

Unravelling vivianite formation in-situ in intertidal sediments: The role of P-adsorbed ferrihydrite as a precursor

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Vivianite, a ferrous phosphate mineral, can be an important phosphorus (P) sink in non-sulfidic, reducing, iron (Fe) and P-rich environments such as coastal sediments. The formation and burial of vivianite might enhance P sequestration and thus can have a positive impact on water quality. It remains unclear whether vivianite forms via spontaneous nucleation or from a surface-controlled dissolution-precipitation process leading to a progressive mineral transformation of iron (oxyhydr)oxides, such as ferrihydrite (Fh), to vivianite. Additionally, the detection and quantification of vivianite in sediments remains challenging and estimates of the contribution of vivianite to total P are often derived from geochemical calculations.

In this study, we investigated the formation of vivianite in intertidal sediments in-situ by incubating mesh-bags containing ⁵⁷Fe-enriched Fh with and without adsorbed P mixed with sediment for seven weeks in three intertidal flats in Northern Germany. Based on the sediment geochemistry, vivianite formation was predicted to form in two of the three intertidal flats. The ⁵⁷Fe-enrichment of the Fh enabled us to trace specifically Fh transformation products in the incubated mineral-soil mixes by ⁵⁷Fe-Mössbauer spectroscopy. In addition, Fe- and P K-edge X-ray absorption spectroscopy (XAS) was used as a complementary method to identify and quantify bulk Fe and P transformation products. Further, during the experiment, porewater chemistry at the field sites was regularly monitored.

Seven weeks after deploying the mesh-bags in the sediments, the ⁵⁷Fe-enriched (P-adsorbed) Fh was completely transformed. Reductive dissolution of (P-adsorbed) Fh resulted in the formation of various reduced and intermixed-valence iron minerals such as siderite and green rust. When P was adsorbed to Fh, vivianite formation dominated over siderite formation at the two sites predicted to favor vivianite formation. When vivianite formed it contributed only up to 11% to the total Fe pool based on Mössbauer spectroscopy and Fe K-edge XAS, while it contributed up to 60% to the total P pool, highlighting the importance of vivianite as a P retention phase. The use of ⁵⁷Fe-enriched Fh combined with Mössbauer spectroscopy enabled us to detect and quantify vivianite formation in-situ in different intertidal sediments, suggesting vivianite formation through surface-controlled dissolution-precipitation process in the environment.