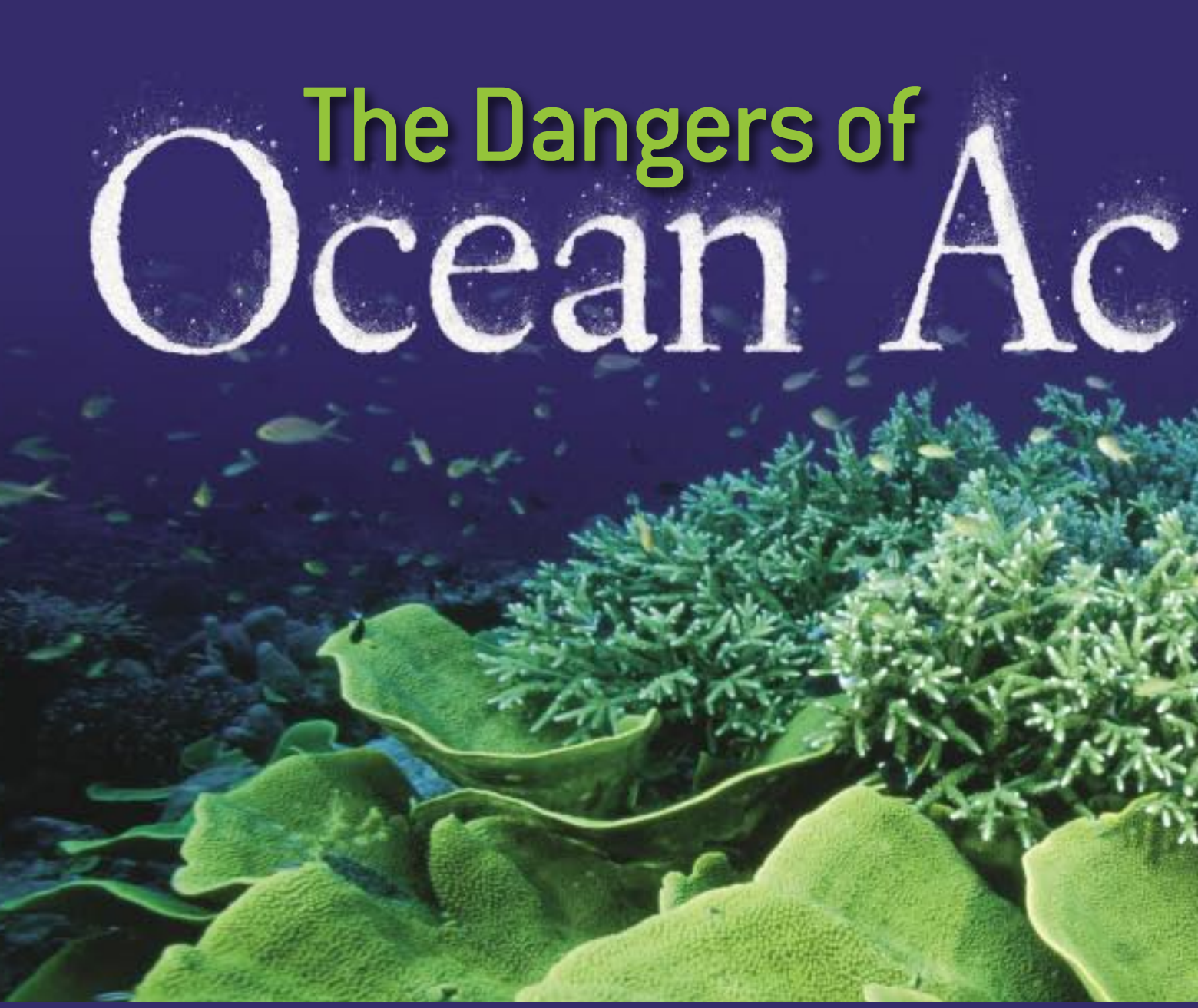
The Dangers of Ocean Ac



Much of the carbon dioxide given off from the burning of acid balance of seawater. The repercussions for marine

trial production of carbon-dioxide over the next 50 years." In other words, they wanted to figure out how dire the situation would be today. That they had to argue the importance of such observations now seems astonishing, but at the time scientists did not know for certain whether the carbon dioxide spewing out of tailpipes and smokestacks would indeed accumulate in the atmosphere. Some believed that it would all be absorbed benignly by the sea or be happily taken up by growing plants on land.

far from industrial activity and vegetation as anyone could get: the South Pole. Another was at a newly established weather station atop Mauna Loa in Hawaii.

