benthic foraminifera).

Discussion

Effect of decreasing $[\text{CO}_3^{2-}]$ and pH, and increasing $p\text{CO}_2$ on dissolution rates

Broadly, dissolution rates of all substrates in this study increased with decreasing $[\text{CO}_3^{2-}]$ and pH. However, the rate of dissolution and total amount of CaCO_3 dissolved for most of the biogenic substrates were large enough to partly influence the seawater chemistry in the reactor. The observed change in $[\text{CO}_3^{2-}]$ between start and end conditions ranged from 1-11 $\mu\text{mol kg}^{-1}$, with an average increase of 5 $\mu\text{mol kg}^{-1}$ for the biogenic substrates. This may cause a buffering effect, resulting in an under-estimation of the observed dissolution rates for the given $p\text{CO}_2$ conditions relative to a perfectly non-buffered system. This is particularly evident in the dissolution of *Porolithon*, which caused the greatest overall increase in seawater TA, and therefore the greatest changes to the seawater inorganic carbon chemistry. The resultant buffering effect is likely the reason that the dissolution rates of the coralline algae *Porolithon* had the lowest observed dependence on changes in seawater chemistry (Fig. 3).

The buffering effect observed in these experiments is likely highly relevant for carbonate dissolution occurring in closed systems or systems with restricted flow-through, such as in sediment pore waters. In laboratory and model simulations (Andersson, 2005; Morse et al., 2006) buffering in sediments has been shown to result in establishment of a metastable equilibrium with respect to the least stable Mg-calcite mineral phase present. This metastable equilibrium persists until this mineral phase has dissolved completely. As discussed in Section 5.5, this results in a sequential dissolution of Mg-calcites according to mineral stability. leading to sequential dissolution of Mg-calcites according to mineral stability (see *Section 5.5*).

However, the buffering effect of the change in seawater chemistry on the dissolution reaction means that quantification of the relationships between dissolution rate and $[\text{CO}_3^{2-}]/\text{pH}/\text{pCO}_2$ observed using this method includes significant error. Therefore, we have presented only the empirical dissolution rates obtained for specific conditions, rather than a rate law.

The increase in $[\text{CO}_3^{2-}]$ caused by dissolution of the substrate could also have enhanced the importance of surface reactions in the dissolution mechanism. All experiments took place in conditions of $\text{pH} > 7$ and $\text{pCO}_2 < 0.03$ atm, which Rickard and Sjöberg (1983) found to be a “mixed-kinetics” or “transition” region of dissolution for calcite in simple solutions, as in this region both transport (diffusion of H^+ ions to and away from the reacting solid) and surface reactions were rate-controlling. However, the reactions of CO_3^{2-} with H^+ that caused the observed buffering favor the dominance of surface reactions, because progressively less H^+ ions became available for reaction with the solid as the reaction proceeded.

Effect of solid to solution ratio

The dissolution of the bryozoan and coralline algae demonstrated significantly higher rates as well as rate dependence on seawater chemistry than the other substrates. However, this may be because lower solid to solution ratios were used in these experiments (38 and 57% lower for the bryozoan and coralline algae respectively, compared to the average of the other experiments, see *Section 2.4*).

This lower solid to solution ratio reduces the aforementioned buffering effect which could explain the higher observed dissolution rates of these organisms. Furthermore, the low solid to solution ratios may also explain the higher dependence of

the dissolution rates of these substrates on the solution chemistry because the smaller amount of substrate did not change the seawater chemistry to as great an extent as other substrates with roughly equivalent mineral composition and surface area (e.g. benthic foraminifera). This suggests that any buffering effect present in this system would be greatly reduced, resulting in a greater influence of the solution composition on dissolution rates.

