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The diel carbon cycle of the Biosphere 2 ocean

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Abstract

The purpose of this study was to find the dominant processes affecting the diel carbon cycle of the Biosphere 2 ocean from July 27, 1995 to August 14, 1995. Despite excessively low nitrate ($< 0.05 \mu\text{mol l}^{-1}$) and phosphate ($0.00\text{--}0.04 \mu\text{mol l}^{-1}$) values, the Biosphere 2 ocean not only showed large daily TCO_2 changes of $30.5 \pm 7.0 \mu\text{mol kg}^{-1}$ but also a net production of organic carbon and CaCO_3 during the period of this study. A model used to predict pCO_2 values based on measured O_2 concentrations suggested CaCO_3 precipitation and organic carbon production were dominating the average diel ocean pCO_2 signal while the gas exchange with the atmosphere was relatively insignificant to the pCO_2 in the Biosphere 2 ocean. In the first 4 days of the experiment, the alkalinity decreased at a calculated rate of about $10 \mu\text{eq kg}^{-1} \text{d}^{-1}$ while in the following 10 days the model indicated that the alkalinity was nearly constant. The model also confirmed that the positive net production of organic carbon effectively held the pCO_2 in the Biosphere 2 ocean below equilibrium with the atmosphere. Although changes in the gas exchange had a small effect on the diel amplitude of pCO_2 ($255 \pm 84 \mu\text{atm}$), changes in the photosynthetic quotient (PQ) were more significant. A PQ of 1.0 was used in the model to match calculated pCO_2 with measured pCO_2 of the Biosphere 2 ocean. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Biosphere 2; Carbon; Gas exchange; Diel; pCO_2 ; Ocean

1. Introduction

The focus of this study is to understand the major factors that control the carbon chemistry of the Biosphere 2 ocean. As with many coral reefs (Gattuso et al., 1993) and marsh embayments (Nixon et al., 1976), Takahashi et al. (1995) found that

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Biosphere 2's ocean was extremely depleted in nutrients. While nitrate values were found to be below the measurement blank ($0.05 \mu\text{mol kg}^{-1}$) and phosphate values varied from 0.00 to $0.04 \mu\text{mol kg}^{-1}$, there were still large diel changes in oxygen (Langdon and Sweeney, 1995) and total CO_2 (TCO_2) values. In the absence of nutrients we can consider three dominating processes that might affect both the amplitude of the diel signal and the amount of TCO_2 stored in the ocean: gas exchange; photosynthesis; respiration; and CaCO_3 precipitation and dissolution. These three processes are the basis for our carbon cycle model of the Biosphere 2 ocean (Fig. 1).

1.1. Gas exchange

The first element of the TCO_2 budget in the Biosphere 2 ocean is the gas exchange rate. To calculate the effect of gas exchange we used the stagnant film model which separates the well mixed atmosphere and ocean reservoirs with the gradient in the thin film of thickness z (m). Each gas has a particular molecular

