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Diurnal Changes in the Partial Pressure of Carbon Dioxide in Coral Reef Water

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Coral reefs are considered to be a source of atmospheric carbon dioxide because of their high calcium carbonate production and low net primary production. This was tested by direct measurement of diurnal changes in the partial pressure of carbon dioxide (P_{CO_2}) in reef waters during two 3-day periods, one in March 1993 and one in March 1994, on Shiraho reef of the Ryukyu Islands, Japan. Although the P_{CO_2} values in reef waters exhibited large diurnal changes ranging from 160 to 520 microatmospheres, they indicate that the reef flat area is a net sink for atmospheric carbon dioxide. This suggests that the net organic production rate of the reef community exceeded its calcium carbonate production rate during the observation periods.

Photosynthetic organic production and calcium carbonate production occur simultaneously in coral reefs at rates more than 100 times those in the outer ocean (*1*). Photosynthesis acts as a sink of atmospheric CO_2 ($CO_2 + H_2O \rightarrow CH_2O + O_2$), whereas respiration releases the fixed CO_2. Calcium carbonate production, on the other hand, raises P_{CO_2} in seawater ($Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$). It is thought that gross organic production in reefs is high, but net organic production is near zero, because the tropical ocean is typically depleted in nutrients to support net production. Therefore, coral reefs are thought to be a source of CO_2 to the atmosphere (*2*). One model proposes that the glacial-interglacial increase in atmospheric CO_2 levels resulted from the release of CO_2 that accompanies calcium carbonate deposition in reefs (*3*).

Global productions of net organic carbon and calcium carbonate in reefs have been roughly estimated at 20×10^{12} g of C per year (*4*) and 111×10^{12} g of C per year (*5*), respectively, which supports the hypothesis that coral reefs are a net source for atmospheric CO_2 (*2*). However, knowledge of the actual P_{CO_2} changes that accompany reef productions has been uncertain and requires direct measurement of P_{CO_2} changes in reef water (*6*).

We have monitored the change in P_{CO_2} of reef water over Shiraho coral reef on Ishigaki Island in the Ryukyus of Japan (Fig. 1A). Our measurements were made with a compact seawater P_{CO_2} measurement system with a nondispersive infrared gas analyzer (NDIR) and a membrane tube (*7*). The device is most effectively used in a shallow reef area, which is inaccessible to a large research vessel. We made measurements continuously for two three-day periods, from 9 to 12 March 1993 (Fig. 2A) and from 13 to 17 March 1994 (Fig. 2B). In addition to reef water P_{CO_2}, we measured the partial pressure of CO_2 in the atmosphere (p_{CO_2}), light intensity, current direction and speed, and water depth. P_{CO_2} values outside the reef were measured twice: at 12:00 Japan time on 14 March 1994 and at 0:00 Japan time on 16 March 1994.

Shiraho is a typical fringing reef with a reef flat 850 m wide from the shore to the reef edge. This reef is known for its flourishing corals (Fig. 1B) (*8*). The seaward rise (reef crest) is exposed during low tides and separates water on the reef flat from the outer ocean. This situation is ideal for conducting a natural closed-field experiment. During these stagnant periods, the calcium

