



Effects of lower surface ocean pH upon the stability of shallow water carbonate sediments

Sarah Tynan^{*}, Bradley N. Opdyke

Research School of Earth Sciences, Building 47, The Australian National University, Acton, ACT, 0200, Australia

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ABSTRACT

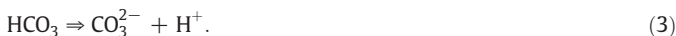
It is predicted that surface ocean pH will reach 7.9, possibly 7.8 by the end of this century due to increased carbon dioxide (CO₂) in the atmosphere and in the surface ocean. While aragonite-rich sediments don't begin to dissolve until a threshold pH of ~7.8 is reached, dissolution from high-Mg calcites is evident with any drop in pH. Indeed, it is high-Mg calcite that dominates the reaction of carbonate sediments with increased CO₂, which undergoes a rapid neomorphism process to a more stable, low-Mg calcite. This has major implications for the future of the high-Mg calcite producing organisms within coral reef ecosystems. In order to understand any potential buffering system offered by the dissolution of carbonate sediments under a lower oceanic pH, this process of high-Mg calcite dissolution in the reef environment must be further elucidated.

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1. Introduction

CO₂ in the Earth's atmosphere has long played a role in maintaining an equable temperature on the surface of the planet, and is naturally cycled through the Earth's atmosphere, biosphere and hydrosphere. The Earth's oceans and sediments act as the main sink and buffer of atmospheric CO₂, and have helped keep the system in a dynamic equilibrium for many millennia. However, anthropogenic perturbation of the Earth's CO₂ cycle has resulted in a dramatic increase in atmospheric CO₂ concentrations, with a consequent increase of CO₂ entering the shallow oceans. Atmospheric CO₂ stood at 379 ppm in 2005. Present levels of atmospheric CO₂ stand at ~390 ppm (Tans, 2010), with worst case scenarios suggesting levels as high as 660–790 ppm by 2100–2150 (IPCC, 2007).

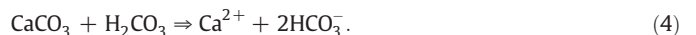
It is the ocean's calcium carbonate (CaCO₃) system that controls its CO₂ buffering capacity. As the ocean absorbs CO₂ carbonic acid is formed (Eq. (1)), which in turn dissociates to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions (Eqs. (2) and (3)):



Thus, as CO₂ is absorbed into the oceans the pH of the surface seawater is lowered. The normal pH of surface seawater is 8.1–8.2.

Predictions are that within the next 100 years, absorption of excess CO₂ into the oceans could result in lowering the oceanic pH to 7.9 (Feely et al., 2001) or even 7.8 (Gattuso et al., 1999). Some modelling predictions see a decrease in ocean pH of 0.7, which would result in an oceanic pH lower than any seen over the past 300 million years (Caldeira and Wickett, 2003).

CO₂ is ultimately absorbed in the oceans through the dissolution of the carbonate minerals calcite, aragonite and high-Mg calcite (Eq. (4)):



This carbonate dissolution occurs largely in the deep, cold regions of the ocean, where calcite is the dominant carbonate mineral. The process of carbonate dissolution in shallow water environments has been considered inconsequential as these waters are generally supersaturated with respect to the carbonate minerals (Andersson et al., 2003). However, saturation states of the carbonate phases are strongly pH dependent. A decrease in surface ocean pH will have serious implications for carbonate precipitation and accretion (Jokiel et al., 2008; Hoegh-Guldberg et al., 2007; Hallock, 2005) and also the stability of existing carbonate sediments. Most susceptible will be the organisms whose skeletons are comprised of the less stable minerals aragonite and high-Mg calcite, both of which are abundant in shallow environments (Morse et al., 2006).

High-Mg calcite with a Mg content of 12 mol% Mg has a stability close to or exceeding that of aragonite (Morse et al., 2006; Walter and Morse, 1984), with stability decreasing as the Mg content increases. Organisms that secrete high-Mg calcite, such as encrusting coralline algae, generally have the role of cementing and holding coral reefs

^{*} Corresponding author. Fax: +61 2 6125 5544.

