KANSAS GEOLOGICAL SURVEY

OPEN-FILE REPORT SERIES 95-56

INFORMAL COMMUNICATIONS OF SCOR WORKING GROUP 104.

Kansas Geological Survey Open-File Report 95-56a:

REFLECTIONS ON THE MEASUREMENT AND SIGNIFICANCE OF CARBON METABOLISM ON CORAL REEFS

S. V. Smith
Centro de Investigación Cientifica y de Educación Superior de Ensenada
(CICESE), Ensenada, Mexico
(Permanent address: Dept. Oceanography, U. Hawaii, Honolulu, HI 96822)

Kansas Geological Survey Open-File Report 95-56b:

CORAL REEF CARBON CYCLE RESEARCH: CONCEPTUAL AND EXPERIMENTAL DESIGN

Robert W. Buddemeier
Kansas Geological Survey, University of Kansas
1930 Constant Ave., Lawrence KS 66047 USA

OCTOBER 1995

INTERNATIONAL COUNCIL OF SCIENTIFIC UNIONS
SCIENTIFIC COMMITTEE ON OCEANIC RESEARCH

Working Group 104 of the Scientific Committee on Oceanic Research has been established to review and report on the topic "Coral Reef responses to global change: the role of adaptation." This open-file report series has been established to provide citable references to the informal papers and documents produced by or contributed to the working group. As these papers may be preliminary and informal in nature those who wish to cite any of them are advised to contact the author(s).

—R.W. Buddemeier, Chair, WG-104

KANSAS GEOLOGICAL SURVEY
OPEN-FILE REPORTS

OFR 95-56 is available for purchase. For price and ordering information, contact the Survey's Publication Sales Office at (913) 864-3965 or e-mail, pubsales@kgs.ukans.edu..

Disclaimer

REFLECTIONS ON THE MEASUREMENT AND SIGNIFICANCE OF CARBON METABOLISM ON CORAL REEFS

A Working Paper Prepared for SCOR WG 104

KANSAS GEOLOGICAL SURVEY

OPEN-FILE REPORT 95-56a

S. V. Smith

Centro de Investigación Cientifica y de Educación Superior de Ensenada

(CICESE), Ensenada, Mexico

(Permanent address: Dept. Oceanography, U. Hawaii, Honolulu, HI 96822)

Introduction

There has been a recent surge of interest in the community metabolism of coral reefs, with emphasis on the role of coral reefs as net sources or sinks for atmospheric CO_2. This interest seems to have been particularly strong among the Japanese scientific community (e.g., Yamamuro et al., 1995; Kayanne et al., 1995; Kraines, 1995), apparently at least in part reflecting the possibility of using reefs and other natural systems as CO_2 scrubbers. As someone who has studied the community metabolism of coral reefs and other ecosystems for 25 years, I find the interest both heartening and disheartening. The heartening aspect is that it is good to see expansion of knowledge about a topic I have worked on for so long. The disheartening aspect is my sense that this recent surge of activity may not be building adequately on the intellectual base of many years of information.

As a specific example, the paper in Science by Kayanne et al. (1995) uses a very limited data set (data from 4 daytime and 2 nighttime periods) from a restricted portion of the reef flat of an apparently heavily stressed coral reef to observe that the portion of one reef which they are studying may be taking up atmospheric CO_2 (Buddemeier, submitted; Gattuso et al., submitted). Kayanne et al. rather casually dismiss the considerable weight of historical data as being of limited value and conclude that reefs (in general) may be a sink for atmospheric CO_2. That study contrasts with a more thoroughly documented study by Gattuso et al. (1993), who concluded that a particular reef flat in French Polynesia was a CO_2 source during the time of their study and provided local confirmation of theoretically based conclusions (Ware et al., 1992) that reefs in general might be slight sources of CO_2 release to the atmosphere. The contrast being made here is not between these differing views, which are a healthy part of scientific advance, but rather between the cautious conclusions drawn by Gattuso et al. (1993) and the generalizations drawn by Kayanne et al. (1995)--each apparently with rather comparable data sets. The highly visible article by Kayanne et al. (1995) has received remarkable media attention which I believe to be quite out of proportion with the importance of this paper.

Because I have been a contributor to the base of information and knowledge about coral reef community metabolism, and because Bob Buddemeier has seen letters I have written to various people attempting to put their papers, manuscripts, or ideas about reefs into a broader perspective, Bob suggested that it would be a useful product for SCOR WG 104 if I were to write a "mini-review" to put this state of knowledge into my perspective of coral reefs and the global carbon budget. In asking me to do this, Bob gave me full permission to reflect my biases in the analysis.

Because I am writing this "review" somewhat removed from ready access to a major library, the bias is stronger than I might like. As such, this has become more of an essay than a review. I have built heavily on my own work and that of my friend and colleague, Don Kinsey. More specifically, I have used much of the material in Kinsey's useful (and considerably less biased) 1985 review of coral reef metabolism. With a few specific exceptions, I have not worried about updating data in that review with more recent site-specific studies, because the studies I know of have not significantly altered the patterns Don reported. I have also relied on Bob Buddemeier to flesh out references I could not readily run down. With these limitations in mind, I hope that this somewhat incomplete essay will serve some purpose.

There are three intermingled points which I wish to address: My first point is to provide an overview of the history of metabolic measurements on coral reefs and related biotic communities. After some reflection, I have deliberately excluded the many physiological studies of corals, algae, and other reef organisms; instead, I have dealt only with measurements at the scale of biotic communities or entire ecosystems. My second point is to provide a summary of the metabolic results drawn from those studies. Finally, because it is clear that much of the present interest is largely spurred by a consideration of reefs as global sources or sinks of atmospheric CO_2, my third point is to put the reef data into a global perspective.

Historical Review

The study by Odum and Odum (1955) on the windward reef flat of Eniwetok (now spelled Enewetak) Atoll is often cited as the beginning of the study of reef community metabolism. The method they used has come to be called "flow respirometry," and most (although not all) subsequent measurements of reef community metabolism have relied on some modification of this technique. That study, conducted in 1954, was seminal in the development of the field of reef community metabolic ecology because of its insightful nature and comprehensive ecological perspective. However it should be recognized that the study was only one (albeit the most detailed) of several investigations into reef metabolism conducted in the Western Pacific during the decade following W.W.II. Sargent and Austin (1949) published estimates of reef flat community metabolic rates on Rongelap Atoll, undertaken in 1946. Work reported by Emery (1962) on Guam was carried out in 1952. General interest in the topic of metabolism reef communities far predates these studies, as evidenced by Japanese work in Palau in the 1930's (see Motoda, 1969 for a "modernization" of the early data). Thus, quantitative estimates of reef community metabolism extend back about 50 years, and understanding that reef metabolism alters the chemistry of waters on coral reefs can be traced back about 60 years.

Should results of the early studies be dismissed as scientific curiosities, of limited quantitative value? Some studies (old and new) have such limited data that they serve little quantitative use. However, as a generality, results from the older data are statistically reasonably in line with more recent estimates of reef metabolism. I am suspicious of results from some individual studies over the record of studies of reef community metabolism. However, there is no strong correlation between the age and the quality of the results. Because of advances in analytical techniques, computer modeling capabilities, and the insight of experience, it is certainly true that modern studies are more sophisticated than the earlier studies. However, as someone who continues to work on the metabolism of aquatic communities, I believe that the early literature on reef community metabolism is about as good as the more recent literature.

Most of the early work was based on changing O_2 concentrations in the water. We have been able to measure O_2 with reasonable precision for some time, and properly chosen systems impart strong, readily measurable concentration signals to the water. The basic quality of data from individual studies is largely dependent upon two considerations: the success with which the investigator chose systems with quantitatively large and unambiguous signals of metabolic changes, and the amount of data which the investigator took the time to collect.

In the late 1950's came the innovation of using CO_2-based estimates of community metabolism on reefs. Besides being more directly relevant to the question of carbon cycling than the O_2 data (which, nevertheless, will be argued to be of great importance in this discussion), the CO_2 measurements have two inherent advantages and one inherent disadvantage. The advantages are as follows: First, CO_2-based measurements can, if properly made, include estimates of both organic metabolism (photosynthesis and respiration) and inorganic metabolism (precipitation of $CaCO_3$); to derive both organic and inorganic metabolism estimates requires that two CO_2-related variables be measured. Second, because of the chemistry of CO_2 versus O_2 (low partial pressure of CO_2 in both water and air, compared to O_2 partial pressures; high concentration of total dissolved inorganic carbon [DIC] in seawater), metabolic signals measured with CO_2 are much less disrupted than O_2 signals by gas flux across the air-water interface.

The single disadvantage of CO_2-based measurements concerns the absolute precision of measurement in the two chemical systems (O_2 v CO_2). O_2 concentration can be measured with somewhat better than 1% relative precision; with the techniques which have been commonly used, DIC can be measured to about 0.3% relative precision. Because there is about 10 times as much DIC as O_2 dissolved in seawater (about 2000 v 200 μmol/liter), the **absolute** precision of the O_2 measurements is better than the precision of the CO_2 measurements. If we assume that we are dealing with organic metabolism involving a 1:1 ratio of O_2 production to CO_2 consumption, it becomes obvious that organic metabolism measured with O_2 flux has the potential to be somewhat more precise.

As far as I can reconstruct, the first quantitative use of CO_2 as a measure of metabolism on shallow marine environments is the work by Park et al. (1958); those authors used variation of pH as a record of metabolism. Because they measured only one CO_2-related variable, their data can only be used to approximate the rate of organic metabolism. Estimates of organic metabolism based on a single variable should be reasonably satisfactory as long as neither calcification nor sulfate reduction is greatly changing total alkalinity. Broecker and Takahashi (1966) measured net changes of DIC and CO_2 partial pressure (pCO_2) on the Bahama Banks (a calcifying, non-reef system) to calculate the integrated DIC fluxes. That system showed net changes in DIC and alkalinity, but little change in pCO_2; this point becomes significant in the later discussion.

About the time of the study by Broecker and Takahashi, Don Kinsey began work on the Australian Great Barrier Reef. Although publication of his measurements of O_2 go back to 1967 (Kinsey and Kinsey, 1967), his earliest publication of CO_2 measurements was in 1972 (data collected in 1967-68). I used a preprint of that publication as a methods reference when I conducted studies on Enewetak Atoll in 1971 (Smith, 1973; Smith and Marsh, 1973). Both Kinsey and I used high precision pH and alkalinity measurements to calculate components of the CO_2 system.

