Invited review

The occurrence, identification and environmental relevance of vivianite in waterlogged soils and aquatic sediments

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ABSTRACT

In this article, we review the nature, occurrence and environmental relevance of the authigenic ferrous iron phosphate mineral vivianite (Fe₃(PO₄)₂·8H₂O) in waterlogged soils and aquatic sediments. We critically discuss existing work from freshwater and marine systems, laboratory studies and microbial batch culture experiments aiming to deduce common characteristics of the mineral’s occurrence, and the processes governing its formation. Vivianite regularly occurs in close association with organic remains in iron-rich sediments. Simultaneously, it is a biogenic mineral product of metal reducing bacteria. These findings suggest that vivianite nucleation in natural systems is directed by the activity of such bacteria and crystal growth is particularly favoured within protected microzones. Taking into account recent findings from coastal marine sediments where vivianite authigenesis has been shown to be coupled to the anaerobic oxidation of methane, small-scale microbially mediated reactions appear to be crucial for the formation of vivianite. Small-scale heterogeneity within the sediment matrix may also explain why saturation calculations based upon bulk pore water constitutions often fail to accurately predict the occurrence of the mineral. Vivianite is not restricted to a specific trophic state of a system. The mineral forms in oligotrophic- as well as in eutrophic waters. However, depending on the iron inventory, the production, supply and degradation of organic matter determine the relative contribution of iron sulphide formation to the iron pool, and the concentration of inorganic phosphate and Fe²⁺ in pore waters. Thus, vivianite authigenesis is also governed by bulk chemical conditions such as the rate of sulphide formation relative to that of Fe²⁺ production. This situation allows stimulation of vivianite formation by iron supplementation aimed at restoring eutrophic lakes. Recent results from coastal marine sediments suggest that vivianite authigenesis is of significance for P burial in the marine realm. Vivianite authigenesis is likely important at the global scale, but has so far largely been ignored.

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Vivianite

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1. Introduction

Vivianite is the most common stable iron phosphate mineral forming in sedimentary environments (Nriagu, 1972; Emerson, 1976; Berner, 1981a). This mineral occurs worldwide in various aquatic systems, such as freshwater and marine sediments, and in terrestrial systems such as waterlogged soils, bogs, hydrothermal deposits and archaeological settings as well as in wastewater sludges (Table 1).

<table>
<thead>
<tr>
<th>System</th>
<th>Location</th>
<th>Identification</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment of freshwater lakes</td>
<td>Lake Åsrum, Norway</td>
<td>By eye</td>
<td>Viv not present in the underlying lagunal and marine sediments</td>
<td>Rosenqvist (1970)</td>
</tr>
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<td></td>
<td>Great Lakes, USA</td>
<td>By eye, microscopy</td>
<td>Viv not directly associated with organic remains although these materials were abundant</td>
<td>Nriagu and Dell (1974)</td>
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<td></td>
<td>Lake Ur, Germany</td>
<td>By eye</td>
<td>Meromictic bog lake</td>
<td>Tessenow (1974)</td>
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<tr>
<td></td>
<td>Lago Maggiore, Italy</td>
<td>By eye, SEM, XRD, Mössbauer spectroscopy</td>
<td>Viv depth layer not in accordance with saturation calculations</td>
<td>Nembrini et al. (1983)</td>
</tr>
<tr>
<td></td>
<td>Toolik Lake, Alaska</td>
<td>By eye, SEM-EDX</td>
<td>Ultra-oligotrophic arctic lake. viv does not occur at the sediment surface but only below the oxic–anoxic interface</td>
<td>Cornwall (1987)</td>
</tr>
<tr>
<td></td>
<td>Narrow Lake, Canada</td>
<td>By eye, XRD</td>
<td>Viv only present in the deep southern basin where the molar S:Fe ratio was higher than in the shallow northern basin</td>
<td>Manning et al. (1991)</td>
</tr>
<tr>
<td></td>
<td>Lake Biwa, Japan</td>
<td>By eye, XRD, X-ray fluorescence</td>
<td>Manganoo viv, high sulphide concentration cause viv dissolution</td>
<td>Nakano (1992), Murphy et al. (2001)</td>
</tr>
<tr>
<td></td>
<td>Lake Busslójön, Sweden</td>
<td>XRD, Mössbauer spectroscopy</td>
<td>Present in preindustrial non-sulphidic sediments</td>
<td>Olsson et al. (1997)</td>
</tr>
<tr>
<td></td>
<td>Baptist Lake, Canada</td>
<td>By eye, SEM-EDX, XD, IR spectroscopy</td>
<td>Influence of groundwater rich in Fe(II) and phosphate</td>
<td>Manning et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>Lake Baikal, Russia</td>
<td>By eye, SEM-EDX, XR, XRD, IR spectroscopy</td>
<td>Manganoo viv, viv grains contain inclusions of plagioclase and pyrite, formation in microenvironments</td>
<td>Fagel et al. (2005), Sapota et al. (2006), Minyu et al. (2013)</td>
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<tr>
<td></td>
<td>Laguna Potrok Aike, Argentina</td>
<td>By eye, SEM-EDX, XR, XRD, IR spectroscopy</td>
<td>Indirect signs of microbially mediated viv formation, uranium-thorium dating of viv</td>
<td>Nuttin et al. (2013), Vuillerm et al. (2013)</td>
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<tr>
<td></td>
<td>Lake Pavin, France</td>
<td>XRD</td>
<td>Viv detected on sinking particles, role of polyphosphates in precipitation of reduced Fe(II) phosphates</td>
<td>Comsis et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>Lake Groß-Glenicke, Germany</td>
<td>By eye, SEM-EDX, XR, XRD, IR spectroscopy</td>
<td>Viv formation triggered by Fe supplement</td>
<td>Rothe et al. (2014)</td>
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<tr>
<td>Sediment of rivers</td>
<td>Lake Øren, Denmark</td>
<td>SEM-EDX, XRD</td>
<td>Identification by XRD on bulk sediment</td>
<td>O’Connell et al. (2015)</td>
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<td></td>
<td>Potomac River, USA</td>
<td>By eye, SEM-EDX</td>
<td>Major control on the occurrence of viv is the presence or absence of amorphous Fe(III) oxihydroxides</td>
<td>Hearn et al. (1983)</td>
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<td></td>
<td>Mississippi River, USA</td>
<td>By eye, X-radiography</td>
<td>Viv consists of radial aggregates of 1–3 mm in diameter and occurs together with other diagenetic minerals (siderite, pyrite, calcite, dolomite, hematite)</td>
<td>Bailey et al. (1998)</td>
</tr>
<tr>
<td></td>
<td>Havel River, Germany</td>
<td>By eye, SEM, XRD</td>
<td>Occurrence of viv associated with a decreased sulfidization in response to a lower primary productivity</td>
<td>Rothe et al. (2015)</td>
</tr>
<tr>
<td>Sediment of canals</td>
<td>Old Birmingham Mainline Canal, UK</td>
<td>SEM-EDX</td>
<td>Viv coexisted with biogenic structures and pyrite framboids</td>
<td>Dodd et al. (2003)</td>
</tr>
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<td></td>
<td>Salford Quays, UK</td>
<td>SEM-EDX, XRD, Raman spectroscopy</td>
<td>Highly contaminated, organic-rich canal bed sediments</td>
<td>Taylor and Boul (2007); Taylor et al. (2008)</td>
</tr>
<tr>
<td>Waterlogged soils</td>
<td>Organic soil, Denmark</td>
<td>XRD, Mössbauer spectroscopy</td>
<td>Viv neoformention in response to Fe(III) reduction following anoxic soil incubation</td>
<td>Heiberg et al. (2012)</td>
</tr>
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<td></td>
<td>Meadow soil, Denmark</td>
<td>By eye, SEM-EDX, XR, XRD, Mössbauer spectroscopy</td>
<td>Dissolution precipitation experiments, viv shows slow precipitation kinetics</td>
<td>Walpersdorf et al. (2013)</td>
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<td></td>
<td>Paddy field soil, Japan</td>
<td>By eye, SEM-EDX, XR, XRD, Mössbauer spectroscopy</td>
<td>Viv attached to aged rice roots XRD detection successful after the minerals exposure to air</td>
<td>Nanzy et al. (2010, 2013), Rodgers (1977)</td>
</tr>
<tr>
<td></td>
<td>River bog, Denmark</td>
<td>XRD</td>
<td>Viv coexisted with siderite, calcite and occasionally pyrite</td>
<td>Postma (1981)</td>
</tr>
<tr>
<td></td>
<td>Amazon Fan, Brazil</td>
<td>By eye, SEM-EDX</td>
<td>Viv occurs below the depth of total sulphate depletion</td>
<td>Burns (1997)</td>
</tr>
<tr>
<td></td>
<td>Yung-An Ridge, South China Sea</td>
<td>SEM-EDX, XR, Raman spectroscopy, IR spectroscopy</td>
<td>Magnesium-rich viv, viv formation influenced by methane induced sulfidization</td>
<td>Hsu et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>Bothnian Sea, Baltic Sea</td>
<td>SEM-EDX, XRD, µXRF, XANES</td>
<td>Anaerobic oxidation of methane triggers viv formation</td>
<td>Egger et al. (2015a)</td>
</tr>
<tr>
<td></td>
<td>Wastewater sludge</td>
<td>SEM-EDX, XR, Mössbauer spectroscopy</td>
<td>P removal through Fe reduction-induced P precipitation</td>
<td>Frossard et al. (1997), Zhang (2012)</td>
</tr>
<tr>
<td></td>
<td>Archaeological settings</td>
<td>By eye</td>
<td>Viv present on the surface of bones and other human remains, important function of microorganisms proposed</td>
<td></td>
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</table>