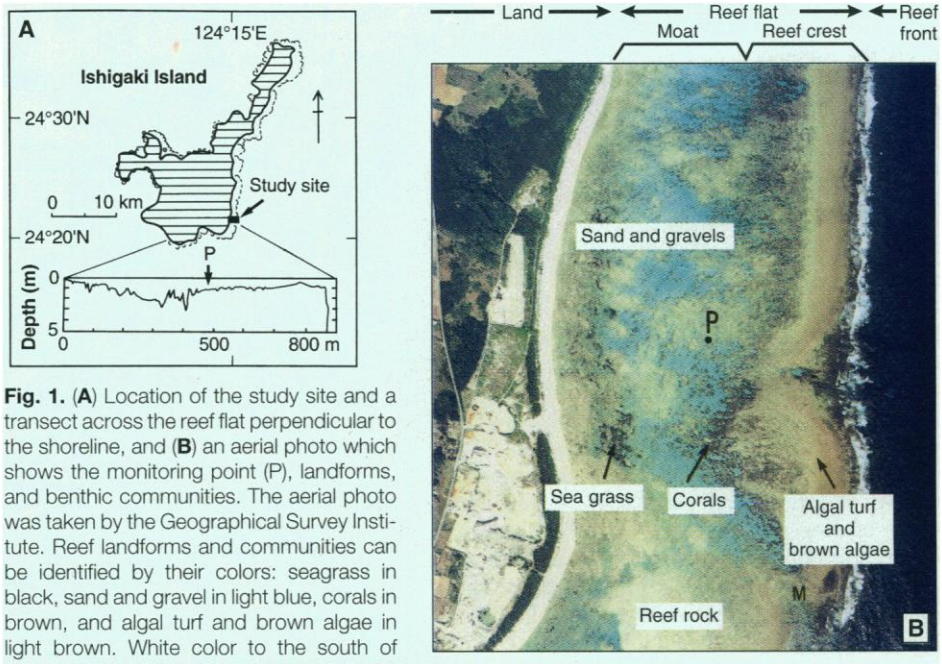

Fig. 1. (**A**) Location of the study site and a transect across the reef flat perpendicular to the shoreline, and (**B**) an aerial photo which shows the monitoring point (P), landforms, and benthic communities. The aerial photo was taken by the Geographical Survey Institute. Reef landforms and communities can be identified by their colors: seagrass in black, sand and gravel in light blue, corals in brown, and algal turf and brown algae in light brown. White color to the south of Shiraho reef shows reef rock covered with sand. The outer reef crest and reef rock are exposed at low tide.

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carbonate production of coral communities has been estimated on the basis of changes in the measured alkalinity values in seawater, and the organic production and respiration have been estimated on the basis of changes in the total CO_2 concentration computed from the measured alkalinity and P_{CO_2} values. The water exchanges on every high tide with adjacent open-ocean water.

We observed a diurnal pattern of reef water P_{CO_2}, with a minimum of 157 μatm during the day and a maximum of 521 μatm during the night (9). The magnitude of the daytime decrease corresponds well with the light intensity. Table 1 shows the averaged light intensity and the averaged P_{CO_2} normalized at 23°C for each daytime and nighttime period. On 16 March 1994, averaged light intensity was at its highest value (720 μmol m^{-2} s^{-1}) and daytime average P_{CO_2} at its lowest value (242 μatm) measured during the observation periods. The relation between the average values of P_{CO_2} and those of light intensity (I) is represented as $P_{CO_2} = 352 - 0.13I$, if we assume linearity. The mean light intensity in March for Ishigaki Island from meteorological observations is 552 μmol m^{-2} s^{-1} (*10*). The corresponding value of P_{CO_2} would be 279 μatm.

Atmospheric p_{CO_2} was almost constant: 348 ± 9 μatm in 1993 and 348 ± 2 μatm in 1994. Compared with the average daytime (279 μatm) and nighttime (352 μatm) P_{CO_2} obtained from the above equation, this reef showed higher daytime CO_2 invasion from air to sea (a difference of 69 μatm) than nighttime evasion (4 μatm). To evaluate the function of reefs in the exchange of CO_2 between air and sea, we must compare the reef P_{CO_2} with the offshore value (322 μatm at 23°C). The estimated mean daytime and nighttime reef water P_{CO_2} values were 43 μatm lower and 30 μatm higher than the offshore value, respectively, which also indicates that the reef serves as a sink of atmospheric CO_2.

The light-dependence of P_{CO_2} changes implies that changes in CO_2 in the Shiraho reef water are caused primarily by the balance of photosynthesis and respiration. To test this, we compared organic carbon and calcium carbonate productions with P_{CO_2} changes during six stagnant periods. During the four daytime stagnant periods (DI to DIV in Table 1), photosynthetic organic production (9 to 16 mmol of C per square meter per hour) exceeded the carbonate production (3 to 7 mmol C m^{-2} $hour^{-1}$). Because the rate of photosynthesis exceeds that of calcium carbonate production by a factor of 1.6 or greater (Table 1), the P_{CO_2} in reef waters decreased during the daytime. During the nighttime stagnant periods (NI and NII in Table 1), the CO_2 production by respiration (−3 and −5 mmol C m^{-2} $hour^{-1}$) was associated with minor carbonate production (−1 and 1 mmol C m^{-2} $hour^{-1}$) and hence caused an increase in P_{CO_2}.

We estimated the daily calcium carbonate and photosynthetic organic productions by measuring pH and alkalinity change on Shiraho reef (*11*). The reef has a net organic production of 110 mmol C m^{-2} day^{-1} (1.3 g C m^{-2} day^{-1}) and a net calcium

Table 1. Relation between P_{CO_2} and light intensity. P_{CO_2} and light intensity are averaged for each daytime (D) and nighttime (N) period. Estimated organic and carbonate productions during six stagnant periods (DI to DIV, NI, and NII in Fig. 2) are also shown.

