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# Wally's Quest to Understand the Ocean's CaCO<sub>3</sub> Cycle

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## Abstract

Aspects of the production and dissolution of CaCO<sub>3</sub> hard parts dominate the literature regarding contemporary marine chemistry and paleoceanography. During my long career I have contributed more than 200 papers related to this subject. In this prefatory article in the first volume of the *Annual Review of Marine Science*, I recount what I consider to be the highlights of my attempts to understand the cycle of CaCO<sub>3</sub> in today's ocean and in oceans of the past. These studies began in the Bahamas in the early 1960s and then quickly graduated to the world ocean. Although much of my research has involved stable and radioisotopes contained in shells and coral directed toward reconstruction of the late Quaternary operation of the earth system, in this review I concentrate on carbonate chemistry and, in particular, the compensation in the deep sea for the overproduction of CaCO<sub>3</sub> by marine organisms.

## INTRODUCTION

Early in my academic career, the ocean's  $\text{CaCO}_3$  cycle caught my attention. Some 45 years later, it remains one of the brightest colors on my research palette. The offer to write the prefatory article for this new addition to the *Annual Reviews* bookshelf gives me the opportunity to recount my accomplishments in this area and to comment on what I feel needs to be done. So, I warn you who have opened these pages that what you are about to read is not the usual review article but rather a more personal account of my attempts to come to grips with this challenging subject.

My first encounter was the result of an invitation from John Imbrie to join him on an expedition to the Bahama Banks. At the time, I was interested in the application of two radio tracers,  $^{14}\text{C}$  and  $^{222}\text{Rn}$ , to the determination of the rate of transfer of gases between the ocean and the atmosphere.  $^{222}\text{Rn}$  is produced by the decay of radium dissolved in sea water and  $^{14}\text{C}$  was created as the result of H-bomb tests. Neither had yet been exploited for this purpose. So, I jumped at Imbrie's offer.

In those days, Taro Takahashi (**Figure 1**), who was teaching at Alfred University, came by Lamont every now and then to troubleshoot our infrared  $\text{CO}_2$  analyzer (and to visit his girlfriend in New York City). During one of these visits, I mentioned the upcoming Bahamas trip. Taro was eager to sign on. He thought it would be interesting to measure  $\text{CO}_2$  partial pressures in the shallow bank waters. So, in June 1963, off we went to Frazers Hog Key to the north of Andreas Island on the eastern rim of Grand Bahama Bank. There, first using a chartered Chalk Airline Widgeon and then a Lerner Lab research vessel, I became an oceanographer. But serendipity stepped in and turned my plan topsy turvy. Instead of being deficient in radon owing to loss to the atmosphere, we found the shallow bank waters to have a sizable excess (Broecker, 1965).



PHOTO CREDIT: BRUCE GILBERT

**Figure 1**

Taro Takahashi.

Through radon measurements on pore waters, we determined that the excess was gained from the underlying sediments. This led, in later years, to a host of ocean bottom radon profiles designed to determine vertical eddy diffusion rates (Broecker et al. 1968). We did find excess  $^{14}\text{C}$  in the bank waters but realized that its distribution could be better used to pin down the residence time of the waters on the bank (Broecker & Takahashi 1966).

The big discovery was Taro's. He realized that by measuring both  $\text{pCO}_2$  and  $\Sigma\text{CO}_2$  he could determine how much  $\text{CaCO}_3$  had been precipitated from each of our bank water samples. Further, by combining his water chemistry with my radiocarbon-based water residence times, we could compute the rate of  $\text{CaCO}_3$  precipitation as a function of the product of carbonate and calcium ion concentrations. As a result of evaporation, waters isolated on the banks undergo sizable increases in salinity and hence in concentration product. Intrigued by the 1963 results, Taro and I organized a second expedition to the Bahamas in the summer of 1964. On the basis of the combined results of these two expeditions we were able to demonstrate that the precipitation rate of  $\text{CaCO}_3$  increased with the increase in the ionic product of calcium and carbonate ion (Broecker & Takahashi 1966). Some 30 years later, Chris Langdon and Taro conducted manipulations of the calcium and carbonate ion concentrations in the indoor tropical lagoon at Biosphere 2 and were able to confirm that the rate of precipitation of  $\text{CaCO}_3$  by coralline algae (akin to those that thrive on the Bahama Banks) depends strongly on the ion product of the calcium and carbonate ion concentrations (Langdon et al. 2000). These studies provide the warning that the  $\text{CO}_2$  we add to the atmosphere by burning fossil fuels and its consequent reduction of the carbonate ion concentration in surface ocean waters are creating an additional stress on the world's already threatened coral communities.

## WHITINGS

It was on this second trip that we encountered a whiting. Anyone who has flown over the Bahama Banks has likely noted white streaks in the water. When I first saw one, I asked the pilot what they were. He replied: "Whitings." Further inquiries into how they formed yielded speculations that fit into two categories:  $\text{CaCO}_3$  spontaneously precipitated from the bank water and  $\text{CaCO}_3$  stirred up from the underlying sediment. When in 1964 we sailed across one of these tens-of-meters-wide plumes, Taro made  $\text{CO}_2$  partial pressure measurements that eliminated the precipitation scenario. If active precipitation of  $\text{CaCO}_3$  was occurring, the waters in the whiting should have had substantially higher  $\text{CO}_2$  partial pressures than the waters on either side. But Taro found absolutely no difference! To check, we made a second pass that produced the same result (Broecker & Takahashi 1966). Then, I got an idea as to how we could nail down Taro's claim. On board our small vessel (with the grand name *Lord Raleigh*) we had a continuous centrifuge for use in connection with  $^{90}\text{Sr}$  measurements. I proposed that we centrifuge enough whiting water to isolate the 30 g of  $\text{CaCO}_3$  needed at that time for a radiocarbon measurement. If, on the one hand, the  $\text{CaCO}_3$  was stirred up from the bottom, it would have the radiocarbon age of 1000–2000 years characteristic of bank sediment. If, on the other hand, the  $\text{CaCO}_3$  was newly precipitated from the bank water, it would have (because of the H-bomb  $^{14}\text{C}$ ) a future age. Months later, measurements back at Lamont showed the  $\text{CaCO}_3$  to be derived from bottom sediment (Broecker & Takahashi 1966). Taro had it right!