Despite the widespread occurrence of vivianite, most notably in lacustrine sediments, its origin, mode of formation, and significance in the global phosphorus (P) cycle are not well understood. Of particular interest are the recent observations from anoxic marine sediments which suggest that the authigenic formation of reduced iron (Fe(II)) phosphates is of much greater importance for the burial of P than previously assumed (Slomp et al., 2013; Dijkstra et al., 2014; Egger et al., 2015a).

The retention of P in aquatic sediments is determined by a cascade of processes which include the deposition on the sediment, the transformation of mainly organic-bound P, immobilization and burial, as well as the percolation to deeper sediment layers (Boers et al., 1998). The immobilization of P and the ability of a sediment to retain P is influenced by the characteristics of the depositional environment, such as the nature of the input source material and the sedimentation rate including the prevailing redox conditions (Ruttenberg and Berner, 1993). The fixation of P within sediments thereby depends on the transport of orthophosphate between solid particles, adsorption-desorption mechanisms, biological assimilation and mineral nucleation, including the formation of iron and calcium phosphates such as vivianite and apatite (Søndergaard et al., 2001).

Bound P may be organic-bound P or inorganic-bound P. Organic-bound P originates from organic matter, which is often the principle source material of P to the sediments and one of the most important pools of P in marine sediments (Ruttenberg and Berner, 1993). In a succession of mineralization processes, organic-bound P can be liberated and the orthophosphate released may be bound in microbial biomass, sorbed by Fe(III) (oxyhydr)oxides, aluminium hydroxides, silicate clays or bound in secondary phosphate minerals authigenically formed during early sediment diagenesis. Autogenic phosphate minerals can constitute a significant pool among the long-term P inventory of sediments.

Most prominently, carbonate fluorapatite is a major burial sink in the ocean (Ruttenberg and Berner, 1993; Slomp et al., 1996; Schulz and Schulz, 2005). In addition to calcium phosphates, ferrous phosphates may significantly contribute to P retention in anoxic sediments, particularly if the sediments are anoxic but non-sulphidic (Gächter and Müller, 2003). Moreover, also oxidised Fe(III) compounds such as ferric (oxyhydr)oxides and ferric phosphates can persist in reductive environments, significantly contributing to P binding under these conditions (Hyacinthe and Van Cappellen, 2004; Lehtoranta et al., 2009). The fundamental processes of sediment diagenesis, authigenic iron mineral formation, and reactivity of iron-bearing minerals, however, are only briefly addressed in this review, since those were recently reviewed by Roberts (2015). By the pioneer work of Einsele (1936) and Mortimer (1941) the tight coupling between the Fe and the P cycle in aquatic environments has been revealed. It is well known that Fe(III) (oxyhydr)oxides form at oxic/anoxic boundaries in lakes and marine water bodies (Ruttenberg and Berner, 1993), crucially influencing the behaviour of orthophosphate, arsenate and trace metals as a result of their scavenging capacity (see Gunnars et al., 2002, and references therein). In the absence of oxygen, the degradation of organic matter by dissimilatory Fe and sulphate reducing bacteria as well as methanogens leads to the liberation of ferric Fe compounds, the production of sulphides (S²⁻) and the formation of iron sulphides (FeS₂), thus, counteracting the functioning of Fe(III) (oxyhydr)oxides in trapping P (Roden and Edmonds, 1997). Simultaneously, Fe(III) (oxyhydr)oxide-P compounds may undergo reductive dissolution in the presence of S²⁻ (Sugawara et al., 1957; Smolders and Roelofs, 1993; Murray, 1995). However, the increased liberation of solutes, such as orthophosphate, Fe²⁺ and Mn²⁺, in response to organic matter decomposition also leads to favourable conditions for the formation of other, non-sulphidic, authigenic minerals such as carbonates ( siderite, carbonate fluorapatite) and phosphates (vivianite) (Suess, 1979).

In this review we will summarise existing knowledge on sedimentary vivianite, including its characteristics and appearance, methodological identification, and its occurrence in various sedimentary settings. From this literature synthesis, we discuss the methodological limitations of vivianite identification and present the factors that appear to controlling the occurrence of the mineral. A conceptualised model of the most important processes governing vivianite formation in sediments, arising from the literature on microbial batch culture experiments is given. We will also discuss the quantitative importance of vivianite authigenesis for P burial, its ecological role in aquatic systems, and the importance of vivianite in the restoration of eutrophied lakes. We conclude with a short perspective on further challenges to be faced in order to uncover the role of vivianite in the global P cycle.

2. Vivianite characteristics and appearance

Vivianite, Fe₃[PO₄]₂·8H₂O, named after the English mineralogist John Henry Vivian (1785–1855), is a hydrous phosphate of ferrous Fe and carbonates in the monoclinic system, space group B2/m. Vivianite is the Fe-rich end-member of the vivianite mineral group (M₃(XO₄)₂·8H₂O, where M = divalent Mg, Mn, Fe, Co, Ni, Cu, Zn, and X = P or As), has a hardness of 1.5–2 (Mohs), and a density of 2.67–2.69 g cm⁻³. The mineral’s structure consists of single (FeO₂(H₂O)₄) and double (Fe₂O₄(H₂O)₄) octahedral groups, linked to each other by PO₄ and H₂O hydroxyl bonds (Rouzies and Millet, 1993). The magnetic properties of vivianite are well known: the mineral is paramagnetic but undergoes antiferromagnetic transition at a Néel temperature of 12 K (Meijer et al., 1967; Frederichs et al., 2003). Further crystallographic properties can be found elsewhere, for example at www.mindat.org.

Vivianite is colourless and translucent in its pristine state. Upon exposure to air, vivianite is known for its vivid bluish to green appearance, which is due to a gradual oxidation of Fe(II) (Hush, 1967) (Fig. 1). Manning et al. (1991) identified pale blue crystals of vivianite in sediments of mesotrophic Narrow Lake, Alberta and noted that the weak colour indicated a low concentration of ferric ions in the vivianite.