E-mail address: sarah.tynan@anu.edu.au (S. Tynan).

together, so lower shallow ocean pH will have a widespread affect on the entire reef community (Hoegh-Guldberg et al., 2007).

While it is accepted that the carbonate dissolution relevant for oceanic CO₂ sequestration occurs at depth, there has been some work carried out regarding shallow water dissolution. Attempts to quantify the potential CO₂ sink offered by shallow carbonate dissolution have produced a range of results: in the early 1980s, it was calculated that high-Mg calcite dissolution presented a possible sink of 2% of annual CO₂ emissions at a 1980 level (Garrels and Mackenzie, 1981); Sabine and Mackenzie (1991) suggested that carbonate sediments in reef shelves and banks offer a sink of up to 0.05 Gt/year; while calculations from Langdon (2000) produced a sink of 6% annual oceanic CO₂ uptake. Sabine and Mackenzie (1995) calculated that dissolution of aragonite could offer a sink for 2.6×10^{16} g (2.6×10^7 Gt) of CO₂.

Other work has produced evidence of the critical pH for carbonate dissolution. Analysis of the pore waters of carbonate sediments in the Bahamas found that dissolution occurred in these waters as soon as pH dropped below 8.0 (Morse et al., 1985). Other studies have found that the lower pH reached simply as a result of natural respiratory and metabolic processes of CO₂ release within reef ecosystems is sufficient to enhance carbonate dissolution (Gattuso et al., 1997; Garcia-Pichel, 2006; Yates and Halley, 2006), evidence that a sustained lowering of ocean pH will cause increased dissolution of carbonate sediments.

This study investigates the effect of a lower ocean pH resulting from increased CO₂ in the surface ocean by attempting to simulate the natural environment through laboratory experiments, using natural carbonate sediments collected from the Great Barrier Reef, Australia.

2. Methods

2.1. Laboratory experiments

Carbonate sediments were collected via grab sample from two sites at Lizard Island, which is located on the Great Barrier Reef, in northern Queensland, Australia (Fig. 1). Sediments were taken from the lagoon area, from ~1 to 2 m depth (Lizard Head) and from a beach location (Coconut Beach). Sediments were dried in sunlight, and were not frozen or refrigerated for transport to the laboratory.

The base of a small fish tank (24 cm × 19.5 cm × 21 cm) was covered with a 1 cm deep layer of sediment, and the tank filled with natural seawater (~9360 mL). Mixing of the water was ensured

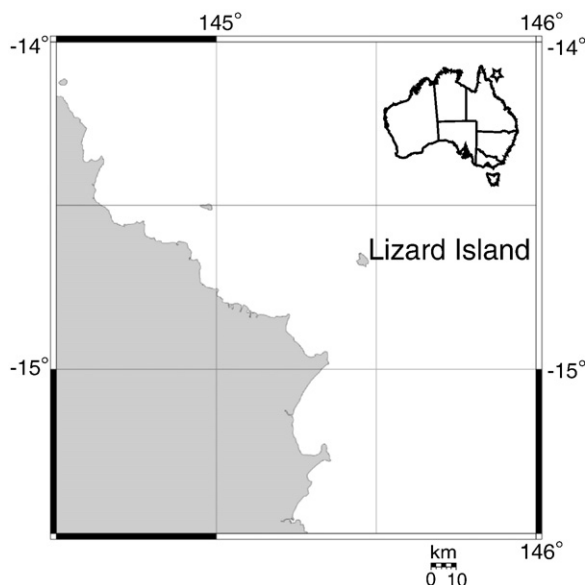


Fig. 1. Location map for Lizard Island. Map created using GMT Online Map Creation website (www.aquarius.geomar.de/omc).

through the use of a small submersible aquarium pump. A Perspex lid was placed over the top of the tank to minimise gas exchange between the water and overlying air. The average temperature in the tank was 23.6 °C with standard deviation of 2.9 °C.

Seawater was collected in clean, well-rinsed containers from Eden and Bateman's Bay, New South Wales, Australia. The water was kept in cold storage, and filtered within 24–48 h after collection through a 0.45 µm Millipore filter to remove any organic matter that could oxidise, and affect the pH of the seawater. Despite the filtering, the water pH tended to drop slowly over time. The seawater was discarded if the pH dropped lower than 7.9.

