THE ACIDIFICATION OF OCEANS OR CLIMATE CHANGE'S EVIL TWIN

The geo-chemistry of calcium carbonate

Sparkling waters are rich in dissolved mineral salts, much more than still waters. A quick comparison of the information labels gives us valuable information to convince ourselves of this.

TYPICAL ANALYSIS/ANALYYSIT (mg/L)		
Sulphate	SO_4^{2-}	430
Bicarbonate	HCO_3^-	245
Calcium	Ca^{2+}	174
Chloride	Cl^-	52.0
Magnesium	Mg^{2+}	51.4
Sodium	Na^+	33.3
Total Dissolved Solids (at 180°C): mg/L		915

Chemical analysis of natural sparkling water

TYPICAL ANALYSIS (mg/l)	
Calcium	27.0
Magnesium	10.5
Potassium	3.5
Sodium	35.3
Bicarbonate	211.8
Chloride	7.6
Sulphate	9.2
pH at source	7.8
Dry residue at 180°C	210.8

Chemical analysis of still water

This high mineral content, clearly visible in the total mineralization indicated on the labels as the "residue" or "extract" when dry, justifies the fact that some of these sparkling waters are recommended by nutritional doctors. Where does such a difference come from? In order to answer this question, it is obviously necessary to point out the responsibility of the only chemical element present in sparkling waters and absent in still waters: CO_2.

A bit of chemistry is needed to deepen the link between the mineralization of sparkling water and CO_2.

All the advertisements for mineral waters insist on the progressive enrichment of the water in mineral elements during its long journey in the rocks of the subsoil. It is therefore a given that the mineral salts present in our water come from the minerals present in the rocks

The CO_2 present in the water will increase its capacity to solubilise (= dissolve) the mineral elements in the rocks. Let's take the example of a mineral that is abundant in water: Calcium and let's look at the solubilisation mechanisms.

Limestone is a solid compound with the formula $CaCO_3$ (we speak of Calcium carbonate). It is shown to dissolve very weakly in pure water according to equation (1):

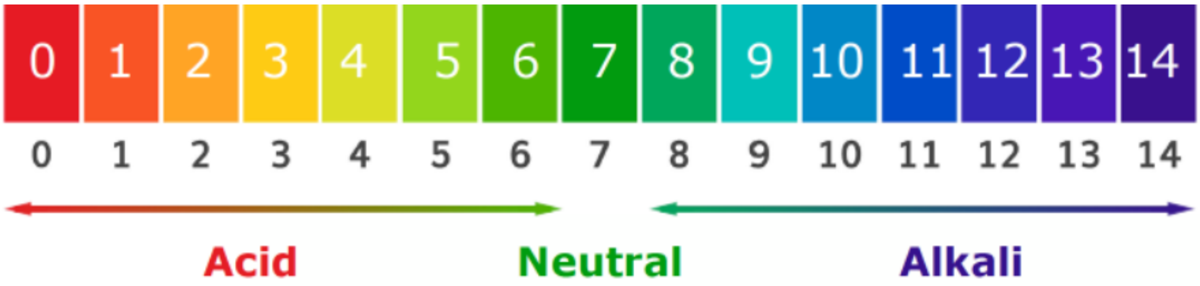
$$\textbf{(1)}\quad CaCO_3\,(s) \rightarrow Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$$

Here we specify that (s) means solid and (aq) means in aqueous solution, i.e. dissolved.

If dissolved CO_2 is present in the water, then the water is enriched with H^+ and HCO_3^- ions according to equation (2):

$$\textbf{(2)}\quad CO_2 + H_20 \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$

H^+ ions are known to all students because they define the hydrogen potential: the pH, which is used to measure the acidity of a solution. The pH scale is shown below:



H_2CO_3 represents carbonic acid and HCO_3^- represents the hydrogen carbonate ion, whose role in the formation of the shells of certain molluscs we will recall later.