The Mauna Loa monitoring has continued (with just one brief interruption) from 1958 to this day. Being not so remote as Antarctica, Hawaii sees carbon dioxide levels rise and fall sharply in step with the Northern Hemisphere's growing season, but at the end of each and every year, the concentration of this heat-trapping gas always ends up higher than it was 12

FRED BAVENDAM *Minden Pictures*

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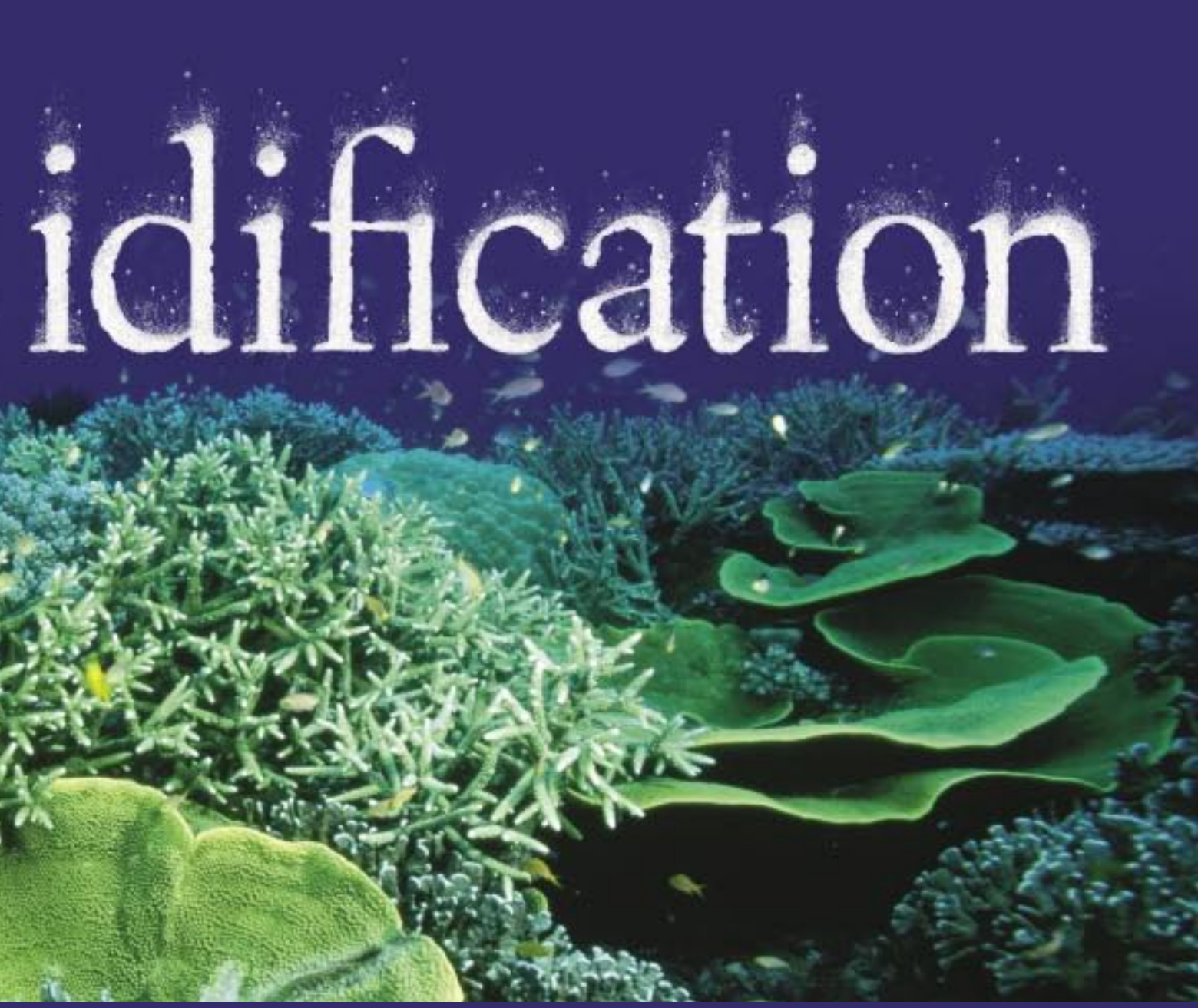


fossil fuels goes into the ocean, where it changes the life may be enormous

BY SCOTT C. DONEY

CORAL REEFS—and the extraordinary biodiversity they support—are under siege from many forces, including exposure to toxic chemicals and direct physical destruction. A less known but perhaps greater threat is the change in ocean chemistry caused by the burning of fossil fuels. Today one third of the carbon dioxide given off in that process enters the ocean, reducing its naturally alkaline pH. This shift toward more acidic conditions diminishes the ability of corals (and many other marine organisms) to grow.

to Revelle long ago that the part that went into the ocean would fundamentally alter the chemistry of seawater. Unlike some aspects of climate change, the reality of this effect—essentially the acidification of the ocean—is not much debated, although its full implications are just now being revealed.

How Unnatural?

THE HALF-CENTURY RECORD that Keeling produced is extremely valuable, but it is too short to place the current situation in context. Scientists have, however, been able to obtain a longer-term perspective by measuring air bubbles trapped in ice cores. From this natural archive they have learned that the atmospheric concentration of carbon dioxide was approximately constant for several thousand years and then began to grow rapidly with the onset of industrialization

in the 1800s. This gas is now about 30 percent more abundant than it was a few hundred years ago, and it is expected to double or triple its former level by the end of this century.

This burgeoning supply of carbon comes largely from the burning of fossil fuels—coal, oil and natural gas. (Cement production and the burning of tropical forests add some, too, but to simplify things, let me gloss over such secondary contributions for the sake of clarity.) Unlike the constituents of living organisms, fossil fuels contain little or none of the radioactive form of carbon: the carbon 14 isotope, which has eight neutrons in the nucleus rather than the usual six. Fossil fuels also display a unique ratio of the two stable isotopes of carbon (carbon 12 and 13). The combustion of these fuels thus leaves a distinctive isotopic signature in the atmosphere. So no one can question where the growing surplus of carbon dioxide comes from.

