



Effect of natural sulfidic conditions on the stability of authigenic vivianite in lake sediment

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Abstract. Phosphorus (P) stored in lake sediments as legacy P can serve as a long-term internal source of eutrophication if environmental conditions shift. One key sedimentary P sink is vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), a ferrous phosphate mineral that forms under anoxic, iron-rich conditions. However, vivianite is unstable in sulfidic environments, where sulfide (S^{2-}) preferentially binds to Fe(II), potentially releasing P back into porewater. In this study, we examined the stability of naturally
15 formed vivianite under in situ sulfidic conditions in Lake Arendsee, a eutrophic lake in northern Germany with elevated sulfate concentrations and deep vivianite-rich sediment layers. Using sediment-filled dialysis chambers (peepers), vivianite-bearing sediment was exposed for 2 and 9 months to varying natural porewater conditions across a redox gradient. Our results show that sediment exposed to sulfidic conditions near the sediment–water interface experienced significant solid phase P loss—up to 41 %—accompanied by increased S content and decreased vivianite signal, as confirmed by Mössbauer
20 spectroscopy and X-ray diffraction (XRD). Most P released originated from vivianite, indicating that sulfide-induced vivianite dissolution was the primary P-mobilization pathway. These findings demonstrate that vivianite can act as a dynamic P source when exposed to sulfidic porewater, with implications for long-term P cycling and lake management. As sulfate inputs to freshwater systems continue to rise, processes that destabilize vivianite may compromise the effectiveness of internal P retention. Consequently, lake restoration strategies must account for sulfur-driven P release mechanisms.

25 1 Introduction

Freshwater eutrophication remains a pressing concern worldwide, driven largely by increased phosphorus (P) concentrations in the water body. To design effective management strategies for controlling P levels in lakes, a thorough understanding of possible P sources is needed. Internal sources of P in the lake sediment can perpetuate eutrophic conditions even when external sources have been curtailed (Schindler, 2006; Søndergaard et al., 2001). While much research has focused on
30 reactive pools of P in the sediment as short-term internal source of P (Hupfer and Lewandowski, 2008; Markovic et al., 2019; Søndergaard et al., 2001; Steinman and Spears, 2020), many questions remain open regarding long-term P retention and release (Søndergaard and Jeppesen, 2020).



During an extended period of eutrophication, P can accumulate in the sediment (legacy P) and forms a reservoir which can potentially become a P source if environmental conditions change (Carey and Rydin, 2011). A common binding partner for P is iron (Fe), and Fe-P phases often constitutes a major part of the solid bound P in the sediment (Boers et al., 1998). Fe(III)-oxyhydroxide particles bind P by surface adsorption, but are sensitive to redox conditions, becoming unstable under the reductive conditions typically found in the sediment. However, they constitute a precursor for long term P sequestration in the form of redox-stable ferrous (Fe(II)) minerals such as vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) (Heinrich et al., 2020; Kubeneck et al., 2025). Vivianite has been observed in many aquatic sediments, and can form substantial reservoirs of legacy P (O'Connell et al., 2015; Rothe et al., 2016). However, vivianite is unstable in the presence of sulfide (S^{2-}), which binds preferentially to Fe(II) forming iron sulfide phases (FeS_x), while releasing P (Wilfert et al., 2020). Consequently, a stable reservoir of vivianite could become a source of dissolved P when exposed to sulfidic conditions. Recent studies have demonstrated this principle by introducing synthetic vivianite in sulfidic environments (Kubeneck et al., 2024; Song et al., 2024). In a changing world, conditions in freshwater systems could shift towards sulfidic by, for example, elevated sulfate (SO_4^{2-}) concentrations, which have increased in freshwater systems over the last decades (Zak et al., 2021).

The behavior of vivianite has been examined extensively in a laboratory setting but is rarely investigated within a natural context, yet this is essential to understand the effects on complex freshwater systems. We showed in earlier work that naturally formed vivianite-bearing sediment from Lake Arendsee, Germany, can be mobilized by increased sulfate reduction and release P via a mesocosm experiment (van Kuppevelt et al., 2025). Based on these findings, the present study investigates this process under natural conditions of the lake itself, specifically the sediment redox gradient which includes sulfate reduction near the sediment surface. Within the sulfidic upper sediment, vivianite is expected to dissolve over time, but should remain stable lower in the sediment, further away from the sulfate reduction zone. To test this hypothesis, we employ a novel method to introduce vivianite-rich sediment taken from deeper layers to various depths, allowing diffusive exchange with the porewater while separating the solid phase to be retrieved at the end of the experiment for examination. To this end, we used dialysis chambers ("peepers") filled with vivianite-bearing sediment separated by a filter membrane to *in situ* porewater conditions at different depths over several months.

2 Materials and Methods

2.1 Study Site

Lake Arendsee (52°52'36.12"N, 11°29'12.12"E) is a dimictic lake in northern Germany formed by salt-karst processes. It spans 5.14 km², with a maximum depth of 49.5 m (mean ~ 29 m) and a relatively long water residence time of approximately 50–60 years (Meinikmann et al. 2015). Beginning in the 1960s and lasting up to today, Lake Arendsee experienced pronounced eutrophication driven by urban discharge from the nearby city of Arendsee. Despite various mitigation efforts, P levels in the water column remain high, sustained by ongoing groundwater-derived P and legacy P inputs (Hupfer et al.,



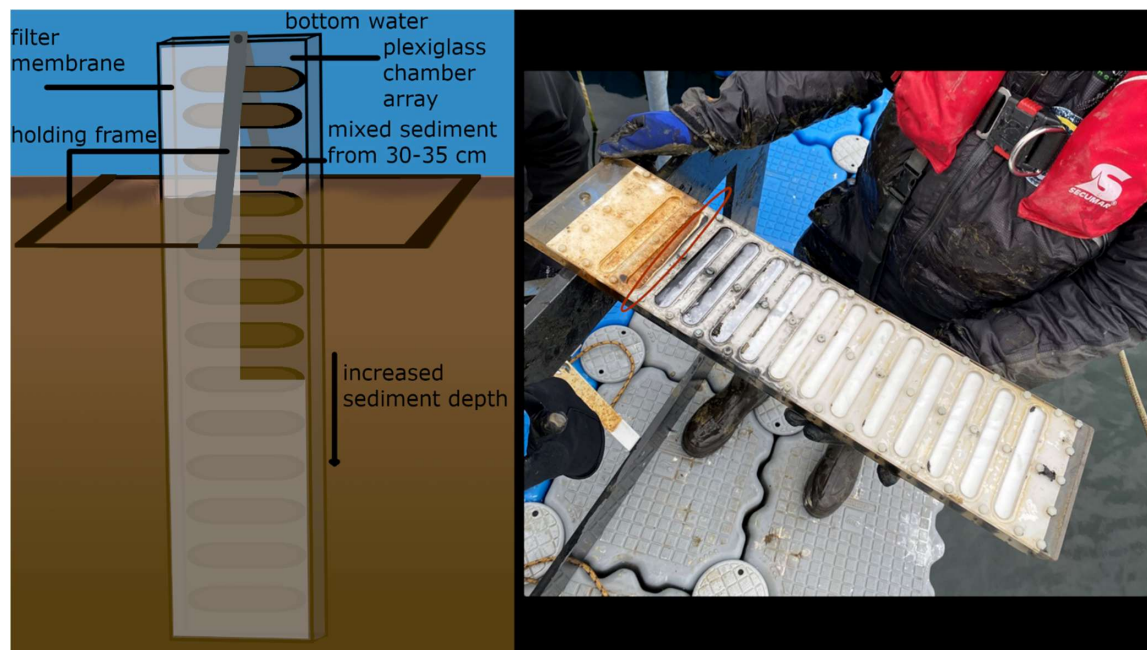
2019). Recent measurements show an annual mean total P concentration of $178 \mu\text{g L}^{-1}$ (2023; [https://www.igb-berlin.de/der-](https://www.igb-berlin.de/der-arendsee)
 65 arendsee).

In addition to elevated P, the lake has considerable sulfate concentrations—around $61 \pm 7 \text{ mg S L}^{-1}$ in January 2023 (van Kuppevelt et al., 2025)—due to groundwater enriched by local gypsum deposits. The uppermost sediment layers are rich in organic matter and produce enough sulfide to form iron sulfide phases, and are relatively low in Fe content ($< 10 \text{ mg Fe g}^{-1} \text{ DW}$). Deeper sediment horizons (below $\sim 25 \text{ cm}$) have a higher total Fe content (up to $50 \text{ mg Fe g}^{-1} \text{ DW}$). Within these
 70 deeper zones, vivianite constitutes a major Fe-bearing phase (Rothe et al. 2015; Scholtysik et al. 2022).