In other words**, <u>the CO_2 dissolved in water is responsible for its acidification.</u>**

Thus the presence of H^+ ions capable of interacting with the $CO3^{2-}$ in equation (1) causes further solubilisation of $CaCO_3$. In other words, solid limestone provides more dissolved Calcium in water. The final equation (3) is therefore established

$$\text{(3)}\quad CaCO3 + H^+ + HCO_3^- \rightarrow Ca(HCO_3)_2 \rightarrow Ca^{2+} + 2HCO_3^-$$

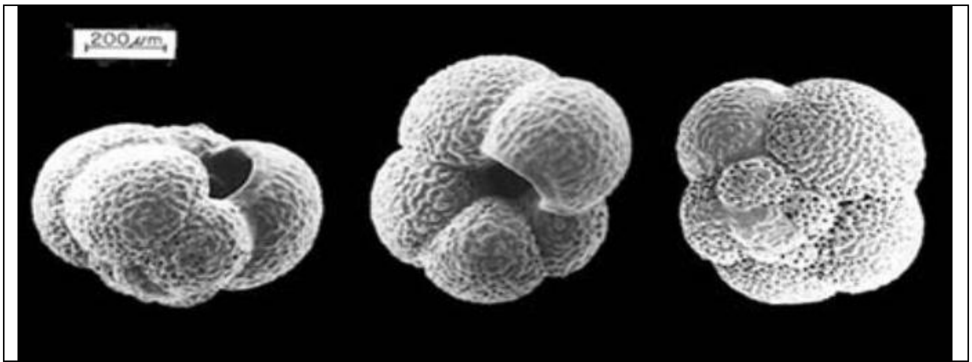
This beautiful chemical demonstration makes it possible to establish that when CO_2 is dissolved in water the capacity of dissolution of solid mineral elements into soluble ions such as Calcium increases.

Other old studies (Lehmann from 1932) show that dissolution is also stronger when the temperature increases.

In summary, solid calcium carbonate (= limestone) is put into solution (=dissolved) all the more easily if the water in the solution is rich in CO_2, i.e. if the water is acidic.

<u>The biological importance of calcium carbonate and the physico-chemical conditions of the ocean</u>

Let us now take the oceanic point of view. Many organisms have a shell (e.g. Molluscs), a carapace (e.g. Crustaceans), a skeleton (e.g. corals) or a test (e.g. Foraminifera), which is largely made of solid calcium carbonate.



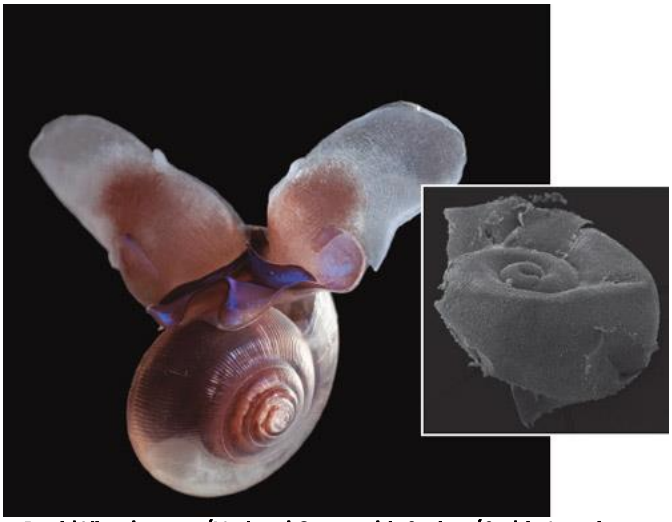
Test of Globigerina pachyderma (Foraminifera) MEB

Studies show that calcium carbonate can only crystallise above a pH of 10. Of course, the water in which marine animals grow does not reach this pH level. It is the organic molecules produced by the living organism, mainly proteins and chitin, that make crystallisation possible at a pH of around 7.

To conclude this rapid presentation of the crystallisation of calcium carbonate by marine organisms, it is obviously necessary to write the chemical equation (4)

$$\textbf{(4)}\ Ca^{2+}(aq) + HCO_3^-(aq) \rightarrow CaCO_2(s) + H^+(aq)$$

We can see that the equation above is the opposite of the equation (3)