The ocean has absorbed fully half of all the fossil carbon released to the atmosphere since the beginning of the Industrial Revolution.

Absorption rates can vary, but today about 40 percent of the carbon dioxide derived from fossil fuel remains in the atmosphere; the rest is taken up by vegetation on land or by the ocean, currently in about equal proportions. The injection of fossil-fuel carbon into the sea is, as of yet, a relatively small addition to the ocean's huge natural reservoir of this element. Detecting and quantifying the uptake, therefore, requires especially precise measurements, ones good to at least one part in 1,000. And because the amounts vary substantially from place to place, the task also demands the resources and perseverance to map carbon concentrations throughout the world.

Overview/CO_2 in the Ocean

- About a third of the carbon dioxide (CO_2) released by the burning of fossil fuels currently ends up in the ocean.
- Absorbed CO_2 forms carbonic acid in seawater, lowering the prevailing pH level (which is slightly alkaline) and changing the balance of carbonate and bicarbonate ions.
- The shift toward acidity, and the changes in ocean chemistry that ensue, makes it more difficult for marine creatures to build hard parts out of calcium carbonate. The decline in pH thus threatens a variety of organisms, including corals, which provide one of the richest habitats on earth.
- Within a century, the surface of the Southern Ocean will become corrosive to the shells of tiny snails that form a key link in the marine food chain within this highly productive zone.

Oceanographers did exactly that in the late 1980s and 1990s, as part of a global assessment that went by two acronyms: JGOFS (for Joint Global Ocean Flux Study) and WOCE (for World Ocean Circulation Experiment).

Those surveys, however, did not in themselves identify what part of the carbon measured is natural and what part derives from the carbon dioxide that people have dumped into the air. In 1996 Nicolas Gruber, now at the University of California, Los Angeles, and two of his colleagues developed an innovative technique for doing so. The application of Gruber's method to all the JGOFS and WOCE data, an exercise completed in 2004, suggests that the ocean has absorbed fully half of all the fossil carbon released to the atmosphere since the beginning of the Industrial Revolution.

Another way to document this process is to make repeated measurements of carbon on the same piece of ocean. One must be careful to distinguish the fossil carbon from the various biological sources of this element in the sea. And the observations need to span a decade or more to reveal the overall trend brought on by the burning of fossil fuels against the background of natural variability. Last year Rik Wanninkhof of the National Oceanic and Atmospheric Administration's Atlantic Oceanographic and Meteorological Laboratory and I led a research expedition to do just such an experiment.

With a party of 31 scientists, technicians and students onboard our research vessel, we spent almost two months sampling the physical and chemical properties of the western South Atlantic, from top to bottom, starting near Antarctica and ending near the equator. This is the very same slice of ocean that I and other scientists had first measured in 1989, when I was a graduate student.

When we compared our observations from 2005 with those made 16 years earlier, we found that the upper few hundred meters of the South Atlantic in general have higher carbon concentrations today than in the recent past, which is consistent with the notion that the sea is taking in atmospheric carbon dioxide. Other oceanographers have found similar trends in the Pacific and Indian oceans as well. But what exactly does this change portend for the marine environment?

