Freshwater shells as monitors of river contaminants

Brian W. Stewart, University of Pittsburgh

Motivation

- Rivers in populated, industrial regions such as western Pennsylvania can be severely impacted by pollution from multiple sources.
- Because contaminant inputs change as new industries emerge or as remediation efforts evolve, it is critical to monitor the effects of these changes, in the past as well as the present.
- We propose to apply a new method for measuring sensitive natural isotope signals in freshwater mussels to develop a record of past changes to Allegheny River water chemistry over the past several decades.

Project Description

- We will test the application of novel Ba and Sr isotope systems by comparing mussel shells (native and invasive) with potential metal sources
  - Dissolved metals in river water
  - Suspended organic matter (food source)
  - Sediment substrate
- We will analyze the shells of multiple mussel species
  - Possible species-dependent vital effects on isotope uptake
  - Determine shell mineralogy by XRD
- We will extend the record back in time
  - Analyze mussel shell growth rings
  - Identify annual changes in metal sources
  - Relate to industrial or other potential pollution inputs

Context

- Sessile species like mussels passively record water chemistry over time
- Shell metal concentrations can be affected by many factors, while isotopes are taken up in a predictable way
  - For example, Ba isotopes are strong indicators of hydraulic fracturing (**Fig. 1**)
  - We are applying novel isotope systems to *reliably* track multiple pollution inputs into surface water over time

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We are developing **new metal isotope tracers** in mussel shells as robust recorders of stream water chemistry over time

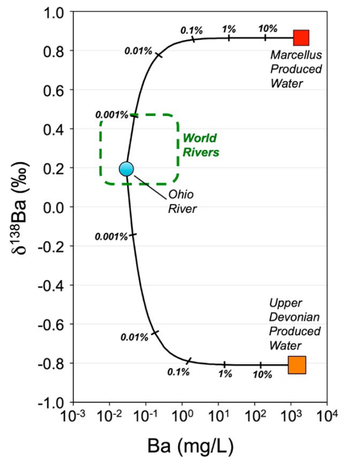

Fig.1: Our group showed that the ratio of $^{138}Ba/^{134}Ba$ (expressed as $\delta^{138}Ba$) varies tremendously between Marcellus Shale "frack" waters and conventional oil and gas well brines. Thus leakage or spills of Marcellus waters will be recorded in freshwater mussel shells as a sharp increase in $\delta^{138}Ba$. Figure from Tieman et al. (2020).

Project Deliverables

- By the end of the funding period, we will have completed the following:
  - Sampling and analysis of coexisting shells and stream water
  - Determine species-dependent (both native and invasive) mass fractionation of Ba and Sr isotopes in shell calcium carbonate
  - Analyzed shell mineralogy (multiple species) by x-ray diffraction
  - Determine the isotopic composition of suspended organic material (mussel food source)
  - Carry out first analysis of past shifts in water chemistry by microsampling shell material in mussels >30 years old
- Within 1-2 years after the end of funding:
  - PhD student Kristi Dobra, lead on this project, will have completed her dissertation
  - We will have submitted at least two scientific journal articles establishing the method
  - We will establish a collaboration with outside freshwater bivalve experts
  - We will submit a proposal a federal agency (e.g., NSF) to expand the work beyond western Pennsylvania

Potential Impact

- The proposed research lays the groundwork for using freshwater bivalve shells as a temporal record of metal inputs into surface water, allowing correlation of changes to water quality to specific sources
- Once the proposed method is developed, it can be applied to any freshwater system that hosts shell-bearing organisms, providing a useful monitoring and recording tool.

References

Tieman, Z.G., Stewart, B.W., Capo, R.C., Phan, T.T., Lopano, C.L., Hakala, J.A. (2020) Barium isotopes track the source of dissolved solids in produced water from the unconventional Marcellus Shale gas play. *Environ. Sci. Technol. 54*, 4275-4285.