

# Carbon fluxes in coral reefs. II. Eulerian study of inorganic carbon dynamics and measurement of air-sea CO<sub>2</sub> exchanges

Michel Frankignoulle<sup>1,\*,\*\*</sup>, Jean-Pierre Gattuso<sup>2,3</sup>, Renzo Biondo<sup>1</sup>,  
Isabelle Bourge<sup>1,\*\*</sup>, Gérard Copin-Montégut<sup>4</sup>, Michel Pichon<sup>3,5,6</sup>

<sup>1</sup>Laboratoire d'Océanologie, Université de Liège, Institut de Chimie Bât B6, B-4000 Sart Tilman, Belgium

<sup>2</sup>Observatoire Océanologique Européen, Centre Scientifique de Monaco, Avenue Saint-Martin, MC-98000 Monaco, Principality of Monaco

<sup>3</sup>Laboratoire de Biologie Marine et Malacologie, URA CNRS 1453, EPHE, Université de Perpignan, F-66860 Perpignan Cedex, France

<sup>4</sup>Observatoire Océanologique, Université Pierre et Marie Curie, BP 8, F-06230 Villefranche-sur-mer Cedex, France

<sup>5</sup>Australian Institute of Marine Science, PMB No. 3, Townsville M. C., Queensland 4810, Australia

<sup>6</sup>Centre de Recherches Insulaires et Observatoire de l'Environnement, EPHE, BP 1013, Moorea, French Polynesia

**ABSTRACT:** Air-sea CO<sub>2</sub> exchanges and the partial pressure of CO<sub>2</sub> were measured in surface water overlying 2 coral reefs: Moorea (French Polynesia, austral winter, August 1992), where coral diversity and surface cover are low, and Yonge Reef (Great Barrier Reef, austral summer, December 1993), where coral diversity and cover are comparatively higher. A procedure is proposed to estimate the potential CO<sub>2</sub> exchange with the atmosphere by taking into account both the saturation level of oceanic seawater and the equilibration process occurring after water leaves the reef. It is shown that both sites were net sources of CO<sub>2</sub> to the atmosphere as a result of the effect of calcification on the dynamics of the inorganic carbon system. The potential global CO<sub>2</sub> evasion from the ocean to the atmosphere is about 4 times higher at Yonge Reef than at Moorea. It is also demonstrated that, at both sites, the major exchange of CO<sub>2</sub> from sea to air occurs as seawater returns to chemical equilibrium after it has crossed and left the reef. The dynamics of inorganic carbon were studied using the so-called homogeneous buffer factor [ $\beta = d \ln(p\text{CO}_2) / d \ln(\text{DIC})$ ] (where  $p\text{CO}_2$  is the CO<sub>2</sub> partial pressure in surface water and DIC is dissolved inorganic carbon), which gave estimates that approximately 80% of the change in inorganic carbon was related to photosynthesis and respiration. This approach showed that the calcification rate was proportional to the net organic production during the day and to the respiration rate at night.

**KEY WORDS:** Coral reefs · Inorganic carbon · Air-sea CO<sub>2</sub> exchanges

## INTRODUCTION

It is not yet certain how much and how quickly excess atmospheric CO<sub>2</sub> is taken up by the oceans (see e.g. Tans et al. 1990, Watson et al. 1991). While the open ocean is close to atmospheric CO<sub>2</sub> equilibrium, the situation in coastal areas is far less certain because

data are so far very sparse. Coastal areas are sites of intense primary production and specific processes (upwelling, river input) which can induce strong variations of dissolved inorganic carbon and associated high air-sea CO<sub>2</sub> fluxes (Mackenzie et al. 1991, Wollast 1991). Air-sea CO<sub>2</sub> exchange in coastal areas is thus a fundamental process which could play a significant role in the global carbon cycle.

Coral reefs are important shallow-water, tropical ecosystems due to their geographical extent (617 000 km<sup>2</sup>, i.e. 15% of the sea floor surface area between 0 and 30 m; Smith 1978). In terms of carbon dynamics, 2

\*E-mail: michel.frankignoulle@ulg.ac.be

\*\*Present address: Université de Liège, Mécanique des Fluides Géophysiques, Unité d'Océanographie Chimique, Institut de Physique (B5), B-4000 Sart Tilman, Belgium

important biological processes occur in these ecosystems: metabolism of organic carbon (photosynthesis and respiration) and metabolism of inorganic carbon (precipitation and dissolution of calcium carbonate).

In the context of the atmospheric carbon budget, marine calcification can have important consequences because this process is known to release dissolved  $\text{CO}_2$  to the surrounding water and can then act as a net source of  $\text{CO}_2$  to the atmosphere. Ware et al. (1992) have demonstrated, using numerical calculations, that 0.6 mol  $\text{CO}_2$  is released in surrounding water for each mole of calcium carbonate precipitated. More recently, Frankignoulle et al. (1994) have shown that the released  $\text{CO}_2$ /precipitated  $\text{CaCO}_3$  ratio reflects a positive feedback to the increasing atmospheric  $\text{CO}_2$ , and it increases from 0.6 (at present atmospheric  $\text{CO}_2$  level) to 0.84 when the  $\text{CO}_2$  partial pressure in surface water ( $p\text{CO}_2$ ) = 1000  $\mu\text{atm}$ . Since coral reefs are characterized by a net organic production close to zero (Kinsey 1983), calcification could play a major role in atmospheric exchange of  $\text{CO}_2$  in coral reefs.

The evidence for  $\text{CO}_2$  release to the atmosphere in coral reefs has recently been demonstrated by Gattuso et al. (1993), who carried out the first field measurements of air-sea  $\text{CO}_2$  exchanges on a coral reef flat (Moorea, French Polynesia, summer 1991). During 24 h experiments, they observed daily variations of the flux direction in agreement with the photosynthesis/respiration cycle:  $\text{CO}_2$  uptake during the day and  $\text{CO}_2$  release at night. They found that over 24 h the net  $\text{CO}_2$  flux from sea to air was approximately 1.5 mmol  $\text{CO}_2$   $\text{m}^{-2}$ . More recently, Kayanne et al. (1995) monitored daily changes in dissolved  $\text{CO}_2$  over a sub-tropical reef (Shiraho reef, Ryukyu Islands, Japan) and concluded that reefs could behave as sinks for atmospheric  $\text{CO}_2$ . Their conclusion that all reefs may behave as sinks for  $\text{CO}_2$  has been questioned (Buddemeier 1996, Gattuso et al. 1996) for several reasons, but mainly because their study site is not representative of the 'standard' reef system as described by Kinsey (1983) and does not allow such generalisation.

