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Diagenetic alteration of iron and phosphorus records below the sulfate-methane-transition-zone in Black Sea sediments

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The sediments of the Black Sea are characterized by vast deposits of iron oxide-rich lake sediments below the current marine sediments. The lake sediments were deposited until ca. 9000 years ago when the former giant lake became connected to the Mediterranean Sea through post-glacial sea level rise. The subsequent downward diffusion of marine sulfate into the methane-bearing lake sediments has led to a multitude of diagenetic reactions in the sulfate-methane-transition zone (SMTZ), including anaerobic oxidation of methane (AOM) with sulfate. While the cycles of sulfur, methane and iron in the SMTZ have been extensively studied (e.g. Jorgensen et al., 2004), relatively little is known about the diagenetic alterations of the sediment record occurring directly below the SMTZ.

Here, we combine detailed geochemical analyses of the sediment and pore water with multicomponent diagenetic modeling to study the diagenetic alterations below the SMTZ at two sites in the Black Sea. We focus on the dynamics of iron and phosphorus and demonstrate that downward sulfidization leads to dissolution of Fe-oxide bound P, Fe-carbonate and vivianite in the lake sediments. Below the sulfidization front, downward diffusing phosphate is bound again in vivianite. Trends in total sediment P with depth are significantly altered highlighting that diagenesis may strongly overprint burial records of P below a lake-marine transition. We also demonstrate that cryptic sulfur cycling cannot explain the observed release of dissolved Fe below the SMTZ. Instead, we suggest that organoclastic Fe-oxide reduction and/or AOM coupled to the reduction of Fe-oxides are the key processes explaining the high concentrations of dissolved Fe at depth in the sediment.

Reference

Jørgensen, B. B., Böttcher, M. E., Lüschen, H., Neretin, L. N. and Volkov, I. I.: Anaerobic methane oxidation and a deep H2S sink generate isotopically heavy sulfides in Black Sea sediments, Geochim. Cosmochim. Acta, 68(9), 2095–2118, 2004.