Fragile guardians of the sea

How decaying shells help preserve the alkalinity of the seas

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▲ **Fig. 1** An example of a sea butterfly. Its wing-like protrusions, which propel it through the water, are called parapodia. Note that the pteropod’s aragonite shell is nearly transparent.

Calcium carbonates produced by sea creatures help to maintain the ocean’s alkalinity – and also serve as a natural sink for anthropogenic carbon dioxide. To better understand essential but obscure deep-sea galvanization processes, Olivier Sulpis of Utrecht University developed an innovative 3D reactive-transport model that shows how seashells assist with preserving calcite grains in seafloor sediments.

Where is the boundary between an organism and its environment? We can visually distinguish trees from the soil, birds from the sky, and seashells from the sea, but looks can be deceiving. We may see hard borders between living and nonliving things, but look deeper: the seemingly solid edges of organisms are actually a porous fabric – as beautiful and profound as any tapestry can be.

Organisms become what they are by exchanging matter with their environment and by reshaping these environments as well. Our eyes and minds may struggle to perceive what happens on a molecular level, but the impact of life’s interplay with the environment can be enormous – perhaps as big as the ocean itself.

Small but significant

Consider, for example, the sea butterfly (**Fig. 1**). “It is like a miniature snail we would see on land, but with wings to fly around in the water,” says Olivier Sulpis, a geochemistry researcher in the Department of Earth Sciences at the Netherlands‘ Utrecht University. Sea butterflies (also called pteropods) are smaller than 1 cm, and they produce their thin, translucent shells from aragonite, a form of calcium carbonate ($CaCO_3$).

Sea butterflies synthesize aragonite from materials found in seawater, including calcium and carbon. When pteropods die, the dissolution of their aragonite shells neutralizes some of the CO_2 which is suspended in seawater. In this way, the world’s vast population of sea butterflies helps to maintain the alkalinity of the ocean. But rising oceanic CO_2 levels could disable sea butterflies from producing their shells in the first place. A shrinking population of aragonite producers could thereby add to a vicious cycle of accelerated acidification.

“Butterflies are ‘first responders’ of ocean acidification because they are so vulnerable,” says Sulpis. Unfortunately, humanity is struggling to interpret the message of these first responders. Sea butterflies are abundant, but not well-known, especially after they die and sink to the deepest parts of the ocean. One theory proposes that dissolving aragonite shells trap and neutralize CO_2 by interacting with calcite (**Fig. 4**, another form of $CaCO_3$) found in seafloor sediment.

This galvanic deep-sea process could be even more important to maintain oceanic alkalinity than the reactions occuring during the lifespan of the creature. Micrometer-scale chemical processes are very difficult to study, especially when they take place one kilometre or more underwater. To better understand this elusive phenomenon, Sulpis has developed a novel three-dimensional model how aragonite interacts with calcite-rich sediments on the seafloor [1].

Sustain life in the ocean in death

Sea butterflies may seem like an unlikely subject for such intense study, but they and their fellow $CaCO_3$ producers have an outsized impact on their environment. During their lives, pteropods cycle through a vertical commute, rising toward the surface at night and descending during the day. They feed on microorganisms and draw calcium and dissolved carbon from the ocean to build their fragile aragonite shells (**Fig. 2**).

„In seawater, calcium and dissolved carbon are everywhere,“ says Sulpis. „They are ideal ingredients to build crystal structures.“ Calcium carbonate compounds are at the basis of many seashells and exoskeletons formed by corals.

The world’s coral reefs are perhaps the most visible oceanic examples of an interwoven network of living and inanimate matter (**Fig. 3**). A healthy reef features living corals that actively synthesize crystal structures from calcium and dissolved carbon. In addition, it consists of dead corals, which continue to interact with their surroundings as they decay. While they sustain a diverse ecosystem of plant and animal life, decomposing corals help maintain the ocean‘s alkalinity and add to the carbonate-rich sediments which cover the seafloor. Dead pteropod shells also contribute to these sediments, though their exact role is actually rather mysterious.

The missing aragonite

Most corals produce their skeletons from calcite, which is the most common $CaCO_3$ compound found in the oceans. As noted earlier, sea butterfly shells are made from aragonite. “Aragonite and calcite are both $CaCO_3$ compounds, but their crystal structures are different. They are built with the same bricks, but the bricks are not arranged the same way,” Sulpis explains. From his perspective, aragonite deserves more consideration for its role in the oceanic carbonate cycle. “We do not know a lot about aragonite, but we are able to estimate how common it is in the shallower waters, where the sea butterflies live,” Sulpis says. “When the shells sink to the ground and reach the deep ocean, the aragonite does not last: Sample cores from deep ocean sediments comprise mostly of calcite.”

