

Threshold of carbonate saturation state determined by a 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 suggest that carbonate dissolution will occur in polar regions and in the deep-sea oceans where saturation state with respect to carbonate minerals (Ω) will be < 1 by 2100. However, carbonate in coral reefs distributed in tropical zones will not dissolve because the major carbonate in such reefs is aragonite, and the saturation state with respect to aragonite (Ω_a) is > 1 . Recent reports demonstrate nocturnal carbonate dissolution in reef reefs, despite $\Omega_a > 1$, probably relate to the dissolution of the minor 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, and it is unknown whether these dissolution processes actually occur under natural conditions. This work describes the measurement of the dissolution rates of coral aragonite and Mg calcite excreted by marine organisms under conditions of $\Omega_a > 1$ with controlled seawater μCO_2 . Laboratory experimental data of the present study show that bulk carbonate sediments sampled from a coral reef start to dissolve at $\Omega_a = 3.7$, and dissolution rates increase with falling Ω_a . Mg-calcite derived from foraminifera and coralline algae dissolved when Ω_a reached 3.4, whereas coralline aragonite started to dissolve when Ω_a was almost 1.0. We show that nocturnal carbonate dissolution of coral reefs occurs mainly by the dissolution of foraminifera and coralline algae in reef sediment.

AT $\Omega_a = 3.4$

AT $\Omega_a = 1.0$

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 to the atmosphere by human activities is taken up by the oceans (Sabine et al., 2004), lowering the pH of surface water and increasing the saturation

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decreasing

net dissolution of

dynamic 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 $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentrations of Ca^{2+} and CO_3^{2-} , respectively, and K_{sp} is a product of the equilibrium concentrations of Ca^{2+} and CO_3^{2-} .

Hence, the formation of the mineral is thermodynamically favorable when $\Omega > 1.0$, but is unfavorable in the case of $\Omega < 1.0$. Oceanic uptake of CO_2 causes an increase in hydrogen ion concentration $[\text{H}^+]$ and a decrease in carbonate ion concentration $[\text{CO}_3^{2-}]$, leading in turn to a decrease in Ω .

Carbonate dissolution can be described as follows:



15 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 increases that buffer capacity. If we are to meaningfully forecast the future change in the carbon balance between the atmosphere and the ocean, and to predict accurately the degree of consequent ocean acidification, it is crucial that we understand this buffer system.

The effect of the calcification performed by marine organisms on the decrease in Ω of seawater has been examined by laboratory experiments that control Ω . For example, Langdon and Atkinson (2005) showed that by 2065 the coral calcification rate will decrease by about 40 % compared with pre-Industrial levels. This estimate was based on laboratory experiments that showed the calcification rate of coccolithophorids decreases with increasing seawater $p\text{CO}_2$. This decrease would impact on the calcifiers themselves, as well as on the ecosystems they constructed.

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varies w/ carbonate

The value of Ω is different among its mineralogy. Aragonite is more soluble than calcite, and at present, Ω_a values range from 1 to 2 in high-latitude regions, and from 3 to 4.5 in low-latitude regions where coral reefs are formed. Therefore, carbonate dissolution at low latitudes (e.g., coral reefs) has not been expected. ~~However, net dissolution under conditions of $\Omega_a > 1$ has been observed at several coral reefs (Boucher et al., 1998; Leclercq et al., 2002; Kayanne et al., 2005; Yates and Halley, 2006; Nakamura and Nakamori, 2009). These previous studies inferred that dissolution in the case of $\Omega_a > 1$ is due to the dissolution of Mg-calcite. Mg-calcite is a carbonate in which some of the Ca is replaced by Mg, giving rise to the mineral dolomite. It is formed by foraminifera, coralline algae, and sea urchins, and exists universally in coral reef areas and occurs widely in the oceans (Moussa et al., 1991). When the Mg content is greater than 8%–12%, Mg-calcite dissolves more readily than aragonite (Plummer and Mackenzie, 1974; Bischoff et al., 1987; Morse et al., 2006).~~

The solubility of Mg-calcite is varied with content of magnesium. In general, minerals with higher Mg content shows higher solubility. Moreover, the solubility of synthetic and biogenic Mg-calcite is different in laboratory experiment, and there is variability in the solubility of biogenic Mg-calcite from different organisms (Morse and Mackenzie, 1990).

