Coral reefs:
sources or sinks of atmospheric CO_2?

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Abstract. Because the precipitation of calcium carbonate results in the sequestering of carbon, it frequently has been thought that coral reefs function as sinks of global atmospheric CO_2. However, the precipitation of calcium carbonate is accompanied by a shift of pH that results in the release of CO_2. This release of CO_2 is less in buffered sea water than fresh water systems; nevertheless, coral reefs are sources, not sinks, of atmospheric carbon. Using estimated rates of coral reef carbonate production, we compute that coral reefs release 0.02 to 0.08 Gt C as CO_2 annually. This is approximately 0.4% to 1.4% of the current anthropogenic CO_2 production due to fossil fuel combustion.

Introduction

CO_2 is a major greenhouse gas which is expected to contribute at least 50%, and perhaps much more (Lashof and Ahuja 1990), to projected global warming. Because coral reefs are conspicuous depositors of calcium carbonate ($CaCO_3$), it may be inferred that, by removing carbonate and bicarbonate ions, the process leaves seawater over the reef undersaturated in inorganic carbon and leads to withdrawal of CO_2 from the atmosphere. Thus, flourishing coral reefs would serve as a hedge against global warming.

However, when calcium carbonate is precipitated, CO_2 is generated rather than consumed (Arrhenius 1896). During the calcification process, the water becomes more acid due to the removal of bicarbonate and carbonate ions, and this change in pH lowers the solubility of CO_2 (Broecker and Takahashi 1966; Stumm and Morgan 1981). The partial pressure of CO_2 increases and, in an open system, CO_2 escapes to the overlying atmosphere.

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The calcification reaction is commonly expressed in the form (e.g. Stumm and Morgan 1981, p. 171):

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + H_2O + CO_2.$$
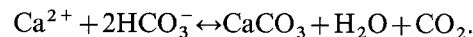
This simplistic representation of the calcification process has resulted in the assumption that for each mole of $CaCO_3$ deposited, a mole of CO_2 is liberated (e.g., Taylor et al. 1991). While this is nearly true in freshwater, the process is reduced in buffered seawater, with the result that only approximately 0.6 moles of CO_2 are liberated per mole of $CaCO_3$ deposited.

Our purpose here is to describe in general terms the processes which occur during precipitation or dissolution of $CaCO_3$ and to show that, in the marine environment, about 0.6 moles of CO_2 will be liberated per mole of $CaCO_3$ deposited. In the short term (hours to days), some or all of the CO_2 liberated during carbonate deposition may be absorbed by biological processes on the reef. However, over extended periods (seasons or longer), coral reefs are a contributing source to global atmospheric CO_2, albeit a minor one when compared with current CO_2 release due to fossil fuel combustion.

Analysis of carbonate precipitation

Characterization of the aqueous CO_2 system at a given temperature and salinity requires measured or assumed values for two variables related to CO_2 (Skirrow 1975; Smith 1985). Practical measurement variables include pH, total alkalinity (TA), dissolved inorganic carbon (DIC), and CO_2 partial pressure (pCO_2). In the paragraphs that follow, we will first indicate the composition of typical reef waters with respect to inorganic C species using estimated average values and pH, and then illustrate the response of those variables to carbonate precipitation in two scenarios.

Globally-averaged pCO_2 of the well-mixed upper layer of the ocean is only slightly less than the globally-averaged pCO_2 of the atmosphere, with a difference of less than 10 µatm (Broecker et al. 1979; Volk and Bacas-

