



Threshold of carbonate saturation state determined by CO₂ control experiment

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Abstract. Acidification of the oceans by increasing anthropogenic CO₂ emissions will cause a decrease in biogenic calcification and an increase in carbonate dissolution. Previous studies have suggested that carbonate dissolution will occur in polar regions and in the deep sea where saturation state with respect to carbonate minerals (Ω) will be <1 by 2100. Recent reports demonstrate nocturnal carbonate dissolution of reefs, despite a Ω_a (aragonite saturation state) value of >1 . This is probably related to the dissolution of reef carbonate (Mg-calcite), which is more soluble than aragonite. However, the threshold of Ω for the dissolution of natural sediments has not been clearly determined. We designed an experimental dissolution system with conditions mimicking those of a natural coral reef, and measured the dissolution rates of aragonite in corals, and of Mg-calcite excreted by other marine organisms, under conditions of $\Omega_a > 1$, with controlled seawater $p\text{CO}_2$. The experimental data show that dissolution of bulk carbonate sediments sampled from a coral reef occurs at Ω_a values of 3.7 to 3.8. Mg-calcite derived from foraminifera and coralline algae dissolves at Ω_a values between 3.0 and 3.2, and coralline aragonite starts to dissolve when $\Omega_a = 1.0$. We show that nocturnal carbonate dissolution of coral reefs occurs mainly by the dissolution of foraminiferans and coralline algae in reef sediments.

1 Introduction

The oceans are a large carbon reservoir that absorbs atmospheric CO₂, which then equilibrates to bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions. More than 30% of the CO₂ emitted into the atmosphere by human activities is taken up by the oceans (Sabine et al., 2004), lowering the pH of surface water and decreasing the saturation state (Kleypas et al., 2006). Future uptake of CO₂ by the oceans is predicted to reduce seawater pH by 0.3 to 0.5 units over the next few decades (Caldeira and Wickett, 2003).

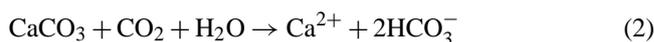
The saturation state of seawater for a given mineral is a measure of the thermodynamic potential for the mineral to form or dissolve. The saturation state of calcium carbonate (Ω) is defined as follows:

$$\Omega = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / K_{\text{sp}}^* \quad (1)$$

where $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ are the concentrations of Ca²⁺ and CO₃²⁻, respectively, and K_{sp}^* is a product of the equilibrium concentrations of Ca²⁺ and CO₃²⁻.

Hence, the formation of calcium carbonate is thermodynamically favorable when $\Omega > 1.0$, but is unfavorable when $\Omega < 1.0$. Oceanic uptake of CO₂ causes an increase in hydrogen ion concentration [H⁺] and a decrease in carbonate ion concentration [CO₃²⁻], leading in turn to a decrease in Ω .

Carbonate dissolution can be described as follows:



As a result, Ω will rise by carbonate dissolution. The carbonate–bicarbonate system acts as a buffer to atmospheric CO_2 levels and ocean acidification. Hence, carbonate dissolution results in an increase to the buffer capacity. If we are to predict future changes in the carbon balance between the atmosphere and the ocean accurately, and the degree of consequent ocean acidification, it is crucial that we understand this buffer system.

Previous studies have mainly investigated the effects of elevated $p\text{CO}_2$ on the net production and calcification of marine organisms by laboratory experiments. For example, Langdon and Atkinson (2005) showed that by 2065 the coral calcification rate will decrease by 40 % to 83 % compared with pre-industrial levels. Data from Gattuso et al. (1998), Leclercq et al. (2000), Marubini et al. (2001, 2002), and Reynaud et al. (2003), meanwhile, predict a decline of only 1 % to 18 %. Although there are differences between low- and high-sensitivity data sets, the calcification rates of marine organisms are expected to decrease.

The value of Ω varies with carbonate mineralogy, and the solubility of Mg-calcite varies according to the magnesium content. In general, minerals with a higher Mg content show higher solubility, but the solubility of synthetic and biogenic Mg-calcite varies under laboratory conditions, and there is variability in the solubility of biogenic Mg-calcite from different organisms (Morse and Mackenzie, 1990).

At present, Ω_a (aragonite saturation state) values are 1 to 2 in high-latitude regions, and 3 to 4.5 in low-latitude regions. Although carbonate dissolution at low latitudes (e.g. coral reefs) was not predicted, net dissolution under conditions of $\Omega_a > 1$ has been observed at several coral reef sites (Boucher et al., 1998; Leclercq et al., 2002; Kayanne et al., 2005; Yates and Halley, 2006; Nakamura and Nakamori, 2009). These studies have shown that dissolution is possible even when $\Omega_a > 1$, due to the high solubility of Mg-calcite. When the Mg content is $> 8\%$ to 12% , Mg-calcite dissolves more readily than aragonite (Plummer and Mackenzie, 1974; Bischoff et al., 1987; Morse et al., 2006).

