

# Measurement of community metabolism and significance in the coral reef CO<sub>2</sub> source-sink debate

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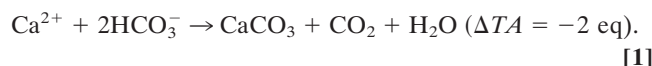
Two methods are commonly used to measure the community metabolism (primary production, respiration, and calcification) of shallow-water marine communities and infer air-sea CO<sub>2</sub> fluxes: the pH-total alkalinity and pH-O<sub>2</sub> techniques. The underlying assumptions of each technique are examined to assess the recent claim that the most widely used technique in coral reefs (pH-total alkalinity), may have provided spurious results in the past because of high rates of nitrification and release of phosphoric acid in the water column [Chisholm, J. R. M. & Barnes, D. J. (1998) *Proc. Natl. Acad. Sci. USA* 95, 6566–6569]. At least three lines of evidence suggest that this claim is not founded. First, the rate of nitrification required to explain the discrepancy between the two methods recently reported is not realistic as it is much higher than the rates measured in another reef system and greater than the highest rate measured in a marine environment. Second, fluxes of ammonium, nitrate, and phosphorus are not consistent with high rates of nitrification and release of phosphoric acid. Third, the consistency of the metabolic parameters obtained by using the two techniques is in good agreement in two sites recently investigated. The pH-total alkalinity technique therefore appears to be applicable in most coral reef systems. Consequently, the conclusion that most coral reef flats are sources of CO<sub>2</sub> to the atmosphere does not need revision. Furthermore, we provide geochemical evidence that calcification in coral reefs, as well as in other calcifying ecosystems, is a long-term source of CO<sub>2</sub> for the atmosphere.

The contribution of an ecosystem to the global carbon cycle primarily results from (i) the balance between organic carbon production (photosynthetic CO<sub>2</sub> fixation) and consumption (respiratory CO<sub>2</sub> release) and (ii) the balance between calcium carbonate precipitation (a source of CO<sub>2</sub>) and dissolution (a sink for CO<sub>2</sub>) (1). Two methods are used to measure community metabolism of calcifying communities in flowing seawater: the alkalinity anomaly technique [pH-TA (2, 3)] and the pH-O<sub>2</sub> technique (4). In a recent paper, Chisholm and Barnes (5) cast doubt on the validity of the former method and suggest that it may explain the recent controversy on the role of coral reefs in the global carbon cycle. The validity of techniques used to estimate the metabolism of coastal marine communities is a critical issue at a time where unprecedented international programs (Land-Ocean Interaction in the Coastal Zone, LOICZ, and European Land-Ocean Interaction Studies, ELOISE) seek to estimate the contribution of the coastal zone to the global carbon cycle.

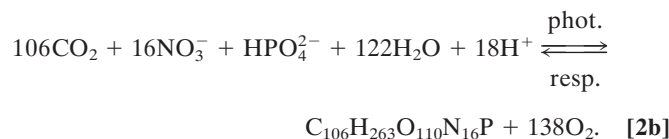
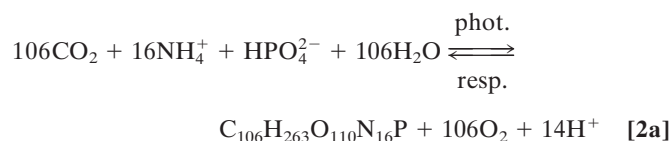
The aim of the present paper is to examine the assumptions involved in the pH-TA and pH-O<sub>2</sub> techniques, to assess the claims of Chisholm and Barnes (5) by using both published and unpublished data, and to address the problem of the effect of reef metabolism on the global carbon cycle, in both the short and the long term.

**The pH-TA Technique.** This technique is based on measurements of pH and total alkalinity (TA) upstream and downstream of a community. These variables are used to calculate the difference between the downstream and upstream concentrations of dissolved inorganic carbon ( $\Delta DIC$ ) by using standard equations that

describe the seawater inorganic carbon system (e.g., ref. 6). The rate of calcification is calculated by using the simple stoichiometric relationship that relates  $\Delta TA$  and community net calcification:



The 1:1 molar relationship between the CO<sub>2</sub> released and the CaCO<sub>3</sub> precipitated holds in freshwater only, and the ratio is lower than 1 in seawater because of its buffering capacity (7). Calcification is therefore a CO<sub>2</sub>-releasing process that can make water in equilibrium with the atmosphere degas, against the initial pCO<sub>2</sub> gradient (8). Total alkalinity and DIC decrease by 2 eq and 1 mol, respectively, for each mole of CaCO<sub>3</sub> precipitated. This change of DIC resulting from calcification ( $\Delta DIC_{\text{calc}}$ ) is then subtracted from  $\Delta DIC$  to provide an estimate of net community production ( $\Delta DIC_{\text{org}}$ ). Further details on the pH-TA technique are given by Smith and Key (2) and Smith and Kinsey (3). The major assumption of this method is that no process other than calcification significantly affects TA during the transit of the water mass above the community investigated. Removal of CO<sub>2</sub> by photosynthesis and its addition by respiration have no effect on TA. However, these processes are coupled with the assimilation and dissimilation of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> which liberate OH<sup>-</sup> or H<sup>+</sup> (or uptake H<sup>+</sup> or OH<sup>-</sup>):



