



Competitive divalent cation incorporation in the ferrous phosphate mineral vivianite

L. Joëlle Kubeneck, Laurel K. ThomasArrigo, Katherine A. Rothwell, Ruben Kretzschmar Soil Chemistry Group (https://soilchem.ethz.ch), CHN, ETH Zurich, 8092 Zurich, Switzerland.

luisa.kubeneck@usys.ethz.ch

Background

The chemical form in which phosphorus (P) is bound in soils and sediments influences its bioavailability. Under reducing, non-sulfidic conditions, it has been shown that vivianite, $Fe_3(PO_4)_2 \cdot 8 H_2O_1$, is a major P burial phase in coastal sediments.¹ Significant isomorphic substitution of ferrous iron (Fe(II)) by Mn and/or Mg in natural vivianites has been reported.² The substitution of Fe(II) in the vivianite structure might have the potential to enhance vivianite formation in environments, which are Fe(II)-limited.

Research Objectives

- Understanding the competition between divalent Mg & Mn incorporation into vivianite
- Determining how salinity, representing an estuarine gradient, influences divalent cation incorporation
- Studying the effect of substitution on mineralogical characteristics and P sequestration

Experimental Approach



Reaction conditions:

- pH 7.0 ± 0.1, anoxic
- 24 hrs equilibrium time
- Fe(II) limiting reactant
- Variable ratios of (Mn+Mg)/Fe & concentrations of artificial seawater (0, 3, 6 & 9 psu)

Results

Without competition, Mg and Mn are equally incorporated at a salinity of 0 psu





Analysis includes:

- Total elemental composition (ICP-OES)
- XRD with Rietveld refinement
- Raman spectroscopy
- Fe K-edge EXAFS spectroscopy
- And others

Conclusions & Outlook

- (1) Presence of Mn has a negative effect on Mg incorporation into vivianite
- Substitution of Fe(II) by Mg/Mn can (2) enhance vivianite formation under Fe(II)limiting conditions
- (3) Analysis is ongoing – first preliminary insights:
 - Salinity likely leads to smaller crystal size based on Rietveld refinement
 - Further solid-phase characterization is in progress, including Raman, XRD, and XAS

Oxic cond.

Pure

Mn-rich

Mn&Mg-rich Mg-rich

References:

¹Egger et al. 2015, GCA, 169, p. 217-235 ²Rothe et al. 2016, EARTH-SCI REV, 158, p. 51-64

This research is part of a project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme ((788009-IRMIDYN-ERC-2017-ADG).

Salinity has a negative effect on Mg incorporation



Fig. 2: Elemental solid phase ratio of substituted vivianites formed at three different salinities. 50 *Left group: initial aqueous Mg/Fe ratio varied* from 0.18 (3 psu), 0.33 (6 psu) and 0.55 (9 psu). Right group: Competition between Mn & Mg. Initial aqueous Mn/Fe ratio was 0.52 at all salinities, while the Mg/Fe ratio varied from 0.18, 0.33 and 0.55.

 Presence of Mg enhances vivianite formation under Fe(II)-limiting conditions

%

When Mn & Mg are both present, Mn outcompetes Mg for incorporation

Мn

Salinity does not have an effect on Mn incorporation



Fig. 3: % of aqueous P removed from solution via vivianite formation at variable initial aqueous Mg/(Mg+Fe) concentrations at ≈ 0 psu.