2.2 Experimental Setup

To investigate the effect of natural porewater conditions of lake Arendsee on naturally formed vivianite, we designed a setup using an array of dialysis chambers (peepers), based on a method for porewater analysis developed by Hesslein (1976). This method allows exchange of dissolved compounds between the chambers and the outer environment through a filter
 75 membrane, while keeping the sediment inside the chambers physically separated from the lake sediment.

The method was adapted for our experiment by filling the chambers with portions of the same homogenized sediment collected from a vivianite-rich depth (Fig. 1). This way, different portions of the same sediments were exposed to porewater conditions at different depths.





80 **Figure 1: Left: Schematic of the sediment peeper (SedP) setup. Sediment from a specific depth is exposed to different porewater conditions by loading it in the peeper chambers, separated by a permeable membrane. Right: Photograph of the actual peeper right after retrieving after 9 months of exposure. Note the line on the membrane of the second chamber from the top, marking the sediment-water interface (red circle).**

The sediment-filled peepers (SedP) consisted of two custom-made plexiglass samplers with 14 chambers each (chamber width: 14.5 cm; height: 2 cm; depth: 1.8 cm; chamber distance: 2 cm; volume: 53 mL). Prior to use, the peepers and accompanying cover plates were soaked in 1 %v/v hydrochloric acid for 24 h and thoroughly rinsed with distilled water. Dialysis membranes (0.2 µm) were carefully cropped to fit exactly between the sediment peeper and cover.

The sediment peepers were filled with sediment and assembled on-site at Lake Arendsee prior to deployment at the lake bottom in June 2022, according to the following procedure. Vivianite-rich sediment for filling the peepers was collected using a UWITEC gravity corer ($\varnothing = 9$ cm) from a floating monitoring platform near the deepest point of the lake (52°53'23.2"N 11°27'38.1"E). A total of ten cores were collected and sliced, selecting the vivianite-rich sediment fraction between 30–35 cm below the sediment-water interface (SWI), which was pooled in a ziplock bag. Care was taken to prevent oxygen exposure by using multiple layers of airtight plastic bags with no trapped air. The pooled sediment was homogenized by kneading the bag thoroughly for 15 minutes. After mixing, a subset of the pooled sediment was collected in three 50 mL Falcon tubes for baseline analyses, and the remainder was immediately transferred to the peeper to minimize oxygen exposure. The chambers were filled completely with the mixed sediment to prevent air enclosure, and the surface around the chambers was cleaned with paper towels before placing the filter membrane and tightly screwing on the cover.

Porewater profiles of the surrounding sediment were investigated in parallel using the established equilibrium method described by Hesslein (1976). Here, the chambers are filled only with distilled water which then equilibrates with the local porewater composition. For these porewater peepers (PwP), two plexiglass samplers were used (double array of 2×58 chambers; chamber width: 6 cm; height: 0.6 cm; depth: 1.7 cm; chamber distance: 0.4 cm; volume: 6.3 mL) which allowed for a depth resolution of 1 cm. The PwP were acid washed (same as for SedP) and assembled in the lab a day before deployment. The chambers were filled with distilled water and covered by a fitted membrane (0.2 µm), making sure no air bubbles were enclosed (Hesslein, 1976). The prepared PwP were placed in a container with distilled water which was then treated with N₂ gas to remove oxygen for 12 hours before deployment.

The two SedP and two PwP were anchored to separate, custom made holding frames and adjusted to hold the top of the peeper circa 10 cm above the sediment, once inserted. The peepers were deployed directly into Lake Arendsee. Each peeper was positioned at locations within 20 m of the platform and slowly lowered to the bottom with ropes which were then secured to the platform.

110 2.3 Peepers Retrieval and Sampling Procedure

The two sets of parallel SedP and PwP were retrieved at 2 months and 9 months after deployment. The first set (SedP2m; PwP2m) was retrieved in August 2022, constraining the peeper's exposure to the summer period, when temperatures and



primary production were maximal, and during which the lake was constantly stratified. The second set (SedP9m; PwP9m) was retrieved in March 2023, throughout winter, when bottom waters were mixed.

115 Upon retrieval, each peeper was hoisted carefully from the lake bottom, removed from the frame and cleaned, and the chambers were immediately sampled.

Before sampling the SedP, the SWI was marked based on visible staining of the filter membrane corresponding to the different redox conditions, where red-brown Fe(III) phases indicated the oxic top sediment, and black precipitation the anoxic sediment below (Fig. 1). After carefully cutting and opening the membrane, the sediment was transferred from each
 120 chamber to a 50 mL airtight container. All samples were cooled immediately after sampling and stored at 5 °C before further processing and analysis.

Porewater was extracted from the chambers of the PwP as follows: 2 mL was collected as is and fixed with 200 µL of 2 % zinc acetate, to prevent losses of volatile H₂S for later analysis of the sulfide concentration, with the methylene blue method (Cline, 1969). 2 mL was collected and filtered through a 0.2 µm syringe filter (to sterilize it) for quantification of dissolved
 125 sulfate, nitrate (NO₃⁻) and chloride (Cl⁻) by ion chromatography (IC, Metrohm Compact IC; conductivity detector). 10 mL was acidified by adding 0.1 mL 3.75 M HNO₃ for analysis of soluble reactive P (SRP) and ammonium (NH₄⁺) concentrations using continuous segmented flow analysis (AutoAnalyzer 3 HR; SEAL Analytical, Inc.). The acidified subsamples were also analyzed for total elemental P (TP), Fe, S and Mn concentrations by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 7400 Duo Full MFC; Thermo Fisher Scientific Inc.). The full array of
 130 measured elements in the porewater and the resulting concentration profiles can be found in Fig. S1.

2.4 Sediment Processing and Solid Phase Characterization

The baseline sediment and SedP sediment samples were processed within a day after collection to minimize oxidation effects. Each sediment sample was first homogenized by stirring, and then subsamples were immediately collected for wet analyses: Duplicate subsamples of 0.5 g were used for dry weight (DW) measurements, to estimate water content by
 135 calculating the difference in sample weight before and after drying at 105 °C, and the dried sample was further heated at 450 °C to obtain loss on ignition (LOI) to estimate the volatile fraction. Subsamples of 0.6 g were also taken of the wet sediment for sequential P extractions - described in the next section - to estimate the different forms of P in the samples. The remainder of the sediment was frozen at -20 °C and subsequently freeze-dried for further solid phase characterization, which are described in the following sections. Part of the freeze-dried sediment was ground using a specialized mill (XRD-Mill
 140 McCrone, Retsch). Both coarse and ground freeze-dried sediment was stored in a dry and dark cupboard at room temperature in airtight containers, but no further measures were taken to prevent oxidation.

2.4.1 Sequential P Extraction

The different P fractions were separated from the sediment samples based on their specific reactivity, using a sequential extraction method based on the protocol originally developed by Psenner (1984) and modified by Wang (2021). In short,



145 0.6 g of wet sediment was sequentially exposed to different extractants targeting distinct sediment P pools. At each step, P was dissolved into the liquid fraction and separated from the solids via centrifugation (10 min, 1000 rpm).

The targeted P pools and related extractants were, in order: 1) loosely bound P (H₂O-P), using deoxygenated Millipore H₂O; 2) Fe(II) bound P (Bipy-P), using 0.2 %w/w 2,2'-bipyridine; 3) Reducible P binding phases, including Fe(III)-P (BD-P), using a solution of 0.11 M sodium bicarbonate and 0.11 M sodium dithionite; 4) Fe-P minerals and organic bound P (NaOH-P), using 0.1 M sodium hydroxide; 5) Recalcitrant P phases, including Ca bound P (residual-P), as non-extracted P. The NaOH-P fraction was further distinguished in a fraction containing reactive P (SRP) measured directly in the extract (NaOH-SRP), and non-reactive P fraction (NaOH-NRP), calculated as the difference between the SRP and total P (TP) concentrations. The NaOH-NRP includes bound P forms such as organic P, while NaOH-SRP contains unbound orthophosphate released from mineral phases including vivianite, when not (completely) extracted by bipyridine or during
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 155 the BD extraction which targets surface-oxidized vivianite. Vivianite is thus likely found distributed across the Bipy-P, BD-P, and NaOH-SRP fractions

TP was measured in all extracts as SRP after digestion with 0.2 M potassium peroxydisulfate. SRP concentrations were measured photometrically with the molybdenum blue method (Murphy and Riley, 1962), using a Spekol 1500 spectrophotometer (Analytik Jena GmbH). Additionally, to further investigate the mineral origin of the P fractions, Fe
 160 concentrations were measured in the Bipy and BD extracts by atomic absorption spectroscopy (AAS pinAAcle 900T). The solid phase content of each fraction per dry gram of sediment was calculated from the extract concentrations using DW as measure of porosity.