Based on these results, the solid to solution ratio appears to have had a significant effect on the rates measured using this method; therefore it is not meaningful to compare the rates of different substrates obtained at different solid to solution ratios. For these reasons, the results obtained for the bryozoan and coralline algae are excluded from discussions of the effect of mineralogy and surface area on the relative dissolution rates of the substrates studied. The trends observed for the rest of the substrates with respect to mineralogy and surface area are consistent with observations of the coralline algae and the bryozoan.

Effect of mineralogy on dissolution rates

Dissolution rates at all $p\text{CO}_2$ levels increased with increasing Mg-content (Fig.5), except in the case of the mixed sediment, which contains up to 23% 15-mol% Mg-calcite, but is mostly (~ 70%) aragonite (Andersson et al. in prep). The dissolution rates of the mixed sediment were between those of the barnacle, composed of 2.4 mol% Mg, and the sea urchin, with an Mg-content of 12.5 mol%. This is consistent with the observation that the stability of aragonite is close to that of Mg-calcites with 8-12 mol% Mg.

These results support the hypothesis that Mg-calcites, because of their lower thermodynamic stability (relative to pure calcite) could act as “first responders” to OA,

dissolving more quickly than calcite under equivalent conditions. This idea has been subject to some controversy, mostly surrounding the solubility of biogenic Mg-calcites in seawater. There are essentially two experimental solubility curves for biogenic Mg-calcites, known as the “minimally prepared” (Plummer and Mackenzie 1974) and the “best-fit” (Bischoff et al., 1987; Walter and Morse, 1984) solubility curves. These terms refer to differences in the sample preparation, as for the “best-fit” solubility the samples were annealed and treated to remove organic matter before evaluating their stability, while the samples for the “minimally prepared” curve were not. The results of these two curves are highly dissimilar, as the “best-fit” curve shows that biogenic Mg-calcites between 16-20 mol% are only slightly more soluble than aragonite, while according to the “minimally prepared” curve Mg-calcites in this same composition range are approximately 500% more soluble than aragonite (Morse et al., 2006).

The empirical dissolution rates determined in this study avoid this uncertainty in biogenic Mg-calcite solubility by comparing absolute dissolution rates determined at specific conditions for both biogenic calcites and Mg-calcites of varying content. Using this measure, it appears that Mg-content does have a significant impact on the dissolution rates of biogenic carbonates.

Relationship of BET surface area to dissolution rates and BET surface area-normalized dissolution rates

The BET surface area-normalized dissolution rates increased as a function of specific surface area for most substrates (Fig.5), but it was not a linear relationship. This is consistent with the observations of Walter and Morse (1985) and Cubillas (2005) that the BET surface area appears to be a significant over-estimate of the reactive surface

area, and is not a reliable normalizing factor for dissolution rates (Fig.6). This stems from the fact that BET measurements quantify the specific surface area (total surface area per weight) which is not necessarily the same as the reactive surface area (total surface area available for reaction) for biogenic carbonates, which often have very complex microstructures. To accurately normalize dissolution rates to surface area, the reactive surface area must be known. At this point, there is no reliable method to measure this.

However, the specific surface area can still be useful as measure of the relative microstructural complexity of the biogenic substrates, and in this study the dissolution rates did increase as a function of the BET surface area. However there were a few notable exceptions to this trend, which suggests that at least in some cases thermodynamic stability, rather than microstructural complexity, was the deciding factor. The dissolution rates of the barnacle were significantly higher than those of the Iceland spar, despite the fact that its Mg-content was only slightly ($\sim 1\text{mol}\%$) higher. This could be attributed to the very large difference in surface area between the two, as the Iceland spar had a specific surface area of only $0.01\text{ m}^2\text{ g}^{-1}$ compared to that of the barnacle, which was over 100 times higher at $1.90\text{ m}^2\text{ g}^{-1}$. The barnacle had the second highest specific surface area measured, second only to that of the coralline algae *Porolithon* and over twice that of the other coralline algae, which had the next highest surface area. Despite this very high surface area, the barnacle had the lowest dissolution rates of all the biogenic substrates at all levels, likely because it was composed of almost pure calcite. Additionally, the mixed sediment, despite having an intermediate surface area compared to the other biogenic substrates ($0.50\text{ m}^2\text{ g}^{-1}$) had the next-lowest dissolution rates, after the barnacle. This may be because the sediment was mostly aragonite, which is more

stable than the >12 mol% Mg-calcite that the remaining biogenic substrates were composed of.

