Impacts of seawater saturation state ($\Omega_A = 0.4 - 4.6$) and temperature (10, 25 °C) on the dissolution kinetics of whole-shell biogenic carbonates

Justin B. Ries^{1†}, Maite N. Ghazaleh², Brian Connolly², Isaac Westfield¹, Karl D. Castillo²

¹*Department of Marine and Environmental Sciences, Northeastern University, Nahant, Massachusetts, 01908, United States of America*

²*Department of Marine Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, 27514, United States of America*

[†]Author for correspondence email: j.ries@neu.edu; +1 (781) 581-7370 ext. 342; 430 Nahant Road Nahant, MA 01908

KEYWORDS: dissolution kinetics, ocean acidification, global warming, gross calcification, gross dissolution, net calcification, calcium carbonate, marine calcifier, calcareous organism

ABSTRACT

Anthropogenic increase of atmospheric $p\text{CO}_2$ since the Industrial Revolution has caused seawater pH to decrease and seawater temperatures to increase—trends that are expected to continue into the foreseeable future. Myriad experimental studies have investigated the impacts

23 of ocean acidification and warming on marine calcifiers' ability to build protective shells and
 24 skeletons. No studies, however, have investigated the combined impacts of ocean acidification
 25 and warming on the whole-shell dissolution kinetics of biogenic carbonates. Here, we present the
 26 results of experiments designed to investigate the effects of seawater saturation state ($\Omega_A = 0.4 -$
 27 4.6) and temperature ($10, 25\text{ }^{\circ}\text{C}$) on gross rates of whole-shell dissolution for ten species of
 28 benthic marine calcifiers: the oyster *Crassostrea virginicus*, the ivory barnacle *Balanus*
 29 *eburneus*, the blue mussel *Mytilus edulis*, the conch *Strombus alatus*, the tropical coral
 30 *Siderastrea siderea*, the temperate coral *Oculina arbuscula*, the hard clam *Mercenaria*
 31 *mercenaria*, the soft clam *Mya arenaria*, the branching bryozoan *Schizoporella errata*, and the
 32 coralline red alga *Neogoniolithon* sp. These experiments confirm that dissolution rates of whole-
 33 shell biogenic carbonates decrease with calcium carbonate (CaCO_3) saturation state, increase
 34 with temperature, and vary predictably with respect to the relative solubility of the calcifiers'
 35 polymorph mineralogy [high-Mg calcite ($\text{mol\% Mg} > 4$) > aragonite > low-Mg calcite ($\text{mol\%}$
 36 $\text{Mg} < 4$)], consistent with prior studies on sedimentary and inorganic carbonates. Furthermore,
 37 the severity of the temperature effects on gross dissolution rates also varied with respect to
 38 carbonate polymorph solubility, with warming ($10 - 25\text{ }^{\circ}\text{C}$) exerting the greatest effect on
 39 biogenic high-Mg calcite, an intermediate effect on biogenic aragonite, and the least effect on
 40 biogenic low-Mg calcite. These results indicate that both ocean acidification and warming will
 41 lead to increased dissolution of biogenic carbonates in future oceans, with shells/skeletons
 42 composed of the more soluble polymorphs of CaCO_3 being the most vulnerable to these
 43 stressors. The effects of saturation state and temperature on gross shell dissolution rate were
 44 modelled with an exponential asymptotic function ($y = B_0 - B_2 \cdot e^{B_1 \cdot x}$) that appeals to the general
 45 Arrhenius-derived rate equation for mineral dissolution [$r = (C \cdot e^{-E_a/RT})(1-\Omega)^n$]. Although the

dissolution curves for the investigated biogenic CaCO_3 exhibited exponential asymptotic trends similar to those of inorganic CaCO_3 , the observation that gross dissolution of whole-shell biogenic CaCO_3 occurred (albeit at lower rates) even in treatments that were oversaturated ($\Omega > 1$) with respect to both aragonite and calcite reveals fundamental differences between the dissolution kinetics of whole-shell CaCO_3 and inorganic CaCO_3 . Thus, applying stoichiometric solubility products derived for inorganic CaCO_3 to model gross dissolution of biogenic carbonates may substantially underestimate the impacts of ocean acidification on net calcification (gross calcification minus gross dissolution) of systems ranging in scale from individual organisms to entire ecosystems (i.e., net ecosystem calcification). Finally, these experiments permit rough estimation of the impact of CO_2 -induced ocean acidification on the gross calcification rates of various marine calcifiers, calculated as the difference between net calcification rates derived empirically in prior studies and gross dissolution rates derived from the present study. Organisms' gross calcification responses to acidification were generally less severe than their net calcification response patterns, with aragonite mollusks (bivalves, gastropods) exhibiting the most negative gross calcification response to acidification, and photosynthesizing organisms, including corals and coralline red algae, exhibiting relative resilience.

1. INTRODUCTION

Daily mean atmospheric carbon dioxide ($p\text{CO}_2$) exceeded 400 ppm at the Mauna Loa (Hawaii) observatory in May 2013 (Tans and Keeling, 2013), an approximate 43% increase from the pre-Industrial-Revolution level of 280 ppm (IPCC, 2007). This increase in atmospheric $p\text{CO}_2$ has caused surface seawater pH to decline by approximately 0.1 units (Brewer, 1997; Caldeira and Wickett, 2003; Orr et al., 2005; IPCC, 2007) and surface seawater temperatures to increase

by approximately 1 °C (IPCC, 2013; Kleypas et al., 2005). Atmospheric $p\text{CO}_2$ is predicted to increase to between 700 and 900 ppm by the end of the 21st century, which should cause sea surface pH to decrease by an additional 0.3 to 0.4 units (Brewer, 1997; Caldeira and Wickett, 2003; Orr et al., 2005; Raven et al., 2005; IPCC, 2013; Füssel, 2009; Egleston et al., 2010) and surface seawater temperatures to increase by 2 to 4 °C (IPCC, 2013; Eakin et al., 2008; Donner, 2009) over the same timeframe. This decrease in seawater pH will reduce the seawater concentration of carbonate ions ($[\text{CO}_3^{2-}]$), which marine calcifiers use to build their calcium carbonate (CaCO_3) shells and skeletons.

Myriad experimental studies (too numerous to mention here) have demonstrated that CO_2 -induced ocean acidification impairs calcification within many species of marine calcifiers. Review articles by Kleypas et al. (1999, 2005), Langdon (2000), Hoegh-Guldberg et al. (2007), Fabry et al. (2008), Doney et al. (2009), Hendricks et al. (2010), and Kroeker et al. (2013) provide excellent summaries of the many studies conducted to date. Several studies also suggest that calcification within some species of marine calcifiers is not impacted and, in some cases, is actually enhanced by moderate elevations in atmospheric $p\text{CO}_2$ (e.g., Iglesias-Rodriguez et al., 2008; Wood et al., 2008; Ries et al., 2009; Rodolfo-Metalpa et al., 2010, 2011; Fabricius et al., 2011; Castillo et al., 2014).

The process of shell-building (i.e., ‘net calcification’) within marine calcifiers inhabiting near-undersaturated waters results from the balance of forming new shell through active calcification (i.e., ‘gross calcification’) and losing old shell through dissolution (i.e., ‘gross dissolution’; e.g., Ries, 2011a, 2011b; Rodolfo-Metalpa et al., 2011). Benthic marine calcifiers inhabiting restricted coastal waters can experience seawater $p\text{CO}_2$ that is higher than equilibrium $p\text{CO}_2$ for surface seawater in the open ocean due to seasonal cycles in the respiration of organic

carbon and/or upwelling and/or water mixing (e.g., Feely et al., 2008; Andersson and Mackenzie, 2012; Andersson and Gledhill, 2013). Calcifiers inhabiting these restricted coastal environments are already experiencing seawater that is undersaturated or nearly undersaturated with respect to their shell mineralogy, which supports the gross dissolution of exposed shell (e.g., Andersson et al., 2005, 2006, 2008, 2011; Morse et al., 2006; Andersson and Mackenzie, 2012; Andersson and Gledhill, 2013) and either biologically mediated gross calcification or gross dissolution beneath healthy tissue (e.g., Wood et al., 2008; Ries et al., 2009; Rodolfo-Metalpa et al., 2010, 2011; Fabricius et al., 2011). Furthermore, this dissolution of biogenic carbonates is predicted to increase by more than 200% by year 2300 under business-as-usual scenarios (Kleypas et al., 2005; Andersson et al., 2005, 2006, 2008, 2011; Morse et al., 2006; IPCC 2007; Andersson and Mackenzie, 2012; Andersson and Gledhill, 2013; Pickett and Andersson, 2015).

Although numerous studies have investigated the impact of CO₂-induced ocean acidification on organisms' rates of net calcification (gross calcification minus gross dissolution), relatively few studies have endeavored to isolate the effects of ocean acidification on the gross dissolution (e.g., Morse et al., 1979; Keir, 1980; Kennish and Lutz, 1999; Cubillas et al., 2005; Bednaršek et al., 2012; Pickett and Andersson, 2015) or gross calcification (e.g., Comeau et al., 2010; Rodolfo-Metalpa et al., 2011; Cohen and Fine, 2012) of marine calcifiers' shells and skeletons. And none has investigated the combined impacts of warming and acidification on these processes. Indeed, it is presently unclear which of these two processes (gross dissolution vs. gross calcification) is most directly impacted by ocean acidification (e.g., Andersson et al., 2008, 2011; Ries et al., 2009; Ries, 2011a, 2012; Rodolfo-Metalpa et al., 2011; Andersson and Gledhill, 2013; Pickett and Andersson, 2015).

This manuscript presents the results of 47-day laboratory experiments investigating the independent and combined effects of seawater saturation state ($\Omega_A = 0.4 - 4.6$) and temperature (10, 25 °C) on rates of whole-shell gross dissolution for 10 species of marine calcifiers that span a range of carbonate polymorph mineralogies (low-Mg calcite, high-Mg calcite, and/or aragonite): the oyster *Crassostrea virginicus*, the ivory barnacle *Balanus eburneus*, the blue mussel *Mytilus edulis*, the conch *Strombus alatus*, the tropical coral *Siderastrea siderea*, the temperate coral *Oculina arbuscula*, the hard clam *Mercenaria mercenaria*, the soft clam *Mya arenaria*, the branching bryozoan *Schizoporella errata*, and the coralline red alga *Neogoniolithon* sp. Gross calcification rates for a subset of these species are also roughly estimated from the difference between their previously determined net calcification rates (Ries et al., 2009; Castillo et al., 2014) and their empirically derived gross dissolution rates (this study).

1.1 Overview of prior work on the dissolution kinetics of CaCO_3

The dissolution kinetics of calcium carbonate minerals comprise a vast body of theoretical and empirical research that has now been explored for more than half a century. The field has received such widespread attention because of its relevance to a broad range of industries and scientific disciplines. Industrial applications relevant to CaCO_3 dissolution include antifouling of marine and freshwater structures (e.g., turbines, boat hulls), descaling of pipes and industrial reactors, art conservation, ceramics, dentistry, vascular and soft-tissue decalcification, mineralogical sequestration of fossil-fuel derived CO_2 , the development of oil and gas reservoirs, and the mineralogical sealing of oil and gas wells. Calcium carbonate dissolution is also relevant to countless scientific subjects, including the global carbon cycle, sedimentary diagenesis, the formation, abundance and distribution of limestones, the evolution of ocean chemistry, fossil preservation, lysocline dynamics, buffering of the seawater carbonate system, and the biological

and sedimentary responses to ocean acidification and warming. Because many natural waters exist near the CaCO_3 precipitation-dissolution divide, the CaCO_3 - CO_2 - H_2O system has become a model for the empirical exploration of mineral dissolution kinetics.

Although a thorough review of prior studies investigating the dissolution kinetics of CaCO_3 minerals is beyond the scope of the present contribution, a brief overview of the field is presented below. Readers seeking a more comprehensive treatment of the subject are directed to reviews by Plummer et al. (1979), Morse (1983), Mackenzie et al. (1983), Morse and Mackenzie (1990), Morse and Arvidson (2002), Morse et al. (2006), Morse et al. (2007), and Andersson and Gledhill (2013).

The majority of studies investigating the dissolution kinetics of CaCO_3 minerals have focused on synthetic carbonates, primarily calcite (Alkattan et al., 1998; Amrhein et al., 1985; Arakaki and Mucci, 1995; Arvidson et al., 2003; Arvidson and Luttge, 2010; Baumann et al., 1985; Berner and Morse, 1974; Berner, 1978; Busenberg and Plummer, 1986; Chou, et al., 1989; Compton et al., 1989; Compton and Pritchard, 1990; Compton and Unwin, 1990; Dreybrodt, 1981; Dreybrodt and Buhmann, 1991; Dreybrodt et al., 1996; Finneran and Morse, 2009; Garrels et al., 1960; Garrels and Wollast, 1978; Gledhill and Morse, 2004, 2006a, 2006b; Gutjahr et al., 1996; Hales and Emerson, 1996; He and Morse, 1993; Kralj and Brečević, 1995; Lafon, 1978; Liu and Dreybrodt, 1997; Morse and Berner, 1972; Morse et al., 1979; Plath et al., 1980; Plummer and Busenberg, 1982; Plummer and Wigley, 1976; Plummer et al., 1978; Pokrovsky et al., 2005, 2009; Pokrovsky and Schott, 1999, 2002; Sjöberg and Rickard, 1984; Schott et al., 2009; Sjöberg, 1976, 1978; Svensson and Dreybrodt, 1992; Thorstenson and Plummer, L.N., 1977, 1978; Walter and Morse, 1985; Weyl, 1958, 1965; Wollast and Reinhard-Derie, 1977; Wollast, 1990; Xu et al., 2012; Bertram et al., 1991; Bischoff, 1998; Casey and Sposito, 1992).

These studies generally support the theoretical assertions that the rate of CaCO₃ mineral dissolution can be reliably modelled by the general equation for mineral dissolution rate (cf. Gledhill and Morse, 2004, 2006a, 2006b; Morse and Arvidson, 2002):

$$r = k \cdot (1 - \Omega)^n,$$

where r = surface-area-normalized dissolution rate, k = a rate constant, Ω = saturation state of the solution with respect to the CaCO₃ mineral of interest, and n = reaction order. The rate constant of the reaction (k) can be modelled from the Arrhenius equation (cf. Gledhill and Morse, 2004, 2006a, 2006b; Morse and Arvidson, 2002) as:

$$k = C \cdot e^{-E_a/RT},$$

where C = a pre-exponential factor, E_a = Arrhenius activation energy of the reaction, R = gas constant, and T = absolute temperature (Kelvin).