Morse and Mackenzie (1990) divided the solubilities of Mg-calcite into three major categories: (1) Plummer and Mackenzie (1974) solubility; (2) the “best-fit” biogenic Mg-calcite solubilities (Bischoff et al., 1987; Walter and Morse, 1984); and (3) synthetic Mg-calcite solubilities (Bischoff et al., 1987; Mucci and Morse, 1984). Of these, category 1 has the highest values for Mg-calcite solubility, with the solubility of 12% to 15% mol Mg-calcite exceeding aragonite solubilities by a factor of five. Category 2 shows significantly higher solubilities than category 3 due to the instability of biogenic factors, although the overall trend in category 2 is similar to that in category 3. While categories 2 and 3 reflect the thermodynamic solubilities of biotic and abiotic Mg-calcite, it is likely that category 1 reflects kinetic (rather than thermodynamic) factors, including the retention of reactive surface particles due to minimal sample cleaning and

lack of annealing (Bischoff et al., 1993; Morse et al., 2007). However, category 1 does reflect reactivity in nature.

The relationship between Ω and the kinetic dissolution rate of synthetic and biogenic calcium carbonates in the laboratory has been described by Keir (1980). Hales and Emerson (1997) reviewed the result of Keir (1980) and made corrections to their original measurements. However, these dissolution rates are not consistent with those obtained from field observations. Moreover, no Mg-calcite dissolution experiments have been performed using natural seawater and used total alkalinity or dissolved inorganic carbon in estimating Ω_a values and dissolution rates. Indeed, it is $p\text{CO}_2$ that alters Ω_a ; consequently, laboratory studies need to set Ω_a values using $p\text{CO}_2$ to attain consistency with the environment. It is essential to determine the relationship between Ω and the kinetic dissolution rate of biogenic Mg-calcite in order to understand naturally buffering systems.

The aim of this work is to clarify the relationship between Ω_a and the rate of Mg-calcite dissolution. We measured the dissolution rate of coralline aragonite and Mg-calcite excreted by several organisms under conditions of $\Omega_a > 1$, using an experiment system that controlled $p\text{CO}_2$ in seawater. We measured the Ω_a threshold of biogenic Mg-calcite, calculated by total alkalinity (A_T) and dissolved inorganic carbon (C_T).

2 Methodology

2.1 Experimental design

We designed an experimental system with conditions matching those of a natural coral reef. Carbonate sediments were collected from Shiraho reef and prepared with minimal treatment (ultrasonic cleaning and drying). Shiraho reef ($24^\circ 22' \text{N}$, $124^\circ 15' \text{E}$) is situated at the southeast coast of Ishigaki Island. Natural seawater was used for the dissolution experiment and the Ω_a value of the seawater was controlled by CO_2 , rather than by HCl or NaOH.

The experimental system (Fig. 1) consists of four components: a seawater tank, a dissolution chamber, a CO_2 gas unit, and a flow-through analyzer for A_T and C_T . The experimental procedure is described below.

First, CO_2 gas (420 to 2210 ppm) levels were prepared using the CO_2 gas unit, imitating CO_2 conditions similar to those close to the present day (420 ppm), $2 \times$ pre-industrial levels (~ 560 ppm), $4 \times$ pre-industrial levels (~ 1120 ppm), and $8 \times$ pre-industrial levels (~ 2240 ppm). Seawater in the tank was circulated through the seawater line (bypass line) for 10 to 12 hours to allow the seawater and introduced CO_2 to equilibrate. The $p\text{CO}_2$ was then checked with a non-dispersive infrared gas analyzer (NDIR: LI-820, LI-COR). After the $p\text{CO}_2$ had stabilized, A_T and C_T were determined using the flow-through analyzer before the experiment began. Samples were placed in the dissolution chamber, and

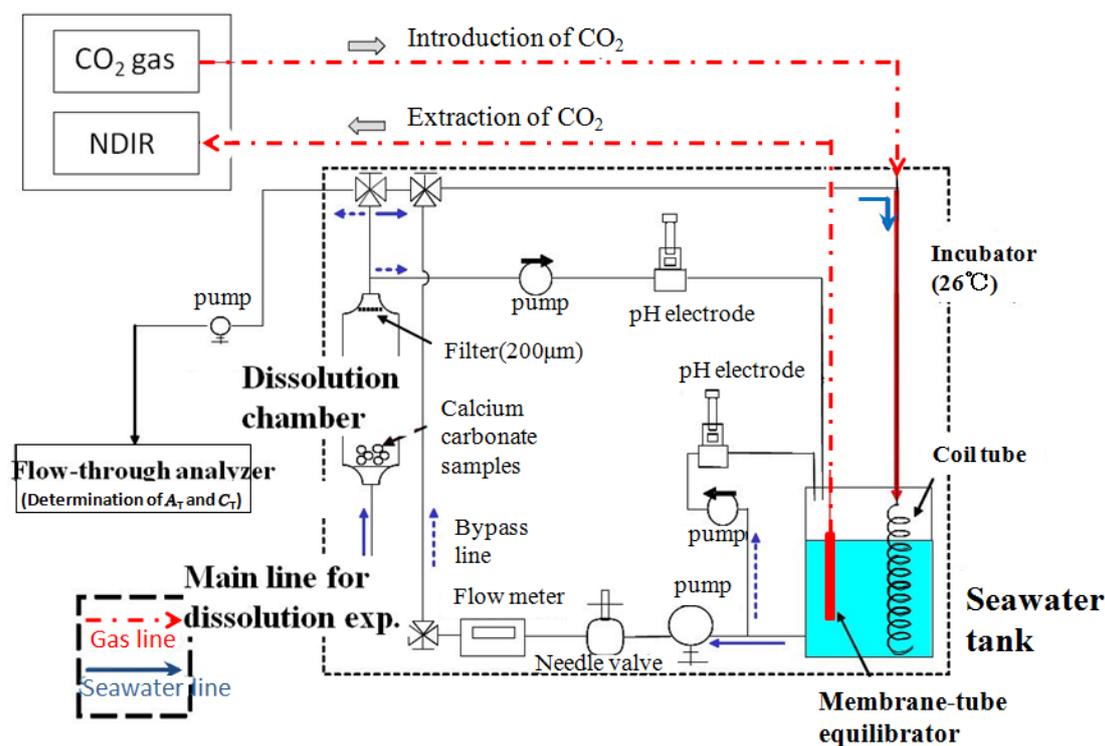


Fig. 1. Experimental set-up.

seawater was circulated through the seawater line (dissolution line). A_T and C_T were measured again after several hours, both in the middle and at the end of the experiment. The experiment was performed as a time series, and A_T and C_T were analyzed periodically through its duration.