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-calcites solubilities (Bischoff et al., 1987; Mucci and Morse, 1984). Category (1) has the highest values for Mg-calcite solubility for all categories. For example, solubility of 12–15 mol Mg % calcites exceed aragonite solubilities by a factor of 5. The difference between (1) and (2) comes from sample treatments. Although previous studies used the same biogenic samples, there are several Mg-calcite solubilities and precise values are not decided. In neither case were the dissolution rates obtained consistent with field observations. Moreover, neither of these studies used total alkalinity and dissolved inorganic carbon when estimating their Ω_{CaCO_3} values and dissolution rates. Indeed, in

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the environment, it is $p\text{CO}_2$ which changes Ω_{a} ; consequently, laboratory studies may need to use $p\text{CO}_2$ to set Ω_{a} in order to attain consistency with the environment.

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 $\Omega_{\text{a}} > 1$ using an experiment system which controlled $p\text{CO}_2$ in seawater. In this paper, we measured threshold of biogenetic Mg-Calcite by not thermodynamic equilibrium but keeping $p\text{CO}_2$ constant experiment for simulating field condition. The dissolution system was designed such that Ω_{a} is controlled by $p\text{CO}_2$. Ω_{a} is calculated by measurements of total alkalinity (A.T) and dissolved inorganic carbon (C.T).

2 Methodology

2.1 Experimental design

The experimental system (Fig. 1) consists of four units with seawater and gas lines connecting these units: seawater tank, dissolution chamber, CO_2 gas unit, and flow-through analyzer for A.T and C.T. Each of these units is described below.

2.1.1 Seawater tank

Tanked
 CO_2 gas was introduced from a CO_2 gas unit and was dissolved in seawater by using a 3.5-m coiled tube. Seawater was stored in the tank within a rectangular bottle (9 l). Seawater $p\text{CO}_2$ was checked using a membrane tube and a non-dispersive infrared gas analyzer (NDIR) (Saito et al., 1995).

2.1.2 Dissolution chamber

Using a pump, seawater was introduced to the dissolution chamber from the seawater tank. Dissolution samples were set in this chamber, which was 600 ml in volume and

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*with small holes to allow for bubbling + equilibration w/ seawater.
+ CO_2 amended water allowed to prevent loss of*

2.1.3 CO_2 gas unit

Gas mixtures of CO_2 at concentrations between 400 and 2210 ppm were generated 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. We used an NDIR, (LI-COR, LI-820) to monitor $p\text{CO}_2$ in the seawater.

2.1.4 Flow-through analyzer

The sample seawater was introduced directly through the flow-through analyzer (Kimoto Electric Company Limited) by switching the flow line (Kimoto et al., 2001; Watanabe et al., 2004). A Certified Reference Material standard seawater (A. Dickson, University of California) was used to calibrate the flow line. Sodium carbonate solutions made on site were used for the C.T calibration. The precision of analysis for A.T and C.T was $\pm 3 \mu\text{mol kg}^{-1}$ for each.

2.2 Experimental procedure

1. CO_2 gas (420–2210 ppm) was prepared from the CO_2 gas unit.
2. Seawater in the tank was circulated inside the seawater line (bypass line) for 10–12 h to allow the seawater and introduced CO_2 to equilibrate. The $p\text{CO}_2$ was then checked with a pH electrode (annular ring type, pHC2401, Radiometer Analytical, France) and also by NDIR.
3. After the pH and $p\text{CO}_2$ had stabilized, A.T and C.T were determined before the dissolution experiment began.

4. Samples were placed in the dissolution chamber, and seawater was circulated inside the seawater line (dissolution line).
5. A_T and C_T were measured again after several hours, at the end of the experiment. — measured were ?

5 2.3 Samples

For the dissolution experiment, seawater was collected from a depth of 500 m at 34.7° N, 139.4° W (near Izu Island, Japan). 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 (24°22' N, 124°15' E). The sediment was collected during August 2007, and the coral and coralline algae were obtained during October 2007.