Over the next several years, Kinsey and I were the only two people I am aware of who were routinely using (with our colleagues) measurement of DIC changes as a record of reef community metabolism. In 1978 we published several papers on the methodology of reef metabolic measurements in the handbook by edited by Stoddart and Johannes (Kinsey, 1978; Smith and Kinsey, 1978; Marsh and Smith, 1978; Smith, 1978a).

Our major period of collaboration occurred when Don Kinsey came to the University of Hawaii in 1976 to earn his Ph.D. "under" me (Kinsey, 1979) (I was as much student as mentor). An early product of that collaboration was the conclusion

(Smith and Kinsey, 1976) that reefs show consistent patterns of modal community calcification rates. Kinsey and I have each further developed those ideas into estimates of modal rates of both organic and inorganic metabolism (Kinsey, 1979, 1983, 1985; Smith, 1983, 1988). In summarizing estimates of gross organic metabolism, we and other authors have tended to co-mingle data collected by both O_2 and CO_2 based methodology. For purposes here, it is convenient to convert those estimates to molar fluxes of carbon. I round off the values and express them as rates per square meter, on an annual basis.

The Kinsey and Smith conclusions about reef metabolism are based on about 40 sites described in the scientific literature. Some of these sites represent multiple studies or multiple sites in the same general geographic location; thus, the actual number of geographic locations is somewhat smaller than this. The Kinsey/Smith conclusions can be summarized as follows: Active reef flat communities (the systems for which the most data are available) both produce and consume about 200 moles of organic C m^{-2} yr^{-1}; these systems precipitate about 40 moles C m^{-2} yr^{-1} as $CaCO_3$; Most of a coral reef clearly does not consist of the high-metabolism reef flats. Whole reef systems (flats, slopes, lagoons, rubble areas, etc.) apparently produce and consume about 100 moles organic C m^{-2} yr^{-1} and precipitate around 10 moles C m^{-2} yr^{-1} as $CaCO_3$. Limited evidence suggests that the upper limit for organic production is about 700 moles C m^{-2} yr^{-1}, and that the upper limit for calcification of portions of reefs is around 120 moles C m^{-2} yr^{-1} (Figure 1). Individually, of course, these rates are largely (and appropriately) reported as hourly and daily rates, reflecting the short timespans involved in the measurement. I find it convenient to present the averages here in terms of annual rates, fully recognizing the characteristics of the individual data.

The wide range of published values suggests that it is impossible to use any one study as a benchmark of average reef performance. Some reefs appear to be net organic carbon producers; some appear to be consumers. Systems receiving high organic loading are likely to be net heterotrophic; those receiving high inorganic loading are likely to be net autotrophic. It is probably also true that stressed reefs tend to lose the calcifying portion of the community. Few studies, other than some of those by Kinsey, are of sufficient duration to lend confidence that the difference between primary production (P) and respiration (R) represents anything more than the statistical artifact of short term data sets or specific local site selection. At the same time, it is clear from the collection of data that modal rates of P and R do emerge (Figure 1). Of particular importance is the observation that the mean P and the mean R for these sites cannot be distinguished from one another statistically. This point is obvious from both histograms (Figure 1) and a scatter diagram (Figure 2). The rates recently reported by workers at two sites in the Ryukyus (Kayanne et al., 1995; Kraines, 1995) both differ from one another substantially and fall within the general scatter of data in the literature, emphasizing the perils of generalizing excessively from a single study.

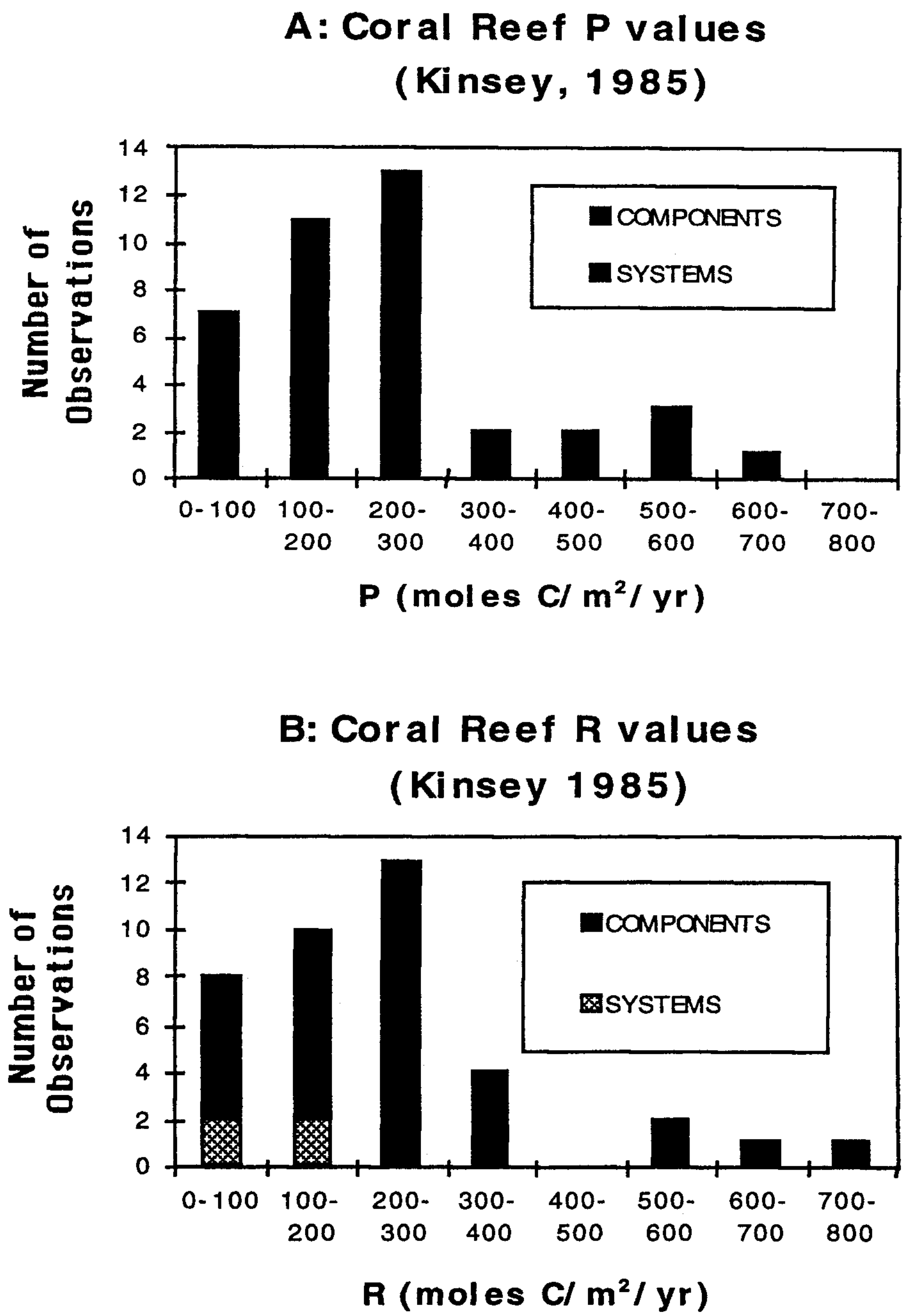

Figure 1. Histograms illustrating gross primary production and respiration rate in various coral reef communities (data from Kinsey, 1985). Note the similarity between the two histograms, both in distribution and modal distributions of the two metabolic rates.

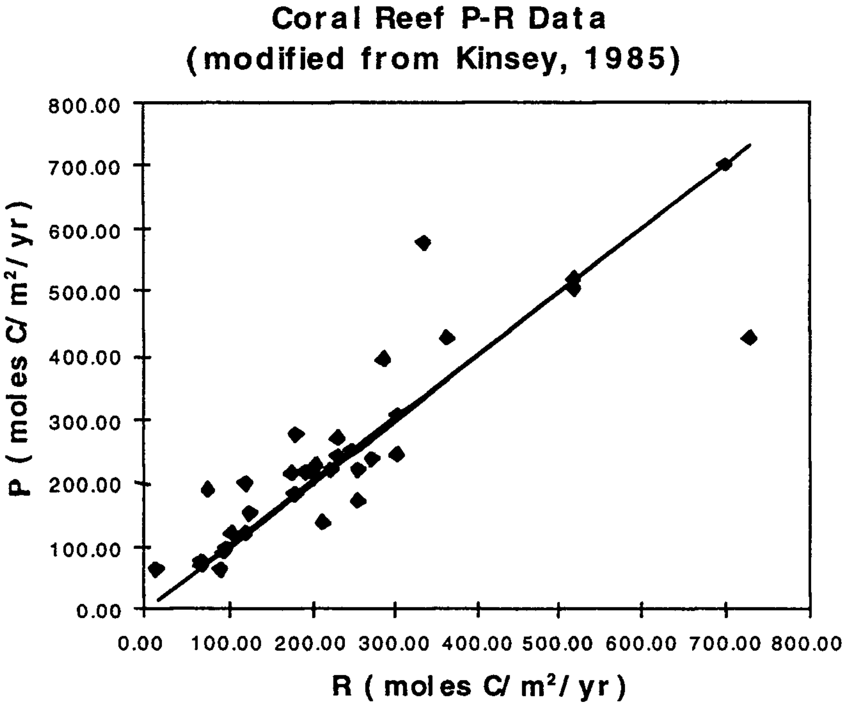

Figure 2. Scatter diagram of respiration versus gross primary production for various coral reef communities (data from Kinsey, 1985); more recent data do not differ significantly. The line on the diagram is the 1:1 line; note that the data are well described by that line.

Kinsey's (1985) review includes studies of numerous sites in the Australian Great Barrier Reef; various locations in the Hawaiian Islands; atolls throughout the Pacific; Guam; various sites in the Indian Ocean; and the Caribbean Sea. Figure 3 is a compilation of geographic locations from which I know reef metabolism data to be available in published, thesis, or manuscript form. The recent Japanese work is a welcome addition, because of the addition of data from reefs in East Asia. Perhaps the major gap in geographic coverage concerns the reefs of Southeast Asia. This gap is troubling in terms of generalizing about global reef metabolic performance, because the area is apparently second only to the Great Barrier Reef region in terms of reef area (Smith, 1978b). The area is also subject to high human population pressure (Wilkinson et al., 1994) and intense loading of riverborne terrigenous materials (Milliman and Syvitski, 1992), so there is reason to suppose that reefs of this region might function differently than reefs elsewhere. One might hypothesize, for example, that the metabolism of these reefs would be strongly influenced by loading with both inorganic nutrients and organic material.