This paper presents data related to daily changes of inorganic carbon and air-sea  $\text{CO}_2$  fluxes measured at a single back reef station (Eulerian approach). The objectives of this work are (1) to complement observations previously made at Moorea during austral winter, (2) to compare results obtained in a reef subject to relatively intense anthropogenic stresses (Moorea) with a pristine reef (Yonge Reef, Great Barrier Reef, Australia), (3) to discuss the respective influence of processes which drive air-sea  $\text{CO}_2$  fluxes over the reef flat (i.e. mainly initial seawater conditions, metabolic and physical effects), (4) to estimate the overall metabolism effect on atmospheric  $\text{CO}_2$  budget and to compare it with air-sea flux data measured over the reef

itself, and (5) to use inorganic carbon thermodynamical equations to estimate the ratio of organic to inorganic metabolisms from this Eulerian approach.

## MATERIAL AND METHODS

Data presented here were obtained during 2 field trips, one at Moorea (Tiahura Barrier Reef, July-August 1992) and the other at Yonge Reef (December 1993). Community structure and composition of both sites are well known. Information regarding the study sites is given in a companion paper (Gattuso et al. 1996 in this issue).

To assess the effect of reef metabolism on air-sea exchange of  $\text{CO}_2$ , measurements of inorganic carbon and related parameters were carried out over three 24 h periods at a back reef station at each site. Discrete seawater samples were taken at oceanic stations. The current patterns across the reefs were relatively simple: water moved from the ocean across the reef and its velocity was modulated by tide. Back reef stations are therefore ideal sites at which to study the effect of reef metabolism on oceanic seawater.

The sampling protocol involved measurements of air-sea  $\text{CO}_2$  exchange, determination of  $\text{CO}_2$  partial pressure in surface water (indirect method), as well as hydrological and meteorological parameters (salinity, water temperature, tide, atmospheric pressure, solar radiation, wind speed and air temperature).

$p\text{CO}_2$  was calculated from measurements of pH and total alkalinity (TA). At both sites, total alkalinity was sampled each hour and measured using the classical Gran electrotitration method (Gattuso et al. 1993). pH was measured using commercial combination electrodes, but sampling intervals and procedures were different between Moorea and Yonge Reef. At Moorea, the electrode (Radiometer, GK2401C) was installed on an *in situ* data-logger and measurements were carried out each half hour at seawater temperature (Gattuso et al. 1996). Calibration was made using National Bureau of Standards (NBS) standards and reproducibility was pH 0.007.

At Yonge Reef, the pH electrode (Ross type, Orion) was installed aboard the research vessel in a cell continuously thermoregulated with surface seawater. A computerized interface was used to carry out 1 measurement every minute. Correction to *in situ* temperature from the cell temperature (0.1 to 0.5°C) was made according to Perez & Fraga (1987). The Ross-type electrode was calibrated using Tris buffer, as proposed by Dickson (1993), on the total proton scale [pH(Seawater scale, SWS)]. The reproducibility of pH measurement was  $\pm 0.2$  mV, which corresponds to an error of pH 0.004.

pCO<sub>2</sub> and the CO<sub>2</sub> speciation were calculated according to the pH(SWS) scale (total proton, mol kg<sup>-1</sup>) using the CO<sub>2</sub> acidity constants of Goyet & Poisson (1989), the CO<sub>2</sub> solubility coefficient of Weiss (1974) and the borate acidity constant of Hansson (1973). The total borate molality was calculated using the Culkin (1965) ratio to salinity. The error in pCO<sub>2</sub>, calculated from errors in pH and TA, was about 2% (6 μatm when pCO<sub>2</sub> = 350 μatm). When pH was calibrated using NBS standards, CO<sub>2</sub> dissociation constants of Mehrbach et al. (1973) were used and the error in pCO<sub>2</sub> was estimated to be about 3% (8 to 10 μatm when pCO<sub>2</sub> = 350 μatm).

Dissolved oxygen was determined in each site at the same frequency as pH (i.e. every half hour at Moorea and every minute at Yonge Reef) using a galvanic electrode (Kent Eil) at Moorea and a polarographic electrode (Orbisphere) at Yonge Reef. Sensors were calibrated against air-saturated seawater and a sodium dithionite solution as zero. Saturation oxygen levels were calculated according to the algorithm of Benson & Krause (1984).

Solar radiation was measured continuously (every minute) using a LI-COR (LI-192SA) quantum sensor which integrates light from 400 to 700 nm and yields data expressed in μmol photons m<sup>-2</sup> s<sup>-1</sup>. Tides at Moorea were calculated using the simplified harmonic method (SHM package) and harmonic coefficients of Matavaï (Tahiti) from Admiralty Charts Tables. Wind speed was measured using a hand anemometer. On the Great Barrier Reef, tide and meteorological parameters (wind speed, air and water temperatures, atmospheric pressure) were monitored (10 min) using a WLR 5 and a weather station (Aanderaa Instruments) respectively.

Air-sea CO<sub>2</sub> exchanges were measured using the bell method described by Frankignoulle (1988). This method involves the deployment of a closed incubator on the sea surface and the detection of initial (10 min) CO<sub>2</sub> variations in the gas phase with a LI-COR 6252 infra-red gas analyser. The analyser was calibrated using pure nitrogen (zero) and a commercial standard for CO<sub>2</sub> (350 ± 3 μatm). The infrared analyser was also used to measure the atmospheric partial pressure of CO<sub>2</sub>. As far as possible, measurements were carried out every half hour at both sites. The exchange coefficient was calculated using Henry's law:

$$F = K\alpha\Delta PCO_2 \quad (1)$$

where  $F$  is the flux (in mol m<sup>-2</sup> s<sup>-1</sup>),  $K$  is the exchange coefficient (in m s<sup>-1</sup>),  $\alpha$  is the CO<sub>2</sub> solubility coefficient (in mol m<sup>-3</sup> atm<sup>-1</sup>) and  $\Delta PCO_2$  is the CO<sub>2</sub> gradient through the air-sea interface (water-air, in atm).