The major size fraction of coral reef sediment was from -1.0 to 0.0 ϕ (1–2 mm), from which 800 particles were separated for each dissolution experiment. The mineralogy of each sample was identified by X-ray diffraction (XRD) analysis. The sample consisted of coral, foraminifera, 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 coralline algae and foraminifera were 16.5 ± 0.4 and 13.3 ± 0.4 mol %, respectively, and the coral was pure aragonite.

2.4 Calculation

20 The A_T of seawater increases by 2 moles for every 1 mole of carbonate dissolution. The carbonate dissolution rate is measured by analyzing the change in A_T ; however, not only carbonate dissolution but also salinity changes affect the A_T . Hence, it is necessary to exclude the influence of salinity. Using Eq. (3), A_T was standardized to a constant salinity, and the dissolution rate was then calculated:

$$25 \quad nA_T = A_T \times S_{\text{average}} / S_{\text{sample}} \quad (3)$$

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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 salinity during each experiment. $C.T$ 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: *over the course of the experiment?*

10 $R = \Delta nA_T / 2 \times m_v \times M \times 100 / (m_s \times t)$ (4)

where ΔnA_T is the difference in nA_T during the experiment, m_v is the weight of seawater, M is the molecular weight of calcium carbonate (=100), m_s is the weight of the carbonate sample, and t is the duration of the experiment. Because A_T and C_T are both analyzed directly in the experimental system, the amount of seawater in the experiment system decreases during the experiment. m_s is the average weight over the course of the experiment. *↑*

ρCO_2 and Ω_{a} of the seawater 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 full pH range (0–14) was used in all calculations, employing the equilibrium constants (K_1 and K_2) reported by Mehrbach et al. (1973).

3 Evaluation of the experiment system

3.1 Evaluation for remaining water

Due to the design of the system, a small amount of seawater remains in the pump and tubing at the end of each run. This is a problem because interpretation of the results requires a reasonable mass balance. To assess the amount of retained water,

5 pilot experiments were performed with seawater and pure water. After initial seawater loading, the conductivity was measured and the system emptied. The system was then loaded with pure water and the conductivity measured. Using the decreasing salinity as a conservative tracer, the conductivity measurements were used to assess how much salt was left in the system, and hence how much water remained in the system after emptying. This process revealed that about 10 ml of water was retained in the system after emptying.

3.2 Evaluation for salinity change

10 The salinity varies over the course of the dissolution experiment, mainly due to evaporation. This is a problem because salinity is used to interpret the results of the experiments.

15 In our experiment system, pCO_2 and Ω_a of seawater are controlled by the continuous bubbling of CO_2 into the seawater. Therefore, seawater continuously evaporates and the salinity rises. Seawater temperature is controlled at 26°C, and the main variable controlling salinity change is the quantity of the flowing gas. Table 1 contains a series of CO_2 volume flows with the resultant salinities. It is clear that the salinity increases in direct proportion to the gas mass flow. Therefore, we calibrated the salinity during the experiment according to the salinity after the experiment, from the relationship between the gas mass flow and the rate of salinity change. 20 This relationship was validated between blank and sample runs under the following conditions: $pCO_2 = 1120$ ppm, gas flow rate = 400 $ml\ min^{-1}$, $\Omega_a = 1.83$, and salinity change = $0.01\ h^{-1}$ (by using a gas flow of 400 $ml\ min^{-1}$; see Table 1).

25 Figure 3 shows a time series of A_T without salinity calibration, and Figure 4 shows a time series with calibration. A_T increased for the blank experiment without a carbonate sample, but after salinity calibration the change in nA_T was about $2-3\ \mu\text{mol kg}^{-1}$, and this value was within the error range of the measurement. The results for all of the dissolution experiments were calibrated using this procedure.

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4 Results

Temperature, pCO_2 & corresponding Ω_a values for ~~for~~ bulk sediment, foraminifera, coralline algae, & coral experiment (already mentioned)

5 The results of the experiments are listed in Table 2. pCO_2 and Ω_a were calculated from A_T and C_T . The results of the bulk dissolution experiment are shown in Figs. 5 and 6. The experiments were performed for 6.0–11.5 h. During the experiments, nA_T varied between 6 and $25\ \mu\text{mol kg}^{-1}$. No increase in nA_T was observed when pCO_2 was 420 ppm, and the change in nA_T was greatest when pCO_2 was about 2030 ppm.