2.4.2 Elemental Composition

165 Small subsamples of freeze-dried sediment (50 mg) were used for determining total element concentrations, to analyze variation in elemental composition between peeper chambers. Aliquots of dry sediment were first ground, then added to a mix of 37 %w/w HCl and 65 %w/w HNO₃ with a volumetric ratio of 1:3, and microwave digested using a pressurized microwave oven (µPrep-A, MLS 169 GmbH). The digestate was diluted to an exact volume and the concentration was then determined by ICP-OES for the elements of main interest (P, Fe, S, Mn and Ca). This yielded the total amount of element
 170 dissolved by the procedure, which was used to calculate the solid phase molar content per gram of dry sediment (µmol g⁻¹ DW).

2.4.3 Scanning Electron Microscopy

Qualitative and non-destructive phase characterization of the freeze-dried sediment was achieved by scanning electron
 175 microscopy (SEM). Analysis of microscale sample topography was performed on the coarse freeze-dried samples (after gold coating) with a scanning electron microscope (SEM; JEOL JSM-6480LV) detecting secondary electron (SE) at an



accelerating voltage of 15 kV and working distance of 10 mm. SEM was coupled with energy dispersive X-ray spectroscopy (EDS, X-act detector) for analysis of the spatial element distribution. The SEM images and EDS maps were processed with the JEOL SEM Control User Interface, which included a built-in function to compute relative elemental concentrations from the summed spectra of an area. The overlay of topographical features and elemental distribution allowed us to qualitatively identify certain Fe minerals, for which the elemental composition then was estimated.

2.4.4 X-ray Diffraction

Crystalline phases were identified by powder X-ray diffraction (XRD) analysis (Bruker D2 Phaser; Co $K_{\alpha 1}$ source; SSD160 detector; $10^\circ < 2\theta < 90^\circ$; divergence slit: 1 mm; measurement time: 6h; step size: 0.6 s; rotating: 10 rpm; scatter screen: 3 mm; Fe filter: 2.5; secondary Soller collimator: 2.5°) of the freeze-dried and ground sediment. The obtained diffractograms were compared to reference patterns of the Crystallography Open Database within Bruker's DIFFRAC.EVA software to identify individual minerals. Since all samples originated from the same mixed sediment, their matrix was assumed to be similar, and differences in mineral content between different samples were semi-quantitatively determined by comparing the reported net area as measure of intensity of characteristic reflections for specific minerals (vivianite).

2.4.5 Mössbauer Spectroscopy

Further quantitative analysis of Fe phases was performed on the starting sediment and three selected samples from distinct depths (chambers: 1, 3 and 10 from the top) of the SedP9m were further investigated using ^{57}Fe Mössbauer spectroscopy. The samples were chosen to include sediment exposed to the bottom water (top chamber: 5.5–3.5 cm above SWI), to the reactive upper anoxic zone (chamber 3: 2.5–4.5 cm below SWI), and to the deeper anoxic conditions from which the sediment originates (chamber 10: 30.5–32.5 cm below SWI).

The measurements were performed at the TU Delft Reactor Institute, Mekelweg 15 Delft, the Netherlands. The instrument used a ^{57}Co (Rh) source and constant-acceleration spectrometer, and was calibrated with $\alpha\text{-Fe}$, and measurements were performed at a temperature of 295 K. With Mössbauer spectroscopy measurement at such temperature, it is challenging to distinguish Fe(III) in oxidized vivianite from other Fe(III) phases or Fe(II) S_x , which may lead to vivianite content underestimation. To provide consistency to the measurements, sediments samples were prepared by simply storing the freeze-dried sediment in air, to allow vivianite to reach full oxidation. With the assumption that oxidation was similar across samples, the vivianite Fe(III) signal was then forced during fitting (30 % of the Fe(II) signal), following the strategy of Prot (2021). This preparation likely also affected iron sulfide phases, but the oxidized product (FeSO₄) gave a similar signal (Dyar et al., 2013) and these were collectively fitted. Further discussion on this approach can be found in the Supplementary Discussion. The obtained Mössbauer spectra were fitted with the Mosswin software (Klencsár 1997), retrieving the different Mössbauer parameters, characteristic of each Fe phase ("fingerprint mode"). In this case, the isomer shift (IS [mm s^{-1}], which provides information on the chemical environment of Fe atoms); the quadrupole splitting (QS [mm s^{-1}], which



provides further information on the chemical environment and "crystal asymmetry" of the Fe atoms); the line-width (Γ [mm s⁻¹]) and the spectral contribution [%], which is related to the mineral abundance in molar percentage of total Fe.

210 2.5 Data Analysis and Calculations

All data were further analyzed and refined using R v4.4.1. Values for bottom water composition were calculated by the average of the PwP elemental concentrations above the SWI. Concentration gradients for Fe and sulfide in the porewater were determined by fitting a linear model through the linear part of the respective measured gradient profiles, using the `lm()` function of R, which also provided values for the standard error and significance. From the obtained gradient, the diffusive
 215 flux was calculated using Ficks first law of diffusion for sediments (Eq. 1) (Boudreau, 2013; Lavery et al., 2001).

$$J_c = -\varphi \cdot \frac{D_c}{\theta^2} \cdot \frac{\partial C}{\partial x} \quad (1)$$

Where J_c is the flux of compound c (Fe or sulfide), calculated with the specific diffusion coefficient D_c , and the concentration gradient $\partial C/\partial x$. The tortuosity θ^2 is estimated with the porosity φ using the relation of Boudreau (2013) (Eq.
 220 2).

$$\theta^2 = 1 - \ln(\varphi^2) \quad (2)$$

The sum of the P fractions quantified by sequential extraction was subtracted from the total P value measured with ICP-OES (solid-PICP-OES) to calculate the fraction of P resistant to extraction (residual-P).

The vivianite-bound Fe content (vivianite-Fe) was estimated by multiplying the spectral contribution of Fe in vivianite from
 225 Mössbauer spectroscopy with the Fe content measured by ICP-OES (solid-FeICP-OES). The pool of vivianite-bound P (vivianite-P) was then estimated using the stoichiometry of vivianite (Fe:P 3:2), correcting for a fixed percentage of Mn impurities determined by SEM-EDS, as cationic substitution of Fe by Mn can be significant in natural vivianite (Kubeneck et al., 2023; Rothe et al., 2016).

The changes in sediment composition resulting from the experiment were investigated by comparing the SedP sediments
 230 between different depths, and with the baseline sediment. Relationships between co-occurring compositional changes were inspected using Pearsons correlation coefficient (R) to investigate the underlying mechanisms (Kubeneck et al., 2024).



3 Results

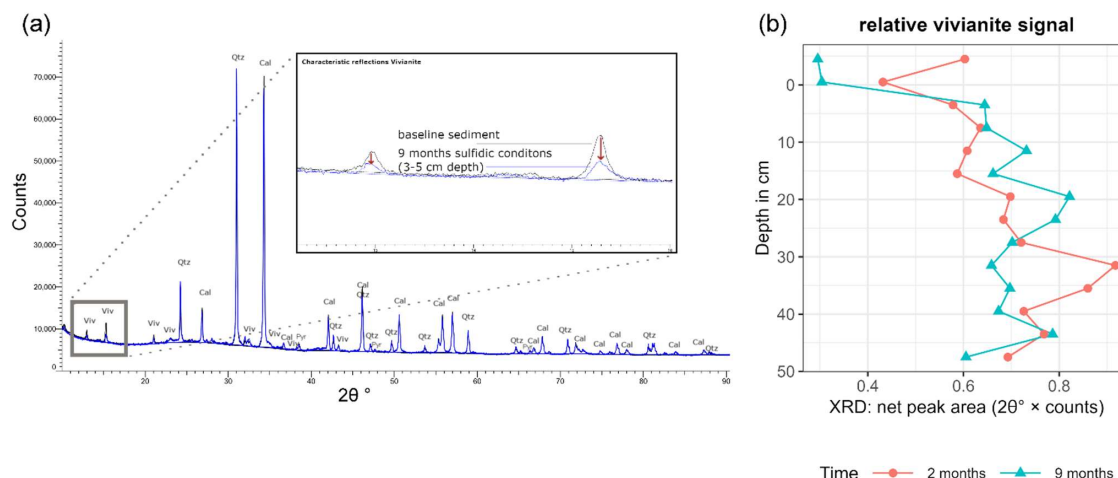


Figure 2: (a) X-ray diffraction (XRD) patterns of the sediment samples showing characteristic reflections for the identified minerals. Peaks corresponding to vivianite (Viv), pyrite (Pyr), quartz (Qtz) and calcite (Cal), are labelled. The inset highlights the main vivianite reflections in both the initial sediment and the sample collected from the SedP nine months later (3–5 cm depth), indicating a clear decrease in peak intensity after treatment. This reduction in peak intensity suggests a decline in the crystalline vivianite content over time, likely due to the geochemical conditions affecting its stability. (b) Semi-quantitative XRD results show the signal of vivianite as function of depth and demonstrate their evolution during the study period.