The conditions for each experiment are listed in Table 1. Temperature in the incubator was maintained at 26 °C and the dissolution experiment was performed at seven different $p\text{CO}_2$ levels for bulk sediment, four levels for coralline algae and foraminiferans, and three levels for coral.

2.2 System components

Seawater tank: CO_2 gas was introduced to the seawater by using a 3.5 m coiled tube with a single small hole to allow for bubbling and equilibration. The coiled tube is made of fluorocarbon polymers and is a closed system. Seawater $p\text{CO}_2$ in the tank was monitored continuously by using a membrane tube and NDIR similar to the system used by Saito et al. (1995).

Dissolution chamber: By using a pump, seawater was introduced to the dissolution chamber (600 ml) from the seawater tank. Carbonate samples for dissolution experiments were placed in this chamber. Mesh filters (200 μm) were affixed to both sides of the chamber to prevent loss of samples.

CO_2 gas unit: Gas mixtures of CO_2 at concentrations between 420 and 2210 ppm were prepared by mixing CO_2 free

gas (passed through soda lime traps to remove trace CO_2) with pure CO_2 using two mass flow controllers, and then dissolved in seawater. The gas flow rate was 400 ml min^{-1} in all experiments.

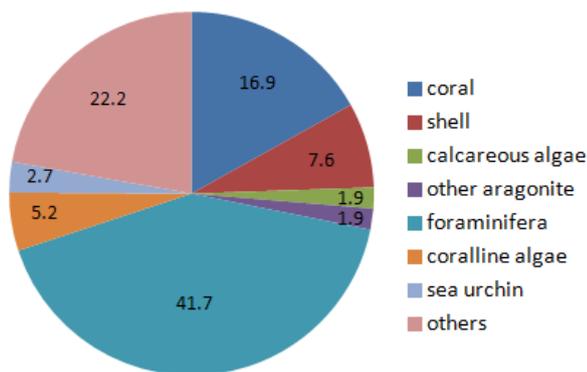
Flow-through analyzer: The sample seawater was introduced directly to the flow-through analyzer (Kimoto Electric Company Limited) by switching the flow line (Kimoto et al., 2001; Watanabe et al., 2004). Certified reference materials (A. Dickson, University of California) were used to calibrate the system. Sodium carbonate solutions were used for the C_T calibration. The analytical accuracies of A_T and C_T were within 3 $\mu\text{mol kg}^{-1}$ and standard deviations of A_T and C_T were 1.1 $\mu\text{mol kg}^{-1}$ and 2.1 $\mu\text{mol kg}^{-1}$ respectively (Kimoto et al., 2002; Watanabe et al., 2004).

2.3 Samples

For the dissolution experiment, we used commercially available seawater (Nihon-Aquarium-Service Co., Ltd.) collected from a depth of 500 m at 34.7° N, 139.4° W (near Izu Islands, Japan) and sterilized by UV rays. The seawater was filtered using a 0.45 μm capsule filter. The carbonate samples used were coral, coralline algae, and sediment sampled from Shiraho reef at Ishigaki Island, Japan. We collected these samples from the surface sediment layer using a scoop. The sampling point was 600 m from the shoreline, in the center of a shallow lagoon in the Shiraho reef, where typical

Table 1. Condition for each experiment.

Samples	Incubator temperature	seawater:sample (by weight)	$p\text{CO}_2$ [ppm]	Ω_a
Bulk sediment	26 °C	310:1	420, 590, 750, 820, 1110, 1290, 2030	3.5, 2.9, 2.5, 2.4, 1.9, 1.7, 1.2
Coralline algae	26 °C	310:1	570, 830, 1070, 2000	2.9, 2.3, 1.8, 1.2
Foraminifera	26 °C	310:1	510, 570, 1240, 2210	3.2, 2.9, 1.7, 1.1
Coral	26 °C	310:1	1070, 1550, 2100	1.9, 1.6, 1.1

**Fig. 2.** Composition of sediment samples (%).

coral zonation could be seen. The sediment was collected in August 2007, and the coral and coralline algae in October 2007. Samples were cleaned in an ultrasonic bath sonicator and dried at 40 °C for about 12 h.

The major size fraction of the coral reef sediment was from -1.0 to 0.0ϕ (1 to 2 mm), from which 800 particles were separated for each dissolution experiment. We consider that our dissolution experiment represents the actual reef environment, because this size fraction (1 to 2 mm) represents 40 % of the size spectrum within the reef sediments. The mineralogy of each sample was identified by X-ray diffraction (XRD) analysis. The samples consisted of coral, foraminiferans, and coralline algae (see Fig. 2). The MgCO_3 content was estimated by the position of the peak X-ray strength (Goldsmith and Graf, 1958). The magnesium contents of the coralline algae and foraminiferans were 16.5 ± 0.4 and $13.3 \pm 0.4 \text{ mol } \%$, respectively, and the coral was pure aragonite.

