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Vivianite represents a major sink for phosphorus in methanogenic coastal surface sediments

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Studies of authigenic phosphorus (P) minerals in marine sediments typically focus on authigenic carbonate fluorapatite, which is considered to be the major sink for P in marine sediments and can easily be quantified with the SEDEX sequential extraction method for P (Ruttenberg, 1992). The role of other potentially important authigenic P phases, such as the reduced iron (Fe) phosphate mineral vivianite (Fe(II)3(PO4)*8H_2O) has so far largely been ignored. This is likely partly due to the fact that the SEDEX method does not distinguish between vivianite and P associated with Fe-oxides. In this study, we show that vivianite can be quantified in marine sediments by combining the SEDEX method with more direct technical and analytical tools such as scanning electron microscope energy dispersive spectroscopy (SEM-EDS) and powder X-ray diffraction (XRD) of wet-sieved sediment samples, as well as synchrotron-based microanalysis (X-ray absorption near-edge structure, XANES) of resin-embedded sediments.

Our results demonstrate that vivianite represents a major burial sink for P below the sulfate/methane transition zone in Bothnian Sea sediments, accounting for up to 50 % of the total P burial. The vivianite in the brackish sediment contains significant amounts of Mn ($\sim$ 4-8 wt.%) but lower contents of Mg ($\sim$ 1-3 wt.%) similar to vivianite obtained from freshwater sediments. We further show that anaerobic oxidation of methane (AOM) drives a sink-switching from Fe-oxide bound P to vivianite by causing the release of both phosphate (AOM with sulfate and Fe-oxides) and ferrous Fe (AOM with Fe-oxides) to the porewater allowing supersaturation with respect to vivianite to be reached. Our results indicate that methane likely plays a key role in providing conditions that allow for vivianite authigenesis in coastal surface sediments. We suggest that vivianite formation may provide an important burial sink for P in many brackish coastal environments worldwide.

References:
Ruttenberg K. C. (1992) Development of a sequential extraction method for different forms of phosphorus in marine sediments. lim 37, 1460–1482.