tow 1989). Although substantial deviations from the global average do occur (Volk and Bacastow 1989; Watson et al. 1991), the approximate equilibrium can be used for calculations in the regime of coral reefs without significant error. Under the assumed equilibrium conditions, the amount of CO_2 dissolved in water may be taken to be proportional to the atmospheric partial pressure of CO_2. Because current pCO_2 of the atmosphere is slightly greater than 350 µatm (Adams et al. 1990), a value of pCO_2 in seawater of 350 µatm may be assumed, and this provides one of the requisite variables. The pH of typical sea water is approximately 8.2 (Smith 1973; Brown et al. 1989, p 97). This value provides a second known variable and allows the computation of the remaining variables of relevance using equations and parameters available in standard references (e.g., Skirrow 1975; Stumm and Morgan 1981). Our computations consider the major ions (carbonate, bicarbonate, hydrogen, and borate) so that the aqueous CO_2 system is described by eight equations in 10 unknowns. Given any two of these unknowns (e.g., pCO_2 and pH) the remaining eight parameters can be solved using algebraic and numerical methods. (Note: Derivations of all equations used in the computations and listings of the corresponding FORTRAN programs are available from J. Ware and M. Reaka-Kudla. The results of these computations are summarized in Table 1 A.)

Suppose a volume of this sea water is sealed, with no overlying gas layer, so that it cannot exchange CO_2 with the atmosphere or the surrounding water. If a given amount of $CaCO_3$ is precipitated, say 0.05 mM (millimoles per liter), results approximating those in Table 1 B would be observed. The pH has decreased to 8.13; this increase in acidity is accompanied by a decrease in both carbonate $[CO_3^{2-}]$ and bicarbonate $[HCO_3^-]$ concentrations and an *increase* in dissolved CO_2. The increase in dissolved CO_2 causes an increase in pCO_2 to 409 µatm.

Table 1. Initial and final conditions of variables after precipitation of 0.05 mM of $CaCO_3$ in sea water with an initial pH of 8.2. Atmospheric pCO_2 is 350 µatm, salinity $=35‰$, and temperature $=25°$ C. (Units: mM = millimoles per liter; meq/l = milliequivalents per liter)[a]

Conditions	Initial values (A)	Final values	
		Sealed volume (B)	Open volume (C)
Equivalent pCO_2 in water, µatm	350	409	350
$[CO_2]$, mM	0.0101	0.0118	0.0101
$[HCO_3^-]$, mM	1.726	1.710	1.661
$[CO_3^{2-}]$, mM	0.219	0.184	0.203
pH	8.200	8.128	8.183
TA, meq/l	2.272	2.172	2.172
DIC, mM	1.955	1.905	1.874
ΔDIC, mM	0	-0.0500	-0.081

[a] Constants used in these computations are: $pK_1 = 5.9677$, $pK_2 = 9.0966$; $pK_w = 13.9947$; $pK_B = 7.3230$ (boron); $\alpha = 0.028885$ (CO_2 solubility constant); $\beta = 0.012140$ (total borate constant)

The total alkalinity, TA, has decreased by 0.10 meq/l (milliequivalents per liter) because the calcium ion has a charge of plus 2. DIC has decreased by 0.05 mM, representing the loss of carbon to solid $CaCO_3$. Since pCO_2 in our sealed volume is now higher than that of the surrounding atmosphere, CO_2 would be *released* if the sealed volume were allowed to equilibrate with the atmosphere. Upon exposure to the atmosphere (Table 1 C), pCO_2 decreases to atmospheric levels, and pH increases slightly (to 8.18) but not to the initial level of 8.2. DIC has decreased by approximately 0.081 mM from the initial value. Clearly, 0.05 mM of this loss in carbon is due the carbon deposited in $CaCO_3$. The other 0.031 mM has been converted to CO_2 gas and has escaped from our volume. In other words, for each unit of CO_2 lost in the form of $CaCO_3$ precipitated in normal sea water, an additional 0.62 units is lost from the original amount of DIC present due to release of CO_2.