Other empirical studies have shown that the dissolution kinetics of synthetic CaCO₃ minerals can also be influenced by a range of factors not included in the general equation for mineral dissolution rate, such as inorganic impurities (Alkattan et al., 2002; Akin and Lagerwerff, 1965; Arvidson et al., 2006; Berner, 1967; Buhmann and Dreybrodt, 1987; Eisenlohr et al., 1999; Garrels et al., 1961; Gutjahr et al., 1996; Harstad and Stipp, 2007; Lea et al., 2001; Morse, 1986; Mucci and Morse, 1984; Mucci et al., 1989; Nestaas and Terjesen, 1969; Salem et al., 1994; Sjöberg and Rickard, 1984; Terjesen et al., 1961; Vinson and Lüttge, 2005; Walter and Hanor, 1979), organic impurities (Barwise et al., 1990; Compton and Sanders, 1993; Suess, 1970; Teng and Dove, 1997), crystal surface properties (Compton et al., 1986; Hillner et al., 1992a, 1992b; Jordan and Rammensee, 1998; Lasaga and Luttge, 2001; Liang and Baer, 1997; Liang et al., 1996; MacInnis and Brantley, 1992, 1993; Schott et al., 1989; Shiraki et al.,

2000; Sjöberg and Rickard, 1985; Teng, 2004; Van Cappellen et al., 1993; White and Peterson, 1990), and ion transport adjacent to the crystal surface (e.g., Liu and Dreybrodt, 1997).

A smaller body of work has investigated the dissolution kinetics of biogenic CaCO_3 minerals. The majority of these studies have focused on the dissolution kinetics of bulk CaCO_3 sediments, often with the aim of constraining reactions involved in the evolution of sedimentary porewater, early-to-late stage sedimentary diagenesis, lithification, and sedimentary buffering of the seawater carbonate system (Andersson et al., 2007; Andersson et al., 2009; Archer et al., 1989; Balzer and Wefer, 1981; Berger, 1967; Buhmann and Dreybrodt, 1985a, 1985b; Burdige et al., 2008, 2010; Burdige and Zimmerman, 2002; Boucher et al., 1998; Friedman, 1964; Gehlen et al., 2005a, 2005b; Hales and Emerson, 1996; Hales et al., 1994; Honjo and Erez, 1978; Jahnke and Jahnke, 2004; Kinsey, 1985; Langdon et al., 2000; Leclercq et al., 2002; Milliman, 1978; Morse, 1978; Morse et al., 2006; Peterson, 1966; Pickett and Andersson, 2015; Rude and Aller, 1991; Silverman et al., 2007a, 2007b; Schmalz, 1965; Tynan and Opdyke, 2011; Walter et al., 1993; Walter and Burton, 1990; Yates and Halley, 2006). These studies generally investigate bulk mixtures of biogenic CaCO_3 minerals that, in some cases, have been substantially altered themselves through neomorphism, diagenetic conversion, laboratory cleaning, and/or natural loss of organic impurities and protective organic layers.

Numerous studies have also investigated the dissolution kinetics of specific types of biogenic CaCO_3 shells and skeletons (Bischoff et al., 1983, 1987; Cubillas et al., 2005; Plummer and Mackenzie, 1974; Walter and Morse, 1984, 1985; Walter, 1985). However, most of these studies involved the heavy treatment, via pulverization and/or chemical cleaning, of the shells and skeletons as the investigators sought to eliminate the effects of organic impurities, protective organic coverings, and shell and/or crystal geometry on the dissolution kinetics of the biogenic

mineral (c.f., Morse and Arvidson, 2002). Although studies investigating mechanically and/or chemically treated shells and skeletons provide important insight into the dissolution kinetics of sedimentary biogenic carbonates, they are not ideal for constraining the whole-shell dissolution kinetics that are relevant to predicting organismal responses to CO₂-induced ocean acidification and warming.

Pickett and Andersson (2015) have published the most recent and comprehensive investigation of dissolution kinetics of biogenic carbonates. In their seminal study, they evaluated the impact of pCO₂ ranging from 3000 to 5500 µatm on the dissolution rates of pulverized shells of 5 species of marine invertebrates that produce calcite of varying Mg-content: a barnacle, a foraminifera, a bryozoan, an urchin, and two species of coralline algae. They found that dissolution rates increased predictably with increasing pCO₂, increasing Mg-content of calcite, and increasing microstructural surface area. Like prior studies on biogenic carbonates, this study utilized crushed shells in order to make their results relevant to sedimentary porewater systems and buffering of the seawater carbonate system. Modification of shell geometry and surface area through mechanical grinding, however, makes it challenging to apply their results to whole shell dissolution kinetics and the biological process of shell-building.

A handful of studies have investigated the dissolution kinetics of untreated, whole-shell biogenic carbonates. The earlier of these studies (Friedman, 1964; Schroeder and Siegel, 1969; Land, 1967) focused mainly on the diagenetic stabilization of high-Mg calcite to form more stable low-Mg calcite and dolomite. As such, these experiments were carried out at temperatures and saturation states that are not relevant to conditions predicted for the future oceans. Moreover, rates of CaCO₃ dissolution in these experiments were typically not documented with the precision and accuracy needed for comparing results amongst organisms and/or experiments

(Morse and Arvidson, 2002) or for interpreting these results in the context of future oceanic change.

More recent investigations of whole-shell dissolution kinetics (e.g., Bednaršek et al., 2012; Keir, 1980; Morse et al., 1979) were conducted with greater scientific rigor and over solution parameters more relevant to future oceanic change, however, these studies have largely been focused on planktonic calcifiers (e.g., foraminifera, coccolithophores, pteropods) due to their role in shelf, slope and deep-sea sedimentation.

Kennish and Lutz (1999) and Powell et al. (2008) conducted long-term field-based experiments and Glover and Kidwell (1993) conducted controlled laboratory experiments investigating the dissolution kinetics of bivalve shells, mainly from a taphonomic perspective (i.e., to determine the potential for preserving bivalve shells in the fossil record). And in a controlled laboratory experiment investigating dissolution rates of whole oyster shells over the pH range 7.2 to 7.9, Waldbusser et al. (2011) found that oyster shell dissolution rates increased with decreasing seawater pH, except between pH 7.4 and 7.2, and that fresh shells dissolved faster than weathered shells, which dissolved faster than dredged shells.

Finally, Nash et al (2013) conducted short-term (10-day) laboratory experiments investigating the dissolution rates of crustose coralline algae over the pH range 7.7 – 8.3 and found that algal skeletons rich in the less soluble dolomite mineral exhibited slower rates of dissolution than algal skeletons rich in the more-soluble Mg-calcite mineral.

Here, we seek to build upon this foundation of research investigating carbonate dissolution kinetics by conducting the first systematic analysis of whole-shell dissolution kinetics at various saturation states and temperatures for a range of benthic calcifying taxa spanning various polymorph mineralogies (aragonite, low-Mg calcite, high-Mg calcite).

2. MATERIALS AND METHODS

2.1 Specimen collection

Live organisms were collected, pursuant to local, state, and federal regulations, from the following localities: *Mytilus edulis* (blue mussel) and *Crassostrea virginica* (oyster) from Buzzards Bay, Massachusetts; *Balanus eburneus* (ivory barnacle), *Schizoporella errata* (branching bryozoan), and *Strombus alatus* (conch) from the Gulf of Mexico off the coast of Florida; *Neogoniolithon* sp. (red algae) from the Atlantic Ocean off the coast of Florida; *Mercenaria mercenaria* (hard clam) and *Mya arenaria* (soft clam) from Nantucket Sound off the coast of Massachusetts; *Oculina arbuscula* (temperate coral) from the Atlantic Ocean off the coast of North Carolina; and *Siderastrea siderea* (tropical coral) from the western Caribbean Sea off the coast of southern Belize. Prior to the start of the experiment, specimens were euthanized in 95% ethanol, gently cleaned of living tissue, rinsed in 95% ethanol to remove salts, and air-dried for 14 days. A small of cyanoacrylate epoxy (3-4 droplets) was used to re-attach left and right bivalve shells (clams, mussels, oysters) in order to mimic their articulated postures while alive. Initial dry weights were then obtained with a *Cole Parmer Symmetry PR 410* analytical balance.

2.2 Experimental conditions

Eighteen specimens of each species were submerged for 47 days in six sets of three-way replicated experimental $p\text{CO}_2$ /temperature ($\pm\text{SD}$) treatments: (1) $497\pm79\ \mu\text{atm}/10.1\pm0.2^\circ\text{C}$; (2) $4144\pm1194\ \mu\text{atm}/10.1\pm0.1^\circ\text{C}$; (3) $5841\pm1323\ \mu\text{atm}/10.0\pm0.2^\circ\text{C}$; (4) $535\pm76\ \mu\text{atm}/24.9\pm0.2^\circ\text{C}$; (5) $4870\pm1045\ \mu\text{atm}/24.9\pm0.2^\circ\text{C}$; and (6) $9212\pm1839\ \mu\text{atm}/25.0\pm0.2^\circ\text{C}$ (Table 1). The control $p\text{CO}_2$ gases were compressed air sourced from outside the building. The elevated $p\text{CO}_2$ gas mixtures were formulated by mixing pure compressed CO_2 with compressed air using *Aalborg*

digital solenoid-valve mass flow controllers. The 34 L experimental tanks were formulated at salinity ($\pm$ SD) of 32.0 ($\pm$ 0.1) with *Instant Ocean Sea Salt* mixed with deionized water and sterilized with addition of HgCl_2 (400 μL of saturated HgCl_2 solution per L seawater). Although the trace elemental composition of *Instant Ocean Sea Salt* differs subtly from that of natural seawater, its major and minor elemental composition, as well as its carbonate chemistry, was found to be the most similar to that of natural seawater when compared with eight other commercial sea salt mixes (Atkinson and Bingman, 1998). Seawater within each aquarium was continuously filtered (757 L h^{-1}) with a hanging power filter that contained a nylon-floss activated-carbon filter cartridge. Circulation and turbulence of seawater within aquaria were maintained with a 400 L h^{-1} powerhead in order to mimic flow conditions on the seafloor, as prior studies (e.g., Comeau et al., 2014) have shown that flow rates impact net calcification rates of benthic organisms. No illumination was provided to the aquaria. Each aquarium was covered with a transparent 3-mm thick plexiglass sheet and both the aquarium and the attached filtration system were wrapped with cellophane to promote equilibration between the gas mixtures and the experimental seawaters and to minimize evaporative water loss. Seawater temperatures ($\pm$ SD) were maintained at the 25°C target temperature with 50 watt heaters and at the 10°C target temperature with 1 hp aquarium chillers. Each week, 250 mL seawater samples were obtained in ground-glass stoppered borosilicate glass bottles for the analysis of dissolved inorganic carbon (DIC) and total alkalinity (TA). Seventy-five percent seawater changes were performed weekly. Deionized water was also periodically added to the experimental aquaria in order to replenish water lost through evaporation and maintain the target salinity of 32.

2.3 Measurement and calculation of carbonate system parameters

Temperature within the experimental aquaria was measured every other day (Table 1) with a NIST-calibrated partial-immersion organic-filled glass thermometer. Salinity was measured every other day (Table 1) with a *YSI 3200* conductivity meter with a *YSI 3440* cell (K=10) that was calibrated with seawater standards of known salinity provided by the laboratory of Prof. A. Dickson of Scripps Institute of Oceanography. Seawater pH was measured every other day with a *Thermo Scientific Orion 2 Star* benchtop pH meter with an *Orion 9156BNWP* pH probe, calibrated with 7.00 and 10.01 *Orion* NBS buffers traceable to NIST standard reference material (for slope of the calibration curve) and with seawater standards of known pH provided by the laboratory of Prof. A. Dickson (for y-intercept of the calibration curve). Seawater dissolved inorganic carbon (DIC; Table 1) was measured via coulometry (*UIC 5400*) and total alkalinity (TA; Table 1) was measured via closed-cell potentiometric Gran titration.

Seawater $p\text{CO}_2$, pH, carbonate ion concentration ($[\text{CO}_3^{2-}]$), bicarbonate ion concentration ($[\text{HCO}_3^-]$), aqueous CO_2 , and aragonite saturation state (Ω_A) were calculated with the program *CO₂SYS* (Lewis and Wallace, 1998), using Roy et al. (1993) values for the K_1 and K_2 carbonic acid constants, the Mucci (1983) value for the stoichiometric aragonite solubility product, and an atmospheric pressure of 1.015 atm.

2.4 Determination of whole-shell dissolution rates

Whole-shell dissolution rates were determined from the difference in whole-shell dry-weight between the beginning and end of the 47-day experiment. At the completion of the experiment, specimens were rinsed in 95% ethanol to remove salts and air-dried for 14 days. Dry weights of the specimens were obtained with a *Cole Parmer Symmetry PR 410* analytical balance. Gross dissolution rates were calculated as the percent change in dry-weight (change in

dry weight divided by initial dry weight) in order to correct dissolution rates for initial shell surface area (proportional to mass), and normalized to the duration of the experiment (in days).

2.5 Modeling dissolution as a function of aragonite saturation state and temperature

Maximum likelihood non-linear hierarchical mixed effects modelling was employed to develop species-specific algorithms that predict shell dissolution rate as a function of aragonite saturation state and temperature (Table 2, 3). The general form of the model is an exponential asymptotic function that appeals to the general Arrhenius-derived rate equation for mineral dissolution [$r = (C \cdot e^{-E_a/RT})(1-\Omega)^n$; terms defined above]:

$$y = B_0 - B_2 \cdot e^{B_1 \cdot x}$$

where y = dissolution rate, B_0 = asymptote, B_1 = rate of approaching asymptote, B_2 = y -intercept and x = saturation state of seawater (cf. Gledhill and Morse, 2004, 2006a, 2006b; Morse and Arvidson, 2002). Akaike's Information Criterion (AIC) was used to investigate various forms of B_0 and B_1 , including treatment of each species and temperature combination as a structural unit [degrees of freedom (DF) = 8; AIC = -691.6], treatment of each species as a structural unit with temperature affecting only B_1 (DF = 8; AIC = -697.4), and treatment of each species as a structural unit with temperature affecting both B_1 and B_0 (DF = 9, AIC = -703.6). Since treatment of each species as a structural unit with temperature affecting both B_1 and B_0 yielded the lowest AIC, B_1 and B_0 were modeled as:

$$B_1 = b_{1.int} + b_{1.temp} + u_1,$$

$$B_0 = b_{0.int} + b_{0.temp} + u_0,$$

where $b_{0.int}$ and $b_{1.int}$ represent the fixed effects of aragonite saturation state, $b_{0.temp}$ and $b_{1.temp}$ represent the fixed effects of temperature, and u_0 and u_1 represent species-specific

random effects. Thus, the maximum likelihood non-linear mixed effects model of dissolution rate (y) as a function of aragonite saturation state (Ω_A) and temperature is:

$$y = (b_{0.int} + b_{0.temp} + u_0) - B_2 \cdot e^{(b_{1.int} + b_{1.temp} + u_1) \cdot \Omega_A}.$$

Fixed effects ($b_{1.int}$, $b_{1.temp}$, $b_{0.int}$, $b_{0.temp}$) were defined via normalized least squares regression analysis. Species-specific random effects parameters (u_0 , u_1) were predicted via Log-Cholesky parametrization.

