What Corals are Dying to Tell Us About CO, and Ocean Acidification

BY KEN CALDEIRA

Remarks from the eighth annual Roger Revelle Commemorative Lecture. This lecture was created by the Ocean Studies Board of the National Academies in honor of Dr. Roger Revelle to highlight the important links between ocean sciences and public policy. This year, the speaker was Ken Caldeira, and the lecture was held on March 5, 2007, at the Baird Auditorium in the Smithsonian National Museum of Natural History in Washington, D.C.

Emissions of carbon dioxide are causing the oceans to become more acidic. Recent experiments show that this ocean acidification threatens many ocean ecosystems. The ancient past may provide a cautionary tale, indicating what might happen if we change ocean chemistry too much too fast.

AN EXTINCTION EVENT 65 MILLION YEARS AGO

Sixty-five million years ago, a comet slammed into the Yucatán Peninsula, just north of what is now the Mexican city of Merida (see Pope et al., 1998 for a review). This comet, perhaps six miles in diameter, would have ejected enough soot and dust into the atmosphere to blot out the sun for months or longer. The ensuing cold and darkness would have caused the widespread death of plants and the animals that fed on them (Pope et al., 1997). This event, known as the Cretaceous-Tertiary boundary

KEN CALDEIRA (kcaldeira@globalecology. stanford.edu) is a senior staff member in the Department of Global Ecology, Carnegie Institution of Washington, Stanford, CA, USA. extinction, marked the end of the dinosaurs that walked on land. Every land animal larger than a cat disappeared.

This massive extinction event also affected the oceanic realm (Zachos et al., 1989). Marine Plesiosaurs became extinct, as did many other marine organisms. The pattern of marine extinctions at the end of the Cretaceous tells a cautionary tale for the future.

Surface waters are the most productive areas of the ocean, the site where nutrients and sunlight are converted into foodstuffs by the photosynthetic activity of marine algae, particularly microscopic phytoplankton. The most productive areas are found in coastal waters, which serve as nursery areas for many marine species. In the open ocean, the productivity of the surface waters also supports life in the depths—the remains of upperocean organisms sink to the bottom and feed the deep-dwelling animals that never see sunlight.

Clams, oysters, reef-building corals, and many other creatures in shallow- and deep-water ecosystems build calcium carbonate shells and skeletons. Calcium carbonate structures can also be found in minute organisms, such as some types of phytoplankton and the foraminifera, unicellular marine amoebae (Figure 1).

Calcium carbonate is key to understanding what happened at the Cretaceous-Tertiary extinction event. The word "Cretaceous" comes from the Latin word creta, meaning chalk, a form of calcium carbonate. The famous white cliffs of Dover consist of chalk deposited during the Cretaceous period in the form of billions of shells of microscopic organisms. These organisms were mostly coccolithophores, single-celled algae enclosed within calcium carbonate shells. Hence, the Cretaceous is named for the chalky deposits produced by abundant marine microorganisms with calcium carbonate shells.

But, when the comet slammed into Earth at the end of the Cretaceous, everything changed. Just about every marine species that built shells or skeletons out of calcium carbonate became either rare or extinct. Coral reefs disappeared from the fossil record for at least two million years. Nearly all plankton with calcium carbonate shells became extinct, not to return for another half million years or so. Many species of



Image: D. Reef CoralImage: E. Sea UrchinImage: E. Sea UrchinImage: D. Reef CoralImage: E. Sea UrchinImage: E. Deep Sea Coral

Figure 1. Many marine organisms make shells or skeletons out of calcium carbonate. Upper row: pelagic organisms that live in the open ocean. Lower row: benthic animals that live in shallow habitats (D and E) or in deep waters (F). All of these organisms are threatened by ocean acidification, but the corals and pteropods appear to be most at risk. A. USGS; B. Victoria J. Fabry, California State University San, Marcos; C. Jeremy Young, The Natural History Museum, London, UK; D-F. NOAA

mussels disappeared. About ten million years passed before marine ecosystems re-evolved the wealth of carbonate species that were found before the extinction event. On the other hand, diatoms—phytoplankton with shells made of silica—persisted through the extinction event. Dinoflagellates—a kind of plankton that forms a plastic-like cyst in sediments—also survived this event unharmed. In addition, many organisms that lived on the deep seafloor seemed to have survived, even if they had shells or skeletons that were made of calcium carbonate.