As far as I am aware, Kinsey's PhD dissertation, which included data from several sites on Heron Island, One Tree Island, and Lizard Island, Australia; and Kaneohe Bay and Johnston Island, Hawaii, remains the most comprehensive study of coral reef metabolism. Don eventually returned to the Australia Institute of Marine Science and collected additional data from several other reefs of the Great Barrier Reef (see Kinsey 1988, 1991; Kinsey and Hopley, 1991). Other of Kinsey's papers are listed in his 1985 review.

One other small, but important, paper by Kinsey (1978) merits attention. In 1976 Brewer and Goldman had pointed out that alkalinity is altered not only by calcification, but also by uptake or release of nitrate and ammonium. While that paper was specifically dealing with plankton metabolism, Don and I were concerned that readers might conclude that alkalinity flux is not valid to estimate reef calcification. It is also well established that sulfate reduction alters alkalinity (Berner et al., 1970; Gaines and Pilson, 1972). Don therefore went through the calculations to point out the rather small degree to which changing nitrogen and sulfate concentrations could be expected to perturb estimates of reef calcification. Sulfate is particularly interesting in this regard. High rates of sulfate reduction have been reported on coral reefs (e.g., Skyring and Chambers, 1976; Walter et al., 1993). However because there are only low concentrations of Fe or other reduced metals in most coral reef sediments, most of the sulfide released is apparently eventually re-oxidized back to sulfate without raising the alkalinity of the reef waters. Therefore the net effect of sulfate reduction on the alkalinity of open water in reef systems appears to be small. More recent work at the oganismal level has further confirmed the validity of the alkalinity approach (Chisholm and Gattuso, 1991).

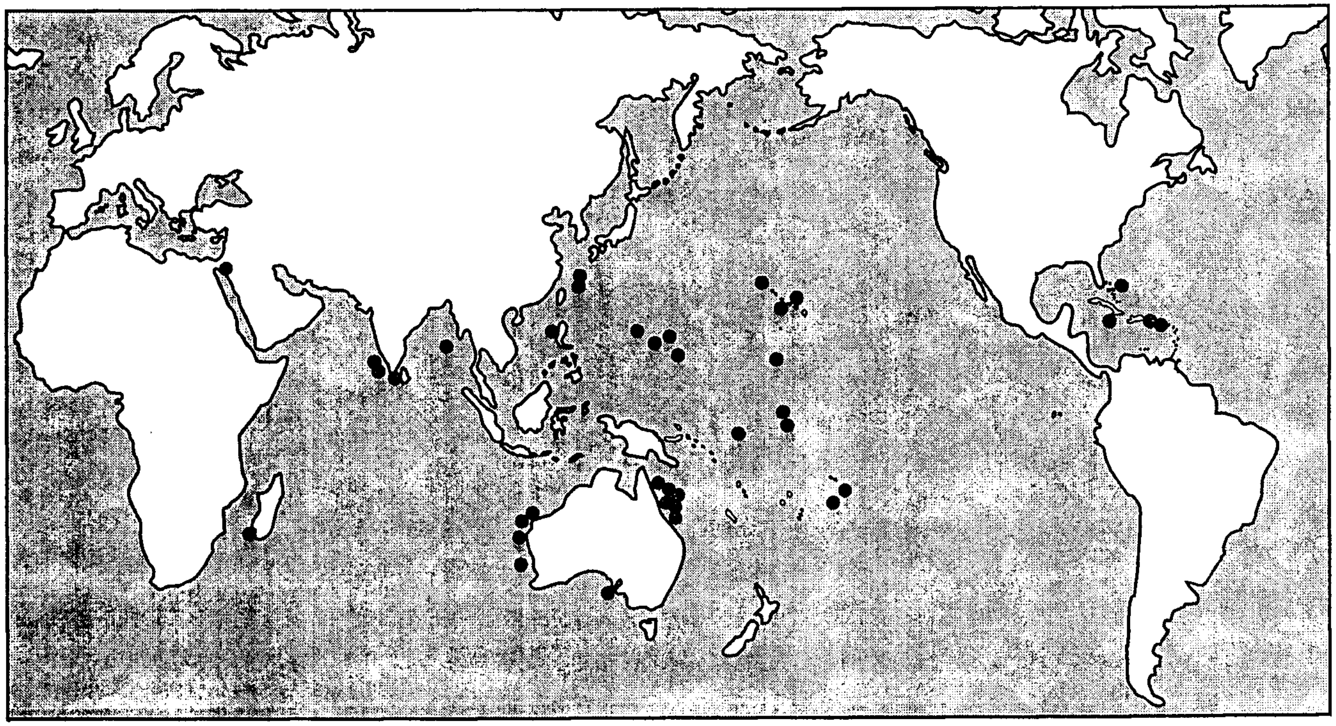

Figure 3. Map showing the distribution of coral reef and related metabolic studies. The solid circles indicate coral reef sites for which reef metabolic data are available; the open circles are site of non-reef metabolic studies. Data shown on this map include citations by Kinsey (1985), as well as other studies.

Aside from the collaboration mentioned above, my own work on reef metabolism largely went in a somewhat different direction from that of Don Kinsey. Although I have made limited flow and standing water respirometry measurements at a variety of sites, I published only one site-specific paper other than my Enewetak work dealing with flow respirometry. That publication dealt with the high-latitude reefs of the Houtman Abrolhos Islands, Western Australia (Smith, 1981). My activities shifted for the most part to larger scale measurements in semi-isolated water bodies (both lagoonal reefs and other semi-enclosed systems), using water, salt and DIC/nutrient budgets in order to estimate the integral performance of these systems.

My initial opportunity for such study was serendipity, a study of the lagoonal reefs of Fanning Atoll (Smith and Pesret, 1974). Upon reflection, I recognized that instantaneous metabolism studies (mostly via flow respirometry) cannot usually provide a robust estimate of net (P-R) or of P/R ratios different from unity. Pretty obviously, many reef communities show P/R ratios near unity. There is some error in P and R determined individually. Although DIC-based metabolic estimates are less subject to errors from gas flux than are O_2-based estimates, there nevertheless is some flux of CO_2 gas across the air-sea interface. This flux is very dependent on wind and turbulence regimes which can only be approximated with models of gas flux across the air-sea interface, usually with rather poor data on the local wind field anyway.

An interesting sidelight of the Fanning studies was the suggestion that cabonate mineral saturation state may influence the rate of $CaCO_3$ precipitation by calcifying ecosystems. Various authors have subsequently discussed this possibility further (e.g., Smith and Buddemeier, 1992; Buddemeier, 1994; Buddemeier and Fautin, in press a,b; Holligan et al., 1993), although there remains a paucity of experimental data.

Moreover, inspection and common sense (as well as papers going back to Smith and Marsh (1973), Kinsey (1979), and various other papers summarized by Kinsey (1985)), make it obvious that portions of reefs must be autotrophic while other portions are heterotrophic. There is also time variability, which is also not well accounted for by short-term studies (which tend to be made during good weather).

It was well established by the late 1970's that communities within coral reefs exhibited high and roughly predictable primary production; there did not seem to be a lot gained by repeating that observation. I reasoned that flow respirometry was not ordinarily a quantitatively reliable method for estimating net community metabolism near 0 in individual, more or less balanced communities within a coral reef, and provided a very poor approach to evaluating the net metabolic effects of interlinked communities within entire reef systems. It seemed obvious to me that the role of reefs in terms of material exchanges with the adjacent ocean, the sediments, and the atmosphere was an issue of net, not gross, metabolism, and was best evaluated for the entire reef system taken as a whole.

Some sort of direct integrated record was required in order to estimate the deviation of net community metabolism from 0.

The water, salt, and DIC budget approach initially seemed an ideal method to estimate net reef performance. Enclosed lagoonal reef systems integrate the metabolic record of changing water composition for periods ranging from many days to a few months. The obvious problem emerged that, while calcification could be so-estimated from changes in alkalinity, the remainder of the DIC flux was attributable to some unknown partitioning between net organic metabolism and net gas flux. It occurred to me during work at Canton Atoll (Smith and Jokiel, 1978) that the net uptake of dissolved inorganic phosphorus (DIP) should record organic metabolism. DIP, like alkalinity, has no gas exchange to complicate the record. Dissolved inorganic nitrogen (DIN) cannot be used in a similar fashion, because of the well known fact that reefs fix and export nitrogen (e.g., Webb et al., 1975; Wiebe et al., 1975).

The problem, of course, was figuring on how to scale between DIP uptake and organic C uptake. The initial guess was to use the Redfield C:P ratio (106:1) (Pilson and Betzer, 1972; Smith and Jokiel, 1978). Subsequent studies (Atkinson and Smith, 1983) demonstrated that benthic plants are better characterized by a ratio near 550:1. It now appears, from both sediment composition and independent considerations of CO_2 gas flux, that net organic C uptake in various reef systems is around 300 times the net DIP uptake.

Various budgets based on the combination of DIC and nutrient data have subsequently been made for both reef (Smith et al., 1984; Smith, 1984) and non-reef (Smith and Atkinson, 1983; Smith and Veeh, 1989) systems dominated by carbonate sediments. My colleagues and I summarized the reef studies by concluding (Smith, 1988; Crossland et al., 1991) that reef system net production is about 4 mol m^{-2} yr^{-1}. Using this net production estimate with the gross production and respiration rates cited above for reef systems (~ 100 mol m^{-2} yr^{-1}) leads to the suggestion that the P/R ratio of reefs is about 1.04.

This brings me back to my initial concerns about flow respirometry: It is impossible in almost any reef to use flow respirometry in order to distinguish P and R within 4% of one another. While I believe that some individual studies have described P and R differing by substantially more than this amount, many reefs clearly exhibit P near R. Those authors who have concluded that P and R are about equal on the reef systems they have studied are, in my view, exhibiting a careful and realistic appraisal of what can be learned from their data: In most flow respirometry studies, estimates of gross metabolic rates are probably reasonable; estimates of net metabolism in most cases are probably not reliably distinguished from 0.