The BET normalized dissolution rates, shown in Fig.6, show the Iceland spar, which had the lowest surface area and lowest Mg-content, dissolving several times faster per surface area than the rest of the carbonates, which all have surface areas at least an order of magnitude larger. In fact, the ranking of the BET-normalized rates among the substrates at equivalent $[\text{CO}_3^{2-}]$ concentrations follows lowest>highest surface area almost exactly in all cases, and is not correlated with which substrates caused the highest total changes to total alkalinity, or with the mineral composition of the substrates. This indicates, in agreement with the conclusion of Keir (1980), Walter and Morse (1984), and Cubillas (2005), that BET measurements over-estimates the reactive surface area for biogenic carbonates, and are not a reliable normalizing factor for dissolution rates.

Comparison to previous laboratory experiments

Compared to the experiments of Walter and Morse (1985) using a pH-stat reactor and a variety of shallow-water biogenic calcites, Mg-calcites, and aragonites, the magnitude of the dissolution rates observed in this study is much lower. However, compared to the experiments of Keir (1980) in a flow-through reactor using artificial seawater and several benthic biogenic calcites, the observed rates are similar (Fig.7). These discrepancies may be because Walter and Morse (1985) used much smaller grain sizes (majority 37-125 μm , largest 300 μm in one experiment) than those employed in this study and most of the experiments of Keir (1980) (>62 μm -1cm).

Walter, Morse and Keir all observed that dissolution rates were highly dependent on grain size. Using the relationship between dissolution rate constant and substrate grain

size determined by Walter and Morse (1984b), the results of Walter and Morse (1985) and Keir (1980) were extrapolated to the median grain size (925 μm) and $[\text{CO}_3^{2-}]$ range (20-45 $\mu\text{moles kg}^{-1}$) used in this study. Under these conditions, the range of the results of both studies is comparable to those observed here (Fig.8). However, both results show a higher dependence of dissolution rates on seawater chemistry, which may be because in the two experimental set-ups employed in those papers (pH-stat and flow-through) there is little or no potential for any buffering effect resulting from dissolution of the experimental substrates.

Phosphate, which is a known inhibitor of calcite dissolution, can cause significant increase in the observed reaction order of calcite dissolution (from $n=2.8$ in phosphate-free seawater to $n=3.4$ in seawater with phosphate, deKanel and Morse (1978)) varied between this study (0.30-0.73 $\mu\text{mol kg}^{-1}$), Walter and Morse (1985) ($<1 \mu\text{mol kg}^{-1}$) and Keir (1980) (phosphate-free artificial seawater). However, because the magnitude of the rates determined in all studies at the same grain size and seawater chemistry are comparable, it does not seem that this variation had a significant effect.

The results of this study were also compared to the results of Yamamoto et al. (2011), which were extrapolated to the $[\text{CO}_3^{2-}]$ concentrations used in this study. Yamamoto (2011) obtained dissolution rates of foraminifera, coralline algae, coral, and mixed sediment in seawater at varying aragonite saturation states, all >1 using a flow-through reactor, in order to determine the threshold aragonite saturation state for Mg-calcites. Their measured rates were much smaller than those documented here, even when extrapolated to the much lower $[\text{CO}_3^{2-}]$ concentrations used in this study ($\sim$ an order of magnitude in most cases). However the grain size employed was much larger, and

because the rates were determined under such a different carbonic chemistry regime (all experiments were conducted in seawater super-saturated with respect to aragonite) the dissolution mechanism may have been entirely different, i.e. much stronger control of surface reactions and little to no influence of transport control (Morse and Arvidson, 2001).