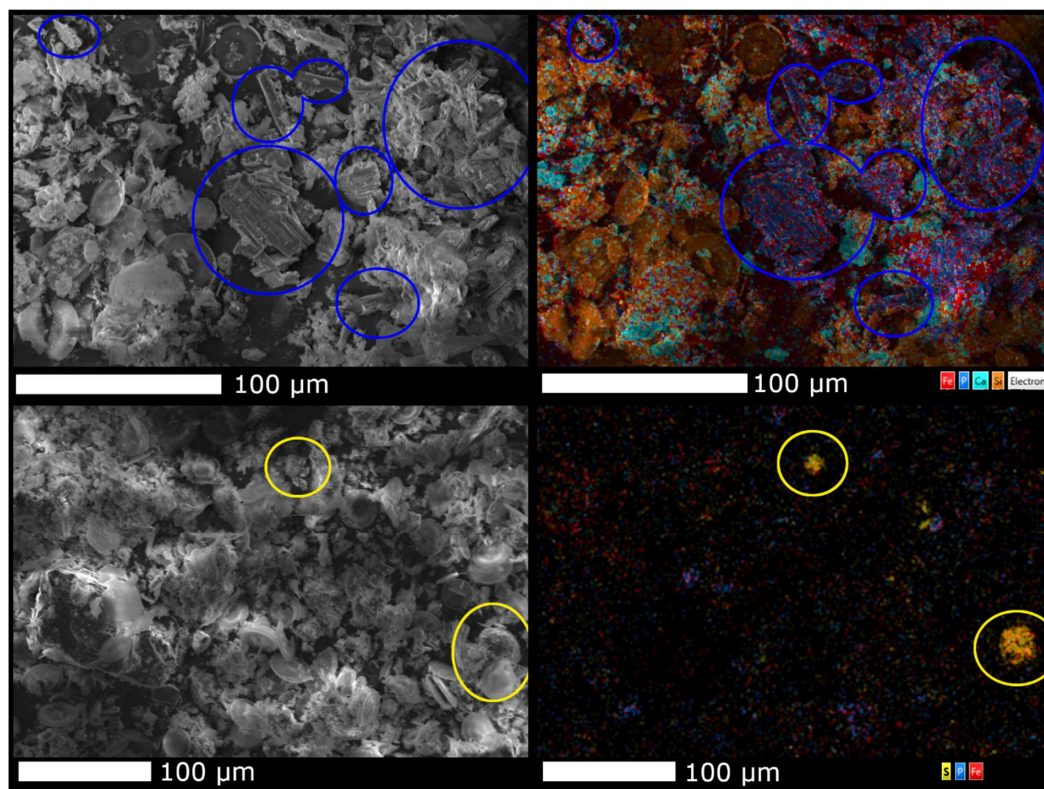
3.1 Sediment Characteristics

The baseline elemental composition measured by ICP-OES of the sediment from lake Arendsee which was used in the SedP is shown in Table 1, as well as the sequentially extracted P pools and Mössbauer results of the baseline sediment. It shows the relatively high Fe content ($699 \pm 24 \mu\text{mol g}^{-1} \text{ DW}$) found typically at this location (Findlay et al., 1998; Scholtysik et al., 2022). Present Fe-phases were shown by XRD characterization to be crystalline vivianite and pyrite (Fig. 2a), which was confirmed by SEM-EDS investigation where both vivianite crystals and pyrite nodules were identified by their characteristic crystal habits and well-defined element stoichiometry (Fig. 3). Also, EDS analysis of individual vivianite crystals revealed substantial Mn content, with a Fe:Mn stoichiometry of 100:11. Further investigation of the vivianite content by Mössbauer spectroscopy indicated that 35 % of total Fe could be attributed to vivianite, which translated into 90 % of solid-PICP-OES, once corrected for the Mn content. However, compared to sequential extractions, the Bipy-P fraction, which should target the vivianite P pool, only accounted for a small part of the total P (8–9 %), despite the high vivianite content. Instead, the P extraction data showed that sediment P was found predominantly in two P fractions: redox sensitive P (BD-P) and metal-bound P (NaOH-SRP). These two P fractions accounted for 75–78 % of solid-PICP-OES in the baseline sediment.



255 **Table 1: Composition of the baseline sediment loaded in the sediment peepers. Element concentrations were measured by ICP-OES and represent the total elemental content of the selected elements in the solid phase. The speciation of the P content was further investigated by sequential extractions, the various fractions indicating sediment P pools with different reactivity. The vivianite content was quantified by Mössbauer spectroscopy as percentage of the total Fe content and was used together with the ICP-OES results to calculate an absolute value for Fe and P bound as vivianite in the sediment.**

Elemental content							
Element		Fe	P	Ca	Mn	S	
ICP-OES analysis	$\mu\text{mol g}^{-1}$	699 ± 24	200 ± 3	$2.6 \pm 0.1 \times 10^3$	78 ± 7	382 ± 12	
	DW						
	ratio mol:mol	Fe:P	3.50		Fe:S	1.83	
Sequential extractions/P fractions							
Extractant <i>Fraction</i>		H ₂ O	Bipy	BD	NaOH <i>SRP</i>	NaOH <i>NRP</i>	Residual
Extracted P	$\mu\text{mol g}^{-1}$	7 ± 5	13 ± 5	92 ± 18	38 ± 17	3 ± 2	49 ± 10
	DW						



260 **Figure 3:** Electron microscopy pictures of the dried mixed baseline sediment. On the left are the SEM-secondary electron images and on the right the EDS map of the same area. The top image shows a cluster of vivianite crystals (blue circles), identified by their characteristic tabular crystal form, and confirmed by the EDS with the overlap of the Fe and P maps and a Fe:P stoichiometry of 3:2, typical for vivianite. The bottom figures show an area with pyrite nodules (yellow circles), which consist of small framboidal crystals found throughout the sediment.

265 3.2 Porewater and Bottom Water Conditions

The concentration gradient of ammonium, SRP, TP, Fe, Mn, sulfide and sulfate- in the chambers of the PwP across the sediment–water interface (SWI) and as function of sediment depth are shown in Fig. 4. After 2 months, the peeper, experienced anoxic conditions at every depth including the part exposed to the bottom water. After 9 months, oxygen was present in the bottom water near the SWI as result of winter water mixing. Due to these contrasting oxygen conditions at the
 270 bottom water, the concentration profiles for the two timepoints resulted different in the water column and SWI, while they were similar deeper in the sediment.

The bottom water conditions determined by the PwP measurements are summarized in Table 2. At both timesteps, the Fe concentration was below the detection limit. Concentrations of ammonium and P were higher at 2 months although they



were still found in the bottom water at 9 months, while Mn and sulfide concentrations were measured in the bottom water at 2 months but below detection limit in the bottom water after 9 months. Conversely, sulfate concentrations were lower at 2 months compared to 9 months.

Table 2: bottom water concentrations measured in the top chambers of the PwP. Differences between timesteps are a result of different redox conditions in the bottom water, with anoxic conditions during summer stratification (PwP2m), and oxic conditions during winter mixing (PwP9m).

Concentration ($\mu\text{mol L}^{-1}$)	PwP2m	PwP9m
Fe	< 0.1	< 0.1
Mn	14 ± 0.5	< 0.1
Ammonium-N	150 ± 22	13 ± 4
TP	19 ± 2	7 ± 0.2
SRP	18 ± 3	6 ± 0.2
TS	640 ± 47	881 ± 35
Sulfate-S	673 ± 25	786 ± 9
Sulfide-S	168 ± 52	0.3 ± 0.1

The upper 20 cm of sediment in both timesteps contained no measurable Fe in the porewater, but Fe concentrations increased with depth below 20 cm in a linear fashion with $13.7 \pm 0.6 \mu\text{mol L}^{-1} \text{ cm}^{-1}$ for PwP2m and $19.1 \pm 1 \mu\text{mol L}^{-1} \text{ cm}^{-1}$ for PwP9m, which translated to an upward flux of respectively 30 and $42 \mu\text{mol m}^{-2} \text{ d}^{-1}$

Directly below the SWI, the porewater concentration of ammonium and Mn increased with depth following a similar trend in both PwP2m and PwP9m, where the slope of the gradient decreases with depth. Elevated ammonium concentrations indicate ongoing organic matter mineralization.

