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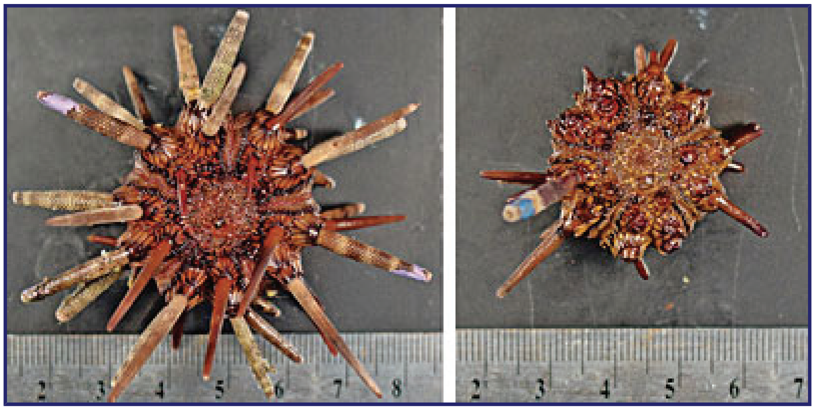
Off-Balance Ocean

Acidification from absorbing atmospheric CO_2 is changing the ocean's chemistry

Rachel Petkewich

PEOPLE CAN'T walk on water, but scientists say the carbon dioxide emitted by humans into the atmosphere has started to leave noticeable footprints on the ocean.

Scientists have been concerned for years that lower ocean pH caused by absorption of CO_2 emissions could decrease calcification processes underlying the growth of shells and corals' hard exteriors. Besides studying that phenomenon, they are investigating how acidification alters the concentration and behavior of the ocean's trace metals, some of which are nutrients for marine life. They are also looking into some unexpected consequences of ocean acidification, such as disruptions to sound propagation and transmission of chemical cues. Some scientists believe the net effect of these and other yet undiscovered changes may threaten the survival of a wide variety of marine organisms.



Justin Ries (both)
View Enlarged Image

Contrast Calcifying organisms, such as these sea urchins grown in seawater acidified with 400 ppm CO_2 (left)—the current level in the ocean—produce spines that are truncated by dissolution when reared in seawater acidified with 2,850 ppm CO_2 (right), an extreme level for lab tests. Numbered scale in centimeters

Increased use of fossil fuels has caused the levels of CO_2 in the atmosphere to nearly double since the Industrial Revolution. "Over the past 200 years, the oceans have absorbed approximately 550 billion tons of CO_2 from the atmosphere, or about a third of the total amount of anthropogenic emissions over that period," says Richard A. Feely, a senior scientist with the National Oceanographic & Atmospheric Administration's Pacific Marine Environmental Laboratory, in Seattle. That means the ocean currently absorbs about 22 million tons of CO_2 per day, he adds.

Marine scientists who have measured the pH of the ocean's surface waters for decades see that it has been dropping. They say that the pH is currently about 8.1, down from about 8.2 in the 18th century. If CO_2 emissions continue at current rates, they expect the pH to fall by approximately 0.3 more units in the next 50–100 years. And as the ocean becomes more acidic, scientists anticipate myriad changes to the ocean's chemistry.

Changing pH is likely to affect many aspects of biochemistry, development, and reproduction for many marine organisms, says Donald C. Potts, an evolutionary biologist at the University of California, Santa Cruz. Whether these organisms can adapt and survive remains to be seen, he adds.

For example, almost all reaction rates are pH dependent, so acidification may change processes in the ocean ranging from enzyme activity to the adsorption of metals onto particle surfaces in seawater, says Frank J. Millero, a professor of marine and physical chemistry at the University of Miami.

Many sea organisms without shells, such as anemones and jellyfish, may be especially susceptible to even the smallest changes in ocean pH because their internal pH tends to vary with that of the surrounding seawater. These organisms cannot actively regulate their internal pH as mammals do.

Although marine mammals can regulate their internal pH, ocean acidification could still affect how they function. Peter G.

Brewer, an ocean scientist at Monterey Bay Aquarium Research Institute (MBARI), in Moss Landing, Calif., says, "What most people don't get is just the sheer scale of the changes that are going on and the multiple ways that acidification can have further impact on the ocean."