But the mechanism propelling the resuspension remained to be identified. Three decades later, during a visit to the marine lab in St. Petersburg, I was stunned to find that scientists there remained convinced that whittings were created by spontaneous crystallization of  $\text{CaCO}_3$ . The local United States Geological Survey (USGS) people had gone so far as to propose whittings as a sink for fossil fuel  $\text{CO}_2$ . When I read them the riot act, they challenged me to come up with a resuspension

mechanism. This led me to recollect that the *Lord Raleigh's* Captain George had warned us that swimming in whittings was dangerous: "They're loaded with lemon sharks." Questions about the sharks' behavior revealed that they hunted prey electronically rather than visually. Hence, they have a big advantage over the fish that swim blind in the darkness of the whittings. I thought: "Aha, it's the sharks that stir up the sediment. Like spiders, they create food traps!" As far as I know, the folks in St. Petersburg still opt for spontaneous crystallization as an explanation and I haven't yet encountered anyone who has picked up on my shark idea (Broecker et al. 2000). But hopefully someday the world will awaken to the truth!

## COMPENSATION DEPTH

In those early days, thoughts about what controlled the chemistry of the ocean remained quite primitive. Occupied by my immediate research, I didn't give these more esoteric aspects of my subject much attention. But, when I read papers by the Scandinavian chemist Sillen (1961, 1967), I was jarred into action. His contention was that the chemical composition of the ocean is at thermodynamic equilibrium with its sediment. How boring, I thought. Although there is no question that the laws of thermodynamics must be obeyed, I also knew that the organisms that inhabit the ocean certainly exert a strong influence on the concentration of at least those constituents such as  $\text{SiO}_2$ ,  $\text{PO}_4$ , and  $\text{NO}_3$  that are essential to plant growth. So, I began to think about the ocean in kinetic terms. Certainly its chemical composition was driven toward thermodynamic equilibrium. But, I reasoned, many of the constituents of its salt did not reside in the sea long enough to reach this state. Rather, their concentrations were controlled by a kinetic balance between supply and removal.

As an example, I pondered the control on the depth of the boundary between abyssal sediments from which all the raining calcite ( $\text{CaCO}_3$ ) had been dissolved and mid-depth sediments from which little of this calcite had been dissolved. In the 1960s the conventional thinking was that the control on the depth separating these two realms was thermodynamic and hence was related to the fact that the solubility of calcite was enhanced by increasing pressure and decreasing temperature. If so, the transition depth was dictated only by water temperature. I came to realize that this was dead wrong. Instead, the transition depth was dictated by chemical economics. In today's ocean, marine organisms produce roughly four times more calcite than the ingredients required for its manufacture are supplied to the ocean. Hence something has to give: Either the rate of manufacture must be curtailed or the overproduction of calcite must be compensated by dissolution. Because surface ocean waters are highly supersaturated with respect to calcite, there is no chemical limit on how much calcite organisms produce. Hence, the control must be via dissolution. Further, because the concentration of calcium ions in today's ocean is two orders of magnitude larger than that of carbonate ions, the control must involve adjustment of the deep sea's carbonate ion concentration. If, at any given time, the burial of  $\text{CaCO}_3$  were to exceed supply, the concentration of carbonate ion could be drawn down and as a consequence, the calcite compensation depth (CCD) would shoal. This process would continue until a balance between burial and supply was reestablished. I found it hard to believe that no one had stated the obvious. So I did (Broecker 1971).

On a hot day in mid-August 2007, I sit in my air conditioned office in Lamont's old Geochemistry Laboratory writing with my #2 pencils. I started the day by answering the reviews of my paper entitled "A need to improve reconstructions of the fluctuations in the carbonate compensation depth over the course of the Cenozoic." The plea in this paper is for an improved reconstruction of the depth of the so-called calcite saturation horizon in all three oceans over the course of the Cenozoic. This reconstruction offers three valuable pieces of information. One is that it fixes the ratio of calcite production by marine organisms to the supply of calcite ingredients. Another is

that this reconstruction provides a constraint on the chemical composition of past oceans in that the depth of the saturation horizon is linked to the product of the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions. Finally, as is the case for today's ocean, differences in this transition depth between ocean basins provide clues regarding the distribution of nutrient constituents in the deep sea.

At this point, it is important to make the distinction between the depth in the ocean we wish to reconstruct (i.e., the calcite saturation horizon) and the depth that is actually reconstructed (i.e., the CCD). The latter lies several hundred meters deeper than the former. Reconstructions focus on the CCD rather than on the saturation horizon for practical reasons. Separating the abyssal sea floor, where sediments have lost all their  $\text{CaCO}_3$  to dissolution, and the mid-depth sea floor, where  $\text{CaCO}_3$  is largely preserved, is a several-hundred-meter-thick transition zone. The  $\text{CaCO}_3$  content of sediments in this zone undergoes a decline with water depth that has a characteristic shape. It starts gradually, steepens, and then becomes gradual again. The shape of the upper part of the transition zone is a consequence of the high  $\text{CaCO}_3$  content of the material raining to the sea floor. To date these reconstructions are based on  $\text{CaCO}_3$  content, which presents a problem because the initial phases of dissolution produce only very small changes in  $\text{CaCO}_3$  content. As a consequence, for sediments with high  $\text{CaCO}_3$  contents, it is not possible to say from this measurement alone whether or not any dissolution has occurred. This becomes clear only when dissolution has sizably reduced the  $\text{CaCO}_3$  content. Hence, reconstructions have focused on the depth at which the  $\text{CaCO}_3$  content has been reduced to 20%. This depth has been termed the CCD.