2.4 Calculation

The A_T of seawater increases by 2 moles for every 1 mole of calcium carbonate dissolution. The carbonate dissolution rate is measured by analyzing the change in A_T . Salinity changes also affect the A_T . Hence, small salinity changes that occurred due to evaporation over the course of the experiment were corrected for by using pre-determined relationships between gas flow and salinity change rate. Dry gas

Table 2. Relationship between change of gas flow, salinity and A_T .

Gas Flow [ml min ⁻¹]	Δ Salinity [h ⁻¹]	ΔA_T [$\mu\text{mol kg}^{-1} \text{ h}^{-1}$]*
50	0.0045	0.308
300	0.0085	0.584
500	0.0264	1.803

*Assuming that initial $A_T = 2350 \mu\text{mol kg}^{-1}$

is required to produce the exact $p\text{CO}_2$ values, so the bubbling of CO_2 into the seawater causes evaporation, and the salinity rises during each experiment. Table 2 shows a series of CO_2 volume flows with the resultant salinities after 7 h. Salinity increases in direct proportion to the gas mass flow, allowing it to be calibrated during the experiment according to the post-experiment salinity value. Figures 3 and 4 show time series of A_T without and with salinity calibration. A_T increased even in the experiment without a carbonate sample; however, after salinity calibration, the change in nA_T (normalized total alkalinity) was about 2 to 3 $\mu\text{mol kg}^{-1}$, a value within the error range of the measurement. Using Eq. (3), A_T was standardized to a constant salinity, and the dissolution rate was then calculated:

$$nA_T = A_T \times S_{\text{average}}/S_{\text{sample}} \quad (3)$$

where nA_T is the normalized total alkalinity ($\mu\text{mol kg}^{-1}$), representing the total alkalinity standardized to the salinity; S_{average} is the average salinity during all the experiments; and S_{sample} is the calibrated salinity according to Table 2. C_T was also standardized to salinity, and nC_T (normalized dissolved inorganic carbon, $\mu\text{mol kg}^{-1}$) was obtained. Salinity was measured using a salinometer (PORTASAL 8410A, Guildline Instruments Limited). IAPSO (International Association for Physical Sciences of the Ocean) standard seawater was used for calibration. The precision of salinity analysis is ± 0.003 .

Dissolution rates were calculated as follows:

$$R = \Delta nA_T/2 \times m_w \times M \times 100/(m_s \times t) \quad (4)$$

where ΔnA_T is the difference in nA_T over the course of the experiment, m_w is the weight of seawater, M is the molecular weight of calcium carbonate (=100), m_s is the average weight

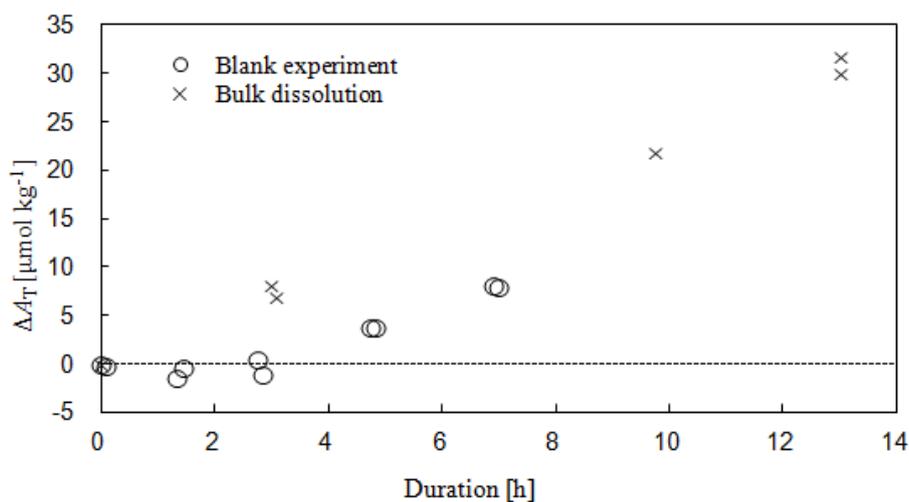


Fig. 3. Blank experiment and bulk dissolution (before salinity calibration).

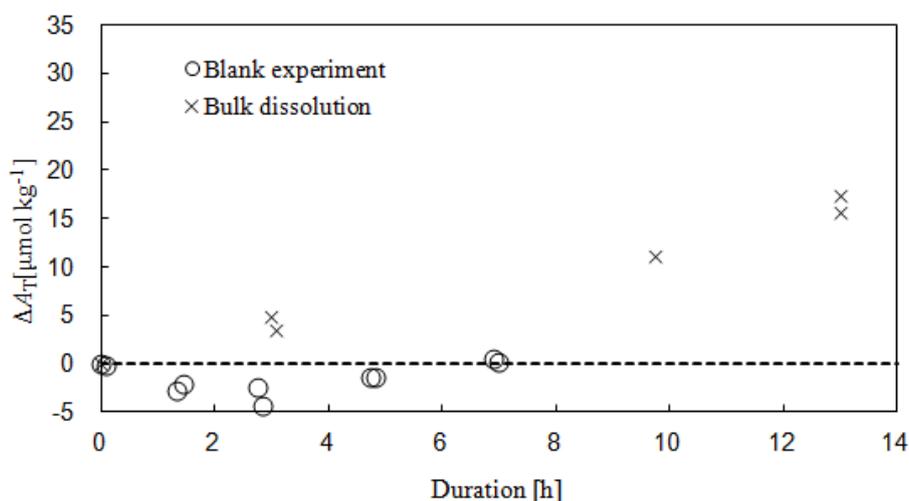


Fig. 4. Blank experiment and bulk dissolution (after salinity calibration).

