

Calcium carbonate production and carbon dioxide flux on a coral reef, Okinawa

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Abstract—Calcification, photosynthesis and respiration were investigated on a coral reef community, Rukan-sho, Okinawa in order to determine the role of calcification associated with carbon dioxide flux. Based on the data measured during the daytime in October 1993, rates of net organic carbon production (OP) and calcification (CA) were estimated at $9.3 \text{ mmol m}^{-2}\text{h}^{-1}$ and $5.3 \text{ mmol m}^{-2}\text{h}^{-1}$, respectively. The respiration rate was $6.0 \text{ mmol m}^{-2}\text{h}^{-1}$ and calcification was negligible at night. The comparison of CO_2 release by calcification ($3.2 \text{ mmol m}^{-2}\text{h}^{-1}$, which is estimated by “0.6 rule” and calcification rate) with the net organic carbon production indicates that the coral reef metabolism played a sink role for atmospheric carbon dioxide during daytime, whereas it acted as a source at night.

INTRODUCTION

The deposition and dissolution of CaCO_3 provides information towards understanding the global oceanic carbon cycle. MACKENZIE and GARRELS (1966) demonstrated the necessity of calcite and/or aragonite precipitation as mechanisms for the removal of excess dissolved Ca^{2+} and HCO_3^- from the oceans to maintain the chemical mass balance between rivers and oceans. The reaction can release CO_2 according to



As a result of CaCO_3 overgrowth experiments on calcite seeds in seawater, WOLLAST *et al.* (1980) reported that 0.6 mole of CO_2 was released from seawater for one mole of CaCO_3 precipitated in seawater. Results of CO_2 chemical equilibrium calculation (e.g. KANO, 1990; WARE *et al.*, 1991; TSUNOGAI, 1993) confirm the Wollast *et al.* experiment, classified by WARE *et al.* (1991) as the “0.6 rule”.

In short, the “0.6 rule” can be explained as the amount of CO_2 gas released to the atmosphere due to reaction (1). Since the released CO_2 gas can be transformed to bicarbonate and carbonate ions in seawater, 1 mole of CaCO_3 precipitation can release only 0.6 mole of carbon dioxide to the atmosphere. Based on the “0.6 rule”, it was concluded that coral calcification is a source of CO_2 to the atmosphere. However, the “0.6 rule” has not been verified by in situ coral reef measurements.

Furthermore, calcification in the above equation has been considered in the absence of biological activities. I consider that the carbon cycle of coral reef ecosystem is complex and influenced by biological processes, such as organic production (photosynthesis), respiration and calcification. This study examined the carbon dioxide flux related to calcification on an Okinawan coral reef in order to evaluate whether the coral reefs are sources or sinks for atmospheric carbon dioxide.

FIELD AND METHODS

Rukan-sho

Rukan-sho is located 15 km west of Itoman City, Okinawa (see Fig. 1(a)). The island is a small atoll (or platform reef) which may be divided into two geomorphological zones, the reef (water depth: -1.0 to -1.3 m) and lagoon (water depth: -2 to -4 m) as shown in Fig. 1(b). The reef has a rich coral reef fauna and flora. Mean water depths were measured using a plastic tape and the bathymetric map was drawn as Fig. 1(b).

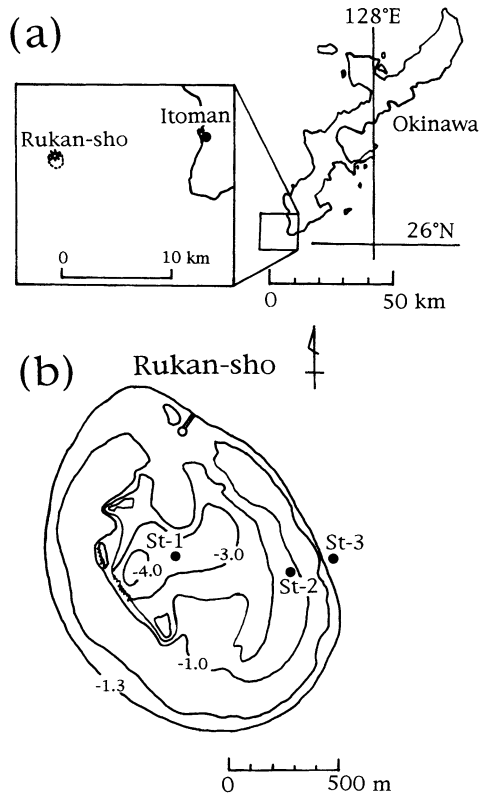


Fig. 1. (a) Location of Rukan-sho. (b) Bathymetric map showing study sites.