A reconstruction of the CCD over the course of the Cenozoic was made possible by the availability of cores recovered as part of the Deep Sea Drilling Program. Each record obtained from a region of the sea floor now covered with red clay revealed a down-hole transition from  $\text{CaCO}_3$ -free to  $\text{CaCO}_3$ -rich sediment. The explanation for this transition was provided by geophysicists, who showed that as sea floor spreading carries the oceanic crust away from its birth place at a mid-ocean ridge crest, it gradually cools; as it cools, its thickness shrinks. This shrinkage causes the sea floor to gradually deepen and at some point it passes through the saturation horizon for the mineral calcite into the realm of dissolution. The fossils of marine plankton in these cores allow geologists to establish the age of the sediment with 20%  $\text{CaCO}_3$  and hence, the time at which the drop below the CCD occurred. On the basis of the sinking rate equations provided by geophysicists, the elevation of the sea floor is backtracked to the time it passed through the CCD. In this way, the Cenozoic history of the CCD has been reconstructed. The last comprehensive paper on this subject was written by Van Andel (1975). On the basis of this reconstruction, the CCD appears to have remained in the range of  $4.5 \pm 0.6$  km. This result means that the area of the sea floor from which the raining calcite hard parts are dissolved has remained close to 70% of the total area of the sea floor. Puzzling to me is that this result implies that, despite the many changes in both the organisms inhabiting the Cenozoic ocean and the factors controlling the supply of ingredients (volcanism, tectonism, continental erosion, etc.), the extent of overproduction of calcite by marine organisms has remained more or less the same.

In an ideal ocean, the depth offset between the CCD and the saturation horizon would be constant in both space and time. If this were the case, the temporal fluctuations in the CCD depth would reflect those of the saturation horizon. However, this is clearly not the case. Rather, the magnitude of the offset varies with the vertical gradient in carbonate ion concentration, with the rain rate of  $\text{CaCO}_3$ , with the ratio of  $\text{CaCO}_3$  to other constituents of the sediment, and even with the identity of the  $\text{CaCO}_3$  entities (see below). In today's ocean, the range in the offset is comparable to the 0.6-km fluctuations in the CCD for times past. So, if we are to confirm these fluctuations, it will be necessary to find ways to improve the reconstructions. A discussion of how this might be accomplished is presented below. But let me first introduce another line of inquiry for which the same tools are required.

## GLACIAL TO INTERGLACIAL CHANGES

The paleoclimatology community was stunned by the announcements in 1980 by Swiss and French scientists that measurements of the CO<sub>2</sub> content on air trapped in polar ice showed that the CO<sub>2</sub> content of the atmosphere was as much as 30% lower than its preindustrial value during peak glacial time (Berner et al. 1979, Delmas et al. 1980). I had pondered how the existence of CO<sub>2</sub> changes might be demonstrated by measurements made on deep-sea sediments, so I pounced on this discovery and published a paper proposing that the lowering could be explained by the release during erosion as the result of the glacial sea level drop of phosphorus and nitrogen stored in continental shelf sediments deposited during interglacial high stands of the sea (Broecker 1981, 1982). As with many subsequent scenarios designed to explain the glacial lowering of the atmosphere's CO<sub>2</sub> content, my explanation was soon shown to be inadequate.

A second quite different scenario was published by Berger & Keir (1984) shortly thereafter. They proposed that erosion and dissolution of CaCO<sub>3</sub> deposited in coral lagoons and on carbonate banks during interglacial high sea stands was responsible for the low CO<sub>2</sub> content of the glacial atmosphere. Intuition might suggest that because the dissolution of CaCO<sub>3</sub> adds carbon to the ocean, it should cause the CO<sub>2</sub> partial pressure to rise. But, in reality, it does just the opposite. The reason is that the Ca<sup>2+</sup> created during dissolution adds two moles of positive charge for each mole of carbon added. To maintain the required balance between the number of negative charges and the number of positive charges, the carbonate ion content of the water increases and its CO<sub>2</sub> content decreases. This is why in our Bahama Bank study, Taro Takahashi endeavored to find an increase in CO<sub>2</sub> resulting from the precipitation of CaCO<sub>3</sub>. Hence, Berger's scenario predicted that the dissolution of CaCO<sub>3</sub> during glacial time should have caused the ocean's carbonate ion concentration to increase and, as a result, the CCD should have shoaled. If the entire 30% reduction in CO<sub>2</sub> were generated in this way, the deepening would have been on the order of two kilometers. Such a change would stand out like a sore thumb in sediments deposited near today's CCD, for rather than having lost most of its CaCO<sub>3</sub> to dissolution, the underlying glacial-age sediment should have experienced little or no dissolution. The fact that only small differences exist between glacial and interglacial sediments put Berger's coral reef hypothesis in a coffin next to the one that housed my shelf-nutrient hypothesis.

Although it clearly failed to explain a major portion of the glacial lowering of atmospheric CO<sub>2</sub> content, Berger's hypothesis ignited an interest in determining whether CaCO<sub>3</sub> dissolution had played even a minor role. However, because the glacial to interglacial differences in CCD depth are small, it was clear that improved strategies would be required. Again, before I discuss these new strategies, I must describe yet another motivation.

## CALCITE DISSOLUTION IN THE BIOTURBATED ZONE

As part of my Ph.D. thesis, I conducted radiocarbon dating of the CaCO<sub>3</sub> in deep-sea sediments. My goal was to pin down the timing of the faunal change that accompanied the termination of the last period of glaciation. During the course of these measurements, I was puzzled by the several-thousand-year ages I obtained for core tops. One thought was that the upper several centimeters of the sediment are blasted away as the piston core enters the sediment. Another was that reworked (i.e., preaged) material was deposited along with material newly formed in the overlying surface waters. When I made my first voyage on Columbia's research vessel *Vema* in 1965, I realized that that part of the problem had to do with the shipboard extrusion of piston cores. Each 10-ft section was laid out on deck and the sediment was extruded by pulling the pipe away from the sediment. The core-top sediment was the first to emerge and, because it was



PHOTO CREDIT: GAIL DERR

## Figure 2

Tsung-Hung Peng.

poorly consolidated, it slumped out to form a wedge in the tray. Using the palm of his hand, the “core describer” pushed the sediment wedge back to its original shape. Of course, in so doing, he mixed together the material that formed the wedge.

Although this observation helped me to understand why piston cores had several-thousand-year-old top ages, this turned out to be only part of the answer. A graduate student at the time, Tsung-Hung Peng (**Figure 2**), and I got hold of samples from a box core and did a closely spaced set of down-core radiocarbon measurements. We found that those from the upper eight centimeters yielded radiocarbon ages close to 3500 years and that only further down the core did the regular progression of increasing ages commence (Peng et al. 1979). Further, a line drawn through this age progression extrapolated to near zero age at the core top. Because the material in the box core was not disturbed, we knew that the high ages were not an artifact of either core-top loss or disturbance by the core describer. Nor could this phenomenon be due to the incorporation of preaged material. Rather, it had to be due to what has become known as bioturbation. Worms in their quest for food ingest and then expel sediment and in the process stir the upper portion of the sediment column. Only when the sediment is buried beyond the reach of these organisms does layer by layer accumulation begin.