of the carbonate sample over the course of the experiment, and t is the duration of the experiment. Due to the design of the system, a small amount of seawater remains in the pump and tubes at the end of each run. However, we can confirm that only a small amount of seawater (10 ml = less than 0.5 % of total volume) remained in the pump at the end of each experiment, and this was corrected for when determining the mass balance of A_T . Seawater $f\text{CO}_2$ and Ω_a values were calculated from A_T , C_T , seawater temperature, and salinity, using the calculation program CO2sys (<http://cdiac.esd.ornl.gov/oceans/co2rprt.html>; DOE, 1994). The total scale for

pH was used in all calculations, employing the equilibrium constants (K_1 and K_2) reported by Mehrbach et al. 1973; refit by Dickson and Millero, 1987).

3 Results

The conditions for each experiment are listed in Table 1 and the results of all experiments are listed in Supplementary Material Table 1. The results of the bulk dissolution experiment are shown in Fig. 5. During the experiments, nA_T varied

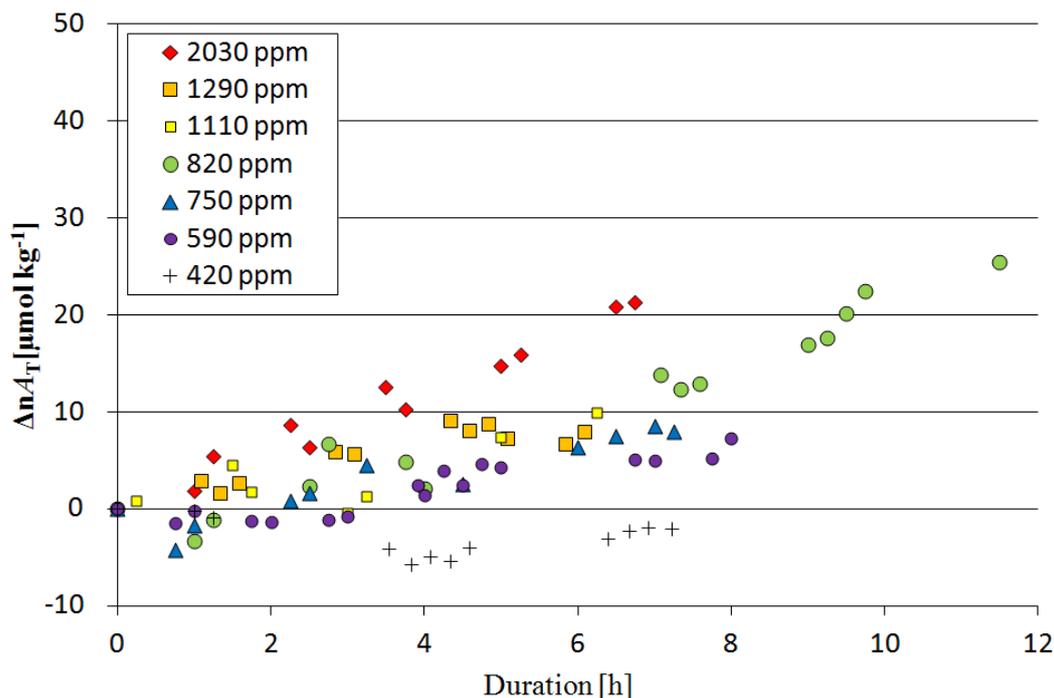


Fig. 5. The result of bulk dissolution experiment (nA_T and duration).

between 6 and 25 $\mu\text{mol kg}^{-1}$. No increase in nA_T was observed when $p\text{CO}_2$ was 420 ppm, and the change in nA_T was highest when $p\text{CO}_2$ was 2030 ppm.

Figure 6 shows the average dissolution rates, calculated from nA_T changes, plotted against averaged Ω_a . The average dissolution rate was fastest ($4.0 \times 10^{-3} \% \text{ h}^{-1}$) when Ω_a was 1.3 and slowest when Ω_a was 3.7.

Similarly, Fig. 7 shows the results of dissolution experiments on coralline algae, foraminiferans, and coral, together with those of the bulk sediment. In all cases, the dissolution rate increases as Ω_a decreases. The threshold value of foraminiferan and coralline algal dissolution is $3.0 < \Omega_a < 3.2$, and that of the bulk sediment is $3.7 < \Omega_a < 3.8$. The dissolution rate of the coral shows no significant change when $1.5 < \Omega_a < 2.0$.

4 Discussion

At any given value of Ω_a , the relative dissolution rate is typically in the order of coralline algae > foraminiferans = bulk sediment > coral (Fig. 7). As in earlier studies (Bischoff et al., 1993; Morse et al., 2006, 2007), the differences among samples presumably resulted from the solubility differences of minerals with varying Mg content.