The oxidation characteristics of vivianite have been studied in detail: when ferrous Fe is oxidised, water molecules are substituted by hydroxyl groups to offset the valence change. Vivianite oxidation proceeds slowly at room temperature and stabilises at a Fe³⁺ concentration of 50% total Fe (Rouzies and Millet, 1993). Nriagu (1972) noted that blue oxidised vivianite was almost indefinitely stable under laboratory conditions. Rouzies and Millet (1993) pointed out that at values higher than 50% Fe³⁺, vivianite alters to metavivianite (Fe²⁺+Fe³⁺+PO₄³⁻(OH)₂·6H₂O). Metavivianite should be distinguished from vivianite by its altered X-ray reflections (Roth et al., 2014). Further oxidation is favoured at higher temperatures, and results in the formation of poorly crystalline mixed valence or ferric Fe phosphate phases, for example lipscombite (Fe²⁺+Fe³⁺+PO₄³⁻(OH)₂), santabarbaraite (Fe³⁺+PO₄³⁻(OH)_2·5H₂O) and strengite (FePO₄·2H₂O) (Nriagu, 1972; Nriagu and Dell, 1974; Pratesi et al., 2003). In a calcareous medium, vivianite oxidation results in the formation of a poorly crystalline Fe(III) oxide (lepidocrocite, γ-Fe₂O₃+OH(OH)) (Roldán et al., 2002). The oxidation of vivianite may explain why additions of vivianite prevent Fe deficiencies in plants growing on calcareous soils (Rombolá et al., 2003).

Vivianite regularly contains significant amounts of Mn and/or Mg, which substitute for Fe in the vivianite lattice. In general, the amount of trace metals in vivianite is an indicator of the surrounding geochemical conditions, and vivianite formed in polymetallic ore deposits contains higher abundances of trace elements than minerals formed in reducing aquatic environments (Tessadri, 2000). Regularly, crystal aggregates appear to consist of “manganooxid” vivianite (Nakano, 1992), or of a mixture of vivianite and ludlamite (Fe,Mn,Mg)₃[PO₄]₂·4H₂O or barcite ([Mg,Fe]₃[PO₄]₂·8H₂O). Nodules enriched in Mn have been reported mostly from freshwater systems such as lake- and canal
aggregates in a study from Taylor et al. (2008) that showed that early diagenetic situ immobilization of heavy metals, such as copper, in soils. Additionally, the high effectiveness of synthesized vivianite nanoparticles for the immobilization of heavy metals, such as Zn and other contaminants such as As, has been demonstrated (Frossard et al., 1997; Sapota et al., 2006; Taylor et al., 2008). Baricite, the Mg analogue of vivianite, was reported from an Fe-rich cold seep sediment off western Taiwan (Hsu et al., 2014), and the authors noted that this Mg-rich vivianite might not be as common in freshwater systems as in marine systems because of low magnesium concentration in lacustrine and riverine sediments. Burns (1997) detected vivianite nodules “with considerable amounts of Mg” in Amazon Fan sediments, Brazil.

Moreover, Frossard et al. (1997) found sand-sized vivianite and baricite in air-dried waste-water sludge. Vivianite forms an important component of metal cycling in contaminated sediments as confirmed in a study from Taylor et al. (2008) that showed that early diagenetic vivianite may act as a sink for Zn and other contaminants such as As during its formation. In another study, Liu and Zhao (2007) emphasized the high effectiveness of synthesized vivianite nanoparticles for the immobilization of heavy metals, such as copper, in soils.

Vivianite nodules and concretions are often of similar habitus. They are described as “hemispheres” (Müller and Förstner, 1973), “spherical aggregates” (Hearm et al., 1983), “tightly packed spherules” (Henderson et al., 1984) and “large oolithic” nodules (Nakano, 1992) with diameters ranging from a few micrometres to centimetres. The aggregates consist of “radiating lath-shaped crystals and needle-like masses” (Taylor et al., 2008), “distinct elongated prismatic” (Zwaan and van der Sluys, 1971) or “rod shaped” (Frossard et al., 1997) crystals. In a laboratory experiment Zelibor et al. (1988) studied the morphological characteristics of vivianite crystals grown in agar gels. The authors suggested that the combination of the gel medium in the pore spaces and the natural electric field in the upper sediments, could be contributing causes to explain the spherical aggregates of vivianite crystals found in nature. In a study about the occurrences of vivianite in Quaternary swamp and surface deposits in the Auckland area, New Zealand, Rodgers (1977) noted that the “spheroids” consisted of “millimetre long needles” which “often appear to radiate from a void”.

The rough surface and the “euhedral form of crystals on particle surfaces” (Hearm et al., 1983), as well as inclusions of diatom shells and other organic debris (Rothe et al., 2014), are a natural indicator of the authigenic origin of vivianite (Fig. 1). From the random orientation of the crystalallites on the surface of vivianite microconcretions, Sapota et al. (2006) concluded that pore spaces in the sediment were not confined by extensive compaction, and hence vivianite formation must have taken place in an early diagenetic environment in surface sediments. Other investigators (Cosmidis et al., 2014; Rothe et al., 2014, 2015) identified vivianite nodules within the first centimetre of freshwater lake and river sediments. These findings allow for the conclusion that vivianite can form rapidly during early diagenetic transformations. In contrast, in an attempt to date authigenic vivianite from Laguna Potrok Aike, Argentina using uranium-series, Nuttini et al. (2013) concluded that the formation of vivianite “seems to be a long lasting process after burial and does not permit estimating precise and reliable diagenetic precipitation ages”.

3. Methods of vivianite identification

By far the most simple approach includes the identification of vivianite nodules by naked eye taking advantage of the characteristic colour change of the mineral on exposure to air (Rosenqvist, 1970; Olsson et al., 1997; Brauer et al., 1999; Nanzyo et al., 2013; Rothe et al., 2014), and subsequent microscopic and/or chemical analysis. Sedimentary vivianite has been identified and characterised by methods including X-ray powder diffraction (XRD) (Postma, 1981; Manning et al., 1991; Taylor et al., 2008; Heiberg et al., 2012; Cosmidis et al., 2014; Rothe et al., 2014), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) (Hearm et al., 1983; Stamatakis and Koukouzas, 2001; Dodd et al., 2003), infrared (IR) spectroscopy (Fagel et al., 2005; Hsu et al., 2014), Raman spectroscopy (Taylor et al., 2008; Milucka et al., 2012) and Mössbauer spectroscopy (Nembrini et al., 1983; Manning et al., 1991; Frossard et al., 1997). Additionally, the magnetic properties of vivianite have been used to identify and quantify vivianite in sediments (Frederichs et al., 2003; Rothe et al., 2014).

Because vivianite is highly sensitive to oxidation, its identification by XRD has been reported to be difficult by some authors (Bricker and Troup, 1973; Olsson et al., 1997; März et al., 2008), suggesting that vivianite rapidly looses its characteristic crystal structure upon exposure to air. However, this assertion has been questioned by others (Rodgers, 1977; Suess, 1979; Manning et al., 1991; Frossard et al., 2014; Rothe et al., 2014). That the crystal structure of vivianite remains stable upon exposure to air at room temperature is supported by the oxidation characteristics of vivianite (Rouzies and Millet, 1993), and...
the observation that the gradually oxidised mineral is stable under laboratory conditions (Nriagu, 1972).

Successful XRD detection appears to depend on the amount of vivianite present in the sample, the size and crystallinity of nodules, and the reflections from other mineral phases which may interfere with those of vivianite (Emerson and Widmer, 1978). The XRD measurements of bulk sediment samples, and samples naturally enriched in vivianite, showed that about a 5% weight of vivianite was necessary to detect the mineral by XRD, i.e. that at least the three most intense peaks are clearly visible (Rothe et al., 2014).

The direct and unambiguous identification of vivianite in sediments is not always easy because phosphate minerals usually comprise only a small part of a sediment matrix (Lindsay et al., 1989). Thus, indirect approaches such as pore water equilibrium calculations, and sequential P extractions have been widely used to predict the occurrence of vivianite in natural systems. However, simultaneously these indirect approaches limit the validity and specificity of findings with regard to the factors and conditions leading to the formation of the mineral.