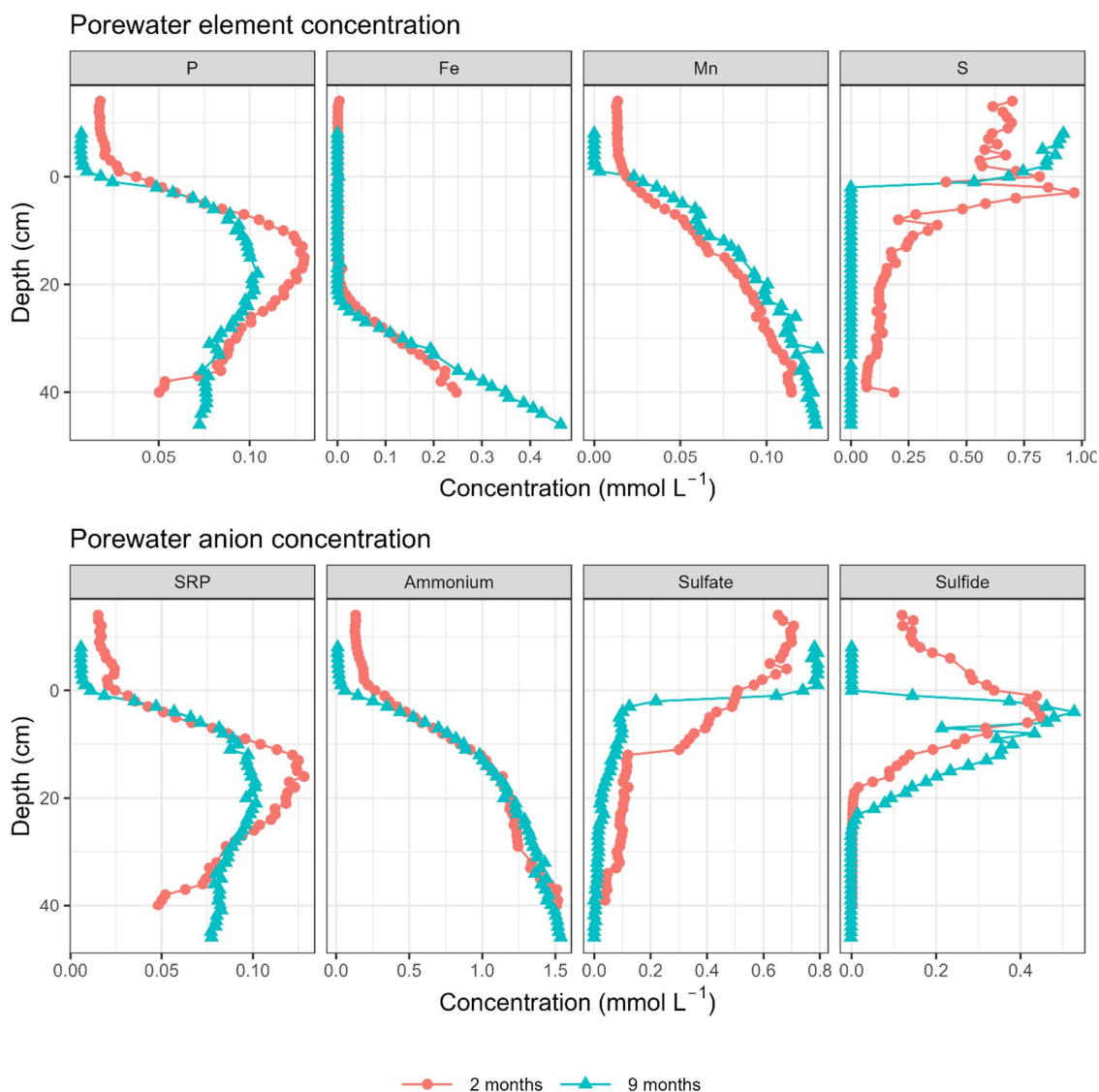
TP concentrations were about 20–60 % higher than the SRP concentrations in the porewater of the upper sediment, while the difference narrowed to 0–10 % higher TP in the porewater below 10 cm depth. TP and SRP followed the same trend in concentration for both timesteps, increasing with depth below the SWI, reaching a maximum at around 15 cm depth below the SWI and then gradually decreasing with depth. The P concentration maximum was 0.13 mmol L^{-1} in PwP2m, and 0.10 mmol L^{-1} in PwP9m.

The sulfate concentration profiles showed a concentration trend with increased depth towards zero, more gradual to a depth of 10 cm for PwP2m, and more sharply for PwP9m.

Sulfide concentrations in the upper sediment increased over depth and were highest at a depth of 5 cm below the SWI at both timesteps, up to 0.45 mmol L^{-1} for PwP2m and 0.53 mmol L^{-1} for PwP9m. Below the maximum, the sulfide concentration decreased gradually reaching approximately 0 mmol L^{-1} at 25 cm depth. Assuming that the sulfide gradients were



approximately linear between 12–19 cm depth, a downward flux was estimated of $44 \mu\text{mol m}^{-2} \text{d}^{-1}$ for PwP2m and $76 \mu\text{mol m}^{-2} \text{d}^{-1}$ for PwP9m.



300

Figure 4: Porewater distributions of porewater element (top) and anion (bottom) concentrations in the sediment in August 2022 and March 2023, respectively 2 and 9 months after the start of the experiment measured using the porewater peeper technique. The plots show phosphorus (P), iron (Fe), manganese (Mn), sulfur (S), soluble reactive phosphorus (SRP), ammonium, sulfate, and



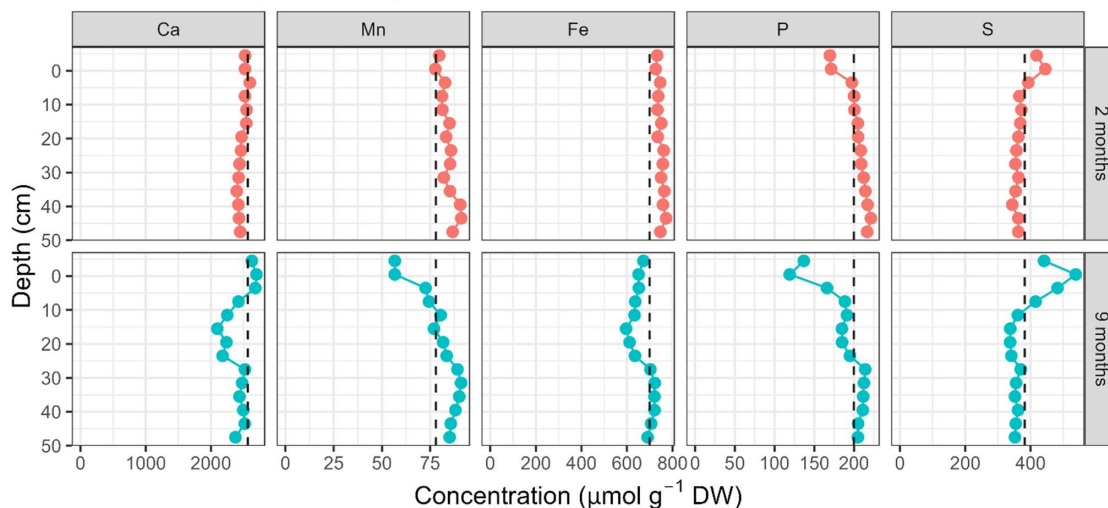
305 sulfide concentrations at two sampling times: 2 months (red circles) and 9 months (blue triangles). Overall, higher P and SRP concentrations are observed at 2 months. Fe and Mn concentrations increase with depth, and sulfate concentrations decrease with depth, while sulfide increases, reflecting enhanced sulfate reduction in the sediment.

3.3 Sediment Composition Changes

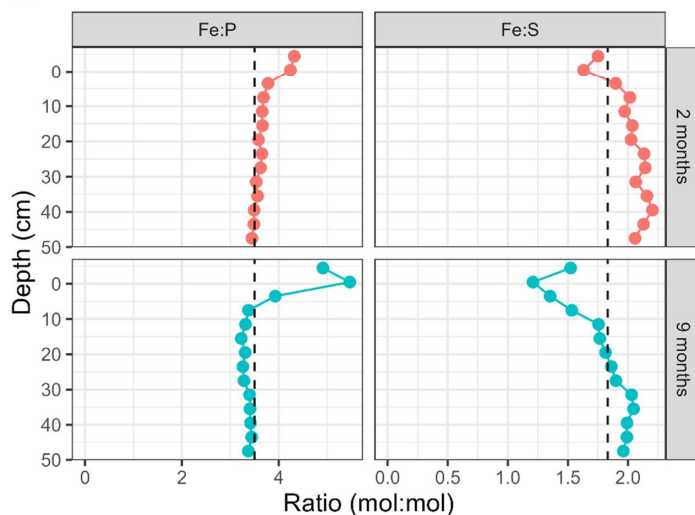
310 Changes in sediment composition in the SedP as result of exposure to natural porewater conditions were found primarily in the upper chambers, with slight differences in SedP2m, and more pronounced differences in SedP9m. In particular, part of the sediment in the top 4 chambers of the PwP turned to a light brown color in a distinct layer near the filter interface, while the sediment in the deeper chambers showed the same black-grey color as the baseline sediment. In SedP9m, the SWI was clearly marked by a red-brown line on the filter paper (Fig. 1).