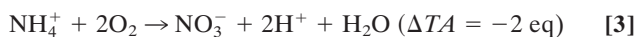
The forward reactions induce  $\Delta TA$  of, respectively, -0.13 and +0.17 equivalents per mole of fixed CO<sub>2</sub>. Eqs. 2a and 2b are based on the Redfield C:N:P atomic ratio that was derived for marine plankton (9). Distinct ratios were found in other communities leading to a stoichiometry of photosynthesis and respiration different from those shown here. The stoichiometry found in benthic marine plants (10) results in a  $\Delta TA$  of +0.06 eq per mole of fixed CO<sub>2</sub>.

Nitrification (Eq. 3) and sulfate reduction (Eq. 4) also significantly alter TA:

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Kinsey (11) has demonstrated that processes 2–4 are likely to cause errors of less than 5% on the net community calcification in a number of reefs. There certainly are environments, such as sedimentary lagoons, in which reaction 4 can be significant (11). Organic acids can significantly contribute to total alkalinity in eutrophic environments (12), but their concentration is likely to be very low in most reef settings. Additionally, organic acid alkalinity behaves nearly conservatively in organic rich estuaries of Georgia (12). Extending these observations to the open ocean and to coral reefs, which have both similar DOC concentrations but much lower levels of organic acids than estuaries, seems reasonable. Errors in the absolute total alkalinity should thus be minor and relatively constant. Because community metabolism deals with changes in *TA*, not absolute values, the effects are negligible. Finally, the validity of the alkalinity anomaly technique to estimate coral calcification has been repeatedly established (3, 13, 14).

**The pH-O<sub>2</sub> Technique.** This technique was first introduced by Barnes (4) to circumvent the major drawback of the pH-*TA* method. There is no simple way to monitor *TA* remotely, by probe, as the water mass flows over the community; it is therefore required that discrete seawater samples be taken for subsequent measurements of *TA* in the laboratory to calculate  $\Delta TA$ . The pH-O<sub>2</sub> technique uses relationships between  $\Delta \text{O}_2$  and  $\Delta DIC_{\text{org}}$ , the metabolic quotients<sup>†</sup>, to estimate net community production and respiration from changes in the concentration of dissolved oxygen.  $\Delta DIC_{\text{calc}}$  is then calculated by subtracting  $\Delta DIC_{\text{org}}$  from the upstream *DIC* value, and  $\Delta TA$  and net community calcification are estimated by using the stoichiometric relationships described above (Eq. 1). This approach is attractive because precise and reliable sensors are available to monitor both dissolved oxygen and pH in the field, and application of the technique requires fewer determinations of *TA* (to estimate upstream *DIC*) than the pH-*TA* technique. However, this technique also requires the use of assumed values of the metabolic quotients, thus introducing uncertainty into the calculated metabolic parameters. Any biogeochemical process that has an O<sub>2</sub>:CO<sub>2</sub> stoichiometry different from the assumed metabolic quotients interferes with the pH-O<sub>2</sub> technique. In particular, note that this is the case with nitrification (Eq. 5), which consumes 2 mol of O<sub>2</sub> per mol of NH<sub>4</sub><sup>+</sup> nitrified. The pH-O<sub>2</sub> technique is therefore affected by nitrification just as much as the pH-*TA* technique.

**Estimation of Air–Sea CO<sub>2</sub> Fluxes.** The contribution of ecosystems to exchange of CO<sub>2</sub> between ocean and atmosphere can be estimated by using direct measurements (15, 16) or using parameters of community metabolism (1). A simple expression was derived to estimate the amount of *DIC* ( $F_{\text{CO}_2}$ ) that needs to be exchanged with the atmosphere to restore the carbonate equilibrium (1):

$$F_{\text{CO}_2} = -P_g + R + \Psi G \quad [5a]$$

or

$$F_{\text{CO}_2} = -P_n + \Psi G, \quad [5b]$$

where the community gross primary production ( $P_g$ ), net primary production (or net ecosystem production,  $P_n$ ), respiration

<sup>†</sup>Community net photosynthetic quotient ( $PQ_{\text{net}} = \Delta \text{O}_2 / \Delta DIC_{\text{org}}$ ) and community respiratory quotient ( $RQ = \Delta DIC_{\text{org}} / \Delta \text{O}_2$ ).