10 Figure 6 shows the average dissolution rates, calculated from nA_T changes, plotted against averaged Ω_a . The average dissolution rate was fastest ($0.004\ %\ h^{-1}$) when Ω_a was 1.3 and slowest when Ω_a was 3.7.

15 Similarly, Fig. 7 shows the results of dissolution experiments on foraminifera, coralline algae, and coral. In all cases, the dissolution rate increases as Ω_a decreases. Threshold of foraminifera and coralline algae are $3.0 < \Omega_a < 3.2$, and that of bulk sediment is $3.7 < \Omega_a < 3.8$. The dissolution rate of coral shows no significant change when $1.5 < \Omega_a < 2.0$.

15 5 Discussion

From Fig. 7, the dissolution rate was highest for coralline algae, followed by foraminifera and then coral. Consistent with previous work (Morse et al., 2006, 2007; Bischoff et al., 1993), the results show that higher dissolution rates were observed for samples with higher Mg-calcite contents.

20 Because the grain size and other properties of the samples were as consistent as possible, the differences in dissolution rates between samples were probably caused by differences in the instability (i.e., solubility) of the minerals.

5.1 Relationship between solubility and Ω_a

25 We compared the solubilities measured in previous studies (Morse and Mackenzie, 1990) with those obtained in the present study from the threshold of coralline algae

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WHAT DOES "THRESHOLD" MEAN THIS TIME

and foraminifera. The solubility of Mg-calcite of biogenic origin is shown in two different ways: Plummer-Mackenzie solubility (Plummer and Mackenzie, 1977) and biogenic best-fit solubility (Walter and Morse, 1984; Bischoff et al., 1987). For example, the Ω value of Mg-calcite (16 mole % $MgCO_3$) is 0.2 by the former method and 0.8 by the latter when $\Omega_a = 1.0$. This discrepancy may originate from differences in pretreatment and the experimental method (Bischoff et al., 1993; Morse et al., 2006). For example, carbonate samples were washed in an ultrasonic bath and then dried for the Plummer-Mackenzie method, whereas for the biogenic best-fit solubility they were not only washed in an ultrasonic bath, but also chemically treated with H_2O_2 to remove organic matter.

In the present work, $-\log(K_{sp}^*)$ of coralline algae ($16.5 \text{ mol} \pm 0.4 \text{ Mg\%}$) and foraminifera ($13.3 \text{ mol} \pm 0.4 \text{ Mg\%}$) are -7.80 and -7.82 , respectively. Our samples were cleaned only by ultrasonic bath and dried at 40°C for about 12 h, following Plummer and Mackenzie (1974). The solubilities calculated in the present study are similar to those estimated using the Plummer-Mackenzie method, and are comparable to those obtained from field data because the minimum processing employed in this study results in a state similar to that in the sediment. Such analyses of the solubility of foraminifera and coralline algae are important because dissolution in the sediment may influence observations and hence the results of palaeoceanographic studies.

20 5.2 Evaluation of Mg-calcite dissolution

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

$$\text{Bulk: Dissolution rate } (\% \text{ h}^{-1}) = -0.0015 \times \Omega_a + 0.0056 \quad (5)$$

$$\text{Foraminifera: Dissolution rate } (\% \text{ h}^{-1}) = -0.0027 \times \Omega_a + 0.0081 \quad (6)$$

$$25 \text{ Coralline algae: Dissolution rate } (\% \text{ h}^{-1}) = -0.0045 \times \Omega_a + 0.0143 \quad (7)$$

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WHAT DOES THIS MEAN?

Definition of threshold needs to be explained earlier.

According to Eqs. (5)–(7), threshold of bulk sediment, meaning bulk dissolution rate is equal zero, is $3.7 < \Omega_a < 3.8$, and that of foraminifera and coralline algae are $3.0 < \Omega_a < 3.2$. Difference of these values comes from "other minerals".