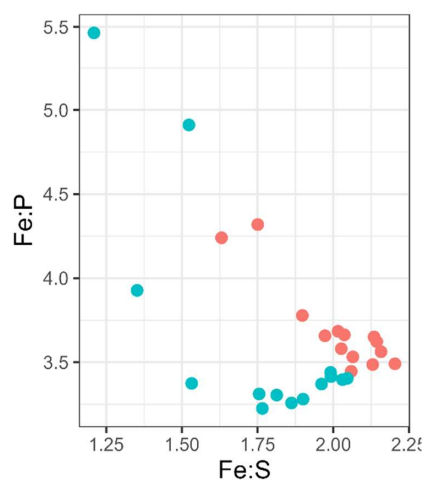
A Sediment solid phase composition



B Elemental ratios



C



315 **Figure 5:** (a) Elemental composition of the sediment solids inside the chambers exposed for 2 and 9 months to porewater of different depths. The elemental abundance was determined after digestion by ICP-OES and here shown for selected elements. The dashed line represents the value measured in the mixed baseline sediment (before the start of the experiment). (b) The calculated molar ratios of Fe:P and Fe:S, and (c) the relation between them. The correlation between Fe:P increase and Fe:S decrease suggests P mobilization from the sediment was coupled with S binding.



320 3.3.1 Elemental Composition

The sediment of the SedP showed compositional gradients over depth, signifying deviations from the baseline sediment as result of exposure to the different porewater conditions (Fig. 5). The deeper chambers showed the smallest change from the baseline, while the primary changes took place in the top 2 chambers of SedP2m (sediment depth: -4.5 cm to 0.5 cm) and top 3 chambers of SedP9m (sediment depth: -4.5 cm to 4.5 cm). The sediment in these chambers was depleted in P by
325 respectively 15 % and 30 % and enriched in S by 13 % and 27 % for SedP2m and SedP9m compared to the baseline, as measured by ICP-OES. Furthermore, the top two chambers of SedP9m had about 27 % less Mn in the solid phase than the baseline sediment, while the Mn content of SedP2m remained unchanged. The solid phase content of Ca and Fe in the upper sediment did appear stable for both timepoints but showed a slight decrease (10–15 %) between 7–24 cm depth in SedP9m.

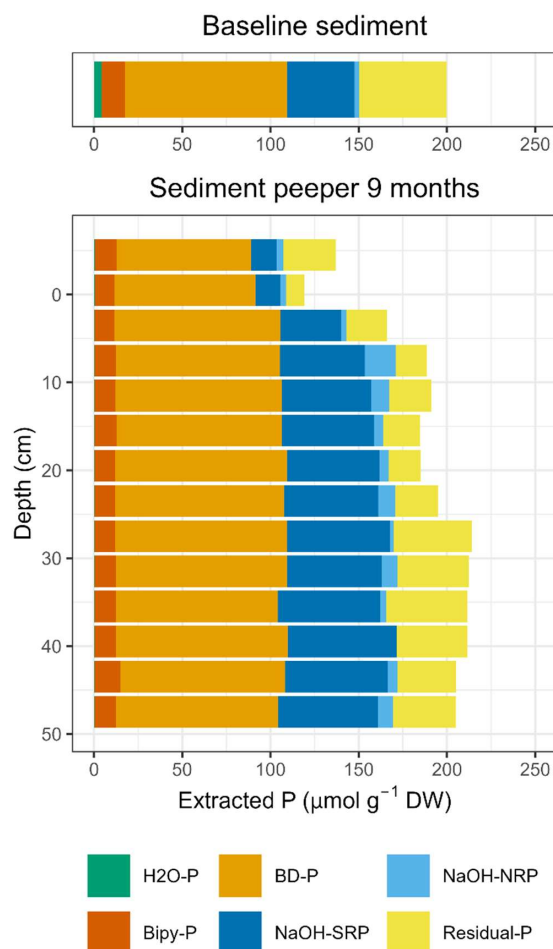


Figure 6: Abundance of the sequentially extracted P fractions for the baseline sediment (values listed in Table 1) and in the sediment retrieved from the 9 months peeper. The stacked bars show the distribution of different operationally defined P fractions at each depth: loosely adsorbed P (H₂O-P), bicarbonate-dithionite extractable P (BD-P), bicarbonate-buffered dithionite-bipy P (Bipy-P), NaOH-extractable soluble reactive P (NaOH-SRP), NaOH-extractable non-reactive P (NaOH-NRP), and residual P. In the baseline sediment, BD-P and NaOH-SRP are the dominant fractions. After 9 months, the depth profiles show limited vertical variation in the unaffected lower chambers, while >10 cm depth is depleted in solid phase P. In particular the proportion of NaOH-SRP is reduced here, while BD-P remains abundant throughout the sediment.

3.3.2 P and Fe Speciation

The P sequential extraction results of the SedP9m show that the decrease in solid phase P in the upper chambers was, in proportion, the largest in the NaOH-SRP fraction, decreasing by 70 % compared to the baseline, which accounted for circa



340 50 % of the lost solid- $P_{ICP-OES}$. The second largest change was found in the BD-P pool, which decreased by 25 % in the upper chambers of sediment, while the Bipy-P fraction remained equally low at all depths (Fig. 6).

The solid phases identified in the sediment by XRD and SEM-EDS were largely the same both in the upper and lower chambers of the SedP and the baseline sediment. However, while the XRD signal did not significantly vary for most minerals between the different samples, it did vary for the characteristic reflections of vivianite (Fig. 2b). Namely, vivianite
 345 peak intensity positively correlated ($R = 0.76$, $p = 3 \times 10^{-6}$) with the decrease in solid- $P_{ICP-OES}$ in the top chambers of both SedP. This showed that a decrease in solid-bound P coincided with a decrease in crystalline vivianite, possibly becoming the source of the mobilized P. The loss of P from vivianite in SedP9m was further investigated by Mössbauer spectroscopy, which confirmed a decrease in vivianite content in the upper sediment samples after 9 months of exposure, which showed lower vivianite spectral contribution compared to the start, in favor of sulfidic phases ($FeS/FeSO_4$) (Table 3). Concurrent
 350 with the observed patterns in P and S content and speciation, the sample from a depth of 30.5–32.5 cm showed no substantial deviation from the baseline sediment in vivianite or $FeS/FeSO_4$ signal (Table 3). The vivianite-Fe from Mössbauer as fraction of the solid- $Fe_{ICP-OES}$ yielded a value for vivianite-P (Fig. 7), which was respectively 90 and 64 $\mu mol\ g^{-1}$ DW less than the baseline sediment for the upper samples (5.5–3.5 cm above and 2.5–4.5 cm below SWI), and 6 $\mu mol\ g^{-1}$ DW for the lower sample (30.5–32.5 cm).

355 **Table 3: The Mössbauer fitted parameters of the sediments at different depths, measured at 295 K. The spectra and fitting can be found in Fig. S2. In addition to the distinct spectra of the A and B sites of vivianite, a spectral contribution of oxidized Fe of about 30 % of the total vivianite was forced in the fitting. The remaining signal could be attributed to iron sulfide (FeS), as well as its oxidation product ($FeSO_4$) formed during sample preparation.**

Sample	IS ($mm \cdot s^{-1}$)	QS ($mm \cdot s^{-1}$)	Γ ($mm \cdot s^{-1}$)	Phase	Spectral contribution (%)	Mineral
Sediment baseline	1.22	3.03	0.31 [^]	Fe_{II}^{2+}	11	Vivianite site B
	1.21	2.40	0.31 [^]	Fe_I^{2+}	12	Vivianite site A
	0.46*	0.59*	0.48*	Fe^{3+}	11	Oxidized vivianite
	0.35	0.80	0.56	Fe^{2+}	65	$FeS / FeSO_4$
SedP9m-0 5.5–3.5 cm above SWI	1.19	3.03	0.38 [^]	Fe_{II}^{2+}	7	Vivianite site B
	1.18	2.32	0.38 [^]	Fe_I^{2+}	6	Vivianite site A
	0.46*	0.59*	0.48*	Fe^{3+}	6	Oxidized vivianite
	0.36	0.78	0.61	Fe^{2+}	82	$FeS / FeSO_4$
SedP9m-3 2.5–4.5 cm below SWI	1.22	3.03	0.30 [^]	Fe_{II}^{2+}	7	Vivianite site B
	1.20	2.38	0.30 [^]	Fe_I^{2+}	9	Vivianite site A
	0.46*	0.59*	0.48*	Fe^{3+}	7	Oxidized vivianite
	0.34	0.78	0.59	Fe^{2+}	76	$FeS / FeSO_4$
SedP9m-10	1.22	2.95	0.37 [^]	Fe_{II}^{2+}	13	Vivianite site B

