

Western Kentucky University
TopSCHOLAR®

Mammoth Cave Research Symposia

11th Research Symposium 2016

Apr 19th, 9:30 AM

Potential Evidence for Arsenic Mineralization in Mussel Shells in the Upper Green River Basin, Kentucky

Autumn Turner

Crawford Hydrology Laboratory, Western Kentucky University, autumn.turner610@topper.wku.edu

Chris Groves

Crawford Hydrology Laboratory, Western Kentucky University, chris.groves@wku.edu

Aaron Celestian

Natural History Museum of Los Angeles County

Albert Meier

Department of Biology, Western Kentucky University, albert.meier@wku.edu

Follow this and additional works at: http://digitalcommons.wku.edu/mc_research_symp

 Part of the [Animal Sciences Commons](#), [Forest Sciences Commons](#), [Geology Commons](#), [Hydrology Commons](#), [Other Earth Sciences Commons](#), and the [Plant Sciences Commons](#)

Recommended Citation

Autumn Turner, Chris Groves, Aaron Celestian, and Albert Meier, "Potential Evidence for Arsenic Mineralization in Mussel Shells in the Upper Green River Basin, Kentucky" (April 19, 2016). *Mammoth Cave Research Symposia*. Paper 3.
http://digitalcommons.wku.edu/mc_research_symp/11th_Research_Symposium_2016/Day_two/3

This is brought to you for free and open access by TopSCHOLAR®. It has been accepted for inclusion in Mammoth Cave Research Symposia by an authorized administrator of TopSCHOLAR®. For more information, please contact todd.seguin@wku.edu.

Potential Evidence for Arsenic Mineralization in Mussel Shells in the Upper Green River Basin, Kentucky

Autumn Turner¹, Chris Groves¹, Aaron Celestian² and Albert Meier³

¹ Crawford Hydrology Laboratory, Western Kentucky University

² Natural History Museum of Los Angeles County

³ Department of Biology, Western Kentucky University

Introduction

Harvesting and burning of fossil fuels results in the release of numerous derivatives known to be detrimental to the environment and its fauna. Environmental conditions within Kentucky's Green River Basin are impacted by emissions from various regional coal burning power plants. Emissions from these activities contribute to acid deposition/precipitation. Coal burning increases atmospheric CO₂ concentrations that in turn lower rainfall pH, and sulfur within the mineral pyrite (FeS₂) often contained within coal can be oxidized to contaminate rainwater with sulfuric acid. Other byproducts associated with coal power production include toxic metals including mercury and arsenic that can be deposited onto land and water surfaces.

Together, these major contributors to surface water acidification can pose substantial threats to aquatic biota, particularly among calcifying organisms. Aquatic systems are very sensitive to associated changes in water chemistry and concerns exist that biodiversity may suffer as a consequence. Economic motivations have called for study into the effects of lowered pH on the dissolution of calcite shells in marine molluscs as it relates to community and population health. The results of these studies indicated that decreases in pH lead to significantly higher mortality rates in juvenile mussels, including death by dissolution (Green, 2004) and impaired periostracum repair in adults (Rodolfo-Metalpa, 2011). Less well studied is whether human impacts on atmospheric chemistry with regard to pH or other characteristics may be impacting, and whether evidence for these impacts is present in the shells of mollusks such as mussels in fresh water ecosystems. These organisms are an important component of the biodiversity within Kentucky's Green River Basin.

The purpose of this exploratory study sought to determine whether there is mussel shell evidence of ecological impact of emissions from regional coal power production including the TVA Paradise Fossil Plant and others by examining shell mineral constituency of *Actinonaias ligamentina*, a common freshwater mussel species. We examined shell material collected in about 2000 (Kirkland, 2002) from Lawler Bend on the Green River, several kilometers upstream from Mammoth Cave National Park (MACA). This part of the Green River Basin has been shown to be impacted by fallout from coal combustion, with historically lowered rainfall pH and elevated sulfate concentrations based on data from the Houchin Meadow atmospheric monitoring station near MACA (NADP, 2016).

