

Competitive incorporation of Mn^{2+} and Mg^{2+} in the ferrous phosphate mineral vivianite

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The ferrous phosphate mineral vivianite can play a substantial role in phosphorus (P) sequestration in various environments such as coastal sediments and under reducing, non-sulfidic conditions vivianite likely acts as a permanent burial sink. Thus, authigenic vivianite formation might enhance P burial and therefore has a positive impact on water quality. Depending on the local environmental geochemistry, ferrous iron (Fe^{2+}) can be substituted by other divalent cations such as manganese (Mn^{2+}) and magnesium (Mg^{2+}). The incorporation of Mn^{2+} and/or Mg^{2+} is likely to change vivianite's mineralogical characteristics and may subsequently influence vivianite's reactivity. Despite the importance of divalent cation substitution in vivianite in the environment, questions remain whether Mn^{2+} or Mg^{2+} are preferentially incorporated and how their incorporation alters vivianite's mineralogy.

Here, we studied the competitive incorporation of Mn^{2+} and Mg^{2+} into vivianite by conducting aqueous coprecipitation experiments at pH 7. Furthermore, we assessed the influence of ionic strength, resembling an estuarine gradient, on the incorporation of Mn^{2+} and/or Mg^{2+} . Using a combination of X-ray powder diffraction, X-ray absorption spectroscopy, Mössbauer spectroscopy, and electron microscopy, we provide insights into changes in vivianite mineralogy due to Mn^{2+} and Mg^{2+} incorporation.

Our results of 19 different vivianites show that up to 50% of Fe^{2+} can be substituted by Mn^{2+} and Mg^{2+} in the vivianite structure, with a preferential incorporation of Mn^{2+} over Mg^{2+} . Increases in ionic strength resulted in a decrease in divalent cation incorporation. Furthermore, spectroscopic and electron microscopy data reveals that substitution lead to changes in crystal size and crystal morphology. Following from our results, we will discuss how ionic strength impacts divalent cation incorporation into vivianite and how these changes in the vivianite structure and morphology may impact its reactivity in the environment. We will conclude with a discussion on how divalent cation substitution may make the identification of vivianite in natural samples more challenging.