Although the shells and skeletons of the ten species investigated were composed of a range of calcium carbonate polymorphs (low-Mg calcite, high-Mg calcite, aragonite) with different solubility products, dissolution rates of all specimens were plotted and modelled with respect to the aragonite saturation state of seawater. This facilitated direct comparison of the dissolution responses of the different species (i.e., under equivalent future pCO_2 scenarios) and avoided problems associated with bi-mineralic shells and with assigning solubility products to Mg-calcites of undetermined solubilities (see Pickett and Andersson, 2015). Should the reader prefer, the y-axes of the dissolution curves can be easily transformed to the appropriate polymorph since saturation states of calcium carbonate polymorphs are related by constant proportions. This transformation would only expand or compress the dissolution curve along its x-axis; it would not materially alter the shape of the curve.

2.6 Estimation of gross calcification rates

Net calcification rates under a range of acidified treatments at 25 °C have been previously determined for eight of the investigated organisms (Ries et al., 2009; Castillo et al., 2014). These measurements of net calcification represent the balance of gross calcification at the site of calcification and gross dissolution of previously formed shell/skeleton (Rodolfo-Metalpa et al., 2011). Gross calcification rates for eight of the investigated taxa were estimated by subtracting

their empirically derived gross dissolution rates (this study) from their empirically derived net calcification rates derived by Ries et al. (2009; all taxa except *S. siderea*) and Castillo et al. (2014; *S. siderea* only) at the aragonite saturation states employed in the Ries et al. (2009) and Castillo et al. (2014) studies (Table 4). Although aragonite saturation states employed in the dissolution experiment (this study) did not perfectly align with the aragonite saturation states employed in the prior studies from which net calcification rates were derived, non-linear mixed effects regressions were employed to interpolate gross dissolution rates at aragonite saturation states equivalent to those employed in the studies by Ries et al. (2009) and Castillo et al. (2014; Table 4). It should be noted that this approach to estimating gross calcification assumes that the gross dissolution of dead shell material is representative of the gross dissolution that would affect the shells of living organisms. Thus, values of gross calcification derived by subtracting measured gross dissolution from measured net calcification should be treated as estimates only. Indeed, the objective here is to identify general patterns of gross calcification amongst the organisms across a range of saturation states, rather than to generate highly accurate gross calcification rates for a given species at a given saturation state.

3. RESULTS

3.1 Effect of Ω_A on gross dissolution

All ten species of calcifiers exhibited gross dissolution curves that were asymptotic in nature. Dissolution rates were relatively constant in the treatments that were oversaturated with respect to organisms' predominant polymorph, and then predictably increased exponentially in the undersaturated treatments. Notably, gross dissolution of shells and skeletons of all investigated taxa were also observed in each of the oversaturated treatments ($\Omega_A > 1$) and at both

temperatures (10, 25 °C), albeit at much slower rates than observed in the undersaturated treatments (Figure 1).

The asymptotic shape of the gross dissolution response curves allows them to be reliably modelled with an exponential asymptotic function ($y = B_0 - B_2 \cdot e^{B_1 \cdot x}$; terms define above), which appeals to the general Arrhenius-derived rate equation for mineral dissolution [$r = (C \cdot e^{-E_a/RT})(1-\Omega)^n$; terms defined above; cf. Gledhill and Morse, 2004, 2006a, 2006b; Morse and Arvidson, 2002].

Normalized least squares non-linear regression analysis was employed to define the following fixed effects of the dissolution rate model: $b_0.int = -0.0250$ ($p=0.0052$); $b_0.temp = -0.0012 \cdot T + 0.0119$ ($p=0.0054$); $b_2 = 0.6379$ ($p<0.0001$); $b_1.int = -5.0299$ ($p=0.0000$); and $b_1.temp = 0.0816 \cdot T - 0.8155$ ($p<0.0001$; Table 2A). These statistically significant ($p<0.01$) fixed effect parameters yield the following model of dissolution rate (y) as a function of aragonite saturation state (Ω_A) and temperature (T):

$$y = (-0.0250 + -0.0012 \cdot T + 0.0119 + u_0) - 0.6379 \cdot e^{(-5.0299 + 0.0816 \cdot T - 0.8155 + u_1) \cdot \Omega_A},$$

which can be condensed to:

$$y = -0.0131 - 0.0012 \cdot T + u_0 - 0.6379 \cdot e^{(-5.8454 + 0.0816 \cdot T + u_1) \cdot \Omega_A}.$$

Species-specific random effects parameters (u_0 , u_1) were predicted via Log-Cholesky parameterization (Table 2B), resulting in species-specific models of skeletal dissolution from $\Omega_A = 0$ to $\Omega_A = 5$ as a function of aragonite saturation state and temperature (Figure 1).

3.2 Effect of polymorph mineralogy on gross dissolution

Relative dissolution rates of the various shells and skeletons tracked the relative solubility of their predominant CaCO_3 polymorph: high-Mg calcite > aragonite > low-Mg calcite (Table 5; Figure 2). Largely high-Mg calcite shells [i.e., branching bryozoan (cf. Smith, 2014; Taylor et

al., 2009) and coralline red algae] exhibited faster dissolution than predominantly aragonite shells (i.e., conch, tropical coral, temperate coral, hard clam and soft clam), which in turn experienced greater dissolution than predominantly low-Mg calcite shells (i.e., oyster, barnacle, mussel; see Ries (2011b) for mineralogical assays of the various species). However, dissolution rates did not track Mg-content of the two high-Mg shells—the bryozoa (ca. 6 mole-% Mg; cf. Smith, 2014; Taylor et al., 2009) had higher dissolution rates than the more Mg-rich coralline red algae (> 20 mole-% Mg; Ries, 2011b).

3.3 Effect of temperature on gross dissolution

Gross dissolution rates were modeled using the general equation $y = B_0 - B_2 \cdot e^{B_1 \cdot x}$ and averaged at both 10.1 °C (±0.2) and 25.0 °C (±0.2) over $\Omega_A = 0$ to $\Omega_A = 5$. Dissolution rates at 10 °C were significantly ($p < 0.01$) lower than at 25 °C (Tables 2, 5; Figures 1, 2). Shell/skeletal polymorph mineralogy impacted this effect of temperature on dissolution rate (Table 5; Figure 2). Shells/skeletons composed predominantly of high-Mg calcite exhibited a stronger temperature-dissolution relationship than shells/skeletons composed largely of aragonite, which in turn exhibited a stronger temperature-dissolution relationship than shells/skeletons composed mostly of low-Mg calcite.

3.4 Estimated gross calcification in response to ocean acidification

Gross calcification rates under 25 °C for the oysters, blue mussels, conchs, tropical corals, temperate corals, hard clam, soft clam, and coralline red algae were estimated by subtracting gross dissolution rates at 25 °C in the present study from net calcification rates at 25 °C in the Ries et al. (2009) and Castillo et al. (2014) studies (Table 4; Figure 3). These organisms' gross calcification response patterns to acidification were generally less severe (i.e., less steeply sloped) than their net calcification response patterns, as the latter incorporated the

effects of gross dissolution of exposed shell/skeleton. The two exceptions were the temperate and tropical corals, which exhibited similarly shaped but vertically offset gross calcification and net calcification response curves. Estimated gross calcification response patterns were most negative for the predominantly aragonite mollusks (conch, hard clam, soft clam), were flat for the predominantly calcite mollusks (oyster, mussel), were threshold in shape for the temperate coral (i.e., gross calcification declined drastically at the highest $p\text{CO}_2$ treatment), and parabolic in shape for the tropical coral and coralline red algae (i.e., gross calcification increased under moderately elevated $p\text{CO}_2$ but declined under the highest $p\text{CO}_2$ treatment).

4. DISCUSSION

4.1 Effect of Ω on gross dissolution rate

The observation that the gross dissolution curves for the investigated biogenic CaCO_3 exhibited trends similar to those of inorganic CaCO_3 and could be reasonably modelled with an exponential asymptotic function ($y = B_0 - B_2 \cdot e^{B_1 \cdot x}$; terms define above) that appeals to the general Arrhenius-derived rate equation for mineral dissolution [$r = (C \cdot e^{-E_a/RT})(1-\Omega)^n$; terms defined above; cf. Gledhill and Morse, 2004, 2006a, 2006b; Morse and Arvidson, 2002] suggests that the whole-shell dissolution kinetics of the investigated biogenic CaCO_3 generally conform to the dissolution kinetics of inorganic CaCO_3 , as shown previously for shallow water marine carbonate sediments (e.g., Walter and Morse, 1985) and crushed biogenic carbonates (Pickett and Andersson, 2015).

However, the observation that gross dissolution of biogenic CaCO_3 occurred even in treatments that were oversaturated ($\Omega > 1$) with respect to both aragonite and calcite (albeit at much slower rates than in the undersaturated treatments) indicates that there are fundamental differences between the gross dissolution kinetics of biogenic and inorganic CaCO_3 , with

biogenic carbonates exhibiting greater vulnerability to dissolution than abiogenic carbonates, particularly at oversaturated conditions. These results contrast the work of Cubillas et al. (2005), which showed that biogenic carbonates dissolve more slowly than abiogenic carbonates of equivalent mineralogy when normalized to reactive (BET) surface area, and at equivalent rates when normalized to geometric surface area.

The observed gross dissolution of biogenic CaCO_3 in oversaturated treatments could arise from various factors, including the dissolution of more soluble trace mineral phases, such as amorphous calcium carbonate (e.g. Weiner et al., 2003; Addadi et al., 2003), vaterite (Lowenstam and Abott, 1975) or brucite (Schmalz, 1965), or from the disaggregation of organic matrices that may bind together clusters and/or layers of biogenic carbonate minerals within shells and skeletons (e.g., Allemand et al., 1998; Glover and Kidwell, 1993). However, it is unlikely to have arisen from microbial-induced dissolution (e.g., Tribollet et al., 2009; Glover and Kidwell, 1993), as the experimental seawaters were poisoned with HgCl_2 for the duration of the experiment. Regardless of the precise mechanism that is responsible for the gross dissolution of biogenic carbonates in the oversaturated treatments, these results suggest that applying stoichiometric solubility products derived for inorganic carbonates to model gross dissolution of biogenic carbonates may substantially underestimate the impacts of ocean acidification on net calcification (gross calcification minus gross dissolution) of calcifying systems ranging in scale from individual organisms to entire ecosystems [as discussed in Andersson and Gledhill (2013) and Pickett and Andersson (2015) in the context of ‘net ecosystem calcification’].

The observation that dissolution was observed within all of the investigated species, despite many of these species possessing some sort of organic covering on their outer surface

(e.g., the periostraca for the 5 mollusk species investigated), indicates that such organic coverings do not, on their own, prevent shell dissolution.

4.2 Effect of CaCO₃ polymorph mineralogy on gross dissolution rate

Marine calcifiers build their shells from either the aragonite and/or calcite polymorphs of calcium carbonate, the latter of which can occur as either low-Mg (< 4 mole-% Mg) or high-Mg (> 4 mole-% Mg) phases. The aragonite polymorph is more soluble than the pure calcite phase. However, the solubility of calcite increases with increasing Mg-content, such that calcite with approximately 12 mole-% Mg has a solubility equivalent to that of aragonite. Shells and skeletons composed of aragonite and/or high-Mg calcite are therefore expected to be more deleteriously impacted by ocean acidification than those composed of low-Mg calcite (e.g., Andersson et al., 2007).

The present study reveals that gross dissolution rates at $\Omega_A = 0.6$ and $T = 10$ and 25 °C generally track shell/skeletal polymorph mineralogy (i.e., higher-Mg calcite > aragonite > lower-Mg calcite; Table 5; Figure 2). High-Mg calcite shells [i.e., branching bryozoa (cf. Smith, 2014; Taylor et al., 2009) and coralline red algae] exhibited more rapid dissolution than predominantly aragonite shells (i.e., conch, tropical coral, temperate coral, hard clam and soft clam), which in turn experienced faster dissolution than predominantly low-Mg calcite shells (i.e., oyster, barnacle and mussel). Notably, however, dissolution rates did not track Mg-content of the two high-Mg calcite shells—the bryozoan (ca. 6 mole-% Mg) had higher dissolution rates than the more Mg-rich coralline red algae (> 20 mole-% Mg). Pickett and Andersson (2015) also observed that crushed specimens of bryozoa had faster dissolution rates than crushed specimens of coralline red algae, despite the bryozoa's lower Mg-content. They attributed this trend to the

bryozoan skeletons possessing proportionally more microstructural surface area than the coralline algae.

These results are consistent with the assertion that marine calcifiers that produce the more soluble phases of CaCO_3 (i.e., aragonite and high-Mg calcite) will be more vulnerable to the effects of ocean acidification than calcifiers that secrete less vulnerable phases (i.e., low-Mg calcite and dolomite; Andersson et al., 2008; Kuffner et al., 2008; Ries et al., 2009; Nash et al., 2013), although these trends can be moderated by differences in the microstructural surface area of the shells (Pickett and Andersson, 2015). These results are also consistent with the hypothesis that the average Mg-content of marine carbonate sediments may decrease with increasing ocean acidification, due to the preferential dissolution of the more soluble higher-Mg phases (e.g., Morse et al., 2006; Andersson et al., 2008). This could ultimately lead to an oceanic state that favors the formation and preservation of low-Mg calcite shells and skeletons (historically known as ‘calcite seas’) over aragonite and high-Mg calcite shells and skeletons (‘aragonite seas’; e.g., Mackenzie and Pigott, 1981; Sandberg, 1983; Andersson et al., 2006, 2008), despite that the relatively elevated Mg/Ca ratio of modern seawater (molar $\text{Mg/Ca} = 5$) kinetically favors the formation of aragonite and high-Mg calcite (‘aragonite seas’; cf. Ries, 2010).

4.3 Effect of temperature on dissolution rates

The results of the present study show that dissolution rates of all 10 species investigated were significantly ($p < 0.01$; Table 3) greater at a temperature of 25 °C than at a temperature of 10 °C (Table 2, 5; Figures 1, 2A). These results are consistent with the general equation for mineral dissolution rate that models the rate constant of the dissolution reaction from the Arrhenius equation [$r = (C \cdot e^{-E_a/RT})(1-\Omega)^n$; see prior section for description of terms; cf. Gledhill and Morse, 2004, 2006a, 2006b; Morse and Arvidson, 2002], where increasing ‘T’ (temperature)

results in increasing ‘ r ’ (surface-area-normalized dissolution rate). Temperature also has a mitigating effect on dissolution because the solubility of CO_2 in seawater decreases with increasing temperature, resulting in increased Ω_A (cf. Andersson et al., 2008). Importantly, the results of the present study reveal that the increased rates of CaCO_3 dissolution that accompany a temperature change from 10 to 25 °C outweigh any decrease in dissolution rate resulting from the temperature-induced increase in Ω_A (Figure 1).

Furthermore, the magnitude of the temperature effect (10, 25 °C) on dissolution rate was linked to shell/skeletal polymorph mineralogy (Table 5; Figure 2). The effect of temperature on dissolution rates (quantified as the difference in average dissolution rate at 10 and 25 °C) was generally greater for high-Mg calcite shells/skeletons than for aragonite shells/skeletons, which were in turn generally greater than for low-Mg calcite shells/skeletons (Figure 2). These results suggest that both ocean acidification and warming will disproportionately impact dissolution rates of shells and skeletons composed of the more soluble phases of calcium carbonate (i.e., higher-Mg calcite and aragonite).

