Biogenic Fish-gut Calcium Carbonate is a Stable Amorphous Phase

Berko Award Application

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Although most oceanic $CaCO_3$ production is attributed to planktonic organisms such as coccolithophores, foraminifera and pteropods, a lesser-known source originates from the intestinal tracts of marine boney fish. As part of a unique osmoregulation strategy, marine fish actively drink seawater and precipitate biogenic calcium carbonate, which facilitates water absorption and maintains Ca^{2+} homeostasis. The focus of my research has been to investigate some of the fundamental characteristics of this novel biomineral, namely the morphology, composition and behavior in seawater pre- and post-excretion. Due to previous identification of fish carbonates as Mg-calcite, sensitive preparation procedures and analytical tools were employed to preserve the original state of the mineral and to detect minute changes in the mineral structure.

FTIR spectroscopy and SEM imaging revealed that fish carbonate minerals are in fact formed and maintained as a stabilized amorphous calcium carbonate (ACC) phase, with an exceptionally high Mg content (the highest yet reported among biogenic ACC). Furthermore, when fish carbonates were incubated in varying seawater pH, the carbonate ion concentration doubled on average in samples containing fish carbonates, significantly increasing ($p<0.01$-0.0001) the alkalinity value. We believe that the substantial Mg ion incorporation, along with other as yet identified macromolecules, are responsible for the stability of the mineral throughout its residence in the intestinal tract, as well as its high solubility characteristic.

With a better understanding of the biomineral's basic properties and its behavior in seawater, we present a practical application of our data, estimating that fish carbonate products contribute modestly to the present marine environment. And in regard to the potential role fish may play in future seawater conditions, our study suggests fish could provide beneficial seawater buffering to micro-environments, such as niches found in coral reefs.