**Table 1. Effect of community metabolism on the seawater carbonate system and air–sea CO<sub>2</sub> flux**

$G/P_n$ , mol/mol	$\Delta TA / \Delta DIC$ , equivalent/mol	$F_{\text{CO}_2}$ , mol
1.0/0.0 (net calcification only)	–2.0/–1.0	+0.6 ↗
1.67/1.0	–3.33/–2.67	0.0 →
1.0/1.0	–2.0/–2.0	–0.4 ↘
0.0/1.0 (net photosynthesis only)	0.0/–1.0	–1.0 ↘

*G*, net community calcification; *P<sub>n</sub>*, net community primary production,  $\Delta TA$ , change in total alkalinity;  $\Delta DIC$ , change in the concentration of dissolved inorganic carbon;  $F_{\text{CO}_2}$ , amount of DIC that needs to be exchanged with the atmosphere in order to restore the carbonate equilibrium. The arrows indicate the direction of the air–sea CO<sub>2</sub> flux: ↗, evasion; →, no flux; ↘, invasion. The small changes in total alkalinity resulting from assimilation and excretion of nutrients associated with production and degradation of organic carbon were neglected.

(*R*), and net calcification (*G*) are expressed in molar units, and  $\Psi$  is the molar ratio of CO<sub>2</sub> released by calcification to calcium carbonate precipitated. Positive  $F_{\text{CO}_2}$  indicate CO<sub>2</sub> evasion (sea to air flux) and negative  $F_{\text{CO}_2}$  indicate CO<sub>2</sub> invasion (air to sea flux). Frankignoulle *et al.* (7) have shown that  $\Psi = 0.6$  for seawater displaying the following characteristics:  $p\text{CO}_2 = 356 \mu\text{atm}$ ,  $TA = 2370 \mu\text{eq kg}^{-1}$ , temperature = 25°C and salinity = 35 (1 atm = 101.3 kPa).

This relationship enables us to compute values of the  $G/P_n$  ratio that are important to identify the effect of coral reefs on seawater  $p\text{CO}_2$  (Table 1). The critical ratio that causes no change in  $p\text{CO}_2$  (and no air–sea CO<sub>2</sub> flux) is  $G/P_n = 1.67$ . The system becomes a source of CO<sub>2</sub> when  $G/P_n > 1.67$  and a sink for CO<sub>2</sub> when  $G/P_n < 1.67$ . Most reef flats exhibit  $G/P_n$  ratios higher than 1.67/1.0 because their metabolism of organic carbon is nearly balanced ( $P_g/R \approx 1$ ,  $P_n \approx 0$ ) (13). It has therefore been suggested that most reef flats can be expected to cause CO<sub>2</sub> evasion to the atmosphere (1), a prediction that has been confirmed by a limited number of direct measurements (15, 16).

**Discrepancy Between the pH-*TA* and pH-O<sub>2</sub> Techniques Reported by Chisholm and Barnes.** These authors (5) investigated the community metabolism of a fringing reef flat at Lizard Island (Great Barrier Reef, Australia). Salinity ranged from 1 to 3 units below normal values because of heavy rainfall before the measurements. They estimated the rate of community calcification (*G*) by using both the pH-*TA* and the pH-O<sub>2</sub> techniques. During daylight, *G* estimated from pH-O<sub>2</sub> data was similar to that estimated from pH-*TA* data (41.0 and 36.8 g CaCO<sub>3</sub> m<sup>–2</sup>). However, the two methods did not compare well at night: there was net CaCO<sub>3</sub> dissolution according to the pH-O<sub>2</sub> data ( $G = -15.5 \text{ g CaCO}_3 \text{ m}^{-2}$ ) and net CaCO<sub>3</sub> deposition according the pH-*TA* technique ( $G = 4.7 \text{ g CaCO}_3 \text{ m}^{-2}$ ).

Consequently, the pH-*TA* technique provided estimates of annual rates of net calcification higher than the pH-O<sub>2</sub> technique (ca. 15.1 vs. 9.3 kg CaCO<sub>3</sub> m<sup>–2</sup> yr<sup>–1</sup>, respectively). The former rate was deemed unrealistically high for a reef exhibiting only 0–10% of live coral cover.

