

# Researching ocean buffering

Just like our bodies, oceans have natural buffering capacity. This is good news, because a constant pH is important for marine life. Seawater contains ions, such as chloride and sodium from salt, as well as calcium, hydrogencarbonate and carbonate ions that are essential for living organisms that produce calcium carbonate skeletons. These ions are part of the buffering process.

The oceans' natural buffer is the carbonate/hydrogencarbonate system. This maintains pH between 8.1 and 8.3, in a series of equilibrium reactions.



This chemical equilibrium between various chemical forms of carbon and hydrogen ions (protons) forms a buffering system that is the most important factor controlling the pH of seawater.

## The dynamic ocean environment

There's a lot going on in the oceans, including changes to the chemical environment, and this has an impact on pH.

Le Chatelier's principle tells us that an increase in concentration of dissolved carbon dioxide causes the equilibrium to move to the right. This leads to increased concentration of hydrogencarbonate and hydrogen ions, and lower pH.

At the oceans' current pH level another equilibrium reaction that involves some of the same species also takes place.



Although this reaction doesn't involve a change in pH, it does use up carbonate ions and produces hydrogencarbonate ions. Most of the carbon in today's oceans is in the form of hydrogencarbonate, rather than carbonate ions or carbonic acid.



photo: Liza Naude, Stock.xchng

## Ocean acidification

The amount of carbon dioxide produced has increased because of human activity, largely through burning fossil fuels. This has led to increased concentration of carbon dioxide in the atmosphere and also in the oceans.

A higher concentration of dissolved carbon dioxide in the ocean has resulted in an increase in the concentration of hydrogen ions. And that means the ocean pH has decreased as  $\text{pH} = -\log_{10}(\text{H}^+)$ .

This pH change is referred to as acidification. Even though the ocean pH is above 7 (which is on the basic side of neutral), pH is moving in a direction towards more acid composition.

The pH at the oceans' surface has declined by about 0.1 pH unit in the past 200 years; and it's predicted that it could drop a further 0.3-0.6 pH units by the end of the century, depending on how much additional  $\text{CO}_2$  is emitted into the atmosphere. The pH scale is logarithmic, which means even this seemingly small decline equates to a doubling of hydrogen ion concentration.

This is bad news because data from gases trapped in ice cores shows that current ocean pH is already lower than it has been for 800 000 years.



photo: 'Industry smoke' by Uwe Hermann



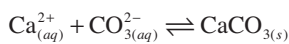
photo: Oceans Institute

## Tipping the buffering balance

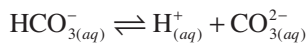
Calcium carbonate minerals, present on the deep ocean floor below what is called the saturation horizon, constantly dissolve and thereby increase the alkalinity of seawater, which offsets the decline in pH. But there is a problem: these minerals dissolve much more slowly than the current uptake of carbon dioxide by the oceans, and that leads to increased ocean acidity and lower pH. Furthermore, CO<sub>2</sub> uptake occurs at the surface of the ocean, far from the deep ocean floor, so this critical zone experiences the most rapid increase in ocean acidification.

## Ocean acidification and marine organisms

Marine organisms that have shells or exoskeletons constructed of calcium carbonate ultimately depend on the presence of carbonate ions to form their skeletons.



Because the concentration of carbonate ions in seawater is much less than the concentration of hydrogencarbonate ions, organisms are also able to convert hydrogencarbonate ions from seawater into carbonate to build their skeletons. This process produces hydrogen ions, which the organism must expel into the environment.



Getting rid of hydrogen ions takes energy, and the higher the concentration of hydrogen ions in the surrounding seawater, the greater the energy needed by this process. So for these organisms there's less energy left over for other important life processes, such as reproduction.

Shell-building marine organisms play key roles in the marine ecosystem, as they provide food and possibly shelter for other animals. Plankton is one of these organisms and they also play an important role in the ocean where they absorb massive volumes of carbon dioxide. If plankton numbers decrease then the concentration of carbon dioxide in the ocean and atmosphere will increase faster, compounding the problems.

The sensitivities of marine organisms to increasing ocean acidification aren't well understood, so the outcomes of increased carbon dioxide concentration are currently unknown. What is known is that changes to the ocean ecosystem will have a flow-on effect, so science needs to find some answers. Scientific research has an important role to play in understanding past and present conditions in the ocean, so forecasts for the future can be made.



photo: Coral outcrop, Flynn Reef by Toby Hudson

## Coral reefs in the spotlight

Coral reefs are unique ecosystems that form living habitats for a diverse range of organisms. Researchers at The University of Western Australia are investigating exactly how increasing levels of atmospheric carbon dioxide might be impacting on these ecosystems.