There is an explanation for the “missing” aragonite: In deep-sea environments, the dissolving aragonite chemically interacts with calcite, thereby protecting the latter compound from dissolving. However, this theory cannot be tested by studying the oceanic aragonite cycle directly.

An „embarrassing“ gap

According to Sulpis, it is embarrassing how little is known about open-ocean aragonite cycling. The estimates in published papers how much calcium carbonate exists in the form of aragonite range from ten to ninety percent. The scarce knowledge of aragonite cycling stems from the difficulty of conducting research in the deeper parts of the ocean due to the limited ability to place sensitive instrumentation there. Referred to Sulpis, it is nearly impossible to observe reactions

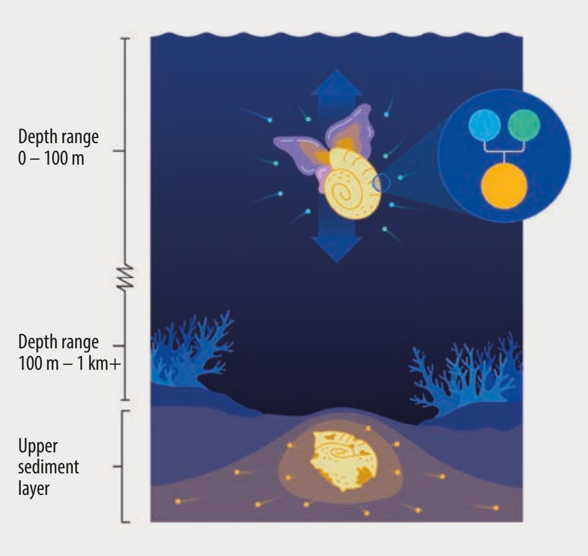

Fig. 2 An illustration of pteropod‘s role in the oceanic carbonate cycle. Living sea butterflies draw calcium and carbon dioxide from sea water to build their shells, which consist of calcium carbonate in the form of aragonite. After pteropods die, their shells sink to the seafloor, where their $CaCO_3$ shells decompose. This decomposition helps sustain the alkalinity of the oceans and builds up carbonate-rich sediments over time.

in seawater at this scale and depth since the environment is almost inaccessible. Physically removing specimens from deep-sea sediment is also challenging, especially when the materials to be studied are so fragile. “It is really hard to recover sea butterfly shells with a sediment trap,” says Sulpis. It takes too much time to retrieve them so that they are likely to have dissolved. Therefore, there is a lack of good data about calcium carbonate reactions at deep sea pressures and temperatures.

Previous attempts to mathematically model the behavior of calcium carbonate in seawater have treated all $CaCO_3$ as calcite, rather than creating separate models of aragonite. In addition, existing diagenetic ‚continuum‘ models do not take into account what is happening at the scale of a single grain, or a single pore in a seashell. Besides, older models have rendered $CaCO_3$ grains as smooth, uniform objects, which is not accurate. In contrast, these grains are complex and heterogenous micrometer-scale shapes with insides and outsides.However, some simplifications are necessary, but it is preferable to replicate the actual shapes as closely as possible, at the smallest scale possible. „Before deciding to simplify some structures, we wanted our simulation to confirm that these simplifications would not compromise results,“ asserts Sulpis.

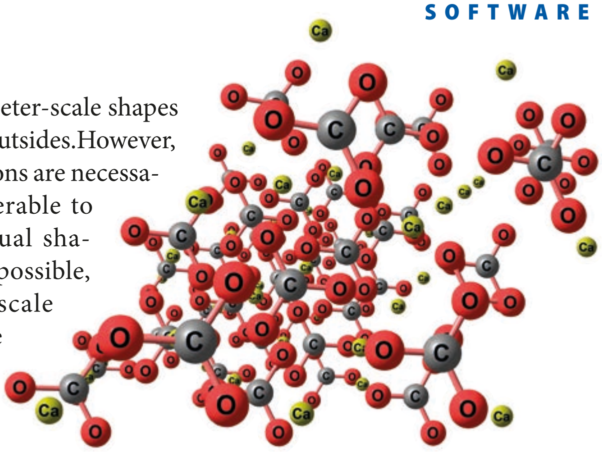

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Fig. 4 A schematic of the molecular structure of calcite.