This conclusion is robust to variations in pH and pCO_2 (varying less than 10% for pH from 8.1 to 8.3 and pCO_2 from 300 to 400 µatm), so that our choice of initial conditions does not greatly affect the results. Had the reaction been run in reverse and calcium carbonate been dissolved instead of precipitated, CO_2 would have been *absorbed* in exactly the same relative amounts. The specific result that only 0.62 moles of CO_2 are liberated for each mole of $CaCO_3$ precipitated in seawater is due to the buffering effect of seawater. In freshwater, approximately one mole of CO_2 is liberated for each mole of $CaCO_3$ precipitated. That this "0.6 rule" is not a purely computational phenomenon has been demonstrated experimentally by Wollast et al. (1980).

Global reef carbonate production estimates

Most coral reefs appear to show maximal production rates of about 10 to 12 kg $CaCO_3$ m^{-2} y^{-1}, while substantial portions of reef flats appear to produce approximately 4 kg $CaCO_3$ m^{-2} y^{-1} (Smith and Kinsey 1976; Buddemeier and Smith 1988; Kinsey and Hopley 1991). These rates may be high in comparison to the metabolic performance of reef systems as a whole (which may contain substantial areas of relatively unproductive inter-reef habitat). Consequently, these rates should not be extrapolated to the global area of reefs. A reasonable regional average for gross $CaCO_3$ production of reef provinces (as defined in Smith 1978) is approximately 1.5 [± 0.5] kg m^{-2} y^{-1} (Smith and Kinsey 1976; Smith 1983; Buddemeier and Smith 1988; Kinsey and Hopley 1991). As an example, the recent study by Hubbard et al. (1990) for an entire reef system on St. Croix indicated that total carbonate production averaged 1.2 kg m^{-2} y^{-1}.

The much higher rates determined for recent reefs during the Holocene transgression (Adey 1978; Davies et al. 1985; Fairbanks 1989; Chappell and Polach 1990) may be viewed as representative upper limits for net reef growth. These rates could be renewed if significant sea level rises occur in combination with current predictions of global temperature increase. However, only those relatively small areas of reef development that are presently limited

in upward growth by contemporary sea levels and upon which increases in global temperature do not exert a negative impact would respond with increased growth. For the present, therefore, we use a value of 1.5 [$\pm$0.5] kg $CaCO_3$ m^{-2} y^{-1} in the following calculations.

Limits on CO_2
released by reef carbonate precipitation

The estimated gross $CaCO_3$ production of 1.5 [$\pm$0.5] kg m^{-2} y^{-1} corresponds to 180 [$\pm$60] g C m^{-2} y^{-1} which, by the "0.6 rule", would result in the release of 108 [$\pm$36] g C m^{-2} y^{-1} as CO_2. Smith and Veeh (1989) have pointed out that much of the CO_2 released during $CaCO_3$ precipitation in calcifying ecosystems is taken up by net organic production instead of being released to the atmosphere immediately. As discussed by Crossland et al. (1991), reef systems produce about 36 g C m^{-2} y^{-1} in net organic production. This figure represents the maximum amount of CO_2 released by carbonate deposition processes that could be incorporated into organic production. Much of the net organic production must be exported from the reef (otherwise organic material would accumulate on the reef) and some of this organic matter is probably oxidized elsewhere, releasing the CO_2 absorbed during calcification. However, for the purposes of providing a conservative lower bound, we consider that all the net organic production offsets CO_2 production from calcification. Therefore, as a lower limit, reef carbonate prodcution would release approximately 108 [$\pm$36] − 36 = 72 [$\pm$36] g C m^{-2} y^{-1} to the atmosphere.

As an upper limit on reef CO_2 production, one could consider that only the organic material buried in reef sediments is prevented from oxidation and subsequent release of CO_2 to the atmosphere. Reef sediments contain on the order of 0.4% organic carbon by weight (Crossland et al. 1991), which corresponds to the loss of 6 [$\pm$2] g C m^{-2} y^{-1}. It follows that as much as 102 [$\pm$34] g C m^{-2} y^{-1} may be released to the atmosphere in response to carbonate production. (Note: The slight reduction in uncertainty is due to the fact that the 0.4% figure applies not only to the original estimated average but also to the original estimated uncertainty).