At this point, you the reader might ask, what does bioturbation have to do with the  $\text{CaCO}_3$  cycle and the CCD? The answer is plenty! Another one of my graduate students, George Kipphut, was the first to make the connection (Peng et al. 1977). We had been thinking that the radiocarbon age of the  $\text{CaCO}_3$  in the bioturbated zone could be approximated by mass,  $M$ , of  $\text{CaCO}_3$  in the mixed layer divided by the rain rate,  $R$ , of  $\text{CaCO}_3$  to the sea floor as follows:

$$\text{Age}(\text{kyrs}) = \frac{M(\text{g}/\text{cm}^2)}{R\left(\frac{\text{g}/\text{cm}^2}{\text{kyr}}\right)}$$



Because of radiocarbon decay within the mixed layer, the relationship is actually a bit more complicated:

$$Age = \tau \ln \left( 1 + \frac{M}{\tau R} \right),$$

where  $\tau$  is the mean lifetime of radiocarbon atoms, i.e., 8.25 kyrs (see Peng et al. 1977 for derivation). Take, for example, a situation where the mass of the  $\text{CaCO}_3$  in the mixed layer is  $6 \text{ g cm}^{-2}$  and the rain rate of  $\text{CaCO}_3$  is  $2 \text{ g cm}^{-2} \text{ kyr}^{-1}$ . If radiodecay is neglected, the  $^{14}\text{C}$  age comes out to be 3.00 kyr. With the inclusion of radiodecay, the age comes out to be 2.56 kyr.

Kipphut pointed out that if  $\text{CaCO}_3$  dissolution occurred within the bioturbated zone, provided the mixing depth remained unchanged, the radiocarbon age would be reduced (Peng et al. 1977). Suppose that dissolution had reduced the mass of  $\text{CaCO}_3$  in the mixed layer from  $6 \text{ g cm}^{-2}$  to  $4 \text{ g cm}^{-2}$ , then the radiocarbon age would be only 1.79 kyr.

A surprise came when a test of this idea was conducted. Radiocarbon ages were performed on box cores taken by Woods Hole's Dan McCorkle at a series of water depths along the equator in the western Pacific (Broecker et al. 1999). As expected, the greater the water depth, the lower the core-top  $\text{CaCO}_3$  content. Because  $^{14}\text{C}$  dates from beneath the bioturbated zone revealed that the accumulation rate of the non- $\text{CaCO}_3$  material remained unchanged along the traverse, it could be assumed that the rain to the sea floor of  $\text{CaCO}_3$  was the same at each site and therefore that the decrease in  $\text{CaCO}_3$  content with water depth was the result of ever greater extents of dissolution induced by the pressure effect on the solubility of calcite. To our surprise, instead of decreasing with water depth, the core-top radiocarbon age increased dramatically.

It took a third Lamont-Doherty graduate student, Rachel Oxburgh, to explain this result. She challenged our assumption that the dissolution occurred within the sediment pores. Instead, she posited that dissolution occurred while the grains rested on the sea floor, before they were mixed into the sediment. In this case, an increase in the core-top  $^{14}\text{C}$  age with water depth would be expected, because the input of  $\text{CaCO}_3$  to the sediment would correspondingly decrease (Oxburgh 1998).

Although in hindsight Oxburgh's explanation seems obvious, at the time we were blinded by measurements of pore water pH made using microelectrodes slowly ratcheted into the sediment from bottom landers. These results suggested that respiration  $\text{CO}_2$  released by bacteria (and worms) into the sediment pore waters lowered their pore water carbonate ion content, promoting dissolution within the bioturbated zone. Although these microelectrode measurements have been made in several areas, not enough information is available to demonstrate how the ratio of sea floor dissolution to within-sediment dissolution changes with water depth. At the saturation horizon any dissolution would have to occur within the sediment pores; with increasing depth below this horizon an ever-greater portion of the dissolution would be expected to occur on the sea floor before the grains were buried. Further, Jahnke & Jahnke (2004) made an interesting case that perhaps  $\text{CaCO}_3$  coatings on the calcite grains dissolve rather than the grains themselves. The coatings, presumed to form in contact with the overlying bottom water, are transported into the sediment by bioturbation. Coatings form when grains are in contact with supersaturated bottom water and then redissolve when bioturbated into undersaturated pore water. Following up on this idea, I showed that at a site on the Atlantic's Ceara Rise where electrode measurements of pore water pH documented sizable dissolution, there was no evidence that calcite had been dissolved from the sediment (Broecker & Clark 2003).

Having dragged you through this discussion of bioturbation and its impact on radiocarbon ages, you might now ask, "What does this have to do with reconstructing past saturation horizon depths?" The answer, as I discuss below, is that one of the things that influences the offset between

the saturation horizon and CCD is the fraction of dissolution that takes place on the sea floor. The CCD is defined as that depth at which the sediment  $\text{CaCO}_3$  content is reduced to 20%, and it is located in waters that are highly undersaturated with respect to the mineral calcite. The radiocarbon evidence suggests that under these conditions a major fraction of the dissolution occurs on the sea floor before the grains are buried.

## DISSOLUTION INDICES

It is clear from these examples that more must be learned about the factors that influence the extent of calcite dissolution in the deep sea. Although the  $\text{CaCO}_3$  content provides useful information, this measurement alone cannot provide the answers we seek. Some more direct indices of dissolution are required. Early on it was realized that as foraminifera shells thin by dissolution they eventually break into pieces; hence, the higher the ratio of fragments to whole shells, the more extensive the dissolution. Although certainly a potential candidate for the sought-after index, fragmentation has two major drawbacks. The most obvious drawback is that it is highly labor intensive. At least 300 whole shells and shell fragments must be examined using a binocular microscope. Further, because the shells of some species of foraminifera are more fragile than those of others, they break up more easily. Hence the proper calibration of a fragmentation index would require an immense effort. This challenge has yet to be met.