4.1 Relationship between solubility and Ω_a

We compared the solubilities obtained in this study with those measured previously (Morse and Mackenzie, 1990)

using the Ω_a threshold of coralline algae and foraminifera. The solubility of biogenic Mg-calcite is calculated using two different methods: Plummer–Mackenzie solubility (Plummer and Mackenzie, 1974) and biogenic best-fit solubility (Walter and Morse, 1984; Bischoff et al., 1987). The Ω value of Mg-calcite (16 mole % Mg) is 0.2 by the former method and 0.8 by the latter, when $\Omega_a = 1.0$. This discrepancy originates from differences in pretreatment and the experimental method (Bischoff et al., 1993; Morse et al., 2006). For example, the Plummer–Mackenzie method carbonate samples were washed in an ultrasonic bath and then dried, whereas for the biogenic best-fit solubility they were not only washed in an ultrasonic bath, but were chemically treated with H_2O_2 to remove organic matter.

In the present work, the $-\log(K_{sp}^*)$ values of coralline algae ($16.5 \text{ mol} \pm 0.4 \text{ mole \% Mg}$) and foraminiferans ($13.3 \text{ mol} \pm 0.4 \text{ mole \% Mg}$) are 7.80 and 7.82, respectively, and according to Plummer and Mackenzie (1974), $-\log(K_{sp}^*)$ value of 12.7 mole % Mg is 7.82. Our samples were cleaned only in an ultrasonic bath and dried at 40 °C for about 12 h, following Plummer and Mackenzie (1974). The solubilities calculated in this study are similar to those reported by Plummer and Mackenzie (1974), and are comparable to those obtained from field data, because the minimal processing employed in this study resulted in a state similar to that occurring in the sediment. Moreover, a significant dissolution rate of coral was obtained even when $\Omega_a = 1.1$. Since Ω_a (calculated from A_T and C_T) has an error of 0.05, biogenic aragonite starts to be dissolved where

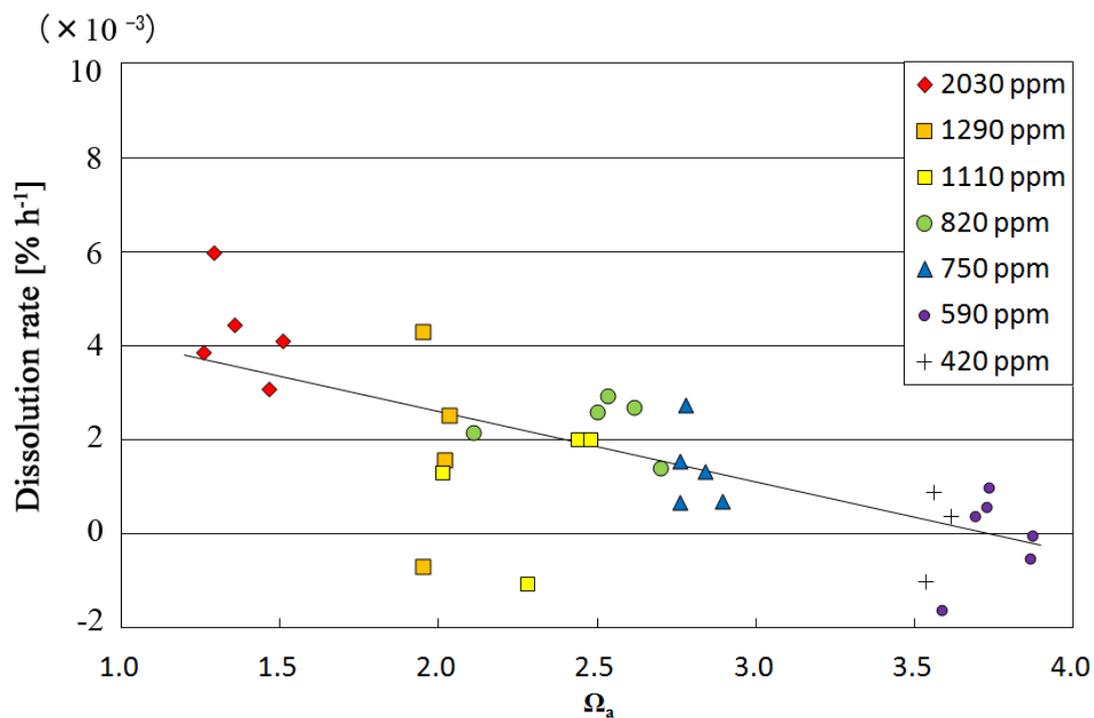


Fig. 6. The relationship between average dissolution rate and Ω_a (bulk).