Parameter	Day of March 1993						Day of March 1994						
	9		10		11		13	14		15		16	
	D	N	D	N	D	N	N	D	N	D	N	D	N
Averaged P_{CO_2} (μatm)	319	327	336	367	270	365	411	322	385	302	377	242	255
Averaged light intensity (μmol m^{-2} s^{-1})*	556	0	197	0	519	0	0	111	0	137	0	720	0
Stagnant period	DI†	NI†						DII	NII	DIII		DIV	
Organic production (mmol C m^{-2} $hour^{-1}$)	11	−3						13	−5	9		16	
Carbonate production (mmol C m^{-2} $hour^{-1}$)	7	−1						4	1	5		3	

*Micromoles of photosynthetically available radiation. †Productions were measured 400 m south of site P in Fig. 1B.

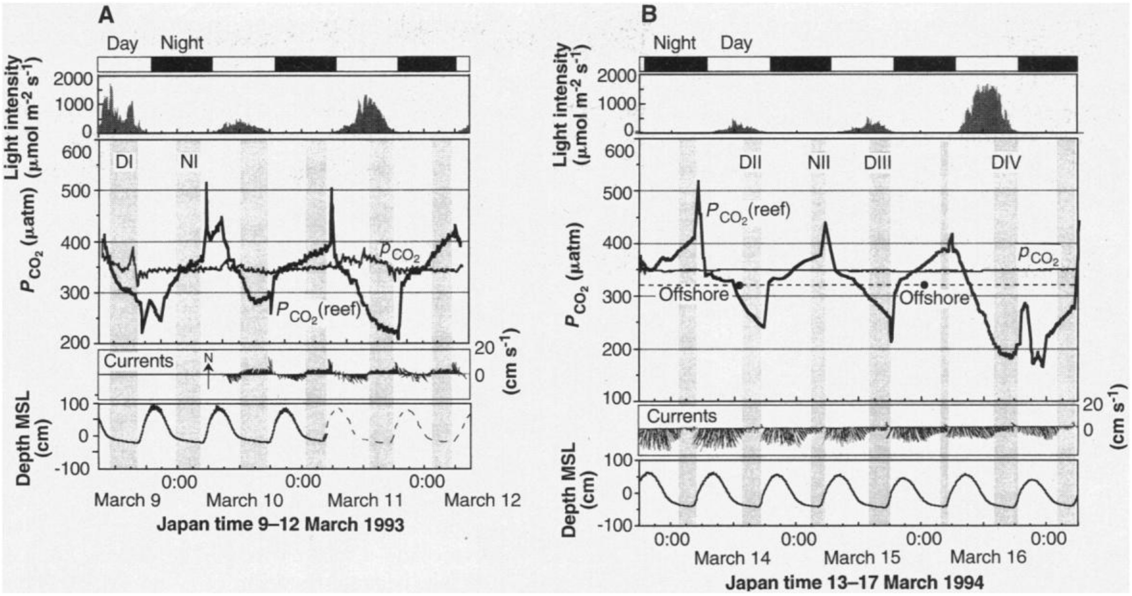

Fig. 2. Changes in reef water P_{CO_2} and atmospheric p_{CO_2} together with light intensity, current direction, current speed, and water depth for the periods from 9 to 12 March 1993 (**A**) and from 13 to 17 March 1994 (**B**). The combined standard uncertainties for the P_{CO_2} values were ±10 μatm in 1993 and ±5 μatm in 1994 (*7*). The 1994 values were more precise because we improved the stability of the measuring system. Two offshore P_{CO_2} values at midday and at midnight were the same (322 μatm), which suggests they were constant as shown by the dashed line. The stagnant periods are represented by shaded vertical bars identified by changes in water depth and currents. The spikes of P_{CO_2} just after the stagnation correspond with those of the currents from the mouth of the reef (M in Fig. 1B). This flow pushes the water south of the station, where dense corals make the P_{CO_2} change larger. MSL, mean sea level. Japan time is universal time plus 9 hours.

carbonate production of 100 mmol C m^{-2} day^{-1} (1.2 g C m^{-2} day^{-1}) in March 1993 (*12*). The ratio of organic production to calcium carbonate production is 1.1. The ratio was almost the same in August 1992 (1.0). The ratio of organic carbon production to calcium carbonate production required to maintain seawater P_{CO_2} at a constant value of 350 μatm has been calculated to be 0.6 (*2*). When the ratio exceeds these values, reefs serve as a sink of CO_2 (*13*). The ratio for Shiraho reef exceeds these threshold values, which is consistent with our P_{CO_2} measurements.

On Moorea barrier reef, French Polynesia, CO_2 evasion from sea to air was observed at a backreef site, and it was concluded that reefs are a source of CO_2 (*6*). In contrast, at a reef front (corresponding to the reef crest in this study) site, CO_2 flux from air to sea was observed (*14*). These results suggest that different reef zones act differently as to CO_2 fluxes and that the highly productive zone such as the reef front acts as a sink of CO_2.