The quantitative values derived for P-R from the DIP budgetary approach can be faulted because of the large and uncertain scaling factor for conversion of DIP flux to and organic C metabolism, and because of the possibility that some of the DIP uptake is abiotic (sorption) or otherwise not directly related to net metabolism. At the same time, dismissal of the nutrient budget approach because reefs fix nitrogen is unwarranted and reflects a basic misunderstanding of what has been done with a DIP budget. It is exactly because reefs do fix nitrogen that phosphorus, but not nitrogen, is a reasonable proxy to establish the net flux from nutrient data. The further point is that phosphorus, but not nitrogen, tends to be exhausted in reef systems with long water residence times. At this point, however, I am willing to leave this debate concerning DIP-based estimates of reef net production, and to turn to another approach to the CO_2 system of coral reefs and other shallow-water calcifying communities. That topic is a consideration of the CO_2 partial pressure of water in these systems.

Beginning with my initial Enewetak work, I have published CO_2 partial pressure (pCO_2) calculations for the systems I have studied. Such pCO_2 calculations based on pH and alkalinity should be precise to somewhat better than 10 μatm, although inaccuracies in the absolute pH measurements are likely to render the accuracy somewhat poorer than that estimate. Precision, not accuracy, is of primary importance here, because one is generally considering changes in pCO_2 between the oceanic feed water and the water in these systems. The general pattern which emerges is that the pCO_2 shift as water ages in these systems tends to be remarkably small. Sometimes there is a decrease during the aging process; sometimes there is an increase; sometimes the change is effectively 0. The safe conclusion to draw from these observations would seem to be that, on average, the net effect of reef metabolism on aqueous pCO_2 tends to be small. This is an interesting conclusion, and one which we explore below.

Following on the paper by Ware et al. (1992), we can describe $CaCO_3$ precipitation (on reefs or from any other aqueous medium) by the following equation for HCO_3^- and Ca^{2+} uptake out of water and into the solid phase:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O.$$

Because of the carbonate buffer capacity of seawater, some of the "CO_2 release" implied by the above reaction is actually retained in the seawater as an elevated concentration of dissolved free CO_2. Once the CO_2 partial pressure of the system has returned to equilibrium with the overlying gas phase after $CaCO_3$ precipitation, the real ratio of CO_2 atmospheric release to $CaCO_3$ precipitation in order to maintain pCO_2 constant under present conditions of CO_2 partial pressure is more like 0.6 (see Frankignoulle et al., 1994, for a discussion of the change in this ratio with changing pCO_2). The important point to note is that, for every mole of $CaCO_3$ precipitated out of seawater (using seawater bicarbonate, not atmospheric CO_2), about 0.6 additional moles of seawater bicarbonate are converted to CO_2 which eventually may escape to the atmosphere. Reef calcification delivers CO_2 to the atmosphere, rather than taking it up. It should be emphasized that CO_2 release with calcification is not peculiar to reefs; for example, exactly this same phenomenon has been documented for coccolithophore blooms (Holligan et al. 1993). While some authors have had some initial confusion on this point, this fundamental characteristic of carbonate chemistry now seems to be reasonably well accepted.

Organic metabolism can also be represented by a simple equation:

$$CO_2 + H_2O \leftrightarrow CH_2O + O_2 .$$

Running the reaction from left to right describes primary production; from right to left represents respiration. Organic carbon production takes up CO_2 from the water, causing gas influx from the atmosphere; respiration reverses that flux. Total alkalinity is not affected by this reaction (ignoring nutrient effects; Smith and Key, 1975), so the net CO_2 gas flux induced by this reaction should (with time) exactly compensate the net DIC removal from (or addition to) seawater due to metabolism.

Calcification and net P-R by reefs thus tend to push the pCO_2 in opposite directions. The implication of pCO_2 neutrality as a "common condition" for reefs is that organic production on modern reefs may tend to take up the free CO_2 generated by calcification, before that CO_2 escapes to the atmosphere. That is, organic metabolism may take up about 60% as much DIC into organic C (either particulate or dissolved; POC, DOC) as does $CaCO_3$ precipitation. As a general concept, this idea has been explored in some detail for a non-reef calcifying system (Spencer Gulf; Smith and Veeh, 1989). Interestingly, it is also implicit in the study by Broecker and Takahashi (1966) of the Bahamas Banks. Both of these systems, with water residence times approaching a year, show little net change of CO_2 partial pressure as water ages in these systems, even though there is no obvious reason why the two processes of organic and inorganic carbon metabolism should so nearly cancel one another out. Gattuso et al. (in press) explore this concept further.

Summary of Metabolic Studies

We can use the observations of the last few paragraphs and the net calcification rate estimate for reef systems of 10 mol m^{-2} yr^{-1} to suggest that net production by coral reef systems may tend to be around 6 mol m^{-2} yr^{-1}. These conditions are suggested to describe "average reefs," not individual reefs. Considering the fact that the DIP-derived estimate of net production (4 mol m^{-2} yr^{-1}) and this calcification-derived estimate are largely independent of one another, they are remarkably close. If more data tend to suggest that the pCO_2 of reef systems tends to diminish somewhat, then the conclusion will be that net production is somewhat higher than 60% of net calcification; if, on average, pCO_2 goes down, then net production will be somewhat lower than 60%.

Buddemeier (pers. comm. and submitted) has recently re-raised a point which has been previously made (e.g., by Broecker and Takahashi, 1966) as another possible approach to estimating net production. If the calcification rate of a system is known, then why isn't the ratio of organic to inorganic carbon in reef sediments, multiplied by the calcification rate, a reasonable estimate of net production? The organic to inorganic C ratio in reefs is typically something less than 0.1, suggesting that P-R might be less than 1 mol m^{-2} yr^{-1}. A problem of unknown magnitude in such an estimate is the differential transport of reef systems. It is well established from DOC gradients that DOC is transported away from reefs, and it is likely that POC not intimately associated with inorganic matter is similarly removed differentially. The magnitude of these fluxes is not well established, but it seems safe to conclude that P-R must be something greater than 1 mol m^{-2} yr^{-1}.

From the various estimates offered above, it seems likely that coral reefs are, on average, slight net producers of organic matter; somewhere between about 1 and 10 mol m^{-2} yr^{-1} (i.e., a P/R ratio of 1.01 to 1.1) seems almost certain to bracket the reasonable range of net production. Despite recent statements to the contrary, Ware et al. (1992) did not "assume that reefs are a source of CO_2." Because a calcification rate of around 10 mol m^{-2} yr^{-1} should lead to CO_2 gas flux to the atmosphere of about 6 mol m^{-2} yr^{-1}, CO_2 uptake from the atmosphere by organic metabolism and CO_2 release to the atmosphere by inorganic carbon metabolism balance one another to within at most ± 4-5 mol m^{-2} yr^{-1}. While individual reefs (or portions of reefs) will inevitably deviate from this pattern, at least over short periods of time, it seems foolhardy to generalize from any single study to the metabolic performance of coral reef systems as a whole.

Global Considerations

The next point of this essay is to put these data into some sort of global context. I estimated some years ago that coral reefs occupy an area of some 0.6×10^{12} m^2 in the global ocean (Smith, 1978b). It is my understanding that recent studies by ICLARM do not greatly alter this estimate (John McManus, personal communication), but let us use 10^{12} m^2 as perhaps an upper limit on the area of coral reefs and non-reef communities dominated by organisms commonly found on reefs.

From the information summarized above, $CaCO_3$ precipitation by coral reefs, extrapolated over such an area, might total as much as 10^{13} moles/yr. this would lead to up to about 6×10^{12} moles/yr of gas evasion. Organic carbon production and consumption by these communities might account for up to 10^{14} moles per year of CO_2 gas invasion and evasion, respectively; but we can guess that the net flux associated with organic metabolism would be invasion approximately offsetting the CO_2 release associated with calcification. The prudent conclusion about reef-mediated CO_2 exchange with the atmosphere would seem to be that reefs pump a maximum of 10^{14} moles per year of CO_2 back and forth across the air-sea interface, but that the net transfer is likely to be something less than ±5 x 10^{12} moles/yr. My guess is that the actual transfer is substantially less than this.

For comparison, marine primary production and consumption each pump about 4-10 x 10^{15} moles of CO_2 back and forth between the ocean and atmosphere (again, with little net flux, although I believe there is a slight net CO_2 release to the atmosphere) (Schlesinger, 1991; Smith and Hollibaugh, 1993). The gross metabolic performance of coral reefs is therefore about a 1-2 % term in the marine biotic gross CO_2 pump. Other marine communities, including other shallow water communities, are more significant in terms of gross flux and seem more likely to contribute significantly to net flux.

I conclude this essay by observing (again) that we know a great deal about the dynamics of reef metabolism. Our knowledge is founded on the data accumulated over about 50 years. We gain nothing, and lose a great deal, by not using that accumulated data effectively. I further suggest that a more interesting exercise than trying to make reefs quantitatively more important in the global carbon cycle than is supported by objective evidence would be to speculate and experiment on why the inorganic and organic portions of this pump are apparently in such close balance with one another on coral reefs.

REFERENCES

Atkinson, M., and S. V. Smith. 1983. C:N:P ratios of benthic marine plants. Limnol. Oceanogr. **28**: 568-574.

Berner, R. A., M. R. Scott., and C. Thomlinson. 1970. Carbonate alkalinity in the pore waters of anoxic marine sediments. Limnol. Oceanogr. **15**: 544-549.

Brewer, P. G., and J. C. Goldman. 1976. Alkalinity changes generated by phytoplankton growth. Limnol. Oceanogr. **15**: 544-549.

Broecker, W. S., and T. Takahashi. 1966. Calcium carbonate precipitation on the Bahama Banks. Jour. Geophys. Res. **71**: 1575-1602.

Buddemeier, R. W. 1994. Symbiosis, calcification, and environmental interations. pp. 119-131 In Doumenge, F. (ed.) Past and Present Biomineralization Processes. Bulletin de l'Institut océanographique, Monaco no. spécial 13.

Buddemeier, R. W. Submitted. Technical Comment, Science.

Buddemeier, R. W. and D. G. Fautin. In press, a. Global CO2 and evolution among the Scleractinia. In Allemand, D. and J.-P. Cuif (eds) Biomineralization 93: Proceedings of the Sevent International Biomineralization Symposium. Bulletin de l'Institut océanographique, Monaco no. spécial 14.

Buddemeier, R. W. and D. G. Fautin. In press, b. Saturation state and the evolution and biogeography of symbiotic calcification. In Allemand, D. and J.-P. Cuif (eds) Biomineralization 93: Proceedings of the Sevent International Biomineralization Symposium. Bulletin de l'Institut océanographique, Monaco no. spécial 14.