The Perspex lid over the tank had two ports on the top, where a pH electrode (SERA 8921-0) and a tube for adding CO₂ gas were inserted. The pH probe and CO₂ gas tube were connected to a battery powered pH controller (SERA Ceramic CO₂ Control System 8005-7), and CO₂ cylinder (Soda Stream CO₂ 301, 1000PSI, certified 99.9% pure CO₂) respectively. The CO₂ cylinder was attached to a SERA 8013-2 pressure regulator, which was controlled by a switch within the pH controller. The system injected CO₂ gas according to the desired pH set on the meter and the valve closed when the pH probe measured the target pH in the chamber. The CO₂ gas travelled from the cylinder through the tubing to the tank, and then was dispersed in the water through very small diameter gas permeable tubing. Although it was intended to regulate the injection of the CO₂ gas such that pH consistently decreased or remained constant over the duration of the experiment, in some cases, the input of CO₂ gas was erratic and thus pH values fluctuated within some experiments.

Water samples of approximately 120 mL were taken every one to 3 h during the day. Where experiments ran for more than one day, samples were not taken throughout the night. Samples were filtered through 4.5 µm Millipore filters and stored in plastic acid washed, airtight Nalgene bottles. Experiment duration was varied, depending on the results. Most experiments ran for approximately one week.

The pH electrode was calibrated prior to each experiment, using TPS pH Buffers 4.00 and 9.23, which are electrometrically referenced to standard buffers traceable to NIST SRM's 1861f and 1861i. pH measurement accuracy was within 0.1.

2.2. Analysis

2.2.1. Alkalinity titrations

Alkalinity titrations were performed immediately following sample collection using a Metrohm 716 DMS Titrino to obtain the concentration of HCO₃⁻ and CO₃²⁻, as an indication of dissolution of CaCO₃. Titrations were performed to an endpoint pH of 3.8 and were repeated at least twice, until results were replicated within 1% (~20 µmol L⁻¹). 0.01 M HCl was used for the titrations. The titration procedure was standardised via calibration of the HCl with NaOH, the concentration of which was determined via titration of a known precise weight of potassium hydrogen phthalate (KHP) AR grade.

2.2.2. ICP-AES

Water samples were analysed for Mg²⁺ and Ca²⁺ at The Australian National University, using a Varian Vista Pro Axial Geometry Inductively Coupled Plasma Atomic Emission Spectrometer, with an argon plasma maintained by the interaction of a radio frequency (RF) field and ionised argon gas, which operates at approximately 8000 K. Upon the sample's introduction to the plasma, excited cations emit light of varying intensities at known wavelengths throughout the spectrum. The light emitted by the excited atoms is then channelled through a cone to the detector that then measures the intensity of light for the cations of interest at the relevant wavelengths required. To calibrate the instrument, a set of standards of known concentration, along with a blank, are run to obtain intensity/concentration points for each element and zero concentration respectively. The

calibration standards are reanalysed regularly to account for any instrument drift. The error is <5% for the instrument.

The conditions used for this study were:

Calcium wavelength – 315.887 nm
 Magnesium wavelength – 279.800 nm
 Strontium wavelength – 407.771 nm
 Power: 1.00 kW
 Plasma flow: 15.0 L/min
 Auxiliary flow: 1.50 L/min
 Nebulizer flow: 0.90 L/min
 Replicate read time: 1.00 s
 Instrument stabilization delay: 15 s
 Replicates: 3

The standards were prepared from 1000 ppm AccuTrace Reference Standards supplied by AccuStandard Inc.

Water samples were diluted in a 1:3 ratio with 2% HNO₃ to accommodate the high Na concentration of seawater.

2.2.3. XRD

To determine the mineralogy of each of the sediment samples, X-ray diffraction analysis was carried out with a SIEMENS D501 Bragg-Brentano diffractometer equipped with a graphite monochromator and scintillation detector, using CuK α radiation. The sample was ground in an agate mortar in acetone, and supported on a quartz single-crystal low-background holder. The scan range was 2 to 70° 2-theta, at a step width of 0.02°, and a scan speed of 1° per minute.