A simulated deep dive

For a deeper understanding of how calcite and aragonite interact at the seafloor, Sulpis developed a three-dimensional model using the COMSOL Multiphysics® software. This model allows moving virtually among the boundaries between oceanic organisms and their environment. It enables researchers to simulate the dissolution reactions occurring among aragonite and calcite grains and the seawater that surrounds them. The water’s alkalinity, density, and chemical composition were set to match typical deep-sea conditions. The team modeled various solids and simulated their interactions with seawater and seafloor sediment. Sulpis also added seashell models, based on scans of actual specimens, to his sediment-water interface. The *H. inflatus* pteropod shell (**Fig. 5**), for example, is based on a CT scan of a specimen from the Cariaco Ba-

Fig. 3 A healthy coral reef consists of living corals as well as calcium carbonate structures left behind by now-dead corals.

Kristin Hoel via Unsplash

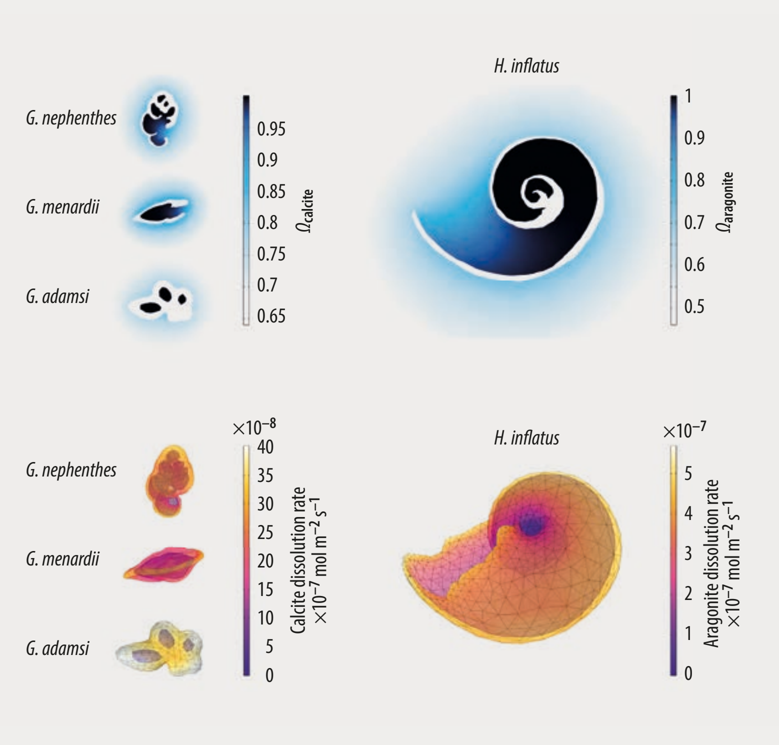

Fig. 5 Simulation images of four pteropod species' seashells, showing changes after being submerged for one minute. The highlighted *H. Inflatus* shell is made of aragonite, while the others consist of calcite. The $CaCO_3$ saturation levels (top, blue) in the surrounding seawater are compared to the rate at which the shells dissolve (bottom). Note that the intricate inner shapes of the shells appear to have little effect on saturation levels.

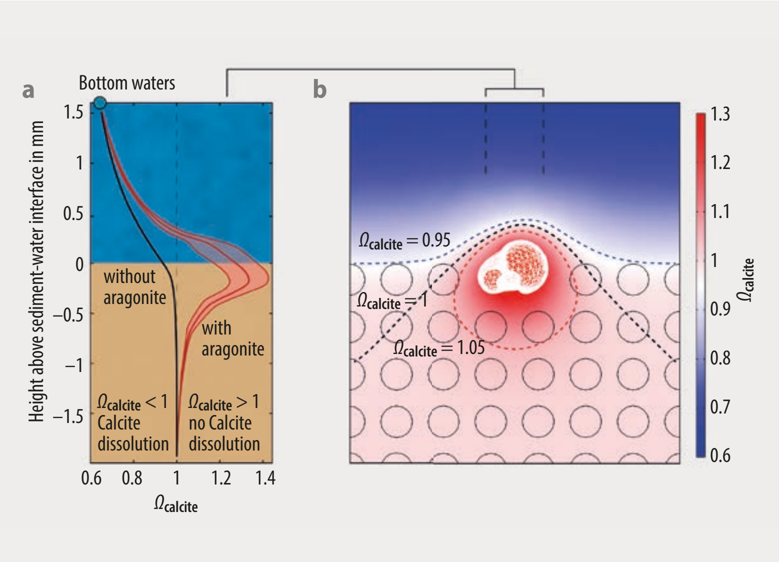

Fig. 6 The tendency for calcite dissolution differs above, at, and below the sediment-water interface (a). In the absence of aragonite, calcite will continue to dissolve (black) while the presence of the shell will prevent calcite from dissolving (red). A simulation (b) shows how a dissolving pteropod shell affects the boundary zone around the sediment-water interface: Grains of calcite (circles) are suspended in the sediment; the presence of aragonite prevents their dissolution (red).

sin off the coast of Venezuela. Such three-dimensional images enabled the simulation to take the irregular shape of a shell into account during its dissolution.