What could explain this pattern of extinction? Nearly every organism that lived in the upper ocean and used calcium carbonate to build its shell or skeleton died off during the Cretaceous extinction event. Organisms that lived in the deep ocean or did not need calcium carbonate had a much better chance of survival.

The comet that struck the Yucatán blasted a giant crater, now hidden beneath more recent sediments (Figure 2). The Yucatán Peninsula is basically a giant block of calcium carbonate—formed from the skeletons of ancient marine organisms—but including significant amounts of calcium sulfate (the substance used in making gypsum wallboard).

When the comet blasted into the Yucatán, the impact heated the calcium

sulfate to high temperatures and pressures very rapidly, and this caused the release of sulfur dioxide and other sulfur compounds into the atmosphere. In the atmosphere, these compounds reacted with oxygen and water to form sulfuric acid. Even if as little as 5% of the sulfur released by the impact of the comet were to rain down on the ocean as sulfuric acid, it would still be enough to make upper-ocean waters corrosive to the calcium carbonate shells and skeletons of marine organisms.

The pattern of extinction that occurred in the ocean at the Cretaceous-Tertiary boundary could be explained by the sequence of events that acidified the upper ocean. However, the amount of sulfur that rained down on the ocean would not have been enough to acidify the entire ocean. Within a few years, the acidic surface waters would have mixed with the vast waters of the ocean depths, restoring the chemistry of the upper ocean to an environment suitable for corals, coccolithophores, and other carbonate-shelled creatures. But it was too late—they were already gone.

Because the upper ocean acidification lasted only a year or two, some corals managed to survive the harsh environmental change and prospered when the conditions improved. But, it took two million years for them to become abundant enough to leave a trace in the fossil record and ten million years before corals recovered to their pre-extinction levels of diversity. And, it took 500,000 years before new species of calcium-carbonateproducing plankton evolved from their shell-less cousins. Again, it took many more millions of years to recover preextinction levels of species diversity.



Figure 2. The extinction of the dinosaurs is linked to the impact of a comet 65 million years ago. The comet hit Earth near the northwest tip of the Yucatán Peninsula (A) and formed a crater (B), named Chicxulub, that is roughly 180 km in diameter. The image in B is a horizontal gradient map of the Bouguer gravity anomaly over the Chicxulub crater. The Yucatán coast is shown as a white line. A striking series of concentric features reveals the location of the crater. A. NASA; B. Alan Hildebrand, Mark Pilkington, and Martin Connors



CARBON DIOXIDE, OCEAN CHEMISTRY, AND MARINE LIFE

So, what is the relevance of this ancient extinction event for our modern marine environment? The burning of fossil fuels produces carbon dioxide, a greenhouse gas that causes atmospheric warming and drives climate change. An early paper describing this effect was written in 1896 by the Swedish chemist Svante Arrhenius. The title of the paper was, "On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground." Why did Svante Arrhenius refer to carbonic acid rather than carbon dioxide?

Carbon dioxide dissolved in water forms carbonic acid, much in the same way that sulfur oxides become sulfuric acid (Doney, 2006). In the late nineteenth century, it was common to refer to CO_2 as "carbonic acid" because this reaction took place so readily. Could the "carbonic acid" that we are releasing into the atmosphere from the burning of fossil fuels have the same effect on the marine environment that sulfuric acid had 65 million years ago at the end of the Cretaceous period?

To answer this question, we need to understand something about Earth's long-term carbon cycle. Carbon dioxide is naturally supplied to the atmosphere, ocean, and biosphere by various geologic sources, such as volcanoes, terrestrial hydrothermal vents (such as those at Yellowstone National Park), and undersea mid-ocean ridge hydrothermal vents. In round numbers, these sources add up to about a half a billion tons of carbon dioxide per year. This carbon dioxide accumulates in the atmosphere, traps heat, and prevents Earth from sinking into a deep freeze. But, if carbon dioxide kept accumulating in the atmosphere, Earth would become an oven because it would retain too much heat.

