Silicon — Foe or Friend?

Do you know the concentration of silicate in a typical coral reef environment, where it comes from or what happens to it?

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Figure 1

For some aquarists, one of the advantages to having a reef aquarium is that one gets to play the role of a minor god. The fate of a mesocosm of organisms is in your hands, as you control how the system is constructed and populated. All inputs and outputs of the system are under your influence, if not complete control.
What many people discover is that playing a minor god is substantially more difficult than they initially thought or hoped it would be. As they are humbled by various plagues and devastations racking what they hoped would be a utopian aquatic paradise, they seek the experience and wisdom of others. Some of what they hear is valuable information, some of it just plain wrong. Some of what they hear has a sliver of truth to it, but it has been exaggerated and distorted by ignorance and endless retellings. It is into this gray zone that we forge in this article, into the land of silicon, filled with mystery, frustration and exaggerations.

The color of fear in the American Revolution was red...the redcoats were coming and all that. In the ’50s, the color of fear was again red, with the rise of the Soviet Union to nuclear superpower status. But in the ’90s, one of the colors of fear for reefkeepers was golden-brown: The color of diatoms, nourished by their ally, silicate.

If one believed everything one hears about silicate on the aquarium newsgroups, one would soon “know” diatoms and silicate are to be avoided at all costs. One hears tales of would-be aquatic utopias overtaken by diatoms, the evil ones that eat silicate and smother prized corals. The stories have grown so strong and so polarized in their endless retellings that I find myself forced to take polite exception to what you may have heard about this widely misunderstood element. If you have read the newsgroups or read aquarium magazine articles, you know that silicate and diatoms are the enemy. Perhaps you will be shocked, dismayed and horrified to learn that I am... a diatom sympathizer.

Of course, many of you will never be turned to the side of the golden brown. To you, I say: Know thine enemy. While the newsgroups are filled with stories of individuals who wage ware against silicon with high-tech weaponry, I’ve yet to hear a detailed discussion of the role of silicate in marine ecosystems in the aquarium literature. I doubt many of you know the concentration of silicate in a typical coral reef environment, where it comes from or what happens to it.

Silicon Chemistry
Silicon belongs to the same group of elements as carbon (see Figure 1) and shares some properties with it. Elemental silicon has no known role in biology. The biologically relevant form is the +4 oxidation state, which in biological systems is almost invariantly covalently bonded to four oxygen atoms that sit at the corners of a tetrahedron around a central silicon atom.
There are a number of variations in the hydration state of these SiO_4 centers. In silicic acid, the simplest form, the four corner oxygens are part of hydroxyl groups, giving it a composition of $Si(OH)_4$. Silicic acid is a weak acid. The first deprotonation reaction is half complete at a pH of 9.47, giving $Si(OH)_3OH^-$. A second deprotonation reaction is half complete at a pH of 12.6. So, at seawater conditions (pH 8.1 on the oceanographic pH scale), approximately 96 percent of the silicic acid is in the form of $Si(OH)_4$ and four percent is ionized.

The other extreme end of silicate hydration is quartz, SiO_2, which could be thought of as completely dehydrated $Si(OH)_4$. Quartz is the least soluble form of silicon found in nature. There are many intermediate hydration forms, which could be described as $SiO_2(H_2O)_x$, where x varies between 0 (quartz) and 2 (silicic acid.) The biogenic opal formed by diatoms is one example of an amorphous, solid, polymeric form of silicic acid that is more hydrated than quartz, but much less hydrated than free silicic acid. Biogenic opal is substantially more soluble than crystalline quartz.

The reluctance of silicic acid to ionize at neutral pH is one reason why it is difficult to remove from tap water. Because the vast majority of it is unionized at neutral pH, mixed-bed ion exchange columns do not bind it efficiently. Also, because it is not strongly ionized, it does not have the tight hydration shell that simple ions typically carry in water. So, silicic acid passes through many reverse osmosis (nanofiltration) membranes fairly readily. Some newer membranes have higher rejection rates than older cellulose triacetate (CTA) or thin film composite (TFC) membranes, and they are available on the aquarium market.