Consider the ocean chemistry-sound connection. Brewer and his MBARI colleagues published a study showing that at lower pH, the ocean will absorb less sound at low frequencies and essentially become noisier (*Geophys. Res. Lett.* **2008,** *35,* L19601; C&EN, Oct. 6, 2008, page 47). The researchers suggest that mammals dependent on sonar may be able to communicate over longer distances, although they would have to deal with more background distractions. "I think it shocked a lot of people that something as strange as that could be impacted, but it is absolutely true," Brewer says.

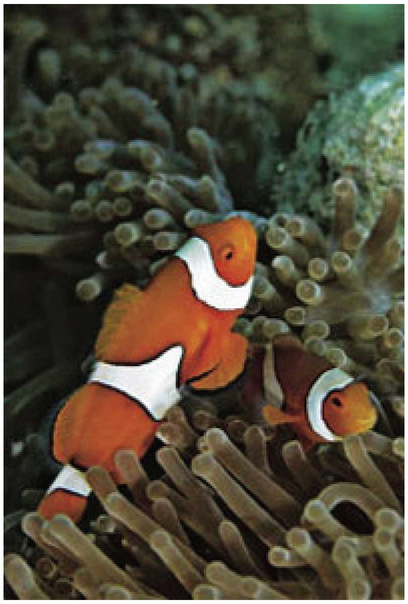
Fish fall between simple organisms and mammals with regard to pH regulation. Most fish can easily regulate small changes in pH. Few studies have examined the effects of ocean acidification on fish, but Philip L. Munday, a coral reef expert at James Cook University, in Australia, and colleagues recently reported how acidification impairs olfaction and homing ability in orange clownfish larvae. In laboratory studies, they found that larvae raised in seawater acidified with CO_2 to pH 7.8, which is the pH level predicted for 2100 at current CO_2 emission rates, had difficulty discriminating between different chemical cues (*Proc. Nat. Acad. Sci. USA* **2009,** *106,* 1848; C&EN, Feb. 9, page 30).

Such olfactory cues help guide larvae back to reefs so they can locate adult habitats at the end of their larval phase. Disrupting that sensory ability could affect whether or not larvae from a broad range of marine species can find a home, Munday says.

THE SPEED at which acidification is occurring is a particular concern to ocean scientists. The "Monaco Declaration," a statement released on Jan. 30 by 155 ocean scientists from 26 countries, sums up their discussions at a symposium in Monaco last October. "We are deeply concerned by recent, rapid changes in ocean chemistry and their potential, within decades, to severely affect marine organisms," they wrote in the statement, adding that "severe damages are imminent."

They pointed specifically to acidification-related decreases in shellfish weights and slowed growth of coral reefs, among other problems. "Increasing acidity and related changes in seawater chemistry also affect reproduction, behavior, and general physiological function of some marine organisms, such as oysters, sea urchins, and squid," the scientists wrote. They added that field studies suggest impacts of acidification on some major marine organisms that produce calcium carbonate structures may already be detectable.

Adding CO_2 to seawater affects calcifying organisms by upsetting the natural equilibrium of calcium carbonate chemistry in the ocean. When CO_2 dissolves in seawater, it forms carbonic acid, which can dissociate into hydrogen ions and bicarbonate ions. Those hydrogen ions are likely to react with carbonate ions to form more bicarbonate. "Some of that bicarbonate comes at the expense of the carbonate, which is the form of carbon that some organisms use in calcification," says Justin Ries, a marine geochemist at the University of North Carolina (UNC), Chapel Hill.


Proc. Natl. Acad. Sci. USA

Losing Nemo Acidified seawater disrupts the homing ability of orange clownfish.

In addition, "a critical factor is that at the present time, Ca^{2+} concentration in the ocean happens to be at its lowest level in more than a half-billion years," geologist Steven M. Stanley of the University of Hawaii, Manoa, wrote in an article in *Chemical Reviews* (**2008,** *108,* 4483). Reduced carbonate concentration in combination with low calcium levels results in exceptionally low calcium carbonate levels in seawater, he wrote.