Thus, the total range of CO_2 released to the atmosphere by coral reefs appears to be on the order of 36 to 136 g C m^{-2} y^{-1} which, when multiplied by the global reef area of 6$\times$10^{11} m^2 (Smith 1978), yields 2.2 to 8.2$\times$10^{13} g C y^{-1}. Thus, coral reefs probably are contributing between 0.02 and 0.08 gigatons (Gt) of C as CO_2 to the atmosphere each year. To put this amount of CO_2 release in perspective, the anthropogenic release of CO_2 by fossil fuel combustion in 1988 was approximately 5.7 Gt C y^{-1} (World Resources 1990, Table 24.4). Therefore, coral reefs are adding CO_2 to the atmosphere at 0.4% to 1.4% of the current rate of anthropogenic production due to fossil fuel combustion.

We note one other CO_2 pathway related to reef $CaCO_3$ production. Any carbonate material that is transported off the reef and subsequently sinks below the carbonate compensation depth (CCD) will be dissolved with a resulting *absorption* of CO_2. While it may take hundreds or thousands of years for the absorption of this CO_2 in mid- to deep-ocean water to affect surface waters (Williamson and Holligan 1990), this pathway can be considered to be approximately in steady state. In the steady-state, this absorption would further decrease the contribution of reefs to global atmospheric CO_2. If we take the figure of Hubbard et al. (1990) that 25% of $CaCO_3$ production is transported off-reef and make the limiting assumption that all of this material is transported below the CCD, the figures quoted above do not change appreciably (the range of the total reef contribution would be 0.1% to 1.1% of the CO_2 released due to fossil fuel combustion).

Discussion

While we have spoken of coral reefs as releasing CO_2 to the atmosphere, this may be, strictly speaking, not correct. On the whole, the world's oceans are a sink for the CO_2 emitted by fossil fuel combustion (Broecker et al. 1979; Tans et al. 1990). Because it is impossible to determine the exact fate of the CO_2 emitted by any specific process, and because the ocean overall is a net sink for CO_2, a more accurate statement with regard to the fate of the CO_2 emitted by carbonate precipitation on coral reefs is as follows: Over periods of decades, the carbonate precipitation on coral reefs results in a reduction in the global absorption of CO_2 from the atmosphere to the ocean surface waters of between 0.02 to 0.08 Gt C y^{-1} as CO_2. On a geological time scale this process cannot continue indefinitely without replacement of the carbonate ions and a restoration of the pH balance; this is accomplished via various feedback processes associated with volcanism, metamorphism, and weathering of terrestrial sedimentary rocks (Berner et al. 1983; Marshall et al. 1988). On the much shorter time scales associated with current greenhouse predictions, this global carbon cycle does not need to be balanced. Since the total DIC of the world's oceans is approximately 38,000 Gt C (Skirrow 1975), we can be confident that the process described above can continue without geochemical limitations for at least several centuries, which is the time scale of greatest current interest.

Given the magnitude of current uncertainties about the global CO_2 budget (e.g., Tans et al. 1990), it is clear that coral reefs are not major participants in global CO_2 balance. Indeed, to our knowledge, the activities of coral reef organisms have yet to be included in any world-wide CO_2 balance equations. Nevertheless, it is important that the role of coral reefs in global carbon cycles be accurately understood.

In conclusion, we have shown that coral reefs are net producers of CO_2 and therefore contribute to the global greenhouse effect. It should be emphasized that this production is part of the normal CO_2 cycle and that the natural greenhouse effect, to which coral reefs have been contributing since the Mesozoic, is necessary for maintaining the earth's temperature in a range that is capable of sustaining life. In contrast, the liberation of CO_2 (and

other "greenhouse gases") by fossil fuel combustion, changing agricultural practices, and other human industry is enhancing this natural greenhouse effect. On a global scale, the magnitude of the reef-generated CO_2 is small compared to current human-induced perturbations.

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