4.4 Surface area effects

Calcifying organisms utilize a broad range of microstructures in the construction of their shells and skeletons. Carriker et al. (1991), for example, documented 4 discrete microstructural groups within a single oyster shell, each with potentially unique dissolution kinetics. Walter and Morse (1985) also showed that relative dissolution rates of carbonate sediments were impacted by their reactive surface area. And Kidwell (2000) argued that shell microstructure is a key factor in determining whether a species is ultimately preserved in the fossil record, or lost to dissolution. It is therefore likely that both shell micro-structure and macro-structure played a role in determining relative dissolution rates of the different shell types investigated in the

present study. For instance, the 6 mole-% Mg calcite skeletons of the bryozoa dissolved more rapidly than the more soluble > 20 mole-% calcite skeletons of the coralline red algae. Pickett and Andersson (2015) recently attributed a similar trend that they observed for crushed samples of bryozoa and coralline red algae to the bryozoan skeleton having a higher surface-area-to-volume-ratio than the skeleton of the coralline red algae. However, the irregular geometry and relatively large size of the shells investigated in the present study precluded analysis of their reactive surface areas via traditional methods, such as morphometric analysis and Brunauer–Emmett–Teller (BET) gas adsorption. Instead, geometric effects were controlled for by normalizing shell dissolution rates to starting shell mass, which should generally be proportional to surface area.

4.5 Gross calcification responses to elevated $p\text{CO}_2$

Estimation of gross calcification rates (Table 4; Figure 3) from empirically derived net calcification (Ries et al., 2009; Castillo et al., 2014) and gross dissolution (this study) reveals that all eight taxa, including the conch, hard clam, and coralline red algae that exhibited net dissolution under the highest $p\text{CO}_2$ treatment, were able to continue calcifying on a gross basis in all four $p\text{CO}_2$ treatments (including the treatment undersaturated with respect to aragonite). Notably, the organisms' gross calcification response patterns to acidification were generally less severe (i.e., less steeply sloped) than their net calcification response patterns. This suggests that the shape of an organism's net calcification response pattern to ocean acidification—particularly in conditions approaching or exceeding undersaturation with respect to their mineral polymorph—is largely influenced by the gross dissolution of their shell or skeleton, rather than simply by their gross calcification under those conditions.

The observation that gross calcification response patterns were most negative for the predominantly aragonite mollusks (conch, hard clam, soft clam), were flat for the predominantly calcite mollusks (oyster, mussel), were threshold in shape for the temperate coral, and parabolic in shape for the tropical coral and coralline red algae (Table 4; Figure 3), is consistent with prior observations that marine calcifiers' exhibit highly variable responses to ocean acidification (Ries et al., 2009; Kroeker et al., 2010; Hendricks et al., 2010).

Ries et al. (2009) attributed these differential responses to a confluence of factors, including the relative solubility of their mineral polymorph, the extent to which they utilize organic coverings (e.g., epicuticles in crustacea, periostraca in mollusks, calcicoblastic epithelia in corals) to protect their shells or skeletons from external seawater, the extent to which they utilize CO₂ directly via photosynthesis, and their relative ability to remove protons from their calcifying fluid in order to deprotonate HCO₃⁻ to generate CO₃²⁻ for calcification (see Ries, 2011b, Jokiel, 2011, and Bach, 2015, for further discussion). The observation that the aragonite mollusks exhibited a more negative response than the calcite mollusks (Figure 3) is consistent with the assertion that shell polymorph mineralogy plays a role in determining differential gross calcification responses to ocean acidification *within* taxonomic classes. However, the observation that the high-Mg calcite coralline red algae, which produce a highly soluble polymorph of CaCO₃, exhibited the most positive gross calcification response to acidification (Figure 3) suggests that polymorph mineral solubility is not the primary factor controlling polyphyletic trends in gross calcification responses to ocean acidification.

The observation that the mollusks, which are thought to maintain their calcifying fluid at pH similar to that of seawater (e.g., Crenshaw, 1972), generally exhibited a more negative gross calcification response to acidification than the corals and algae, which are thought to maintain

their calcifying fluids at a substantially elevated pH (Al-Horani, 2003; Cohen et al., 2009; Krief et al., 2010; Ries, 2011b, Trotter et al., 2011; Venn et al., 2011; Anagnostou et al., 2012; McCulloch et al., 2012; Holcomb et al., 2015), is consistent with the assertion that organisms' ability to elevate pH at the site of calcification is an important factor in determining cross-taxonomic trends in gross calcification responses to ocean acidification (Ries et al., 2009).

Lastly, the observation that the photosynthesizing organisms that were investigated (corals and coralline algae) exhibited more positive gross calcification responses to CO₂-induced ocean acidification (i.e., parabolic in shape for the tropical corals and coralline algae) than the non-photosynthesizing organisms investigated (mollusks) suggests that an organisms' ability to utilize CO₂ directly via photosynthesis may also influence cross-taxonomic trends in gross calcification responses to ocean acidification. In brief, moderate increases in *p*CO₂ may fertilize photosynthesis in some symbiont bearing corals and coralline algae, thereby providing additional energy for calcification and resulting in a positive calcification response to moderate ocean acidification (i.e., defining the up-slope of the parabola). Under extreme elevations in *p*CO₂, when aqueous CO₂ is no longer limiting for photosynthesis, the insults of reduced CaCO₃ saturation state may outweigh the benefits of increased (or CO₂-saturated) photosynthesis, resulting in a negative calcification response to extreme ocean acidification (i.e., defining the down-slope of the parabola). More thorough discussions of the competing effects of CO₂-enhanced photosynthesis versus CO₂-impaired calcification in determining corals' calcification response to ocean acidification are available in Ries et al. (2009) and Castillo et al (2014).

5. CONCLUSIONS

Whole-shell dissolution experiments conducted across a range of saturation states ($0.4 < \Omega_A < 4.6$) and temperatures (10, 25 °C) on ten species of marine calcifiers revealed the following:

(1) Dissolution rates of whole-shell biogenic carbonates decrease with CaCO_3 saturation state, increase with temperature and vary predictably with respect to the relative solubility of the calcifiers' polymorph mineralogy [high-Mg calcite (mol% Mg > 4) > aragonite > low-Mg calcite (mol% Mg < 4)], consistent with prior studies on sedimentary and inorganic carbonates. These results indicate that both ocean acidification *and* warming will increase dissolution rates of biogenic carbonates in future oceans.

(2) The severity of the temperature effects on gross dissolution rates varied with respect to carbonate polymorph solubility, with warming (10 – 25 °C) exerting the greatest effect on biogenic high-Mg calcite, an intermediate effect on biogenic aragonite, and the least effect on biogenic low-Mg calcite.

(3) Gross dissolution curves for the investigated biogenic CaCO_3 were similar in shape to those of inorganic CaCO_3 and could be reasonably modelled with an exponential asymptotic function ($y = B_0 - B_2 \cdot e^{B_1 \cdot x}$) that appeals to the general Arrhenius-derived rate equation for mineral dissolution [$r = (C \cdot e^{-E_a/RT})(1-\Omega)^n$].

(4) Gross dissolution of whole-shell biogenic CaCO_3 occurred even in treatments that were oversaturated ($\Omega > 1$) with respect to both aragonite and calcite, indicating that fundamental differences exist between the dissolution kinetics of whole-shell and inorganic CaCO_3 .

Therefore, applying stoichiometric solubility products derived for inorganic carbonates to model gross dissolution of biogenic carbonates may substantially underestimate the impacts of ocean acidification on net calcification (gross calcification minus gross dissolution) of calcifying

systems ranging in scale from individual organisms to entire ecosystems (i.e., net ecosystem calcification).

(5) Rough estimates of the impact of ocean acidification on the gross calcification rates of various marine calcifiers were calculated from the difference between net calcification (determined in prior studies) and gross dissolution (determined in present study). Organisms' gross calcification responses to acidification were generally less severe than their net calcification response patterns, with aragonite mollusks (bivalves, gastropods) exhibiting the most negative gross calcification response to acidification, and photosynthesizing organisms (corals, coralline red algae) exhibiting greater resilience.

6. ACKNOWLEDGEMENTS

We thank K. Horvath and T. Courtney for valuable input and assistance. We thank C. Pelejero and an anonymous referee for their thorough reviews. This research was supported by NOAA awards NA13OAR4310186 (to JBR and KDC) and NA14NMF4540072 (to JBR), the UNC-Chapel Hill IDEA Program (NSF award #1107897), and NSF awards OCE-1437371 and OCE-1459706 (to JBR).

7. REFERENCES

- Addadi, L., Raz, S. and Weiner, S. (2003) Taking advantage of disorder: amorphous calcium carbonate and its roles in biomineralization. *Advanced Materials* 15, 959-970.
- Akin, G.W. and Lagerwerff, J.V. (1965) Calcium carbonate equilibrium in aqueous solutions open to the air: II. Enhanced solubility of a CaCO_3 in the presence of Mg^{2+} and SO_4^{2-} *Geochimica et Cosmochimica Acta* 29, 353-360.

- 654 Al-Horani, F.A., Al-Moghrabi, S.M. and DeBeer, D. (2003) The mechanism of calcification and
655 its relation to photosynthesis and respiration in the scleractinian coral *Galaxea fascicularis*.
656 Marine Biology 142, 419-426.
- 657 Alkattan, M., Oelkers, E.H., Dandurand, J.-L. and Schott, J. (1998) An experimental study of
658 calcite and limestone dissolution rates as a function of pH from -1 to 3 and temperature
659 from 25 to 80 C. Chemical Geology 151, 199-214.
- 660 Alkattan, M., Oelkers, E.H., Dandurand, J.-L. and Schott, J. (2002) An experimental study of
661 calcite dissolution rates at acidic conditions and 25° C in the presence of NaPO₃ and MgCl₂.
662 Chemical Geology 190, 291-302.
- 663 Allemand, D., Tambutté, É., Girard, J.-P. and Jaubert, J. (1998) Organic matrix synthesis in the
664 scleractinian coral *Stylophora pistillata*: role in biomineralization and potential target of the
665 organotin tributyltin. The Journal of Experimental Biology 201, 2001-2009.
- 666 Amrhein, C., Jurinak, J.J. and Moore, W.M. (1985) Kinetics of calcite dissolution as affected by
667 carbon dioxide partial pressure. Soil Science Society of America Journal 49, 1393-1398.
- 668 Anagnostou E., Huang K.F., You C.F., Sikes E.L., and Sherrell R.M. (2012) Evaluation of boron
669 isotope ratio as a pH proxy in the deep sea coral *Desmophyllum dianthus*: Evidence of
670 physiological pH adjustment. Earth and Planetary Science Letters 349–350, 251-260.
- 671 Andersson, A.J., Bates, N.R. and Mackenzie, F.T. (2007) Dissolution of carbonate sediments
672 under rising pCO₂ and ocean acidification: observations from Devil's Hole, Bermuda.
673 Aquatic Geochemistry 13, 237-264.
- 674 Andersson, A.J. and Gledhill, D. (2013) Ocean acidification and coral reefs: effects on
675 breakdown, dissolution, and net ecosystem calcification. Annual Review of Marine Science
676 5, 321-348.

- 677 Andersson, A.J., Kuffner, I.B., Mackenzie, F.T., Jokiel, P., Rodgers, K.S. and Tan, A. (2009) Net
678 loss of CaCO_3 from a subtropical calcifying community due to seawater acidification:
679 mesocosm-scale experimental evidence. *Biogeosciences* 6, 1811-1823.
- 680 Andersson, A.J. and Mackenzie, F.T. (2011) Ocean acidification: setting the record straight.
681 *Biogeosciences Discussions* 8, 6161-6190.
- 682 Andersson, A.J., Mackenzie, F.T. and Bates, N.R. (2008) Life on the margin: implications of
683 ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers. *Marine*
684 *Ecology Progress Series* 373, 265-273.
- 685 Andersson, A.J., Mackenzie, F.T. and Lerman, A. (2005) Coastal ocean and carbonate systems in
686 the high- CO_2 world of the Anthropocene. *American Journal of Science* 305, 875-918.
- 687 Andersson, A.J., Mackenzie, F.T. and Lerman, A. (2006) Coastal ocean CO_2 -carbonic acid-
688 carbonate sediment system of the Anthropocene. *Global Biogeochemical Cycles* 20.
- 689 Andersson, A.J. and Mackenzie, F.T. (2012) Revisiting four scientific debates in ocean
690 acidification research. *Biogeosciences* 9, 893-905.
- 691 Arakaki, T. and Mucci, A. (1995) A continuous and mechanistic representation of calcite
692 reaction-controlled kinetics in dilute solutions at 25° C and 1 atm total pressure. *Aquatic*
693 *Geochemistry* 1, 105-130.
- 694 Archer, D., Emerson, S. and Reimers, C. (1989) Dissolution of calcite in deep-sea sediments: pH
695 and O_2 microelectrode results. *Geochimica et Cosmochimica Acta* 53, 2831-2845.
- 696 Arvidson, R.S., Collier, M., Davis, K.J., Vinson, M.D., Amonette, J.E. and Luttge, A. (2006)
697 Magnesium inhibition of calcite dissolution kinetics. *Geochimica et Cosmochimica Acta* 70,
698 583-594.

- 699 Arvidson, R.S., Ertan, I.E., Amonette, J.E. and Luttge, A. (2003) Variation in calcite dissolution
700 rates: A fundamental problem? *Geochimica et Cosmochimica Acta* 67, 1623-1634.
- 701 Arvidson, R.S. and Luttge, A. (2010) Mineral dissolution kinetics as a function of distance from
702 equilibrium – new experimental results. *Chemical Geology* 269, 79-88.
- 703 Bach, L.T. (2015) Reconsidering the role of carbonate ion concentration in calcification by
704 marine organisms. *Biogeosciences* 12, 4939-4951.
- 705 Balzer, W. and Wefer, G. (1981) Dissolution of carbonate minerals in a subtropical shallow
706 marine environment. *Marine Chemistry* 10, 545-558.
- 707 Barwise, A.J., Compton, R.G. and Unwin, P.R. (1990) The effect of carboxylic acids on the
708 dissolution of calcite in aqueous solution. Part 2. d-, l- and meso-Tartaric acids. *Journal of*
709 *the Chemical Society, Faraday Transactions* 86, 137-144.
- 710 Baumann, J., Buhmann, D., Dreybrodt, W. and Schulz, H.D. (1985) Calcite dissolution kinetics
711 in porous media. *Chemical Geology* 53, 219-228.
- 712 Bednaršek, N., Tarling, G.A., Bakker, D.C.E., Fielding, S., Jones, E.M., Venables, H.J., Ward,
713 P., Kuzirian, A., Leze, B. and Feely, R.A. (2012) Extensive dissolution of live pteropods in
714 the Southern Ocean. *Nature Geoscience* 5, 881-885.
- 715 Berner, R.A. (1967) Comparative dissolution characteristics of carbonate minerals in the
716 presence and absence of aqueous magnesium ion. *American Journal of Science* 265, 45-70.
- 717 Berner, R.A. (1978) Rate control of mineral dissolution under earth surface conditions. *American*
718 *Journal of Science* 278, 1235-1252.
- 719 Berner, R.A. and Morse, J.W. (1974) Dissolution kinetics of calcium carbonate in sea water: IV.
720 theory of calcite dissolution. *American Journal of Science* 274, 108-134.

