Magnesium: Calcium's Little Sister

Magnesium is an interesting atom that has tremendous biological and chemical relevance to reef tanks.

By Randy Holmes-Farley

Magnesium is an interesting atom that has tremendous biological and chemical relevance to reef tanks. Fortunately for reefkeepers, it is present in abundance in seawater and is depleted only slowly. Consequently, maintenance of magnesium levels is not typically a big issue if using an appropriate salt mix. Nevertheless, magnesium is a very important ion and engenders much discussion among hobbyists. In this article I'll try to add to the extensive writings that Craig Bingman has published in the past.

First, a little background on magnesium. In seawater, magnesium is invariably present in the form of a divalent cation, Mg++. It is present in seawater at a concentration of about 1300 ppm, and that concentration does not vary appreciably with depth or location in the world (besides estuaries and other places where all ions are distorted). In seawater, Mg ions outnumber Ca ions by a factor of 5. Most magnesium in seawater is present as the free ion hydrated with tightly bound water molecules. Some of it, however, forms tight ion pairs (i.e., soluble complexes) with negatively charged ions, such as sulfate, bicarbonate, carbonate, borate, fluoride and hydroxide.

Interestingly, the average residence time for a magnesium ion in seawater is tens of millions of years, substantially longer than calcium (a few million years) and aluminum (100 years), but less than sodium (about 250 million years). In a sense, this is an indication of how reactive magnesium is: it stays in seawater a long time because it's fairly unreactive, but it does get taken out of solution more readily than does sodium.

Another interesting characteristic of ions is whether they are excluded from organisms, actively taken up or just “allowed” to be present. Like sodium and sulfate, the relative concentration of magnesium in organisms is approximately the same as in seawater. More than anything else, this probably results from the fact that there is plenty of magnesium present, and that it is used by organisms for many purposes. Chloride, on the other hand, is actively rejected by organisms, and most other ions are substantially concentrated.

Why Do We Talk So Much About Magnesium?

So what is it about magnesium that gets reefkeepers talking about it so much? Is it the fact that it is important for many enzymes? No. Is it the fact that it's important for the skeletons of many organisms in reef tanks? No. It's because reefkeepers have become infatuated with measuring and “optimizing” the levels of calcium and alkalinity in their tanks, and the fact that magnesium can play a role in these levels.

What does magnesium have to do with calcium and alkalinity? Good question. In order to answer that, one has to have a basic understanding of the calcium and carbonate systems in seawater. This system is detailed in many reef-oriented publications, so I won't go into it in great detail. Suffice to say that calcium carbonate is supersaturated in seawater, meaning that given enough time calcium ions will interact with carbonate ions and precipitate as calcium carbonate. If you run the concentration of either too high, $CaCO_3$ will start to precipitate. Magnesium interferes with this process, permitting both calcium and carbonate to be elevated above where they would be in the absence of magnesium.

How does magnesium interfere with precipitation of $CaCO_3$? Two ways have been suggested, and these are detailed below. The first involves magnesium poisoning the surface of growing $CaCO_3$ crystals, slowing the precipitation. The second involves the interaction between soluble magnesium ions and soluble carbonate ions, forming an ion pair and effectively lowering the free concentration of carbonate that is available to precipitate with calcium.

Measurement of the Impact of Magnesium on the Calcium/Carbonate System

In Stephen Spotte's book Captive Seawater Fishes there is an extensive discussion of the impact of magnesium on the calcium/carbonate system. Buried in that discussion is a set of data that indicates the magnitude of the impact that magnesium can have. In this experiment, batches of artificial seawater were made up with varying magnesium and carbonate levels. The scientists then measured how long it took for calcium carbonate to precipitate from each solution. Not surprisingly, the higher the carbonate was raised, the more rapid was the precipitation of calcium carbonate.

More interestingly, the magnesium levels were found to have a very large impact on the rate of precipitation. In batches with no magnesium, and at natural calcium and elevated carbonate levels, calcium carbonate was found to precipitate in minutes. With a natural seawater level of magnesium added to that mix, the precipitation was delayed to 13 to 20 hours.

With double the natural magnesium concentration, the precipitation was delayed to 22 to 29 hours.

Even more strikingly, at a lower level of carbonate (closer to that of natural seawater and probably similar to that in many reef tanks), precipitation was delayed from a few minutes in the absence of magnesium to 750 hours in the presence of natural levels of magnesium. Consequently, we conclude that magnesium has a big impact on the rate of precipitation of calcium carbonate (a fact that has been confirmed by many researchers).

Poisoning of Growing $CaCO_3$ Surfaces

In Captive Seawater Fishes, poisoning of growing $CaCO_3$ surfaces is presented as the only explanation involving magnesium for the delay in precipitation of $CaCO_3$, and there is an extensive discussion there about how this takes place. Like many real life problems, this one is not easy to fully explain with simple chemistry, but I'll try! To get an idea of the complications involved, however, Spotte says “The study of carbonate minerals involves nuances of solubility that pose some of the most difficult problems in chemical oceanography and geochemistry.”