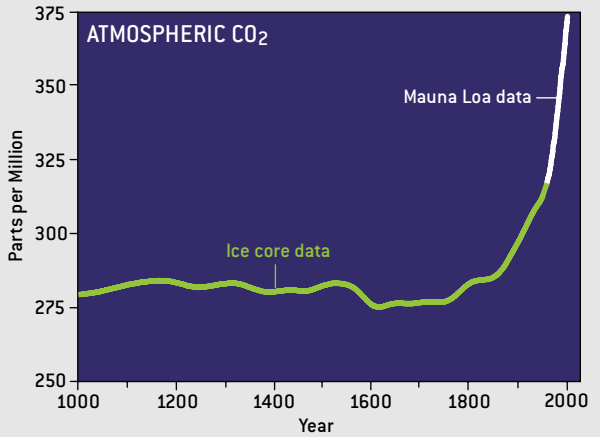
Ocean Chemistry 101

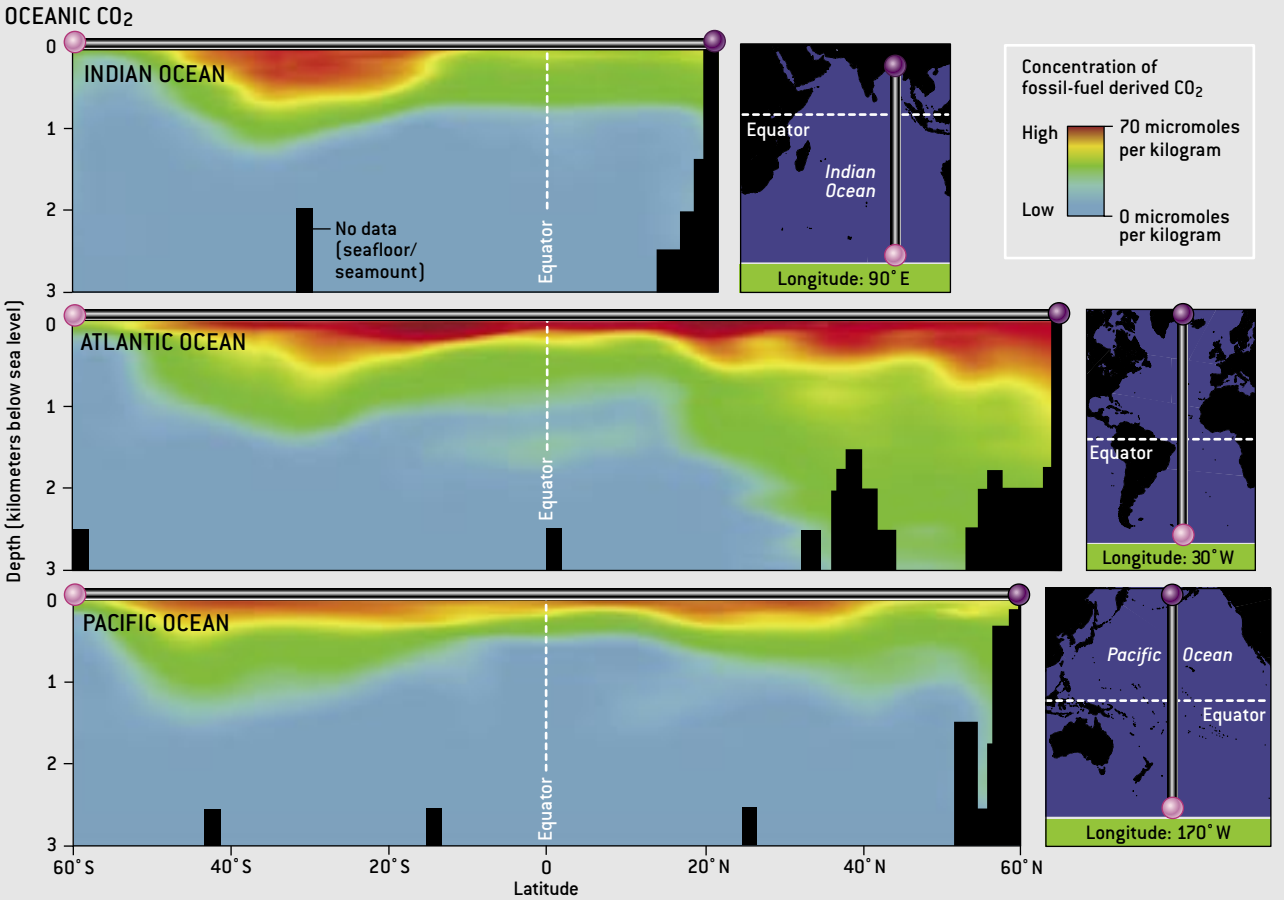
EXPLAINING THE IMPLICATIONS of these shifts in oceanic conditions requires, alas, a review of some freshman chemistry. But bear with me; it is really not that painful. Carbon dioxide (CO_2) combines with water to form carbonic acid (H_2CO_3), the same weak acid found in carbonated beverages. Like all acids, this one releases hydrogen ions (H^+) into solution, in this case leaving both bicarbonate ions (HCO_3^{-1}) and, to a lesser extent, carbonate ions (CO_3^{-2}) also swimming around. A small fraction of the carbonic acid remains in solution without dissociating, as does a little carbon dioxide. The resulting brew of carbon compounds and ions is thus rather complex.

CO_2: FROM ATMOSPHERE TO OCEAN

The concentration of carbon dioxide in the atmosphere has mounted considerably over the past century or so. This worrisome trend is well documented (*right*) by a combination of two techniques: the examination of air bubbles trapped in glacial ice (*green segment*, which shows 75-year averages) as well as direct measurements of the atmosphere (*white segment*, which reflects the annual average determined at a weather station situated atop Mauna Loa on the big island of Hawaii).

Large as it is, the increasing concentration of carbon dioxide in the atmosphere would have been even greater had not much of it been absorbed by the sea, a phenomenon that detailed oceanographic surveys have now documented. The cross sections below show where about half of this fossil-fuel effluent now resides—in the upper portions of the world's oceans.

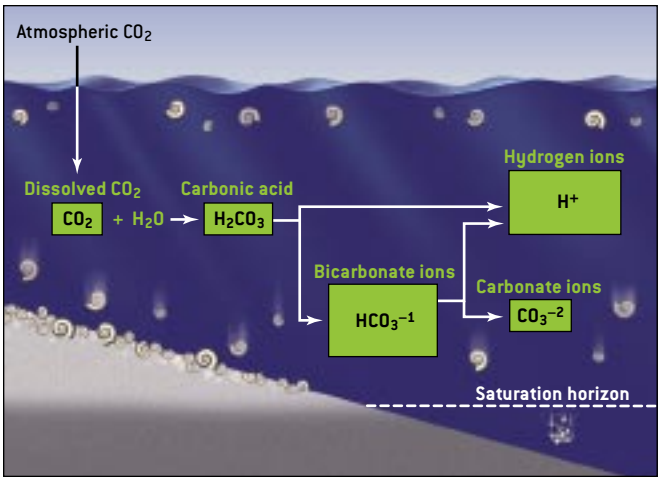




JEN CHRISTIANSEN; SOURCES: CARBON DIOXIDE INFORMATION ANALYSIS CENTER AT OAK RIDGE NATIONAL LABORATORY (http://cdiac.ornl.gov/ftp/trends/co2/lawdome.combined.dat and http://cdiac.ornl.gov/ftp/ndp001/maunaloa.co2) (*atmospheric CO_2 data*); ROBERT KEY *Princeton University* (*oceanic CO_2 cross section data*)