The results were interpreted using the SIEMENS software package *Diffracplus Eva* (2000), and quantitative estimates, to ascertain the proportions of calcite, aragonite and low- and high-Mg calcite, along with the unit cell sizes of the Mg-calcites were performed with the program CSIRO Siroquant 2.5 (2000).

The proportions of calcite, aragonite and Mg-calcite were calculated, along with the unit cell sizes of the Mg-calcite, which was used to estimate the mol% Mg of the sample.

2.2.4. Grain size analysis

A representative sample from each sediment type was wet-sieved through a series of sieves, from 400 μ m to 100 μ m in 100 μ m divisions. The different size fractions were then weighed to ± 0.01 g.

3. Results

3.1. Sediment analysis

3.1.1. Mineralogy

X-ray Diffraction analysis of the sediment samples identified aragonite, high-Mg calcite and calcite, along with insignificant amounts of halite, quartz, and possibly albite. Further analysis using the CSIRO Siroquant 2.5 program (2000) showed that the calcite peaks were slightly offset from the peaks of pure calcite, indicating two different types of high-Mg calcite – a low-Mg calcite with peaks similar to pure calcite, and a more Mg-enriched phase. The Siroquant analysis also yielded approximate quantities of each phase (Table 1), along with the unit cell parameters of the high-Mg calcite, which were used to ascertain the mol% Mg of the calcite (Mackenzie et al., 1983). The two Mg-calcite phases identified in the sediment types were

Table 1
Mineralogy of each sediment type, as per XRD and Siroquant analysis.

	Calcite (%)	Aragonite (%)	High-Mg calcite (%)	Other (%)
Coconut Beach	3	39	55	3
Lizard Head	4	57	36	3

Table 2
Grain size analysis of each sediment type.

	0–100 μ m (%)	100–200 μ m (%)	200–300 μ m (%)	300–400 μ m (%)	>400 μ m (%)
Coconut Beach	9.10	31.43	2.96	0.32	56.18
Lizard Head	0.26	4.07	10.50	12.57	72.55

found to contain ~9 and 18.5 mol% Mg respectively. The errors associated with calculation of the unit cell sizes are in the order of 0.001, and so are unlikely to significantly affect (>1 mol%) the mol% Mg determination of the calcite phases.

As the mol% Mg increases, the stability of the calcite decreases, with calcite of about 12 mol% Mg being roughly equal in stability to aragonite (Walter and Morse, 1984). Approximately 55% of the Coconut Beach sediment was found to be 18.5 mol% Mg-calcite while this phase comprised only 36% of the Lizard Head sediment (Table 1).

3.1.1.1. Grain size analysis. Results from the grain size analysis (Table 2) show that the Coconut Beach sediment contains 35 times more of the smallest (0–100 μ m) grain size fraction.

3.2. Laboratory experiments

3.2.1. Dissolution vs. precipitation

For ease of comparison, the results from all of the laboratory experiments were compiled and were plotted to show change in alkalinity as a function of pH. Positive values (increase in alkalinity) are indicative of dissolution, and negative values (decrease in alkalinity) are indicative of precipitation. As replicates were repeated to within 1% (~20 μ mol L⁻¹), this error will translate to a range of Δ alkalinity of 0 \pm 20 μ mol L⁻¹ in which values likely do not represent any real significant change in alkalinity. Fig. 2 shows the range of results produced by the various experiments for each sediment type.

The vast majority of values from the Lizard Head sediment experiments plot below the zero line (Fig. 2a). It is evident that even at lower pH precipitation dominates the system for this sediment type.

