Coupled dynamics of CH_4-S-Fe-P in Black Sea sediments

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Surface sediments in the deep basin of the Black Sea are underlain by extensive deposits of iron (Fe) oxide-rich lake sediments that were deposited prior to the inflow of marine Mediterranean Sea waters ca. 9000 years ago. The ongoing downward diffusion of marine sulfate into the methane (CH_4)-bearing lake sediments has led to a multitude of diagenetic reactions in the sulfate-methane transition zone (SMTZ). While the cycles of sulfur (S), CH_4 and Fe in the SMTZ have been extensively studied, relatively little is known about their impact on sedimentary phosphorus (P) and the biogeochemical processes occuring below the SMTZ.

In this study, we combine detailed geochemical analyses with multicomponent diagenetic modeling to demonstrate that sulfate-mediated anaerobic oxidation of CH_4 substantially enhances the downward sulfidization of the lake deposits. This drives the release of Fe oxide bound P to the pore water and subsequent formation of authigenic Fe(II)-P minerals below the sulfidization front. We further show that downward migrating sulfide becomes partly re-oxidized to sulfate by reaction with oxidized Fe minerals, fueling a cryptic S cycle with slow rates of sulfate reduction in the deep limnic deposits. However, our results reveal that cryptic S cycling is unlikely to explain the observed release of dissolved Fe^{2+} below the SMTZ. Instead, we suggest that CH_4 oxidation coupled to the reduction of Fe oxides may provide a possible mechanism for the apparent Fe oxide reduction at depth in the sediment.

The coupled CH_4-S-Fe-P dynamics described here may strongly overprint burial records of Fe, S and P in depositional marine systems subject to changes in organic matter loading or water column salinity. Such diagenetic alterations should not be interpreted as primary sedimentary signals.