One simple result of all this dissolving and dissociating is the increase in hydrogen ion concentration, which chemists normally quantify in terms of the familiar pH scale. A drop by one pH unit corresponds to a 10-fold increase in the concentration of hydrogen ions, making the water more acidic, whereas a change of one unit upward corresponds to a 10-fold decrease, making the water more alkaline. Neutral pH (that of pure water) is 7. The pH of pristine seawater measures from 8 to 8.3, meaning that the ocean is naturally somewhat alkaline.

The absorption of carbon dioxide has already caused the pH of modern surface waters to be about 0.1 lower (less alkaline) than it was in preindustrial times. Unless civilization modifies its appetite for fossil fuels soon and in a significant way, ocean pH will fall an additional 0.3 by 2100. In a troubling prediction of the more distant future, Ken Caldeira, an oceanographer at the Carnegie Institution of Washington, suggests that ocean pH several centuries from now will be lower than at any time in the past 300 million years.



CARBON DIOXIDE absorbed from the air combines with water to form carbonic acid. A portion of this compound persists in the ocean, but most of it dissociates into acidifying hydrogen ions along with bicarbonate ions. Some of the latter also dissociate, forming carbonate ions and yet more hydrogen ions. These chemical changes cause an upward shift in the "saturation horizons" for calcite and aragonite—the water levels deep in the sea below which shells of marine organisms made of these minerals dissolve.

These shifts in pH may seem small, but they provide ample cause for alarm. Notably, recent experiments indicate that the change will prove harmful to some forms of marine life—in particular, to organisms that depend on the presence of carbonate ions to build their shells (or other hard parts) out of calcium carbonate ($CaCO_3$).

At first this concern appears paradoxical. After all, if some of the carbon dioxide absorbed by the sea dissociates into carbonate ions, one might expect that there should be plenty to go around, even more than would have been available otherwise. That logic, though, is flawed because it neglects the effect of all the hydrogen ions that are also created, which tend to combine with carbonate ions, forming bicarbonate ions. The net result is thus a reduction in the concentration of carbonate ions.

The worry is that a lowering of pH (and thus of carbonate ion concentration, which is expected to drop by half over this century) will hamper the ability of certain organisms to make calcium carbonate, so much so that these organisms will then have difficulty growing. Some of the most abundant life-forms that could be affected in this way are a type of phytoplankton called coccolithophorids, which are covered with small plates of calcium carbonate and are commonly found floating near the surface of the ocean (where they use the abundant sunlight for photosynthesis). Other important examples are planktonic organisms called foraminifera (which are related to amoeba) and pteropods (small marine snails). These tiny creatures constitute a major food source for fish and marine mammals, including some species of whales.

Biologists also fear what might happen to corals, which despite their plantlike appearance are actually colonies of small animals related to sea anemones. They feed by filtering plankton out of the water, and they secrete calcium carbonate skeletons, which accumulate over time to form coral reefs—some of the most productive and biologically diverse ecosystems in the ocean. Coralline algae (algae that also secrete calcium carbonate and often resemble corals) contribute to the calcification of many reefs, too. The Great Barrier Reef off the coast of Australia, for instance—the largest biological structure in the world—is simply the accumulation of generation after generation of coral and coralline algae. Less obvious examples occur deeper down in the sea, where cold-water coral communities dot continental margins and seamounts, forming important fish habitats.

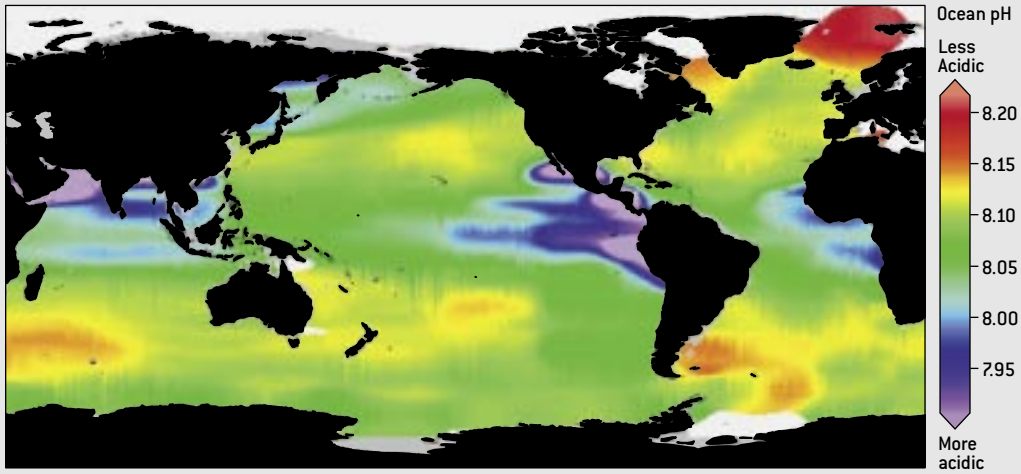
Shallow-water corals owe their beautiful colors in part to symbiotic algae, which live inside the coral cells. In response to various forms of environmental stress, these algae sometimes leave their hosts, exposing the white calcium carbonate skeleton underneath. Such "bleaching" events can be brought on by extreme warmth, for example. And some scientists sus-

JEN CHRISTIANSEN (*top*); CHRIS SABINE *NOAA Pacific Marine Environment Laboratory* (*bottom*)

THE OCEAN'S CHANGING ACIDITY

Measurements taken in the top 50 meters of the ocean reveal that pH varies considerably from place to place. Scientists expect oceanic pH to decrease in the years ahead.