The other main technique used for removing silicic acid from water is to use a deionization resin that is charged with only hydroxide ion. As impurities in the water bind to the resin, hydroxide ion is released, and the pH in the resin chamber goes up. As the pH increases, silicic acid is converted into ionized silicate, and it can then be bound to the deionization resin and removed from the product water.Click image to enlarge

Figure 2

Silicon Geochemistry

Silicon is one of the most abundant elements in the crust of the earth. A simplified version of the silicon cycle in nature is that silicon enters the hydrosphere as it is released from eroding rocks on land. It is carried to the sea in both soluble form and in small particles of silicate minerals suspended in the water. The concentration of silicon in mean “world river water” is 218 micromoles per kilogram of river water (13.1 parts per million as SiO2). Figure 2 shows the concentration of silicon in the world ocean (IRI/LDEO Data Explorer; Conkright et al. 1994, Levitus et al. 1994). You can see plumes of red (high silicate) where rivers empty into the ocean, with their fresh load of silicate. However, over most of the ocean surface, the silicate concentration is very low. Biological processes keep its concentration low in ocean surface water.

Diatoms and other groups of marine organisms absorb silicate from the water and convert most of it into skeletal materials. Diatoms are the main consumers of silicate in the ocean, followed by sponges and a number of protist groups. Some higher organisms have small requirements for silicon, which will be described later. The skeletons of dead diatoms sink from the surface waters into the depths of the ocean, where the diatom skeletons gradually dissolve. The silicate dissolved in the ocean depths comes back to the surface of the ocean in areas with upwelling currents. There are several such areas visible in Figure 2, perhaps the most prominent of these being off the western coast of South America.

Diatom uptake, death, sinking and dissolution followed by upwelling currents constitutes the biological and physical “pump” that gives rise to the oceanic distribution of silicate, along with silicate input from rivers. Silicate is far from saturated throughout the ocean, and biological processes keep it undersaturated at the surface of the ocean. This is in contrast to calcium carbonate, another major skeletal building block of marine organisms, where removal of CO2 from the ocean surface makes the top layer of the ocean supersaturated with respect to all forms of calcium carbonate.

You will also notice a very strong correlation between silicate concentration and latitude. Between 30 N and 30 S, the approximate range of coral reefs, the oceanic concentration of silicate is quite low. In the polar regions, silicate concentrations are substantially higher. A concentration of 5 micromoles per kilogram of seawater or less is typical. Although there is definitely a trend to higher silicate concentrations in the ocean depths, where the mean silicate concentration is over 100 micromoles per kilogram at 1,000 meters depth, the concentration of silicate is very low through the photic region of the tropical ocean, where the organisms that inhabit our aquaria live.

“Mean tap water” has a composition similar to “mean river water” and the concentration of silicate in mean river water is about 40 times higher than the silicate concentration in surface seawater in the tropics. So, here is our first problem and one that the aquarium community seems quite familiar with: Some tap water is loaded with silicate and it can certainly promote diatom blooms in reef tanks.

Silicon and Aquarium Husbandry

Diatoms are interesting in that they are the major group of algae that have an absolute requirement for silicate. But we all know it takes nitrogen, phosphorus and other essential micronutrients to grow hair algae and other unsightly types of algae in a reef aquarium. Diatoms have the same requirements, with the additional, absolute requirement for silicon for growth. So, it takes more than just silicate to grow diatoms, and if diatoms are growing, they are growing by using nutrients that might otherwise fuel the growth of other types of algae. Unfortunately, this is completely lost in the popular aquarium literature.

Moreover, diatoms are very easily controlled by herbivores. Most of the herbivorous snails sold in the aquarium trade are primarily diatom predators. By limiting silicate input into an aquarium without similar attention to other nutrients, you aren’t just selecting against diatoms. You are selecting for other types of algae, some of which may be considerably more difficult to control biologically than diatoms. If I had to pick one type of nuisance algae in my aquarium, I’d pick diatoms every time.

Diatoms also sequester nutrients into nice little packages that are relatively easily removed by foam fractionators. Some of the “grit” apparent in dried skimmate consists of diatom skeletons. They are relatively easily dislodged from the surfaces of the aquarium with a cleaning magnet. Every time you clean diatoms off the front glass of your aquarium, you are essentially feeding the system with phytoplankton. Diatoms also dominate the assimilatory nitrate reduction of the world’s oceans. So, they are quite good at converting something you might not want accumulating in your aquarium — nitrate — into a valuable food source for many marine organisms.

I will be the first to admit that some areas have problematic concentrations of silicate in tap water and that it is a nuisance when the silcate concentration of a system containing other inorganic nutrients is high. However, given the advantages of having some diatom growth in a reef aquarium, it is clear they are not the scourges of the aquarium world they are made out to be. I'd even go so far as to suggest it might be good for your system as a whole to have enough silicate in the water as to warrant cleaning the front glass with a cleaner magnet every day or two. I believe the "center of mass opinion" in the aquarium community now is that silicate should be kept so low as to absolutely minimize the need for this activity.

