Do hyperenriched black shales correspond with periods of elevated atmospheric O_2?

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Hyperenriched black shales (HBS) contain anomalously high levels of organic carbon and a wide variety of trace elements, in particular Mo, Se, Zn, Ni, Cu, U, and V, and, in some cases, Cr, Co, Ag, Au, PGE, and REE. The source of metals has been controversial, but recent research (e.g. [1]), suggests that seawater could be the source for most redox-sensitive elements.

HBS occur at particular times during Earth history, for example in the Early Cambrian to Early Ordovician (Niutitang Fm., S. China; Arthur Creek Fm., N. Australia; Alum Shale, Sweden and Norway), Middle Devonian (Popovich Fm. W. USA; Canol Fm., NW Canada), Middle Carboniferous (Linton, Heath and Chattanooga Fms. USA; Lisburne Group Alaska; Mecca Quarry Shale of the Midcontinent USA), Middle to Late Permian (Kuperschiefer, N. Europe; Phosphoria Fm., USA). Based on Se contents and Se/Co ratios in marine pyrite, periods of HBS deposition occur at peaks of atmosphere-ocean oxygenation [2]. This seems to be counter-intuitive as it suggests that periods of global ocean anoxia suitable for HBS formation coincide with elevated atmospheric O_2.

We suggest the following scenario that may explain this enigma. Cycles start with increased erosion related to continental uplift, which deliver a high nutrient flux of trace metals to the oceans, promoting planktonic productivity and related oxygen release to the atmosphere. The downward flux of organic matter produces widespread anoxia and draws down trace metals, with ultimate deposition of organic-rich HBS in marginal basins, epeiric seas, and on continental shelves. These coupled mechanisms produced nutrient-rich and anoxic-sulfidic deep oceans with HBS peaks at 490-525 Ma, 385-400 Ma, 310-335 Ma, 250-275 Ma, 205 Ma, 130 Ma, and the present day.

[1] Lehmann, B., et al., (2007), Highly metalliferous carbonaceous shale and Early Cambrian seawater: *Geology*, v. **35**, p. 403–406. [2] Large RR., et.al., (2014), Trace element content of sedimentary pyrite as a new proxy for deep-time ocean-atmosphere evolution: *Earth and Planetary Science Letters*, v. **389**, p. 209-220.