Areas of relatively low pH (signifying more acidic conditions) arise mostly through the natural upwelling of deeper waters. Those zones, such as in the east equatorial Pacific, might be good places for scientists to study the effects expected to prevail over wider areas in the future.



pect that the acidification of the ocean (or more properly, the reduction in the ocean's slightly alkaline state) also tends to prompt such episodes.

Survival of the Thickest?

BUT CORALS and other calcifying marine organisms could be affected by acidification in even more significant ways—their shells might actually disintegrate. Drop a piece of chalk (calcium carbonate) into a glass of vinegar (a mild acid) if you need a demonstration of the general worry: the chalk will begin dissolving immediately. Gaining a fuller understanding of which life-forms are most at risk of such a fate requires another short chemistry lesson.

The calcium carbonate in corals or in the shells of other marine creatures comes in two distinct mineral forms: calcite and aragonite. And some calcite-secreting organisms also add magnesium to the mix. Aragonite and magnesium calcite are more soluble than normal calcite. Thus, corals and pteropods, which both produce aragonitic shells, and coralline algae, which manufacture magnesium calcite, may be especially susceptible to harm from ocean acidification.

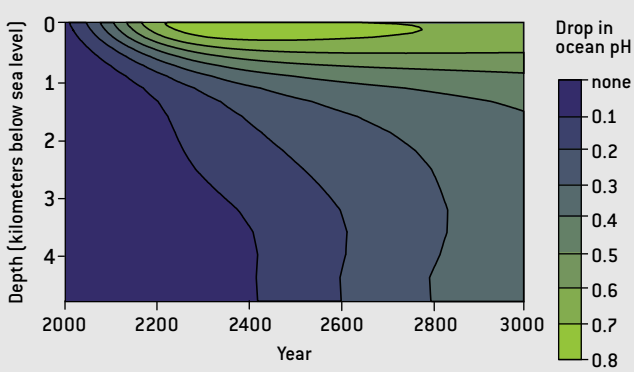
The solubility of calcium carbonate depends fundamentally on the carbonate ion concentration (and therefore indirectly on pH), but it also hinges on several other variables, including temperature and pressure. Under modern conditions, many deep, cold waters are acidic enough to dissolve calcium carbonate shells. They are said to be "undersaturated." Shallow, warm surface waters are described as "supersaturated" with respect to both calcite and aragonite, meaning that these minerals have no tendency to dissolve. The transition between supersaturated and undersaturated conditions is referred to as the saturation horizon: the level below which things begin to dissolve.

The influx of carbon dioxide from the atmosphere has caused the saturation horizons for aragonite and calcite to shift closer to the surface by 50 to 200 meters compared with where they were positioned in the 1800s. And recent studies indicate that further widespread shoaling will take place over the next several decades. Thus, as the ocean becomes more and more acidic, the upper, shell-friendly portion will become thinner. That is to say, less and less of the sea will remain hospitable for calcifying organisms.

Early on, many scientists reasoned that ocean acidification would pose only a minor problem, because surface waters would remain supersaturated—at least with respect to calcite, the robust form of calcium carbonate. In the late 1990s Christopher Langdon, a marine biologist at the University of Miami, conducted an elegant experiment to test this surmise: he manipulated the water chemistry over an artificial coral reef that had been set up in a huge tank at Columbia University's Biosphere II laboratory (which, rather incongruously, is located in the middle of the Arizona desert). Strikingly, he found that the rate of calcium carbonate production in the corals declined with lower pH, although the water remained considerably supersaturated with respect to aragonite. Shortly afterward, Ulf Riebesell of the Alfred Wegener Institute for Polar and Marine Research in Germany and his colleagues demonstrated a similar stunting of planktonic coccolithophorids. Laboratory experiments are now available to show the deleterious effects of increased carbon dioxide (and the lower pH that results) for all the major groups of marine organisms that have hard parts made of calcium carbonate.

As the ocean becomes more and more acidic, the upper, shell-friendly portion will become thinner.

Because cold waters are naturally less supersaturated than warm ones for the various forms of calcium carbonate, high-latitude and deep water ecosystems may be the first to suffer from ocean acidification. Polar surface waters most likely will



Although acidification of the sea (as measured by the drop in pH) has so far been small, scientists expect larger shifts in the future. The greatest changes will take place near the surface, but over time the full depth of the ocean will feel these effects.