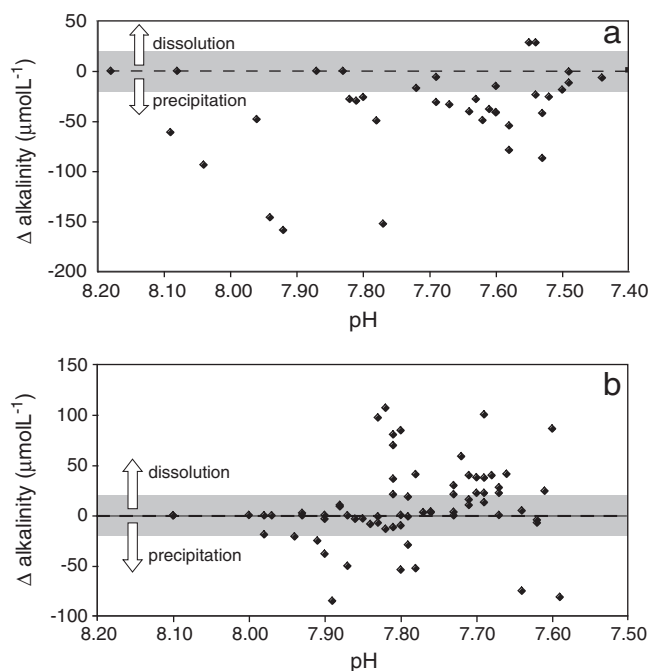


Fig. 2. Change in alkalinity as a function of pH from experiments using a. Lizard Head sediments and b. Coconut Beach sediments. Values that lie above the zero line indicate dissolution of CaCO₃, values below the zero line indicate precipitation of CaCO₃.

In contrast, most of the Coconut Beach experiments show a relatively clear dissolution path (Fig. 2b). At pH greater than 7.8, precipitation dominates the system. Below this value, while there is still some precipitation, dissolution is clearly starting to occur. The majority of the highly negative values in the Coconut Beach plot come from a single experiment, which shows a dissolution pattern much closer to those of the Lizard Head sediment experiments.

3.2.2. Re-precipitation of a low-Mg calcite

In some experiments, where alkalinity decreases as a result of precipitation, there is a corresponding increase in Mg^{2+} and Ca^{2+} . This indicates dissolution of a high-Mg calcite and re-precipitation of another calcite of lower Mg content (Fig. 3). This phenomenon is not evident in all of the experiments, but mainly those which sediments that contain a high proportion of high-Mg calcite. Alkalinity, Mg^{2+} , and Ca^{2+} data are reported in a Supplemental data table.

Furthermore, the proportions of Mg^{2+} and Ca^{2+} that are produced by the dissolution reactions are not consistent throughout the experiments. However, common to all the experiments that show dissolution is an unexpectedly high amount of Mg^{2+} as compared to Ca^{2+} , as shown in Fig. 4.

4. Discussion

Although the Lizard Head sediments were air-dried prior to running the experiments, it is possible that some remnant organisms were still present in the material, resulting in some biologically-induced $CaCO_3$ precipitation, which could account, at least in part, for the alkalinity signal exhibited in Fig. 2a.

Another, possibly more important, factor in the enhanced dissolution measured in the Coconut Beach sediment experiments is the markedly higher (55% compared to 36%) proportion of high-Mg

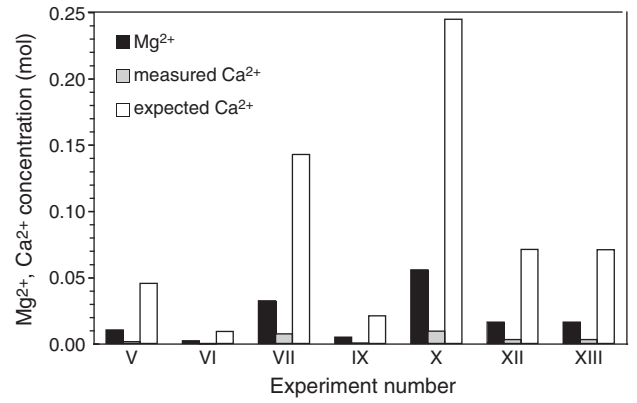


Fig. 4. Comparison of Mg^{2+} , measured Ca^{2+} and expected Ca^{2+} (calculated from dissolution of 18.5 mol% Mg-calcite).

calcite in the Coconut Beach sediment, emphasising the importance of high-Mg calcite in any reef sediment dissolution regime.