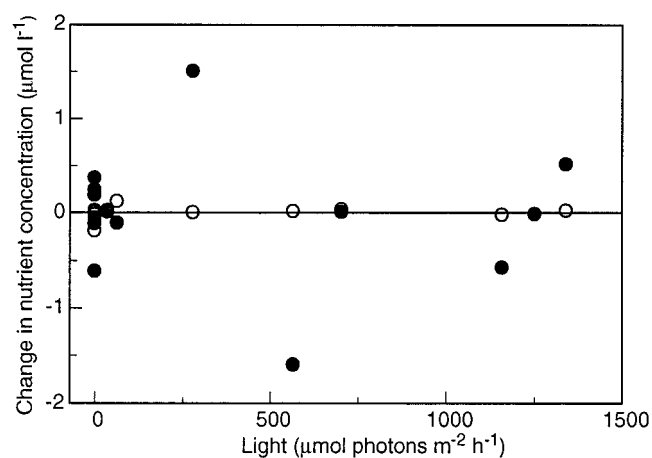
Chisholm and Barnes (5) infer that substantial decomposition of organic matter, due to the low salinity at the time of the experiments, explains the high rate of calcification estimated with the pH-*TA* technique. They then generalize this suggestion and conclude that “(D)ata presented herein question the long standing assumption that the carbonate equilibrium of seawater above most reefs is principally controlled by photosynthesis, respiration, calcification and solution of reef rock.” Chisholm and Barnes (5) invoke two processes that may have affected the total alkalinity during their experiments: the formation of phosphoric acid due to organic matter decomposition (Eqs. 2a

and **2b**) and a “considerably greater amount of nitric acid via oxidation of ammonium by nitrifying bacteria” (Eq. 3).

We will evaluate this claim by using three approaches: (i) assessing whether the rate of nitrification required to explain the discrepancy between the two methods at Lizard Island is realistic, (ii) examining whether high rates of organic matter decomposition and nitrification are likely in two other sites, and (iii) checking the consistencies of measured  $\Delta TA$  and  $\Delta TA$  estimated by the pH-O<sub>2</sub> technique, as well as metabolic quotients, at these sites.

**Estimation of the Nitrification Rate Required to Explain the Discrepancy Reported by Chisholm and Barnes.** The decomposition of organic matter releases NH<sub>4</sub><sup>+</sup> (**2a**) that can be subsequently nitrified (**2b** and **3**). It either increases *TA* by 0.13 eq per mol of carbon respired (**2a**) or decreases *TA* by 0.17 eq per mol of carbon respired (**2b**). Nitrification (**3**) decreases *TA* by 2 eq per mol of ammonium nitrified. None of these processes was measured by Chisholm and Barnes (5), but one can estimate the rates required to explain the nighttime difference in calcification between the  $\Delta TA$  and pH-O<sub>2</sub> techniques ( $-47 + 155 = 108$  mmol CaCO<sub>3</sub> m<sup>-2</sup>). Because the difference was attributed to calcification, the change in *TA* is two times higher than the change in CaCO<sub>3</sub>. Therefore, the two processes invoked by Chisholm and Barnes (5) must have decreased *TA* by 216 meq m<sup>-2</sup> or, assuming a 12:12 h photoperiod, 18 meq m<sup>-2</sup> h<sup>-1</sup>. They estimate that the effect of nitrification was considerably higher than that of organic matter decomposition. Let us assume that those processes accounted for, respectively, 90% and 10% of the excess change in *TA*. Therefore, the rate of nighttime nitrification must have been around 8 mmol m<sup>-2</sup> h<sup>-1</sup> ( $18 \times 0.9/2$ ). Nitrification is known to occur in corals (17) and coral reefs (18). However, the rates reported are much lower than 8 mmol m<sup>-2</sup> h<sup>-1</sup>. Webb and Wiebe (18) reported rates ranging from 0.4 to 39  $\mu\text{mol m}^{-2} \text{h}^{-1}$  (mean = 10.4  $\mu\text{mol m}^{-2} \text{h}^{-1}$ ;  $N = 6$ ) at Enewetak. Two reviews compile rates of nitrification measured in marine sediment (19) and in coastal marine environments (20). The highest rate was measured in North Sea sediments and reaches 1.4 mmol m<sup>-2</sup> h<sup>-1</sup> (21). Also, coral reef waters lack the substrate required for intense nitrification because ammonium concentration typically ranges between 0.2 and 0.5  $\mu\text{mol liter}^{-1}$  (22). Ammonium enrichment experiments carried out on sediment of the Lizard Island reef flat have shown that a significant ammonium uptake is obtained when its concentration in the overlying water is 5 mmol liter<sup>-1</sup> (J. W. Bishop, personal communication). Note that the nighttime uptake rate [ $2.35 \pm 0.44$  ( $\pm\text{SD}$ ) mmol m<sup>-2</sup> h<sup>-1</sup>] is still three times lower than that supposed to have occurred at the same site. It is therefore concluded that the nitrification rate required to support the Chisholm and Barnes hypothesis is very unlikely to occur as it is much higher than the rates measured in a coral reef and other marine environments by 1 to 3 orders of magnitude.

