

## OCEAN SCIENCE

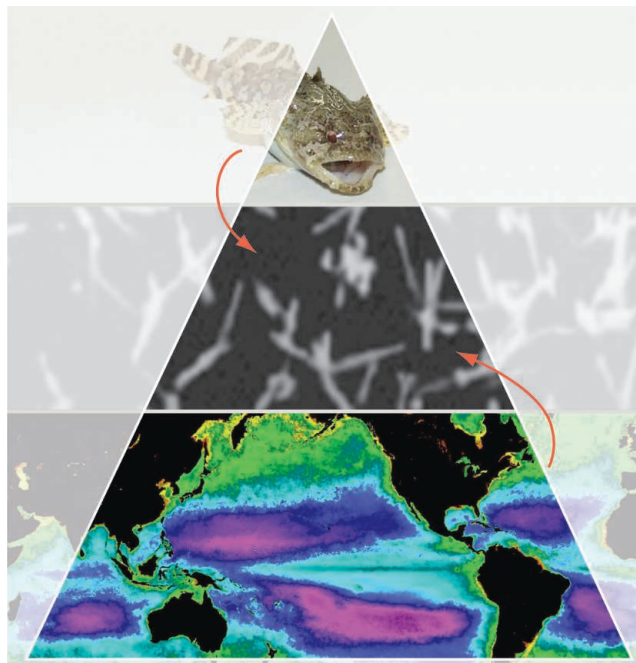
# Animal Function at the Heart (and Gut) of Oceanography

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Far more biomass is contained in marine primary producers than in marine animals at higher levels of the food chain. This relation suggests that animals—particularly secondary consumers such as fishes—must play a negligible role in elemental cycling in the world's oceans (1). However, given that the midwater ecosystem is the largest on Earth, with over 99.5% of the habitable space (2), the activity and metabolism of oceanic animals across great depth ranges, especially in productive regions, should perhaps not be discounted (3, 4). Unfortunately, marine animal biomass, distribution, and function are not sufficiently well known to fully reconcile these opposing views (5). On page 359 of this issue, Wilson *et al.* (6) elucidate a physiological pathway, common to all marine bony fishes, that seems to contribute substantially to the marine inorganic carbon cycle.

The first clue to a possible role of fish in the marine inorganic carbon cycle came from studies of toadfish, *Opsanus beta*. In 1991, while investigating the fate of urea-derived carbon, Walsh *et al.* observed pellets in the toadfish's gut (7), which were later found to be a metastable form of calcite that contains large amounts of magnesium. The source of these "gut rocks" was not immediately obvious, but Walsh *et al.* reasoned that if common to all fish, they might contribute to the inorganic carbon cycle.

More than a decade of detailed physiology has revealed how and why gut rocks form. As far as is known, all bony fishes regulate their internal osmolarity at a level considerably lower than that of seawater and, in seawater, must drink to remain hydrated. However, absorption of the imbibed fluid by the intestine is osmotically limited by the concentrated ions in sea-



**An unexpected role.** Fishes at the top of the trophic pyramid are traditionally considered unimportant for biogeochemical cycles because of the loss of energy as one moves from low to higher levels in the food chain. This stylistic pyramid shows how marine fish, as first discovered in the toadfish *Opsanus beta* (top), produce precipitated carbonates ("gut rocks") within their intestines (middle) (6) and make a substantial contribution to the global calcium carbonate cycle (bottom) (estimated  $\text{CaCO}_3$  concentrations for the world oceans).

water. Active acid-base regulation facilitates precipitation of the divalent ions as gut rocks and promotes fluid absorption. This appears to be a universal phenomenon critical to the survival of all marine-adapted bony fishes.

For most of the past century, substantial dissolution of calcium carbonate ( $\text{CaCO}_3$ ) was believed to occur only in the deep waters that are undersaturated with respect to the various phases of calcium carbonate. However, more recent observations of water column alkalinity reveal that substantial dissolution of calcium carbonate must be occurring at depths well above this "chemical lysocline" (8). The most likely explanation is dissolution of more soluble forms of calcium carbonate, such as the aragonitic shells of pteropod mollusks. More studies on  $\text{CaCO}_3$  are needed, particularly in remote regions like the Southern Ocean (9), but current estimates of such sources fail to explain all of the mysterious

Animal physiology has a substantial impact on the marine inorganic carbon cycle, for example, through the formation of calcium carbonate "gut rocks" in bony fish.

alkalinity. One possible source is the high-magnesium calcite from which gut rocks are formed; its lysocline is shallower than that for other forms of carbonate, and gut rocks would therefore dissolve at shallower depths. However, few oceanographers took note of Walsh's gut rock hypothesis.

Wilson *et al.* have now modeled the size, composition, and abundance of marine fish across the global ocean using two different approaches. Each relies on satellite-derived estimates of global primary productivity from phytoplankton and the conversion of organic matter from one trophic level or link in the food chain to the next (10) (see the figure). It is thus imperative, particularly in this era of climate change, that satellite assets be maintained and expanded via consistent national investment to produce quality imagery (11) that can be used not only to assess traditional phytoplankton concentrations but also to model top-down linkages in the food chain (6, 12, 13). Because of the immensity of the oceans, small

variations in model assumptions can swell into vastly different global results. Nevertheless, when coupled with global models and estimates of sea surface temperature, the present analysis predicts substantial fish carbonate production across the world ocean—enough to explain at least one-quarter of the increased alkalinity, or 3 to 15% of total oceanic carbonate production.