Density separation of water-free sediment using different concentrations of a sodium polytungstate solution (3Na₂WO₄·9WO₃·H₂O) is an easy and reliable approach to enrich sedimentary vivianite in the high-density (ρ>2.3 g cm⁻³) sediment fraction (Rothe et al., 2014, 2015). The enrichment of natural vivianite allows a direct identification of vivianite by XRD, a detailed microscopic analysis of mineral grains, and a quantitative determination of the amount of vivianite present in the sediment. An alternative approach to determining the amount of vivianite in the high-density sediment fraction, is magnetic hysteresis measurements, which take advantage of the paramagnetic nature of vivianite (Rothe et al., 2014).

3.1. Thermodynamic calculations: potentials and limitations

Ultimately, crystal growth depends on thermodynamic principles and a mineral nucleates from solution if the mineral saturation state is above the equilibrium value. The solubility constant of vivianite has been examined by Rosengqvist (1970) and Nriagu (1972), and the principle stability of vivianite and the conditions favourable for its formation have been derived from these thermodynamic considerations (Nriagu, 1972; Nriagu and Dell, 1974; Postma, 1981). Vivianite is stable at pH conditions from 6 to 9, and its formation is favoured by high activities of ferrous Fe and orthophosphate in pore waters. Such conditions are commonly found in organic and Fe-rich waterlogged soils and sediments where reducing conditions persist but sulphide (S²⁻) production is low.

Thermodynamic equilibrium calculations have been widely used to predict the occurrence of vivianite and other authigenic minerals in various environmental settings. However, supersaturated pore water may only serve as an indicator for the conditions at which the formation of a specific mineral is possible. Supersaturation does not directly indicate an active mineral formation because reaction kinetics ultimately control the crystallization of mineral grains. In their study, Emerson and Widmer (1978) demonstrated by flux calculations that vivianite growth is rather controlled by surface processes, than by the diffusion of solutes. Subsequently, other investigators confirmed that there is no equilibrium control by vivianite with respect to pore water orthophosphate and Fe²⁺ concentration (Postma, 1981; Boers and de Bles, 1991; Walpersdorf et al., 2013), and that supersaturated pore waters may or may not indicate the occurrence of the mineral within a sediment (Rothe et al., 2014) (Fig. 2).

Some authors have noted the weakness of pore water evidence of vivianite determined from ion activity product calculations. Cornwell (1987) noted in his study about authigenic P minerals in an arti lake that “pore water evidence is not sufficient to determine authigenic mineral precipitation: the mineral must be identified within the sediment”. Murphy et al. (2001) concluded that discrepancies between pore water observations (s supersaturation) and proven mineral precipitation indicates that “vivianite formation and stability in sediments is not completely understood” (referencing Boers and de Bles (1991)). In their review about phosphate chemistry in lake sediments Syers et al. (1973) concluded: “Application of the solubility product is useful for predicting which P compounds are thermodynamically stable or which P compounds can theoretically form. It is difficult, if not impossible, however, to take the findings obtained with “pure” systems in the laboratory and solubility predictions based on thermodynamics and to extrapolate these to the extremely complex environment in lake sediments, in which reactions kinetics may be modified by other dissolved species and solid phases.”

Solubility product calculations should be done with care because the validity of results is limited due to the following constraints: (i) calculations are based upon activity coefficients which are not very accurate, especially for trivalent ions; (ii) there is complexation, in particular in the presence of organic compounds which increases the solubility and kinetically retards nucleation; and (iii) small particles (nano-/micrometre-sized) normally have higher solubilities than do large bulk particles. Furthermore, it is important to consider that all solubility product calculations are based upon macroscopic measurements for example using pore water samplers with a theoretical resolution of millimetres to centimetres (Hesslein, 1976). However, mineral nucleation and crystal growth take place on a nano- to micrometre scale, and might be associated with specific solid phases and the activity of microorganisms. Thus, small-scale in situ conditions within microenvironments are not well represented by such saturation calculations (Dodd et al., 2003; Glasaer et al., 2005). Lastly, careful sample handling is a prerequisite to perform accurate solubility product calculations, preventing oxygen contamination of samples and subsequent changes in concentration of dissolved metal ions and orthophosphate (Rothe et al., 2014).

3.2. Sequential phosphorus extraction procedures

To determine the chemical character of P binding forms in soils and sediments, sequential P fractionation techniques use solvents with different chemical properties including acids, bases and reducing agents (Ruttenberg, 1992; Ruban et al., 1999; Lukkari et al., 2007). There are various protocols available, with different operationally defined P forms. Most of them address inorganic P forms (Ruban et al., 1999) to differentiate between loosely adsorbed (exchangeable) P, Fe-bound P, apatite-P, and residual P.

Ferric Fe compounds and the P associated with these compounds (by adsorption or by chemical binding) are sensitive to redox changes and may be liberated under anoxic conditions. Thus, the Fe associated P from strictly anoxic sediments has been attributed to stable ferrous Fe phosphate minerals such as vivianite, or to ferric Fe phases which resist reductive dissolution (Hyacinthe and Van Cappellen, 2004). However, none of the existing extraction schemes differentiates between ferrous and ferric Fe–P compounds, nor specifically targets vivianite. Thus, the occurrence of reduced Fe(II) phosphates may be plausible in these cases, however, a direct identification of the specific Fe phosphate mineral is missing.

Based upon results presented by Williams et al. (1980) and Nembrini et al. (1983), freshly precipitated vivianite has been considered to be liberated within the redox-sensitive Fe-bound P fraction (Jilbert and Slomp, 2013; Dijkstra et al., 2014) of the SEDSEX P extraction (citrate–dithionite–bicarbonate extraction, CDB-P (Ruttenberg, 1992)). In contrast, Rothe et al. (2015) noted that synthetic and natural vivianite was not entirely liberated in one single extraction step (bicarbonate–dithionite, BD–TP) targeting the Fe-bound P phases of the sequential extraction procedure of Psenner et al. (1984). The results Rothe et al. (2015) presented suggest that vivianite liberation depends on the crystallinity of the mineral and highly-crystalline vivianite is not entirely liberated during the extraction targeting Fe-bound P (for example CDB extraction of
4. Vivianite occurrence and formation mechanisms

Vivianite has been reported from reductive environments and occurs in sediments of lakes, rivers, canals, peat bogs, swamps, river fans and cold seep settings; it has been also identified in coastal marine sediments as well as in waterlogged soils (Table 1). Records include quaternary, postglacial, modern and surface deposits. Vivianite also occurs in sewage sludge and as a weathering product in hydrothermal veins. Vivianite formation is not limited to soils and sediments, the mineral has been also identified within the water column of a meromictic Fe-rich crater lake (Cosmidis et al., 2014). The mineral appears to be totally clear and this further complicates the interpretation of sequential P extractions with regard to the occurrence of reduced Fe(II) phosphates and vivianite. Although P extractions estimate the portion of P that may become bioavailable under certain environmental conditions and the portion of P which is stably bound, the many types of naturally occurring P species classified within a few extraction steps, mean that sequential P extraction procedures are only an approximate approach (Lukkari et al., 2007; Hupfer et al., 2009).

Direct association of vivianite crystal aggregates with organic remains appears to be a common feature, although it is not ubiquitous. Tessenow (1974) detected spherical vivianite nodules in a bog lake (Lake Ursee, Germany) and some of these nodules were grown on the remains of leaves and fibres. Stoops (1983) found vivianite associated with decaying roots, or alone inside root channels in a soft bog of the Belgian Campine. Henderson et al. (1984) reported vivianite encrusting fragments of decayed wood and fossil bone in swamp, lake and surface deposits of the Auckland area (New Zealand), and recently, Nanzyo et al. (2013) demonstrated that vivianite crystal aggregates grow on and within decaying rice roots in a paddy field soil, Japan. Also Stamatakis and Koukouzas (2001) reported that vivianite frequently replaces leaves and faecal pellets in lacustrine clayey diatomite deposits, Thessaly, Central Greece. Moreover, vivianite has been identified in teeth and bones of dead bodies buried in waterlogged conditions, in close proximity to a source of Fe (McGowan and Prangnell, 2006). Other investigators have found vivianite crystallities in close association with algal remains such as diatom shells.