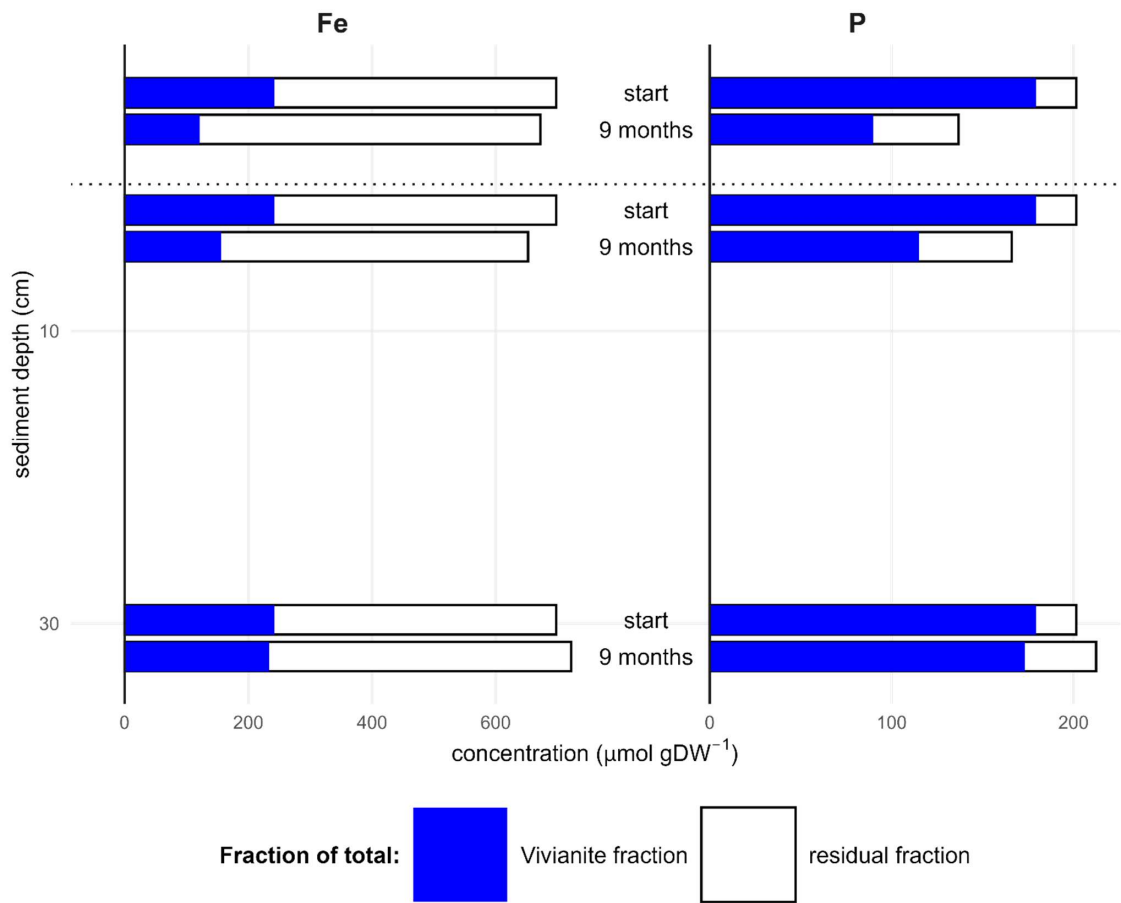


30.5–32.5 cm	1.21	2.31	0.37^	Fe ₂ ²⁺	9	Vivianite site A
below SWI	0.46*	0.59*	0.48*	Fe ₃ ³⁺	10	Oxidized vivianite
	0.36	0.80	0.61	Fe ₂ ²⁺	68	FeS / FeSO ₄

Experimental uncertainties: Isomer shift: I.S. ± 0.01 mm s⁻¹; Quadrupole splitting: Q.S. ± 0.01 mm s⁻¹; Line width: Γ ± 0.01

360 mm s⁻¹; Spectral contribution: ± 3 %.

* Fixed fitting parameter. ^Coupled fitting parameters.



365 **Figure 7: Quantification of vivianite fraction by Mössbauer spectroscopy. The vivianite-Fe fraction is displayed with full blue bars, as part of the solid-FeICP-OES. The vivianite-P fraction was calculated from the vivianite-Fe fraction using the stoichiometry of**



vivianite (3:2 Fe:P) and represented in the same way as part of the solid- $P_{ICP-OES}$. For each depth, the top bar shows mixed baseline sediment, while the bottom bar shows the 9 months sediment sample.

4 Discussion

370 4.1 Influence of Porewater Conditions on P Retention

Exposing vivianite-rich deep sediment to the porewater conditions near the sediment surface led to clear alteration of the P reservoir, in particular in the most reactive zone directly above and below the SWI. Here, decreased solid- $P_{ICP-OES}$ content indicates P mobilization from the solid phase.

375 The P mobilization was coupled with S immobilization, as evidenced by a significant negative correlation between solid phase P and S abundance throughout the sediment ($R = 0.837$, $p = 3 \times 10^{-8}$). This suggests that S cycling played an important role and explains the concurrence of porewater sulfide at the affected sediment depth.

Sulfide is known to affect the stability of Fe phases, and can mobilize P by interacting with P-bearing Fe phases (Chen et al., 2021; Kubeneck et al., 2024; Zhao et al., 2019). Sulfide can either reduce Fe(III) phases associated with P (Roden and Edmonds, 1997) or react directly with Fe^{2+} by forming FeS_x phases (Song et al., 2024; Wilfert et al., 2020). Since the
 380 sediment was taken from an anoxic mature horizon, very little P was bound in reducible phases (i.e. Fe(III) phases), and 90 % of all P was observed to be bound as vivianite. Sulfide-driven reductive dissolution of P-bearing Fe(III) phases is therefore unlikely to have contributed importantly.

P bound in vivianite was the largest P pool at the start, while exhibiting the most change at the end of the experiment. This was demonstrated by XRD analysis, which showed a diminished vivianite signal in affected sediment compared to the
 385 baseline sediment, and by a similar trend in the Mössbauer results. Our findings suggest that direct reaction of sulfide with vivianite was a significant source of mobile P, consistent with previous laboratory and mesocosm studies (van Kuppevelt et al., 2025; Song et al., 2024; Wilfert et al., 2020). Mössbauer analysis provided furthermore direct quantitative evidence of the vivianite transformation: In both upper sediment layers analyzed by Mössbauer spectroscopy after 9 months (5.5–3.5 cm above and 2.5–4.5 cm below SWI), the estimated loss of vivianite-P (respectively 90 and 64 $\mu\text{mol g}^{-1}$) was the same order of
 390 magnitude yet higher than the loss of solid- $P_{ICP-OES}$ (respectively 64 and 34 $\mu\text{mol g}^{-1}$ DW). This is strong evidence that the dissolution of vivianite is the major mechanism of P mobilization, but it does not provide a proper mass balance, since the vivianite-P value was calculated from the Mössbauer spectra using several assumptions and is likely not very accurate (see Supplementary Discussion).

The FeS phases formed during this reaction remain in the solid phase, which explains the observed S increase. Solid phase
 395 Fe showed a weak positive correlation with P ($R = 0.53$, $p = 0.003$), suggesting P release was only partly accompanied by Fe release. Since this deviation in Fe content was minimal compared to the P and S changes, the molar Fe:P ratios increased and molar Fe:S ratios decreased (Fig. 5b), which indicates S replacing P in binding to Fe. Elemental analysis by ICP-OES of the



solid phase showed that the stoichiometry of S increase and P decrease was between 1–3 S:P. This indicates that less than 2 mol S was bound per mol of Fe released from vivianite (Fe:P of 3:2), suggesting a stoichiometry of Fe-monosulfides (FeS) rather than pyrite (FeS₂) in the precipitated phase. XRD results did indeed not show clear evidence of crystalline pyrite formation, while Mössbauer results did suggest an increase of FeS in the affected sediment. These observations are in line with previous reports on phases formed by the reaction of sulfide and Fe²⁺ in lake sediments (Kraal et al., 2013; Kubeneck et al., 2024; Rickard, 2012).