In short, while magnesium carbonate is not supersaturated in seawater (or in reef tanks), and will not precipitate on its own, magnesium is attracted to calcium carbonate surfaces where the carbonate ions are already held in place by the calcium ions. With the carbonate ions held in place, magnesium finds this an attractive place to precipitate. A similar effect happens for phosphate and many organics, where they precipitate onto the calcium ions that are held in place by the carbonate ions — but that's another story for another day.

When calcium carbonate (as calcite or aragonite) is placed into seawater, calcium carbonate rapidly begins to precipitate onto the fresh surface. After a short time, however, a thin coating of $Mg/CaCO_3$ (magnesian calcite) begins to form as magnesium pushes its way into the growing surface. Eventually, the surface contains a substantial amount of magnesium. The extent to which this happens depends on the underlying mineral, and is apparently much more extensive on calcite than aragonite (perhaps another reason that aragonite dissolves more readily than calcite). It also depends upon the relative amounts of calcium and magnesium in the water. Regardless, a new type of material is formed that contains both calcium and magnesium.

This new mineral surface containing both calcium and magnesium is not a good nucleating site for precipitation of additional calcium carbonate (as aragonite or calcite), and precipitation of additional $CaCO_3$ slows down substantially. Consequently, seawater and reef tanks are readily supersaturated with respect to calcium carbonate.

Ion Pairing of Magnesium to Carbonate

A second factor in the impact of magnesium on calcium and alkalinity levels involves the ion pairing of magnesium to carbonate in solution. The magnitude of this effect is likely smaller than the surface poisoning effect, but it may still be significant to the calcium and alkalinity levels attainable in reef tanks. To understand how this works, let's start back at the equation governing the equilibrium solubility of calcium carbonate in water. From the solubility product we have

$$K_{sp} = [Ca^{++}] \times [CO_3^{--}]$$

(This means the concentration of the calcium times the concentration of the carbonate equals a constant, Ksp, the solubility product constant. This is easily thought of as follows: it takes one Ca^{++} and one CO_3^{--} to come together to form $CaCO_3$, so as the concentration of either rises you are more likely to get them to come together, and so when you reach a certain amount of both, precipitation will begin).

But that is the freshman chemistry simplification. It really should read:

$$K_{sp} = ?c \times [Ca^{++}] \times ?o \times [CO_3^{--}]$$

where ?c and ?o are the activity coefficients of the calcium and carbonate respectively. These factors take into account the fact that some of the calcium and carbonate may be tied up or otherwise prevented from easily interacting with each other. In seawater, there are many things that contribute to the activity coefficient, but magnesium is one, and Millero quantifies this effect in his book Chemical Oceanography. In seawater, more than half of the carbonate ions present at any given point in time are ion-paired to magnesium, and this substantially reduces the free concentration of carbonate ions available to precipitate with calcium.

Before suggesting the magnitude of this effect, let me turn the solubility equation around a bit.

$$\text{Saturation state} = (?c \times [Ca^{++}] \times ?o \times [CO_3^{--}])/K_{sp}$$

The saturation state is a measure of how much calcium and carbonate are in solution. If the saturation state = 1, then the solution is exactly saturated. If it is above 1, the solution is supersaturated. If it is below 1, the solution is undersaturated. Natural seawater has a saturation state of 3 to 5, so it is substantially supersaturated. The higher the supersaturation, the more "pressure" there is for CaCO3 to precipitate from solution.

The interesting data presented by Millero is as follows:

If you put CO3-- into pure sodium chloride solution at the salinity of natural seawater, you get a certain activity coefficient, ?o = 0.164. Alternatively, if you put it into a mixture of sodium chloride and magnesium sulfate at natural seawater salinity and in the appropriate ratios for natural seawater, you get a lower activity coefficient, ?o = 0.134. The magnesium has lowered the activity coefficient substantially (being an anion, the sulfate would have a small impact on the activity coefficient of carbonate, also an anion).

What does this mean? Well, if we look at the saturation state equation using these values, we find that for a given concentration of calcium and carbonate, the supersaturation is lower when magnesium is present than when it is not.

Alternatively, for a given saturation state, the concentration of calcium and carbonate will be higher in the presence of magnesium. How big is the effect?

Let's say we have a certain saturation state with 400 ppm calcium in the presence of magnesium. With everything else unchanged, removing all of the magnesium (and replacing it with sodium) will result in the same saturation state at a calcium level of 327 ppm. Thus, if reef tank seems to be maxing out Ca++ at 400 ppm, then without any Mg++ it might max out at 327 ppm (through this effect alone and assuming that the calcium and alkalinity is being limited by precipitation, not by the amount being supplemented to the tank).

Note, however, that this isn't the perfect answer. It is examining the difference between having and not having Mg++ in pure sodium chloride solution, not in natural seawater. The answer in the latter case may be different. Nevertheless, it gives an idea of what magnitude of effect magnesium might be expected to have through mechanisms involving reduction of the activity of the carbonate ions in solution.

I hope this article provides reefkeepers with an understanding of how magnesium is playing a role in the calcium/carbonate system in their tanks. As is usually the case, these kinds of discussions do not tell us what levels of magnesium are optimal or how far above or below natural seawater one can safely keep a reef tank. Nevertheless, understanding what is happening in our tanks can help lead us to solutions to vexing problems, as well as to provide us with an appreciation for the great complexities that nature provides in our tanks.