The dynamics of inorganic carbon were studied in terms of the so-called homogeneous buffer factor  $\beta$

(see Sundquist & Plummer 1981), which is a convenient parameter for discussion of which process is responsible for inorganic carbon variations:

$$\beta = \left( \frac{\Delta pCO_2}{pCO_2} \right) \left( \frac{\Delta DIC}{DIC} \right)^{-1} = \frac{d \ln(pCO_2)}{d \ln(DIC)} \quad (2)$$

The homogeneous buffer factor  $\beta$  can be obtained from a data set by plotting  $\ln(pCO_2)$  versus  $\ln(DIC)$ . When dissolved CO<sub>2</sub> is the inorganic species involved in the carbon exchange (e.g. air-sea exchange), this buffer factor is the so-called Revelle factor and its value is about 12 for average seawater conditions. The factor can be significantly different from 12 if processes other than uptake or release of dissolved CO<sub>2</sub> occur. Frankignoulle (1994) recently proposed a relationship which allows calculation of  $\beta$  when organic and inorganic carbon metabolisms occur simultaneously ( $r^2 = 0.9994$ ,  $p < 0.0000$ ):

$$\beta = -7.02 + 0.186 \times \%C_{org} \quad (3)$$

where  $\%C_{org}$  is the percentage of change in inorganic carbon concentration due to organic metabolism (photosynthesis and respiration). This equation was obtained by taking into account both CO<sub>2</sub> and H<sub>3</sub>O<sup>+</sup> uptake as suggested by Redfield et al. (1963). The buffer factor displays a wide range of values depending on the inorganic species involved in the CO<sub>2</sub> dynamics. It ranges from -7 (only carbonate change,  $\%C_{org} = 0$ ) to +12 ( $\%C_{org} = 100$ ).

## RESULTS

### Moorea (austral winter)

Fig 1 shows air-sea CO<sub>2</sub> fluxes, pCO<sub>2</sub>, water temperature, irradiance, tide and oxygen saturation obtained over 3 diel cycles at Moorea during July and August 1992.

As already mentioned by Gattuso et al. (1993), air-sea CO<sub>2</sub> fluxes displayed strong daily variations with CO<sub>2</sub> invasion during the day and CO<sub>2</sub> evasion at night. Measurements of daily variations in pCO<sub>2</sub> showed that (1) pCO<sub>2</sub> changed from about 240 μatm during the day to 400 μatm at night, in good agreement with metabolic processes (superimposition of diurnal photosynthetic CO<sub>2</sub> uptake and the production of dissolved CO<sub>2</sub> by respiration and calcification) and (2) the shift of the direction of air-sea CO<sub>2</sub> fluxes was in perfect agreement with that of the sign of the CO<sub>2</sub> gradient through the interface which drives the fluxes (Eq. 1).

Dissolved O<sub>2</sub> varied inversely with pCO<sub>2</sub> and corresponded closely with related metabolic processes, displaying strong over-saturation during the day (up to 160%) and under-saturation at night. Tidal range was

