

Metals in black shales

BERND LEHMANN^{1*}

^{1*} Technical University of Clausthal, Mineral Resources,
bernd.lehmann@tu-clausthal.de

Post-Archean marine black shales with organic carbon content of several wt% have long been known to be enriched in a broad metal spectrum. These metals reflect accumulation of biogenic matter with a composition relatively close to that of planktonic organisms. A suite of redox- and particle-sensitive metals also accumulates through precipitation/adsorption from seawater and reflects the environmental conditions of the ocean bottom water as a function of bacterial respiration/organic matter degradation. Oxidic conditions are characterized by enrichment of Mn and locally Ba, whereas suboxic (also denitrifying) conditions typically have high P, and in places high V or Cr concentrations; anoxic and euxinic conditions (both sulfate reducing) may display V, U, Mo, and Ni enrichments..

Advanced organic matter decay under reducing conditions will release Ni, Cu, Zn from biogenic matter which may be incorporated in pyrite or in other sulfides. Consequently, Ni, Cu, Zn may indicate the original presence of organic matter even if partially or totally lost after deposition. Lateral facies variation with distinct metal zoning between these different depositional environments corroborates the general model, which, at very advanced reaction progress, is best preserved in restricted and stratified Early Cambrian basins on the Yangtze Platform of South China. Hydrodynamically induced winnowing of hardground with oolitic Mo-S-C and Ni sulfide compounds has here produced spectacular metal tenors in the % range in euxinic portions, grading into suboxic V-rich black shale (V in illite), with huge stratigraphically equivalent phosphorite deposits in oxic/suboxic settings, as well as 10s of meter thick "stone coal" (sapropelite).

Anoxic/euxinic marine environments may also provide the reducing milieu for focussed seafloor metal precipitation from hydrothermal fluids related to sediment-hosted massive sulfide systems (Cu-Pb-Zn-Ag-Ba), as documented by the presence of host basal black shale units in many SEDEX massive sulfide ore deposits (such as Rammelsberg, Germany; HYC, Australia; Howards Pass and Sullivan, Canada; Red Dog, USA). Basal black shale is also found related to Late Archean/Early Proterozoic banded iron formation (Minas Gerais and Carajás, Brazil).

Black shales preserve their reducing lithology with geological time and may then act as epigenetic traps for redox-sensitive metals in a broad hydrothermal ore deposit spectrum. Examples are orogenic gold and Carlin-type gold deposits where gold deposition is controlled by carbonaceous host rocks, or unconformity-related uranium deposits which are controlled by graphite-rich basement rocks. Roll-front/sandstone-hosted uranium deposits are also controlled by reducing host rocks within a much wider oxidizing depositional environment. The same applies to the European Kupferschiefer and Central African copper shale deposits where basinal brines leach postorogenic red bed/molasse basins and Cu (Co) + other minor redox-sensitive elements are deposited at thin carbonaceous rock units.

Links between sediment reactivity, sediment oxygen demand, and the N isotope effect of benthic N loss: Model and field observations

MORITZ F. LEHMANN^{1*} AND MOHAMMAD ALKHATIB²

¹ Universität Basel, Department for Environmental Science, Basel, Switzerland, moritz.lehmann@unibas.ch (* presenting author)

² GEOTOP, UQAM-GRIL, Département des Sciences Biologiques Montreal, Canada, alkhatib.mohammad@courrier.uqam.ca

Abstract

We report ¹⁵N/¹⁴N ratios of pore water nitrate and reduced dissolved nitrogen (RDN=DON+NH₄⁺) in sediments from various marine environments, where microbial nitrate reduction has previously been identified as a significant sink for fixed nitrogen (N). In order to address the combined isotope effects of benthic N-cycle processes (ϵ_{sed}) on the water column nitrate pool and to assess the dependence of ϵ_{sed} on various environmental factors, we calculated the net fluxes of dissolved N across the sediment-water interface from simulated pore water profiles corresponding to denitrification under varying sedimentation regimes. The model simulations suggest that differences in sediment reactivity and sediment oxygen demand have a significant effect on the geometry of the oxic layer and the denitrification zone, and thus on the expression of the biological N-isotope effect of denitrification in the water column. Model predictions were confirmed by observational benthic isotope flux data from an estuarine environment characterized by gradients in organic matter (OM) reactivity, bottom water oxygen concentrations, as well as benthic respiration rates. In agreement with the model, observed values for ϵ_{sed} ranged between 1 and 6 ‰ and diffusion-limitation of nitrate to the depth of denitrification was identified as the main cause of the general under-expression of the biological fractionation (>20‰) at the sediment water interface. The pore water RDN pool in the sediments was enriched in ¹⁵N relative to the water column so that the (OM reactivity-controlled) efflux of RDN to the water column acts to enhance ϵ_{sed} . ϵ_{sed} reflects the $\delta^{15}\text{N}$ of the N₂ lost from marine sediments and thus best describes the isotopic impact of N elimination on the oceanic fixed N pool. Our mean value for ϵ_{sed} (4.6‰) is larger than assumed by earlier work, questioning current ideas with regards to the state of balance of the modern N budget.