Focustronic Educational Program

Secrets of Coral Calcification

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**Liming / saturation index**

What is decisive for whether lime can be formed at all is the concentration of the two ions that are to be combined, ie. the concentration of calcium (Ca\(^{2+}\)) and carbonate (CO\(_{3}^{2-}\)).

Let us repeat the formula for when lime is formed:

\[ \text{Ca} + \text{CO}_3 \rightarrow \text{CaCO}_3 \]

By multiplying the concentration of Ca by the concentration of CO\(_3\) and dividing this product by a so-called solubility constant, Ksp, we get a value called the saturation index, \(\Omega\). The saturation index in a natural sea water for the calcium-carbonate-form calcite is 5, and for aragonite it is 3. This means that aragonite dissolves slightly more easily than calcite.

The formula for saturation index, \(\Omega\), thus looks like this:

\[ \Omega = \frac{[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]}{\text{Ksp}} \]

- If \(\Omega < 1\), the solution of calcium and carbonates is unsaturated, and there are no conditions for lime to be formed at all. On the contrary, already formed lime dissolves.
- If \(\Omega = 1\), a solution is saturated. There are now chemical conditions for calcium-carbonate to be formed.
- If \(\Omega > 1\), the solution is supersaturated and the conditions are then even higher for lime to be formed and spontaneous precipitation occurs if there is no inhibitors presents.

In a normal sea water (pH 8.2, Ca 410 and dKH 7.0), as mentioned above, there is a saturation index (\(\Omega\)) of 3 for aragonite and 5 for calcite, ie. calcium and carbonate are supersaturated. Why does it then not precipitate spontaneously? Major reason of that is actually that Magnesium to some extent cover the CaCO\(_3\) surface, and in that way prevent from spontaneous precipitation.

In addition to the calcium and carbonate concentrations, the pH value also plays a major role for calciumcarbonate-formation. The reason is that the pH value controls the carbonate concentration. We remember from previous article about KH, that a pH increase shifts the carbonate chain to the right, and thus gives an increase of the carbonate concentration (CO\(_3\)),

\[ \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \]

A pH increase forces the reaction going to the right
which in turn increases the saturation index ($\Omega$) for CaCO$_3$. However, since the pH value is a logarithmic scale, this means that a pH increase with e.g. 1 unit gives a 10 times doubling of the carbonate content and a pH increase with e.g. 0.3 units gives a doubling of the carbonate concentration ($10^{0.3} = 2$).

More simply: This means that if we increase the pH value by 0.3, it will be twice as easy for lime to be formed (due to the doubling of the CO$_3$ concentration).

Spontaneous calcification and biologic calcification

With spontaneous calcification we mean calcification that occurs outside a living organism, thus simply the combination of Ca and CO$_3$ to CaCO$_3$, driven by the saturation index ($\Omega$) described above.

With biological calcification we mean calcification that occurs inside a living organism, like a coral. This process is facilitated by same factors that the spontaneous, but as this also is an active process taking some energy, the coral can create its skeleton even under suboptimal conditions, even if it’s harder for the coral to do that of course.

The Zooxanthellae and calcification

With this knowledge, we now have a model in which way the zooxanthellae facilitate the biological lime formation in the coral:

When the zooxanthellae’s photosynthesis run at high speed, CO$_2$ is consumed. The reduction in carbon dioxide means that we get a pH increase local in the coral. The pH increase in turn means that the dominant HCO$_3$ ions is more easily converted to CO$_3$ ions. And, when the content of CO$_3$ ions rises, the probability of the formation of CaCO$_3$ increases. So in this way, the light, with the help of the zooxanthellae, facilitate the skeleton formation by the coral.
Other factors that can affect calcification

Add to this there are more actors that will affect calcification, both the biological in the coral and the spontaneous. The list also contains some of the factors we already have mentioned.

Temperature

Increased temperature increase calcification. The reason is that the solubility constant for \( \text{CaCO}_3 \), \( K_{sp} \), is lower at higher temperature.

Strontium

Many experience that an increase in Sr have a positive effect on calcification. One of the possible reason is that Sr, with its resemblance of the Ca ion, is a sort of precursor, that can trigger the formation of \( \text{CaCO}_3 \) crystals. Compare the mechanism with a growing snowball, starting with a very small ball, where the small starting-ball is the strontium. One of the evidence for this theory is that we know that Sr is incorporated into the aragonite crystal structure in the coral. However, the exact mechanism how Sr facilitate the skeleton formation in the coral is not known.

Phosphate

Phosphate will bind to \( \text{CaCO}_3 \) structures in a similar way that Mg do, and in that way inhibit further precipitation. This inhibiting effect concerns both the biological \( \text{CaCO}_3 \) formation as the spontaneous, as scientist have found phosphate inside the cell matrix at elevated phosphate levels. Some author say that this inhibiting properties of phosphate occurs already at levels above 0.08 ppm. However there are sometimes seen tanks with very high phosphate levels, like 0.2 ppm or more, and still corals that seems to growth very well. The reason of this is not fully explained, but could maybe be explained that these corals of some reason do not incorporate the phosphate into the cell matrix, or maybe is overcompensated by a correspondingly higher pH.

pH

An increase of pH increase the level of \( \text{CO}_3 \) in a logarithmic way, giving higher possibilities to formate \( \text{CaCO}_3 \). This applies both to the spontaneous and biological \( \text{CaCO}_3 \) formation, as the coral doesn't have to use so much energy to create \( \text{CaCO}_3 \) crystals when the saturation index is higher.

KH/Carbonate hardness

An increase of KH giving higher levels of \( \text{CO}_3 \) in a linear way (=if you double KH you double the \( \text{CO}_3 \) concentration), thus increase the saturation index, giving higher possibilities to formate \( \text{CaCO}_3 \), both the spontaneous and the biological in the coral.

Calcium

An increase of Ca increase the saturation index, and thus increase the possibility to spontaneous formate \( \text{CaCO}_3 \). But, on the contrary to the KH, increased Ca seems not to increase skeleton formation speed in coral as long as the Ca levels are above 360 ppm. This is
maybe due to that calcium transport into the coral cell is an active process, so as long as the calcium concentration outside the cell is above 360 ppm, its always same inside.

**Magnesium**

An increase of Mg, will due to mechanism described above (Mg covers the CaCO₃ crystals), make it some harder to formate CaCO₃. A decrease of Mg, will in short term make it easier for coral to formate CaCO₃, as the crystals is now not poisoned by Mg. But as low Mg, due to its facilitating of spontaneous precipitation, Ca and CO₃ will be consumed very fast, and thus in long term actually low Mg will also lower the overall calcification process. So for Mg the key is to have high levels enough to prevent spontaneous precipitation, but not that high so the calcification is too hard. Ideal level is like that we have in natural sea water.

/Jonas Roman