During the early 1990s, Elizabeth Clark (**Figure 3**) and I stumbled onto what we thought of as an automated means of measuring fragmentation. This method involved determining both the amount of  $\text{CaCO}_3$  in the greater-than-63- $\mu$  fraction and the total amount of  $\text{CaCO}_3$  in a sediment sample (Broecker & Clark 1999). The ratio of these two amounts was dubbed the size index and was based on measurements in hundreds of sediment core-top samples from throughout the tropical ocean. We found that in sediments shallow enough to have experienced little dissolution, the ratio nearly always fell in the range  $0.55 \pm 0.05$ . Further, in waters deemed to be undersaturated with respect to calcite, the index decreased linearly with water depth. Also, when plotted against what we termed pressure-normalized carbonate ion content, all the measurements scattered about a single straight line. I thought we had discovered the long-sought-after dissolution index.

But our euphoria vanished when analyses of glacial-age sediments forced us to the conclusion that during peak glacial time the index for sediments that had experienced little dissolution appears to have been closer to 0.45 than to 0.55. Our tentative explanation was that the contribution of coccoliths (smaller than our 63- $\mu$  cutoff) was greater during glacial than during interglacial periods (Broecker & Clark 2001). Because at the time we had no way to measure coccoliths, our quest to apply our index to glacial-age sediments stalled.

At an American Geophysical Union (AGU) meeting in San Francisco at about that time, Pat Lohmann took me aside and recommended that I look into his dissolution index (Lohmann 1995). This index involved weighing 50 shells of a given foraminifera species picked from a narrow size fraction. The idea was that the weight provided a measure of the shell-wall thickness; the greater the extent of dissolution, the thinner the walls. Because our size index method was in limbo at this point, we picked up on Pat's suggestion. Using our size index samples, we did shell-weight calibrations and then carried out a series of down-core measurements on sediments from the Ceara Rise in the eastern equatorial Atlantic; we were rewarded with evidence for strong dissolution events corresponding to MIS 5d, MIS 5b, and the MIS 5a-4 boundary (Broecker & Clark 2002).

But then the roof caved in on this method as well. Stephen Barker (**Figure 4**) found as part of his Cambridge University Ph.D. dissertation that the weights of core-top *Globigerina bulloides* from northern Atlantic cores varied with the carbonate ion concentration of the water in which they grew (Barker & Elderfield 2002). This opened the door to the possibility that the wall thicknesses



PHOTO CREDIT: PATRICIA CATANZARO

### Figure 3

Elizabeth Clark.

of foraminifera shells varied with other environmental factors that influenced their growth. With our eyes opened to this possibility, we realized that our own results from high latitude South Atlantic cores showed this effect (Broecker & Clark 2004). Foiled again! Discouraged, we put this whole enterprise aside and turned our attention to other projects.

In 2006, the opportunity arose to examine the contribution of coccoliths to our size index. It came in the person of Tzu-Chien Chiu (**Figure 5**), a former Lamont graduate student, who for a year had served as a discussion leader in Columbia College's freshman Frontiers of Science course. I suggested that before returning home to Taiwan she do one year of postdoctoral research under my direction. One of the projects I dangled before her was measuring the contribution of coccoliths to the  $\text{CaCO}_3$  in Ontong-Java Plateau cores. She bit.

We decided to split the material into four size fractions:  $<20 \mu$ ,  $20\text{--}38 \mu$ ,  $38\text{--}63 \mu$ , and  $>63 \mu$ . The small fractions were examined by electron microscopy. We found that the  $<20\mu$   $\text{CaCO}_3$  entities were dominantly coccoliths and the  $20\mu\text{--}38\mu$   $\text{CaCO}_3$  entities were dominantly juvenile foraminifera shells and shell fragments. In the core-top sample from a 2.3-km depth core



PHOTO CREDIT: G. HAARHOFF

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**Figure 4**

Steve Barker.



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**Figure 5**

Tzu-Chien Chiu.

(where little dissolution had occurred), roughly half of the  $\text{CaCO}_3$  was supplied by coccoliths ( $<20\ \mu$ ) and approximately half was supplied by foraminifera ( $>20\ \mu$ ).

The surprise came when Tzu-Chien Chiu made similar measurements on an Ontong-Java core top from a 4.0-km core. She found that the ratio of foraminiferal  $\text{CaCO}_3$  to coccolith  $\text{CaCO}_3$  was 2.5 times lower than that in the shallower core. On the basis of radiocarbon-derived accumulation rates and the assumption that the  $\text{CaCO}_3$  rain was the same at these two nearby sites, she found that whereas approximately 75% of the foraminiferal  $\text{CaCO}_3$  had dissolved, only approximately 7% of the coccolith  $\text{CaCO}_3$  had dissolved (Chiu & Broecker 2008). Not only were coccoliths an important component of our size index, but they were also the dominant component. Further, because nearly the same fraction of foraminifera  $\text{CaCO}_3$  was dissolved from each of the three larger size fractions and because no foraminifera fragments appeared in the  $<20\text{-}\mu$  fraction, shell breakage clearly produced mainly fragments greater than  $63\ \mu$  in size. So what we had viewed for so long as a fragmentation index had nothing to do with fragmentation. Rather, it was a measure of the differential dissolution of foraminifera and coccoliths!

In an attempt to document whether the dissolution that took place at 4.0-km depth occurred on the sea floor or within the sediment, we obtained radiocarbon ages on the  $<20\text{-}\mu$  and  $>20\text{-}\mu$  material. To the extent that the dissolution of the foraminifera calcite occurred within the sediment, the  $^{14}\text{C}$  age should have been smaller than that of the coccolith calcite. But what we found was that the foraminifera fraction age was consistently older than that for the coccolith fraction (**Table 1**). Puzzled by this result, we did similar paired  $^{14}\text{C}$  analyses for six other samples. As shown in **Table 1**, in every one, be it deep or mid-depth, Ontong-Java (Pacific) or Ceara Rise (Atlantic), Holocene or glacial, we found the same thing—the foraminifera were always older than the coexisting coccoliths. Although the analysis on the 4.0-km depth core appeared to confirm that the dissolution must have occurred largely before burial, we were puzzled by the consistency of the sign of the age difference.