**Do High Rates of Nitrification and Release of Phosphoric Acid Occur at Other Sites?** These processes should induce significant changes in the nutrient concentration of the water mass as it flows across the reef flat. However, as mentioned by Gattuso *et al.* (23): “The contribution of nutrients to changes in total alkalinity was negligible at Yonge reef since there was no or very small changes in nutrient concentrations during the transects (data not shown).” The data are shown in Fig. 1. The changes in NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> during the transect experiments were not statistically significant different from 0 ( $P = 0.09$ – $0.97$ ), whether at night or during the day. The average areal fluxes are  $-0.019$  mmol PO<sub>4</sub><sup>3-</sup> m<sup>-2</sup> h<sup>-1</sup> and  $0.083$  mmol NH<sub>4</sub><sup>+</sup> m<sup>-2</sup> h<sup>-1</sup>. We therefore conclude that no significant nitrification took place at the time of measurement. It is likely that a similar situation prevailed at Moorea. Recent observations demonstrate that no nitrification

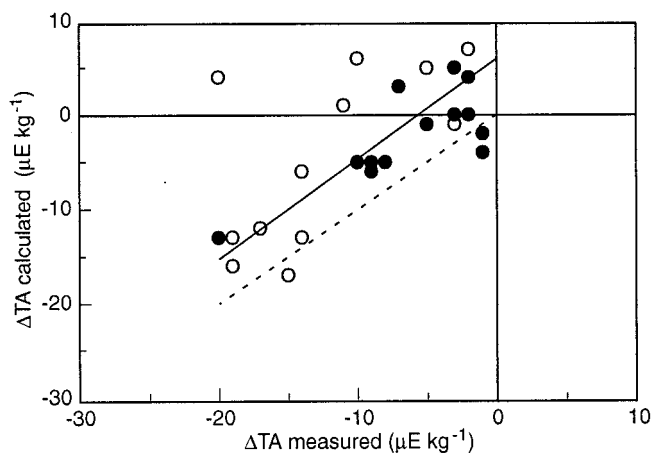


**Fig. 1.** Changes in the concentrations of phosphorus (squares) and ammonium (circles) during transects carried out at Yonge Reef (J.-P.G., M. Pichon, B. Delesalle, C. Canon, and M. Frankignoulle, unpublished results). Dissolved inorganic nutrients were measured on a Skalar multichannel segmented flow autoanalyzer (57). The analytical method is based on that of Tréguer and Le Corre (58) modified to ensure a suitable accuracy and sensitivity to low concentration levels, as well as the linearity of the response over a wide range of concentrations.

takes place in a reef located in southern Japan (24): NH<sub>4</sub><sup>+</sup> does not change significantly, there is no release of NO<sub>3</sub><sup>-</sup> at any time, and a significant NO<sub>3</sub><sup>-</sup> uptake was measured at night (as opposed to NO<sub>3</sub><sup>-</sup> release if nitrification occurred).

**Comparison of the pH-TA and pH-O<sub>2</sub> Data at Other Sites.** The relationship between measured  $\Delta TA$  and  $\Delta TA$  estimated by the pH-O<sub>2</sub> method can be investigated by using the data sets collected on two Pacific barrier reef flats at Moorea and Yonge Reef by Gattuso *et al.* (15, 23). The two methods are well correlated ( $r = 0.68$ ;  $P < 0.001$ ; Fig. 2). The slope of the geometric regression line is not significantly different from 1 and the y intercept ( $6 \mu\text{eq kg}^{-1}$ ) is significantly different from 0. Several limitations of the pH-O<sub>2</sub> method could explain such slight discrepancy. First, pH and *DIC* are known to provide poor estimates of *TA* (e.g., ref. 26) and the accuracy of calculated  $\Delta TA$  depends on the accuracy of both pH and O<sub>2</sub>. If one sets the error of the latter variables to very small values (0.003 unit for pH and  $3 \mu\text{mol kg}^{-1}$  for O<sub>2</sub>), the resulting error on  $\Delta TA$  is  $7 \mu\text{eq kg}^{-1}$ . Such an error is within the ranges of measured  $\Delta TA$  (see Fig. 2). Second, the estimate of  $\Delta TA$  is very sensitive to the correction because of air–sea O<sub>2</sub> exchange ( $F_{\text{O}_2}$ ). The largest difference between  $\Delta TA$  measured and  $\Delta TA$  estimated by the pH-O<sub>2</sub> method shown in Fig. 2 ( $24 \mu\text{eq kg}^{-1}$ ) could result from an inaccuracy of  $F_{\text{O}_2}$  of only 20%. Chisholm and Barnes (5) estimated  $F_{\text{O}_2}$  from a relationship between the gas exchange coefficient and wind speed. This procedure does not properly account the effect of inner turbulence due to stresses other than wind (current and bottom topography). Frankignoulle *et al.* (16) demonstrated that the CO<sub>2</sub> gas exchange coefficient, which exhibits a similar response to wind speed and inner turbulence than the O<sub>2</sub> gas exchange coefficient, is underestimated by more than 50% when turbulence is not taken into account.