A team at the ARC Centre of Excellence in Coral Reef Studies, led by Professor Malcolm McCulloch, is investigating responses of coral reefs to changes in ocean chemistry.





## Information from coral cores

When marine organisms build their calcium carbonate shells and skeletons, other elements, such as boron, are incorporated. Professor McCulloch measures the concentration of boron and carbon isotopes in the skeletons of corals by testing core samples.

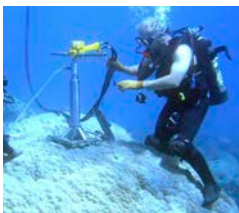


photo: Oceans Institute

Corals can live for hundreds of years, so samples from older corals, or parent corals, allow Professor McCulloch to build up a picture of ocean chemistry over a long period of time.

Boron is used in these studies as it is incorporated into coral skeletons. Like carbon, boron has a set of pH-sensitive reactions that involve conversion of boric acid to borate ions. Boron also has two stable isotopes,  $^{10}\text{B}$  and  $^{11}\text{B}$ , and the relative concentrations of these two isotopes depends on ocean pH. Professor McCulloch's research has shown that  $^{11}\text{B}$  levels are dropping, which indicates decreasing pH. This research has already shown that ocean pH has decreased over the past 200 years, from 8.12 to approximately 8.06 pH units.

The study also compared the concentration of the stable isotope  $^{13}\text{C}$  in coral core samples to the more common isotope  $^{12}\text{C}$ .  $^{13}\text{C}$  is present in normal atmospheric carbon dioxide. It is also present in fossil fuels, but in far lower quantities relative to  $^{12}\text{C}$ . As carbon dioxide from burning fossil fuels mixes with atmospheric carbon dioxide, the relative percentage of  $^{13}\text{C}$  decreases. In this way measurement of  $^{13}\text{C}/^{12}\text{C}$  ratios allows scientists to measure the impact of human industry.

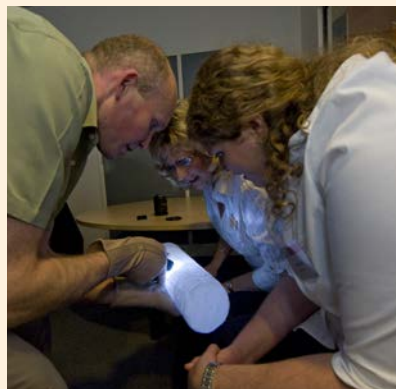
Core samples showed corresponding drops in  $^{13}\text{C}$  and  $^{11}\text{B}$ , which demonstrate a link between increasing industry and lowering of ocean pH.



Professor McCulloch's research is continuing and addresses questions such as: How will corals cope with chemical changes in the ocean? Will our reefs disappear altogether or will some be able to relocate? Are some corals more resilient than others? What is the critical level of atmospheric carbon dioxide beyond which corals are unable to produce calcium carbonate skeletons?

## Krill in the spotlight

Researcher Robert King, biologist with the Australian Antarctic Division of the Department of Environment and Heritage, is looking into how ocean acidification might impact on one of the marine systems most important animals, krill.



Krill are thought to have the largest biomass of any multi-cellular animal species on the planet. In the Southern Ocean alone there are an estimated 500 million tonnes of krill. These tiny organisms are an integral part of the marine ecosystem, particularly as they form an important food source for many marine animals, including commercial fish species.

Increased ocean acidification is a potential threat to the future abundance of krill. Robert King and his team have been able to determine the effect of increased levels of dissolved carbon dioxide on growth and development of krill.

What they found was when they tripled levels of carbon dioxide in the ocean, krill seemed to be doing just fine; but when they doubled it again, krill larvae failed to hatch. These results are concerning, when predicted carbon dioxide levels are four times current levels by the end of this century.

The research team is currently investigating the impact of a range of carbon dioxide concentrations on the different stages in the krill lifecycle.

### What are krill?

Krill is a general term used to describe multiple species of free-swimming, open ocean crustaceans. Antarctic krill are about 6 cm long, and weigh around a gram.



Photo: 'Antarctic krill, *Euphausia superba*' by Uwe Kils