JEN CHRISTIANSEN; SOURCE: "ANTHROPOGENIC CARBON AND OCEAN pH," BY K. CALDEIRA AND M. E. WICKETT IN *NATURE*, VOL. 425; SEPTEMBER 25, 2003

THE AUTHOR

SCOTT C. DONEY is a senior scientist in the department of marine chemistry and geochemistry at the Woods Hole Oceanographic Institution. He began pursuing oceanographic studies while an undergraduate at the University of California, San Diego, and ultimately obtained a doctorate in chemical oceanography in 1991, after completing a program jointly administered by the Massachusetts Institute of Technology and the Woods Hole Oceanographic Institution. Among his other professional activities, Doney serves on the NASA Orbital Carbon Observatory science team and is chair of the Ocean Carbon and Climate Change Scientific Steering Group, which is a part of the U.S. Global Change Research Program.

MARINE ORGANISMS at risk from the increasing acidification of the ocean include the corals and coralline algae commonly found in reef communities, as well as foraminifera and coccolithophorids, which are abundant in most surface waters. Also under threat, particularly in cold, polar waters, are a variety of small marine snails called pteropods.

Coral (*Millepora tenella*)

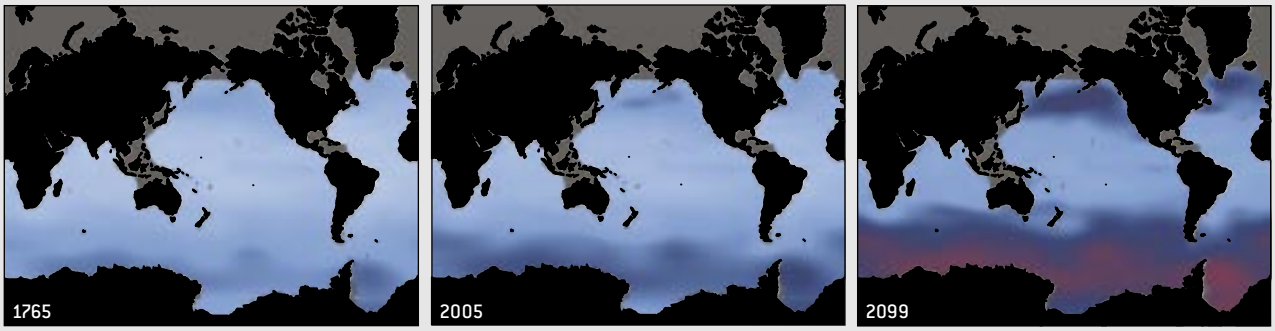
Coralline algae (*Amphiroa anceps*)

become undersaturated for aragonite before the end of this century. One worrisome possibility, based on the work of Victoria J. Fabry of California State University, San Marcos, is that polar pteropods will simply disappear altogether. Or perhaps they will be forced to migrate to lower, warmer latitudes, assuming that they can adapt to those environments. No one knows how a sharp decrease in pteropod numbers will affect other parts of the marine ecosystem. But the fact that these small snails are a key link in the food chain in the Southern Ocean (which supports large populations of fish, whales and seabirds) is ample cause for concern.

High-latitude calcareous phytoplankton and zooplankton might share a similar fate, although their declines would come decades later because their shells are formed from calcite, the less soluble form of calcium carbonate. Deep coral communities will probably suffer, too, particularly those in the western North Atlantic along the path of water that contains high concentrations of carbon from fossil-fuel emissions.

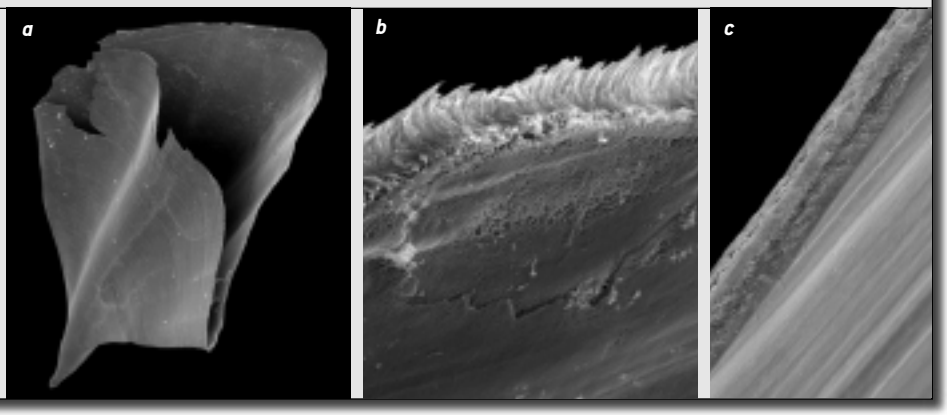
THE (RAGGED) FUTURE OF ARAGONITE

Diminishing pH levels will weaken the ability of certain marine organisms to build their hard parts and will be felt soonest and most severely by those creatures that make those parts of aragonite, the form of calcium carbonate that is most prone to dissolution. The degree of threat will vary regionally.

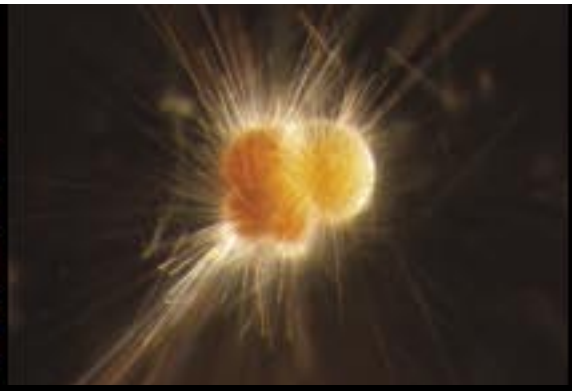


Before the Industrial Revolution (*left*), most surface waters were substantially "oversaturated" with respect to aragonite (*light blue*), allowing marine organisms to form this mineral readily. But now (*center*), polar surface waters are only marginally oversaturated (*dark blue*). At the end of this century (*right*), such chilly waters, particularly those surrounding Antarctica, are expected to become undersaturated (*purple*), making it difficult for organisms to make aragonite and causing aragonite already formed to dissolve.