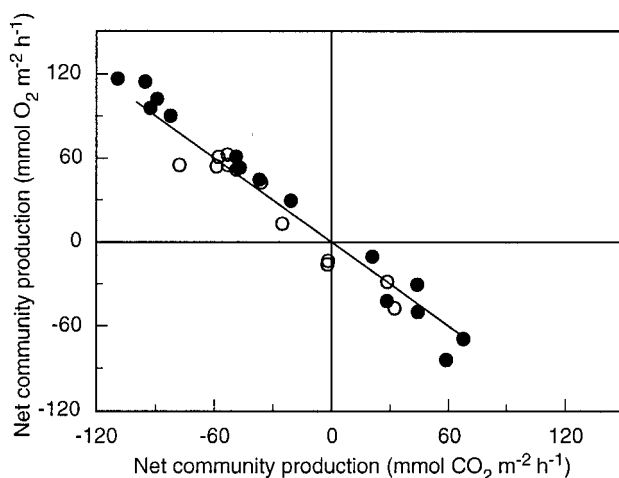
It is worth emphasizing that the site investigated at Moorea (as well as at Yonge Reef) is a barrier reef and not a fringing reef as claimed by Chisholm and Barnes (5). The Tiahura reef system is much closer to the coast than Yonge reef and is subject to a relatively intense human pressure (25). However, the barrier reef is not greatly affected by the land because (i) it is hydrodynamically isolated from it by a channel exhibiting a very strong current and (ii) the water mass impinging on the reef crest only contains ca. 10% of water recirculated through the nearby pass (Wolanski *et al.*, ref. 25).



**Fig. 2.** Change in total alkalinity estimated by the pH-O<sub>2</sub> technique as a function of measured change in total alkalinity. Data at Moorea (open circles) and Yonge Reef (filled circles) are from Gattuso *et al.* (23). The 1:1 and the geometric regression lines ( $y = 6 + 1.06x$ ;  $N = 27$ ;  $r = 0.68$ ) are shown as dotted and plain lines, respectively.

The rates of net community production obtained by the pH-O<sub>2</sub> and pH-TA techniques should not be consistent if high rates of nitrification and release of phosphoric acid occur, and anomalous values of metabolic quotients should be found. That did not happen at Moorea (1992) or at Yonge Reef (Fig. 3). Net community production rates estimated with both techniques were consistent and highly correlated ( $r^2$  was 0.93 and 0.98, respectively, at Moorea and Yonge Reef). The slopes were not statistically different from 1. The data set collected at Moorea in 1991 cannot be analyzed in a similar way because the CO<sub>2</sub> data were not reliable, because of a relatively poor accuracy of the pH measurements (15).

The average respiratory quotient ( $RQ$ ) was  $0.9 \pm 0.2$  at Moorea ( $N = 2$ ) and  $0.8 \pm 0.1$  at Yonge Reef ( $N = 3$ ). It was significantly lower than 1 ( $P = 0.04$ ) at Yonge Reef.  $PQ_{net}$  was  $1 \pm 0.1$  at Moorea ( $N = 5$ ) and  $1.1 \pm 0.1$  at Yonge Reef ( $N = 10$ ); they were not significantly different than 1 ( $P > 0.25$ ). True  $PQ$  was not significantly different at Moorea ( $1.07 \pm 0.06$ ;  $N = 10$ ) and Yonge Reef ( $1.08 \pm 0.03$ ;  $N = 12$ ). Therefore, the metabolic quotients measured at these two sites are perfectly



**Fig. 3.** Net community production estimated using the O<sub>2</sub> and CO<sub>2</sub> techniques at Yonge Reef (filled circles) and Moorea (open circles) (23). The 1:1 line is shown.

normal and agree with those with those obtained by various authors at other sites (e.g., ref. 27). The nutrient data, the comparison of measured and estimated TA, as well as the consistency of the metabolic quotients demonstrate that none of the processes invoked by Chisholm and Barnes (5) distorted the parameters of community metabolism measured at Moorea and Yonge Reef.

**Contribution of Coral Reefs to the Carbon Cycle.** After questioning the reliability of the results obtained using the pH-TA technique, Chisholm and Barnes (5) implied that the distortion of the estimates of community production and calcification, mostly due to nitrification, observed at Lizard Island may “explain apparent anomalies in the metabolic performance of reefs close to land and reconcile the different experimental findings that have given rise to the CO<sub>2</sub> debate.” The so-called “CO<sub>2</sub> debate” relates (i) to a discrepancy between short-term measurements and estimates of air-sea CO<sub>2</sub> fluxes over reef flats by two of the authors (J.-P. G. and M. F.), and some estimates measured by other authors and (ii) to the long-term role of coral reefs on the global carbon cycle.