Evolution of the Evidence

In an evolving sequence of events, we began by analysis of shell thin-section (Figure 1) within a transect across annually deposited shell layers with Raman Spectroscopy. In



Figure 1: Scanned image of *Actinonaias ligamentina* shell thin section used in Raman Spectroscopy mineral analysis.

this process samples are excited with a laser beam, and analysis of the resulting electron scattering emanating from the regions where the beam impacts the sample provides information on molecular vibrations in the system, which in turn can be used as a “fingerprint” to identify the constituent molecules present. For solid mineral samples, comparison of these data with existing libraries of spectrum data can identify constituent minerals present that make up a sample. As expected, the great bulk of the shell through the central region was composed of calcium carbonate

(CaCO₃) in the form of aragonite. However, bands on the inside and outside of the shell showed a different distribution of Raman Spectra (Figures 2 and 3). An analysis of one of these spectra (Figure 4) to our surprise indicated the presence of the relatively rare ferrous sulfate-arsenate mineral bukovskyite (Fe₂(AsO₄)(SO₄)(OH)·7H₂O), also historically known as the poisonous “clay of Kutná Hora.” Figure 4 shows a comparison of the sample’s Raman spectrum with the library standard, showing a close correlation of relevant peaks. If the mineral is indeed found within the shell, it may suggest that these organisms have directly bioincorporated the material into the shells during formation of annuli. To our knowledge, bukovskyite has never been identified or described as present in the shells of freshwater mollusks.

An immediate question that arises would be to identify the sources of these various constituents, in this case arsenic (As), sulfur (S) and iron (Fe). It is clear that coal burned through the years at regional power plants over the tens of years that the mussel growth represented contains the mineral pyrite, particularly coal from western Kentucky

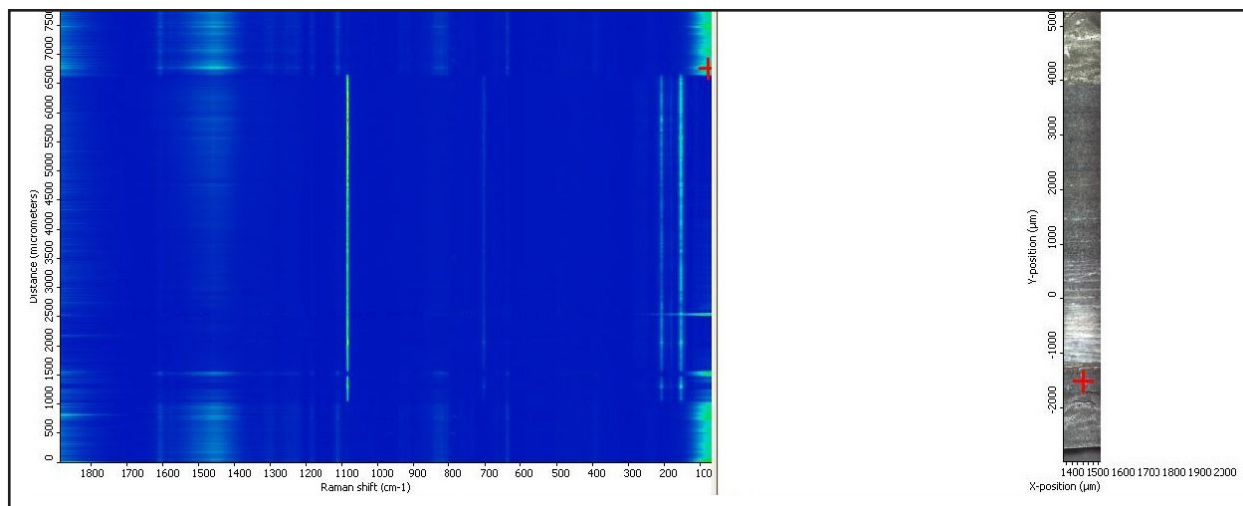


Figure 2: Distance vs. Raman shift for entire section of *Actinonaias ligamentina* shell analyzed.