Study sites

Three sites fixed for the field observations are shown in Fig. 1(b). They are located on the center of the lagoon (Site-1), the back reef (Site-2) and the outer reef (Site-3), respectively. The observations were carried out on 17 and 18 October 1993. At low tide, the sea level was 0.8 m lower than the mean sea level and almost all of the reef front was emerged for a few hours. During the low tide, water samples were collected every 20 minutes at Site-2 where tide pools had formed. Seawater samples were also collected at Site-1 and Site-3 for the determination of pH, total alkalinity (TA), total carbon dioxide (DIC), *p*CO₂ and salinity (see Table 1). At these three sites, the samples were collected from just below the water surface (~5 cm) using plastic cylinders (7 cm in diameter, 15 cm in length), which were sealed under water without atmospheric contact.

Analytical methods

The salinity was determined by a salinometer (YEO-KAL, 601 MKIII, Australia). Seawater was stored in 250 ml plastic bottles and kept in a cooling box after sampling, and transported to the laboratory for analyses of pH and total alkalinity. Within several hours, the pH was measured at 25°C using a pH-meter (Toa

Table 1. Results of a study undertaken in Rukan-sho on 17–18 October 1993

Sample No.	Time	T (°C)	Salinity	pH(NBS) (at 25°C)	TA (meq/kg)	DIC (mmol/kg)	pCO ₂ (μ atm)
(Site-1)	17/10/93						
1-1	14:00	28.3	34.815	8.346	2.248	1.853	257
1-2	15:33	28.3	34.821	8.342	2.238	1.847	-
	18/10/93						
1-3	0:03	27.3	34.792	8.188	2.275	1.954	346
1-4	2:03	27.1	34.792	8.198	2.291	1.967	354
1-5	3:50	27.0	34.804	8.186	2.300	1.994	358
(Site-2)	17/10/93						
2-1	13:20	29.5	34.834	8.434	2.144	1.697	250
2-2	13:40	30.0	34.839	8.463	2.114	1.639	243
2-3	14:00	30.1	34.838	8.477	2.092	1.616	-
2-4	14:20	30.2	34.852	8.489	2.078	-	218
2-5	14:40	30.0	34.857	8.495	2.061	1.570	184
2-6	15:00	30.0	34.862	8.504	2.048	1.552	174
2-7	15:20	29.8	34.866	8.513	2.031	1.529	163
2-8	15:40	29.8	34.873	8.516	2.012	1.514	155
	18/10/93						
2-9	1:40	26.8	34.815	8.005	2.266	2.040	557
2-10	2:00	26.8	34.816	7.975	2.260	2.052	618
2-11	2:20	26.7	34.819	7.943	2.266	2.068	645
2-12	2:45	26.7	34.823	7.914	2.267	2.082	681
2-13	3:00	26.6	34.825	7.907	2.264	2.084	846
2-14	3:20	26.6	34.827	7.874	2.264	2.095	900
(Site-3)	17/10/93						
3-1	16:25	27.4	34.786	8.271	2.294	1.926	331

T: temperature, TA: total alkalinity and DIC: total carbon dioxide.
The *p*CO₂ was measured at 25°C using the OHTAKI *et al.* (1993) method.

Electronic, HM-60, Japan). Total alkalinity was measured by potentiometric titration with 67 mM HCl in 0.65 M NaCl solution at 25°C, within 2 days (BUTLER, 1982). Seawater samples for total carbon dioxide (DIC) and $p\text{CO}_2$ determinations were collected in 100 ml Pyrex vials with rubber stoppers. The samples for DIC measurements were poisoned to terminate biological activity with a saturated HgCl_2 solution (0.1 ml) soon after sampling, and stored in a refrigerator. DIC was measured coulometrically (Carbon dioxide coulometer, UIC Model 5012, USA). The partial pressure of CO_2 was determined using NDIR (Shimadzu, URA-106, Japan) (OHTAKI *et al.*, 1993).

RESULTS AND DISCUSSION

The results are listed in Table 1. Figure 2 shows the variations in pH, TA and DIC between day and night at Site-2. The figure clearly demonstrates the changes in pH, TA and DIC of seawater in the coral reef community which was periodically subjected to a cessation of water flow for a few hours, and also the distant differences between these variables during the day and night.

Calcification

The total alkalinity (TA) of seawater on a coral reef mainly changes in response to the precipitation and dissolution of CaCO_3 . The alkalinity depletion method (SMITH and KINSEY, 1978) can be applied to estimate the rate of calcification. Because of seawater evaporation, the alkalinity changes in proportion to the salinity. Therefore