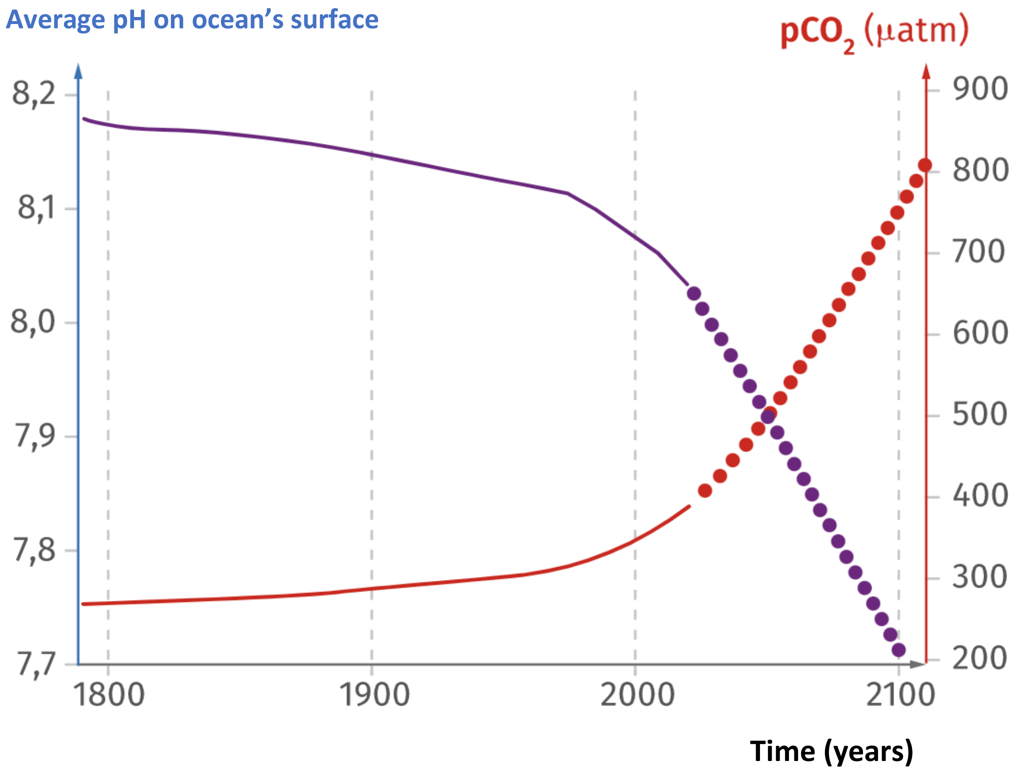


The subtle balance between the crystallisation of calcium carbonate, which is essential for living beings, and the dissolution of this same calcium carbonate in the water depends on two main parameters: the acidity of the environment resulting from its CO_2 content and the temperature.

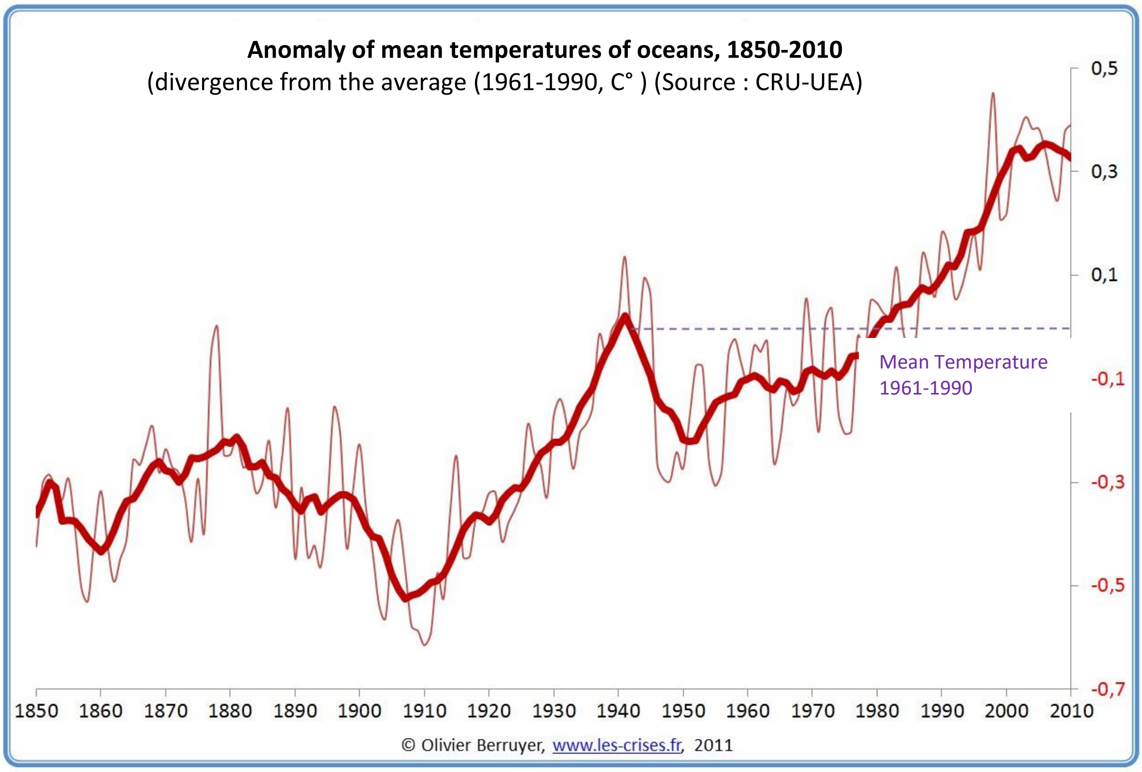
A recent study estimates that by the middle of the century, the calcification of microscopic algae and corals will be reduced by 10 to 50%.

