



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 ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) 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 Fe^{2+} in pore waters. Thus, vivianite authigenesis is also governed by bulk chemical conditions such as the rate of sulphide formation relative to that of Fe^{2+} 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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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 1

Compilation of the natural occurrence of vivianite (viv) in aquatic and terrestrial systems worldwide, drawn from the scientific literature between 1970 and 2015.

System	Location	Identification	Remarks	Reference
Sediment of freshwater lakes	Lake Åsrum, Norway	By eye	Viv not present in the underlying lagunal and marine sediments	Rosenqvist (1970)
	Great Lakes, USA	By eye, microscopy	Viv not directly associated with organic remains although these materials were abundant	Nriagu and Dell (1974)
	Lake Ur, Germany	By eye	Meromictic bog lake	Tessenow (1974)
	Lago Maggiore, Italy	By eye, SEM, XRD, Mössbauer spectroscopy	Viv depth layer not in accordance with saturation calculations	Nembrini et al. (1983)
	Toolik Lake, Alaska	By eye, SEM-EDX	Ultra-oligotrophic arctic lake, viv does not occur at the sediment surface but only below the oxic–anoxic interface	Cornwell (1987)
	Narrow Lake, Canada	By eye, XRD	Viv only present in the deep southern basin where the molar S:Fe ratio was higher than in the shallow northern basin	Manning et al. (1991)
	Lake Biwa, Japan	By eye, XRD, X-ray fluorescence	Manganovan viv, high sulphide concentration cause viv dissolution	Nakano (1992), Murphy et al. (2001)
	Lake Bussjösjön, Sweden	By eye	Present in preindustrial non-sulphidic sediments	Olsson et al. (1997)
	Baptiste Lake, Canada	XRD, Mössbauer spectroscopy	Influence of groundwater rich in Fe ²⁺ and phosphate	Manning et al. (1999)
	Lake Baikal, Russia	By eye, SEM-EDX, XRD, IR spectroscopy	Manganovan viv, viv grains contain inclusions of plagioclase and pyrite, formation in microenvironments	Fagel et al. (2005), Sapota et al. (2006), Minyuk et al. (2013)
	Laguna Potrok Aike, Argentina	By eye, SEM-EDX, XRD	Indirect signs of microbially mediated viv formation, uranium–thorium dating of viv	Nuttin et al. (2013), Vuillemin et al. (2013)
	Lake Pavin, France	XRD	Viv detected on sinking particles, role of polyphosphates in precipitation of reduced Fe(II) phosphates	Cosmidis et al. (2014)
	Lake Groß-Glienicke, Germany	By eye, SEM-EDX, XRD	Viv formation triggered by Fe supplement	Rothe et al. (2014)
	Sediment of rivers	Lake Ørn, Denmark	SEM-EDX, XRD	Identification by XRD on bulk sediment
Potomac River, USA		By eye, SEM-EDX	Major control on the occurrence of viv is the presence or absence of amorphous Fe(III) oxi-hydroxides	Hearn et al. (1983)
Mississippi River, USA		By eye, X-radiography	Viv consists of radial aggregates of 1–3 mm in diameter and occurs together with other diagenetic minerals (siderite, pyrite, calcite, dolomite, hematite)	Bailey et al. (1998)
Sediment of canals	Havel River, Germany	By eye, SEM, XRD	Occurrence of viv associated with a decreased sulfidization in response to a lower primary productivity	Rothe et al. (2015)
	Old Birmingham Mainline Canal, UK	SEM-EDX	Viv coexisted with biogenic structures and pyrite framboids	Dodd et al. (2003)
Waterlogged soils	Salford Quays, UK	SEM-EDX, XRD, Raman spectroscopy, XANES, EXAFS	Highly contaminated, organic-rich canal bed sediments	Taylor and Boulton (2007); Taylor et al. (2008)
	Organic soil, Denmark	XRD, Mössbauer spectroscopy	Viv neof ormation in response to Fe(III) reduction following anoxic soil incubation	Heiberg et al. (2012)
Bogs	Meadow soil, Denmark	By eye, SEM-EDX, XRD, Mössbauer spectroscopy	Dissolution precipitation experiments, viv shows slow precipitation kinetics	Walpersdorf et al. (2013)
	Paddy field soil, Japan	By eye, SEM-EDX, XRD	Viv attached to aged rice roots	Nanzyo et al. (2010, 2013)
	Swamps, Auckland Area, New Zealand	By eye, XRD	XRD detection successful after the minerals exposure to air	Rodgers (1977)
Marine sediments	River bog, Denmark	XRD	Viv coexisted with siderite, calcite and occasionally pyrite	Postma (1981)
	Amazon Fan, Brazil	By eye, SEM-EDX	Viv occurs below the depth of total sulphate depletion	Burns (1997)
	Yung-An Ridge, South China Sea	SEM-EDX, XRD, Raman spectroscopy, IR spectroscopy	Magnesium-rich viv, viv formation influenced by methane induced sulfidization	Hsu et al. (2014)
Other	Bothnian Sea, Baltic Sea	SEM-EDX, XRD, µXRF, XANES	Anaerobic oxidation of methane triggers viv formation	Egger et al. (2015a)
	Wastewater sludge	SEM-EDX, XRD, Mössbauer spectroscopy	P removal through Fe reduction-induced P precipitation	Frossard et al. (1997), Zhang (2012)
	Hydrothermal deposits	By eye	Viv retains its deep colour even where intensively altered	Robertson (1982), Rodgers et al. (1993)
Archaeological settings	By eye	Viv present on the surface of bones and other human remains, important function of microorganisms proposed	Tessadri (2000), Thali et al. (2011), McGowan & Prangnell (2006, and references therein)	

EXAFS: extended X-ray absorption fine structure; IR spectroscopy: infrared spectroscopy; µXRF: micro X-ray fluorescence; SEM-EDX: scanning electron microscopy with energy dispersive X-ray spectroscopy; XANES: X-ray absorption near edge structure; XRD: powder X-ray diffraction.

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