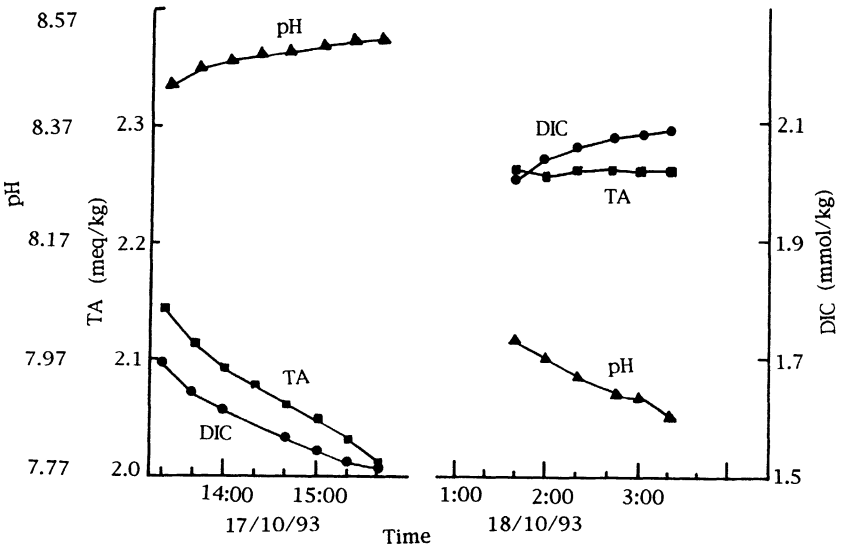


Fig. 2. Variations in pH, total alkalinity (TA) and total carbon dioxide (DIC) at Site-2 on 17-18 October 1993.

a correction for salinity change is needed to calculate the alkalinity depletion.

Total alkalinity at Site-2 decreased from 2.144 to 2.012 meq/kg for 2.33 hours at daytime (see Nos. 2-1 and 2-8 in Table 1). ΔTA is calculated at 0.134 meq/kg ($2.144 \times 34.873/34.834 - 2.012 = 0.134$) after the correction for seawater evaporation. The net hourly calcification rate (CA) is calculated to be 5.3 mmol m⁻²h⁻¹ using the equation:

$$CA = 0.5(\Delta TA) \cdot Z \cdot D/T, \quad (2)$$

where Z is the water depth at Site-2 (0.18 m), D is the density of seawater (1020 kg/m³) and T is the period of the observation (2.33 hours).

From the data shown in Table 1 (Nos. 2-10 to 2-17), no alkalinity change was observed at Site-2 during nighttime. It thus indicates that net calcification did not occur during the night. This finding suggests no calcification at night and the occurrence of diurnal growth-line found in a coral (WELLS, 1963).

Photosynthesis and respiration

Changes in DIC and TA of the surrounding seawater at Site-2 provide data on coral reef community metabolism. Hourly rates of net organic carbon production (OP) during daylight can be estimated as follows:

$$OP = (\Delta DIC - \Delta TA/2) \cdot Z \cdot D/T. \quad (3)$$

Carbon dioxide exchange across the air-seawater boundary on a reef flat is assumed to be negligible on the basis of the calculation (SMITH and KINSEY, 1978). The production rate (OP) at Site-2 is calculated to be 9.3 mmol m⁻²h⁻¹ using the data shown in Table 1 (Nos. 2-1 and 2-8).

Hourly respiration rates (R) at night are similarly calculated as follows:

$$R = (\Delta DIC) \cdot Z \cdot D/T. \quad (4)$$

The rate (R) is estimated to be 6.0 mmol m⁻²h⁻¹ using the data shown in Table 1 (Nos. 2-9 and 2-14).

CO₂ flux at Site-2

The ratio of rates of net organic carbon production to calcification is calculated to be 1.8 (OP/CA = 9.3/5.3). From carbon dioxide chemical equilibria, WARE *et al.* (1991) pointed out that 0.6 mole of CO₂ is liberated as gas to the atmosphere for one mole of CaCO₃ precipitated in seawater (0.6 rule). The ratio (OP/CA) is larger than the value expected by the "0.6 rule", which means the coral reef can take up all the CO₂ generated by calcification and more. Therefore, we may conclude from these preliminary observations that the coral reef community during the day acts as a sink for atmospheric CO₂. However, Fig. 2 and Table 1 showed only respiration at night.

The net CO₂ budget during a day can be estimated with several assumptions,

1) measured calcification, photosynthesis, and respiration rates are representative, and 2) the length of the day and the night are 12 hours each. Since net organic carbon production (OP) and calcification (CA) during the day were $9.3 \text{ mmol m}^{-2}\text{h}^{-1}$ and $5.3 \text{ mmol m}^{-2}\text{h}^{-1}$, respectively, and the respiration rate was $6.0 \text{ mmol m}^{-2}\text{h}^{-1}$ and calcification was negligible at night, the net CO_2 budget of the reef can be calculated at $1.4 \text{ mmol m}^{-2}\text{day}^{-1}$ ($9.3 \times 12 - 5.3 \times 0.6 \times 12 - 6.0 \times 12 = 1.4$). The value, 1.4 is considered almost zero compared with the values of daily OP, CA and R. The resultant calculation suggests that the net CO_2 budget was equally balanced on the coral reef. However, this conclusion is based on several assumptions and a small data set. Therefore, further studies are needed to confirm this result and to expand our current understanding of the carbon dioxide flux on coral reef ecosystems.

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