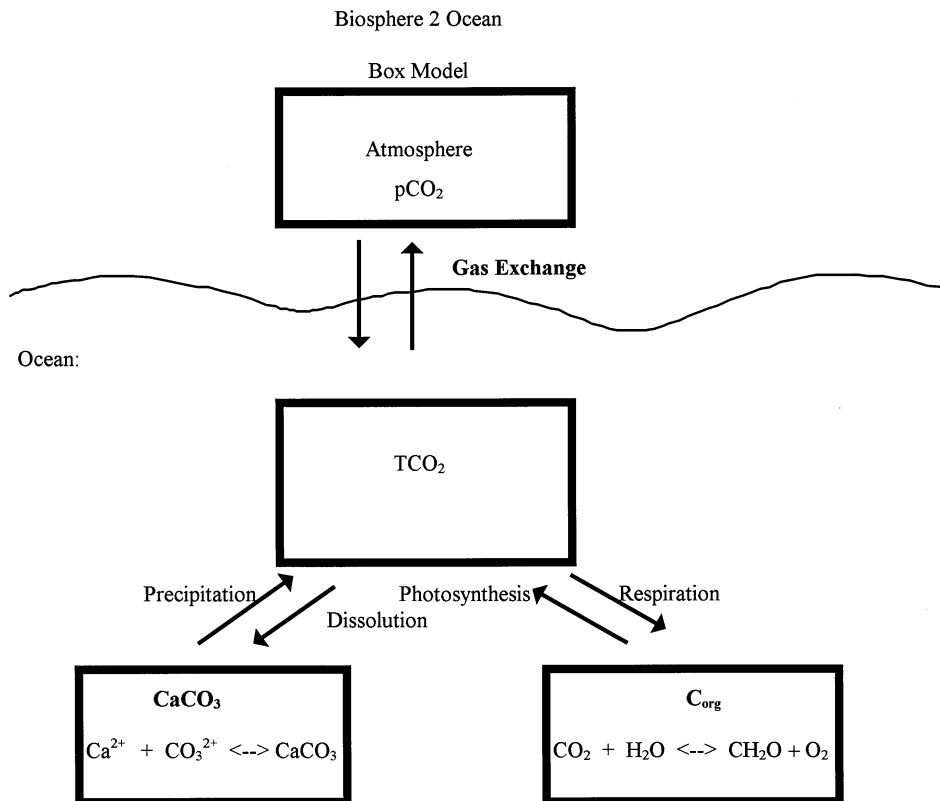


Fig. 1. Biosphere 2 Box Model—this box model represents the three major reservoirs affecting the TCO_2 in the Biosphere 2 ocean.

diffusivity, D ($\text{m}^2 \text{day}^{-1}$), within the thin film. The flux ($\text{mol m}^{-2} \text{d}^{-1}$) of CO_2 into the ocean can then be represented by the equation:

$$\text{Flux CO}_2 = (D/z) \alpha(\Delta p\text{CO}_2) \quad (1)$$

Where α is the solubility constant (mol atm^{-1}) of CO_2 gas (Weiss, 1974). The $\Delta p\text{CO}_2$ (μatm) gradient in the micro layer is calculated using the equation:

$$\Delta p\text{CO}_2 = p\text{CO}_2 \text{ atm} - p\text{CO}_2 \text{ sw} \quad (2)$$

In which $p\text{CO}_2 \text{ atm}$ (μatm) and $p\text{CO}_2 \text{ sw}$ (μatm) are the measured partial pressure of CO_2 in the atmosphere and seawater, respectively.

In this model the rate at which CO_2 gas moves into the ocean is determined by D/z (m/d), the gas transfer coefficient (piston velocity, Broecker and Peng, 1971, 1974, 1982). With the gas transfer coefficient, we can calculate the time it will take for a gas to reach equilibrium using the depth of the mixed layer, h .

In Biosphere 2 ocean we were able to calculate the gas transfer coefficient by artificially supersaturating the ocean with oxygen (to about $250 \mu\text{M}$) and then allowing the value to relax back to a steady state value. The gas transfer coefficient, k ($= D/z$), was then calculated by regressing $\ln(C_t - C_f)$ against time, where C_t is the concentration of oxygen at time t and C_f is the concentration of oxygen at steady state (Langdon and Sweeney, 1995). The average depth was assumed to be 3.6 m (Atkinson, et al., 1999)

$$k = h/(t_2 - t_1) * \ln(C_1 - C_f) / \ln(C_2 - C_f) \quad (3)$$

Since the gas transfer coefficient for oxygen was calculated to be $2.1 \pm 0.2 \text{ m d}^{-1}$ we were able to calculate the gas transfer coefficient for CO_2 by using the diffusivity of each gas at a constant temperature:

$$k_{\text{CO}_2} = k_{\text{O}_2} * (D_{\text{CO}_2} / D_{\text{O}_2})^{1/2} \quad (4)$$

Because the temperature of the gases were the same we assumed that the kinematic viscosity of water is constant (with constant temperature and salinity) so $(D_{\text{CO}_2} / D_{\text{O}_2})$ can be calculated using the relative ratio of the Schmit numbers for CO_2 gas and O_2 gas (Wanninkhof, 1992). This gives a gas transfer coefficient for CO_2 of $2.0 \pm 0.2 \text{ m d}^{-1}$ at 26.0°C .

1.2. Photosynthesis and respiration

In the Biosphere 2 ocean, incubations experiments indicated that the benthic community, the plant matter growing around the edges and at the bottom, seem to be the dominant factor affecting the TCO_2 . The pelagic community, normally a dominant source and sink of TCO_2 in the ocean, does not play an important role in Biosphere 2 ocean. Langdon and Sweeney (1995) used 12 h bottle incubation experiments to estimate that pelagic species of phytoplankton account for about 8% of the net photosynthesis observed in the ocean.