Significance for natural systems and the potential consequences of OA for dissolution of biogenic carbonates in seawater

The pore water-sediment system is a natural environment with restricted mixing and elevated $p\text{CO}_2$ values from decomposition of organic matter (Andersson et al., 2005; Morse et al., 2006; Andersson et al., 2007), conditions analogous to those created in this study. The conditions of this study were designed to be similar to the conditions in the Bermuda sediments in particular, by using substrates representing some of the most common organisms in Bermuda, a grain size corresponding to the dominant size fraction in the Bermuda sediment, and $p\text{CO}_2$ values based on observations and predictions of current and future values in the Bermuda pore water.

These are useful conditions to replicate in the laboratory, because observations of dissolution under current conditions in the Bermuda sediment are well-documented and can be compared to the results obtained in the laboratory, and because the current conditions in the sediment (elevated $p\text{CO}_2$, depressed $[\text{CO}_3^{2-}]$) represent the predicted effects of OA on the carbon chemistry of the rest of the marine environment. Thus, these conditions enable one of the major goals of this study: making connections between laboratory measurements, field observations, and predictions of the future effects of OA.

Numerous laboratory studies and field observations have demonstrated that significant dissolution occurs in shallow water carbonate sediments, and Chave and Schmalz (1965) and Andersson et al. (2007) provided evidence for selective dissolution of Mg-calcite phases from sediment composition and overlying seawater chemistry in Bermuda. These results agree with the findings of this study that at any given $p\text{CO}_2$ value, dissolution rate increases with increasing Mg-content. From the dissolution rates of specific organism skeletons from Bermuda (as opposed to observations of bulk sediment) the results of this study allow predictions of which specific organisms should be expected to be abundant or depleted under high $p\text{CO}_2$ conditions in Bermuda sediments. The coralline algae *Porolithon*, with the highest dissolution rates at all levels, can be expected to selectively dissolve first, and so should be depleted with increasing depth (=increasing $p\text{CO}_2$) in the Bermuda sediment. Conversely, the barnacle, with the lowest dissolution rates and lowest Mg-content, should be represented fairly equally at all depths. A relatively simple field experiment could verify this.

Dissolution rates in the sediments at Devil's Hole in Bermuda were estimated by Andersson et al. (2007) to range between $0.2\text{--}8\text{ mmol m}^{-2}\text{ hr}^{-1}$ based on alkalinity measurements of the overlying waters. Assuming a sediment porosity of 50% and that only the uppermost 0.01m of sediment are responsible for dissolution, the rates obtained in this study range from $33\text{--}121\text{ mmol m}^{-2}\text{ hr}^{-1}$ (the lower bound represents the rate of the barnacle at $p\text{CO}_2 \sim 3,300\text{ }\mu\text{atm}$, and the upper bound represents the rate of the coralline algae *Porolithon* at the highest $p\text{CO}_2$, $\sim 5,000\text{ }\mu\text{atm}$). Measurements in the natural environment represent net dissolution (dissolution-calcification) and are thus lower than measurements of gross dissolution. However, the significantly higher rates obtained in

this study can likely be attributed mostly to differences between the laboratory and natural environment. Although this study represents a step forward in the attempt to connect the laboratory to the field, many differences remain to be addressed. The depressed rates observed in the sediment compared to this study may be due to the fact that the solid to solution ratio used in these reactors ($\sim 6 \text{ g m}^{-3}$) is significantly lower than the solid to solution ratio in a carbonate sediment with 50% porosity ($1,360,000 \text{ g m}^{-3}$). Therefore, the buffering effect seen to depress dissolution rates in this study is likely even more pronounced in the sediment. Additionally, the very well-mixed hydrodynamic conditions in the reactor are significantly different from the less turbulent conditions in the sediment, where the dissolution reaction could potentially be transport-controlled, resulting in a slower rate and lower dependence of the rate on the seawater chemistry. Andersson et al. (2007) also observed that the dominant dissolving phase in the Bermuda sediment may be 16 mol% Mg-calcite (though this finding includes significant uncertainty associated with measurements of seawater Ca^{2+}), which is consistent with the finding of this study that the Mg-calcite in the mixed sediment was 16 mol% Mg-calcite. Beyond these differences in conditions, the rates observed in the field are themselves subject to a certain amount of error because of the uncertainties associated with calculating turbulence and flux, which are needed to estimate dissolution rates in the sediment from TA measurements of the overlying water.