Only one explanation has come to mind. We call it the cereal box effect. It is well known that a size sorting occurs when a cereal box is shaken. The small grains are concentrated toward the bottom and the large grains toward the top. There is no mystery as to why this occurs: The small grains slip through the interstices separating the big grains. But it is obvious that this effect could not occur in sticky sediment. Rather, worms must be called upon to preferentially ingest small particles and then defecate them in the lower portion of the mixed layer. In this case, the ratio of large to small grains would decrease with depth in the bioturbated zone and as a consequence, the

**Table 1 Radiocarbon results on size fractions from cores on the Ontong-Java Plateau in the western equatorial Pacific and from the Ceara Rise in the western equatorial Atlantic. The  $<20\text{-}\mu$  size fraction is made up entirely of coccoliths, and the  $>20\text{-}\mu$  fraction is made up entirely of foraminifera shells and shell fragments (Chiu & Broecker 2008)**

Core number and location	Depth (cm)	$^{14}\text{C}$ age of $\text{CaCO}_3$ ( $>20\ \mu$ ) (years)	$^{14}\text{C}$ age of $\text{CaCO}_3$ ( $<20\ \mu$ ) (years)	$\Delta^{14}\text{C}$ age (years)
MW91-9GGC 15	10–11	7890	6505	1385
0.0° 158°E 2.31 km	42–43	18,690	16,860	1830
MW91-9BC 56	3–4	4815	4120	695
0.0° 162°E 4.04 km	13–14	9390	8290	1100
MW91-9GGC 55	22–23	20,590	18,660	1930
0.0° 162°E 4.04 km				
EW92-9JPC 3	8–9	7365	6075	1290
5.3°N 44.3°W 3.29 km	70–71	12,090	10,610	1480

**Table 2** Profile of size-fraction CaCO<sub>3</sub> distribution in equatorial core MW91-9 BC37 from 2.45-km water depth on the Ontong-Java Plateau. The entries are percents of the total CaCO<sub>3</sub> in four size fractions. The results fail to show any enrichment of foraminifera in the upper portion of the bioturbated zone. Samples provided by Daniel McCorkle, Woods Hole Oceanographic Institution

Depth in core (cm)	Coccoliths >20 μ (%)	Foraminifera		
		20–38 μ (%)	38–63 μ (%)	>63 μ (%)
0–1	48.7	4.2	6.0	41.1
3–4	45.8	5.3	7.8	41.1
6–7	39.6	3.6	6.5	50.3
9–10	42.6	6.3	6.2	44.9

larger grains (i.e., the foraminifera shells) would have a longer residence time in the mixed layer than the small grains (i.e., the coccoliths). High on our list of things to do is to get a series of samples from one of Dan McCorkle's box cores and attempt to confirm the existence of a gradient in size. This test was performed and no size distribution gradient with depth in the mixed layer was found (Table 2).

## HOLOCENE CARBONATE ION DECLINE

Thwarted by our inability to come up with a dissolution index whose calibration is independent of growth conditions, we happened upon a problem for which it could be assumed that these conditions had likely remained unchanged: the ocean's role in the 20-ppm rise in atmospheric CO<sub>2</sub> content during the past 8000 years. For example, if this increase was the result of the deposition during the Holocene of CaCO<sub>3</sub> in shallow tropical reefs and lagoons, then it should have been accompanied by a 6-μmol/kg decrease in the carbonate ion content of deep sea water. Conversely, if this increase was the result of a weakening of the biologic pump, then no change in deep ocean carbonate ion concentration would have occurred. To determine which category of explanation applies, we turned to two of McCorkle's box cores from the Ontong-Java Plateau: one from 2.37-km depth and the other from 4.04-km depth. To check the assumption that growth conditions had remained unchanged, we made down-core size-index and shell-weight measurements on the shallower core and found that, as hoped, both showed no trend over the past 10 kyrs. We were pleased to find that the measurements on the deeper core revealed a decrease in both size index and shell weight during the past 8 kyrs. This decrease eliminated from contention the biological pump explanation, but it also created a dilemma. Although the reduction in carbonate ion content indicated by the decrease in size index ( $8 \pm 2 \mu\text{mol/kg}$ ) was more or less consistent with expectation, the reduction in carbonate ion content indicated by the decrease weight of *Pulleniatina obliquiloculata* shells ( $19 \pm 6 \mu\text{mol/kg}$ ) was far larger than expected (Broecker & Clark 2007). Making matters more complicated, the radiocarbon age of the core-top CaCO<sub>3</sub> (4 kyr) requires that these decreases must be considered minima, because they record what occurred during only approximately half of the 8-kyr time interval.

I have no ready answer as to why the two results differ. Perhaps it is because the size index is nonlinear. As dissolution proceeds, the solution-resistant foraminifera, such as *Globorotalia menardii*, become dominant as the solution-prone foraminifera, such as *Globigerinoides sacculifer*, dissolve away. If this is the case, then the core-top age-corrected decrease in carbonate ion concentration based on shell weights (>24 μmol/kg) is at least four times larger than the expected drop associated with the atmospheric CO<sub>2</sub> rise (6 μmol/kg). One possible explanation is that during the course of the Holocene the contribution to the deep water mix of the higher preformed

carbonate ion concentration deep water formed in the northern Atlantic has decreased relative to that of the lower preformed carbonate ion concentration deep water formed in the Southern Ocean. However, it is a stretch to attribute the missing 18 or so  $\mu\text{mol/kg}$  to a change in this mix. Clearly, flies remain in the ointment for even this seemingly straightforward application.

## YET ANOTHER STRATEGY

Encouraged by the observation that the record from an intermediate depth core could serve as a reference, we extended the record for two Ontong-Java Plateau cores back to approximately 150 kyrs. As a reference we selected piston core VM24-109 from a depth of 2.37 km. For the dissolution record we selected a nearby giant gravity core from 4.04-km depth.  $^{18}\text{O}$  and the fraction of foraminifera  $\text{CaCO}_3$  for these two cores are shown in **Figure 6**. As can be seen, despite the presumably similar rain rates at the nearby sites, because of dissolution the accumulation rate in the deeper core is half that in the shallower core.

In the shallow core the size index reaches its highest values adjacent to the two Terminations and its lowest values in MIS 5. If, as hoped, dissolution at 2.37-km depth was minimal, then these variations would have to be attributed to changes in the rain ratio of foraminifera to coccoliths. Stephen Barker examined the  $>150\text{-}\mu$  fraction in four samples and found that there was twice as much breakage in the two samples with low foraminifera to coccolith ratios than in the two with high ratios (S. Barker, personal communication). This finding certainly undermines our reference core strategy.