- 721 Bertram, M.A., Mackenzie, F.T., Bishop, F.C. and Bischoff, W.D. (1991) Influence of
722 temperature on the stability of magnesian calcite. *American Mineralogist* 76, 1889-1896.
- 723 Bischoff, W.D. (1998) Dissolution enthalpies of magnesian calcites. *Aquatic Geochemistry* 4,
724 321-336.
- 725 Bischoff, W.D., Bishop, F.C. and Mackenzie, F.T. (1983) Biogenically produced magnesian
726 calcite: inhomogeneities in chemical and physical properties and comparison with synthetic
727 phases. *American Mineralogist* 68, 1183-1188.
- 728 Bischoff, W.D., Mackenzie, F.T. and Bishop, F.C. (1987) Stabilities of synthetic magnesian
729 calcites in aqueous solution: comparison with biogenic materials. *Geochimica et*
730 *Cosmochimica Acta* 51, 1413-1423.
- 731 Bojar, A.V., Bojar, H.P. and Tufar, W. (2012) Mg/Ca and isotopic high resolution record of
732 deep-sea hydrothermal barnacles. In *EGU General Assembly Conference Abstracts*, vol. 14,
733 p. 12862.
- 734 Boucher, G., Clavier, J., Hily, C. and Gattuso, J.P. (1998) Contribution of soft-bottoms to the
735 community metabolism (primary production and calcification) of a barrier reef flat (Moorea,
736 French Polynesia). *Journal of Experimental Marine Biology and Ecology* 225, 269-283.
- 737 Brewer, P.G. (1997) Ocean chemistry of the fossil fuel CO₂ signal: The haline signal of
738 “business as usual”. *Geophysical Research Letters* 24, 1367-1369.
- 739 Buhmann, D. and Dreybrodt, W. (1985a) The kinetics of calcite dissolution and precipitation in
740 geologically relevant situations of karst areas: 1. Open system. *Chemical Geology* 48, 189-
741 211.

- 742 Buhmann, D. and Dreybrodt, W. (1985b) The kinetics of calcite dissolution and precipitation in
743 geologically relevant situations of karst areas: 2. Closed system. Chemical Geology 53, 109-
744 124.
- 745 Buhmann, D. and Dreybrodt, W. (1987) Calcite dissolution kinetics in the system H₂O-CO₂-
746 CaCO₃ with participation of foreign ions. Chemical Geology 64, 89-102.
- 747 Burdige, D.J., Hu, X. and Zimmerman, R.C. (2010) The widespread occurrence of coupled
748 carbonate dissolution/precipitation in surface sediments on the Bahamas Bank. American
749 Journal of Science 310, 492-521.
- 750 Burdige, D.J. and Zimmerman, R.C. (2002) Impact of sea grass density on carbonate dissolution
751 in Bahamian sediments. Limnology and Oceanography 47, 1751-1763.
- 752 Burdige, D.J., Zimmerman, R.C. and Hu, X. (2008) Rates of carbonate dissolution in permeable
753 sediments estimated from pore-water profiles: The role of sea grasses. Limnology and
754 Oceanography 53, 549.
- 755 Busenberg, E. and Plummer, L.N. (1986) A comparative study of the dissolution and crystal
756 growth kinetics of calcite and aragonite. Studies in Diagenesis 105, 139-168.
- 757 Caldeira, K. and Wickett, M.E. (2003) Oceanography: anthropogenic carbon and ocean pH.
758 Nature 425, 365-365.
- 759 Carriker, M.R., Swann, C.P., Prezant, R.S., and Counts, C.L. (1991) Chemical elements in the
760 aragonitic and calcitic microstructural groups of shell of the oyster *Crassostrea virginica*: A
761 proton probe study. Marine Biology 109, 287-297.
- 762 Casey, W.H. and Sposito, G. (1992) On the temperature dependence of mineral dissolution rates.
763 Geochimica et Cosmochimica Acta 56, 3825-3830.

- 764 Castillo, K.D., Ries, J.B., Bruno, J.F. and Westfield, I.T. (2014) The reef-building coral
765 *Siderastrea siderea* exhibits parabolic responses to ocean acidification and warming.
766 Proceedings of the Royal Society B: Biological Sciences 281, 20141856.
- 767 Chou, L., Garrels, R.M. and Wollast, R. (1989) Comparative study of the kinetics and
768 mechanisms of dissolution of carbonate minerals. Chemical Geology 78, 269-282.
- 769 Cohen A., McCorkle D., de Putron S., A. G.G., and Rose K.A. (2009) Morphological and
770 compositional changes in the skeletons of new coral recruits reared in acidified seawater:
771 insights into the biomineralization response to ocean acidification. Geochemistry
772 Geophysics Geosystems 10, Q07005.
- 773 Cohen, S. and Fine, M. (2012) Measuring gross and net calcification of a reef coral under ocean
774 acidification conditions: methodological considerations. Biogeosciences Discussions 9,
775 8241-8272.
- 776 Comeau, S., Edmunds, P.J., Lantz, C.A., and Carpenter, R.C. (2014) Water flow modulates the
777 response of coral reef communities to ocean acidification. Scientific Reports 4,
778 doi:10.1038/srep06681.
- 779 Comeau, S., Gorsky, G., Alliouane, S. and Gattuso, J.-P. (2010) Larvae of the pteropod
780 *Cavolinia inflexa* exposed to aragonite undersaturation are viable but shell-less. Marine
781 Biology 157, 2341-2345.
- 782 Compton, R.G., Daly, P.J. and Houses, W.A. (1986) The dissolution of Iceland spar crystals: the
783 effect of surface morphology. Journal of Colloid and Interface Science 113, 12-20.
- 784 Compton, R.G. and Pritchard, K.L. (1990) The dissolution of calcite at pH < 7: kinetics and
785 mechanism. Philosophical Transactions of the Royal Society of London: Series A,
786 Mathematical and Physical Sciences 330, 47-70.

- 787 Compton, R.G., Pritchard, K.L. and Unwin, P.R. (1989) The dissolution of calcite in acid waters:
788 mass transport versus surface control. *Freshwater Biology* 22, 285-288.
- 789 Compton, R.G. and Sanders, G.H.W. (1993) The dissolution of calcite in aqueous acid: the
790 influence of humic species. *Journal of Colloid and Interface Science* 158, 439-445.
- 791 Compton, R.G. and Unwin, P.R. (1990) The dissolution of calcite in aqueous solution at pH < 4:
792 kinetics and mechanism. *Philosophical Transactions of the Royal Society of London: Series*
793 *A, Mathematical and Physical Sciences*, 1-45.
- 794 Crenshaw, M.A. (1972) The inorganic composition of molluscan extrapallial fluid. *The*
795 *Biological Bulletin* 143, 506–512.
- 796 Cubillas, P., Köhler, S., Prieto, M., Chaïrat, C. and Oelkers, E.H. (2005) Experimental
797 determination of the dissolution rates of calcite, aragonite, and bivalves. *Chemical Geology*
798 216, 59-77.
- 799 Davies, D.J., Powel, E.N., and Stanton Jr. (1989) Relative rates of shell dissolution and net
800 sediment accumulation - a commentary: can shell beds form by the gradual accumulation of
801 biogenic debris on the sea floor? *Lethaia* 22, 207–212.
- 802 Doney, S.C., Fabry, V.J., Feely, R.A. and Kleypas, J.A. (2009) Ocean acidification: the other
803 CO₂ problem. *Marine Science* 1.
- 804 Donner, S.D. (2009) Coping with commitment: projected thermal stress on coral reefs under
805 different future scenarios. *PLoS One* 4, e5712.
- 806 Dreybrodt, W. (1981) Kinetics of the dissolution of calcite and its applications to karstification.
807 *Chemical Geology* 31, 245-269.
- 808 Dreybrodt, W. and Buhmann, D. (1991) A mass transfer model for dissolution and precipitation
809 of calcite from solutions in turbulent motion. *Chemical Geology* 90, 107-122.

- 810 Dreybrodt, W., Lauckner, J., Zaihua, L., Svensson, U. and Buhmann, D. (1996) The kinetics of
811 the reaction $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^-$ as one of the rate limiting steps for the dissolution
812 of calcite in the system $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$. *Geochimica et Cosmochimica Acta* 60, 3375–
813 3381.
- 814 Eakin, C.M., Kleypas, J. and Hoegh-Guldberg, O. (2008) Global climate change and coral reefs:
815 rising temperatures, acidification and the need for resilient reefs. C. Wilkinson, Status of
816 Coral Reefs of the World, p. 29-34.
- 817 Egleston, E.S., Sabine, C.L. and Morel, F.M. (2010) Revelle revisited: buffer factors that
818 quantify the response of ocean chemistry to changes in DIC and alkalinity. *Global*
819 *Biogeochemical Cycles* 24.
- 820 Eisenlohr, L., Meteva, K., Gabrovšek, F. and Dreybrodt, W. (1999) The inhibiting action of
821 intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in
822 aqueous $\text{H}_2\text{O}-\text{CO}_2$ solutions. *Geochimica et Cosmochimica Acta* 63, 989-1001.
- 823 Fabricius, K.E., Langdon, C., Uthicke, S., Humphrey, C., Noonan, S., De'ath, G., Okazaki, R.,
824 Muehllehner, N., Glas, M.S. and Lough, J.M. (2011) Losers and winners in coral reefs
825 acclimatized to elevated carbon dioxide concentrations. *Nature Climate Change* 1, 165-169.
- 826 Fabry, V.J., Seibel, B.A., Feely, R.A. and Orr, J.C. (2008) Impacts of ocean acidification on
827 marine fauna and ecosystem processes. *ICES Journal of Marine Science* 65, 414-432.
- 828 Feely, R.A., Sabine, C.L., Hernandez-Ayon, J.M., Ianson, D. and Hales, B. (2008) Evidence for
829 upwelling of corrosive 'acidified' water onto the continental shelf. *Science* 320, 1490-1492.
- 830 Finneran, D.W. and Morse, J.W. (2009) Calcite dissolution kinetics in saline waters. *Chemical*
831 *Geology* 268, 137-146.

- 832 Friedman, G.M. (1964) Early diagenesis and lithification in carbonate sediments. *Journal of*
833 *Sedimentary Research* 34.
- 834 Füssel, H.-M. (2010) Review and quantitative analysis of indices of climate change exposure,
835 adaptive capacity, sensitivity, and impacts. World Bank, Washington, DC.
- 836 Garrels, R.M., Thompson, M.E. and Siever, R. (1960) Stability of some carbonates at 25 degrees
837 C and one atmosphere total pressure. *American Journal of Science* 258, 402-418.
- 838 Garrels, R.M., Thompson, M.E. and Siever, R. (1961) Control of carbonate solubility by
839 carbonate complexes. *American Journal of Science* 259, 24-45.
- 840 Garrels, R.M. and Wollast, R. (1978) Equilibrium criteria for two-component solids reacting
841 with fixed composition in an aqueous phase; example, the magnesian calcites; discussion.
842 *American Journal of Science* 278, 1469-1474.
- 843 Gehlen, M., Bassinot, F.C., Chou, L. and McCorkle, D. (2005a) Reassessing the dissolution of
844 marine carbonates: I. Solubility. *Deep Sea Research Part I: Oceanographic Research Papers*
845 52, 1445-1460.
- 846 Gehlen, M., Bassinot, F.C., Chou, L. and McCorkle, D. (2005b) Reassessing the dissolution of
847 marine carbonates: II. Reaction kinetics. *Deep Sea Research Part I: Oceanographic Research*
848 *Papers* 52, 1461-1476.
- 849 Gledhill, D.K. and Morse, J.W. (2004) Dissolution kinetics of calcite in NaCl–CaCl₂–MgCl₂
850 brines at 25° C and 1 bar pCO₂. *Aquatic Geochemistry* 10, 171-190.
- 851 Gledhill, D.K. and Morse, J.W. (2006a) Calcite dissolution kinetics in Na–Ca–Mg–Cl brines.
852 *Geochimica et cosmochimica acta* 70, 5802-5813.
- 853 Gledhill, D.K. and Morse, J.W. (2006b) Calcite solubility in Na–Ca–Mg–Cl brines. *Chemical*
854 *Geology* 233, 249-256.

- 855 Glover, C.P., and S.M. Kidwell (1993) Influence of organic matrix on the post-mortem
856 destruction of molluscan shells. *Journal of Geology* 101, 729-747.
- 857 Gutjahr, A., Dabringhaus, H. and Lacmann, R. (1996) Studies of the growth and dissolution
858 kinetics of the CaCO_3 polymorphs calcite and aragonite II. The influence of divalent cation
859 additives on the growth and dissolution rates. *Journal of Crystal Growth* 158, 310-315.
- 860 Hales, B. and Emerson, S. (1996) Calcite dissolution in sediments of the Ontong-Java Plateau: In
861 situ measurements of pore water O_2 and pH. *Global Biogeochemical Cycles* 10, 527-541.
- 862 Hales, B., Emerson, S. and Archer, D. (1994) Respiration and dissolution in the sediments of the
863 western North Atlantic: estimates from models of in situ microelectrode measurements of
864 porewater oxygen and pH. *Deep Sea Research Part I: Oceanographic Research Papers* 41,
865 695-719.
- 866 Harstad, A. and Stipp, S.L.S. (2007) Calcite dissolution: Effects of trace cations naturally present
867 in Iceland spar calcites. *Geochimica et Cosmochimica Acta* 71, 56-70.
- 868 He, S. and Morse, J.W. (1993) The carbonic acid system and calcite solubility in aqueous Na-K-
869 Ca-Mg-Cl- SO_4 solutions from 0 to 90° C. *Geochimica et Cosmochimica Acta* 57, 3533-
870 3554.
- 871 Hendricks, I.E., Duarte, C.M., Alvarez, M. (2010) Vulnerability of marine biodiversity to ocean
872 acidification: A meta-analysis. *Estuarine, Coastal, and Shelf Science* 86, 157-164.
- 873 Hillner, P.E., Gratz, A.J., Manne, S. and Hansma, P.K. (1992a) Atomic-scale imaging of calcite
874 growth and dissolution in real time. *Geology* 20, 359-362.
- 875 Hillner, P.E., Manne, S., Gratz, A.J. and Hansma, P.K. (1992b) AFM images of dissolution and
876 growth on a calcite crystal. *Ultramicroscopy* 42, 1387-1393.