Conclusion

The significant dependence of dissolution rates on the seawater carbonate chemistry, and the observed increase in rates with Mg-content, indicate that dissolution rates of biogenic carbonates will increase significantly as a result of ocean acidification, and that Mg-calcites and the organisms that secrete them could be especially vulnerable to these changes. These results also confirm the findings of Keir (1980), Walter and Morse (1985), and Cubillas (2005) that BET surface areas are not a reliable normalizing factor for dissolution rates, and highlight the need for an accurate method to measure the reactive surface area of biogenic carbonates.

Figure 1 A schematic of the free-drift reactor used for all experiments.

Figure 2 The results of the control experiments described in Section 2.3.3. All data points represent the average of the results of the two reactors, and all error bars represent the range of those results.

Figure 3 The dissolution rates obtained for all substrates, normalized to the sample weight and plotted versus the average $[\text{CO}_3^{2-}]$ (a), average pCO_2 (b) and average pH (c). These are the average values as determined from the initial and final conditions, so the error bars in the x-direction represent the range of conditions during the experiment. The error bars in the y-direction represent the range in rate values obtained from the two reactors.

Figure 4 The dissolution rates obtained for all substrates, normalized to the BET specific surface area, shown as a function of average $[CO_3^{2-}]$ concentration. The error bars in the x-direction represent the range of $[CO_3^{2-}]$ over the course of the experiments, and the errors in the y-direction represent the range in rates obtained from the two reactors.

Figure 5 The dissolution rates (across all substrates) normalized to substrate weight, shown as a function of the mol % Mg. The error bars in the x-direction represent a 0.4 mol% uncertainty in the Mg-content, determined via repeated analysis of Iceland Spar.

Figure 6 The dissolution rates (across all substrates) normalized to BET surface area, shown as a function of the mol % Mg. The error bars in the x-direction represent a 0.4 mol% uncertainty in the Mg-content, determined via repeated analysis of Iceland Spar.

Figure 7 The results of Keir (1980) and Walter and Morse (1985), converted to the units used in this study. The $[CO_3^{2-}]$ concentrations were calculated using the K_{sp} , Ω , salinity, and calcium and magnesium concentrations reported in their work. The closed symbols represent the data from Walter and Morse (1985), and the open symbols are from Keir (1980). Purple symbols represent high Mg-calcites (9-20 mol%) and blue symbols represent calcites or calcites with unknown Mg-content (Keir (1980) did not determine the Mg-content of his samples).

Figure 8 The results of Keir (1980) and Walter and Morse (1985), extrapolated to the median grain size used in this study by using the results of Walter and Morse (1984b) on the dependence of dissolution rate on grain size. The dissolution rates were calculated assuming that the reaction orders determined for each substrate remained constant over all grain size, and the rate constant has a linear dependence on grain size (see Walter and Morse (1984b), Fig.4). The colored symbols are results from this study, and the grey and black symbols are the results of Walter and Morse (1985) and Keir (1980), respectively.

Table 1 The mineralogy and surface area of the substrates used in this study.