In low nutrient but highly productive environments such as coral reefs it has been shown that the plant organisms generally rely on recycled nutrients. In particular,

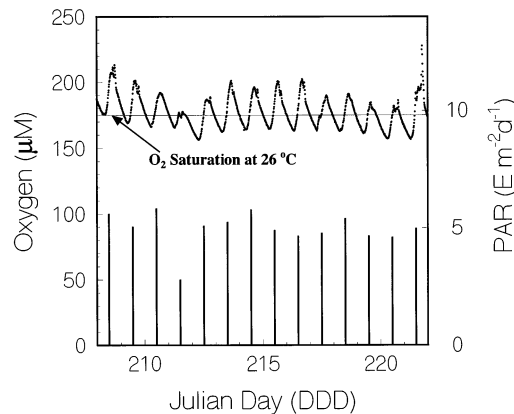


Fig. 2. Biosphere 2 O_2 —this shows the oxygen concentration in the Biosphere 2 ocean measured every 15 min from July 27 (JD 208) to August 12, 1995 (JD 222). the vertical line represent the total integrated PAR for each day. The vertical lines are centered at 1200 h each day.

uptake of NH_3 increases in place of NO_3^- which yields a photosynthetic quotient (PQ) of about 1.1 in many algae (Laws, 1991) and as low as 1.0 in coral reef environments (Porter, 1980; Barnes, 1983; Barnes and Devereux, 1984). With a PQ of 1.1, the algae in the Biosphere 2 ocean will take up one mole of CO_2 for every 1.1 moles of O_2 that they produce assuming that the only available nutrients in the system are those provided by NH_3 and not NO_3^- .

The Biosphere 2 ocean is unique because there is no wave action forcing the surface water oxygen above a saturated concentration. This allows us to assume that oxygen concentrations are only changing as a result of organic carbon production, oxidation or gas exchange. Since it has been observed (Fig. 2) that the average daily oxygen concentration in Biosphere 2 ocean is above saturation at 26°C, Langdon and Sweeney (1995) have estimated a positive net production rate of O_2 to be $10.8 \mu\text{mol kg}^{-1} \text{d}^{-1}$. This would imply that organic carbon was also produced at a rate of $10.8 \mu\text{mol kg}^{-1} \text{d}^{-1}$ with a PQ of 1.0. A net positive production implies that the TCO_2 is being constantly reduced throughout the study and may only be balanced by input of CO_2 gas from the atmosphere or dissolution of $CaCO_3$.

1.3. $CaCO_3$ precipitation and dissolution

Between March and June of 1995, Takahashi et al. (1995) made pCO_2 and TCO_2 measurements in Biosphere 2 ocean which demonstrated a 0.77 equivalents change in alkalinity for every mole of TCO_2 consumed. This implied that there were 0.39 mol $CaCO_3$ precipitated for every mol of TCO_2 consumed. Takahashi et al. (1995) also observed that the mean rate of decrease in alkalinity was $19 \mu\text{eq kg}^{-1} \text{d}^{-1}$ ($9.5 \mu\text{mol of } TCO_2 \text{ kg}^{-1} \text{d}^{-1}$). Without an adequate time series of TCO_2 measurements to calculate alkalinity changes during the full 14 day experiment in August 1995, we

have used estimated changes in alkalinity and measured changes in O_2 to predict pCO_2 . The predicted pCO_2 was then compared with the measured value during the study period.

2. Methods

All measurements referred to in this experiment were done from July 19, 1995 (Julian day (JD) 200) to August 23, 1995 (JD 235) from a sampling platform in the Biosphere 2 ocean. In that time the salinity and temperature were held constant at 36.2 ± 0.5 pss and $26.0 \pm 1.0^\circ C$ through the use of heat exchangers and additions of fresh water. Initially, an airlift was used to insure proper circulation of water throughout the ocean was achieved during additions of 37.6 kg $Na_2CO_3 \cdot xH_2O$. On July 27, 1995 (JD 208) at 0655 the airlift was turned off and left off until August 14, 1995 (JD 226) at 1000. The model used data collected from July 27, 1995 (JD 208) through August 12, 1995 (JD 222) when the airlift was off.

