Post-depositional vivianite formation alters sediment phosphorus records

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Phosphorus (P) concentrations in sediments are frequently used to reconstruct past environmental conditions in freshwater and marine systems, with high values thought to be indicative of high primary productivity. Recent studies suggest that post-depositional formation of vivianite, an iron(II)-phosphate mineral, might significantly alter trends in P with sediment depth.

Here, we investigate P dynamics in a sediment record from the Bornholm Basin that was retrieved during the IODP Baltic Sea Paleoenvironment Expedition 347 in 2013, and which consists of lake sediments overlain by brackish-marine deposits. Combining bulk sediment geochemistry with micro-analysis using scanning electron microscope energy dispersive spectroscopy (SEM-EDS) and synchrotron-based X-ray absorption spectroscopy (XAS), we demonstrate that manganese- and magnesium-rich vivianite is present in the lake sediments just below the transition to the brackish-marine sediments (at 11.5 to 12 m sediment depth).

A reactive transport model was used to show that vivianite is formed where phosphate, diffusing down from the organic-rich, brackish-marine sediments, meets pore waters rich in dissolved iron in the lake sediments. Transient model simulations indicate that the peak in vivianite, which currently makes up the majority of total P at that depth, originally occurred at the lake-marine transition (9 to 10 m) and moved downwards due to changes in the depth of a sulfidization front. This key role for free porewater sulfide in vivianite stability is confirmed by experiments in which the mineral was subjected to sulfidic conditions.

Our work highlights that post-depositional vivianite formation can strongly alter sedimentary P records, particularly in systems that are subject to environmental perturbation, such as a change in primary productivity, which can be associated with a lake-marine transition.