

Rapid high amplitude variability in Baltic Sea hypoxia during the Holocene

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Hypoxia (oxygen <2ml/L) is widespread in the modern Baltic Sea and has occurred intermittently throughout the Holocene. Previous studies based on the occurrence of laminated sediments have shown that during the Holocene Thermal Maximum (HTM) and Medieval Climate Anomaly (MCA), hypoxic conditions were present in the deep basins of the Baltic Sea. However, high-resolution, quantitative reconstructions of past hypoxia are lacking. Here we present sediment records of molybdenum enrichment (Mo/Al), organic carbon content (C_{org}) and the ratio of organic carbon to total phosphorus (C_{org}/P_{tot}) which facilitate the first detailed comparison between modern and past hypoxic conditions in the Baltic Sea. We show that the previously identified intervals of widespread hypoxia were in fact characterized by multiple centennial-scale hypoxic events, interrupted by periods of more oxic conditions. This rapid high amplitude variability in hypoxia intensity was likely forced by climatic oscillations – which influence the ventilation rate of the Baltic Sea – and amplified by positive feedbacks in the P cycle, which control export productivity. We show that the modern hypoxic event has a similar intensity to the most extreme past events, implying a maximum potential intensity of both hypoxia and productivity in the Baltic Sea. However, modern hypoxia intensified more rapidly than any past event, confirming the role of anthropogenic nutrient loading in forcing this coastal marine system into its current hypoxic state.

Crystallization of schwertmannite from Na-rich solutions

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Schwertmannite is a ferric oxyhydroxysulphate ($Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$) formed in acid waters that may play a key role in the removal of toxic elements from aqueous solutions. It is generally accepted that this metastable phase is transformed into goethite and jarosite-like compounds, which infer changes in the chemical composition of aqueous solutions. Here, the objective is studying the crystallization of schwertmannite from sodium-rich solutions at ambient temperature and its stability during aging processes. For this purpose, a set of experiments was carried out by mixing $Fe_3(SO_4)_2$ (0.16M) and NaOH (0.5M) parent solutions which were kept at constant stirring (250 rpm) for specific reaction periods (1, 7, 14 and 21 days) at 25°C. Nature of the solids were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The surface of the solids was analyzed by X-ray photoelectron spectroscopy (XPS) and the binding energies of Fe2p_{3/2}, S2p, Na1s, and O1s core levels were obtained to determine the chemical state of the species. A colloidal mixture of dark brown colour is obtained at the beginning of the reaction, which changed to brown-reddish colour at the end of the period of reaction (21 days). Changes of colour in the mixture are associated with the evolution of the nature of solids as the aging process progresses. XRD reveal that the solid obtained in the early stage of experiments (1day) seems to be amorphous and evolves to a poorly crystalline phase. This phase matches with the pattern of schwertmannite which was recognized as a mineral in spite of its poor crystalline character (Bigam *et al.* 1994). Any other phases have not been identified in these diffractograms. SEM images show grains of higher size ($\approx 50 \mu m$) coexisting with grains of lower dimension ($< 5 \mu m$) in the entire aging process. All the particles displaying a shapeless morphology. The overall XPS spectra reveal the presence of sodium on the surface of schwertmannite. The binding energies obtained for Na, Fe, S and O suggest that sodium is adsorbed on the surface of the precipitates but a chemical bond is not established with iron, sulfur or oxygen. Thus, sodium has not been incorporated in the crystal structure of schwertmannite, which remains stable throughout the entire aging process at the experimental conditions used in the present work.

Bigam J.M., Carlson L. and Murad E. (1994) *Mineralogical Magazine*, **58**, 641-648.