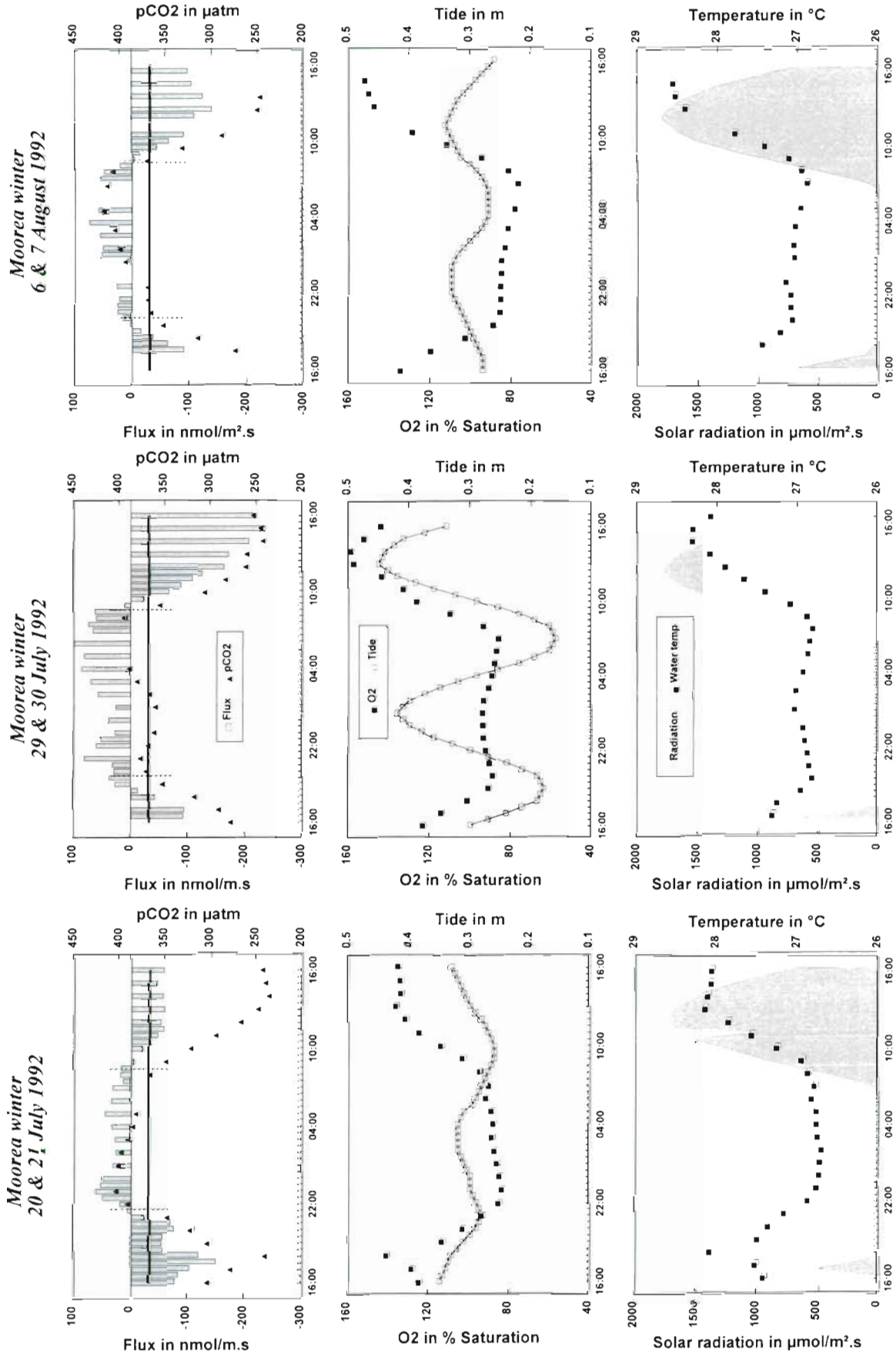


Fig. 1 Variations in air-sea CO<sub>2</sub> fluxes (positive value for evasion), CO<sub>2</sub> partial pressure, dissolved oxygen saturation level, tide, water temperature and irradiance during three 24 h cycles carried out at the back reef at Moorea. pCO<sub>2</sub> was calculated from pH and total alkalinity, tide was calculated using the SHM package. Irradiance data were obtained using a 10-point moving average, with 1 measurement taken per minute. On flux/pCO<sub>2</sub> graphs, vertical lines indicate when pCO<sub>2</sub> was at atmospheric equilibrium (~355 µatm) and the horizontal line represents the negative flux attributed to the initial oceanic under-saturation (this flux, -32 nmol m<sup>-2</sup> s<sup>-1</sup>, was estimated using the measured oceanic pCO<sub>2</sub> and the average exchange coefficient observed in the reef flat)

quite small at Moorea and the maximum signal was approximately 30 cm during the second cycle. Water temperature ranged between 27 and 28.5°C and its variation was driven by solar radiation.

### Yonge Reef (austral summer)

Fig. 2 shows the results obtained at Yonge Reef in December 1993. The partial pressure of CO<sub>2</sub>, air-sea CO<sub>2</sub> fluxes and dissolved oxygen displayed changes similar to those observed at Moorea. At this site, both pCO<sub>2</sub> and air-sea flux variations were high, with values ranging from 250 to 700 µatm and from -250 to +700 nmol m<sup>-2</sup> s<sup>-1</sup> respectively. Tide appeared to be an important forcing process at Yonge Reef, with a semi-diurnal signal of 3.5 m during the third cycle. The highest flux and pCO<sub>2</sub> observed values were recorded during the nocturnal low tide period. Water temperature variations, ranging from 26 to 28.5°C, were driven by both tide and solar radiation with minima associated with nocturnal low tide and maxima associated with maximal incoming radiation.

### Daily atmospheric budgets at the back reef

Daily integration of air-sea CO<sub>2</sub> fluxes measured at the back reefs and shown in Figs. 1 & 2 was carried out for both sites (Table 1). As already suggested by flux patterns in Fig. 1, the Moorea winter computation yields negative values (CO<sub>2</sub> invasion), whereas positive values were found at Moorea and at Yonge Reef in summer (CO<sub>2</sub> evasion). There is a major difference in oceanic pCO<sub>2</sub> between sites and seasons: the oceanic surface water was in equilibrium with the atmosphere at Moorea in summer and at Yonge Reef (pCO<sub>2</sub> ≈ 350 µatm), whereas it was under-saturated at Moorea in winter (pCO<sub>2</sub> ≈ 326 atm).

## DISCUSSION

### Potential budgets of air-sea CO<sub>2</sub> fluxes

The seasonal change observed at Moorea in the surface oceanic water is due to a temperature effect and is in good agreement with pCO<sub>2</sub> measurements carried out in French Polynesia by Y. Dandonneau (pers. comm.). The oceanic water at Moorea in winter was therefore a sink for atmospheric CO<sub>2</sub> before it reached the reef. This initial condition has to be taken into account to estimate the net effect of reef metabolism on the air-sea CO<sub>2</sub> flux budget. A simple procedure enables one to take into account the fact that oceanic

Table 1 Daily integration of measured air-sea CO<sub>2</sub> fluxes (positive values for evasion) at the back of the reef (S: summer, W: winter). The single value for Moorea summer is from Gattuso et al. (1993)

|        | Daily atmospheric CO <sub>2</sub> fluxes (mmol m <sup>-2</sup> d <sup>-1</sup> ) |          |              |
|--------|--|----------|--------------|
|        | Moorea S   | Moorea W | Yonge Reef S |
| Diel 1 | +1.5   | -1.2     | +2.7         |
| Diel 2 | -  | -2.1     | +6.5         |
| Diel 3 | -  | -1.1     | +3.2         |

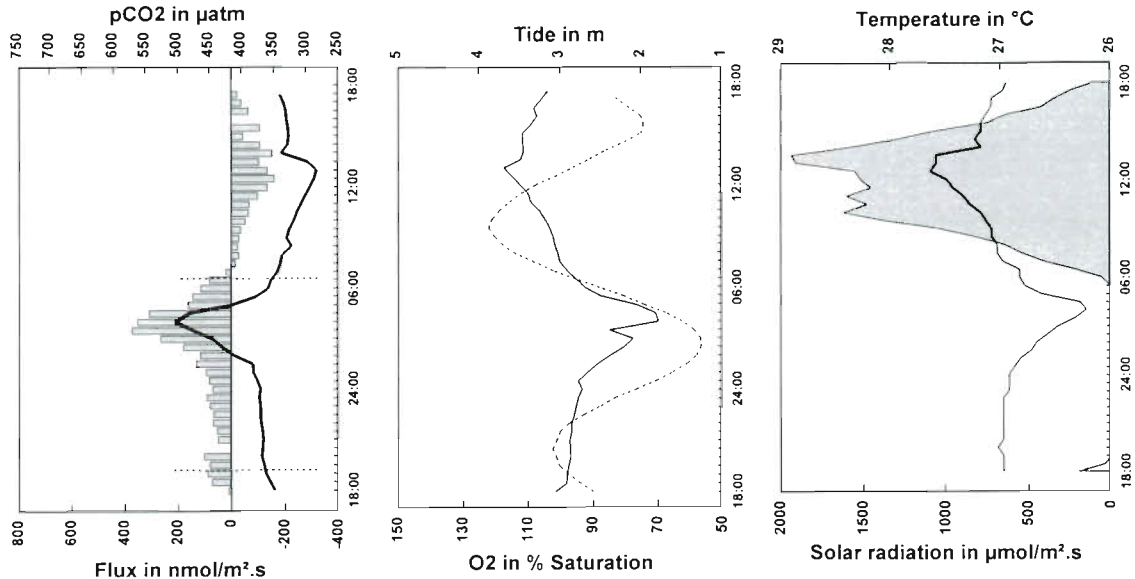
water impinging on the reef is not always in equilibrium with the atmosphere. It also takes into account the fact that air-sea CO<sub>2</sub> exchange is a slow process which continues after the water mass has left the reef system.