Chisholm, J. R. M., and J.-P. Gattuso. 1991. Validation of the alkalinity anomaly technique for investigating calcification and photosynthesis in coral reef communities. Limnol. Oceanogr. **39**:458-462.

Crossland, C. J., B. G. Hatcher, and S. V. Smith. 1991. Role of coral reefs in global ocean production. Coral Reefs **10**: 55-64.

Emery, K. O. 1962. Marine Geology of Guam. U. S. Geol. Surv. Prof. Pap. 403-B, 76 pp.

Frankignoulle, M., C. Canon, and J.-P. Gatusso. 1994. Marine calcification as a source of carbon dioxide: positive feedback of increasing atmospheric CO_2. Limnol. Oceanogr. **39:** 458-462.

Gaines, A., Jr., and M. E. Q. Pilson 1972. Anoxic water in the Pettaquamscutt River. Limnol. Oceanogr. **17**: 42-49.

Gattuso, J.-P., M. Frankignoulle, S. V. Smith, and R. Wollast. Submitted. Technical Comment, Science.

Gattuso, J.-P., M. Pichon, B. Delesalle, and M. Frankignoulle. 1993. Community metabolism and air-sea CO_2 fluxes in a coral reef ecosystem (Moorea, French Polynesia). Mar. Ecol.--Prog. Ser. **96**: 259-267.

Gattuso, J.-P., M. Pichon, and M. Frankignoulle. In press. Biological control of air-sea CO_2 fluxes: effect of photosynthetic and calcifying organisms and ecosystems. Mar. Ecol. Prog. Ser.

Holligan, P. M., et al. 1993. A biogeochemical study of the coccolithophore, *Emiliana huxleyi*, in the North Atlantic. Global Biogeochem. Cycles **7**: 879-900.

Kayanne, H., A. Suzuki, and H. Saito. 1995. Diurnal changes in the partial pressure of carbon dioxide in coral reef water. Science **269**: 214-216.

Kinsey, D. W. 1972. Preliminary observations on community metabolism and primary productivity of the pseudo-atoll reef at One Tree Island, Great Barrier Reef. pp. 13-32 In: Proc. of the Symp. on Corals and Coral Reefs, Cochin.

Kinsey, D. W. 1978. Productivity and calcification estimates using slack-water periods and field enclosures. UNESCO Monogr. Oceanogr. Meth. **5**: 439-468.

Kinsey, D. W. 1979. Carbon turnover and accumulation by coral reefs. PhD dissertation, U. Hawaii, 248 pp.

Kinsey, D. W. 1983. Standards of performance in coral reef primary production and carbon turnover. pp. 209-218 In: D. J. Barnes (ed.) Perspectives on Coral Reefs. Australian Institute of Marine Science, Townsville.

Kinsey, D. W. 1985. Metabolism, calcification and carbon production. 1. Systems level studies. Proc. 5th Internat. Coral Reef Congr., Tahiti. **4**: 505-526.

Kinsey, D. W. 1988. Coral reef system response to some natural and anthropogenic stresses. Galaxea **7**: 113-128.

Kinsey, D. W. 1991. The coral reef: an owner-built, high-density, fully-serviced, self-sufficient housing estate in the desert--or is it? Symbiosis **10**: 1-22.

Kinsey, D. W., and D. Hopley. 1991. The significance of coral reefs as global carbon sinks--response to Greenhouse. Palaeogeog., Palaeoclim., Palaeoecol. **89**: 363-377.

Kinsey, D. W., and B. E. Kinsey. 1967. Diurnal changes in oxygen content of the water over the coral reef platform at Heron Island. Aust. Jour. Mar. Freshwat. Res. **18**: 23-34.

Kraines, S. 1995. Construction of a model of mass flux in a coral reef. M.S. Thesis, U. Tokyo, 86 pp.

Marsh, J. A., Jr., and S. V. Smith. 1978. Productivity measurements of coral reefs in flowing water. UNESCO Monogr. Oceanogr. Meth. **5**: 361-378.

Milliman, J. D., and J. P. M. Syvitski. 1992. Geomorphic/tectonic control on sediment discharge to the ocean: the importance of small mountainous rivers. J. Geol. **100**: 525-544.

Motoda, S. 1969. An assessment of primary productivity of a coral reef lagoon in Palau, Western Caroline Islands, based on the data obtained during 1935-37. Records Oceanogr. Works in Japan **10**: 65-74.

Odum, H. T., and E. P. Odum. 1955. Trophic structure and productivity of a windward coral reef community on Eniwetok Atoll. Ecol. Monogr. **25**: 291-320.

Park, P. K., D. W. Hood., and H. T. Odum. 1958. Diurnal pH variation in Texas Bays, and its contribution to primary production estimation. Publ. Inst. Mar. Sci. Texas **5**: 47-64.

Pilson, M. E., and S. B. Betzer 1972. Phosphorus flux across a coral reef. Ecology **54**: 581-588.

Sargent, M. C., and T. S. Austin. 1949. Organic productivity of an atoll. Trans. Amer. Geophys. Union **30**: 245-249.

Schlesinger, W. H. 1991. Biogeochemistry: An Analysis of Global Change. Academic, San Diego, 443 pp.

Skyring, G. W., and L. A. Chambers. 1976. Biological sulphate reduction in carbonate sediments of a coral reef. Aust. Jour. Mar. Freshwater Res. **27**: 595-602.

Smith, S. V. 1973. Carbon dioxide dynamics: record of organic carbon production, respiration, and calcification in the Eniwetok reef flat community. Limnol. Oceanogr. **18**: 106-120.

Smith, S. V. 1978a. Alkalinity depletion to estimate the calcification of coral reefs in flowing water. UNESCO Monogr. Oceanogr. Meth. **5**: 397-404.

Smith, S. V. 1978b. Coral reef area and the contributions of reefs to processes and resources of the world's oceans. Nature **273**: 225-226.

Smith, S. V. 1981. The Houtman Abrolhos Islands: carbon metabolism of coral reefs at high latitude. Limnol. Oceanogr. **26**: 612-621.

Smith, S. V. 1983. Coral reef calcification. pp. 240-247 In: D. J. Barnes (ed.) Perspectives on Coral Reefs. Australian Institute of Marine Science, Townsville.

Smith, S. V. 1984. Phosphorus versus nitrogen limitation in the marine environment. Limnol. Oceanogr. **29**: 1149-1160.

Smith, S. V. 1988. Mass balance in coral reef-dominated areas. pp. 209-226 In: B.-O. Jansson (ed.) Coastal-Offshore Ecosystem Interactions. Springer, Berlin.

Smith, S. V., and M. J. Atkinson. 1983. Mass balance of carbon an phosphorus in Shark Bay, Western Australia. Limnol. Oceanogr. **28**: 625-639.

Smith, S. V., and R. W. Buddemeier. 1992. Global Change and coral reef ecosystems. Annu. Rev. Ecol. Syst. **23**:89-118.

Smith, S. V., S. Chandra, L. Kwitko, R. C. Schneider, J. Schoonmaker, J. Seeto, T. Tebano, and G. W. Tribble. 1984. Chemical stoichiometry of lagoonal metabolism. University of Hawaii Sea Grant Report CR-84-02, 30 pp.

Smith, S. V., and J. T. Hollibaugh. 1993. Coastal metabolism and the oceanic organic carbon balance. Reviews of Geophysics. **31:** 75-89.

Smith, S. V., and P. L. Jokiel. 1978. Water composition and biogeochemical gradients in the Canton Atoll lagoon. Atoll Res. Bull. **221**: 15-53.

Smith, S. V., and G. S. Key. 1975. Carbon dioxide and metabolism in the marine environment. Limnol. Oceanogr. **20**: 493-495.

Smith, S. V., and D. W. Kinsey. 1976. Calcium carbonate production, coral reef growth, and sea level rise. Science **194**: 937-939.

Smith, S. V., and D. W. Kinsey. 1978. Calcification and organic carbon metabolism indicated by carbon dioxide. UNESCO Monogr. Oceanogr. Meth. **5**: 469-484.

Smith, S. V., and J. A. Marsh. 1973. Organic carbon production on the windward reef flat of Eniwetok Atoll. Limnol. Oceanogr. **18**: 953-961.

Smith, S. V. and F. Pesret. 1974. Processes of carbon dioxide flux in the Fanning Island lagoon. Pac. Sci. **28**: 225-245.

Smith, S. V., and H. H. Veeh. 1989. Mass balance of biogeochemically active materials (C, N, P) in a hypersaline gulf. Est. Coast. Shelf Sci. **29**: 195-215.

Walter, L. M., S. A. Bischof, W. P. Patterson, and T. W. Lyons. 1993. Dissolution and crystallization in modern shelf carbonates: evidence from pore water and solid phase chemistry. Phil. Trans. R. Soc. Lond. A **344**: 27-36.

Ware, J. R., S. V. Smith, and M. L. Reaka-Kudla. 1992. Coral reefs: sources or sinks of atmospheric CO_2 ? Coral Reefs **127**: 127-130.

Webb, K. L., W. D. Dupaul, W. Wiebe, W. Sottile, and R. E. Johannes 1975. Enewetak (Eniwetok) Atoll: aspects of the nitrogen cycle on a coral reef. Limnol. Oceanogr. **20**: 198-210.

Wiebe, W. J., R. E. Johannes, and K. L. Webb 1975. Nitrogen fixation in coral reef community. Science **188**: 257-259.

Wilkinson, C. R., L. M. Chou, E. Gomez, A. R. Ridzwan, S. Soekarno, and S. Sudara. 1994. Status of coral reefs in Southeast Asia: threats and responses. pp. 311-317 In Ginsburg, R. N. (compiler), Proceedings of the Colloquium on Global Aspects of Coral Reefs: Health, Hazards, and History, 1993. University of Miami.

Yamamuro, M., H. Kayanne, and M. Minagawa. 1995. Carbon and nitrogen isotopes of primary producers in coral reef ecosystems. Limnol. Oceanogr. **40**: 617-621.