Additionally, the Coconut Beach sediment has over 10 times the amount of the $<100 \mu m$ grain size fraction. This could also be a factor in the enhanced dissolution, although it has been proposed that grain size does not play a significant role in enhancing dissolution until the grains have a diameter smaller than $0.1 \mu m$ (Bathurst, 1975). Unfortunately, analysis to this precision was not conducted on any of the samples used in this project.

The results from the different experiments are somewhat varied. Not all experiments show dissolution of carbonate, and in the experiments where dissolution did occur, it occurred in markedly different amounts. Why there is such disparity in the results of the various experiments is unclear, though the nature of the experiments

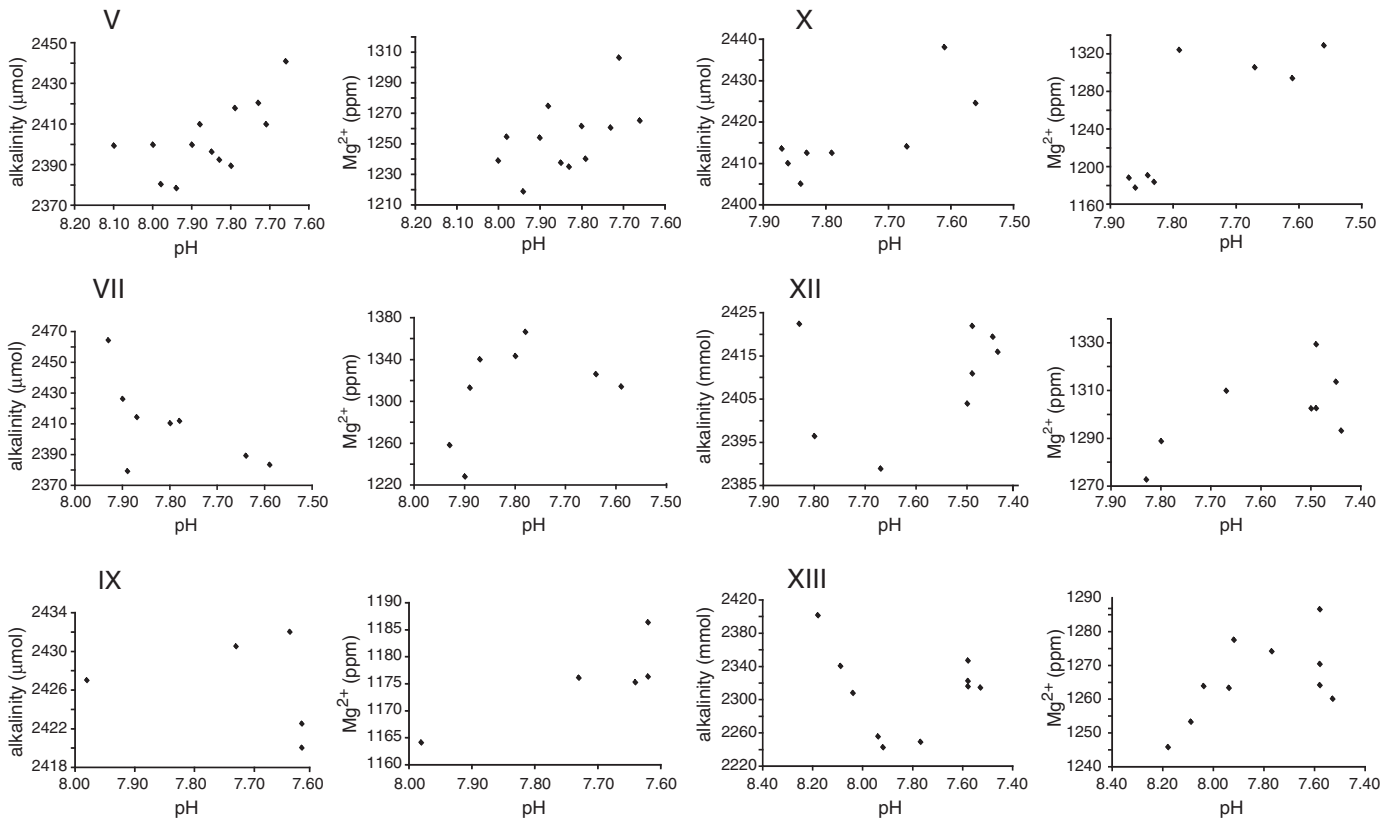


Fig. 3. Results from experiments showing an initial decrease in alkalinity, accompanied by an increase in Mg^{2+} .

dictates that the sediment samples will not be homogenous across all of the experiments, which could account for differences in the results. Clearly evident is the dominance of high-Mg calcite in any dissolution signal seen at these pH values.