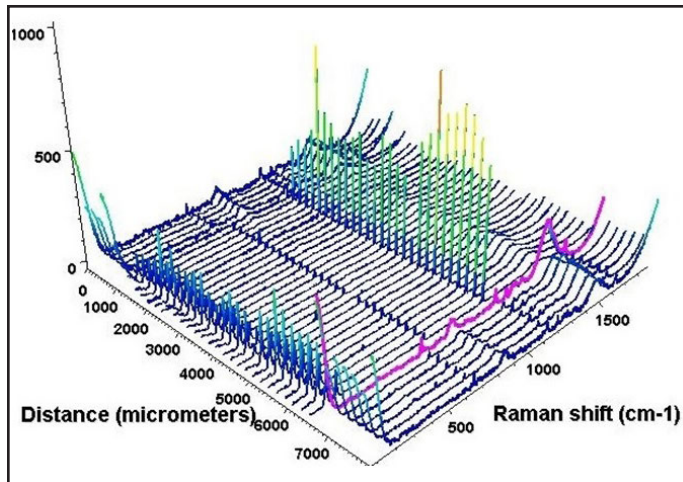


Figure 3: Topographic representation of Raman spectra generated from entire *Actinonaias ligamentina* shell analysis.

that was burned during years before being augmented/replaced by lower sulfur coals from Wyoming's Powder River Basin. Within coal, arsenic can be associated with pyrite as 1) arsenic-rich pyrite, within which some iron has been replaced by arsenic up to about 10% by weight, 2) as the mineral arsenopyrite (FeAsS), or 3) as arsenate (AsO_4^{3-}) (Huggins et al. 1993; Huffman et al., 1994). Upon combustion, within coal ash this is generally present as arsenate species.

Our team decided that an additional, independent identification of the presence of bukovskyite, or at least arsenic, would be important to confirm the Raman spectroscopy results. We first investigated the thin section under a Scanning Electron Microscope (SEM) with attached capacity for Energy Dispersive Spectroscopy (EDS), which has the ability to provide elemental analysis for near surface layers. Examining the regions that had shown the unusual spectra, and not knowing whether the bukovskyite, if present, was evenly disseminated throughout that region of the shell or was isolated as discrete particles, we focused the fine (micron scale) beam on

heterogeneous light and dark spots and found no indication of arsenic. It is not clear from these results whether there 1) is not arsenic in the samples, 2) whether we did not examine the right microscopic sites, or 3) whether arsenic is present but at concentrations below the detection limit of the EDS technology.

We then worked to digest in acid solutions an amount of powdered sample, from another of Kirkland's (2002) shells collected downstream from the first one that had already been ground to run the resulting fluid on Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES) which is able to measure trace elements with high sensitivity. After dissolving in a hydrochloric/nitric acid solution there was still some insoluble residue, and so a second digestion using hydrofluoric acid was completed. There was still a small amount of insoluble material present and so a third digestion, using a lithium tetraborate dissolution technique at 1050°C . A small amount of insoluble residue remained still. ICP OES analysis of the fluid showed no arsenic above the detection limit, and Raman Spectroscopy analysis of the insoluble crystals indicated that these are made of quartz. We are uncertain as to whether there was no arsenic in this sample, or whether what was present was below the detection limit. Ongoing efforts will work to grind samples from the same shell from which the bukovskyite Raman spectrum was obtained, and to repeat this analysis with a larger quantity of shell material digested.

Conclusions

Although the Raman spectrum showing a close match to bukovskyite is consistent with the potential presence in the Upper Green River basin of arsenic-bearing pyrite species or byproducts from coal combustion, at this