CORAL REEF CARBON CYCLE RESEARCH: CONCEPTUAL AND EXPERIMENTAL DESIGN

KANSAS GEOLOGICAL SURVEY

OPEN-FILE REPORT 95-56b

Robert W. Buddemeier

Kansas Geological Survey, University of Kansas

1930 Constant Ave., Lawrence KS 66047 USA

Preface:

This paper is an expanded version of an abstract submitted to the International Workshop on Carbon Cycling and Coral Reef Metabolism, Miyakojima, Japan, October 16-25, 1995; because it addresses the relationships among coral reef community structure, function, and the carbon cycle, it is also being circulated as a working paper of SCOR Working Group-104. Although it is a stand-alone document, it is best read in conjunction with the working paper of Smith (1995), which addresses the history and significance of reef community metabolism measurements in much more detail than the summary treatment presented here. As a working paper it is intended to be conceptually complete, but does not necessarily contain the level of citation and literature review appropriate to a formal publication.

Introduction:

In spite of the likelihood that carbon fluxes due to coral reef metabolism can only be a minor component of the global carbon cycle, there is persistent interest in exploring the question of whether coral reefs represent sources or sinks for atmospheric carbon dioxide. This paper examines the methods and requirements for making such a determination.

Two definitions are critical, and often ignored in the design and interpretation of individual experiments: what is a source or sink, and what is a coral reef.

Sources, Sinks, Inventories, and Fluxes:

A source of atmospheric CO_2 is any process (or reservoir) that produces a transfer of CO_2 into the atmosphere from another compartment of the exchangable carbon cycle; the term sink is normally used to refer to the material where carbon resides after it is extracted from the atmosphere (e.g., terrestrial biomass, soil organic matter, etc.). Any flux of CO_2 into or out of the atmosphere can be called a source or sink, but a critical component of the definition is the time scale. The mixing time of the atmosphere is a few years, so definition of a source or sink is problematic unless it results in a net change over that time scale. From a climatic standpoint, material removed from the atmosphere must be sequestered for a minimum of many decades (more realistically, centuries to millennia) before it can be considered a sink. Because the atmosphere is the reference reservoir and because its carbon dioxide dynamics are relatively well known, the problem of source definition is less critical.

Figure 1 presents a simplified schematic of some of the major pathways and reservoirs of carbon related to reef systems. Net community production (the difference between photosynthesis (P) and respiration (R), also termed "excess" production: E = P - R) is a potential sink for atmospheric CO2, just as net calcification (precipitation - dissolution) is a potential source. The simplified relevant reactions are $CO_2 + H_20 \longrightarrow H_2O + O_2$ (P, or -R), and $2HCO_3^- + Ca^{++} \longrightarrow CaCO_3 + CO_2$. Neither sink nor source are actual, however, unless the integrated net reactions proceed as written, and the products are protected from further reaction and re-exchange with the atmospheric carbon cycle. In an actual reef system, organic and inorganic production tend to counterbalance each other in terms of atmospheric fluxes; the degree to which they counterbalance each other in source/sink behavior is more difficult to assess.

Figure 1 shows three possible destinations for the net organic and inorganic products of reef metabolism. They may end up in the local reef or reef-derived, or they may be exported to other oceanic compartments (here simplified as the shallow and deep ocean). To a first approximation, sediments are usually considered to be out of exchange with the atmosphere, but in actuality they are the site of active biogeochemical reactions and cannot be treated as inert (Tribble et al., 1989; Tribble et al., 1990; Walter et al., 1993); these issues are discussed further below.

A key issue for this discussion is the question of whether the transport of material fractionates the inorganic and organic products in such a way as to enhance either source or sink behavior. Transport of material to the deep ocean can effective removal from the short-term carbon cycle; although both inorganic and organic products are likely to react at depth, there re-equilibration with the atmosphere will be postponed for hundreds to thousands of years (oceanic turnover times). Downslope transport of material is known to occur at shelf edges and on atoll slopes, but the fraction of total production following this path is very poorly known. Because of the extensive sediment trapping on shallow shelve, banks and lagoons and the approximate equivalence of reef accretion and reef production rates (Buddemeier and Smith, 1988) it

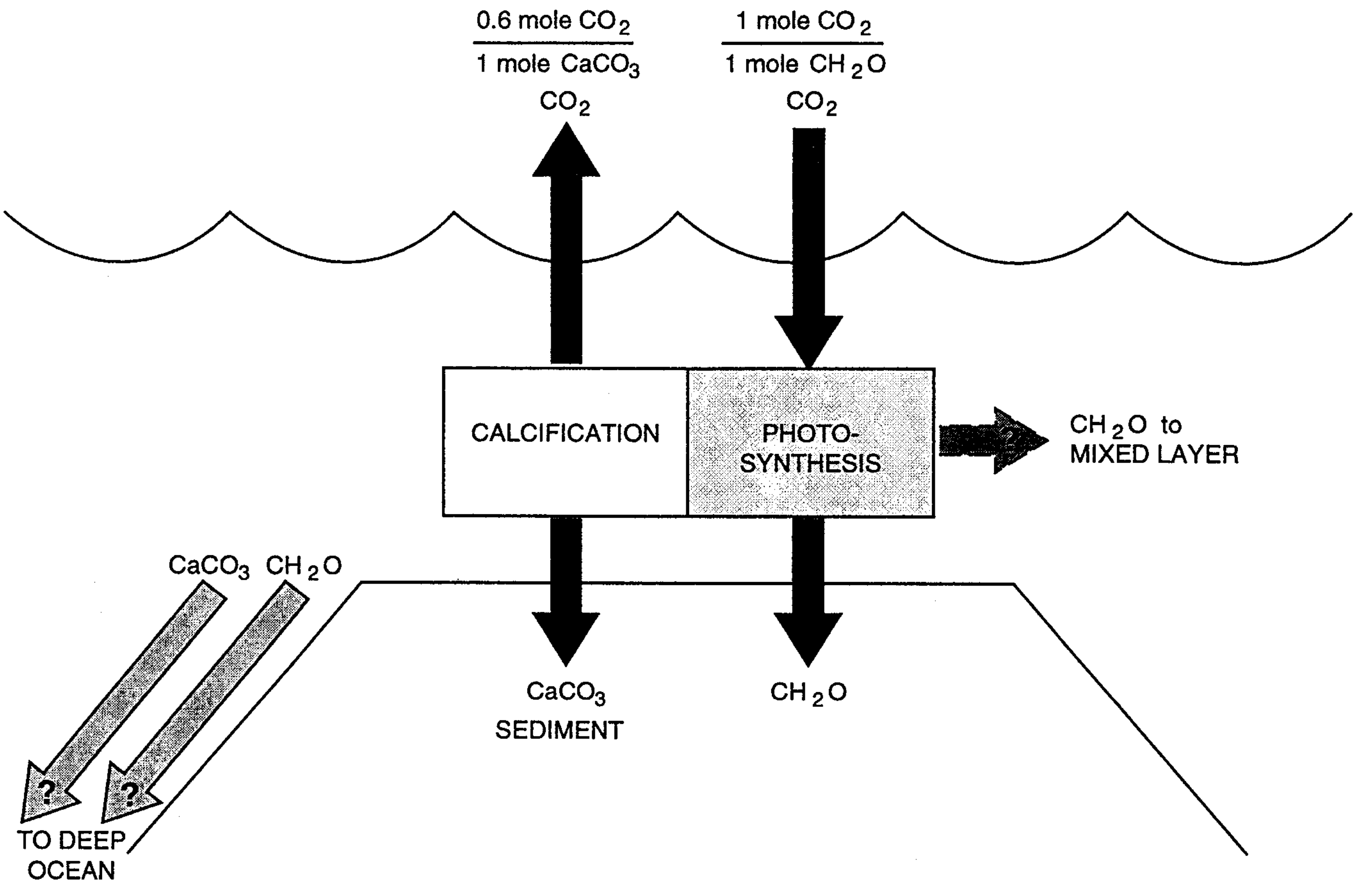

Figure 1: A schematic representation of reef-related carbon fluxes and reservoirs. If net calcification and net photosynthesis are positive, then their products must be transported to one of the reservoirs indicated (sediment, deep ocean, or surface ocean). Only in the case where the amount of organic carbon buried in the sediment or transported to the deep ocean is > 0.6 x the amount of carbonate carbon similarly transported can reef metabolism be considered a sink for atmospheric CO_2.

is normally assumed that a substantial majority of shallow water production is retained within the depth range of the oceanic mixed layer. For the material transported downslope, density will be a factor; solid carbonates will sink more readily than free organic matter. The carbonates removed will carry with them included or attached organic matter, so to a first approximation we can assume that transport to the deep ocean will remove organic and inorganic carbon in the same proportions as burial in the shallow sediments.

A more significant potential fractionating mechanism is transport of material out of the reef system to the surface ocean. Although oceanic "alkalinity plumes" around reef areas testify to some off-reef transport of carbonate materials, loss of organic material in the form of POC and DOC is probably proportionally more important because of the buoyancy and reactivity of organic material. Mobilization of reef organic matter has been reported by a numerous authors (Coles and Strathman, 1973; Marshall, 1965; Marshall et al., 1975). Indications of the significance of this flux are reported by Johannes (1967), who estimates that the carbon exported from reefs by coral mucus production is equivalent to about 40% of the coral respiration; he also cites studies reporting that normal oceanic phytoplankton/zooplankton ratios are shifted dramatically in favor of zooplankton in the vicinity of coral reefs. If it is correct that the net productivity of reef systems is of the same order of magnitude as the surrounding oceans (Crossland et al., 1991), this observation implies that a significant fraction of the reef primary production is exported to and consumed in locations away from the reef. This is an important consideration in metabolic estimates of fluxes; if respiration is separated in time or space from photosynthesis, local or short-term measurements may suggest a sink where, on a more realistic scale, none actually exists.

Reefs, Reef Communities, and Reef Organisms:

The term "coral reef" is applied to many structures and communities, and the terminology used by other disciplines is not necessarily appropriate for "reef" classification in terms of carbon cycle behavior. The most rigorous and traditional definition might be an community in which the benthos is dominated by calcifying reef organisms, living on top of a carbonate structure produced by that community or its predecessors. Examples of this are oceanic atolls (especially those with relatively small emergent areas) and outer shelf barrier reefs, as in the central Great Barrier Reef. Such communities are normally found to be primarily autotrophic, although this is not an intrinsic requirement of the definition.

However, geologists may focus on the carbonate structure without close attention to its presently living community, and ecologists apply the term to mixed communities in which there may be net heterotrophy, terrigenous influences, or other communities (e.g., seagrasses) that are not an obligate part of the "pure" coral reef community. Figure 2 depicts a gradient in "reef community" types from seaward to landward. Stressed or coastal coral communities often contain a much higher ratio of non-calcifying to calcifying organisms, and therefore may exhibit a higher organic to inorganic production ratio, making them appear to be larger potential CO_2 sinks (Gattuso et al., 1995). This may in some cases be true, but the error lies in ascribing this behavior to a "coral reef community;" the actual sink behavior is the product of (for example) a seagrass or algal community that not only is not an intrinsic part of the coral reef community, but may even be competing with or replacing it.