A large number of reports demonstrate that coral reef ecosystems, mostly barrier reef flats, are sources of carbon dioxide to the atmosphere because of their low net fixation of CO<sub>2</sub> via photosynthetic processes (net community production is close to 0) and rather large release of CO<sub>2</sub> by precipitation of calcium carbonate (1, 7, 8, 15, 16, 23, 28–30). The reef investigated at Moorea by Gattuso *et al.* (15) did not “apparently release(d) CO<sub>2</sub> to the atmosphere” as is suggested by Chisholm and Barnes (5). Air-sea CO<sub>2</sub> evasion was not only inferred by using an indirect method based on community metabolism data but was also directly measured. Similar measurements carried out at Moorea (in a different season) and Yonge Reef provided the same result (16). The reversal of the measured air-sea CO<sub>2</sub> flux that occurs during late morning and early night takes place when the seawater  $pCO_2$  computed from pH and TA is approximately 355  $\mu\text{atm}$ , the value of atmospheric  $pCO_2$  at the time of measurement (16). This demonstrates that estimation of seawater  $pCO_2$  from pH and TA is satisfactory. There was a 1 to 2 orders of magnitude difference in the daily air-sea CO<sub>2</sub> fluxes estimated from direct measurements and from parameters of the community metabolism (16, 23). These authors have provided several considerations that could explain such a difference. The point, however, is that they both indicate a CO<sub>2</sub> efflux to the atmosphere. Also, Chisholm and Barnes (5) did not realize that these two approaches used the same TA data.

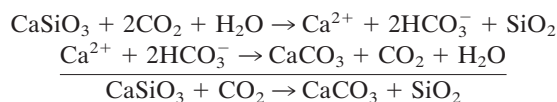
Some recent reports suggest, however, that some reef flats are sinks for atmospheric CO<sub>2</sub> (31–34). Some of the later conclusions are, however, hampered by the techniques used, the limited data sets, and the representativity of the study sites (35) and are not consistent with reef sediment geochemistry (36). It is significant that most studies suggesting that reefs may be sinks of CO<sub>2</sub> were carried out on fringing reefs, which are more likely subject to anthropogenic stresses than other reef systems. There is an increasing number of reefs shifting from coral-dominated to algal-dominated states (e.g., refs. 37–39) because of factors related, to some extent, to human-induced changes. The effect of these changes on the ecosystem function are poorly known, but it has often been suggested that they lead to an increase in the community excess production and a decrease in community calcification (36, 40, 41). These responses may shift the ecosystem from a CO<sub>2</sub> source for the atmosphere to a CO<sub>2</sub> sink (42, 43). Critics of the Shiraho (Ryukyu Island, Japan) reef study by Kayanne *et al.* (31) did not “argue . . . that the reef must have been dominated by noncalcareous algae . . .” as stated by Chisholm and Barnes (5). They based their argument on qualitative surveys carried out in December 1994 (M. Pichon, personal communication) and October 1995 (J.-P.G., unpublished obser-

vations) which showed that the Shiraho reef flat exhibits large areas with 100% algal cover and that the sedimentary area located along the shore harbors seagrass beds (42).

Therefore, the conclusion that “average” coral reef flats are sources of CO<sub>2</sub> to the atmosphere (1) still stands. Whereas average coral reef flats behaves as sources of CO<sub>2</sub> for the atmosphere, reefs are essentially balanced ecosystems. Compared with reef flat studies, integrated studies encompass a much larger area, include considerably more sedimentary zones (hence a much lower community net calcification) and integrate the CO<sub>2</sub>-related signals over many days. It was shown that the CO<sub>2</sub> flux associated with calcification and the CO<sub>2</sub> flux associated with organic metabolism almost exactly offset in Spencer Gulf (not a coral reef but nevertheless a calcifying system; ref. 44). Similar investigations in atolls reached a similar conclusion (e.g., ref. 45). Calcification makes the system degas CO<sub>2</sub>. Organic metabolism makes the CO<sub>2</sub> flux go either in or out, depending on trophic status. Because most reefs seem to be marginally autotrophic, the tendency of organic metabolism will be one of slight CO<sub>2</sub> invasion. Our point is that there is a tendency of the two processes of organic production and calcification to at least compensate one another in complete reef systems while CO<sub>2</sub> invasion due to organic metabolism is overwhelmed by the CO<sub>2</sub> released by calcification in most reef flats.