The pronounced effects of porewater conditions on the sediment composition were located near the SWI. This zone displayed a stark redox gradient but also experienced a significant change in redox conditions over time as result of stratification and overturning of the dimictic lake. While the availability of oxygen for part of the year could have played a role in transforming the sediment composition, the change also occurred in the permanently anoxic upper sediment. Oxidative dissolution of vivianite could theoretically mobilize P, but this would result in the formation of Fe(III) phases and S mobilization. The depletion of solid-phase Mn in the oxic zone is evidence for the mobilization of Mn phases and implies oxidative processes which also could have affected Fe. Decreased Fe/S ratios above the SWI suggest that this effect was minor compared to the sulfide phase formation during the anoxic season. Overall, our findings are in line with previous studies showing that vivianite is resistant to dissolution by oxidation and can structurally persist even under fully oxic conditions (Banke et al., 2025; Heinrich et al., 2020; Metz et al., 2024).

4.2 Implications for Freshwater Systems

While S cycling is widely recognized as important for P cycling, most studies have focused on the short-term mobilization of P by sulfide and the limiting effect on P sequestration (Chen et al., 2016; Van Diggelen et al., 2014; Zak et al., 2006; Zhao et al., 2019). However, the role of sulfide on long-term internal P loading is less studied and described as a lowered P-binding capacity in sulfidic environments. This simplification overlooks the effect of changing conditions, yet the long-term development of trophic conditions is dependent on the ongoing P balance, and sudden eutrophication can occur if a P sink becomes a P source. The potential for remobilization of legacy P pools has been to control long-term P retention (Gächter and Müller, 2003; Katsev et al., 2006; Roden and Edmonds, 1997). Vivianite in particular can form substantial P reservoirs in eutrophic lakes, and its vulnerability to sulfidic conditions forms a potential risk (Kubeneck et al., 2024; van Kuppevelt et al., 2025).

Our experiment demonstrates that mobilization of legacy vivianite can occur under natural conditions triggered by simple disturbance such as upheaval of deeper sediment to the sulfate reduction zone. While we demonstrated the effect by purposefully moving sediment such mobilization could also occur during dredging or natural events like storms. The P loading from this source can be substantial: The magnitude of P release from the sediment peeper was in the order of 10 mg m⁻² d⁻¹ over a period of 9 months, which is comparable to the annual benthic P release rate of lake Arendsee (Hupfer et al., 2019). Sulfidation of the vivianite can also influenced environmental factors such as temperature, OM availability and sulfate concentrations (Sørensen et al., 1981; Zak et al., 2021). Hence, a change in conditions can result in an increased



sulfate reduction and instigate P mobilization (Han et al., 2023; Zhao et al., 2021; Zhou et al., 2022). It is ultimately conceivable that an initial P loading event instigates a feedback loop where the induced eutrophication leads to increased sulfide production which mobilizes more vivianite-P. This hypothesis needs further testing, as observations of legacy P mobilization are scarce, while there are at the same time many cases of sudden eutrophication events (Gonsiorczyk et al., 2024; Ho et al., 2019).

Although sulfide in the sediment prevents vivianite formation (Heinrich et al., 2022; Lamers et al., 2002; Rothe et al., 2015), sulfidic conditions can coexist with vivianite reservoirs, as the example of Lake Arendsee shows. In Lake Arendsee, past external P loading initially produced vivianite sequestration via geochemical focusing of Fe and Mn. As Fe(III) depleted and organic matter availability increased over time as result of increasingly eutrophic conditions, vivianite formation halted and sulfide production became dominant (Scholtysik et al., 2022). We hypothesize that during this transition, mobilization of P from legacy vivianite could have caused internal P loading, hence contributing to the rapid increase in eutrophic conditions in the mid-20th century (Findlay et al., 1998; Scharf, 1998). To test this hypothesis, the total volume of mobilized vivianite needs to be investigated, and compared to other sources of P at the time, since external P loading likely also increased during this period (Scharf, 1998). The significance of this process and the relative contribution of vivianite to internal P loading might have been minor in lake Arendsee (the vivianite reservoir is constrained to the deepest part (Scholtysik et al. 2022)), investigation would nevertheless provide insight in the role of legacy vivianite P during eutrophic transition, and evidence for a positive feedback could have implications for other lakes as well. The P release from vivianite likely slowed down over time when the reaction front gradually depleted the vivianite reservoir from above and migrated downwards, while increased sedimentation buried the vivianite reservoir further, resulting in a larger distance from the sulfide source at the top sediment, which lowered the sulfide flux towards the reaction front (Passier et al., 1996). Vivianite mobilization then halted when the sulfide flux at the reaction front stoichiometrically matched the upwards Fe flux from the deep sediment. The flux calculations based on our porewater results suggest this is the case today, as the downwards sulfide flux was respectively 1.5 and $1.8 \times$ the upwards Fe flux. Previous studies have shown that present day internal P loading in lake Arendsee is mainly governed by mineralization of organic matter (Hupfer et al., 2019; Hupfer and Lewandowski, 2005), hence vivianite sulfidation is not likely to be a significant source of P in lake Arendsee. Still, under different conditions this can change in the future

4.3 Considerations for lake management

The example of Lake Arendsee demonstrates the potential of P loading from legacy pools of vivianite P. Our experiment shows the strong difference in vivianite mobilization depending on transport of sulfide to the vivianite horizon. sulfide flux reaching the vivianite depends on the sulfide production in the sulfate reduction zone, minus the sulfide lost during diffusion. The maximal capacity for long-term S immobilization is ultimately limited by the influx of Fe and other metals from the deep sediment and catchment, and the mass balanced with sulfate influx determines if S or Fe accumulates over time (Passier et al., 1996).



Sulfide-driven internal processes should be considered by lake eutrophication managers. The examination of P, S and Fe mass balances along with sediment analyses, can help to explain sudden increases in P concentrations, or long-term internal P loading. Management strategies could include limiting sulfate inputs, introducing alternative P binding agents, or increasing Fe availability.

Furthermore, when planning any type of intervention measure, it is important to assess unintentional effects that these may cause on sulfur cycling and possible P mobilization. Dredging, for example, can extract P reservoirs from the lake, remove the reactive upper sediment, or even bring deeper layers of vivianite-bearing sediment to the surface, where it would become vulnerable to sulfidation. Chemical measures to lower freshwater P concentrations — including Fe amendment — not only could prove inefficient in the long-term but could also have an adverse effect when it increases sulfate reduction, for example when using sulfate salts.

5 Conclusions

By exposing vivianite-rich deep sediment to contrasting natural porewater conditions in Lake Arendsee, we demonstrate that redox-stable Fe–P minerals are not necessarily stable under sulfidic conditions. When brought into contact with sulfide-containing porewater near the sediment–water interface, the sediment lost up to 41 % of its solid-phase phosphorus within nine months. Multiple lines of evidence (ICP-OES, sequential extraction, XRD, and Mössbauer spectroscopy) consistently indicate that this phosphorus loss was primarily driven by the dissolution of vivianite.

Phosphorus mobilization was tightly coupled to sulfur immobilization, reflected in the strong negative correlation between solid-phase P and S and in declining Fe:S ratios. The observed stoichiometry suggests that sulfide reacted directly with Fe(II) from vivianite to form iron monosulfides, thereby destabilizing the mineral structure and releasing phosphate. This confirms that sulfide-induced vivianite dissolution represents a viable pathway for internal phosphorus loading under natural conditions.

Importantly, the extent of vivianite mobilization was dependent on sulfide supply and transport. While experimental exposure near the sediment surface triggered substantial P release, present-day in situ flux calculations indicate that sulfide and upward Fe fluxes are currently close to balance, limiting ongoing vivianite dissolution in the lake. This highlights that the vulnerability of vivianite reservoirs is governed not only by their presence, but by the balance between sulfide production, diffusive transport, and iron availability.

Our findings demonstrate that legacy P stored in vivianite can become reactive when environmental conditions shift toward enhanced sulfate reduction. As sulfate concentrations continue to increase in many freshwater systems, sulfur-driven destabilization of vivianite may compromise long-term sediment P retention. Lake restoration and management strategies should therefore explicitly consider sulfur cycling, particularly when evaluating interventions such as dredging, iron amendment, or measures that may alter sulfate inputs or organic matter mineralization.



Overall, this study shows that vivianite is not merely a permanent burial sink for phosphorus, but a dynamic and condition-dependent reservoir whose stability is tightly linked to sulfur cycling.



500 **Data availability**

The data underlying this study are archived at Zenodo under <https://doi.org/10.5281/zenodo.22829542>. The dataset will be made publicly available upon publication of this manuscript.

Supplement link

The link to the supplement will be included by Copernicus, if applicable.

505 **Author contributions**

HvK and MH designed the experiment. Experimental setup and analysis was carried out by HvK. CB helped with Mössbauer interpretation and discussion. HvK prepared the manuscript with revisions from MH and CB.

Competing interests

The authors declare that they have no conflict of interest

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Review statement

- 525 The review statement will be added by Copernicus Publications listing the handling editor as well as all contributing referees according to their status anonymous or identified.

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