A relatively low estimate of global reef net organic production was based on a mean reef production rate of 0.1 g C m^{-2} day^{-1} (*4*), which in turn was based primarily on measurements from three atolls (*15*). In that study, net production for the whole reef was calculated from changes in total carbon and alkalinity in enclosed lagoon water with a long residence time (50 days). Decomposition of organic matter predominated in such lagoons, and thus, the estimate might have been low. The low estimate of net organic production is also based on underestimates of the contribution of nitrogen fixation (*4*), which provides new nutrients for net organic production in the coral reef. Coral reefs, on the other hand, are known to be active sites of nitrogen fixation (*16*). Our P_{CO_2} measurements and our estimate of high net organic production indicate that reefs might serve as a sink, not a source, for atmospheric CO_2.

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7. H. Saito *et al.*, in press. We used a membrane instead of a spray as an equilibrator. Gaseous CO_2 diffuses through the membrane into flowing air inside the membrane tube, and its CO_2 concentration is measured by NDIR. P_{CO_2} changes in seawater were monitored continuously with the combined standard uncertainties of ±10 μatm in 1993 and ±5 μatm in 1994 estimated from NDIR calibration and vapor correction.
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9. The P_{CO_2} data are in situ values in microatmospheres (1 μatm = 0.101325 Pa). The study site is situated on a reef flat (mean depth of 200 cm) surrounded by coral patches. We set the P_{CO_2} measurement system 50 cm above the reef floor. The water was well mixed vertically by currents >2 cm s^{-1}. We measured the water temperature and salinity at the same time we measured P_{CO_2}. The maximum changes in temperature and salinity were 2°C and 0.1, and the estimated thermodynamical effects of these changes on P_{CO_2} at 350 μatm were 30 and 1.5 μatm [R. F. Weiss, R. A. Jahnke, C. D. Keeling, *Nature* **300**, 511 (1982)], respectively, except for the night from 13 to 14 March 1994 when the temperature changed 4°C. Therefore, the large P_{CO_2} change of more than 300 μatm was mainly the result of biological metabolism.
10. The global solar radiation was observed at Ishigaki Local Meteorological Observatory 5 km west of Shiraho reef. The mean light intensity (photosynthetically available radiation in micromoles per square meter per second) for March was calculated from the radiation records (megajoules per square meter) from 1986 to 1990 with the relation described by K. S. Baker and R. Frouin [*Limnol. Oceanogr.* **32**, 1370 (1987)] and A. Morel and R. C. Smith [*ibid.* **19**, 591 (1974)].
11. Estimation procedures were based on those of S. V. Smith [*ibid.* **18**, 106 (1973)] and are described by A. Suzuki [*Bull. Geol. Surv. Jpn.* **45**, 573 (1994)].
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13. The coexistence of photosynthesis and calcification in reefs has been documented [H. Kayanne and S. Miyachi, *Biofutur* **106**, 76 (1991); T. A. McConnaughey, *Bull. Inst. Oceanogr. (Monaco)* **13**, 137 (1994); A. Suzuki, T. Nakamori, H. Kayanne, *Sediment. Geol.*, in press].
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Flotation of Diamond in Mantle Melt at High Pressure

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Experiments show that diamond floats in a primitive mantle melt at around 20 gigapascals and 2360°C and in a melt formed by partial melting of the transition zone at about 16 gigapascals and 2270°C. These observations constrain magma densities at high pressure. Diamond precipitated or trapped in a silicate melt at the base of the transition zone or the lower mantle floats and has been accumulating in the transition zone since early in Earth's history. Thus, the transition zone could be a reservoir of diamond.

Density difference between solid and liquid governs the chemical differentiation in the Earth's interior; in particular, the olivine-silicate melt density crossover at high pressure could produce serious influences (*1*, *2*). Density measurements at high pressure and high temperature have suggested that olivine floats in komatiite and peridotite melts at depths below 250 km (*3*, *4*). However, the existence of a density crossover between olivine and a magma in the Earth is still uncertain because flotation of olivine in the equilibrium mantle melt has not yet been observed in the experiments. Kitamura (*5*) suggested that diamond might float in mantle melt at high pressure and speculated that a diamond-rich layer might form during solidification of a terrestrial magma ocean.

We conducted density measurements of peridotite melts at high pressure by sink-float experiments with diamond as a density marker. The experiments were carried out in an MA-8–type multianvil apparatus (*6*). The starting materials (Table 1) were simplified compositions of primitive peridotite, PHN1611 (*7*), and the melt by partial melt-

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