The mole fraction of CO_2 in dry air 1 m above the Biosphere 2 ocean was made using a non-dispersive infrared gas analyzer (LICOR Model LI-6251). Calibration of the instrument was performed using four Biosphere 2 supplied CO_2 standards. Each standard was calibrated at Lamont using a gas chromatograph equipped with a flame ionization detector. The gas chromatograph was calibrated using a coulometer and P-V-T measurements of pure CO_2 gas (99.998%). The pCO_2 in air was computed using the measured barometric pressure, water vapor pressure at the seawater temperature, and the barometric pressure. The precision of the measurement is estimated to be about $\pm 0.5\%$ of the measured value.

Measurement of the pCO_2 sea water was done by pumping water from 1 m below the surface into a 20 l equilibrator chamber through a shower head ($25\text{--}30\text{ l min}^{-1}$) which facilitated rapid exchange of CO_2 between the liquid and the gas phase. The equilibrated air was then passed through a infrared gas analyzer (LICOR Model LI-6251) alternatively with the atmospheric pCO_2 gas samples. Calibration of the infrared analyzer done using Biosphere 2 supplied CO_2 standards (as described above). Each value was measured over a 3 min time interval. The pCO_2 in the seawater was computed using the measured barometric pressure, water vapor pressure at the equilibration temperature, and the barometric pressure. The precision of the measurement is estimated to be about $\pm 0.5\%$ of the measured value.

TCO_2 samples were collected in 250 ml Pyrex glass bottles sealed with a ground glass stopper that had been lubricated by silicon grease. Each sample was initially collected in a 5 l Niskin bottle at 1 m depth. Five hundred ml of seawater were allowed to drain into the sample bottles through a 0.6 m of bubble-free Tygon tubing. The tubing was then removed from the bottle leaving a small amount of head space between the stopper and the liquid. Once the sample was removed from Biosphere 2 each sample was poisoned with 250 μl of 50% saturated mercuric chloride to prevent any biological alteration of the sample. This experimental procedure yielded an average standard deviation in replicate samples of $\pm 2.0\ \mu\text{mol kg}^{-1}$.

In this study all values of alkalinity have been calculated using methods similar to those described by Peng et al. (1987). For the above calculations the following equilibrium constants were used: the solubility of CO_2 in water measured by Weiss (1974), the dissociation constants of CO_3^{2-} and HCO_3^- tested by Mehrbach et al. (1973) and the boric acid dissociation constant measured by Dickson (1990). Alkalinity can be calculated using measured values of TCO_2 and pCO_2 at a given salinity, temperature and nutrient levels to an accuracy of about $30 \mu\text{eq kg}^{-1}$ (Takahashi et al. 1995). However, the calculated value will give a precision of about $2 \mu\text{eq kg}^{-1}$.

Oxygen values were collected by an ENDECO 1133 pulsed oxygen sensor placed 1 m below the Biosphere 2 ocean surface. The electrode was calibrated against daily oxygen samples analyzed by Winkler titrations (Strickland and Parson, 1972). The oxygen sensor took a sample of the oxygen every 4 min and an analog voltage was logged by Biosphere 2's data acquisition system every 15 min. Chris Langdon reported that the calibration accuracy was $\pm 3.7 \mu\text{M}$ during the period of July 26–29. Calibrations made after that time have increased to $\pm 8.9 \mu\text{M}$.

The light measurements were made with a Licor sensor with PAR quantum response and a cosine collector. This sensor was located at a depth of 2.15 m.

3. Results and discussion

3.1. Field results

On July 24, 1995 (JD 205) at 1545 the first of two additions of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ were added to the Biosphere 2 ocean to maintain a supersaturated concentration of aragonite. Before the two additions of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$, the average TCO_2 measured was $1819.0 \pm 18.5 \mu\text{mol kg}^{-1}$ and the pCO_2 had an average daily value of $817 \pm 51 \mu\text{atm}$. By July 27, 1995 (JD 208) at 0655 all of the 37.6 kg $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ had been completely mixed (confirmed by measurements of TCO_2 in two different areas in the Biosphere 2 ocean) and the airlift was turned off. With the addition of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ the average daily pCO_2 had fallen down to $646.8 \pm 55.2 \mu\text{atm}$ (Fig. 3a) and the average TCO_2 rose to a value of $1928.9 \pm 18.4 \mu\text{mol kg}^{-1}$ (Fig. 3b).