Vivianite formation appears to be favoured under organic-rich conditions which typify the minerals occurrence and its environment (Henderson et al., 1984). Readily degradable organic debris may enhance the development of reducing microenvironments, and simultaneously serve as an important orthophosphate source. Such conditions are common in the vicinity of effluent from water sewage plants (Hearn et al., 1983), septic plume systems (Robertson et al., 1998), and in sediments receiving high anthropogenic wastewater and nutrient loadings (Goslar et al., 1999; Dodd et al., 2003; Taylor et al., 2008). Moreover, P supply may be naturally enhanced by P-rich ground water percolating through sediments (Manning et al., 1999). Vivianite has been identified in all these settings.

It is well accepted that Fe(III) (oxyhydr)oxides play an important role in vivianite formation. As these compounds efficiently scavenge orthophosphate, but are subject to microbial and chemical reduction (Melton et al., 2014), they serve as a source for Fe$^{2+}$ and orthophosphate, and may therefore act as an important precursor phase for vivianite. Tessenow (1974) concluded that the “reduction of sedimented Fe(III) hydroxophosphate complexes” and the “rapid solution of Fe...
and [...] orthophosphate under anoxic conditions is of particular importance for the accumulation of Fe$^{2+}$ and orthophosphate in pore waters, and finally vivianite precipitation. Fagel et al. (2005) proposed for Lake Baikal, in Siberia, Russia, that the ferrosulfic hydroxylphosphates \(\text{Fe}_2\text{S}_x\text{O}_y\text{H}_z\) precipitated at the sediment surface dissolve further below, in more reducing conditions, and subsequently lead to direct precipitation of vivianite from pore waters (citing Nriagu and Dell, 1974). A similar conclusion was drawn by Sapota et al. (2006), suggesting that Fe(III) (oxyhydr)oxide-rich particles may have adsorbed sufficient amounts of orthophosphate during periods of slow sedimentation and subsequently allowed vivianite to form. Manning et al. (1991) showed that in Narrow Lake, Alberta, Canada, the main sink of orthophosphate switches, with increasing depth of burial, from adsorption on ferric oxides to incorporation into vivianite. Hearn et al. (1983) identified that the presence or absence of amorphous ferric oxy-hydroxides controlled the occurrence of vivianite in Potomac River sediments (USA). However, they found vivianite concentrated in a coarse-sand dredge spoil in a surface layer which contained less ferric oxy-hydroxides than did the layers without vivianite. They proposed that amorphous Fe(III) (oxyhydr)oxides react with pore water orthophosphate to form stable ferric Fe phosphates preferentially to the formation of vivianite.

The reductive dissolution of Fe(III) (oxyhydr)oxides and the accompanying release of orthophosphate appear to be important triggers for vivianite formation. In meromictic Lake Pavin (Massif Central, France), Cosmidis et al. (2014) attributed the precipitation of vivianite to the reductive dissolution of Fe(III) (oxyhydr)oxides and mixed valence Fe phosphates. In laboratory incubation experiments with soil slurries, Heilberg et al. (2012) and Walpersdorf et al. (2013) showed that vivianite formed during anoxic treatment in response to reductive dissolution of Fe(III). In wastewater sludges, Zhang (2012) detected vivianite after addition of amorphous Fe(III) oxyhydroxide (\(\alpha\)-FeOOH), and proposed that P removal was triggered through an “Fe reduction-induced precipitation”. Recently, Reed et al. (2016) highlighted that transport of Fe from shelf sediments to deep basins is a crucial process enhancing vivianite formation in deep anoxic and sulphidic regions of the Baltic Sea. Using a reactive–transport model, the authors demonstrated that episodic reoxygenation events encourage the retention of Fe(III) (oxyhydr)oxides and Fe-bound P in sediments, thus leading to enhanced vivianite formation (Reed et al., 2016).

The supply of S relative to that of Fe appears to be another important factor influencing the formation of vivianite, by controlling Fe$^{2+}$ concentration in pore waters. Vivianite preferentially forms in "non-sulphidic" systems, where the rate of S$^{2-}$ production does not exceed that of the Fe$^{2+}$ supply (Berner, 1981b; Gächter and Müller, 2003; Rothe et al., 2015). Indeed, a variety of factors are important and may affect vivianite formation, such as redox conditions, degradability of organic matter, microbial community composition, resorption potential by remaining Fe(III) (oxyhydr)oxides and silicate clays, orthophosphate release, temperature, and pH. Ultimately, decisive for the formation or absence of vivianite in natural systems is, however, the availability of reactive Fe representing the key factor and leaving its imprint in the sediment record. If almost all reactive Fe in the sediment is bound by S$^{2-}$, pore water Fe$^{2+}$ concentrations are too low to allow vivianite to form. However, FeSx and vivianite commonly coexist as long as sufficient Fe is available (Stoops, 1983; Olsson et al., 1997; Brauer et al., 1999; Dodd et al., 2003; Vullémin et al., 2013; Rothe et al., 2015).

It has been proposed that the sedimentary S:Fe ratio (total S:reactive Fe; reactive Fe represents the proportion of total Fe extracted by sediment digestion with aqua regia) can be used to indicate the conditions that explain the presence or absence of vivianite (Rothe et al., 2015). A S:Fe ratio smaller than 1.5 indicates that there is excess Fe relative to that of S, and vivianite formation is not restricted by the supply of Fe (see below). Olsson et al. (1997) found vivianite only in pre-1900 sediments which had a low S content. In contrast, vivianite was absent from post-1900 sediments which had a higher S content. The authors proposed that under low primary production and low S supply, sediments acted as an efficient P sink through the formation of vivianite but increased S$^{2-}$ production significantly decreased the sequestration of Fe-associated P forms (Olsson et al., 1997). Through eutrophication and the elevated production and degradation of organic matter as well as through increased SO$_4^{2-}$ levels, the supply of S relative to that of Fe is favoured, leading to deteriorated conditions for vivianite formation. In many marine sediments there is excess dissolved S$^{2-}$ relative to dissolved Fe$^{2+}$ (Berner, 1970, 1981a), because the SO$_4^{2-}$ concentration is about 100 times higher in seawater than in freshwater. In marine sediments, biogenic apatite is a much more common authigenic phosphate phase than vivianite (Ruttenberg and Berner, 1993; Burns, 1997). The role played by reduced Fe(II) phosphates in P burial in these systems has largely been disregarded so far. However, vivianite may be favoured in estuarine and fan sediments, as well as in productive shelf seas which are characterised by a higher supply of Fe and organic matter than the deep ocean. Until now, only a few studies have identified vivianite in such systems (Burns, 1997; Hsu et al., 2014; Egger et al., 2015a).

Recent studies, however, indicate that the formation of reduced Fe(II) phosphates is favoured in organic- and Fe-rich sediments both within, and below the sulphate/methane transition zone (SMTZ). This is the zone where high concentration of orthophosphate and Fe$^{2+}$ are present in pore waters, and S$^{2-}$ has already precipitated (März et al., 2008; Jilbert and Slomp, 2013; Slomp et al., 2013; Hsu et al., 2014). For the Bothnian Sea, Egger et al. (2015a) provided evidence for vivianite formation below a shallow SMTZ, suggesting that methane plays a crucial role in providing conditions favourable for vivianite authigenesis. The results indicated that the microbiologically mediated anaerobic oxidation of methane with sulphate and Fe drives a sink-switching from Fe(II)/III oxo-bound P to vivianite. Egger et al. (2015a) concluded that vivianite “likely represents an important burial sink for P in coastal systems worldwide”. Thus, the formation of reduced Fe(II) phosphates such as vivianite might be of much greater importance for the global P cycle than previously assumed.