The procedure can be summarized as follows (see also Fig. 3): (1) Oceanic conditions (pH, TA, salinity and temperature) are used to calculate the total dissolved inorganic carbon concentration (DIC). Assuming constant TA, the oceanic pCO<sub>2</sub> is set to 355 µatm in order to derive the DIC concentration corresponding to atmospheric equilibrium. The difference between these DIC values is the amount of CO<sub>2</sub> that has to be exchanged with the atmosphere to restore atmospheric equilibrium ( $\Delta\text{DIC}_o$ ). (2) The same procedure is applied at the back reef and yields  $\Delta\text{DIC}_{br}$ . At the back reef, where DIC displays daily changes,  $\Delta\text{DIC}_{br}$  is calculated every hour and is then integrated over 24 h. (3) The difference  $\Delta\text{DIC}_{br} - \Delta\text{DIC}_o$  is the potential atmospheric CO<sub>2</sub> flux resulting from the effect of reef metabolism. (4) To obtain the total reef effect, it is necessary to take into account air-sea fluxes occurring on the reef flat itself (i.e. before the water reaches the back reef station). These are not included in the above calculation. Fluxes over the reef flat can be estimated from air-sea CO<sub>2</sub> fluxes measured at the back reef by integration over the water column, which is a good estimation because the water column is shallow and well-mixed.

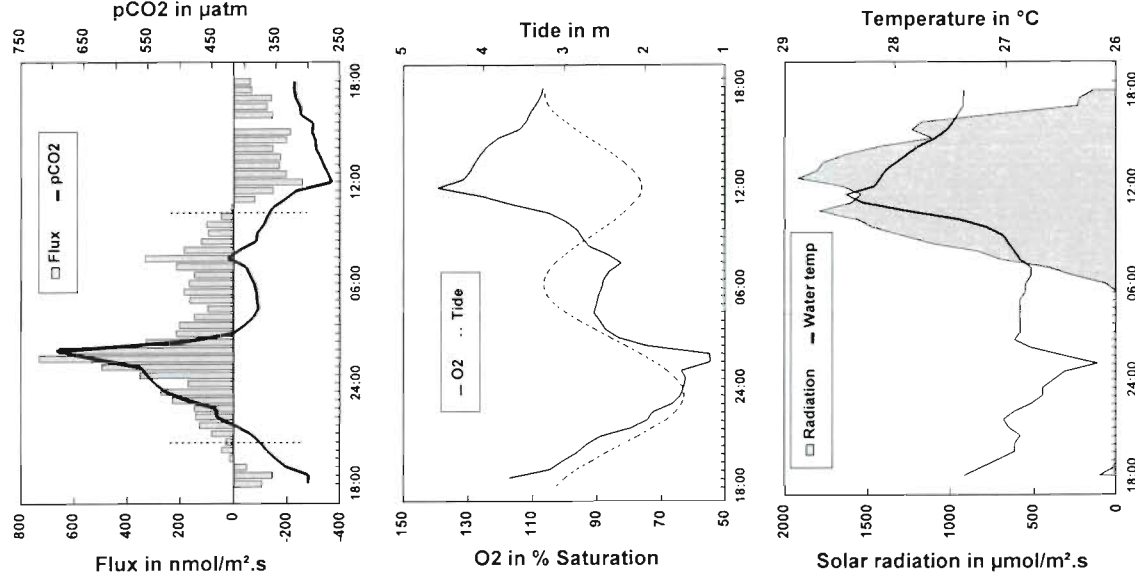
Results are called 'potential air-sea CO<sub>2</sub> fluxes' because they assume that the water mass goes back to atmospheric equilibrium after crossing the reef. This procedure enables estimation of the reef effect in terms of CO<sub>2</sub> thermodynamics in seawater. The potential air-sea CO<sub>2</sub> fluxes obtained for both sites are shown in Table 2.

We conclude that (1) at Moorea in winter, the observed under-saturation in the ocean (326 µatm) induces an oceanic air-sea CO<sub>2</sub> flux that corresponds to an invasion of 20 µmol kg<sup>-1</sup> to reach equilibrium. Since oceanic water was at equilibrium in front of Yonge Reef, the corresponding  $\Delta\text{DIC}_o$  is zero, (2) at Moorea in winter, a smaller air-sea CO<sub>2</sub> flux was necessary to equilibrate the system at the back reef than