From July 27, 1995 (JD 208) to August 1, 1995 (JD 213), we continued to sample for TCO_2 measurements (Fig. 3b) at times that corresponded to daily maxima and minima of pCO_2 . Over this 6 day period the TCO_2 of the Biosphere 2 ocean showed a daily amplitude of $30.5 \pm 7.0 \mu\text{mol kg}^{-1}$. While the average TCO_2 remained fairly constant throughout this period, the calculated alkalinity decreased from a high of $2128 \pm 9 \mu\text{eq kg}^{-1}$ to a low of $2084 \pm 9 \mu\text{eq kg}^{-1}$ (Fig. 3c). This trend was interrupted by one cloudy day (JD 210) which increased the average TCO_2 by almost $20 \mu\text{mol kg}^{-1}$ and increased the alkalinity by about $14 \mu\text{eq kg}^{-1}$ in the next 2 days. After August 1, 1995 (JD 213) measurements of TCO_2 were not taken until after the airlift was turned back on August 14, 1995 (JD 226). On August 19, 1995 (JD 231) the TCO_2 was as high as $2050 \mu\text{mol kg}^{-1}$ and the calculated alkalinity had risen to $2137.7 \pm 0.3 \mu\text{eq kg}^{-1}$ with the airlift on.

The trend in alkalinity that was calculated from the time that the airlift was turned off until a final measurement was made 6 days later (Fig. 3c) illustrated that the calcification process in the Biosphere 2 ocean was not consistent. Further measurements before a final addition of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ on August 19, 1995 (JD 231) indicated a net increase in measured TCO_2 and calculated alkalinity from the time the airlift was turned off on July 27, 1995 (JD 208). Although it was possible that turning the airlift back on enhanced gas exchange and increase the TCO_2 measured, the increased gas exchange should not effect the calculated alkalinity. The only way to increase the alkalinity would be through dissolution of CaCO_3 in the Biosphere 2 ocean.

Because of the addition of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ before the experiment, Fig. 4 showed that the Biosphere 2 ocean was super-saturated with respect to both calcite and aragonite based on solubility constants for aragonite used by Mucci (1983). We assumed that the Ca^{2+} concentration was 8.5 mmol kg^{-1} based measurements made by Takahashi et al. (1995) on June 23, 1995. The only other source of alkalinity might have been from the sediments. Oxidation of organic carbon in the sediments might have led to dissolution in the of CaCO_3 in the pore waters.

The fact that we calculated a net increase in alkalinity over the course of the experiment was even more paradoxical when we considered how much *Amphoroa*, a calcareous algae, was harvested from the Biosphere 2 ocean during the month of

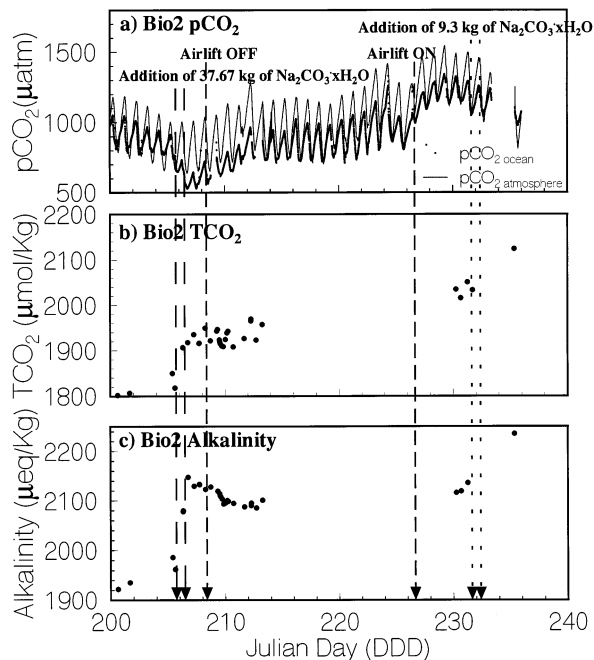


Fig. 3. Biosphere 2 Ocean Study—data collected from July 19, 1995 (JD 200) to August 23, 1995 (JD 235) for a) pCO_2 (b) total CO_2 and (c) calculated alkalinity.