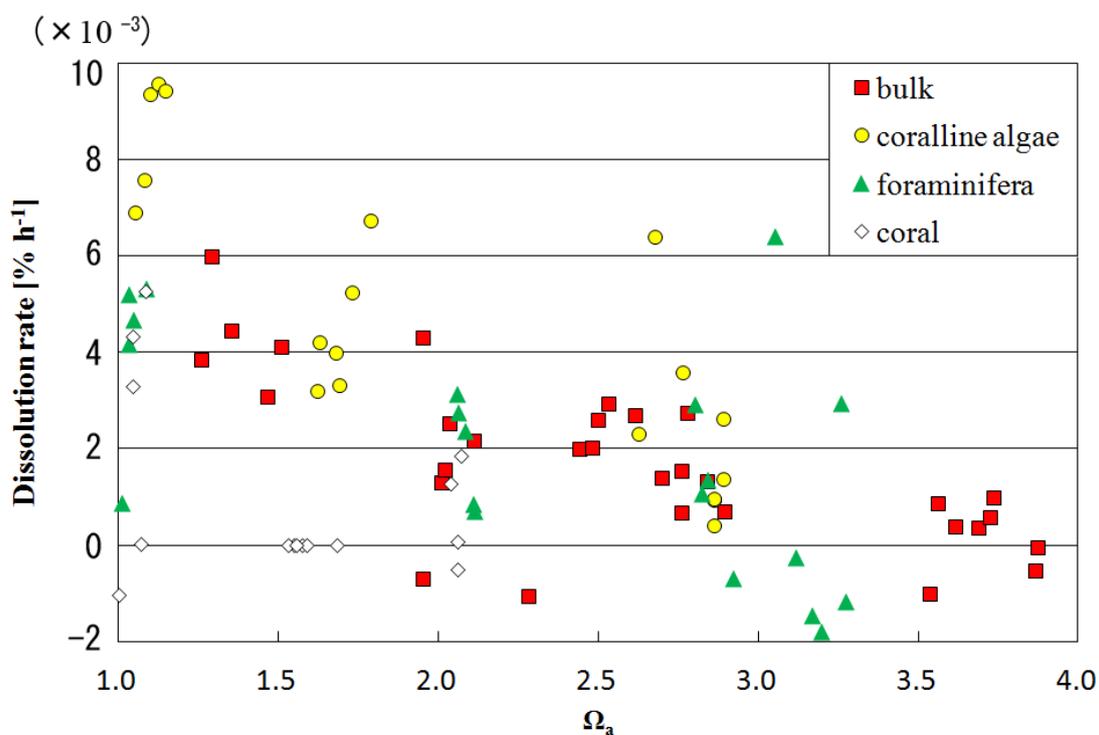


Fig. 7. The relation between average dissolution rate and Ω_a (all samples).

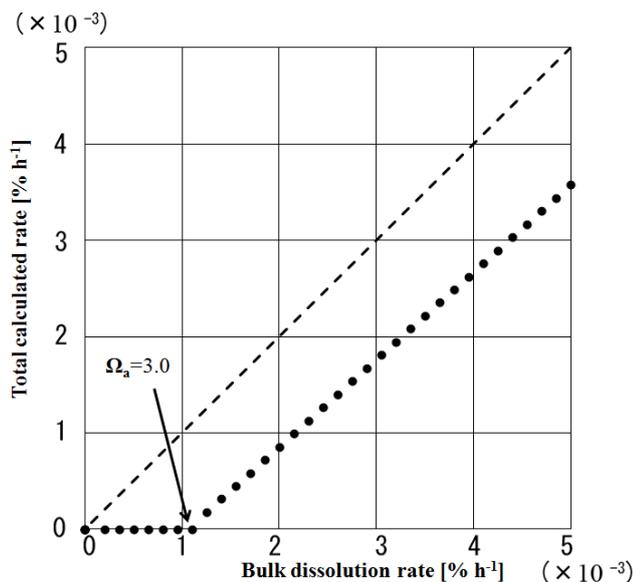


Fig. 8. Relationship between bulk dissolution rate and total calculated dissolution rate.

$1.0 < \Omega_a < 1.1$. Alternatively, biogenic aragonite may be slightly more soluble than synthetic aragonite because of its heterogeneity and instability.

4.2 Evaluation of Mg-calcite dissolution

The relationship between dissolution rate and Ω_a , as obtained from the present experiments, is as follows:

$$\begin{aligned} \text{Bulk sediment : Dissolution rate (i.e. } DR_{\text{bulk}}) (\% \text{ h}^{-1}) & \quad (5) \\ = -0.0015 \times \Omega_a + 0.0056 \end{aligned}$$

$$\begin{aligned} \text{Foraminifera : Dissolution rate (i.e. } DR_{\text{Fora}}) (\% \text{ h}^{-1}) & \quad (6) \\ = -0.0027 \times \Omega_a + 0.0081 \end{aligned}$$

$$\begin{aligned} \text{Corallinealgae : Dissolution rate (i.e. } DR_{\text{CA}}) (\% \text{ h}^{-1}) & \quad (7) \\ = -0.0045 \times \Omega_a + 0.0143 \end{aligned}$$

According to Eqs. (5) to (7), the net dissolution of bulk sediment was zero at $3.7 < \Omega_a < 3.8$ and $3.0 < \Omega_a < 3.2$ for foraminiferans and coralline algae.

Figure 8 shows the total dissolution rate (i.e. the dissolution rate of Foraminifera + coralline algae) plotted against the bulk dissolution rate. The value of the y-axis is given as follows:

$$\begin{aligned} \text{Total calculated dissolution rate} & \\ = DR_{\text{fora}} \times (\text{Foraminifera/Bulk}) + & \quad (8) \\ DR_{\text{CA}} \times (\text{Corallinealgae/Bulk}) \end{aligned}$$

The composition ratio is derived from Fig. 2; in the case of a negative dissolution rate, a value of zero was used, assuming no precipitation of calcium carbonate. In Fig. 8, DR_{bulk}

should be equal to the total calculated dissolution rate (DR) if foraminiferans and coralline algae are the only dissolving grains in the bulk sediment; however, DR is smaller than DR_{bulk} , especially for $\Omega_a > 3.0$.