*Yonge Reef summer  
13 & 14 December 1993*



*Yonge Reef summer  
8 & 9 December 1993*



*Yonge Reef summer  
5 & 6 December 1993*

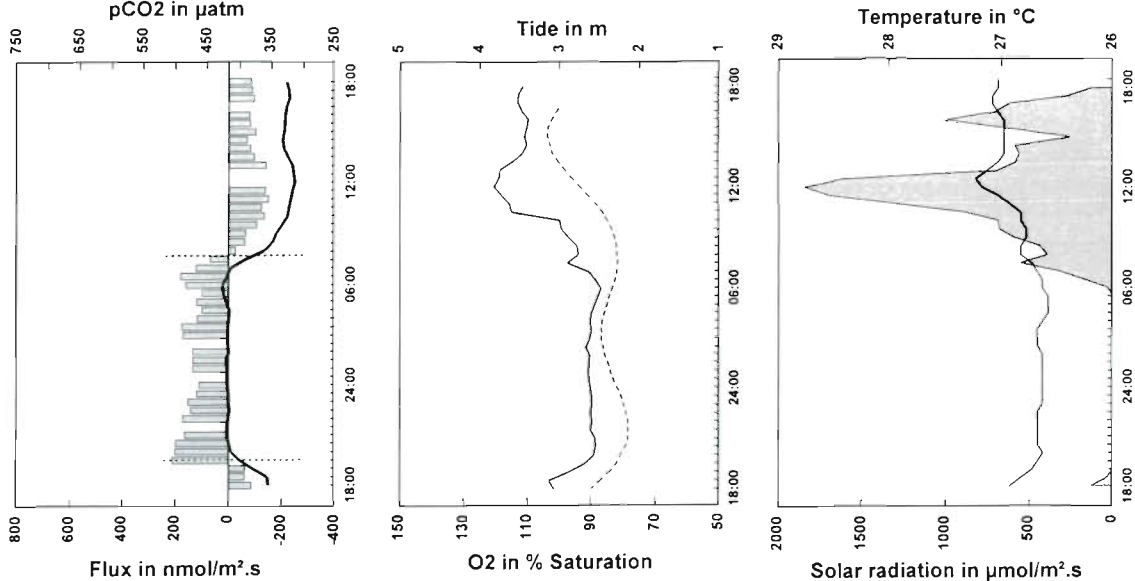


Fig. 2. Variations in air-sea CO<sub>2</sub> fluxes (positive value for evasion), CO<sub>2</sub> partial pressure, dissolved oxygen saturation, tide, water temperature and irradiance during three 24 h cycles carried out at the back reef at Yonge Reef. pCO<sub>2</sub> was calculated from pH and total alkalinity measurements. Irradiance data were obtained using a 10-point moving average, with 1 measurement taken per minute. On flux/pCO<sub>2</sub> graphs, vertical lines indicate when the surface water pCO<sub>2</sub> was at atmospheric equilibrium (~355 µatm)

Table 2. Calculated amounts of CO<sub>2</sub> that must be released by seawater to reach atmospheric equilibrium (355 μatm) at the ocean (ΔDIC<sub>o</sub>) and after crossing the reef (ΔDIC<sub>br</sub>), assuming no calcification (constant TA) during equilibrium. Reef flat values show measured air-sea CO<sub>2</sub> fluxes on the reef flat that allow calculation of the total reef effect and the atmospheric fluxes. Positive values correspond to sea-air fluxes

|        |                          | ΔDIC <sub>o</sub> | Atmospheric C budgets (μmol kg <sup>-1</sup> ) |                         |       | Atmospheric potential budget |
|--------|--------------------------|-------------------|--|-------------------------|-------|------------------------------|
|        |                          |                   | Reef flat                                      | Reef ΔDIC <sub>br</sub> | Total |                              |
| Diel 1 | Moorea (Winter 1992)     | -20               | -0.9   | -1                      | -1.9  | +18.1                        |
|        | Yonge Reef (Summer 1993) | 0                 | +0.8   | +18                     | +18.8 | +18.8                        |
| Diel 2 | Moorea (Winter 1992)     | -20               | -1.6   | 0                       | -1.6  | +18.4                        |
|        | Yonge Reef (Summer 1993) | 0                 | +2.0   | +22                     | +24.0 | +24.0                        |
| Diel 3 | Moorea (Winter 1992)     | -20               | -0.8   | -10                     | -10.8 | +9.2                         |
|        | Yonge Reef (Summer 1993) | 0                 | +1.0   | +6                      | +7.0  | +7.0                         |

in front of the reef, clearly suggesting that the reef was as a net producer of CO<sub>2</sub>, and (3) according to the saturation level, measured daily exchanges on the reef flat range from -1.6 (Moorea) to +2.0 (Yonge Reef) μmol kg<sup>-1</sup>. Except for diel cycles 1 and 2 at Moorea, where calculated exchanges with water after it left the reef were low, the air-sea flux occurring on the reef flat was 1 order of magnitude lower than the exchange necessary to reach equilibrium in water which had left the reef.

Data given in Table 2 are expressed in μmol kg<sup>-1</sup> because they describe the amount of CO<sub>2</sub> that has to be exchanged to reach equilibrium in the observed water masses. Calculations were based upon CO<sub>2</sub> system thermodynamics. To estimate the total effect at each site in terms of CO<sub>2</sub> released to the atmosphere, these data have to be multiplied by the water flow that crosses the reef. The water flow was estimated to be

44 m<sup>3</sup> d<sup>-1</sup> and 129 m<sup>3</sup> d<sup>-1</sup> per meter of reef front for Moorea and Yonge Reef respectively. Moorea and Yonge Reef were therefore (when respectively averaged) sources of 8 g C d<sup>-1</sup> and 28 g C d<sup>-1</sup> respectively or, by taking into account the averaged reef width, 1.8 mmol C m<sup>-2</sup> d<sup>-1</sup> and 5.1 mmol C m<sup>-2</sup> d<sup>-1</sup> respectively.

Finally, data presented in this paper allow a rough estimate of the global carbon dioxide emission from reef ecosystems: assuming that the potential flux is 20 mmol m<sup>-2</sup> d<sup>-1</sup> (i.e. 1 order of magnitude higher than fluxes measured in the field; see Table 2), the global CO<sub>2</sub> flux to the atmosphere is about 0.05 Gt C yr<sup>-1</sup>. This flux represents about 1% of the present anthropogenic input and is in good agreement with the value (0.02 to 0.08 Gt C yr<sup>-1</sup>) computed by Ware et al. (1992).

### Air-sea CO<sub>2</sub> fluxes and wind speed

The magnitude of the air-sea flux is a function of the exchange coefficient,  $K$  (piston velocity; Eq. 1). The estimation of  $K$  is complex because it depends on environmental parameters which are difficult to evaluate (e.g. wind, sea-state, bubbles, surface film; Liss 1983, Wanninkhof 1992). Wind speed is recognized as the dominant factor that influences the exchange coefficient, and relationships that allow the calculation of  $K$  as a function of wind speed have been proposed (Liss & Merlivat 1986, Wanninkhof 1992).