Pteropods form a key link in the food chain throughout the Southern Ocean. For these animals (and creatures that depend on them), the coming changes may be disastrous, as the images at the right suggest. The shell of a pteropod kept for 48 hours in water undersaturated with respect to aragonite shows corrosion on the surface (*a*), seen most clearly at high magnification (*b*). The shell of a normal pteropod shows no dissolution (*c*).



ALEXIS ROSENFELD *Photo Researchers, Inc.* (*fire coral*); KEOKI STENDER *Fishpics Hawaii* (*coralline algae*); WOODS HOLE OCEANOGRAPHIC INSTITUTION (*foraminifer*); STEVE GSCHMEISSNER *Photo Researchers, Inc.* (*coccolithophorid*); RUSS HOPCROFT *University of Alaska–Fairbanks/NOAA* (*pteropod*); JAMES C. ORR *Laboratory of the Science of Climate and the Environment, UMR CEA-CNRS, France* (*map data and pteropod shell images*)



Foraminifer (*Globigerina bulloides*)

Coccolithophorid (*Emiliania huxleyi*)

Pteropod (*Limacina helicina*)

The outlook for coral reefs is even bleaker. For those precious ecosystems, ocean acidification is but one of many environmental stresses, an onslaught that includes greenhouse warming, local pollution, overfishing and habitat destruction. Many coral reefs are already in decline, and ocean acidification may push some over the edge into nonexistence.

Coming Sea Change

AS BAD AS CONDITIONS are expected to be for many marine organisms, there will be some winners, too. Right now very little of the carbon in seawater takes the form of dissolved carbon dioxide, and this scarcity limits the growth of some types of phytoplankton. Many of these species devote precious energy to concentrate carbon dioxide inside their cells, so one might guess that increases in dissolved carbon dioxide will be beneficial to them. Perhaps that will be the case. Not enough is known, however, about this "fertilization" effect to make firm predictions for the future of phytoplankton or to say whether higher carbon dioxide levels will benefit the photosynthetic algae that live inside corals. Many species of marine phytoplankton use HCO_3^{-1} for photosynthesis. And because the concentration of this ion will remain largely unchanged, biologists do not expect that these organisms will experience a significant boost. Some higher plants (sea grasses, for example) use dissolved carbon dioxide directly and probably will benefit from its rising levels, just as plants on land are expected to gain as the atmospheric concentration of this gas increases.

How can scientists better gauge the response of ocean ecosystems to acidification? Most current efforts in this area involve short-term laboratory experiments on single species. Scientists have also mounted small-scale field studies to examine the acute effects that would accompany the deliberate disposal of atmospheric carbon dioxide in the deep sea, one of the various strategies being considered to sequester carbon dioxide and keep it out of the air [see "Can We Bury Global Warming?" by Robert H. Socolow; SCIENTIFIC AMERICAN, July 2005]. Although this work is informative, the results do not translate easily into an understanding of the consequences of long-term, chronic exposure to modestly lower pH. Nor is it straightforward to extrapolate from laboratory studies to whole ecosystems, where many different organisms interact.

One possibility for gaining a more realistic assessment of the problem would be to elevate carbon dioxide levels artificially for months to years in a patch of the ocean or on a coral reef. Experiments involving the large-scale manipulation of carbon dioxide levels are commonly carried out on land, but marine scientists and engineers are just now beginning to explore the logistics for extending this approach to the ocean. Another tactic is to study how marine organisms fare in regions that have long had lower pH, such as the Galápagos Islands, which are bathed in waters that are naturally rich in carbon dioxide.

Yet a third strategy might be to examine the geologic record of times when carbon dioxide concentrations reached much higher levels than that of the present and when ocean pH was presumably much lower—such as during an interval of anomalously warm climate that took place some 55 million years ago (the Paleocene-Eocene Thermal Maximum), when many marine organisms died off. The concern of many scientists today is that the current episode of acidification is taking place more rapidly than anything that has transpired in the past, leaving oceanic species no time to adapt. Although the effects may be hidden from people's view, dramatic alterations in the marine environment appear to be inevitable. SA

Many coral reefs are already in decline, and ocean acidification may push some over the edge into nonexistence.

MORE TO EXPLORE

Anthropogenic Carbon and Ocean pH. Ken Caldeira and Michael E. Wickett in *Nature,* Vol. 425, page 365; September 25, 2003.

Anthropogenic Ocean Acidification over the Twenty-First Century and Its Impact on Calcifying Organisms. James C. Orr et al. in *Nature,* Vol. 437, pages 681–686; September 29, 2005.

Ocean Acidification Due to Increasing Atmospheric Carbon Dioxide. Royal Society, 2005. Available at **www.royalsoc.ac.uk/displaypagedoc.asp?id=13314**