Substrate	mol % MgCO₃	BET SA (m² g⁻¹)
Iceland Spar	1.1	0.01
Benthic Foraminifera (<i>Homotrema rubrum</i>)	13.1	0.25
Gooseneck Barnacle (<i>Pedunculata</i>)	2.4	1.90
Urchin (body, <i>Lytechinus variegatus</i>)	12.5	0.15
Bryozoan	9.3	0.59
Coralline algae ()	12.4	0.69
Coralline algae (<i>Porolithon</i>)	17.4	2.70
Mixed sediment (850-150µm)	15.6	0.50

Table 2 The average starting chemistry of the seawater used for all experiments. Only one nutrient sample was taken for each experiment. Although each experiment included four “batches” of seawater, each batch for each experiment was taken from the same collected seawater, so one nutrient sample was determined to be sufficient.

Substrate	Avg S	Avg TA ($\mu\text{mol kg}^{-1}$)	NO_3^- ($\mu\text{mol kg}^{-1}$)	NO_2 ($\mu\text{mol kg}^{-1}$)	NH_4^+ ($\mu\text{mol kg}^{-1}$)	PO_4^{3-} ($\mu\text{mol kg}^{-1}$)	Si ($\mu\text{mol kg}^{-1}$)
Calcite 1	33.75 ± 0.11	2243.10 ± 0.46	2.66	0.19	2.76	0.60	3.13
Calcite 2	33.66 ± 0.04	2241.07 ± 1.17	2.66	0.19	2.76	0.60	3.13
Benthic foraminifera (<i>Homotrema rubrum</i>)	33.74 ± 0.01	2245.01 ± 5.92	3.18	0.09	0.16	0.64	4.01
Barnacle	33.59 ± 0.06	2238.52 ± 4.33	2.92	0.27	0.36	0.61	2.93
Urchin	33.66 ± 0.07	2243.00 ± 1.86	0.82	0.08	0.74	0.42	2.05
Bryozoan	33.56 ± 0.05	2238.54 ± 3.87	2.60	0.01	not analyzed	0.35	1.78
Coralline algae (<i>name</i>)	33.53 ± 0.04	2236.73 ± 3.17	2.60	0.01	not analyzed	0.35	1.78
Coralline algae (<i>Porolithon</i>)	33.63 ± 0.01	2247.53 ± 0.40	1.24	0.10	not analyzed	0.30	2.01
Sediment	33.62 ± 0.06	2254.34 ± 1.93	1.93	0.22	not analyzed	0.73	3.65
Average	33.64 ± 0.07	2243.09 ± 5.43	2.29	0.13	1.36	0.51	2.72

Table 3 Slope and fit data for the best-fit lines shown in Figure 3(a).

Substrate	Slope	Correlation coefficient (R^2)
Iceland spar	-0.0852	0.75
Benthic foraminifera (<i>Homotrema rubrum</i>)	-0.29	0.98
Gooseneck barnacle (<i>Pedunculata</i>)	-0.14	0.91
Urchin (<i>Lytechinus</i> <i>variegatus</i>)	-0.24	0.97
Bryozoan	-0.33	0.93
Coralline algae	-0.70	0.99
Coralline algae (<i>Porolithon</i>)	0.14	0.96
Mixed sediment (850-1000 μ m)	-0.15	0.96