- 877 Hoegh-Guldberg, O., Mumby, P.J., Hooten, A.J., Steneck, R.S., Greenfield, P., Gomez, E.,
878 Harvell, C.D., Sale, P.F., Edwards, A.J. and Caldeira, K. (2007) Coral reefs under rapid
879 climate change and ocean acidification. *Science* 318, 1737-1742.
- 880 Holcomb M., Venn A.A., Tambutte E., Tambutte S., Allemand D., Trotter J., and McCulloch M.
881 (2014) Coral calcifying fluid pH dictates response to ocean acidification. *Scientific Reports*
882 4, doi:10.1038/srep05207.
- 883 Honjo, S. and Erez, J. (1978) Dissolution rates of calcium carbonate in the deep ocean; an *in-situ*
884 experiment in the North Atlantic Ocean. *Earth and Planetary Science Letters* 40, 287-300.
- 885 Iglesias-Rodriguez, M.D., Halloran, P.R., Rickaby, R.E.M., Hall, I.R., Colmenero-Hidalgo, E.,
886 Gittins, J.R., Green, D.R.H., Tyrrell, T., Gibbs, S.J. and von Dassow, P. (2008)
887 Phytoplankton calcification in a high-CO₂ world. *Science* 320, 336-340.
- 888 IPCC, 2013: Summary for Policymakers. In: *Climate Change 2013: The Physical Science Basis.*
889 *Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental*
890 *Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J.
891 Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University
892 Press, Cambridge, United Kingdom and New York, NY, USA. Jahnke, R.A. and Jahnke,
893 D.B. (2004) Calcium carbonate dissolution in deep sea sediments: Reconciling
894 microelectrode, pore water and benthic flux chamber results. *Geochimica et Cosmochimica*
895 *Acta* 68, 47-59.
- 896 Jokieli, J.P. (2011) Ocean acidification and control of reef coral calcification by boundary layer
897 limitation of proton flux. *Bulletin of Marine Science* 87, 639-657.

- 898 Jordan, G. and Rammensee, W. (1998) Dissolution rates of calcite (1014) obtained by scanning
899 force microscopy: Microtopography-based dissolution kinetics on surfaces with anisotropic
900 step velocities. *Geochimica et Cosmochimica Acta* 62, 941-947.
- 901 Keir, R.S. (1980) The dissolution kinetics of biogenic calcium carbonates in seawater.
902 *Geochimica et Cosmochimica Acta* 44, 241-252.
- 903 Kennish, M.J. and Lutz, R.A. (1999) Calcium carbonate dissolution rates in deep-sea bivalve
904 shells on the East Pacific Rise at 21 N: results of an 8-year in-situ experiment.
905 *Palaeogeography, Palaeoclimatology, Palaeoecology* 154, 293-299.
- 906 Kidwell, S.M. (2001) Preservation of species abundance in marine death assemblages. *Science*
907 294, 1091-1094.
- 908 Kinsey, D.D. (1985) Metabolism, calcification and carbon production. I. System level studies,
909 *Proceedings of the 5th International Coral Reef Congress, Tahiti*, p. 503-542.
- 910 Kleypas, J.A., Buddemeier, R.W., Archer, D., Gattuso, J.-P., Langdon, C. and Opdyke, B.N.
911 (1999) Geochemical consequences of increased atmospheric carbon dioxide on coral reefs.
912 *Science* 284, 118-120.
- 913 Kleypas, J.A., Feely, R.A., Fabry, V.J., Langdon, C., Sabine, C.L. and Robbins, L.L. (2005)
914 Impacts of ocean acidification on coral reefs and other marine calcifiers: a guide for future
915 research (report of a workshop held), p. 18-20.
- 916 Kralj, D. and Brečević, L. (1995) Dissolution kinetics and solubility of calcium carbonate
917 monohydrate. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 96, 287-
918 293.

- 919 Krief S., Hendy E.J., Fine M., Yam R., Meibom A., Foster G.L., and Shemesh A. (2010)
920 Physiological and isotopic responses of scleractinian corals to ocean acidification.
921 *Geochimica et Cosmochimica Acta* 74, 4988-5001.
- 922 Kroeker, K.J., Kordas, R.L., Crim, R., Hendriks, I.E., Ramajo, L., Singh, G.S., Duarte, C.M. and
923 Gattuso, J.P. (2013) Impacts of ocean acidification on marine organisms: quantifying
924 sensitivities and interaction with warming. *Global Change Biology* 19, 1884-1896.
- 925 Kroeker, K.J., Kordas, R.L., Crim, R.N. and Singh, G.G. (2010) Meta-analysis reveals negative
926 yet variable effects of ocean acidification on marine organisms. *Ecology Letters* 13, 1419-
927 1434.
- 928 Kuffner, I.B., Brock, J.C., Grober-Dunsmore, R., Hickey, T.D., Bonito, V., Bracone, J.E. and
929 Wright, C.W. (2008) Biological communities and geomorphology of patch reefs in Biscayne
930 National Park, Florida, USA, in Report OFR 2008-1330. US Geological Survey.
- 931 Lafon, G.M. (1978) Equilibrium criteria for two-component solids reacting with fixed
932 composition in an aqueous phase; example, the magnesian calcites; discussion. *American*
933 *Journal of Science* 278, 1455-1468.
- 934 Land, L.S. (1967) Diagenesis of skeletal carbonates. *Journal of Sedimentary Research* 37.
- 935 Langdon, C., Takahashi, T., Sweeney, C., Chipman, D., Goddard, J., Marubini, F., Aceves, H.,
936 Barnett, H. and Atkinson, M.J. (2000) Effect of calcium carbonate saturation state on the
937 calcification rate of an experimental coral reef. *Global Biogeochemical Cycles* 14, 639-654.
- 938 Lasaga, A.C. and Luttge, A. (2001) Variation of crystal dissolution rate based on a dissolution
939 stepwave model. *Science* 291, 2400-2404.

- 940 Lea, A.S., Amonette, J.E., Baer, D.R., Liang, Y. and Colton, N.G. (2001) Microscopic effects of
941 carbonate, manganese, and strontium ions on calcite dissolution. *Geochimica et*
942 *Cosmochimica Acta* 65, 369-379.
- 943 Leclercq, N., Gattuso, J.-P. and Jaubert, J. (2002) Primary production, respiration, and
944 calcification of a coral reef mesocosm under increased CO₂ partial pressure. *Limnology and*
945 *Oceanography* 47, 558-564.
- 946 Lewis, E. and Wallace, D.W.R. (1998) CO₂SYS: Program developed for CO₂ system
947 calculations, ORNL/CDIAC-105 ed. Carbon Dioxide Information Analysis Center, Oak
948 Ridge National Laboratory, U.S Department of Energy, Oak Ridge, Tennessee.
- 949 Liang, Y. and Baer, D.R. (1997) Anisotropic dissolution at the CaCO₃ (1014)—water interface.
950 *Surface Science* 373, 275-287.
- 951 Liang, Y., Baer, D.R., McCoy, J.M., Amonette, J.E. and Lafemina, J.P. (1996) Dissolution
952 kinetics at the calcite-water interface. *Geochimica et Cosmochimica Acta* 60, 4883-4887.
- 953 Liu, Z. and Dreybrod, W. (1997) Dissolution kinetics of calcium carbonate minerals in H₂O-CO₂
954 solutions in turbulent flow: The role of the diffusion boundary layer and the slow reaction
955 H₂O+ CO₂→ H⁺ + HCO₃⁻. *Geochimica et Cosmochimica Acta* 61, 2879-2889.
- 956 Lowenstam, H.A. and Abbott, D.P. (1975) Vaterite: a mineralization product of the hard tissues
957 of a marine organism (Ascidacea). *Science* 188, 363-365.
- 958 MacInnis, I.N. and Brantley, S.L. (1992) The role of dislocations and surface morphology in
959 calcite dissolution. *Geochimica et Cosmochimica Acta* 56, 1113-1126.
- 960 MacInnis, I.N. and Brantley, S.L. (1993) Development of etch pit size distributions on dissolving
961 minerals. *Chemical Geology* 105, 31-49.

- 962 Mackenzie, F.T., Bischoff, W.D., Bishop, F.C., Loijens, M., Schoonmaker, J. and Wollast, R.
963 (1983) Magnesian calcites; low-temperature occurrence, solubility and solid-solution
964 behavior. *Reviews in Mineralogy and Geochemistry* 11, 97-144.
- 965 Mackenzie, F.T. and Pigott, J.D. (1981) Tectonic controls of Phanerozoic sedimentary rock
966 cycling. *Journal of the Geological Society* 138, 183-196.
- 967 McCulloch M., Trotter J., Montagna P., Falter J., Dunbar R., Freiwald A., Försterra G., López
968 Correa M., Maier C., Rüggeberg A., et al. (2012) Resilience of cold-water scleractinian
969 corals to ocean acidification: Boron isotopic systematics of pH and saturation state up-
970 regulation. *Geochimica et Cosmochimica Acta* 87, 21-34.
- 971 Milliman, J.D. (1978) Dissolution of calcium carbonate in the Sargasso Sea (Northwest
972 Atlantic). Woods Hole Oceanographic Institution.
- 973 Morse, J.W. (1978) Dissolution kinetics of calcium carbonate in sea water; VI, The near-
974 equilibrium dissolution kinetics of calcium carbonate-rich deep sea sediments. *American*
975 *Journal of Science* 278, 344-353.
- 976 Morse, J.W. (1983) The kinetics of calcium carbonate dissolution and precipitation. *Reviews in*
977 *Mineralogy and Geochemistry* 11, 227-264.
- 978 Morse, J.W. (1986) The surface chemistry of calcium carbonate minerals in natural waters: an
979 overview. *Marine Chemistry* 20, 91-112.
- 980 Morse, J.W., Andersson, A.J. and Mackenzie, F.T. (2006) Initial responses of carbonate-rich
981 shelf sediments to rising atmospheric pCO₂ and 'ocean acidification': role of high Mg-
982 calcites. *Geochimica et Cosmochimica Acta* 70, 5814-5830.
- 983 Morse, J.W. and Arvidson, R.S. (2002) The dissolution kinetics of major sedimentary carbonate
984 minerals. *Earth Science Reviews* 58, 51-84.

- 985 Morse, J.W., Arvidson, R.S. and Lüttge, A. (2007) Calcium carbonate formation and dissolution.
986 Chemical Reviews 107, 342-381.
- 987 Morse, J.W. and Berner, R.A. (1972) Dissolution kinetics of calcium carbonate in sea water; I, A
988 kinetic origin for the lysocline. American Journal of Science 272, 840-851.
- 989 Morse, J.W., de Kanel, J. and Harris, K. (1979) Dissolution kinetics of calcium carbonate in
990 seawater: VII. The dissolution kinetics of synthetic aragonite and pteropod tests. American
991 Journal of Science 279, 488-502.
- 992 Morse, J.W. and Mackenzie, F.T. (1990) Geochemistry of sedimentary carbonates. Elsevier.
- 993 Mucci, A. (1983) The solubility of calcite and aragonite in seawater at various salinities,
994 temperatures, and one atmosphere total pressure. American Journal of Science 283, 780-
995 799.
- 996 Mucci, A., Canuel, R. and Zhong, S. (1989) The solubility of calcite and aragonite in sulfate-free
997 seawater and the seeded growth kinetics and composition of the precipitates at 25° C.
998 Chemical Geology 74, 309-320.
- 999 Mucci, A. and Morse, J.W. (1984) The solubility of calcite in seawater solutions of various
1000 magnesium concentrations, $I_t = 0.697$ m at 25° C and one atmosphere total pressure.
1001 Geochimica et Cosmochimica Acta 48, 815-822.
- 1002 Nash, M.C., Opdyke, B.N., Troitzsch, U., Russell, B.D., Adey, W.H., Kato, A., Diaz-Pulido, G.,
1003 Brent, C., Gardner, M., Prichard, J., and Kline, D.I. (2013) Dolomite-rich coralline algae in
1004 reefs resist dissolution in acidified conditions. Nature Climate Change 3, 268-272.
- 1005 Nestaas, I. and Terjesen, S. (1969) Inhibiting effect of scandium ions upon dissolution of calcium
1006 carbonate. Acta Chemica Scandinavica 23, 2519-.

- 1007 Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A.,
1008 Gruber, N., Ishida, A. and Joos, F. (2005) Anthropogenic ocean acidification over the
1009 twenty-first century and its impact on calcifying organisms. *Nature* 437, 681-686.
- 1010 Peterson, M.N.A. (1966) Calcite: rates of dissolution in a vertical profile in the central Pacific.
1011 *Science* 154, 1542-1544.
- 1012 Pickett, M., Andersson, A.J. (2015) Dissolution rates of biogenic carbonates in natural seawater
1013 at different pCO₂ conditions: a laboratory study. *Aquatic Geochemistry*. 10.1007/s10498-
1014 015-9261-3
- 1015 Plath, D.C., Johnson, K.S. and Pytkowicz, R.M. (1980) The solubility of calcite—probably
1016 containing magnesium—in seawater. *Marine Chemistry* 10, 9-29.
- 1017 Plummer, L. and Wigley, T. (1976) The dissolution of calcite in CO₂-saturated solutions at 25° C
1018 and 1 atmosphere total pressure. *Geochimica et Cosmochimica Acta* 40, 191-201.
- 1019 Plummer, L.N. and Busenberg, E. (1982) The solubilities of calcite, aragonite and vaterite in
1020 CO₂-H₂O solutions between 0 and 90° C, and an evaluation of the aqueous model for the
1021 system CaCO₃-CO₂-H₂O. *Geochimica et Cosmochimica Acta* 46, 1011-1040.
- 1022 Plummer, L.N. and Mackenzie, F.T. (1974) Predicting mineral solubility from rate data;
1023 application to the dissolution of magnesian calcites. *American Journal of Science* 274, 61-
1024 83.
- 1025 Plummer, L.N., Parkhurst, D.L. and Wigley, T.M.L. (1979) Critical review of the kinetics of
1026 calcite dissolution and precipitation.
- 1027 Plummer, L.N., Wigley, T.M.L. and Parkhurst, D.L. (1978) The kinetics of calcite dissolution in
1028 CO₂-water systems at 5° to 60° C and 0.0 to 1.0 atm CO₂. *American Journal of Science* 278,
1029 179-216.

- 1030 Pokrovsky, O.S., Golubev, S.V. and Schott, J. (2005) Dissolution kinetics of calcite, dolomite
1031 and magnesite at 25° C and 0 to 50 atm pCO₂. *Chemical Geology* 217, 239-255.
- 1032 Pokrovsky, O.S., Golubev, S.V., Schott, J. and Castillo, A. (2009) Calcite, dolomite and
1033 magnesite dissolution kinetics in aqueous solutions at acid to circumneutral pH, 25 to 150°
1034 C and 1 to 55 atm pCO₂: new constraints on CO₂ sequestration in sedimentary basins.
1035 *Chemical Geology* 265, 20-32.
- 1036 Pokrovsky, O.S. and Schott, J. (1999) Processes at the magnesium-bearing carbonates/solution
1037 interface: II. kinetics and mechanism of magnesite dissolution. *Geochimica et*
1038 *Cosmochimica Acta* 63, 881-897.
- 1039 Powell, E.N., Callender, W.R., Staff, G.M., Parsons-Hubbard, K.M., Brett, C.E., Walker, S.E.,
1040 Raymond, A., and Ashton-Alcox, K.A. (2008) Molluscan shell condition after eight years
1041 on the sea floor—taphonomy in the Gulf of Mexico and Bahamas. *Journal of Shellfish*
1042 *Research* 27, 191-225.
- 1043 Raven, J., Caldeira, K., Elderfield, H., Hoegh-Guldberg, O., Liss, P., Riebesell, U., Shepherd, J.,
1044 Turley, C. and Watson, A. (2005) Ocean acidification due to increasing atmospheric carbon
1045 dioxide. *The Royal Society*.
- 1046 Ries, J. (2010) Review: geological and experimental evidence for secular variation in seawater
1047 Mg/Ca (calcite-aragonite seas) and its effects on marine biological calcification.
1048 *Biogeosciences* 7, 2795-2849.
- 1049 Ries, J. (2011a) Acid ocean cover up. *Nature Clim. Change* 1, 294-295.
- 1050 Ries, J.B. (2011b) Skeletal mineralogy in a high-CO₂ world. *Journal of Experimental Marine*
1051 *Biology and Ecology* 403, 54-64.
- 1052 Ries, J.B. (2012) A sea butterfly flaps its wings. *Nature Geoscience* 5, 845-846.