The process is further complicated by the dissolution behaviour of the high-Mg calcite. The experiments that showed an increase of Mg^{2+} in the water column, accompanied by a decrease in alkalinity, indicate a very rapid dissolution of a high-Mg calcite with subsequent re-precipitation of another calcite of lower Mg content. This process has been documented in previous studies (Tribble et al., 1995). Dissolution of the high-Mg calcites with subsequent re-precipitation of a lower-Mg calcite will offer a quantifiable buffering capacity for shallow-ocean "acidification".

Further indication of this neomorphism or stabilisation process is the disproportionate amounts of Mg^{2+} and Ca^{2+} released into the water column. If the mol% Mg of the high-Mg calcite is taken to be 18.5%, as indicated by the Siroquant 2.5 (2000) analysis, then proportions of Mg and Ca produced by dissolution of this phase should be in the ratio of ~1:4 (18.5:81.5). However, as shown in Fig. 4, this is not the case, with Mg:Ca ranging from 4.4:1 to 12.9:1. This excess of Mg^{2+} indicates that as both Mg^{2+} and Ca^{2+} are produced from the dissolution of the high-Mg calcite, much of the Ca^{2+} is sequestered by the rapid precipitation of a more stable low-Mg calcite. While these results perhaps do not yield a viable quantitative assessment of this reaction, it is clearly evident that a neomorphism from high-Mg calcite to a more stable low-Mg calcite process takes place, and that the reaction takes place quickly, i.e., on a timescale of hours. This reiterates that the high-Mg calcite-precipitating organisms, such as coralline algae, will be among the first to show the detrimental effects of a lower oceanic pH.

It is necessary to note that the Coconut Beach sediments contain an unusually high proportion of high-Mg calcite, with an unusually high mol% Mg. Reef sediments around the globe are heterogeneous, and quantification of the proportions of high-Mg calcite, and the mol% Mg of these calcites is required to assess the effects of the neomorphism of the high-Mg calcite to low-Mg calcite resulting from a drop in ocean pH.

Another consideration is the importance of biological activity in regulating the processes of precipitation and dissolution in reef systems (Leclerq et al., 2002; Garcia-Pichel, 2006; Tribollet et al., 2006; Yates and Halley, 2006), and the need to place the various thermodynamic and chemical studies carried out regarding carbonate dissolution in the context of the complex natural system. Indeed, Morse et al. (2006) provide an excellent synopsis of high-Mg calcite and outline some of the complexities and limitations of using theoretical and inorganic calcite experimental data to interpret the natural world.

5. Conclusion

From the results of this study, it is evident that a decrease in surface ocean pH to levels such as 7.9 or 7.8 due to rising atmospheric CO_2 levels will lead to enhanced dissolution of carbonate sediments in shallow water systems. Significant dissolution of aragonite or low-Mg calcite rich sediment, as indicated by an increase in alkalinity in the experiments, began at a pH of 7.8. However, neomorphism of high-Mg calcite to a more stable, low-Mg calcite occurred as soon as pH began to fall. Organisms that produce high-Mg calcite will become particularly vulnerable as the surface ocean pH drops, and there could be a resultant change in reef biota and a reorganisation of reef structure.

The reaction of high-Mg calcite to rapidly stabilise to a lower-Mg calcite as ocean pH drops will potentially provide an as yet unquantified but significant buffer to ocean "acidification". A more comprehensive understanding of the dissolution behaviour of high-Mg calcite, and indeed, the abundance and distribution of high-Mg calcite is necessary

in order to predict more accurately the effects of lower oceanic pH and the response of the shallow ocean carbonate system.

Supplementary materials related to this article can be found online at doi: 10.1016/j.scitotenv.2010.12.007.

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