

Chalcophile elements as potential recorders of anoxia in estuarine sediments

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Hypoxia or anoxia in modern estuaries and coastal marine waters occurred in many cases before environmental monitoring was routinely performed. The history of natural vs. human causes needs to be clarified in order to correctly design remediation efforts. Previous work points to Mo profiles in dated sediment cores as useful for recording information about the history of anoxia. We investigated fifteen other chalcophile elements in the deep channel sediments of Chesapeake Bay to see if they can provide additional insights. All elements studied are markedly enriched relative to crustal abundances. Excess (above crustal) concentrations for Co, Cu, Zn, Ag, Cd, In, Sn, Sb, Te, Tl, Pb and Bi are highly correlated, suggesting a single process control. After 1940, concentrations of these elements are cyclic (~20 y period). A known climate cycle affecting river inflows has a similar period. However, the years when chalcophile element abundances peaked correspond to times of discharge minima, whereas peak anoxia occurred in years with discharge maxima. Therefore, these elements' deposition fluxes are not controlled by anoxia. We propose that their enrichments originate from aerosol contamination of soils in the watershed. Decade scale variations in discharge vary the mix of contaminated surficial vs. natural weathering products emerging from the watershed. In contrast to the elements studied here, the Mo concentration is exceptionally high in seawater and anthropogenic sources are weak. This accounts for its apparently unique capacity to record information about past redox conditions in estuaries.

Unanswered questions in deep carbon science

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The question of possible abiogenic origins of hydrocarbons is part of the larger problem of the deep carbon cycle. In spite of carbon's importance, many unanswered questions remain regarding the physical, chemical, and biological behavior of carbon-bearing systems at depths greater than a few hundred meters.

Recent results from field, experimental and theoretical studies point to the need for a new broadly interdisciplinary effort to understand deep carbon reservoirs and fluxes, the extent of possible deep abiotic organic synthesis, and the nature and extent of the deep biosphere. The Deep Carbon Observatory is a new international organization devoted to the study of these unanswered questions [1].

Recent findings underscore the need for a focus on deep carbon science. In particular, experimental discoveries of high-P-T organic synthesis from inorganic precursors [2], observations of complex interactions between organic molecules and minerals [3], field evidence for significant outgassing of C-O-H-N volatiles [4], recognition of extensive deep microbial ecosystems [5], and new experimental measurements and theoretical models of carbon sources and sinks [6] demand a careful reappraisal of deep carbon.

[1] <http://dco.ciw.edu>; [2] Kutcherov *et al.* (2002) *Proc. Russ. Acad. Sci.* **387**:789; Scott *et al.* (2004) *PNAS* **101**:14023; [3] Hazen (2006) *Am. Mineral.* **91**:1715; [4] Sohn *et al.* (2008) *Nature* **453**:1236; [5] Roussel *et al.* (2008) *Science* **320**:1046; [6] Oganov *et al.* (2008) *EPSL* **273**:38; Nakajima *et al.* (2009) *PEPI* **174**:202; Zhang & Duan (2009) *GCA* **73**:2099.