The sediment samples consists of 75 % foraminifera, coralline algae, coral, and other aragonite, and 25 % sea urchin (3 %) and "other minerals" (22 %); the latter two components were not included in the calculations. The sea urchin is Mg-calcite with a low $MgCO_3$ content (8.0 mole %), corresponding to a small contribution to the dissolution rate. The "other minerals" are considered to be calcite or Mg-calcite in composition because they did not color with dyeing and over 95 % of sediment at the Shiraho coral reef is carbonate. In this study, we could not distinguish "other minerals" from foraminifera or coralline algae, meaning that we may have underestimated the dissolution rate.

5.3 Comparison between field observation and this study

We compared our result of relationship between bulk dissolution rate and Ω_a , with previous research reported about carbonate dissolution in fields. Because our laboratory result is described by $[\% \text{ h}^{-1}]$, we have to convert the units to $[\text{mmol m}^{-2} \text{ h}^{-1}]$.

If upper 1 cm sand sediment dissolves, and without considering pore water (i.e., Mg-calcite is influenced only by column seawater), dissolution rate $R[\text{mmol m}^{-2} \text{ h}^{-1}]$ is described as follows:

$$20 R[\text{mmol m}^{-2} \text{ h}^{-1}] = DR_{\text{bulk}} [\% \text{ h}^{-1}] \times 0.01 [\text{m}] \times 1 [\text{m}^2] \times 2700 [\text{kg m}^{-3}] \times 0.45 \times 10^2 \\ = 1215 \times DR_{\text{bulk}} (= -0.0015 \times \Omega_a + 0.0056) \text{ according to Eq. (5)} \\ = -1.8 \times \Omega_a + 6.8 \quad (8)$$

25 Density of calcium carbonate is 2700 kg m^{-3} and porosity of coral reef sediment is 0.45 (Morse and Mackenzie, 1990).

Calcification for coral and other calcifiers is observed even during night and decreases total alkalinity (Gattuso et al., 1999). Hence, total alkalinity increase by

results in a decrease of

carbonate dissolution can be observed when gross dissolution is larger than gross calcification. Table 3 shows observed dissolution rate and Ω_{a} . Estimates of net carbonate dissolution range from 0.2 to 3.6 $\text{mmol m}^{-2} \text{h}^{-1}$ when Ω_{a} ranges from 1.0 to 3.1. Andersson et al (2009) calculated gross carbonate dissolution rate by using long-term experiment data and estimated that total dissolution equalled 1.6 $\text{mmol m}^{-2} \text{h}^{-1}$ and 3.74 $\text{mmol m}^{-2} \text{h}^{-1}$ in the control (average Ω_{a} was (2) and in a treatment mesocosms (average Ω_{a} was (1), respectively. From Eq. (8), we can estimate that gross dissolution rates are 3.2 $\text{mmol m}^{-2} \text{h}^{-1}$ and 5.0 $\text{mmol m}^{-2} \text{h}^{-1}$, respectively when Ω_{a} are 2.0 and 1.0. Our result is consistent with previous filed studies.

10 5.4 Future impact for Mg-calcite dissolution

Andersson et al. (2003) suggested that carbonate dissolution has little effect for buffering anthropogenic CO_2 . It is because they applied the solubility value for 15 mol % Mg-calcite from Bischoff et al. (1993). Because their solubility of Mg-calcite is "biogenic best-fit solubility", Mg-calcite does not dissolve even if Ω_{a} decreases below 3.0.

15 Kleypas et al. (2006) suggested that continuous burning of fossil fuels and future uptake of CO_2 by the ocean are predicted to reduce Ω_{a} to 2.0–3.0 until 2100. Our research suggests biogenic Mg-calcite such as coralline algae and foraminifera is more soluble than aragonite and its threshold of dissolution is 3.0–3.2. Mg-calcite dissolution occurs only during night at present, but it will occur during all day in the near future.

20 Kayanne et al. (2005) estimated community calcification rate as 70–127 $\text{mmol m}^{-2} \text{day}^{-1}$ in Shiraho Reef. If average Ω_{a} of daytime becomes 3.0, calcification rate will become 30–50% lower than present rate. On the other hand, according to our result, carbonate dissolution rate will be 1.4 $\text{mmol m}^{-2} \text{h}^{-1}$ (see Eq. 8), which equals at least 33.6 $\text{mmol m}^{-2} \text{day}^{-1}$. Because sand area is about one-third 25 larger than coral area in Shiraho reef (Kayanne et al., 2005), carbonate dissolution will exceed calcification in this reef as average Ω_{a} of daytime decreases below 3.0.