Because we measured both flux and pCO<sub>2</sub> data, we are able to derive values for  $K$  at both sites. Such derivations of  $K$  use Eq. (1) and take into account the salinity and temperature dependence of the CO<sub>2</sub> solubility coefficient. It should be noted that the bell method to measure air-sea CO<sub>2</sub> exchanges suppresses the direct wind effect on the flux such that  $K$  is underestimated. On the other hand, the effect of the inner

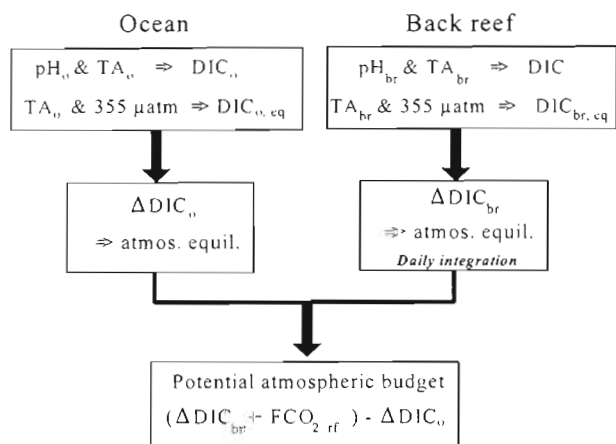


Fig. 3. Procedure used to estimate the global air-sea CO<sub>2</sub> flux for oceanic water crossing the reef (see text). Subscripts o, br, eq and rf refer respectively to the ocean, the back reef, the atmospheric equilibrium and the reef flat

turbulence of a surface layer is clearly taken into account by the bell method but is difficult to reproduce in laboratory experiments, such as with the wind tunnel, which has been used to derive the Liss & Merlivat (1986) relationship. Frankignoulle (1988) discussed results yielded at sea by the bell method over a wide range of wind speeds (from 0 to 14 m s<sup>-1</sup>) and sea-states and suggested that *K*-values obtained by both methods agree within 30%.

Calculated *K*-values are shown versus wind speed in Fig. 4. At Yonge Reef, wind speed was 6 to 11 m s<sup>-1</sup> and thus above the value that is characterized by a stronger influence of wind effect (3.6 m s<sup>-1</sup>; Liss & Merlivat 1986). It is clear from Fig. 4 that most of our set of experimental *K*-values fall between the 2 theoretical curves.

At Moorea in winter, wind speed was most often lower than 6 m s<sup>-1</sup> but corresponding *K* values were higher (about 5 × 10<sup>-3</sup> m s<sup>-1</sup>) than those proposed by the theoretical curves. This observation can be explained by the fact that the reef flat is a turbulent system (depth ≈ 1 m and current ≈ 0.2 m s<sup>-1</sup>) and that this turbulence, independent from the wind, increases the exchange coefficient as detected by the bell method. This effect is masked in Yonge Reef due to higher wind speed, which increases the exchange coefficient. Using the coefficient obtained at low wind speed in Moorea, one can calculate that the averaged daily fluxes obtained at Yonge Reef (2.7, 6.5 and 3.2 mmol m<sup>-2</sup> d<sup>-1</sup>; cf. Table 1) would, under similar turbulence conditions, be respectively equal to 1.9, 3.5 and 1.0 mmol m<sup>-2</sup> d<sup>-1</sup>, i.e. about 50% of the observed values.

Finally, Eq. (1) can be used, with averaged pCO<sub>2</sub> and calculated exchange coefficients, to estimate that 3 to 6 d would be needed to restore equilibrium after water crosses the reef.

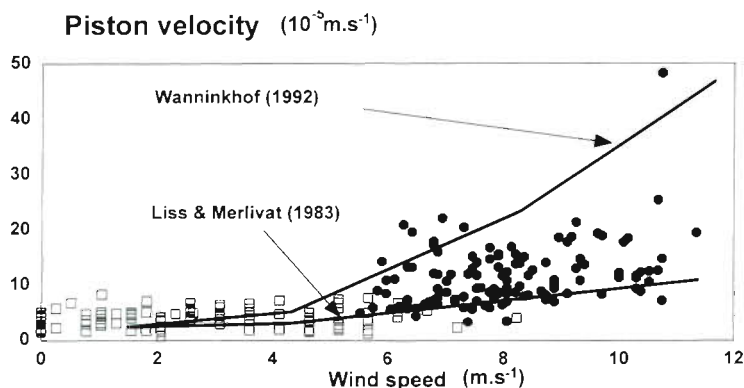


Fig. 4. Piston velocity versus wind speed obtained at Moorea in winter (□) and at Yonge Reef in summer (●). Theoretical curves are also indicated (see text)

Table 3. Regression data obtained by plotting ln(pCO<sub>2</sub>) versus ln(DIC) to yield the homogeneous buffer factor β (slope; cf. Fig. 5)

|        | Homogeneous buffer factors β = dln(pCO <sub>2</sub> )/dln(DIC) |                   |                     |                          |                   |                     |
|--------|--|-------------------|---------------------|--------------------------|-------------------|---------------------|
|        | Moorea (Winter 1992)   |                   |                     | Yonge Reef (Summer 1993) |                   |                     |
|        | β  | %C <sub>org</sub> | %C <sub>inorg</sub> | β                        | %C <sub>org</sub> | %C <sub>inorg</sub> |
| Diel 1 | 6.79   | 74.2              | 25.8                | 8.73                     | 82.7              | 17.3                |
| Diel 2 | 6.53   | 72.8              | 27.2                | 7.65                     | 78.9              | 21.1                |
| Diel 3 | 6.35   | 71.9              | 28.1                | 8.07                     | 81.1              | 18.9                |

### Dynamics of inorganic carbon

pCO<sub>2</sub> displayed strong daily variations at the 2 sites investigated. These were related to metabolic processes that induce changes in the dynamics of total inorganic carbon. Numerous natural processes are liable to modify seawater pCO<sub>2</sub> and its total inorganic carbon content (e.g. Stumm & Morgan 1981): (1) Primary production decreases pCO<sub>2</sub> as a result of uptake of dissolved CO<sub>2</sub> and H<sub>3</sub>O<sup>+</sup>. Respiration has the opposite effect. (2) Calcification increases pCO<sub>2</sub> as a result of chemical equilibration involved with carbonate fixation. (3) Air-sea exchange of CO<sub>2</sub> increases or decreases dissolved CO<sub>2</sub>. (4) Increase in temperature increases pCO<sub>2</sub> due to changes in the CO<sub>2</sub> solubility coefficient and of the carbonic acid equilibrium constants.

Although these processes occur simultaneously, their relative intensity varies throughout the day and according to season. Consequently, the CO<sub>2</sub> distribution at any particular time can be difficult to estimate.