David Liittschwager/National Geographic Society/Corbis; Inset image courtesy of NOAA.

These two graphs below show a continuous rise in the average temperature of the oceans and increasingly intense acidification. The consequences are obvious and inevitable: the disappearance of life forms that need calcium carbonate crystallisation to live.

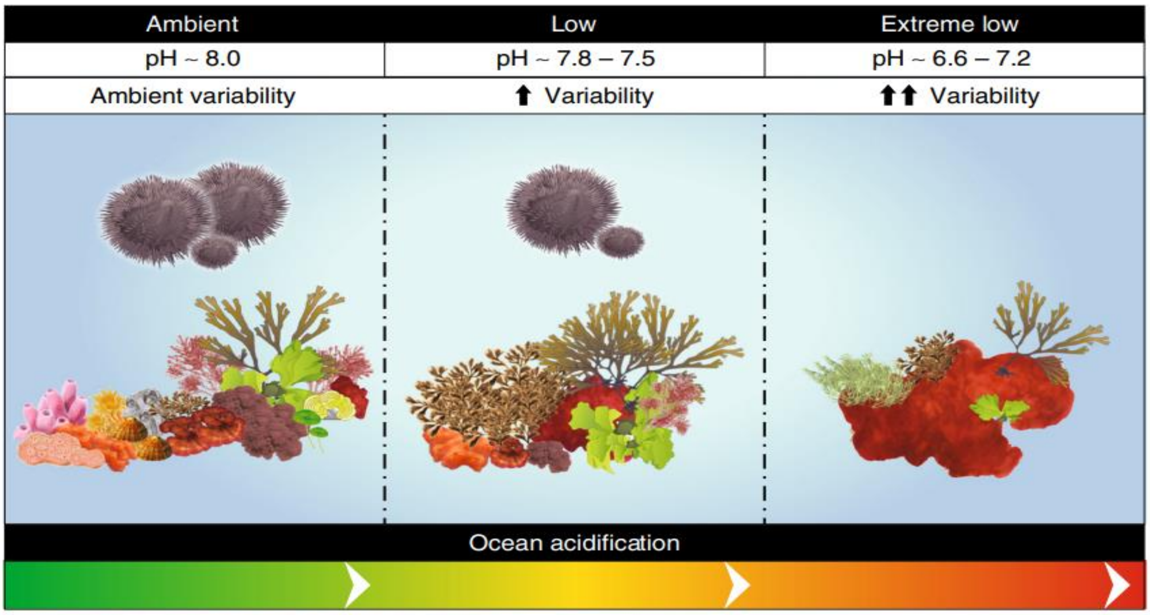


« Functional biodiversity loss along natural CO2 gradients » (DOI: 10.1038/s41467-018-07592-1)



In a paper published in Nature in 2018, authors N Teixido et al consider the loss of marine biodiversity under the IPCC so-called RCP2.6 and RCP8.5 trajectories by 2100. They conclude that ocean acidification will lead to a decrease in species diversity, but that the most important loss will be in the functional richness of marine ecosystems. Communities of organisms exist through interactions between organisms that individually possess genetic and physiological characteristics that allow them to exploit their environment.

The illustration below shows the loss of biodiversity in number of species and functional richness along an acidity gradient. The decrease in pH leads to a drastic loss of all this functional richness.



Ocean acidification, the twin sister of global warming, is the most important change in the world's biome. Assessing the extent of its consequences is scientifically extremely complex, but the current work is particularly alarming!