It is well known that vivianite forms as a result of oxidation–reduction reactions in sediments. Vivianite is often accompanied by an assemblage of authigenic minerals which might be precursors for vivianite, such as ferric and mixed valence Fe phases, or that form at the expense of vivianite. In addition to FeSx, these authigenic minerals include Fe carbonates (such as siderite (Suess, 1979; Brauer et al., 1999)), Fe silicates (such as limonite (Müller and Förstner, 1973)) or other phosphate minerals (such as hydroxylapatite, anapaitite (Stamatakis and Koukouzas, 2001)). However, the formation of these mineral assemblages close to each other cannot be explained by macroenvironmental mineral equilibria alone, which indicates that various microenvironments with different conditions must have existed besides each other during mineral formation (Stoops, 1983). This conclusion is in accordance with the discrepancies reported from pore water equilibrium calculations, and the limitations arising from such calculations. The findings suggest that small-scale processes within the sediment matrix governed by the activity of microorganisms, as well as the porous, heterogeneous sediment matrix itself, play an important function in mineral nucleation.

Specific knowledge on the rate and mechanism of vivianite crystal growth is limited. There is only one study investigating the growth kinetics of pure synthetic vivianite from solution of Mohr’s salt (Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O) and ammoniumdihydrogen and monohydrogen phosphate) at different temperatures (25, 35 and 45°C) in the laboratory (Madsen and Hansen, 2014). The authors found that vivianite exhibits spiral growth at low supersaturation and a combination of this mechanism with surface-nucleation growth at higher supersaturation. From those experiments, Madsen and Hansen (2014) yielded growth rates ranging from 2 × 10$^{-13}$ to 2 × 10$^{-7}$ m s$^{-1}$. Assuming vivianite nodules are able to form rapidly in sediments
(within half a year) this would yield crystals ranging in size between $3 \times 10^{-6}$ and $3 \times 10^{-2}$ m which covers the size of nodules found in natural sediments. Conclusions on the growth mechanism and kinetics of vivianite crystals in natural sediments are, however, limited because sedimentary vivianite forms within a complex reaction matrix where microorganisms may induce mineral nucleation and affect crystal growth.

5. The role of microorganisms in vivianite formation

Microorganisms influence the formation of vivianite in sediments both directly and indirectly. Direct effects are mediated by the supply of orthophosphate, Fe$^{2+}$ and S$^{2-}$, due to their active contribution in organic matter mineralization and the use of electron acceptors such as Fe$^{3+}$ and SO$_4^{2-}$. The indirect effects are by consuming O$_2$, NO$_3^-$, Fe$^{2+}$, and other electron acceptors, thus changing redox conditions, and producing CO$_2$ which lowers the pH. Thus, pore water saturation conditions are mediated by biological processes, and the formation of secondary minerals may be biogenic (Suess, 1979; Vuillemin et al., 2013). Bacteria can thereby induce mineral precipitation by modifying the microenvironment surrounding their cells (such as concentrating ions and changing pH) and/or acting as nucleation sites to overcome kinetic barriers (Sánchez-Román et al., 2015). Thus, nucleation on a biological template can occur before nucleation in a homogenous solution.

Laboratory batch culture experiments show that microorganisms can direct the precipitation of vivianite and other authigenic minerals such as siderite, apatite, and magnetite (Fredrickson et al., 1998; Glaser et al., 2003), suggesting that microorganisms are also actively involved in the formation of these minerals under natural, sedimentary conditions (Vuillemin et al., 2013). The formation of vivianite has been linked to the activity of dissimilatory metal reducing bacteria (DMRB), coupling organic carbon oxidation to Fe(III) reduction (Fredrickson et al., 1998; Zachara et al., 1998; Glaser et al., 2003; O’Loughlin et al., 2013). The DMRB transformed hydrous ferric oxide (HFO) into siderite and vivianite if Fe$^{2+}$ complexing ligands, such as HCO$_3^-$ and HPO$_4^{2-}$ were present in the culture medium. Zachara et al. (1998) observed that biogenic vivianite and siderite were formed through dissimilatory reduction of synthetic and natural Fe(II/III) oxides, and that the formation of vivianite preceded that of siderite.

Vivianite had rapid precipitation rates (7–14 d) and the crystallinity was enhanced in the presence of anthraquinone-2,6-disulfonate (AQDS, a humic acid analogue) (Zachara et al., 1998; Glaser et al., 2003). In the absence of complexing ligands, biogenic Fe$^{2+}$ sorbed to HFO and promoted its solid-state conversion to magnetite or “green rust” (Fredrickson et al., 1998). Green rust is a layered ferrous ferric Fe phosphates during sinking through an anoxic water column, or in bottom sediments, similar to the conversion of green rust into vivianite under reducing orthophosphate-rich conditions as reported by Hansen and Poulsen (1999) (Fig. 4).

6. Ecological role of vivianite in aquatic systems

In many lakes, P is the ultimate limiting nutrient that govern primary productivity. Through vivianite formation in surface sediments, P sequestration can be significantly increased. This increase has consequences for the orthophosphate availability for primary producers in the overlying water, which in turn may result in a change of the N:P stoichiometry and altered algal assemblages.

Immediate effects of vivianite formation on a lake’s P budget are expected, if: (1) vivianite formation significantly contributes to benthic P retention, (2) the formation of the mineral takes place in the recent, early diagenetic sediment layers which are still in close connection to the overlying water, and (3) vivianite is not readily solubilised, and its post-depositional mobility is low.

The observations made on vivianite’s occurrence in sediments and its crystal habit document the early diagenetic nature of vivianite as described in Section 2. The cases in which vivianite has been identified directly at the sediment surface, or within the first centimetre of the sediment (e.g. Cosmidis et al., 2014; Rothe et al., 2014, 2015) can serve as direct proof of its early diagenetic formation. However, vivianite authigenesis does not necessarily occur in close proximity to the sediment surface, but can appear also several metres deep within the sediment, as it might be common for marine settings and in oligotrophic systems with deeper oxygen penetration (Márz et al., 2008).

In contrast, vivianite is often detected in sediment several metres to hundreds of metres deep, and has been used as a proxy to reconstruct paleoenvironmental conditions (for example Brauer et al., 1999; Fagel et al., 2005; Sapota et al., 2006; Minyk et al., 2013; Vuillemin et al., 2013). However, it appears to be difficult to reconstruct the age of the
noodles and their mode of formation (rapid and immediate after sediment deposition, or slow and long lasting) (Nuttin et al., 2013; Vuillemin et al., 2013). Nonetheless, the presence of vivianite in deep sediment layers demonstrates that vivianite can persist many thousands of years within the sediment.

Apart from its common occurrence in lacustrine sediments, not much is known about the quantitative contribution of vivianite in P burial. In recent years, efforts have been made to further elucidate the role of vivianite in P sequestration, using combinations of different kinds of chemical extractions (Egger et al., 2015a), or taking advantage of an enrichment of vivianite nodules after sediment preparation (Rothe et al., 2014). According to Rothe et al. (2014, 2015) and Egger et al. (2015a), 20–40% of total P was bound in vivianite, exemplifying that vivianite authigenesis can be of substantial relevance in P sequestration.

In marine sediments, the role of vivianite in P sequestration has so far largely been ignored. However, as already mentioned in the preceding sections (Sections 4, 5), vivianite authigenesis may be of significance in marine sediments rich in organic matter and Fe. What has been proposed for the Baltic Sea and Black Sea by Jilbert and Slomp (2013) and Dijkstra et al. (2014), and recently demonstrated in the Bothnian Sea sediments (Egger et al., 2015a) is that authigenic vivianite is a significant burial sink for P in coastal sediments. In the same study Egger et al. (2015a) proposed that the formation of vivianite is closely coupled to the anaerobic oxidation of methane. These findings suggest that the mineral represents an important P sink in coastal sediments worldwide.