Approaches to Source/Sink Determination:

At present, we can classify three basic approaches to the determination of sink behavior in terms of the methods available for experimental assessment. Two of them involve determination of production rates and/or the disequilibria that drive fluxes, and one directly measures the reaction products. All have specific -- and different -- limitations and disadvantages. The experimental approaches, which will be discussed with regard to their limiting uncertainties and applications to date, are:

1. Site-specific community metabolism
2. System-level community metabolism
3. Characterization of sequestered materials

All of the methods require some level of regionalization of local (or "point") data, and/or site selection for "representativeness," in order to generalize specific measurements to the global and climatic levels. These processes -- selection and regionalization -- depend critically on the conceptual design, the definition of a coral reef or coral reef community, and the limitations of the methods employed.

Site-specific community metabolism:

Studies of community metabolism typically depend on measurements of the changes in carbon and/or oxygen chemistry in either isolated bodies of water or along a well-defined flow trajectory. Time scales of measurement are typically of hours to a few days, and spatial scales may be meters to a few hundred meters.

Advantages: Relatively high precision and direct measurement of the metabolic reactants and products are possible; determinations can be made of the function of specific communities. Although technologically demanding, the methods can readily be carried out in the field.

Disadvantages: Because of the inherent small spatial and temporal scales, variability is difficult to assess, and extrapolating or regionalizing measurements to larger scales of time and space is almost certainly the limiting uncertainty in the method. The method cannot assess the loss of fixed carbon from the local system, and sediment metabolism

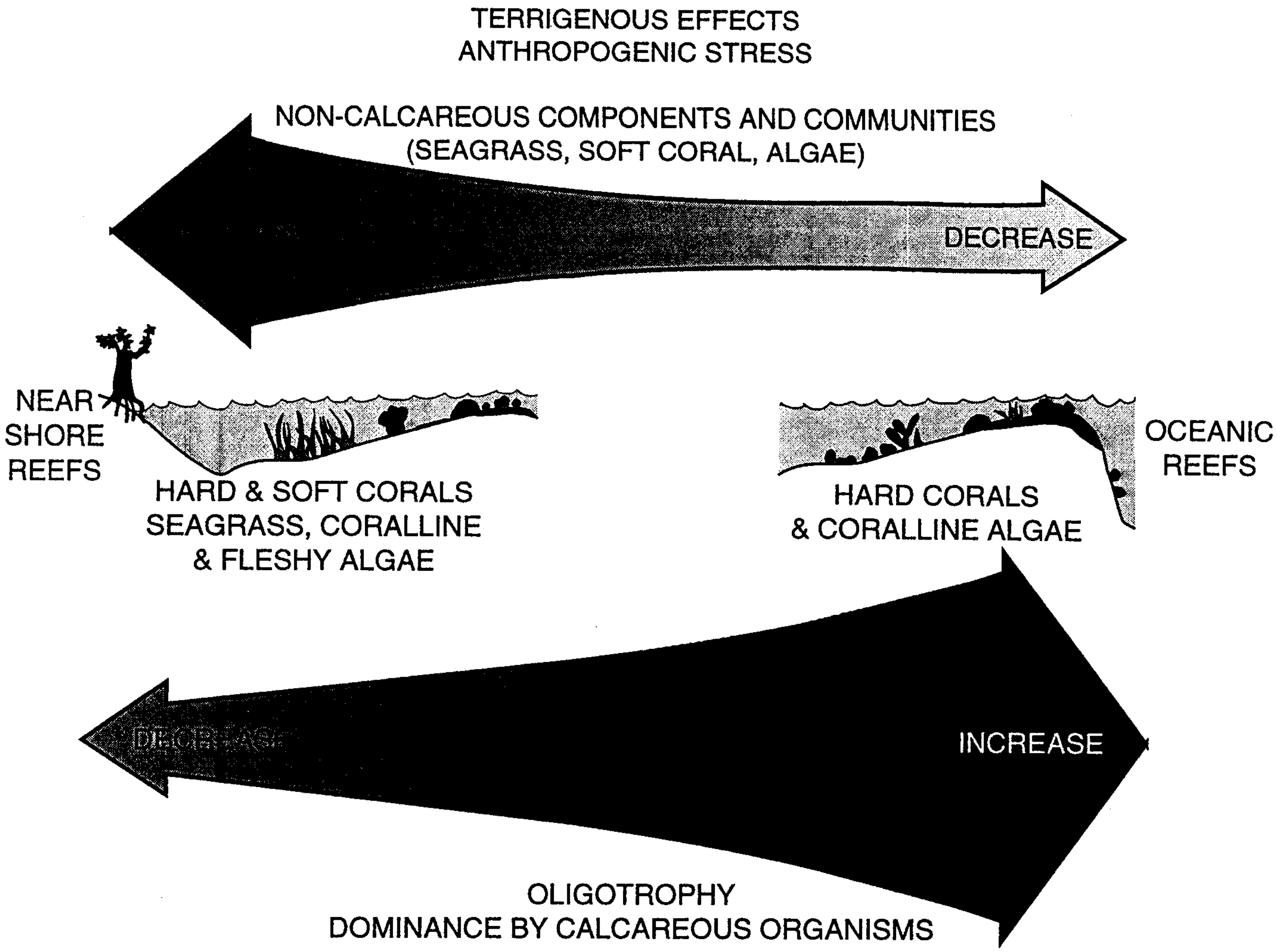

Figure 2: Environmental trends in "coral reef" communities. Terrigenous and human influences are commonly associated with communities having a lower proportion of calcifying organisms. Non-calcifiers may be intimately associated with corals and coralline algae, but are not an obligate part of a strictly defined "coral reef community" such as occurs in many oceanic settings.

contributions may vary on time scales long compared to the period of observation. The method is difficult to apply in high energy environments or in areas where the water volume cannot be defined, both of which may be important to the total flux of CO_2.

Applications to date: Perhaps as many as 50 such studies have been carried out at a wide variety of locations in all oceans. Results are usually expressed as relevant to a specific community type (e.g., reef flat, reef slope, lagoon, etc.). Calcification, and especially photosynthesis and respiration, are highly variable between sites of the same type and at individual sites over time. Gross rates of P and R may fluctuate by factors of 3-4 or even more, making calculation of net rates, extrapolations, and regionalizations highly uncertain. An overview of results (Kinsey, 1985; Smith, 1995) indicates a wide variation in the inferred source or sink behavior of individual sites, but suggests that an overall system average is probably close to zero.

System-level community metabolism:

System-level studies have commonly used nutrient (phosphorus) depletion as an indicator of net organic fixation in combination with alkalinity and salinity changes to assess the metabolism of relatively enclosed, long residence time systems (see discussion by Smith, 1995).

Advantages: This approach integrates over most of the spatial variability of the system, which is probably the greatest uncertainty in combining site-specific studies. It also integrates over longer time scales than most site-specific studies, although it will not (unless repeated) characterize major seasonal or interannual variations.

Disadvantages: The method can be applied only in cases where system geometry and residence times produce a detectable and interpretable signal. Probably the major disadvantage is the need to use assumptions about C:P ratios or other large-scale chemical estimators in order to calculate productivity; because of natural variability in this ratio, there is significant uncertainty in the absolute value of the calculated results.

Applications to date: System-level studies have been carried out at six atoll or island lagoons, plus three other carbonate-producing but not coral reef environments. Results consistently indicate that the carbon flux is either approximately neutral or a small net source to the atmosphere.

Figure 3 provides some perspective on the results of both local and system-level metabolic measurements. It was prepared by pooling all of the P, R, and G values listed by in Table 2 of Kinsey (1985) to produce a mean and standard deviation for each of the indicated reef categories. This calculation implies that each measurement is an

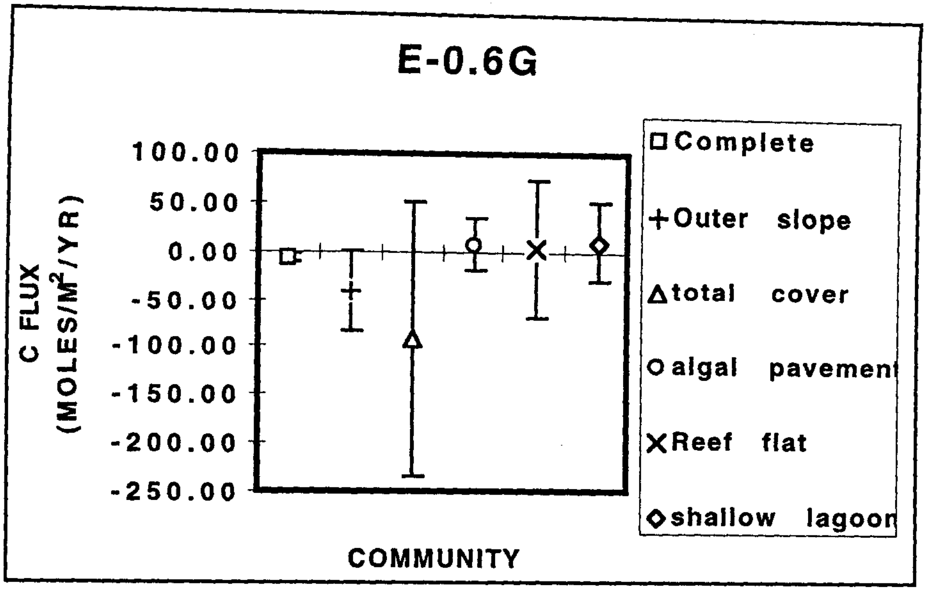

Figure 3: CO_2 flux estimates by community type, obtained by pooling all metabolic data reported by Kinsey (1985) for the indicated categories. Plot is of mean and standard deviaion of the difference between net production (E=P-R) and 0.6 x net calcification (G). Positive numbers indicate a flux of CO_2 from sea to air; negative, from air to sea. None of the numbers are significantly different from zero, but whole-system values show the by far the smallest variance.

equivalent sample of a normal population; although we know that is not a reasonable assumption, the results are instructive nonetheless. The value E - 0.6G is an estimate of the net CO2 flux (negative is a release to the atmosphere, positive is an uptake).