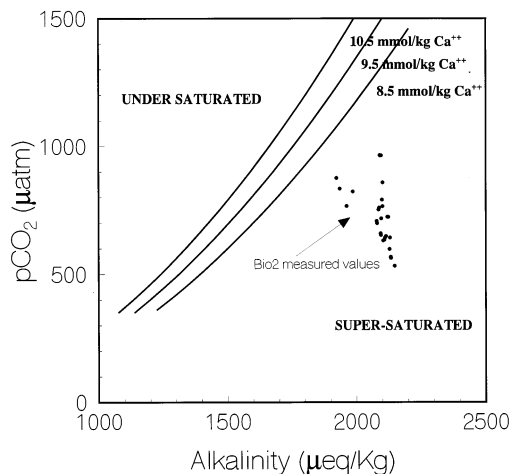


Fig. 4. Aragonite saturation curve for Biosphere 2 ocean—saturation values (—) at 10.5, 9.5 and 8.5 mmol $\text{Ca}^{2+} \text{ kg}^{-1}$. These values are calculated based on constants used by Mucci (1983) at a salinity 36.2 pss and a temperature of 26.0°C. The points represent measured pCO_2 values and calculated alkalinity values using constants from Peng et al. (1987).

August. Rosenthal (personal communication) reported that in the month of August, 1995 about 60 kg of *Amphoroa* was harvested from the Biosphere 2 ocean. If we assumed that the dry weight of *Amphoroa* was 90% CaCO_3 , the volume of Biosphere 2 was $2.6 \times 10^6 \text{ l}$ (Atkinson et al., 1999) and the harvesting of the *Amphoroa* was maintaining a steady state of growth, the alkalinity would be decreasing at a rate of $13 \mu\text{eq kg}^{-1} \text{ d}^{-1}$ due to *Amphoroa* alone. This rate of decrease from *Amphoroa* in month August 1995 was 68% of alkalinity decrease that Takahashi et al. (1995) observed from March through June—a significant contribution. Unfortunately, at no time during our experiment did we see the alkalinity decrease at such a high rate.

3.2. Modelling results

With the help of a model of the carbon system in the Biosphere 2 ocean we have tried to reconstruct how alkalinity might have changed during a 14 day period that the airlift was off. Fig. 4a shows the first model run which predicted the pCO_2 of the Biosphere 2 ocean based on the change in oxygen measured in the ocean (Fig. 2). The model used the calculated gas exchange values for both O_2 and pCO_2 and a PQ value of 1.0 to estimate the change in the pCO_2 every 15 min from July 27, 1995 (JD 208) to August 10, 1995 (JD 222). Although there was a large increase in the observed pCO_2 in latter half of the time series, it was not reflected in the modelled pCO_2 values (Fig. 5a). Without changing the PQ ratio or the gas exchange, the only way to increase the pCO_2 was to decrease alkalinity. As Fig. 3c indicates, there was an average decrease in alkalinity of about $10 \mu\text{eq kg}^{-1} \text{ d}^{-1}$ for

the first 4 days of the experimental period. When we made a similar correction for alkalinity for the whole experimental period we saw a dramatic change in the modelled $p\text{CO}_2$ values (Fig. 5b). In the period of time that the $10 \mu\text{eq kg}^{-1} \text{d}^{-1}$ decrease in alkalinity was actually observed (JD 208–212) we saw a very good match between the modelled $p\text{CO}_2$ and the real $p\text{CO}_2$ measurements. Beyond Julian day 212, the modelled $p\text{CO}_2$ in Fig. 5b quickly increase in value while the measured values plateau. Without TCO_2 measurements after Julian day 213, we were unable to document the actual changes in alkalinity; however, the plateau in the measured $p\text{CO}_2$ values indicate that alkalinity may have been constant after the first 4 days. This result was confirmed in Fig. 5c, which showed a very close fit between the modelled $p\text{CO}_2$ and the measured $p\text{CO}_2$ values, when the alkalinity was held constant after the fourth day of the experimental period. The increase in alkalinity calculated on Julian day 213 (Fig. 3c), further demonstrated that it was unlikely that alkalinity continued to decrease at the initial rate of $10 \mu\text{eq kg}^{-1} \text{d}^{-1}$.