Additonal support for the importance of silicate in marine systems can be found in the scientific literature. In 1997, Barthel and coworkers published an important pair of papers on the uptake of silicate by the sponge Halichondria panicea. The first paper demonstrated a positive correlation between the nutritional status of the sponge and silicon uptake. A positive correlation was found between silicate concentration and silicate uptake by Halichondria panicea.

The second paper was even more interesting. Reincke and Barthel showed that under their experimental conditions, silicate uptake by Halichondria panicea followed the hyperbolic kinetics very common in biological systems. This kinetic signature indicates that some saturable uptake mechanism is operating. The silicate uptake mechanism of this sponge operates at half maximal velocity at 46 micromoles of silicate/kilogram of seawater. This is much higher than a typical ocean surface silicate concentration, and it is one to two orders of magnitude higher than the same kinetic parameter measured in diatoms (e.g., Brzezinksi and Nelson 1996). What this means is quite simple: If you are actually limiting the growth of diatoms in your system by restricting silicate input into the system, you are very probably also severely limiting silicate uptake by sponges, because the uptake mechanism of sponges seems to be much less efficient than the uptake mechanism of diatoms. Perhaps this accounts for some of the usual spectacular failure of ornamental sponges to flourish in aquarium culture. It would be valuable to have more data on kinetic parameters of the silicate uptake mechanism of other species of sponges.

Other recent literature indicates that over evolutionary time, oceanic silicate availibility may have had dramatic effects on the species composition of reef communities. Maldonato and coworkers (1999) have speculated that the dramatic decline of sponge communities from the Jurassic to Cretaceous era reefs may be related to a decrease in dissolved silicate in the oceans over that timescale. They speculate that sponges with an obligate need to form desmas (massive spicules composed of biogenic opal) were forced into deepwater habitats by silicate limitation at a time coincident with a massive evolutionary radiation of diatoms near the Cretaceous-Tertiary boundary. These studies suggest that silicate limitation may have shaped reef communities in the past, and it is not too long a stretch to postulate that perhaps silicate availability affects our ability to successfully keep some types of sponges in our systems. If silicate abundance shaped species diversity over geological time (Racki 1999), so might it shape the abundance of silicate-requiring life in our aquaria.
Figure 3

Silicon in Synthetic Seawater

Several years ago, the silicate concentration or lack thereof in various brands of synthetic seawater was made into a major selling point for certain brands of synthetic seawater. Atkinson and Bingman (1999) analyzed the elemental composition of eight types of synthetic seawater. The results of that study are summarized in Figure 3. Most of the brands are relatively close to oceanic reactive silicate concentrations. Several of the brands contain much more total silicon (determined via inductively coupled plasma spectroscopy analysis) than is truly dissolved in tropical ocean surface water. However, the total silicon concentration in all brands is less than a quarter that found in "mean world river water." In the brands of synthetic seawater with the lowest concentration of silicon, the concentration is less than one tenth that found in mean world river water. The commonsense interpretation of this is that tap water is often a much larger source of silicon input into reef aquariums than are the constituents of "dry" synthetic seawater mixes. Only people who use highly purified water need to be concerned at all about that concentration of silicate in synthetic seawater mixes.

I have a feeling that at least part of the disdain some aquarists have for doing partial water exchanges is because the incoming synthetic seawater has a higher silicon concentration than the water in the aquarium, where silicate has been depleted by diatom growth. Because aquarists have been brainwashed into believing diatoms are unconditionally bad, performing a water exchange is something to be avoided. In areas where the silicate concentration is pathologically high, perhaps this might have been a significant issue prior to recent advancement in water purification technology. Given that partial water exchanges are a very simple way to correct chemical problems in an aquarium, it is very unfortunate that some people are avoiding what could be a profoundly stabilizing influence on the water chemistry in their systems, simply to avoid growing a few diatoms.

Summary and Directions for Future Research

If I were to tell you that there is an organism that can help compete with nuisance algae for nutrients, and will allow you to feed your system phytoplankton simply for the cost of rubbing a magnet on the front glass of your tank, you might be willing to pay quite a lot of money to get such a creature established in your system. Because this organism actively reduces nitrates and packages nutrients in easily skimmable (as well as nutritious) packages, you might be willing to pay even more. I'm hopeful you will not be too disappointed to learn that you already have them in your aquarium, nor too sheepish to learn that you have been doing your damnedest to wipe them out. They are none other than your old enemy, diatoms. One sometimes wonders if the minor aquarium gods always know what they are doing, or what implications their choices might have for their aquatic worlds.