Chisholm and Barnes (5) also state that “(reefs) may release up to 8% (of anthropogenic CO<sub>2</sub>) if they are sources” and quote Gattuso *et al.* (23) to support that statement. The latter paper does not provide such estimate and, to our knowledge, the only estimate of CO<sub>2</sub> release by reefs available in the literature is that of Ware *et al.* (8); 0.4–1% of anthropogenic CO<sub>2</sub> release). Chisholm and Barnes (5) argue that “The fact that carbonate rocks stores 3 10<sup>4</sup> more inorganic carbon than the atmosphere (Skirrow, 1978) shows that reefs are sinks for CO<sub>2</sub> over geological time.” This is a misunderstanding of simple geochemical reactions known since the last century (e.g., ref. 46). Such misconception has been published on several occasions in the 1990s, the first account being, perhaps, that of Karube *et al.* (47), who even proposed that calcification was a possible mechanism for absorbing some of the anthropogenic CO<sub>2</sub> emissions. This misconception recognizes that the massive CaCO<sub>3</sub> deposits associated with past and present reefs are sinks for carbon and makes the erroneous conclusion that they are sinks for atmospheric CO<sub>2</sub>. The oceans contain approximately 50 times more inorganic carbon than the atmosphere. There are three pools of oceanic DIC: HCO<sub>3</sub><sup>-</sup> (90%), CO<sub>3</sub><sup>2-</sup> (9%), and dissolved CO<sub>2</sub> (1%). The latter pool is close to equilibrium with the atmosphere (present *p*CO<sub>2</sub> ca. 360 μatm). The carbon atom incorporated into CaCO<sub>3</sub> is derived from the HCO<sub>3</sub><sup>-</sup> pool, with the consequence that H<sup>+</sup> is liberated and the water gets more acid. The acid pushes an additional amount of HCO<sub>3</sub><sup>-</sup> across into the oceanic CO<sub>2</sub> pool. There is then a physical equilibration between the seawater and atmosphere CO<sub>2</sub> pools, and this physical equilibration pushes CO<sub>2</sub> into the atmosphere.

Berner *et al.* (48) provided a very thorough account of the geochemical control of the changes of atmospheric carbon dioxide over the past 100 million years. Gases released by volcanoes, including H<sub>2</sub>S, NH<sub>3</sub>, CH<sub>4</sub>, and H<sub>2</sub>O, made up much of the highly reducing early atmosphere of earth. Reducing molecules, such as methane, became oxidized to form an early CO<sub>2</sub>-rich atmosphere. The concentration of CO<sub>2</sub> was subsequently controlled by the carbonate-silicate geochemical cycle. The weathering of Ca-Mg silicate rocks followed by precipitation of Ca and Mg in carbonate minerals in the ocean is a major process by which CO<sub>2</sub> is stored. These reactions are described by the Högbom-Urey reactions (49). For example, in the case of calcium silicate:



Additionally, according to Berner *et al.* (48), precipitation of CaCO<sub>3</sub> is an important process and the major way by which CO<sub>2</sub> is returned to the atmosphere. They also demonstrated that a 10% drop in the rate of addition of CO<sub>2</sub> to the atmosphere via oceanic CaCO<sub>3</sub> precipitation (all the other fluxes remaining constant) would result in the complete removal of atmospheric CO<sub>2</sub> in only 30,000 years. There is therefore no doubt that reefs, as well as other calcifying systems, were sources of CO<sub>2</sub> over geological time. Some authors believe that changes in coral reef calcification resulting from variations of sea level and climate are partly responsible for the 80 μatm difference in atmospheric *p*CO<sub>2</sub> (200 vs. 280 μatm) during the last glacial-interglacial period (e.g., ref. 50), although that hypothesis (so-called coral reef hypothesis) was recently challenged (51).

**Conclusions and Perspectives.** The data set collected at Lizard Island by Chisholm and Barnes (5) is puzzling and, so far, unique in the literature. It is, however, very unlikely that the anomalous rates of community metabolism that they reported solely result from high rates of organic matter decomposition and nitrification driven by extreme meteorological conditions prior to the measurements. We conclude that:

1. The high rates of nitrification and release of phosphoric acid that are presumed to have distorted community metabolism data at Lizard Island (5) have not occurred in several sites previously investigated. Therefore, the pH-*TA* method remains widely applicable in most reef systems.
2. The so-called controversy on the role of reef flats as source or sink of CO<sub>2</sub> does not result from a methodological problem related to anomalous changes in total alkalinity at Moorea and Yonge Reef. In our opinion, the results suggesting that two fringing reefs of southern Japan are sinks for atmospheric CO<sub>2</sub> are mostly due to a high surface cover of macrophytes and a low surface cover of corals. A recent paper provides evidence for this (42).
3. Coral reefs are not a quantitatively important component of the present day global carbon cycle as their gross metabolic performance is about a 1–2% term in the marine biotic gross CO<sub>2</sub> pump (28). Nevertheless, they played, together with other calcifying organisms and ecosystems, a quantitatively important role in the long-term control of atmospheric *p*CO<sub>2</sub> by releasing significant amounts of CO<sub>2</sub> (e.g., refs. 48 and 50).

It is our hope that this paper will clarify the assumptions and drawbacks of the methods commonly used to measure the community metabolism of marine communities. Also, the carbon and carbonate cycles of coral reefs are of great interest but the issue of their role in the global carbon cycle is now quite firmly established. There remain, however, many exciting questions of major interest such as the interactions between the two geochemical cycles (28, 52) as well as the consequences of global climatic changes on reef primary production (52) and calcification (37, 52–56).

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