Although the correction for the alkalinity in the first 4 days of the experimental period does help to explain the major differences between the modelled data and the measured data, there is still small inconsistencies in the daily amplitude of the diel signal. The smaller amplitude observed in the modelled $p\text{CO}_2$ value could be explained by the fact that the rate of CaCO_3 precipitation or dissolution was not

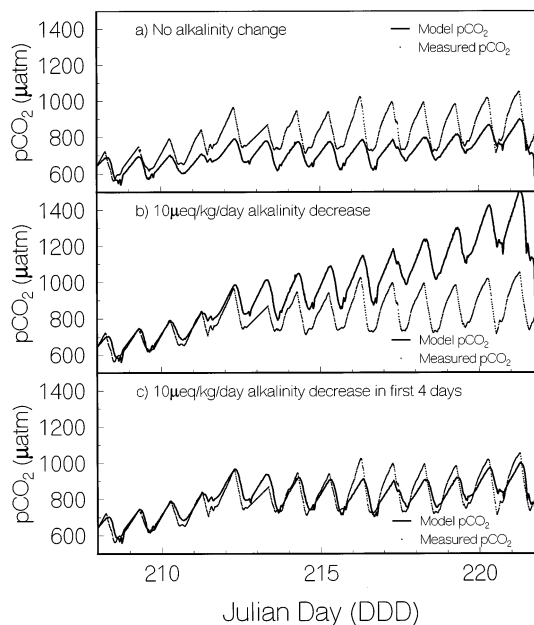


Fig. 5. $p\text{CO}_2$ Model results— $p\text{CO}_2$ values (—)calculated based on the change in O_2 values every 15 min compared with observed results (⋯). This model assumes a piston velocity of 2.1 m d^{-1} for O_2 and 2.0 m d^{-1} for CO_2 along with a PQ value of 1.0. (a) Alkalinity constant (b) decrease in alkalinity ($10 \mu\text{eq kg}^{-1} \text{d}^{-1}$) and (c) decreasing alkalinity ($10 \mu\text{eq kg}^{-1} \text{d}^{-1}$) for the first four diel cycles followed by a constant alkalinity.

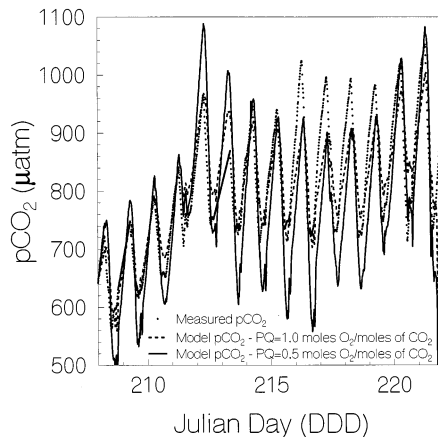


Fig. 6. The effect of a change in the PQ ratio—this figure shows the change in amplitude of the diel $p\text{CO}_2$ values calculated from the change in dissolved oxygen in the Biosphere 2 ocean based on changes in the PQ ratio. The alkalinity in this model decreases for the first 4 days at a constant rate of $10 \mu\text{eq kg}^{-1} \text{d}^{-1}$ and then levels off at a constant value. The piston velocity is set at 2.5 m d^{-1} for CO_2 .

constant throughout a diel period as has been pointed out by many investigations into the coral reef calcification rates (Barnes, 1982; Barnes and Chalker, 1990). In the model we assumed a constant rate of CaCO_3 precipitation which has no diel variability. If precipitation was more rapid at night we might expect to see larger amplitudes in the $p\text{CO}_2$ signal, however, this would contradict the prevailing theory that light enhances calcification rates in coral reefs (Barnes and Chalker, 1990). Fig. 6 illustrates that by decreasing the photosynthetic quotient there was a consequential increase amplitude of the modelled $p\text{CO}_2$ values. It would appear that PQ values that match the amplitude of the measured $p\text{CO}_2$ curve are below values observed in the natural environment (values tend to be between 1.0 and 1.4) (Porter, 1980; Barnes, 1983; Barnes and Devereux, 1984; Laws, 1991). Fig. 7a illustrates that an increase in gas exchange will not affect the amplitude of the $p\text{CO}_2$ values but will bring the average daily values to a steady state more quickly.