The simulation indicates that the inner shape of a shell may not have a significant impact on how it reacts with seawater. "If you look at the top row, it tells us that inside these shells, the trapped water might become completely saturated with $CaCO_3$. This prevents further dissolution along the complex inner surface; the shells dissolve from the outside. These results suggest that some simplifications of a shell's modeled shape will not necessarily affect the results, at least, if the shell is completely surrounded by seawater.

The simulation enables adding a mix of seashells and seawater to calcite-rich sediment (**Fig. 6a**). A dissolving sea butterfly shell exerts a galvanizing action on calcite grains mixed into the sediment (**Fig. 6b**). These grains were rendered as spheres – a simplification based on the results of previous simulations.

The seawater mingling with solids near the sediment-water interface plays a crucial role in this process. However, one-dimensional models use a boundary between seafloor and the water resembling a perfect solid line. In reality, the boundary is varied and seawater is circulating around solids, even below the apparent line of separation. Capturing the gradated boundary between seawater and sediment is one of the advantages of Sulpis's three-dimensional model. As the pteropod shell dissolves, the surrounding seawater becomes saturated with aragonite. This zone of aragonite-saturated seawater chemically interacts with – and protects – the calcite left behind by other organisms (**Fig. 7**).

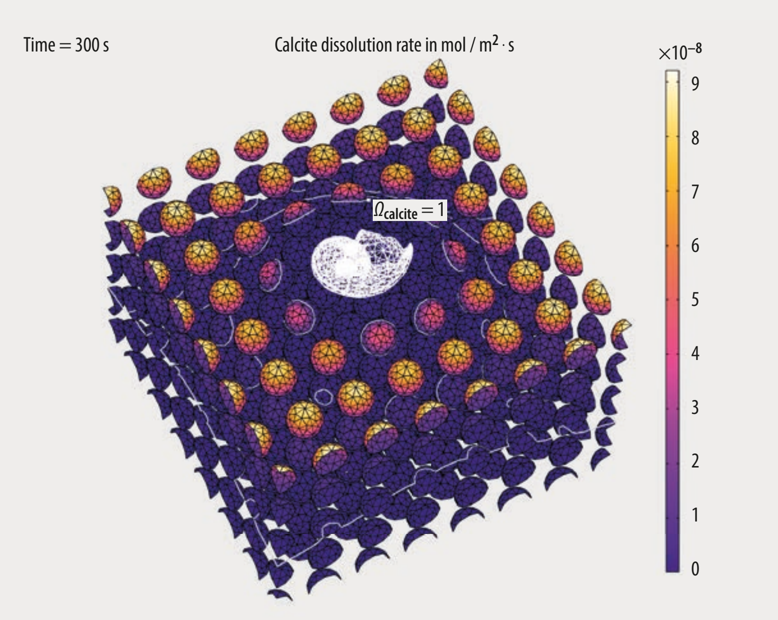

Fig. 7 Simulation results showing how the presence of a pteropod in the seafloor sediment affects the dissolution rates of nearby calcite grains. Lighter colors indicate a more rapid dissolution. A saturation line (white) or isocontour exists where calcite is at equilibrium with its dissolution byproducts: No net dissolution or precipitation occurs.

Helping to mend the seas

Having developed a new means of analyzing underwater micrometer-scale biochemical processes, Sulpis is now exploring how his work can guide further research. As a next step, he wants to replicate these processes in the lab, with calcite and pteropod shells in beakers. So far, experimental results are similar to the outcome of the simulation. Sulpis aims for a better interpretation of the in-situ observations. Toward this end, he and his colleagues have obtained a grant from the Dutch Research Council (NWO) to directly study how aragonite producers shape their environment.

Despite the interaction of the sea shells with the ocean, the greatest impact on the environment stems from humans. Anthropogenic acidification threatens the life-sustaining network of ocean creatures. With this in mind, the understanding carbonate cycles becomes urgent: “Compared to the amount of CO_2 we are adding to the oceans, only a tiny amount is being neutralized,“ says Sulpis. “It might take several thousand years to balance our contribution!”

In a more immediate perspective, people should apply his research and analysis to protect the sea butterflies’ world – and ours. All models are open access and Olivier Sulpis‘s simulations of calcium carbonate seashell dissolution are available for download at *zenodo.org/record/5741613*.

[1] *O. Sulpis* et al., Nat. Commun. **13**, 1104 (2022)

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