- 1053 Ries, J.B., Cohen, A.L. and McCorkle, D.C. (2009) Marine calcifiers exhibit mixed responses to
1054 CO₂-induced ocean acidification. *Geology* 37, 1131-1134.
- 1055 Rodolfo-Metalpa, R., Houlbrèque, F., Tambutté, É., Boisson, F., Baggini, C., Patti, F.P., Jeffree,
1056 R., Fine, M., Foggo, A. and Gattuso, J.P. (2011) Coral and mollusc resistance to ocean
1057 acidification adversely affected by warming. *Nature Climate Change* 1, 308-312.
- 1058 Rodolfo-Metalpa, R., Martin, S., Ferrier-Pagès, C. and Gattuso, J.-P. (2010) Response of the
1059 temperate coral *Cladocora caespitosa* to mid- and long-term exposure to pCO₂ and
1060 temperature levels projected for the year 2100 AD. *Biogeosciences* 7, 289-300.
- 1061 Roy, R.N., Roy, L.N., Vogel, K.M., Porter-Moore, C., Pearson, T., Good, C.E., Millero, F.J. and
1062 Campbell, D.M. (1993) The dissociation constants of carbonic acid in seawater at salinities
1063 5 to 45 and temperatures 0 to 45° C. *Marine Chemistry* 44, 249-267.
- 1064 Rude, P.D. and Aller, R.C. (1991) Fluorine mobility during early diagenesis of carbonate
1065 sediment: An indicator of mineral transformations. *Geochimica et Cosmochimica Acta* 55,
1066 2491-2509.
- 1067 Sandberg, P.A. (1983) An oscillating trend in Phanerozoic non-skeletal carbonate mineralogy.
1068 *Nature* 305, 19-22.
- 1069 Schmalz, R. (1965) Brucite in carbonate secreted by the red alga *Goniolithon* sp. *Science* 149,
1070 993-996.
- 1071 Schott, J., Brantley, S., Crerar, D., Guy, C., Borcsik, M. and Willaime, C. (1989) Dissolution
1072 kinetics of strained calcite. *Geochimica et Cosmochimica Acta* 53, 373-382.
- 1073 Schott, J., Pokrovsky, O.S. and Oelkers, E.H. (2009) The link between mineral
1074 dissolution/precipitation kinetics and solution chemistry. *Reviews in Mineralogy and*
1075 *Geochemistry* 70, 207-258.

- 1076 Schroeder, J.H. (1969) Experimental dissolution of calcium, magnesium, and strontium from
1077 recent biogenic carbonates: a model of diagenesis. *Journal of Sedimentary Research* 39.
- 1078 Shiraki, R., Rock, P.A. and Casey, W.H. (2000) Dissolution kinetics of calcite in 0.1 M NaCl
1079 solution at room temperature: an atomic force microscopic (AFM) study. *Aquatic*
1080 *Geochemistry* 6, 87-108.
- 1081 Silverman, J., Lazar, B. and Erez, J. (2007a) Community metabolism of a coral reef exposed to
1082 naturally varying dissolved inorganic nutrient loads. *Biogeochemistry* 84, 67-82.
- 1083 Silverman, J., Lazar, B. and Erez, J. (2007b) Effect of aragonite saturation, temperature, and
1084 nutrients on the community calcification rate of a coral reef. *Journal of Geophysical*
1085 *Research: Oceans* (1978–2012) 112.
- 1086 Sjöberg, E.L. (1976) A fundamental equation for calcite dissolution kinetics. *Geochimica et*
1087 *Cosmochimica Acta* 40, 441-447.
- 1088 Sjöberg, E.L. (1978) Kinetics and mechanism of calcite dissolution in aqueous solutions at low
1089 temperatures.
- 1090 Sjöberg, E.L. and Rickard, D.T. (1984) Temperature dependence of calcite dissolution kinetics
1091 between 1 and 62° C at pH 2.7 to 8.4 in aqueous solutions. *Geochimica et Cosmochimica*
1092 *Acta* 48, 485-493.
- 1093 Smith, A.M. (2014) Growth and calcification of marine bryozoans in a changing ocean. *The*
1094 *Biological Bulletin* 226, 203-210.
- 1095 Suess, E. (1970) Interaction of organic compounds with calcium carbonate—I. Association
1096 phenomena and geochemical implications. *Geochimica et Cosmochimica Acta* 34, 157-168.
- 1097 Svensson, U. and Dreybrodt, W. (1992) Dissolution kinetics of natural calcite minerals in CO₂-
1098 water systems approaching calcite equilibrium. *Chemical Geology* 100, 129-145.

- 1099 Tans, P. and Keeling, R. (2013) Trends in atmospheric carbon dioxide, National Oceanic and
1100 Atmospheric Administration Earth System Research Laboratory.
- 1101 Taylor, P.D., James, N.P., Bone, Y., Kuklinski, P. and Kyser, T.K. (2009) Evolving mineralogy
1102 of cheilostome bryozoans. *Palaios* 24, 440-452.
- 1103 Teng, H.H. (2004) Controls by saturation state on etch pit formation during calcite dissolution.
1104 *Geochimica et Cosmochimica Acta* 68, 253-262.
- 1105 Teng, H.H. and Dove, P.M. (1997) Surface site-specific interactions of aspartate with calcite
1106 during dissolution: implications for biomineralization. *American Mineralogist* 82, 878-887.
- 1107 Terjesen, S.G., Erga, O., Thorsen, G. and Ve, A. (1961) Phase boundary processes as rate
1108 determining steps in reactions between solids and liquids: The inhibitory action of metal
1109 ions on the formation of calcium bicarbonate by the reaction of calcite with aqueous carbon
1110 dioxide. *Chemical Engineering Science* 14, 277-288.
- 1111 Thorstenson, D. and Plummer, L.N. (1978) Equilibrium criteria for two-component solids
1112 reacting with fixed composition in an aqueous phase; example, the magnesian calcites;
1113 reply. *American Journal of Science* 278, 1478-1488.
- 1114 Thorstenson, D.C. and Plummer, L.N. (1977) Equilibrium criteria for two-component solids
1115 reacting with fixed composition in an aqueous phase; example, the magnesian calcites.
1116 *American Journal of Science* 277, 1203-1223.
- 1117 Tribollet, A., Godinot, C., Atkinson, M. and Langdon, C. (2009) Effects of elevated pCO₂ on
1118 dissolution of coral carbonates by microbial euendoliths. *Global Biogeochemical Cycles* 23.
- 1119 Trotter J., Montagna P., McCulloch M., Silenzi S., Reynaud S., Mortimer G., Martin S., Ferrier-
1120 Pagès C., Gattuso J.-P., and Rodolfo-Metalpa R. (2011) Quantifying the pH ‘vital effect’ in

- 1121 the temperate zooxanthellate coral *Cladocora caespitosa*: Validation of the boron seawater
- 1122 pH proxy. Earth and Planetary Science Letters 303, 163-173.
- 1123 Tynan, S. and Opdyke, B.N. (2011) Effects of lower surface ocean pH upon the stability of
- 1124 shallow water carbonate sediments. Science of the Total Environment 409, 1082-1086.
- 1125 Van Cappellen, P., Charlet, L., Stumm, W. and Wersin, P. (1993) A surface complexation model
- 1126 of the carbonate mineral-aqueous solution interface. Geochimica et Cosmochimica Acta 57,
- 1127 3505-3518.
- 1128 Venn A., Tambutté E., Holcomb M., Allemand D., and Tambutté S. (2011) Live tissue imaging
- 1129 shows reef corals elevate pH under their calcifying tissue relative to seawater. PLoS ONE 6,
- 1130 e20013.
- 1131 Vinson, M.D. and Lüttge, A. (2005) Multiple length-scale kinetics: an integrated study of calcite
- 1132 dissolution rates and strontium inhibition. American Journal of Science 305, 119-146.
- 1133 Waldbusser, G.G., Steenson, R.A., and Green, M.A. (2011) Oyster shell dissolution rates in
- 1134 estuarine waters: effects of pH and shell legacy. Journal of Shellfish Research 30, 659-669.
- 1135 Walter, L.M. (1985) Relative reactivity of skeletal carbonates during dissolution: implications
- 1136 for diagenesis.
- 1137 Walter, L.M., Bischof, S.A., Patterson, W.P., Lyons, T.W., O'Nions, R.K., Gruszczynski, M.,
- 1138 Sellwood, B.W. and Coleman, M.L. (1993) Dissolution and recrystallization in modern
- 1139 shelf carbonates: evidence from pore water and solid phase chemistry. Philosophical
- 1140 Transactions of the Royal Society of London. Series A: Physical and Engineering Sciences
- 1141 344, 27-36.

- 1142 Walter, L.M. and Burton, E.A. (1990) Dissolution of recent platform carbonate sediments in
1143 marine pore fluids. *American Journal of Science* 290, 601-643.
- 1144 Walter, L.M. and Hanor, J.S. (1979) Effect of orthophosphate on the dissolution kinetics of
1145 biogenic magnesian calcites. *Geochimica et Cosmochimica Acta* 43, 1377-1385.
- 1146 Walter, L.M. and Morse, J.W. (1984) Reactive surface area of skeletal carbonates during
1147 dissolution: effect of grain size. *Journal of Sedimentary Research* 54.
- 1148 Walter, L.M. and Morse, J.W. (1985) The dissolution kinetics of shallow marine carbonates in
1149 seawater: A laboratory study. *Geochimica et Cosmochimica Acta* 49, 1503-1513.
- 1150 Weiner, S., Levi-Kalisman, Y., Raz, S. and Addadi, L. (2003) Biologically formed amorphous
1151 calcium carbonate. *Connective Tissue Research* 44, 214-218.
- 1152 Weyl, P.K. (1958) The solution kinetics of calcite. *The Journal of Geology*, 163-176.
- 1153 Weyl, P.K. (1965) The solution kinetics of calcite, 428 ed. Shell Development Company p. 1-59.
- 1154 White, A.F. and Peterson, M.L. (1990) Role of reactive-surface-area characterization in
1155 geochemical kinetic models, ACS symposium series. Oxford University Press, p. 461-475.
- 1156 Wollast, R. (1990) Rate and mechanism of dissolution of carbonates in the system CaCO_3 -
1157 MgCO_3 , *Aquatic Chemical Kinetics: Reaction Rates of Processes in Natural Waters*. John
1158 Wiley & Sons,, New York, p. 431-445.
- 1159 Wollast, R. and Reinhard-Derie, D. (1977) Equilibrium and mechanism of dissolution of Mg-
1160 calcites. *The Fate of Fossil Fuel CO_2* , 479-493.
- 1161 Wood, H.L., Spicer, J.I. and Widdicombe, S. (2008) Ocean acidification may increase
1162 calcification rates, but at a cost. *Proceedings of the Royal Society B: Biological Sciences*
1163 275, 1767-1773.

Xu, J., Fan, C. and Teng, H.H. (2012) Calcite dissolution kinetics in view of Gibbs free energy, dislocation density, and $p\text{CO}_2$. *Chemical Geology* 322, 11-18.

Yates, K. and Halley, R. (2006) CO_3^{2-} concentration and $p\text{CO}_2$ thresholds for calcification and dissolution on the Molokai reef flat, Hawaii. *Biogeosciences Discussions* 3, 123-154.

8. FIGURE CAPTIONS

Figure 1. Gross dissolution rate (%-weight per day) as a function of aragonite saturation state (Ω_A) at 10.1 °C (± 0.02) (solid lines, closed circles) and 25.0 °C (± 0.02) (dashed lines, open circles) for ten species of marine calcifiers. Horizontal dashed lines mark calcification-dissolution divide.

Figure 2. Effects of temperature (10, 25 °C) on rates of gross dissolution at $\Omega_A = 0.6$ for ten species of marine calcifiers. Rate of gross dissolution at 25° C is higher than at 10° C ($p < 0.05$) for all species. Magnitude of temperature effect on dissolution rate is generally proportional to polymorph solubility (high-Mg calcite > aragonite > low-Mg calcite). Inset table shows standard errors (SE) of gross dissolution rates. ‘A’ – aragonite; ‘LMC’ – low-Mg calcite; ‘HMC’ – high-Mg calcite.

Figure 3. Gross dissolution (open circle; estimated from this study), gross calcification (closed circle; net calcification minus gross dissolution), and net calcification [‘x’; from Ries et al. (2009) and Castillo et al. (2014)] response curves [aragonite saturation state (Ω_A) vs. %-weight change per day] at 25.0°C (± 0.02) for eight species of marine calcifiers. Error bars represent standard error.

Table 1

TABLE 1. Average calculated [$p\text{CO}_2$ of gas in equilibrium with seawater ($p\text{CO}_{2(\text{gas-e})}$), pH (seawater scale, pH_{SW}), carbonate ion concentration ($[\text{CO}_3^{2-}]$), bicarbonate ion concentration ($[\text{HCO}_3^-]$), dissolved CO_2 ($[\text{CO}_2]_{(\text{SW})}$), and aragonite saturation state (Ω_{A})] and measured [salinity (Sal), temperature (T), pH, total alkalinity (TA), and dissolved inorganic carbon (DIC)] seawater parameters. SD = standard deviation; N = number of observations.

