



Genesis of heavy sulfides in Holocene sediments of a temporarily anoxic basin

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The texture and stable sulfur isotope composition of iron and manganese sulfides were investigated in the water column and in up to 5 m long sediment cores from the central Landsort Deep, western Baltic Sea. The sediments were deposited during the Holocene brackish phase of the Baltic Sea. In the modern euxinic part of the water column, very minor abundances of single crystals or proto-framboids of pyrite were observed. These are buried in the surface sediment acting as nuclei for further crystallization. In the sediments, the distribution patterns of framboidal pyrite is consistent, with a dynamic history of the dominating weakly-euxinic conditions with regular oxidation events of the euxinic deep part of the water column. When compared to the sulfur isotope composition of dissolved sulfide in the water column, the signatures found in mackinawite and pyrite indicate formation under conditions essentially closed wrt dissolved sulfate below the surface sediment-water interface. The textures together with a strongly zoned sulfur isotope patterns of concretionary authigenic MnS indicates slow growth in a sulfidic pore water gradient that developed towards a system increasingly limited in dissolved sulfate. From a physico-chemical point of view, manganese-calcium solid-solutions should form in the pore waters instead of MnS. We argue, that the inhibitory effect of enhanced phosphate on the carbonate system is responsible for this thermodynamic paradox.