Comparative physiology is a thriving field, but is rarely applied to oceanographic problems. Wilson *et al.* (6) show convincingly that animals, even in the upper trophic levels, can affect elemental cycles via their physiological manipulations. Previous studies have recognized several mechanisms by which animals may contribute to such cycles. For example, many oceanic animals undergo diel vertical migrations from their shallow feeding grounds to depths of several hundred meters, where they continue to excrete respi-

CREDITS: (TOP) USGS; (MIDDLE) FROM (6); (BOTTOM) NASA AQUA MODIS SATELLITE IMAGE

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ratory carbon dioxide, effectively pumping carbon out of the atmosphere to the deep sea (3). Metabolic suppression and anaerobic metabolism, used by some migrators during daytime forays into expansive oxygen minimum zones, may reduce the efficiency of this biological carbon pump in some regions (14). The efficiency of carbon pumping is similarly reduced in the Southern Ocean, where air-breathing mammals and birds are a key component of the food chain. They respire massive amounts of photosynthetically derived carbon back into the atmosphere (13). In contrast, larvaceans increase carbon flux by concentrating particles in their mucus feeding webs that then sink rapidly to depth (15). All these processes depend on the demand for energy, which varies between species by up to three orders of magnitude [see supporting online material (6)].

Despite their potential importance, these and similar phenomena remain

poorly constrained for most oceanic taxa. It is thus difficult to estimate or predict the role of animal function in biogeochemical cycles. The relevant processes must be recognized and quantified, their rates scaled up, and put in the context of global elemental budgets. Wilson *et al.*'s important contribution to our knowledge of the inorganic carbon cycle will hopefully infuse a new appreciation for the role of higher trophic levels in ocean dynamics. Clearly, the field is moving beyond the dismissive viewpoint described by Horne, in which animals were merely a source of "heterogeneity in the sea" [(16), p. 239]. As he noted, "Our element of seawater may well contain an important second phase we have not mentioned—a fish" [(16), p. 3].

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## MATERIALS SCIENCE

# Beyond Biomineralization

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Modern strategies to design advanced materials are often inspired by nature. For instance, during biomineralization, living organisms can impose highly complex shapes and textures with remarkable structural hierarchy upon solid inorganic matter to produce materials that often far exceed the performance of human-made counterparts (1, 2). However, crystallization in purely inorganic systems can also yield smoothly curved forms that resemble those of biomaterials (3). These so-called "biomorphs" are obtained by coprecipitation of barium carbonate (witherite) and silica from alkaline media. A concerted self-assembly process yields nanosized carbonate crystallites that arrange in a highly ordered manner over micrometer lengths, thereby shaping morphologies such as regular helicoids on scales up to millimeters—all in the absence of any complex organic additive or surface scaffold. On page 362 of this issue, García-Ruiz *et al.* use video microscopy to provide insight into several steps decisive for structure evolution and identify a chemical feed-

back process as the driving force for the observed self-organization (4).

A striking similarity between these abiotic biomorphs and most actual biomaterials is their mode of construction, with hierarchical structuring over many length scales and preferential crystallographic orientation. In turn, the chemistry and preparation of the biomorphs are rather simple, thus rendering them excellent model systems to study multiscale interactive self-organizing phenomena.

One of the principles of self-organization explored by García-Ruiz *et al.* is a dynamic, pH-based coupling of equilibria, which induces alternating precipitation of the components. The sensitivity of silicate and carbonate speciation to pH fluctuations in alkaline media, together with pH gradients close to the mineralizing fronts and opposite pH trends in solubility of silica and barium carbonate, are fundamental prerequisites in this context. In other words, an acid and a base (i.e., hydrogen carbonate and silicate) are alternately subject to local neutralization, the latter being directly linked to precipitation. Neutralizing one leads to local conditions under which the other is suddenly out of equilibrium—a situation somewhat reminiscent of the famous

Self-assembly of purely inorganic components can also give rise to complex structures and morphologies once thought restricted to biological materials.

Belousov-Zhabotinsky reaction (5). Silica thereby acts, via precipitation, as an inhibitor for continued carbonate crystal growth first, to stimulate renewed carbonate nucleation later on.

This concept has obvious potential for the design of systems that spontaneously self-assemble to yield highly organized materials. An interesting challenge will be to look for other "acid-base" pairs that would engage in a similar coupled process if conditions are adjusted properly. Simple substitutions such as replacement of barium by one of its alkaline-earth homologs have already been done with success (6, 7). However, the search for alternative reagent pairs should also extend to phenomena beyond those related to pH effects and precipitation; such pairs may be based on a principle analogous to the pH-mineralization feedback. This feedback process teaches us an important lesson: Oscillating precipitation does not necessarily imply periodic structures. The latter arise as a consequence of spatial oscillation, as observed in common banded Liesegang patterns (8). In the present case, oscillation is only of a temporal nature, resulting mainly in encapsulation of carbonate crystallites by silica rather than formation of

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