In lacustrine systems, increased P retention through vivianite authigenesis may partly be induced by the occurrence of plant roots, and the activity of tube-dwelling macrozoobenthos such as chironomid larvae. In both cases, the redox zonation of the sediment is altered by introduction of oxygen into the sediment, leading to zones of Fe(III) (oxyhydr)oxide accumulation and concomitant orthophosphate sorption from the surrounding anoxic pore water (Hölker et al., 2015). Moreover, orthophosphate release and its subsequent accumulation in these zones is favoured through enhanced microbial degradation of organic compounds originating from plant root exudates and the chironomid’s metabolism. The development of microzones with favourable conditions for vivianite formation may particularly occur after the plant roots have died, and burrows are abandoned. Indeed, vivianite crystal aggregates have been detected attached to aged rice roots in a paddy field soil (Nanzyo et al., 2013), and the authors discussed the role of an Fe plaque surrounding the roots for vivianite crystal growth. For chironomids, the effects on benthic element cycling and element budgets and particularly the long-term effects on P sequestration remain largely unknown (Hölker et al., 2015). However, given our current knowledge of the occurrence of vivianite and the role of microbes in biogeochemical cycling of elements and the associated biogenic mineral formation, benthic tube-dwellers may positively affect vivianite authigenesis in surface sediments.

Vivianite has been detected in many anthropogenically influenced sedimentary settings, most notably where P availability was increased. These findings allow for the conclusion that vivianite authigenesis might have been favoured by increased nutrient loadings, and the mineral’s occurrence mirrors human impact on aquatic nutrient cycling. Egger et al. (2015a) concluded that coastal eutrophication leads to a vertical upward migration of the sulphate/methane transition zone within the sediment, shifting the zone of favourable conditions for vivianite formation closer to the sediment surface. It was postulated that anthropogenic fertilization of coastal areas throughout the last century therefore increased the role of vivianite authigenesis in many coastal surface sediments (Egger et al., 2015a). In contrast, in many lacustrine systems, increased nutrient supply led to accelerated eutrophication, including deteriorated oxygen and redox conditions, and the appearance of $S^{2-}$ in the water column, indicating a loss of Fe associated P binding capacity of the sediments. In some cases, vivianite
orthophosphate-rich conditions.

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C106N16P1S0.7Fe0.05, Stumm and Morgan (1981)), more S2- produced with a lower organic matter supply, leading to a higher degree by desulphuration and dissimilatory sulphate reduction than is pro-

The extent of organic matter production and its supply to the sediment have consequences for the formation of vivianite. A higher organic matter supply leads to a higher demand for oxidants, resulting in deteriorated redox conditions and higher reduction rates of Fe3+ and SO42- (Holmer and Storkholm, 2001). Because organic matter is specifically enriched in S compared to Fe (Redfield ratio: C106N16P1S0.7Fe0.05, Stumm and Morgan (1981)), more S2- is produced by desulphuration and dissimilatory sulphate reduction than is produced with a lower organic matter supply, leading to a higher degree of sediment sulphidisation (Berner, 1981a). This affects the availability of Fe2+ in pore waters, and hence also vivianite authigenesis. Neither the SO42- concentration nor the rate of organic matter supply by itself are absolute predictors for the bacterial sulphate reduction rate. Nevertheless, both processes are crucial for the extent of sulphide-and thus vivianite formation.

Recently, Rothe et al. (2015) proposed that the sedimentary S:Fe ratio (total sulphur to reactive iron; reactive iron represents the propor-

In marine systems, SO42- concentrations (~2700 mg L−1) are high enough that bacterial sulphate reduction rates are independent of SO42- in the water. In contrast, in freshwater systems bacterial sulphate reduction rates are affected by the quantity and quality of organic matter, and also by the concentration of SO42-. Although often much higher, freshwater dissolved SO42- concentrations are still regarded to be typically: <27 mg L−1 (Capone and Kiene, 1988), 9.6–28.8 mg L−1 (Caraco et al., 1989), 4.8–29.8 mg L−1 (Marino et al., 1990), 0.96–19.2 mg L−1 (Sinke et al., 1992), 2.2–24.1 mg L−1 (Cook and Kelly, 1992), and 9.6–19.2 mg L−1 (Roberts, 2015).

The German lakes and rivers considered in the present case (Fig. 5) have SO42- concentrations between 42.6 mg L−1 in Lake Groß-Glienicke

Fig. 4. Three proposed mechanisms of vivianite formation in aquatic sediments: (i) vivianite may nucleate directly from pore solution, (ii) its nucleation is directed by a biological template such as the cell wall of microorganisms or organic remains, or (iii) it forms through progressive conversion of ferric iron compounds under reductive, Fe2+- and orthophosphate-rich conditions.

Fig. 5. The sedimentary molar S:Fe ratio (total sulphur to reactive iron) represents the proportion of total iron extracted by sediment digestion with aqua regia) as an indicator of conditions favourable for vivianite authigenesis. Vivianite occurs only at low S:Fe ratios (<1.1), and simultaneously contributes to a comparably higher total phosphorus (P) content (>2 mg gdw−1). Data originate from three lakes and one river in NE Germany (Lake Arendsee, eutrophic; Lake Groß-Glienicke, mesotrophic; lowland river Lower Havel, eutrophic; Lake Groß er Müggelsee, eutrophic). For Lake Arendsee, vivianite formed in the past (1) but not at present (2), due to major qualitative changes in the sediment’s chemical composition resulting from a mining impacted catchment area which explains a comparatively low total phosphorus content at low sulphur:iron ratios. Figure extended from Rothe et al. (2015) under a Creative Commons Attribution license.
Fe averaged to 95.5 ± 20.3 mg g\textsubscript{dw} (Kleeberg (2012)). In lakes with a SO\textsubscript{4}\textsuperscript{2−} concentration of glacial lakes in Germany with 2.9–340 mg L\textsuperscript{−1} (mean 61.6 mg L\textsuperscript{−1}, 321 lakes) (reviewed by Kleeberg et al. (2012)). In lakes with a SO\textsubscript{4}\textsuperscript{2−} concentration below 96–192 mg L\textsuperscript{−1}, the bacterial sulphate reduction rate is considered to be typically first order, and an increase in SO\textsubscript{4}\textsuperscript{2−} concentration will cause an increase in the bacterial sulphate reduction rate (for example Cook and Kelly, 1992).

Usually, it is the rate of SO\textsubscript{4}\textsuperscript{2−} supplied to the benthic zone of SO\textsubscript{4}\textsuperscript{2−} reduction, which limits bacterial sulphate reduction. An exception are mining lakes, where SO\textsubscript{4}\textsuperscript{2−} is scavenged from the water column by Fe(III) hydroxide particles, enhancing the rate of SO\textsubscript{4}\textsuperscript{2−} supply to the reduction zone, and increasing bacterial sulphate reduction (for example Rose and Ghazi, 1997). Some lakes have extremely high concentrations of SO\textsubscript{4}\textsuperscript{2−} with 200–900 mg L\textsuperscript{−1}, and Fe with 25–620 mg L\textsuperscript{−1} (Kleeberg, 1998), but usually these lakes have a low productivity (Nixdorf et al., 2003), and a low supply of organic matter to the sediment. Thus, it remains open, whether the S:Fe ratio can be unrestrictedly applied as an indicator for the presence of vivianite in these extreme environments.

Nonetheless, eutrophic mining lake Golpa IV, Mid-Germany, which was flooded already in 1955, and is today neutral with a pH of 8.35, and a SO\textsubscript{4}\textsuperscript{2−} concentration of 234 mg L\textsuperscript{−1} (Hupfer et al., 1998), seems to fit in the S:Fe concept: a high Fe availability leads to a high P retention (compare with Fig. 5). In the upper 15 cm of sediment (n = 9 horizons) Fe averaged to 95.5 ± 20.3 mg g\textsubscript{dw}, P to 12.6 ± 8.4 mg g\textsubscript{dw}, and S to 54.3 ± 4.0 mg g\textsubscript{dw}, which resulted in a molar Fe:P ratio of 6.2, and a molar S:Fe ratio of 1.0. According to Fig. 5, the latter indicates the presence of vivianite. A direct proof by means of X-ray diffractometry and IR spectroscopy, however, failed at that time, because of the interference with clay minerals (Hupfer et al., 1998).