References

- Andersson, A.J., Bates, N.R., Mackenzie, F.T., 2007. Dissolution of carbonate sediments under rising pCO₂ and ocean acidification: observations from Devil's Hole, Bermuda. *Aquat. Geochem.* 13, 237–264.
- Andersson, A.J., Gledhill, D., 2013. Ocean acidification and coral reefs: effects on breakdown, dissolution, and net ecosystem calcification. *Annu. Rev. Mar. Sci.* 5, 321–348.
- Andersson, A.J., Mackenzie, F.T., 2004. Shallow-water oceans: a source or sink of atmospheric CO₂? *Front. Ecol. Environ.* 2, 348–353.
- Andersson, A.J., Mackenzie, F.T., Bates, N.R., 2008. Life on the margin: implications of ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers. *Mar Ecol Prog Ser* 373.
- Andersson, A.J., Mackenzie, F.T., Gattuso, J.-P., 2011. Effects of ocean acidification on benthic processes, organisms, and ecosystems. *Ocean Acidif.* 8, 122–153.
- Andersson, A.J., Mackenzie, F.T., Lerman, A., 2005. Coastal ocean and carbonate systems in the high CO₂ world of the Anthropocene. *Am. J. Sci.* 305, 875–918.
- Andersson, A.J., Mackenzie, F.T., Ver, L.M., 2003. Solution of shallow-water carbonates: An insignificant buffer against rising atmospheric CO₂. *Geology* 31, 513–516.
- Arakaki, T., Mucci, A., 1995. A continuous and mechanistic representation of calcite reaction-controlled kinetics in dilute solutions at 25 C and 1 atm total pressure. *Aquat. Geochem.* 1, 105–130.
- Archer, D., Emerson, S., Reimers, C., 1989. Dissolution of calcite in deep-sea sediments: pH and O₂ microelectrode results. *Geochim. Cosmochim. Acta* 53, 2831–2845. doi:10.1016/0016-7037(89)90161-0
- Archer, D., Maier-Reimer, E., 1994. Effect of deep-sea sedimentary calcite preservation on atmospheric CO₂ concentration. *Nature* 367, 260–263. doi:10.1038/367260a0
- Bischoff, W.D., Bishop, F.C., Mackenzie, F.T., 1983. Biogenically produced magnesian calcite; inhomogeneities in chemical and physical properties; comparison with synthetic phases. *Am. Mineral.* 68, 1183–1188.
- Broecker, W.S., 1974. Carbonate Dissolution on the Western Flank of the East Pacific Rise.
- Busenberg, E., Plummer, L.N., 1986. A comparative study of the dissolution and crystal growth kinetics of calcite and aragonite. *Stud. Diagenesis* 105, 139–168

- Chan, N., Connolly, S.R., 2013. Sensitivity of coral calcification to ocean acidification: a meta-analysis. *Glob. Change Biol.* 19, 282–290.
- Chave, K.E., Schmalz, R.F., 1966. Carbonate-seawater interactions. *Geochim. Cosmochim. Acta* 30, 1037–1048.
- Cubillas, P., Köhler, S., Prieto, M., Chaïrat, C., Oelkers, E.H., 2005. Experimental determination of the dissolution rates of calcite, aragonite, and bivalves. *Chem. Geol.* 216, 59–77.
- Erez, J., Reynaud, S., Silverman, J., Schneider, K., Allemand, D., 2011. Coral calcification under ocean acidification and global change, in: *Coral Reefs: An Ecosystem in Transition*. Springer, pp. 151–176.
- Friedman, G.M., 1964. Early Diagenesis and Lithification in Carbonate Sediments. *J. Sediment. Res.* 34.
- Gehlen, M., Bassinot, F.C., Chou, L., McCorkle, D., 2005. Reassessing the dissolution of marine carbonates: II. Reaction kinetics. *Deep Sea Res. Part Oceanogr. Res. Pap.* 52, 1461–1476.
- Goldsmith, J.R., Graf, D.L., Heard, H.C., 1961. Lattice constants of the calcium-magnesium carbonates. MINERALOGICAL SOC AMER 1015 EIGHTEENTH ST, NW SUITE 601, WASHINGTON, DC 20036.
- Hales, B., Emerson, S., 1997. Evidence in support of first-order dissolution kinetics of calcite in seawater. *Earth Planet. Sci. Lett.* 148, 317–327.
- Hofmann, G.E., Barry, J.P., Edmunds, P.J., Gates, R.D., Hutchins, D.A., Klinger, T., Sewell, M.A., 2010. The effect of ocean acidification on calcifying organisms in marine ecosystems: an organism-to-ecosystem perspective. *Annu. Rev. Ecol. Evol. Syst.* 41, 127–147.
- Jahnke, R.A., Jahnke, D.B., 2004. Calcium carbonate dissolution in deep sea sediments: Reconciling microelectrode, pore water and benthic flux chamber results. *Geochim. Cosmochim. Acta* 68, 47–59.
- Keir, R.S., 1980. The dissolution kinetics of biogenic calcium carbonates in seawater. *Geochim. Cosmochim. Acta* 44, 241–252.
- Langdon, C., Atkinson, M.J., 2005. Effect of elevated pCO₂ on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment. *J. Geophys. Res. Oceans* 1978–2012 110.