On Earth, silicates, such as granites and basalts, are the most common type of rock. Most of Earth's deep interior is made up of silicate rocks. On the surface, these rocks begin to dissolve as they are rained upon or come into contact with groundwater in the presence of carbon dioxide. This process is known as chemical weathering. When silicate rocks dissolve, they release calcium and other minerals into waters that eventually pour into the ocean. Release of calcium through chemical weathering of silicate rocks followed by the production of calcium carbonate shells and skeletons by marine organisms has removed carbon dioxide from the atmosphere for most of Earth's history. The balance between geologic degassing of carbon dioxide and the weathering and subsequent deposition of carbonate shells and skeletons is what has kept Earth's climate stable over billions of years.

In the Cretaceous, 100 million years ago, it is thought that volcanoes were releasing carbon dioxide perhaps twice as rapidly as they do today. As a result, Earth warmed up, and in the warm, moist environment, silicate rocks dissolved about twice as rapidly, releasing twice as much calcium and driving the formation (and sedimentation) of calcareous marine shells and skeletons. In short, the carbon cycle ran about



Figure 3. Over the past few decades, atmospheric CO_2 has been changing about one hundred times more rapidly than it has changed over the past several hundred thousand years. These graphs show rates of atmospheric CO_2 change in (left) the glacial-interglacial period (thousands of years before present) and (right) in recent time (1950s to present). The ocean's natural chemical buffering system is unable to keep up with these rates of change. *Data from (left) Petit et al. (1999), and (right) Keeling and Whorf* (2005)

twice as fast as it was naturally running up until recent times, but the system remained in balance.

Through fossil-fuel use, we are now emitting 25 billion tons of carbon dioxide into the atmosphere each year. This is nearly 100 times greater than the natural emissions of carbon dioxide from volcanoes and other natural geologic sources (Figure 3). In other words, if we were to cut carbon dioxide emissions to just 2% of current emissions, this would still be enough to double the natural sources of carbon dioxide. Just 2% of current carbon dioxide emissions, if sustained over a long period of time, would be enough to produce the warmer climate experienced on our planet 100 million years ago.

In contrast to current trends, at 2% of today's rate, carbon dioxide would gradually build up in the atmosphere. As the climate warmed, weathering would release more silica and calcium and supply the rapid growth of corals and other calcifying marine organisms—it would be like another Cretaceous. However, we are increasing carbon dioxide by nearly a factor of 100—a whopping 10,000% increase in carbon dioxide emissions. This rate is too high to be balanced by natural weathering processes (Caldeira and Wickett, 2003).

The average person in the world today releases close to 25 pounds (more than 10 kg) of carbon dioxide into the atmosphere each day. The average American emits carbon dioxide about five times more rapidly than the average citizen of the world—over 120 lbs per American per day.

The ocean today is absorbing about 40 lbs (nearly 20 kg) of carbon dioxide each day for each American. With carbon dioxide pollution occurring at this scale, there are bound to be consequences. Even the vast ocean cannot accommodate this scale of pollution, and yet there is barely any appreciation of the impacts of continued fossil fuel combustion on the health of the ocean.

To fully understand the consequences of excess carbon dioxide emissions requires an understanding of carbonic acid chemistry. One thing that all acids have in common is that they increase the activity of hydrogen ions in water—in essence, acids increase the effective concentration of hydrogen ions in water.

Now, let's think about a coral polyp or marine alga trying to assemble a skeleton or shell out of calcium carbonate, which is the product of a positively charged calcium ion, Ca^{2+} , and a negatively charged carbonate ion, CO_3^{2-} . To form calcium carbonate, the coral must be able to absorb both of these ions from seawater. The addition of carbonic acid to seawater (through CO_2 in the atmosphere) produces excess hydrogen ions that react with CO_3^{2-} to form HCO_3^{-} , thereby decreasing the availability of CO_3^{-} to corals and other calcifying organisms (Figure 4).

Currently, the ocean is absorbing carbon dioxide at about one-third the rate that Americans are producing it—the remainder is accumulating in the atmosphere. Although the surface ocean absorbs carbon dioxide quickly, it will take about a thousand years to mix carbon dioxide released today throughout the deep ocean because the upper ocean mixes slowly with the deep ocean (Caldeira and Wickett, 2003, 2005; Orr et al., 2005). With continued emissions over the next century or two, the surface waters will continue to acidify, and even the deep waters of the ocean will be affected (Figure 5).