The sediment samples consist of 75 % foraminiferans, coralline algae, coral, and other aragonite; 3 % echinoids, and 22 % “other minerals”; the latter two components were not included in the calculations. The echinoid test is composed of Mg-calcite with a low MgCO_3 content (8.0 mole % Mg), corresponding to a small contribution to the bulk dissolution rate. The “other minerals” are considered to be calcite or Mg-calcite, because they did not acquire coloration when dyed with $\text{Co}(\text{NO}_3)_2$ (aragonite colors red-purple), and over 95 % of the sediment in the Shiraho reef is carbonate. Any minerals in the minor fraction appear to be much more soluble than the foraminiferans and coralline algae, meaning that we may have underestimated the dissolution rate. However, at least ~ 70 % of the dissolution can be explained from foraminiferan and coralline algal dissolution, and this finding is applicable to reef environments where sediment grains consist mainly of these biogenic carbonates.

4.3 Comparison of the present results with field observations

We compared the results of bulk dissolution rate vs. Ω_a from this study with previous research. Assuming a density of calcium carbonate (D_c) of 2700 kg m^{-3} , a porosity of coral reef sediment (P_c) of 0.45 (Morse and Mackenzie, 1990), the molecular weight of calcium carbonate (M) of 100, and only the uppermost 0.01 m of sediment being responsible for dissolution (d_d), the dissolution rate (R) was converted from $\% \text{ h}^{-1}$ to $\text{mmol m}^{-2} \text{ h}^{-1}$ as follows:

$$\begin{aligned} R[\text{mmol m}^{-2} \text{ h}^{-1}] & = (D_c \times P_c \times d_d / M) \times DR_{\text{bulk}} \quad (9) \\ & = 1215 \times DR_{\text{bulk}} (= -0.0015 \times \Omega_a + 0.0056), \\ & \text{according to Eq. (5)} \\ & = -1.8 \times \Omega_a + 6.8 \end{aligned}$$

Calcification of corals and other calcifiers is observed even at night, and results in a decrease of total alkalinity (Gattuso et al., 1999). Hence, a total alkalinity increase by carbonate dissolution (net dissolution) can be observed when dissolution is greater than gross calcification. Table 3 lists the net dissolution rate and Ω_a values. When Ω_a decreased from 3.1 to 1.0, net carbonate dissolution was observed. Andersson et al. (2009) calculated average rate of total dissolution by using long-term experimental data and estimated values of $1.6 \text{ mmol m}^{-2} \text{ h}^{-1}$ in the control (average $\Omega_a = 2$) and $3.74 \text{ mmol m}^{-2} \text{ h}^{-1}$ in a treatment mesocosm (average $\Omega_a = 1$). From Eq. (8), we can estimate that dissolution rates for our study are 3.2 and $5.0 \text{ mmol m}^{-2} \text{ h}^{-1}$ for Ω_a values of 2.0 and 1.0, respectively. This result is consistent with previous studies.

Table 3. Carbonate dissolution rates reported from carbonate environments and mesocosms.

Reference	Location	Dissolution rate [mmol m ⁻² h ⁻¹]	Ω_a	Benthic condition
Andersson et al. (2007)	Bahama	0.2 to 0.8	1.2 to 1.9	carbonate sediment (20 to 25 m depth) 20 to 30 % coral cover 31 % coral cover
Andersson et al. (2009)	Hawaii mesocosm	2.2 to 3.6	1.0 to 2.0	
Boucher et al. (1998)	Moorea	0.7	–	
Leclercq et al. (2002)	Monaco mesocosm	0.8	Water column: 2.7 to 5.2 Pore water: 1.9	sand community
Suzuki et al. (1995)	Ishigaki	3.0	1.7 to 3.1	19 % coral cover
		1.4	1.8 to 2.6	patch reef 22 %
Yates and Halley (2006)	Hawaii	1.0	1.5 to 2.6	patch reef 10 %
		1.1	2.0 to 2.5	coral rubble
		0.3	2.1 to 2.6	sand bottom

4.4 Future impact of ocean acidification on Mg-calcite dissolution

The burning of fossil fuels and future uptake of CO₂ by the oceans are predicted to reduce Ω_a to 2.0 to 3.0 by 2100 (Kleypas et al., 2006). Because high Mg-calcite is more soluble than both calcite and aragonite, it is the first responder to the decreasing saturation state of seawater (Andersson et al., 2003, 2007, 2009; Morse et al., 2006). The present results show that the threshold Ω_a of biogenic Mg-calcite in taxa such as coralline algae and foraminifera is 3.0 to 3.2. Mg-calcite is dissolved only nocturnally at present, but will eventually begin to dissolve diurnally also.

Kayanne et al. (2005) estimated the community calcification rate to be 70 to 127 mmol m⁻² day⁻¹ for Shiraho Reef. If the average daytime Ω_a value becomes 3.0 and the night-time value becomes 2.0, the carbonate dissolution rate will be 1.4 mmol m⁻² h⁻¹ diurnally and 3.2 mmol m⁻² h⁻¹ nocturnally (see Eq. (9)), which equals at least 55.2 mmol m⁻² day⁻¹. Because the sandy regions are about three times larger than the coral habitats at Shiraho reef (Kayanne et al., 2005), Mg-calcite dissolution in these sands will have a major influence on the Shiraho reef ecosystem. Moreover, the decreased calcification caused by the decline of Ω_a would result in negative net calcification of carbonate ecosystems at Shiraho reef in the future.

Supplementary material related to this article is available online at: <http://www.biogeosciences.net/9/1441/2012/bg-9-1441-2012-supplement.zip>.

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