Numerous published laboratory studies indicate that organisms calcify more slowly under acidic conditions when fewer carbonate ions are available. Carbonate also dissolves from existing calcified structures of organisms at a faster rate in lower pH water, thereby exacerbating the calcification problem.

CORAL REEFS may be degrading from ocean acidification, but the ability of tiny calcifying phytoplankton called coccolithophores to grow in high-CO_2 seawater demonstrates that the marine response to ocean acidification is not uniform. These calcifying organisms build their skeletons by forming crystals of calcium carbonate, and coccolithophores alone produce roughly one-third of the calcium carbonate in today's ocean. M.

Debora Iglesias-Rodriguez of the University of Southampton, in England, and colleagues presented lab evidence, confirmed by data collected from sediment cores, suggesting that the average coccolithophore's mass has grown by 40% over the past 220 years (*Science* **2008,** *320,* 336; C&EN, April 21, 2008, page 43).

UNC's Ries wanted to see if CO_2-induced acidification could affect the crystal structure and composition of calcium carbonate produced by calcifying organisms, which generally form one of two different crystal lattice arrangements: aragonite or calcite. These polymorphs have different solubilities, and Ries wondered if calcifying organisms would alter their polymorphic calcite composition to cope with more acidic water.

He and his colleagues Anne L. Cohen and Daniel McCorkle of Woods Hole Oceanographic Institution recently raised various calcifying organisms in CO_2-acidified water and then used X-ray diffraction, spectroscopy, and microscopy to quantify changes in the organisms' skeletal mineralogy. Of the 18 organisms studied, only tube worms increased their calcite composition in acidified water.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Unexpected Growth Coccolithophores like these may prosper in high-CO_2 seas.

Ries says the results may indicate that some organisms alter their mode of calcification in response to carbonate deficits. He also notes that results from his and others' studies on the effect of elevated CO_2 on calcification suggest that some organisms may adapt by using bicarbonate for calcification. "If they are able to strip away the proton from bicarbonate by manipulating the pH of their calcifying fluid, some organisms may be able to convert bicarbonate back to carbonate at their site of calcification," he says. He adds that this enhanced pH regulation may come at a high energetic cost to the organism.

Changes in carbonate availability, along with decreases in hydroxide concentrations because of decreased pH, will likely have a large influence on trace metals in the acidified ocean too, according to marine chemists. Metals can exist in different chemical forms in seawater. They can be in the free form or interact with other organic ligands or inorganic ions to form complexes in solution. "Normally, the free form is more active in a biological and chemical sense," Miami's Millero says. Copper, for example, in its free form (Cu^{2+}) can be toxic to marine organisms such as phytoplankton.

The ocean's pH can affect how dissolved metals complex with inorganic anions, such as hydroxide and carbonate ions, and with organic ligands, which have not been well characterized, says Robert H. Byrne, a professor at the University of South Florida who studies the physical chemistry of seawater. The concentration of free metals will increase if there is less carbonate and hydroxide to bind, he adds.

Decreases in concentrations of these anions are likely to also affect the concentration and speciation of iron, an essential nutrient for the growth of many organisms. Millero suggests the decrease in pH will slow down oxidation of Fe^{2+} with dissolved oxygen and hydrogen peroxide and increase the solubility of Fe^{3+}. The resulting increase in total available iron may boost the production of phytoplankton in the oceans, but marine chemists differ at this point on whether this boost would ultimately be a boon or a detriment to ocean life.

Marine chemists don't expect that the growing acidity of surface waters will affect the concentrations of all trace metals. For example, Millero says metals that form strong complexes with chloride, such as mercury and cadmium, will not be affected by changes in pH. Because the organic ligands that complex metals in the ocean have not been well characterized, marine chemists have more difficulty predicting how pH will affect metal complexation with organic ligands.

Ocean scientists say acidification of surface waters will likely affect how metals are adsorbed onto biological detritus, which essentially removes metals from surface waters as the debris sinks into the deeper ocean. The adsorption processes are thought to be pH dependent, but there has been little study on the effect so far.

What is known is that the ocean has pulled so much CO_2 from the atmosphere that the resulting levels of carbonic acid could fundamentally change the ocean. To what extent the ocean will continue to acidify and whether marine organisms can adapt to the changes in store remain to be seen.