At today's concentrations, the additional carbon dioxide simply makes it more difficult for many marine organisms to survive. At higher concentrations, the calcium carbonate shells and skeletons of marine organisms will actually start to dissolve. If current carbon dioxide emission trends continue, shells of marine organisms will start dissolving in some parts of the ocean sometime around mid-century.

RESEARCH INTO BIOLOGICAL EFFECTS OF OCEAN ACIDIFICATION

While a few lone scientists were concerned some decades ago about the chemical effects of carbon dioxide on the marine environment, interest really





picked up within the past ten years as a result of a number of experiments on marine organisms and several modeling studies that predict future ocean carbon dioxide concentrations. However, as a field of research, this work is still in its infancy. The following is a very subjective short history that mentions just a few names. I apologize in advance to those who made important contributions that I fail to mention.

In the late 1980s, Brad Opdyke, then working at the University of Michigan, inferred from the geologic record that the chemical condition of the ocean controls the rate of production of carbonate shells and skeletons in the marine environment over geologic time scales. Several researchers, including Chris Langdon from the University of Miami and Jean-Pierre Gattuso (Gattuso et al., 1998) in Villefranche, France, performed experiments on tropical corals that showed coral growth rates slowing dramatically as CO₂ concentrations increased. Joanie Kleypas, at the National Center for Atmospheric Research in Boulder, Colorado, led a ground-breaking study (which included Opdyke, Langdon, and Gattuso) combining model predictions of future ocean chemistry with results coming out of laboratory experiments on corals. This study concluded that coral growth would be severely impeded later this century.

Although the Kleypas et al. (1999) study was alarming, the situation on a natural tropical reef is likely to be even more disturbing. Laboratory experiments examining the effect of high CO_2 on coral growth did not account for predation on corals. In the real world, corals need to grow rapidly enough to keep up



Figure 5. Acidification will continue even if CO₂ emissions are curtailed. Three graphs illustrate anthropogenic CO, emissions (top), atmospheric CO, concentrations (middle), and ocean pH (bottom). Even if emissions are curtailed over the next 250 years, the ocean will continue to acidify as it absorbs more of the atmospheric CO₂, reaching levels that have not been experienced by marine ecosystems for many tens of millions of years.

with the animals that prey on them, a process called bioerosion. Furthermore, sea grasses and other organisms compete for the same space that the corals occupy. For corals to persist in the wild, they must outgrow their predators and their competitors (Figure 6).

Another approach is to evaluate the environmental conditions where corals live today. Tropical corals live in shallow waters (they don't grow below about 150-m water depth) where the calcium carbonate building blocks are readily available. As suggested by Brad Opdyke nearly 20 years ago, the availability of these building blocks largely determines whether the corals can grow rapidly enough to survive bioerosion and ecological competition.

Carbon dioxide dissolves more readily in cold waters, leading to higher concentrations of carbonic acid in the surface waters of polar and subpolar regions. Coral reefs are not found in these colderwater environments. We can characterize the chemistry of the waters in which shallow coral reefs are found today and contrast it with conditions expected later this century under the current trend in carbon dioxide emissions (Figure 7). In several decades, where will the ocean have chemical conditions similar to those where corals are found growing today? The answer is, "Nowhere."

Does this mean that we will do to the ocean over the course of this century what a comet did to the ocean over the course of a single afternoon? Will shallow-water corals go extinct this century, perhaps to re-evolve in several million years?

Nobody can say for sure. First, we could dramatically reduce our carbon



Figure 6. Effect of predation on corals. In the natural world, corals need to grow rapidly enough to withstand predation by fish and other organisms and to compete for space with algae and sea grasses. Ocean acidification reduces the ability of corals to compete ecologically. Hence, the decline of coral reefs could be more rapid than predicted based on laboratory studies of the effects of acidification. *Frank and Joyce Burek*

dioxide emissions, and that would allow corals to survive. Second, corals might be better able to withstand bioerosion and maintain the edge over competitors more effectively than appears at present. (No evidence has been presented in the lab or field suggesting that corals might be able to undergo evolutionary adaptation to survive a more acidified ocean.) Therefore, there is at least a reasonable expectation that if current carbon dioxide emission trends continue, corals will not survive this century.