		497 $\mu\text{atm}/$ 10.1°C	535 $\mu\text{atm}/$ 24.9°C	4144 $\mu\text{atm}/$ 10.1°C	4870 $\mu\text{atm}/$ 24.9°C	5841 $\mu\text{atm}/$ 10.0°C	9212 $\mu\text{atm}/$ 25.0°C
CALCULATED PARAMETERS							
$p\text{CO}_{2(\text{gas-e})}$	(μatm)	497	535	4144	4870	5841	9212
	SD	79	76	1194	1045	1323	1839
	Range	386 - 632	417 - 701	2111 - 5730	3598 - 7723	2395 - 7497	5323 - 12433
	N	20	21	20	21	21	20
pH_{SW}		8.08	8.03	7.26	7.19	7.12	6.96
	SD	0.06	0.05	0.14	0.09	0.12	0.10
	Range	7.98 - 8.18	7.94 - 8.12	7.09 - 7.55	6.98 - 7.31	6.98 - 7.48	6.83 - 7.18
	N	20	21	20	21	21	20
$[\text{CO}_3^{2-}]$	(μM)	198	284	37	54	27	36
	SD	24	24	15	12	10	9
	Range	156 - 241	244 - 317	22 - 71	31 - 73	18 - 59	24 - 56
	N	20	21	20	21	21	20
$[\text{HCO}_3^-]$	(μM)	2629	2297	3154	2980	3261	3315
	SD	97	72	125	94	158	260
	Range	2488 - 2795	2172 - 2448	2920 - 3304	2813 - 3148	3064 - 3486	2917 - 3706
	N	20	21	20	21	21	20
$[\text{CO}_2]_{(\text{SW})}$	(μM)	22	15	184	141	260	264
	SD	4	2	53	30	59	52
	Range	17 - 28	12 - 20	94 - 254	103 - 223	106 - 333	153 - 357
	N	20	21	20	21	21	20
Ω_{A}		3.0	4.6	0.6	0.9	0.4	0.6
	SD	0.4	0.4	0.2	0.2	0.1	0.2
	Range	2.4 - 3.7	3.9 - 5.1	0.3 - 1.1	0.5 - 1.2	0.3 - 0.9	0.4 - 0.9
	N	20	21	20	21	21	20
MEASURED PARAMETERS							
Sal	(psu)	32.03	32.07	31.96	32.02	32.01	32.06
	SD	0.10	0.10	0.09	0.22	0.08	0.12
	Range	31.80 - 32.20	31.90 - 32.30	31.80 - 32.20	31.50 - 32.30	31.90 - 32.20	31.80 - 32.30
	N	48	48	48	48	48	48
Temp	(°C)	10.1	24.9	10.1	24.9	10.0	25.0
	SD	0.2	0.2	0.1	0.2	0.2	0.2
	Range	9.7 - 10.6	24.3 - 25.2	9.9 - 10.6	24.2 - 25.2	9.7 - 10.5	24.8 - 26.1
	N	48	48	48	48	48	48
TA	(μM)	3087	2951	3235	3103	3317	3432
	SD	92	45	140	109	161	285
	Range	2983 - 3287	2897 - 3018	2972 - 3451	2899 - 3292	3116 - 3547	2982 - 3931
	N	21	21	21	21	21	21
DIC	(μM)	2847	2595	3381	3175	3520	3625
	SD	92	58	130	95	187	293
	Range	2723 - 3015	2501 - 2713	3180 - 3585	3024 - 3365	3140 - 3825	3190 - 4030
	N	21	21	21	21	21	21

Table 2

TABLE 2. Summary of statistical parameters for species-specific non-linear mixed effects models of dissolution rate. **(A)** Fixed effects parameters of the general exponential asymptotic function ($y = B_0 - B_2 \cdot e^{B_1 \cdot x}$) used to model dissolution rate (y) as a function of aragonite saturation state (x) and temperature (T). $B_0 = b_0.int + b_0.temp + u_0$; $B_1 = b_1.int + b_1.temp + u_1$; SE = standard error; DF = degrees of freedom. **(B)** Species-specific random effects parameters u_0 and u_1 with condensed equations used to model species-specific dissolution rate (y) as a function of aragonite saturation state (Ω_A) and temperature (T).

(A)

PARAMETER	VALUE	SE	DF	T-VALUE	P-VALUE
B₂	0.6379	0.1128	183	5.6575	0.0000
b₀.int	-0.0250	0.0088	183	-2.8284	0.0052
b₁.int	-5.0299	0.6305	183	-7.9777	0.0000
b₀.temp	0.0012 · T + 0.0119	0.0063	183	-2.8167	0.0054
b₁.temp	0.0816 · T + 0.8155	0.2035	183	6.0101	0.0000

(B)

SPECIMEN	SCIENTIFIC NAME	u_0	u_1	FINAL CONDENSED EQUATION
American oyster	<i>Crassostrea virginicus</i>	0.0129	-1.5334	$y = 0.0015 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-6.6214 \cdot \Omega_A + 0.0816 \cdot T \cdot \Omega_A)$
Ivory barnacle	<i>Balanus eburneus</i>	0.0300	-1.8032	$y = -0.0002 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-7.3788 \cdot \Omega_A + 0.0816 \cdot T \cdot \Omega_A)$
Blue mussel	<i>Mytilus edulis</i>	-0.0302	0.2137	$y = 0.0169 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-7.6486 \cdot \Omega_A + 0.0816 \cdot T \cdot \Omega_A)$
Conch	<i>Strombus alatus</i>	-0.0162	2.4637	$y = 0.0050 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-6.7489 \cdot \Omega_A + 0.0816 \cdot T \cdot \Omega_A)$
Tropical coral	<i>Siderastrea siderea</i>	0.0181	-0.9035	$y = -0.0255 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-6.1874 \cdot \Omega_A + 0.0816 \cdot T \cdot x)$
Temperate coral	<i>Oculina arbuscula</i>	0.0209	-1.1125	$y = -0.0434 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-5.6317 \cdot \Omega_A + 0.0816 \cdot T \cdot \Omega_A)$
Hard clam	<i>Mercenaria mercenaria</i>	0.0147	-0.7760	$y = 0.0078 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-6.9580 \cdot \Omega_A + 0.0816 \cdot T \cdot \Omega_A)$
Soft clam	<i>Mya arenaria</i>	0.0049	2.1016	$y = 0.0045 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-4.5811 \cdot \Omega_A + 0.0816 \cdot T \cdot \Omega_A)$
Branching bryozoan	<i>Schizoporella errata</i>	0.0176	1.2643	$y = -0.0293 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-3.3817 \cdot \Omega_A + 0.0816 \cdot T \cdot \Omega_A)$
Coralline red alga	<i>Neogoniolithon</i> sp.	-0.0124	-0.3420	$y = -0.0082 - 0.0012 \cdot T - 0.6379 \cdot \text{EXP}(-3.7439 \cdot \Omega_A + 0.0816 \cdot T \cdot \Omega_A)$

Table 3

TABLE 3. Species-specific best-fit regressions used to model gross dissolution rate (y) as a function of aragonite saturation state (Ω_A) at 10.1 °C ($\pm$ 0.02) and 25.0 °C ($\pm$ 0.02).

SPECIMEN	SCIENTIFIC NAME	TEMPERATURE (°C)	GROSS DISSOLUTION REGRESSION
American oyster	<i>Crassostrea virginicus</i>	10	$y = -0.010 - 0.638 \cdot \text{EXP}(-6.621 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.028 - 0.638 \cdot \text{EXP}(-6.621 \cdot \Omega_A + 2.039 \cdot \Omega_A)$
Ivory barnacle	<i>Balanus eburneus</i>	10	$y = -0.012 - 0.638 \cdot \text{EXP}(-7.379 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.030 - 0.638 \cdot \text{EXP}(-7.379 \cdot \Omega_A + 2.039 \cdot \Omega_A)$
Blue mussel	<i>Mytilus edulis</i>	10	$y = 0.005 - 0.638 \cdot \text{EXP}(-7.649 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.013 - 0.638 \cdot \text{EXP}(-7.649 \cdot \Omega_A + 2.039 \cdot \Omega_A)$
Conch	<i>Strombus alatus</i>	10	$y = -0.007 - 0.638 \cdot \text{EXP}(-6.749 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.025 - 0.638 \cdot \text{EXP}(-6.749 \cdot \Omega_A + 2.039 \cdot \Omega_A)$
Tropical coral	<i>Siderastrea siderea</i>	10	$y = -0.037 - 0.638 \cdot \text{EXP}(-6.187 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.055 - 0.638 \cdot \text{EXP}(-6.187 \cdot \Omega_A + 2.039 \cdot \Omega_A)$
Temperate coral	<i>Oculina arbuscula</i>	10	$y = -0.055 - 0.638 \cdot \text{EXP}(-5.632 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.073 - 0.638 \cdot \text{EXP}(-5.632 \cdot \Omega_A + 2.039 \cdot \Omega_A)$
Hard clam	<i>Mercenaria mercenaria</i>	10	$y = -0.004 - 0.638 \cdot \text{EXP}(-6.958 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.022 - 0.638 \cdot \text{EXP}(-6.958 \cdot \Omega_A + 2.039 \cdot \Omega_A)$
Soft clam	<i>Mya arenaria</i>	10	$y = -0.007 - 0.638 \cdot \text{EXP}(-4.581 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.025 - 0.638 \cdot \text{EXP}(-4.581 \cdot \Omega_A + 2.039 \cdot \Omega_A)$
Branching bryozoan	<i>Schizoporella errata</i>	10	$y = -0.041 - 0.638 \cdot \text{EXP}(-3.382 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.059 - 0.638 \cdot \text{EXP}(-3.382 \cdot \Omega_A + 2.039 \cdot \Omega_A)$
Coralline red alga	<i>Neogoniolithon</i> sp.	10	$y = -0.020 - 0.638 \cdot \text{EXP}(-3.744 \cdot \Omega_A + 0.816 \cdot \Omega_A)$
		25	$y = -0.038 - 0.638 \cdot \text{EXP}(-3.744 \cdot \Omega_A + 2.039 \cdot \Omega_A)$

Table 4

TABLE 4. Estimated gross dissolution rates (this study), previously derived net calcification rates (Ries et al., 2009 – all species except *S. siderea*; Castillo et al., 2014 – *S. siderea*), and estimated gross calcification rates (net calcification minus gross dissolution) for eight species of marine calcifiers at 25.0 °C (± 0.02) at Ω_A employed by Ries et al. (2009) and Castillo et al. (2014)

SPECIMEN	SCIENTIFIC NAME	SATURATION STATE	GROSS DISSOLUTION REGRESSION	GROSS DISSOLUTION (%-wt per day)	NET CALCIFICATION RATE (%-wt per day)	CALCULATED GROSS CALCIFICATION (%-wt per day)
American oyster	<i>Crassostrea virginica</i>	2.63	$y = -0.028 - 0.638 \cdot \text{EXP}(-6.621 \cdot \Omega_A + 2.039 \cdot \Omega_A)$	-0.02817	0.03167	0.05983
		2.11		-0.02820	0.02667	0.05487
		1.43		-0.02907	0.01833	0.04740
		0.71		-0.05281	0.00500	0.05781
Blue mussel	<i>Mytilus edulis</i>	2.63	$y = -0.013 - 0.638 \cdot \text{EXP}(-7.649 \cdot \Omega_A + 2.039 \cdot \Omega_A)$	-0.01279	0.07333	0.08612
		2.11		-0.01280	0.05167	0.06446
		1.43		-0.01300	0.06000	0.07300
		0.71		-0.02468	0.05167	0.07634
Conch	<i>Strombus alatus</i>	2.28	$y = -0.025 - 0.638 \cdot \text{EXP}(-6.749 \cdot \Omega_A + 2.039 \cdot \Omega_A)$	-0.02473	0.03333	0.05806
		1.93		-0.02478	0.01333	0.03812
		1.51		-0.02523	0.02000	0.04523
		0.68		-0.05064	-0.05167	-0.00103
Tropical coral	<i>Siderastrea siderea</i>	3.97	$y = -0.055 - 0.638 \cdot \text{EXP}(-6.187 \cdot \Omega_A + 2.039 \cdot \Omega_A)$	-0.05517	0.16500	0.22017
		2.83		-0.05517	0.22300	0.27817
		2.50		-0.05519	0.23600	0.29119
		1.06		-0.06289	0.15400	0.21689
Temperate coral	<i>Oculina arbuscula</i>	2.60	$y = -0.073 - 0.638 \cdot \text{EXP}(-5.632 \cdot \Omega_A + 2.039 \cdot \Omega_A)$	-0.07308	0.19667	0.26975
		2.28		-0.07320	0.19333	0.26653
		1.64		-0.07479	0.18500	0.25979
		0.77		-0.11314	0.06333	0.17647
Hard clam	<i>Mercenaria mercenaria</i>	2.63	$y = -0.022 - 0.638 \cdot \text{EXP}(-6.958 \cdot \Omega_A + 2.039 \cdot \Omega_A)$	-0.02190	0.01667	0.03857
		2.11		-0.02192	0.01167	0.03359
		1.43		-0.02246	0.00833	0.03079
		0.71		-0.04131	-0.02333	0.01797
Soft clam	<i>Mya arenaria</i>	2.63	$y = -0.025 - 0.638 \cdot \text{EXP}(-4.581 \cdot \Omega_A + 2.039 \cdot \Omega_A)$	-0.02599	0.29167	0.31765
		2.11		-0.02818	0.12833	0.15651
		1.43		-0.04201	0.00333	0.04535
		0.71		-0.13011	-0.13500	-0.00489
Coralline red alga	<i>Neogoniolithon</i> sp.	3.12	$y = -0.038 - 0.638 \cdot \text{EXP}(-3.744 \cdot \Omega_A + 2.039 \cdot \Omega_A)$	-0.04102	0.09500	0.13602
		2.40		-0.04855	0.24167	0.29021
		1.84		-0.06558	0.17833	0.24391
		0.90		-0.17540	0.06000	0.23540

Table 5

TABLE 5. Effect of temperature and polymorph mineral solubility (high-Mg calcite > aragonite > low-Mg calcite) on average modelled dissolution rate over $\Omega_A = 0.2 - 5.0$ (using Ω_A increments of 0.2) at 10.1 °C (± 0.02) and 25.0 °C (± 0.02). Results ranked by magnitude of temperature effect on average dissolution rate.

SPECIMEN	SCIENTIFIC NAME	AVERAGE DISSOLUTION RATE (weight-% per day)			MINERALOGY*
		10 °C	25 °C	DIFFERENCE	
Blue mussel	<i>Mytilus edulis</i>	-0.0279	-0.0492	0.0213	LMC>A
Ivory barnacle	<i>Balanus eburneus</i>	-0.0456	-0.0673	0.0216	LMC
Hard clam	<i>Mercenaria mercenaria</i>	-0.0388	-0.0611	0.0223	A>>>HMC
Conch	<i>Strombus alatus</i>	-0.0422	-0.0649	0.0227	A>LMC
America oyster	<i>Crassostrea virginicus</i>	-0.0461	-0.0690	0.0230	LMC
Tropical coral	<i>Siderastrea siderea</i>	-0.0746	-0.0987	0.0241	A
Temperate coral	<i>Oculina arbuscula</i>	-0.0949	-0.1209	0.0260	A
Soft clam	<i>Mya arenaria</i>	-0.0538	-0.0867	0.0330	A>>>HMC
Coralline red alga	<i>Neogoniolithon</i> sp.	-0.0754	-0.1228	0.0474	HMC>A
Branching bryozoan	<i>Schizoporella errata</i>	-0.1023	-0.1631	0.0608	HMC>A

*Polymorph mineralogy from Ries et al. (2009; all species except bryozoan and barnacle), Smith et al. (2006; bryozoan), and Bojar et al. (2012; barnacle); A - aragonite; LMC - low-Mg calcite (<4 mol% MgCO₃); HMC - high-Mg calcite (>4 mol% MgCO₃).

Figure 1

Figure 2

Figure 3