The observations of interest from figure 3 are: (1) none of the categories show a mean that is significantly different from zero; (2) the most highly calcifying systems (outer slope and total coral cover) show the greatest tendency toward source behavior; and (3) the standard deviation for system-level measurements is strikingly less than the standard deviations of any of the more localized communities, and the values plotted graphically illustrate the basis for the conclusion (e.g. Smith (1995); Ware et al. (1992)) that reef systems are probably a very small net source of CO_2. These observations emphasize the importance of scale -- reef systems consist of variable component subcommunities whose functions are integrated over time and space scales much larger than those of the typical direct experimental observation.

Characterization of sequestered materials:

This method considers the chemical composition of reef sediments as indicators of source-sink behavior. Calcification releases 0.6 moles of carbon dioxide per mole of carbonate precipitated and photosynthesis takes up one mole of carbon dioxide per mole of carbon fixed. Therefore, if all of the products of the net metabolism are deposited in the sediments, a sedimentary ratio of organic to inorganic carbon >0.6 would indicate a source, while <0.6 would reflect sink behavior -- this ratio is equivalent to 5-6 weight % organic carbon in a sediment that is essentially all carbonate and organic matter.

Advantages: This method views the long-term process over the time scales of sediment deposition, which are generally appropriate to climate considerations. Sampling and analytical techniques are well established, and sediment samples can be taken in environments not amenable to metabolic study. Because extensive, distributed sampling is feasible, regionalization is less of a problem and can be supported with (e.g.) bathymetric and seismic surveys. Sediment analyses can also be used to assess terrigenous contributions or other factors.

Disadvantages: It is known that reefs export organic carbon as DOC and POC; while most of this is probably oxidized rapidly rather than sequestered elsewhere, it must be explicitly addressed in the budgetary estimates. Postdepositional organic inputs or diagenesis may alter the organic/inorganic ratio by pathways that do not imply the same source-sink relationships as primary deposition. Sediment samples integrate over time, but the time period sampled depends on the sediment accumulation rate, so samples from different locations will not necessarily represent the same time periods -- this dictates a long-term, steady-state assumption in combining results. Sampling of near-surface or recent sediments is complicated by possible inclusion of benthic biomass that should not be considered truly sedimentary. Finally, if the community has undergone a recent change, the sediment results may not reflect current performance.

Applications to date: Although substantial data are available in the literature, there has been no systematic application of this to carbon cycle studies. This is probably in part due to the fact that the "source or sink" answer appears to be a foregone conclusion on the basis of sediment analyses -- most carbonate sediments in reef environments have organic/inorganic C ratios an order of magnitude lower than that required for a net carbon sink.

A variety of analyses from active reef systems suggest that typical organic C contents are <1% (organic/inorganic C ratios <0.1) (Emery, 1962; Emery et al., 1954; Smith, 1984; Tribble, 1990). Organic ratios may be higher in close proximity to a high productivity (and usually not coral-reef) source of organic materials. Systems-level surveys of sediments illustrate the effects of reef and other ecosystems. In the Bahamas (which is a carbonate platform of primarily non-coral origin with some coral reef communities) sediment organic levels are quite low except where they can be identified with mangroves, algal communities or seagrass beds (Morse et al., 1985). Brunskill (unpubl. data, pers. commun.) and colleagues at the Australian Institute of Marine Science have performed extensive sediment surveys in the Herbert River region of the Great Barrier Reef, in Exmouth Gulf in Western Australia, and in the Gulf of Papua. The first two locations provide a broad view of primarily reef-derived sediments over scales much larger than that of the reefs themselves. In both cases, sediment organic/inorganic ratios exceed 0.6 only in very limited areas close to the shore or strongly affected by streamflow. The organic/inorganic ratio remains low even in settings where carbonate material is less than 50% of the total sediment mass. These observations tend to reinforce the view of coral reefs as carbon dioxide sources except when they are influenced by or combined with other communities.

Two aspects in which sediments may contribute to some form of carbon sink deserve mention here, both relating to the fact that shallow reef sediments are sites of active bacterial metabolism and diagenesis (see above). When organic carbon is oxidized in the air or in surface ocean water which is in equilibrium with the atmosphere, CO_2 is returned to the atmosphere. However, when it is oxidized in carbonate-containing sediments the CO_2 may be neutralized by dissolution of solid carbonate, with the carbon transferred to the bicarbonate form ($CH_2O + O_2 + CaCO_3 \longrightarrow 2HCO_3^- + Ca^{++}$). If this simply canceled out the atmospheric effects of the original calcification and photosynthesis it would have no impact on source/sink considerations. However, because a mole each of organic and carbonate carbon formed represent a net withdrawal of 0.4 moles of atmospheric CO_2, the 1:1 neutralization in the sediment could be considered a net transfer of carbon from the atmospheric to the oceanic reservoir. Whether or not this represents a genuine sink has not been rigorously examined. However, because reef sediments are 5-10 times too depauperate in organic carbon to represent a sink, and because this consideration could only change the ratio by a factor of about 2, it does not change the basic conclusion but may serve to somewhat reduce the discrepancy between the system metabolism and the sediment-based assessments.

A further related consideration has been pointed out by B. N. Opdyke (pers. commun.). The "titration capacity" of carbonate sediments could in principle convert terrestrial or marine organic carbon into an oceanic inorganic form if there were mechanisms for mixing the two "reactants." This could be a significant sink, but it is important to not that it is not a direct function of the metabolic activity of coral reef (or any other specific) communities; sedimentary microbes are the primary community, operating independently on the organic and inorganic products of other communities.

Evaluation and Conclusion:

Site specific studies are extremely useful for examining community function at small scales, but are generally inappropriate for extrapolating to whole-ecosystem performance, and especially to global and climatic scales. A broad overview of the results of many -- and variable-- site studies is consistent with the smaller number of more uniform findings of whole-system studies; on average, reefs are presently nearly in balance with respect to CO_2 flux, or are possibly a small net source of CO_2. A greater and more interesting discrepancy is between system studies and interpretation of sediment analyses, which suggest that either reefs have been a somewhat stronger CO_2 source over the recent past, or that there are carbon transport and reaction pathways in the present systems that have not been adequately characterized. Where sediment and whole-system metabolism studies are in reasonable agreement, the combined results might be used to calibrate the regionalization of site-specific studies, and to infer by difference the behavior of communities that are not directly measurable.

Identification of the actual -- as opposed to traditionally described -- communities and organisms involved in carbon fixation and transport, and determination of their functional behavior over appropriate scales of time and space, are critical to any effort to define true CO2 source or sink behavior.

The issues of carbon metabolism are not only (or not even primarily) of interest from a carbon-cycle standpoint; they are crucially important to present concerns about reef conservation and management. Many reefs have been damaged by overfishing, and others have been stressed or killed by high inputs of sediment, organic matter, and/or nutrients. If reefs have a higher net productivity than has been generally determined (as would be suggested by carbon sink behavior), they could sustain greater biomass harvesting and possibly higher nutrient or organic inputs. If managers and policy makers respond to an incorrect suggestion of higher productivity by relaxing environmental controls, the global loss of coral reefs could be accelerated. Careful experimental design and interpretation are essential in addressing this sensitive topic.

References:

Buddemeier R. W. and Smith S. V. (1988) Coral Reef Growth in an Era of Rapidly Rising Sea Level: Predictions and Suggestions for Long-Term Research. *Coral Reefs* 7, 51-56.

Coles S. L. and Strathman R. (1973) Observations on coral mucus "flocs" and their potential trophic significance. *Limnology and Oceanography*, 673-678.

Crossland C. J., Hatcher B. G., and Smith S. V. (1991) Role of coral reefs in global ocean production. *Coral Reefs* **10**, 55-64.

Emery K. O. (1962) Marine Geology of Guam. U. S. Geological Survey Professional Paper 403-B.

Emery K. O., Tracey J. L. J., and Ladd H. S. (1954) Geology of Bikini and Nearby Atolls. U. S. Geological Survey Professional Paper 260-A.

Gattuso J. P., Pichon M., and Frankignoulle M. (1995) Biological control of air-sea CO_2 fluxes: effect of photosynthetic and calcifying marine organisms and ecosystems. *Marine Ecology Progress Series* **In press.**

Johannes R. E. (1967) Ecology of organic aggregates in the vicinity of a coral reef. *Limnology and Oceanography* **12**(2), 189-195.

Kinsey D. W. (1985) Metabolism, calcification, and carbon production: I. systems level studies. *Poceedings, Fifth International Coral Reef Congress (Tahiti)* **4**, 505-526.

Marshall N. (1965) Detritus over the reef and its potential contibution to adjacent waters of Eniwetok atoll. *Ecology* **46**(3), 343-344.

Marshall N., Durbin A. G., Gerber R., and Telek G. (1975) Observations on particulate and dissolved organic matter in coral reef areas. *Int. Revue ges. Hydrobiol.* **60**(3), 335-345.

Morse J. W., Zullig J. J., Bernstein L. D., Millero F. J., Milne P., Mucci A., and Choppin G. R. (1985) Chemistry of Calcium Carbonate-Rich Shallow Water Sediments in the Bahamas. **285**(February, 1985), 147-185.

Smith S. V. (1984) Phosphorus versus nitrogen limitation in the marine environment. *Limnology and Oceanography* **29**(6), 1149-1160.

Smith S. V. (1995) Reflections on the measurement and significance of carbon metabolism on coral reefs. Kansas Geological Survey Open-File Report 95-56a.

Tribble G. W. (1990) Early Diagenesis in a Coral Reef Framework. Ph.D.Dissertation (Oceanography), University of Hawaii.

Tribble G. W., Sansone F. J., Li Y. H., Smith S. V., and Buddemeier R. W. (1989) Material Fluxes from a Reef Framework. *Proc. Sixth Int. Coral Reef Symp.*, 577-582.

Tribble G. W., Sansone F. J., and Smith S. V. (1990) Stoichiometric modeling of carbon diagenesis within a coral reef framework. *Geochimica et Cosmochimica Acta* **54**, 2439-2449.

Walter L. M., Bischof S. A., Patterson W. P., and Lyons T. W. (1993) Dissolution and recrystallization in modern shelf carbonates: evidence from pore water and solid phase chemistry. *Phil. Trans. R. Soc. Lond. A* **344**, 27-36.

Ware J. R., Smith S. V., and Reaka-Kudla M. L. (1992) Coral reefs: sources or sinks of atmospheric CO2? *Coral Reefs* **11**, 127-130.