El Niño impact on mollusk shell biomineralization

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Marine macroinvertebrates are ideal sentinel organisms to monitor rapid environmental changes associated with climate change. Chemical proxies from mollusk shells are widely used for detecting variations in seawater parameters (e.g., temperature and productivity) related to such changes. However, the influence of known, and recurrent, climatic events on biological processes during active mineralization, and thus on shell chemistry, is still insufficiently understood.

Analysis of Peruvian cockles from the 1982-83 large magnitude El Niño event show significant alterations in shell biomineralization, linked to microstructural changes and the loss of organic matrix components. These alterations are associated to modifications in magnesium and barium content of aragonite cross lamellar shell layers, while strontium content is nearly constant throughout the event. An increase in magnesium is a possible response of the mollusk specimens to the loss of proteins and the need for the stabilization of amorphous calcium carbonate. Additionally, the increase of barium after the El Niño onset is related to upwelling. Overall, these findings contribute to a better understanding the effects of abrupt climate change on mollusk shell structures, while also offering a new view for proxy application to the reconstruction of El Niño events.

Mobility of trace elements from the Sunbury Shale, eastern Kentucky

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Black shales contain high concentrations of trace elements and may serve as important sources of strategic metals, U and REEs as conventional ore deposits become scarcer. However, the increased use of hydrofracturing for shale gas development as well as possible future mining and processing of black shales for extraction of shale oil could potentially facilitate release of toxic trace elements to hydraulic fracturing or retort process waters, surface water and ground water. Quantifying the concentrations and relative mobility of trace elements from black shales is thus important from both economic and environmental perspectives. A better understanding of trace element mobility from natural weathering of these deposits may also be of use for researchers using outrcop samples to determine paleodepositional conditions.

The Sunbury Shale (lower Mississippian) is one of the youngest units making up the thick Devonian and Mississippian black shale sequence in the Appalachian Basin. This study compares the trace element geochemistry of samples collected from two exposures of Sunbury Shale located < 8 km apart along the eastern margin of the Cincinnati Arch (western flank of the Appalachian Basin). At one site, fresh to minimally weathered samples were collected from a roadcut excavated only a month prior; the second site was a roadcut exposed for ~40 years, wherein the shale was visibly weathered. The Sunbury Shale has, on average, higher levels of trace elements than the much thicker Devonian Ohio Shale that outcrops in the study area (Perkins et al., 2008) and its 5-m thickness readily allowed for comparative sampling of the entire unit from each of the sites. The results indicate that the 40 year period of surface weathering resulted in significant ($\alpha = 0.05$) loss of some trace elements, particularly those associated with sulfides (e.g., Cd, Cu, Ni, Zn). No significant differences were found with respect to the concentrations of Cr, Mo, V that are associated with refractory phases. No significant differences were found with regards to As or Se concentrations, although these elements are also associated with sulfides. This may be due to preferential sorption of these oxyanions under the locally acidic conditions resulting from sulfide oxidation.

[1] Perkins, Piper, and Mason (2008), *Palaeogeography, Palaeoclimatology, Palaeoecology* **265**, 14-29.