The data set presented here allows estimations of the homogeneous buffer factor β (cf. Eq. 2), the value of which highly depends on the process responsible for changes in inorganic carbon concentration (cf. Eq. 3). Fig. 5 shows that the correlation between ln(pCO<sub>2</sub>) and ln(DIC) is very high, with r<sup>2</sup> ranging from 0.96 to 0.99. β values are about 6.5 and 8 at Moorea and Yonge Reef respectively (Table 3). Assuming that changes in dissolved CO<sub>2</sub> induced by air-sea exchange are negligible compared with changes induced by organic metabolism, Eq. (3) allows for the calculation that the proportion of total carbon uptake used for organic metabolism is about 73% at Moorea and 80% at Yonge Reef. These results agree well with those obtained by Gattuso et al. (1996), who determined metabolic parameters on the reef flats (gross photosynthesis, respiration and net calcification) using a Lagrangian technique. The approach proposed here, using pCO<sub>2</sub> and DIC dynamics



at a single station, is an alternative method for determining the relative importance of calcification and the net production. Robertson et al. (1994) recently used this approach to study a coccolithophore bloom in the North Atlantic. Their results suggest that 50% of the uptake of inorganic carbon goes to organic metabolism in this ecosystem.

The assumption that air-sea  $\text{CO}_2$  exchanges are negligible in the above calculation can easily be justified (see also Smith & Veeh 1989, Smith 1995). Although air-sea fluxes are quite important on the reef flat, their magnitude is low compared with metabolic parameters: the daily air-sea  $\text{CO}_2$  fluxes (ca  $1 \text{ mmol m}^{-2} \text{ d}^{-1}$ ; see Table 1) are 2 to 3 orders of magnitude lower than gross primary production, respiration and net calcification ( $-821$ ,  $+730$  and  $-186 \text{ mmol m}^{-2} \text{ d}^{-1}$  respectively in Moorea and  $-1279$ ,  $+1243$  and  $-253 \text{ mmol m}^{-2} \text{ d}^{-1}$  in Yonge Reef; Gattuso et al. 1996).

Fig 5 also shows that  $\beta$  is constant over the entire diel cycle. In terms of  $\text{CO}_2$  chemical dynamics, this means that the amount of uptake or release of dissolved  $\text{CO}_2$  due to any process over the amount of effective carbonate ion uptake for calcification was

constant during the measurements. Since air-sea  $\text{CO}_2$  exchange is negligible compared with metabolic fluxes, the proportions of inorganic carbon for organic metabolism and inorganic metabolism are constant. Thus, the daytime ratio net photosynthesis/calcification and the nighttime ratio respiration/calcification are constant at both sites. This observation is also suggested by the Lagrangian approach and is discussed in detail, in terms of metabolic significance, by Gattuso et al. (1996).

## Conclusions

Both Moorea and Yonge Reef flats were potential sources of atmospheric  $\text{CO}_2$ . The overall fluxes calculated for Yonge Reef are about 4 times higher than for Moorea.

As might be expected, the saturation level of oceanic water with respect to  $\text{CO}_2$  is of prime importance in calculations of the global effect of reef metabolism on the atmospheric budget for  $\text{CO}_2$ . An atmospheric budget cannot be derived from observations made solely over reefs. Data obtained at Moorea in winter have shown that initial (oceanic) conditions can result in air-sea fluxes of  $\text{CO}_2$  over the reef flat whilst overall the reef indeed behaves as a net source of  $\text{CO}_2$ .

$\text{CO}_2$  exchange occurring on the reef flat contributes very little to the air-sea  $\text{CO}_2$  equilibration; most of the equilibration takes place after the water mass has left the reef flat.

These results emphasise the need for further field data to assess the role of coral reefs in terms of atmospheric budget. The wide range of ecological conditions (preservation, biodiversity, photosynthesis versus calcification, etc.) encountered in these ecosystems could be responsible for substantially different conclusions. At any rate, it must be borne in mind that reef systems have a minor role in the present carbon budget (Crossland et al. 1991).

The homogeneous buffer factor  $\beta$  was remarkably constant over 24 h at both sites and can therefore be used to estimate the percentage of the inorganic carbon uptake used for calcification. The constancy of  $\beta$  over 24 h also suggests that calcification is proportional to net production during the day and to respiration rate at night, which is consistent with metabolic rate relations as determined by other techniques.

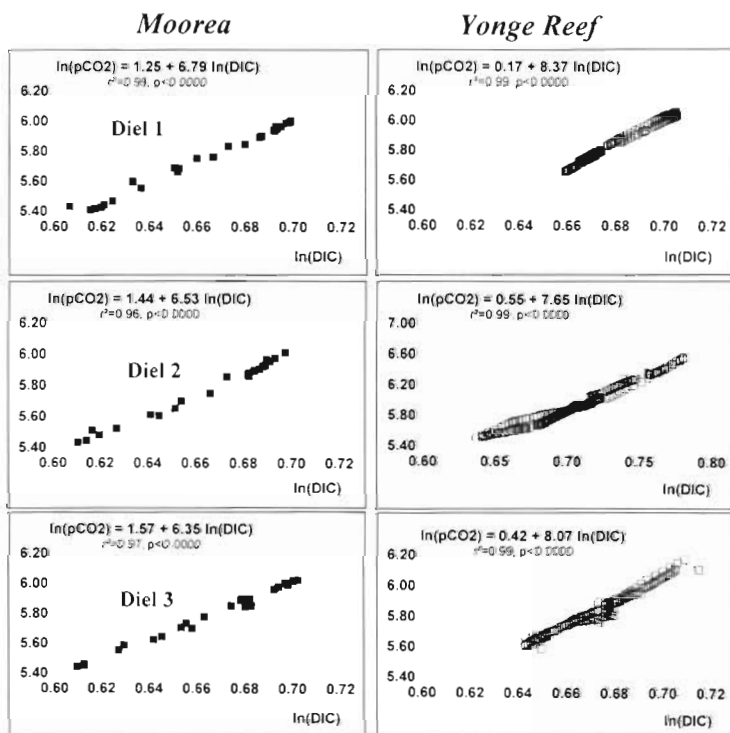


Fig. 5. Plots of  $\ln(\text{pCO}_2)$  versus  $\ln(\text{DIC})$  obtained during diel cycles in order to assess the homogeneous buffer factor  $\beta$  (slope; see text). For the second cycle at Yonge Reef, scales were adjusted to the wider range of observed values.  $\text{pCO}_2$  data were normalized to  $27^\circ\text{C}$  as described by Copin-Montegut (1988)

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