Today's carbon dioxide emissions may be worse for the ocean than the sulfuric acid rain that fell 65 million years ago. After the comet hit the Yucatán, ocean acidification only lasted at most a year or two until the surface waters were diluted by mixing with deeper ocean waters. In contrast, the ocean acidification event of the present is likely to last many thousands of years, much longer than the lifetime of a coral polyp.

And it's not just corals that are vulnerable. Vicky Fabry at the California State University at San Marcos has been studying sea snails, called pteropods, that live in the open waters of the Southern Ocean (Fabry, 1990). These snails may consume up to half of the algal growth in that area, forming a critical component of the Southern Ocean food web that eventually feeds the whales and other top predators in the ecosystem. Fabry's experiments indicate that the shells of these snails will dissolve later this century under current projections of carbon dioxide emissions.

Ulf Riebesell at the Leibniz Institute of Marine Sciences in Kiel, Germany, has performed experiments that subject plankton to different carbon dioxide conditions (Riebesell et al., 2000; Riebesell, 2004). These experiments indicate that plankton are less sensitive



Figure 7. Ocean pH has already decreased by 0.1 unit and may decrease another 0.2 to 0.4 by the end of this century. Left panel: Ocean pH (a measure of acidity) for different latitude bands in preindustrial times, year 2000, and four different scenarios for year 2100. Right panel: Saturation state for two common calcium carbonate minerals, aragonite (e.g., corals, pearls) and calcite (most planktonic organisms). The vertical pink band shows the latitude band where corals commonly grew in preindustrial times (year 1750). The horizontal green band shows that corals are naturally found where the aragonite saturation state is above 3.5. By year 2000, most corals may already have been living in a marginal environment for calcification. All of the projections for year 2100 suggest that ocean pH will fall below what corals have been able to adapt to over the many millions of years of their existence.

to higher CO_2 than corals. However, if CO_2 concentrations continue to increase, plankton also will be unable to construct calcium carbonate shells (Figure 8).

Almost all of these experiments were performed in laboratory environments, not in the field. The few field experiments took place in small enclosures and lasted only a few weeks. Nobody has done the type of long-term experiments necessary to understand how carbon dioxide may affect the reproductive cycles of marine organisms. For example, adult fish may be relatively insensitive to CO₂ changes. Except for the gills, the internal tissues of fish are essentially isolated from ocean chemistry. However, fish eggs and fish larvae may be far more sensitive to changes in ocean chemistry. Even if the fish itself is insensitive to changes in ocean chemistry, its prey may be affected, thus influencing the growth of the fish. The consequences of

acidification on ocean ecosystems will be wide ranging, complex, and difficult to predict—to date, only a few individual species have been studied.

CONCLUSIONS

We know that we are toying with the chemistry of the ocean in a profound way (Raven et al., 2005; Kolbert, 2006; Ruttiman, 2006). We do not know with certainty what the consequences might be. Experiments to date have shown that the chemical changes now occurring in the ocean are likely to be harmful to organisms that build their shells or skeletons out of calcium carbonate. It is likely that a continuation of current trends in carbon dioxide emission will lead to the extinction of corals, which have been around for many millions of years, and may lead to the extinction of other marine species. We do not know what the effects will be on the ecosystems of

the open ocean.

One could speculate that ocean acidification will affect some ocean ecosystems in a way that might be analogous to cutting down a rain forest. Loss of a rain forest means biodiversity is lost. But, invasive, rapidly growing generalists weedy plants—invade and grow. What was once a complex, diverse, ecosystem full of delicate ecological relationships that have developed over the course of evolution, are replaced with simple ecosystems lacking the beauty and diversity and perhaps the resilience of the complex ecosystems they replaced.

In the ocean, the combination of nutrients and light will continue to support living systems. Life is far too robust to be eliminated by a single threat from human activities. But, it may be well within our capability to reduce the complex natural ocean environment to the marine equivalent of weeds.





Preservation of our valued marine ecosystems could also be within our capability. But, it might take reductions in carbon dioxide emissions to very low levels, reductions to levels that may be lower than if global warming were our only concern. Recall that we are now emitting carbon dioxide at a rate that exceeds the natural emission rate by a factor of nearly 100, so that even a 98% reduction in our emissions will more than double the natural carbon dioxide emission rate.

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