Given the close coupling of the Fe-, S-, and P-cycles, any (anthropogenically induced) change in the availability of S and Fe may affect vivianite formation, and hence the P budget. The use of FeSO\textsubscript{4} in wastewater treatment plants, as a measure to eliminate orthophosphate from wastewater, may limit vivianite formation in the effluent water through increased inputs of SO\textsubscript{4}\textsuperscript{2−}. On a larger scale, lignite mining could significantly alter P retention down-stream of former mining areas. While large amounts of Fe(III) (oxyhydr)oxides readily precipitate, the solubilised SO\textsubscript{4}\textsuperscript{2−} is transported further down-stream. This spatially separated supply of Fe and SO\textsubscript{4}\textsuperscript{2−} may improve long-term P retention in one location via vivianite authigenesis, but stimulate SO\textsubscript{4}\textsuperscript{2−}-induced orthophosphate mobilization in another location (Zak et al., 2006), leading to a loss of Fe-associated binding capacity through enhanced sulfidization of sediments.

Fe additions could be used as a lake restoration, decreasing the orthophosphate concentration in the water by stimulating vivianite formation in the sediment. Through a Fe addition, vivianite formation is favoured, because relatively less Fe is bound in sulphidic form, thus, increasing the P binding capacity of the sediment in the long-term.

7. Promoting vivianite formation as a remediation technique to improve water quality

As a consequence of the anthropogenic eutrophication of freshwaters, the in-lake application of P binding agents for P precipitation and inactivation has become an accepted tool aimed at restoring such lake ecosystems (Cooke et al., 2005; Zamparas and Zacharias, 2014). The most common agents are aluminium salts, which inactivate P, thus providing long-term control of P release from sediments. This is, because aluminium salts stably bind orthophosphate regardless of the prevailing redox conditions. Iron is the key element controlling the P binding in aquatic systems because Fe is much more abundant than aluminium in natural systems, and Fe(III) (oxyhydr)oxides are efficient sorption agents for P (Gunnars et al., 2002). Thus, significant amounts of P can be removed from the water body using Fe salts. However, the redox sensitivity of Fe has been regarded as a major disadvantage preventing a long-lasting effect on P mobility (reviewed by Kleeberg et al., 2013). Iron salts such as FeCl\textsubscript{3} and Fe(OH)\textsubscript{3} are not as frequently used in lake restoration as aluminium salts, and many applications have not been successful (Cookie et al., 2005).

Redox-sensitive Fe–P compounds may be liberated once they encounter anoxic conditions, and thus orthophosphate can be released into the water column. However, this process may be modified by the formation of reduced Fe phosphates. Using a conceptual model, Gächter and Müller (2003) emphasized that an increasing ratio of reactive Fe(II) to reactive P leads to enhanced P burial through the formation of solid ferrous Fe phosphates such as vivianite. The more Fe that is available, the less is captured in sulphidic form. Thus, an increased Fe inventory positively affects the P binding capacity of a sediment. There is field evidence for these theoretical considerations: Kleeberg et al. (2012) showed that a single addition of Fe salts to dimictic Lake Groß-Glinicke, Germany, had a beneficial effect on the long-term P cycling in the lake: phosphorus was removed from the water column and chlorophyll-a concentration significantly dropped after the in-lake application of Fe.

Rothe et al. (2014) provided evidence that the Fe application in Lake Groß-Glinicke was the stimulus for vivianite formation in the newly forming sediments. Iron was added in surplus in such a way that not all reactive Fe\textsuperscript{3+} precipitated as solid FeS\textsubscript{2}. After the Fe addition, total sedimentary P content doubled, and vivianite accounted for approximately 40% of the increase in sedimentary P. The redox-sensitivity of Fe appeared to be beneficial for the enhanced immobilization of P. The remaining reactive Fe (not immobilized by the reaction with S\textsuperscript{2−} or bound in vivianite), could migrate upwards with the newly forming sediment due to its continuous reductive dissolution and re-precipitation. The high mobility of Fe led to increased binding of P and vivianite formation even >20 years after the in-lake measure. Kleeberg et al. (2012) emphasized that a lasting effect in terms of P removal and improved water quality can only be maintained, if Fe is provided in surplus. According to Kleeberg et al. (2012), the following aspects need to be considered: (1) external “excess” P input, (2) all in-lake P mobilising and Fe releasing processes by assuming at least a stoichiometric Fe:P ratio of ≥2 (Gunnars et al., 2002), (3) the proportion of Fe associated with organic matter, and (4) the proportion of Fe bound by S\textsuperscript{2−}. However, for the in-lake application of any remediation approach, ultimately only a reduction of the external P load can guarantee a beneficial long-term effect on water quality.

Vivianite formation could also be stimulated in constructed wetland systems. In these engineered systems aiming to assist in treating wastewater (Vymazal, 2007), Fe amendments could improve the immobilization of P in the long-term, and especially under anoxic conditions by increasing the P retention capacity of the sediment through vivianite authigenesis.

8. Summary and perspectives

Although vivianite is common and the site-specific conditions for its formation are well documented, there is insufficient investigation of both the quantitative importance of vivianite authigenesis for the aquatic P cycle, as well as the mechanisms of its nucleation and crystal growth. A review of the recent literature shows that vivianite preferentially forms under iron-rich, non-sulphidic conditions, in close proximity to organic remains, not only in freshwaters but also in the marine realm. Vivianite contributes to increased P sequestration in these systems, although data regarding the quantitative contribution of vivianite to P sequestration are generally sparse. An increased P retention through vivianite authigenesis eases eutrophication. However, when a certain organic matter loading is exceeded (S:Fe > 1.5), increased sediment sulfidization leads to reduced or no vivianite formation, and to a corresponding feedback on water column orthophosphate levels. Vivianite formation is affected by the reductive dissolution of Fe(III) (oxyhydr)oxides and associated orthophosphate release, as well as the
production of sulphides and the formation of iron sulphides. However, it is difficult to further specify the processes leading to mineral nucleation and crystal growth in this complex reaction matrix. Based upon findings from microbial batch culture experiments, vivianite nucleation in natural environments eventually appears in nano- to micrometre sized microenvironments which are sustained by microbial activity. Bacteria can locally induce mineral precipitation by modifying the environment surrounding their cells. This small-scale heterogeneity can explain both the occurrence of an assemblage of secondary minerals in close proximity to each other, and the discrepancies arising from thermodynamic equilibrium calculations aimed at predicting vivianite occurrence in sediments.

Significant progress has been recently made in the detection of vivianite due to the application of heavy-liquid separation, which allows analysis of sediment samples naturally enriched in this mineral. The novel approach allows a renewed search for vivianite in surface sediments where it has previously not been detected, in order to identify factors and processes governing the minerals occurrence, and to assess the quantitative importance of vivianite authigenesis in the aquatic P cycle.

The contribution of vivianite to P burial has not yet been sufficiently quantified. Based on the available data, it is difficult to evaluate the long-term effects on water quality of additional P binding through vivianite formation. New reliable methods need to be established and applied to render new insight. More extensive data is needed on prevailing environmental conditions so that we can better understand the causal relationship between nutrient supply, geochemical conditions within the sediment, and the sediment feedback mechanism in finally retaining more or less P as vivianite. The proposed S:Fe ratio as a certain “threshold” may help in selection of additional waters for case studies.

Phosphorus and nitrogen have been recognized as important elements accelerating eutrophication. In addition to these important nutrients, in future studies the role of SO\textsubscript{4}\textsuperscript{2−} needs more attention. A simultaneously increasing SO\textsubscript{4}\textsuperscript{2−} supply contributes to an immobilization of Fe through the formation of Fe\textsubscript{SO\textsubscript{4}} counteracting remediation efforts. Because seawater is much higher in dissolved SO\textsubscript{4}\textsuperscript{2−} than is freshwater, the role of vivianite has so far been overlooked in marine waters. However, in coastal surface sediments with high organic supply, vivianite formation is induced by a consortium of methane oxidising/sulphate reducing microorganisms, leading to a sink switch from Fe(III) (oxyhydr)oxide-bound P to vivianite. The proposed S:Fe ratio as a certain “threshold” may help in selection of additional waters for case studies.

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