EMPIRICAL DEFINITION OF STABLE CARBON ISOTOPE FRACTIONATION FACTORS IN BIOGENIC HIGH MAGNESIUM CALCITE

Cameron Sam, Sarah Walls[1], Bret Marek[1], Martin Grosell[1], Amanda M. Oehlert
1) *Department of Marine Biology and Ecology, Rosenstiel School of Marine, Atmospheric, and Earth Science*

PROJECT OBJECTIVES

- Measure the $\delta^{13}C$ values of intestinal fluid and ichthyocarbonate
- Calculate the fractionation factor (ε) for ichthyocarbonate formation
- Assess the relationship of ε with mol%$MgCO_3$ content

PROJECT RATIONALE

Ichthyocarbonate is a magnesium-rich carbonate mineral produced in the intestine of marine teleost fish (Wilson et al., 2009). Through ichthyocarbonate production and excretion to the environment, marine fish contribute to both the biological and carbonate pumps, processes which are important controls on atmospheric carbon dioxide concentrations (Grosell and Oehlert, 2023). Ichthyocarbonate is composed of significant proportions of both dietary carbon and seawater dissolved inorganic carbon (DIC; Oehlert et al., 2024), in contrast to other marine calcifiers which principally use DIC. Notably, no value for the fractionation factor between intestinal fluid and ichthyocarbonate has been reported, creating uncertainty in estimates of intestinal fluid δ13C values, and thus the contribution of dietary carbon to ichthyocarbonate formation (Oehlert et al., 2024). Previously, ε was assumed for ichthyocarbonate based on measurements conducted on high magnesium calcite with varying magnesium contents formed in inorganic precipitation experiments (i.e. Jimenez-Lopez et

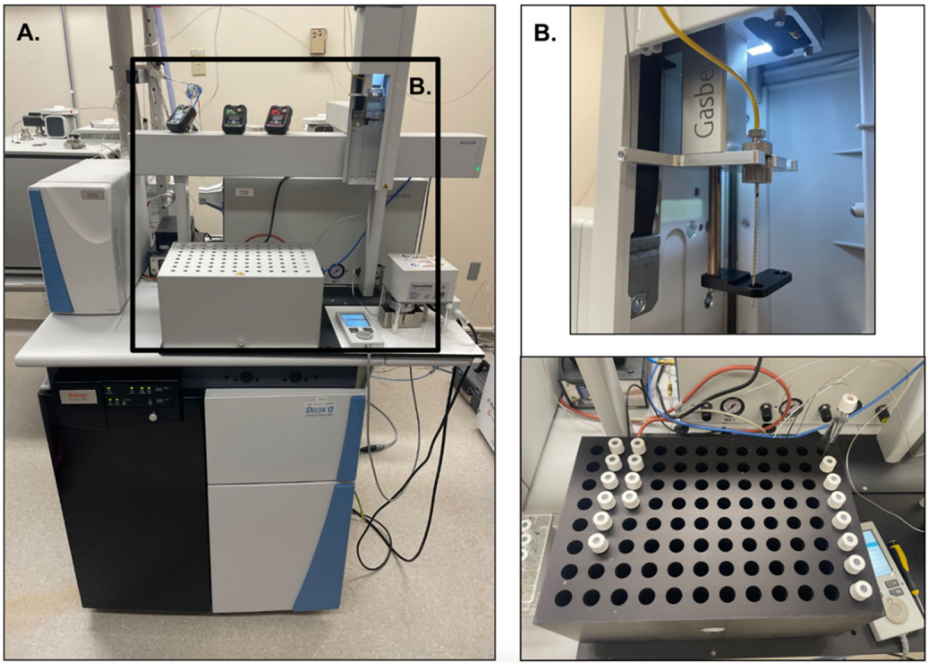

Figure 1: (A) The ThermoFisher Delta Q IRMS + EA Isolink CNS allows for stable isotopic analysis of carbon, nitrogen, and sulfur, (B) The Gasbench Plus allows for measurements of the stable carbon isotopic composition of evolved CO2 gas from acidification of intestinal fluids with H3PO4.

al., 2006) and natural dolomite (Sheppard and Schwarcz, 1970). Based on the high mol%MgCO3 content of ichthyocarbonate (14 – 50‰; Heuer et al., 2012; Salter et al., 2012), the predicted range of ε is + 0.9 – 2.2‰ with increases in ε expected with increasing mol%$MgCO_3$ (Oehlert et al., 2024).

APPROACH

Here we will empirically determine ε by measuring the $\delta^{13}C$ values of intestinal fluid and ichthyocarbonate collected from Gulf toadfish (*Opsanus beta*). Gulf Toadfish were fasted for 3 days, then ichthyocarbonate and intestinal fluid were collected via dissection, along with samples of seawater and excreted ichthyocarbonate. Muscle samples were also collected to fully parameterize the mixing model, which were analyzed on an EA Isolink CNS + Delta Q. The $\delta^{13}C$ values of intestinal fluid, seawater, and ichthyocarbonate were analyzed using the Gasbench Plus + Delta Q. By subtracting the $\delta^{13}C$ values of intestinal fluid from the $\delta^{13}C$ values of ichthyocarbonate, we calculated for the first time the fractionation factor for ichthyocarbonate formation. Additional work to measure the mol%$MgCO_3$ content of ichthyocarbonate and the Mg/Ca ratio of intestinal fluid is underway.

SIGNIFICANCE

We performed the first measurements of paired ichthyocarbonate and intestinal fluid $\delta^{13}C$ values, while developing novel methods for the processing and analysis of intestinal fluid. Additionally, our preliminary analyses suggest the mineralogical fractionation factor of ichthyocarbonate is + 1.62‰. This new measurement will enable researchers to refine estimates of dietary carbon incorporation in ichthyocarbonate, which is one of the top three sources of global marine carbonate production (Wilson et al., 2009; Oehlert et al., 2024) and will provide insight into fractionation factors associated with the formation of biogenic HMC more generally.

REFERENCES

Grosell, M., & Oehlert, A. M. (2023). Staying hydrated in seawater. *Physiology, 38*(4), 178-188.

Heuer, R. M., Esbaugh, A. J., & Grosell, M. (2012). Ocean acidification leads to counterproductive intestinal base loss in the gulf toadfish (Opsanus beta). Physiological and Biochemical Zoology, 85(5), 450-459.

Jimenez-Lopez, C., Romanek, C. S., & Caballero, E. (2006). Carbon isotope fractionation in synthetic magnesian calcite. *Geochimica et cosmochimica acta, 70*(5), 1163-1171.

Oehlert, A. M., Garza, J., Nixon, S., Frank, L., Folkerts, E. J., Stieglitz, J. D., . . . Del Campo, J. (2024). Implications of dietary carbon incorporation in fish carbonates for the global carbon cycle. *Science of the Total Environment, 916*, 169895.

Salter, M. A., Perry, C. T., & Wilson, R. W. (2012). Production of mud-grade carbonates by marine fish: Crystalline products and their sedimentary significance. Sedimentology, 59(7), 2172-2198.

Sheppard, S. M., & Schwarcz, H. P. (1970). Fractionation of carbon and oxygen isotopes and magnesium between coexisting metamorphic calcite and dolomite. *Contributions to Mineralogy and Petrology, 26*, 161-198.

Wilson, R., Millero, F., Taylor, J., Walsh, P., Christensen, V., Jennings, S., & Grosell, M. (2009). Contribution of fish to the marine inorganic carbon cycle. *Science, 323*(5912), 359-362.