By starting with a decreasing the alkalinity value followed by a constant alkalinity value after the first 4 days in the Biosphere 2 ocean model, we were able to match the measured and calculated value of ocean $p\text{CO}_2$ based on the changes in oxygen measured over the study period. However, it is important to address how net production of organic carbon effects the $p\text{CO}_2$ value. Fig. 7b illustrated that with no net production of organic carbon the ocean $p\text{CO}_2$ moved into equilibrium with the atmospheric $p\text{CO}_2$. With a net production of organic carbon Fig. 7c showed that the ocean $p\text{CO}_2$ decreased until it reached a steady state where the amount of CO_2 being added to the ocean through gas exchange equaled the amount being taken out of through organic carbon production. This relationship can be seen in Fig. 3a which showed the ocean $p\text{CO}_2$ maintained an average value that was below that of the atmospheric $p\text{CO}_2$ -indicating that there was a net positive production of organic carbon.

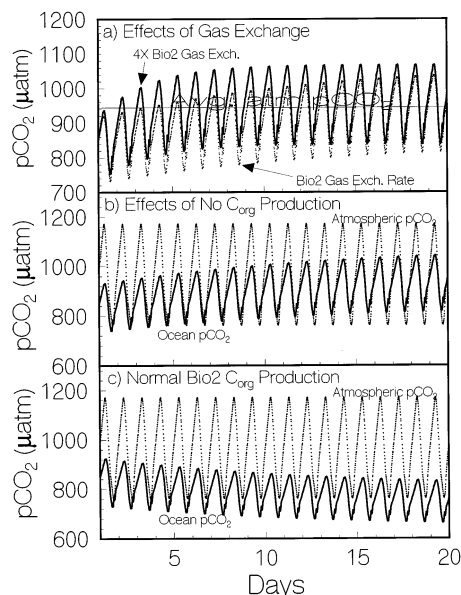


Fig. 7. Normalized models—(a) $p\text{CO}_2$ modelled with changes in gas exchange—this shows the $p\text{CO}_2$ value calculated from changes in O_2 concentrations in a system with no net organic carbon or CaCO_3 production. Shows $p\text{CO}_2$ (---) values based on a piston velocity of 2.5 m d^{-1} . The solid curve illustrates a piston velocity of 10 m d^{-1} . The atmospheric $p\text{CO}_2$ in this model has average value represented by the solid horizontal line and a daily amplitude of $410 \text{ } \mu\text{atm}$. (b) $p\text{CO}_2$ model with no production—this model shows the how the $p\text{CO}_2$ in the ocean changes in relation to the atmospheric $p\text{CO}_2$ if there is no net production of organic carbon. (c) $p\text{CO}_2$ model with Normal Biosphere 2 organic production—this model run shows that given a normal gas transfer coefficient (2.5 m d^{-1}) and a typical August net productivity ($14 \text{ } \mu\text{mol Corg kg}^{-1} \text{ d}^{-1}$) the $p\text{CO}_2$ value will decrease until it has reached an equilibrium value.

4. Conclusion

It was apparent from this study that changes in alkalinity played a major role in the average daily $p\text{CO}_2$ values measured in the Biosphere 2 ocean; however, it was unclear what caused these alkalinity changes. While harvests of *Amphora* indicated that the alkalinity may have decreased by as much as $15 \text{ } \mu\text{eq kg}^{-1} \text{ d}^{-1}$ throughout the month of August, the model showed very erratic shifts in alkalinity which were dominated by periods of constant alkalinity values. If the *Amphora* growth were constant in the ocean during the experimental period then we would have to assume that there was a balancing flux of carbonate ion from the sediment caused by organic carbon oxidation in the sediment. It is also possible that the actual harvesting of *Amphora* from the benthic layer may have enhanced the flux of high alkaline pore water into the overlying water. In the future, the harvesting of *Amphora* will have to be more carefully monitored to determine its affect on the alkalinity in Biosphere 2 ocean.

In addition to the effects of alkalinity, it also has been demonstrated that there was a net production of organic carbon in Biosphere 2 ocean during the study period. We have shown that the organic carbon production was high enough to force the ocean $p\text{CO}_2$ below atmospheric $p\text{CO}_2$ values despite the effects of gas exchange. We can therefore conclude that gas exchange does not play a very significant role in Biosphere 2 ocean.

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