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Table 1. Relationship between change of gas flow, salinity and A_T.

Gas Flow [cc min ⁻¹]	Δ Salinity [h ⁻¹]	Δ A_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 $\mu\text{mol kg}^{-1}$.

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How long
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500 to
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Table 2. Condition for each experiment.

Samples	temperature	seawater(g): sample(g)	μCO_2 [ppm]	at correspondence	<i>Na</i>
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	
Foraminifera	26 °C	310:1	510, 570, 1240, 2210	3.2, 2.9, 1.7, 1.1	
Coralline algae	26 °C	310:1	570, 830, 1070, 2000	2.9, 2.3, 1.8, 1.2	
Coral	26 °C	310:1	1070, 1550, 2100	1.9, 1.6, 1.1	

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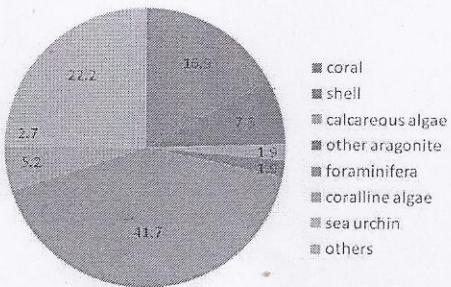


Fig. 2. Component of sediment sample.

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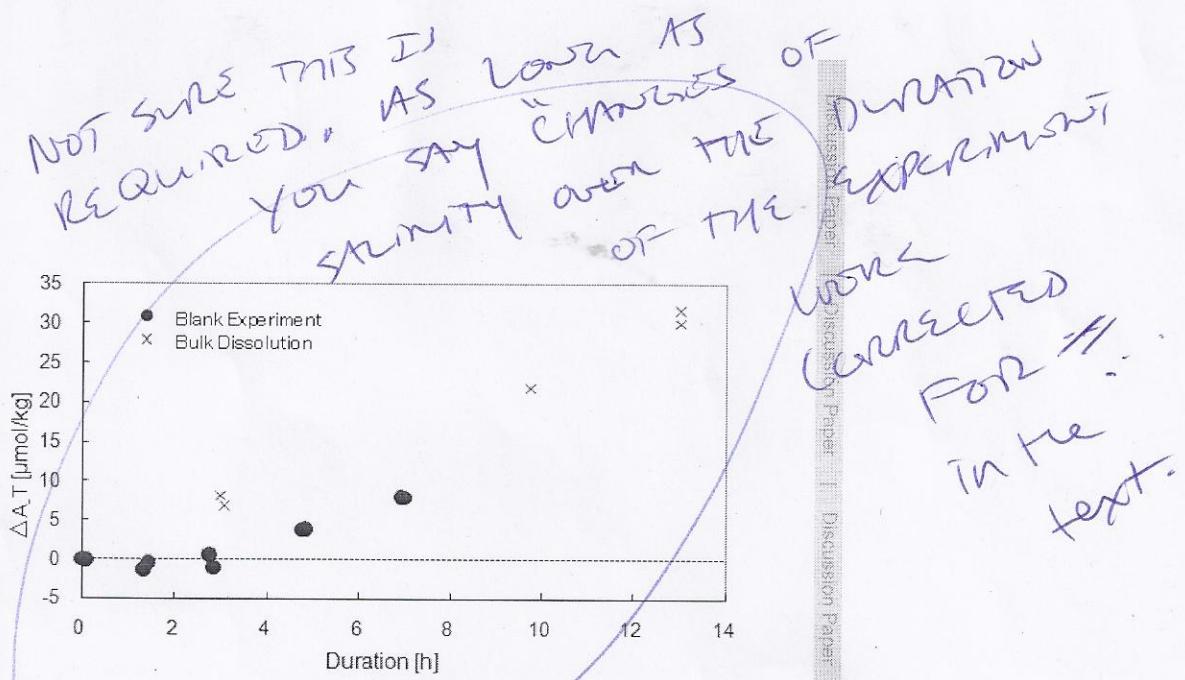


Fig. 3. Blank experiment and bulk dissolution (before salinity calibration).

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