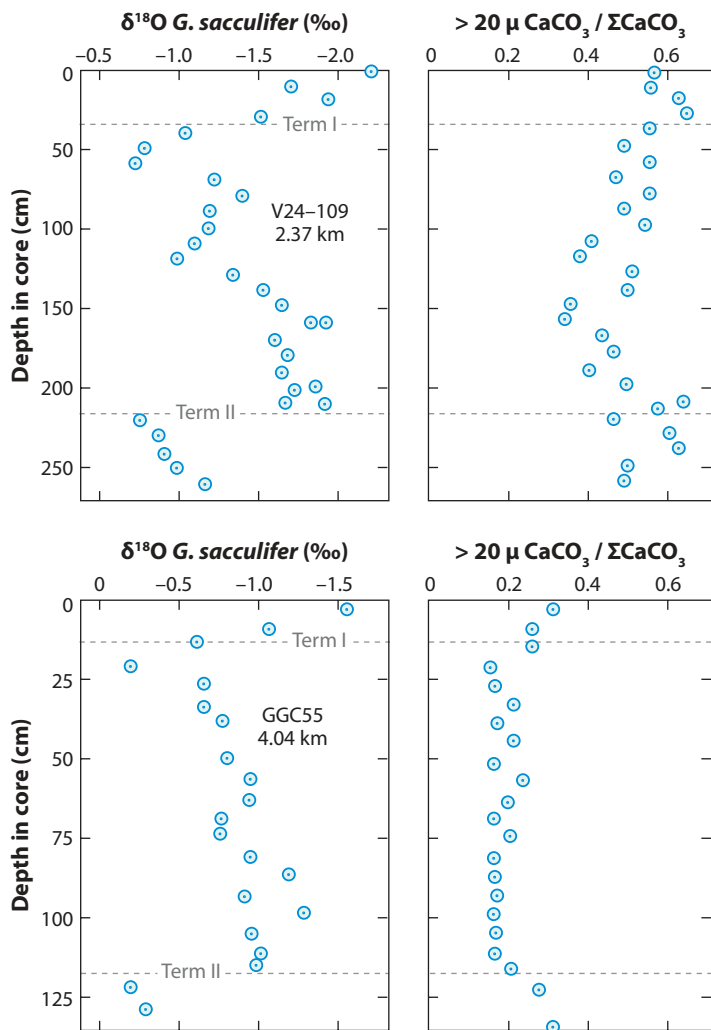
The size indices for the deeper core samples are all considerably lower than those from the shallower core. Putting aside the samples adjacent to the two Terminations, the average ratio of 0.18 in the deep core is approximately 2.5 times lower than the average ratio of 0.48 in the shallow core, a result similar to that found in Chiu & Broecker (2008). So despite our concerted efforts, we have not come up with a satisfactory dissolution index!

## THE PALEOCENE-EOCENE THERMAL EVENT

Yet another problem that requires an understanding of the factors that control the depth of the saturation horizon involves the so-called Paleocene-Eocene thermal event (PETM), an abrupt warming that occurred 55 mya at the Paleocene-Eocene boundary. Well-recorded by oxygen isotope ratios in the shells of planktonic foraminifera from a number of cores taken as part of the Deep Sea Drilling Program, these warmings ranged from 5–9°C in magnitude (Zachos 2005). That this warming was brought about by the addition of a large amount of  $\text{CO}_2$  gas is documented by a prominent dissolution event recorded in a series of deep sea cores from the Walvis Ridge (Zachos et al. 2005). This event is of particular interest because it constitutes an analog for the ongoing buildup of fossil fuel  $\text{CO}_2$ . If the increase in atmospheric  $\text{CO}_2$  responsible for the warming could be reconstructed, it would serve as an index of the sensitivity of the Earth's temperature to greenhouse gases.

Colloquia presented at Lamont-Doherty by Jim Zachos and by Dan Schrag fostered discussions with my colleague Dennis Kent regarding various aspects of the problem. These ranged from the source of the carbon to the details of the stable isotope and  $\text{CaCO}_3$  results. As outlined below, some tantalizing unresolved puzzles regarding the ocean's response currently occupy my aging mind.

The  $^{18}\text{O}$  shift in foraminifera shells is accompanied by a  $\Delta\delta^{13}\text{C}$  of 2–3‰, suggesting that the source of the  $\text{CO}_2$  is  $^{13}\text{C}$ -depleted carbon (Kennett & Stott 1991). One scenario for the origin of this  $\text{CO}_2$  involves the oxidation of methane released from continental margin clathrates



**Figure 6**

Oxygen isotope measurements on *G. sacculifer* shells and size index results for two Ontong-Java Plateau cores, VM24-109 and GGC55. The size index is the fraction of  $\text{CaCO}_3$  in foraminifera (i.e.,  $> 20 \mu$ ) to that in coccoliths (i.e.,  $< 20 \mu$ ) plus that in foraminifera.

(Dickens et al. 1995). Another scenario involves the oxidation of organic matter in the sediment exposed when an epeiric sea desiccated (D. Schrag, personal communication). Still another scenario involves the oxidation of carbon compounds delivered by the impact of a comet (Cramer & Kent 2005). If the  $^{13}\text{C}$  to  $^{12}\text{C}$  ratio for this carbon were known, it would allow the magnitude of the  $\text{CO}_2$  input to be estimated. But the ratio depends on the source. For example, methane hydrates are more  $^{13}\text{C}$  depleted than marine organic matter. Further, all that can be said for cometary carbon is that the  $\delta^{13}\text{C}$  likely lies somewhere in the range of 0 to  $-50\text{‰}$  (Messenger 2000).