- Morse, J.W., Andersson, A.J., Mackenzie, F.T., 2006. Initial responses of carbonate-rich shelf sediments to rising atmospheric $p\text{CO}_2$ and “ocean acidification”: Role of high Mg-calcites. *Geochim. Cosmochim. Acta* 70, 5814–5830.
- Morse, J.W., Arvidson, R.S., 2002. The dissolution kinetics of major sedimentary carbonate minerals. *Earth-Sci. Rev.* 58, 51–84.
- Müller, M., Schulz, K., Riebesell, U., 2010. Effects of long-term high CO_2 exposure on two species of coccolithophores. *Biogeosciences* BG 7, 1109–1116.
- Pandolfi, J.M., Connolly, S.R., Marshall, D.J., Cohen, A.L., 2011. Projecting coral reef futures under global warming and ocean acidification. *Science* 333, 418–422.
- Plummer, L.N., Wigley, T.M.L., 1976. The dissolution of calcite in CO_2 -saturated solutions at 25° C and 1 atmosphere total pressure. *Geochim. Cosmochim. Acta* 40, 191–202.
- Plummer, L.N., Wigley, T.M.L., Parkhurst, D.L., 1978. The kinetics of calcite dissolution in CO_2 -water systems at 5 degrees to 60 degrees C and 0.0 to 1.0 atm CO_2 . *Am. J. Sci.* 278, 179–216.
- Rickard, D., Sjöberg, E.L., 1983. Mixed kinetic control of calcite dissolution rates. *Am. J. Sci.* 283, 815–830.
- Riebesell, U., Zondervan, I., Rost, B., Tortell, P.D., Zeebe, R.E., Morel, F.M.M., 2000. Reduced calcification of marine plankton in response to increased atmospheric CO_2 . *Nature* 407, 364–367. doi:10.1038/35030078
- Ries, J.B., Cohen, A.L., McCorkle, D.C., 2009. Marine calcifiers exhibit mixed responses to CO_2 -induced ocean acidification. *Geology* 37, 1131–1134.
- Silverman, J., Lazar, B., Cao, L., Caldeira, K., Erez, J., 2009. Coral reefs may start dissolving when atmospheric CO_2 doubles. *Geophys. Res. Lett.* 36.
- Sjöberg, E.L., 1976. A fundamental equation for calcite dissolution kinetics. *Geochim. Cosmochim. Acta* 40, 441–447.
- Tribollet, A., Godinot, C., Atkinson, M., Langdon, C., 2009. Effects of elevated $p\text{CO}_2$ on dissolution of coral carbonates by microbial euendoliths. *Glob. Biogeochem. Cycles* 23.
- Walter, L.M., Morse, J.W., 1984. Reactive surface area of skeletal carbonates during dissolution: effect of grain size. *J. Sediment. Res.* 54.
- Walter, L.M., Morse, J.W., 1985. The dissolution kinetics of shallow marine carbonates in seawater: A laboratory study. *Geochim. Cosmochim. Acta* 49, 1503–1513.

Yamamoto, S., Kayanne, H., Terai, M., Watanabe, A., Kato, K., Negishi, A., Nozaki, K., Gattuso, J.-P., 2012. Threshold of carbonate saturation state determined by CO₂ control experiment. *Biogeosciences* 9.