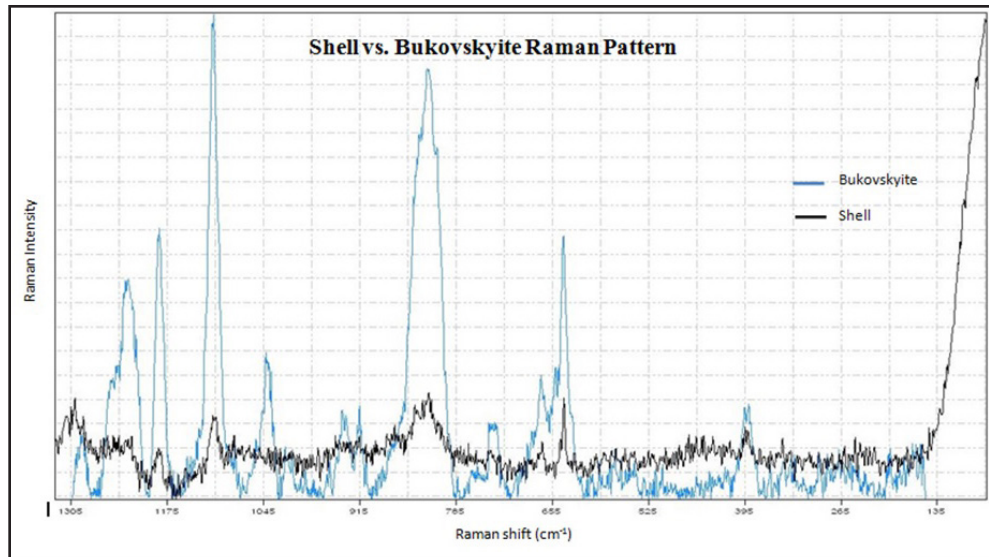


Figure 4: Raman pattern of shell vs. Bukovskyite pattern from CrystalSleuth® mineral database.

stage we are left to further consider what this discrepancy of findings might suggest and how this may affect the prospects for identifying mussel individuals exposed to arsenic species associated with coal combustion. Raman spectroscopy is a powerful tool for determining the mineral constituency of a material and the apparent close match of the spectrum generated from examination of inner and outermost layers of the shell to a known standard spectrum gives cause to continue exploring along these lines. Currently, we have not ruled out the possibility that arsenic is present within the shell sample based on lack of support from EDS spectroscopy for several reasons as discussed above. The point of interest in this research is that if mussels in the Green River are bioincorporating these arsenic derivatives associated with coal combustion fallout processes, it may be possible to reconstruct a biologically preserved record of changes in coal-burning emissions in the region from mussel specimens that were extant in periods coincident with atmospheric conditions prior to Clean Air Act Title IV emission stack modifications

and the switch to burning lower sulfur coal as well as those conditions present post-modifications.

References

- Green, M.A., Jones, M.E., Boudreau, C.L., Moore, R.L., & Westman, B.A. (2004). Dissolution mortality of juvenile bivalves in coastal marine deposits. *Limnology and Oceanography* 49: 727-734.
- Huggins, F.E., Shah, N., Zhao, J., Lu, F. and Huffman, G.P. (1993). Nondestructive determination of trace element speciation in coal and coal ash by XAFS spectroscopy. *Energy & Fuels* (7): 482-489.
- Huffman, G.P., Huggins, F.E., Shah, N. and Zhao, J. (1994). Speciation of arsenic and chromium in coal and combustion ash by XAFS spectroscopy. *Fuel Processing Technology* (39): 47-62.
- Kirkland, R. (2002). *Actiononaias ligamentina as a biomonitor in the Green River: An unique approach for analysis of environmental impacts*. Bowling Green, KY: Western Kentucky University Master's

thesis. Accessed online at: (< <http://digitalcommons.wku.edu/theses/605/> >). (Accessed November 3, 2015).

National Atmospheric Deposition Program. (2016). Weekly samples for site: KY10 (Mammoth Cave National Park-Houchin Meadow). Accessed online at: (< <http://nadp.isws.illinois.edu/nadpdata/weeklyReport.asp?action=weeklyReport.asp&site=KY10&allSites=False&wholestate=False&custom=False&startmonth=01&startyr=2002&endmonth=10&endyr=2015&reportType=html&useType=1&useDescription=Thesis+research&submit=Get+Data&userid=331782> >). (Accessed February 13, 2016).

Rodolfo-Metalpa, R., Houlbreque, F., Tambutte, E., Boisson, F., Baggini, C., Patti, F.P., Jeffree, R., Fine, M. Foggo, A., Gattuso, J.P., and Hall-Spencer, J.M. (2011). Coral and mollusc resistance to ocean acidification adversely affect by warming. *Nature Climate Change* 1: 308-312.