Redox processes in suboxic worlds: The highly different benthic geochemistry of Fe-S-Mn across the chemoclines of Baltic and Black Sea

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Suboxic waters and sediments are complex hotspots of nutrient recycling, metal mobilization and sequestration of organic carbon. Moreover, modern suboxic/anoxic basins are analogs of the ancient global ocean that presumably had a pelagic redox gradient. In this context, comparative analyses of redox processes in geographically distinct basins could provide new insights on the drivers of anoxic ocean processes. Here we present high-resolution benthic geochemical profiles (voltammetric analyses and discrete measurements) along a redox gradient in Baltic and Black Seas, both being coastal productive seas with pelagic anoxia. Our results point to a unique benthic sulfur cycling in Baltic Sea (Gotland Basin) chemocline where sulfide accumulation was limited to the uppermost 100-150 mm of the sediment and moderated by bacterial oxidation at the surface (sulfide consumption 2.7 to 3.4 mmol m^{-2} d^{-1}) and FeS precipitation in deeper layers. In contrast, a similar transect encompassing a benthic redox gradient in the western Black Sea indicated little sulfide accumulation in suboxic sediment porewaters. Instead, high mobility of iron and manganese were detected, with manganese effluxes to the water column. We propose that the different suboxic geochemical pattern is due to the different dynamics of the chemoclines of the two basins: the Baltic Sea is subjected to a stronger atmospheric forcing which results in a more dynamic pelagic redox interface (frequent overlap of O_2 and H_2S) while the Black Sea has a more stable and thicker chemocline without an overlap of O_2 and H_2S. This results in the development of coupled iron-manganese cycling in the Black Sea with the gradual accumulation of solid state metal oxides to sustain the benthic metal shuttle. On the other hand, the Gotland Basin suboxic sediments are less enriched in metals, yielding an excess of sulfide the flux of which provide a suitable niche for benthic sulfide oxidizing community.