If we are to understand what the  $\text{CaCO}_3$  record for the PETM is trying to tell us, one requirement is to characterize the chemistry of the ocean-atmosphere system prior to the event. Unfortunately, with current knowledge only two pieces of paleo information are obtainable. One



is based on the depth of the calcite saturation horizon. When combined with the  $^{18}\text{O}$ -based temperature of deep ocean water, this tells us the product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^-$  ions in the deep ocean. The other is based on the difference between the  $^{13}\text{C}$  to  $^{12}\text{C}$  ratio in nutrient-deficient (i.e., oligotrophic) surface water, and that in deep water in the Pacific Ocean, i.e.,  $\Delta\delta^{13}\text{C}$ . Then,

$$\Sigma\text{CO}_2 = \text{PO}_4^{\text{resp}} \times \left(\frac{\text{C}}{\text{P}}\right)_{\text{org}} \times \frac{\Delta\delta^{13}\text{C}_{\text{photo}}}{\Delta\delta^{13}\text{C}},$$

where  $\Sigma\text{CO}_2$  is the concentration of total dissolved inorganic carbon in deep Pacific water,  $\text{PO}_4^{\text{resp}}$  is the difference between the  $\text{PO}_4^{\text{total}}$  and  $\text{PO}_4^{\text{preformed}}$  in Pacific deep water,  $(\text{C}/\text{P})_{\text{org}}$  is the carbon to phosphorus ratio in organic matter oxidized in the deep Pacific Ocean, and  $\Delta\delta^{13}\text{C}_{\text{photo}}$  is the carbon isotope fractionation during photosynthesis. The Paleocene CCD depth was close to today's value (Van Andel, 1975) and because the temperature dependence of solubility of calcite is small, it can be assumed that the product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^-$  ion concentrations was similar to that of today.  $^{13}\text{C}$  data (B. Cramer, personal communication) suggest that during the Paleocene the Pacific surface to deep Pacific  $\Delta\delta^{13}\text{C}$  was approximately 1.5‰. In addition, estimates of  $\text{PO}_4^{\text{resp}}$ ,  $(\text{C}/\text{P})_{\text{org}}$ , and  $\Delta\delta^{13}\text{C}_{\text{photo}}$  must be made for the Paleocene. Although it is reasonable to assume that the latter two were similar to today's values, the  $\text{PO}_4^{\text{resp}}$  concentration must be pretty much pulled out of the air. If we had it, we could estimate the  $\Sigma\text{CO}_2$  in the pre-PETM ocean.

I have long been impressed by the observation that  $\text{O}_2$ -free waters do not exist in today's abyssal oceans. Only in the Black Sea and along those continental margins subject to intense upwelling are such waters to be found. Furthermore, the presence of shells of benthic foraminifera in all Cenozoic sediments suggests that this has been the case for the past 60 million years. My read on this is that a feedback involving  $\text{PO}_4$  occurs. If a sizable area of the deep sea were to go anaerobic, then as a result burial in the underlying sediment would draw down  $\text{PO}_4$  to the point where the  $\text{O}_2$  demand was reduced until anaerobic conditions were eliminated. As a result I feel that the ratio  $\text{PO}_4^{\text{resp}}$  cannot exceed a fixed limit given by

$$\text{PO}_4^{\text{resp}} < \text{O}_2^{\text{deepsea}} \times \left(\frac{\Delta\text{PO}_4}{\Delta\text{O}_2}\right)_{\text{resp}}.$$

If it is assumed that during the Paleocene the Redfield ratios for raining organic matter and the  $\text{O}_2$  partial pressure in the atmosphere were similar to those of today, then the upper limit of  $\text{PO}_4^{\text{resp}}$  would have differed only because during the Paleocene the deep ocean was approximately  $10^\circ\text{C}$  warmer than today and hence  $\text{O}_2^{\text{preformed}}$  was approximately half of today's value. Therefore, I guess that the  $\text{PO}_4^{\text{preformed}}$  was approximately half of today's value. If so,

$$\begin{aligned} \Sigma\text{CO}_2^{\text{pal}} &= \frac{\text{PO}_4^{\text{resp pal}}}{\text{PO}_4^{\text{resp tod}}} \times \frac{\Delta\delta^{13}\text{C}^{\text{tod}}}{\Delta\delta^{13}\text{C}^{\text{pal}}} \Sigma\text{CO}_2^{\text{tod}} \\ &\cong \frac{1}{2} \times \frac{2}{1.5} \times 2200 \cong 1500 \text{ } \mu\text{mol}/\text{kg}. \end{aligned}$$

The important point is that the  $\Sigma\text{CO}_2$  concentration was likely not much different from today's value. Taken together with the fact that the product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^-$  in the deep Pacific was probably close to today's value, unless the ocean's Ca content was much different, the  $\text{CO}_3^-$  concentration must also have been similar to today's value. Hence one would expect, as in today's ocean, that the response time of  $^{13}\text{C}$  should have been an order of magnitude longer than that of carbonate ion. But the record suggests that these response times were similar. Both appear to have been on the order of  $10^5$  years (Zachos et al. 2005).

With this puzzle in mind, another aspect of the record caught my attention, involving the single-shell foraminifera  $^{13}\text{C}$  record for site 690 reported by Thomas et al. (2002). Whereas surface-dwelling planktics undergo a discontinuous 4‰ decrease in  $\delta^{13}\text{C}$  at 170.78-m depth, the discontinuous drop in  $^{13}\text{C}$  for thermocline-dwelling foraminifera occurs 0.12 m up-core. On the basis of the sedimentation rate of approximately 1 cm kyr<sup>-1</sup> (Farley & Eltgroth 2003), the elapsed time between these two changes is on the order of 10 kyrs. The  $^{13}\text{C}$  drop for benthic foraminifera occurs approximately 0.40 meters up-core from that for surface dwelling planktics, i.e., approximately 40 kyrs later. One explanation for these offsets would be that the large PETM warming stagnated the ocean, cutting off renewal of subsurface waters until some combination of downward mixed and geothermal heat warmed the ocean interior to the point where convection could be renewed.

But this explanation raises two big problems. One is that to acidify the deep ocean and thereby produce the observed drop in  $\text{CaCO}_3$  content downward, mixing must have occurred. The other is that during the 40,000 years of isolation, the deep ocean should have become anaerobic. However, the presence of benthic foraminifera rules this out.

## CONCLUSIONS

Forty-five years of pondering has yet to exhaust my interest in the  $\text{CaCO}_3$  cycle, nor has it led to satisfactory solutions for any of the problems I have tackled. Whether it involves glacial to interglacial time scales or the entire Cenozoic, much research remains to be done. As nature carefully protects her secrets, the greatest pleasure a scientist can get is to pry one loose. In the case of paleocean chemistry, these secrets are recorded mainly in calcite.

## DISCLOSURE STATEMENT

The author is not aware of any biases that might be perceived as affecting the objectivity of this review.

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## Errata

An online log of corrections to *Annual Review of Marine Science* articles may be found at <http://marine.annualreviews.org/errata.shtml>