



1 Direct P K-edge X-ray absorption spectroscopy evidence of phosphorus
2 immobilization in anoxic peat soils

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23 Abstract

24 Rewetting of drained agricultural peatlands is widely promoted to mitigate greenhouse gas
25 emissions, yet concerns remain that reductive dissolution of Fe(III) (hydr)oxides may mobilize
26 bound phosphorus (P) and increase eutrophication risk. However, P concentrations following
27 rewetting can vary by orders of magnitude among peatlands, and the processes controlling this
28 variation remain unclear. In this study, we investigated the mechanisms controlling P retention
29 in a rewetted fen (Løvenborg, Denmark) using synchrotron-based P K-edge X-ray absorption
30 spectroscopy (XAS) and μ -X-ray fluorescence (μ -XRF), bulk soil chemistry, selective
31 extractions, and porewater analyses. The study site is characterized by near-neutral pH (6.8–
32 7.2), elevated calcium (Ca) concentrations (~ 0.5 mM), and substantial pools of ~ 200 mmol
33 oxalate extractable Fe and Al. Fe(III) reduction reached up to 79% of the oxalate-extractable
34 Fe pool, yet dissolved P remained below detection limits (< 0.1 μ M) in all samples,
35 demonstrating a clear decoupling between Fe(III) reduction and P release. Calculated
36 mobilized P greatly exceeded measured porewater P, indicating rapid re-immobilization within
37 the soil matrix. Bulk P K-edge X-ray absorption near-edge structure (XANES) spectra were
38 similar under oxic and anoxic conditions and were dominated by organic and Fe/Al-associated
39 P, with no clear bulk evidence of vivianite or hydroxyapatite. In contrast, μ -XANES data
40 collected from hotspots of P identified using μ -XRF revealed localized domains of Fe- and Al-
41 associated P together with Ca phosphates and vivianite-like Fe(II) phosphate phases that are
42 not observed in bulk spectra. Thermodynamic modeling shows strong supersaturation with
43 respect to vivianite and weaker supersaturation for Ca-P. The results of this study imply that P
44 dynamics in neutral, Ca-rich peat soils are governed by microscale mineralogical heterogeneity
45 that is not captured by bulk analytical techniques, suggesting that conventional Fe-based or
46 bulk redox indicators may overestimate P release following peatland rewetting.



47 **Introduction**

48 Decades of drainage and intensified agricultural fertilization have generated substantial legacy
49 phosphorus (P) pools in lowland peat soils, where P may persist for long periods yet remain
50 susceptible to mobilization under changing environmental conditions (Schmieder et al., 2020;
51 Petersen et al., 2026). Understanding P cycling in anoxic peat soils is therefore critical for
52 assessing the risk of P release associated with re-flooding practices implemented for carbon
53 sequestration and climate change mitigation (Kimmel and Mander, 2010; Lamers et al., 2015).
54 The geochemistry of P under anoxic conditions has been intensively studied (Hoffmann et al.,
55 2009; Kjaergaard et al., 2012), and it is well established that the transition from oxic to anoxic
56 conditions promotes microbial mediated reductive iron dissolution, specifically of Fe(III)
57 (hydr)oxides (herein designated Fe(III)), leading to mobilization of previously sorbed P (Reddy
58 et al., 1999; Gächter and Müller, 2003; Hoffmann et al., 2009).

59 However, laboratory and field-scale observations consistently show that dissolved P
60 concentrations are considerably lower than predicted from the extent of Fe(III) reduction
61 (Florea et al., 2024). This discrepancy indicates that Fe(III) reduction alone does not determine
62 net P release and that secondary immobilization processes operate simultaneously, thereby
63 regulating P dynamics during redox transitions.

64 These processes can include re-sorption of mobilized P onto redox-stable sorbents such as
65 aluminum (Al) oxides or residual Fe(III) oxides, summed up as residual sorption capacity
66 (RSC) (Florea et al., 2024), as well as precipitation of secondary phosphate minerals, including
67 vivianite (Fe-P) and calcium phosphates (Ca-P) (Florea et al., 2026; Egger et al., 2015).
68 Together, these processes may regulate whether rewetted peatlands function as net P sources
69 or sinks under anoxic soil conditions.



70 Mineralogical evidence supports the importance of secondary Fe–P solid formation under
71 anoxic conditions. Previous studies suggested the occurrence of Fe(II)-associated P phases in
72 rewetted peat soils using X-ray diffraction (XRD), Mössbauer spectroscopy, and selective
73 extraction approaches (Florea et al. 2026; Nguyen et al., 2024; Gächter and Müller, 2003),
74 providing strong support for vivianite precipitation following Fe(III) reduction.

75 In parallel, Ca–P precipitation represents a distinct mechanism of P sequestration. Elevated
76 Ca^{2+} activity and porewater pH promote precipitation of Ca–P minerals such as hydroxyapatite
77 (Nriagu and Moore, 1984; Stumm and Morgan, 1996; Reynaud et al., 2022), whereas high
78 Fe(II):P ratios and low sulfide concentrations favor vivianite formation. Identifying the
79 dominant P host phase is critical because Ca–P, vivianite, and resorbed P differ in their stability
80 and sensitivity to environmental change. Ca–P minerals and Al-associated P are generally
81 resistant to redox fluctuations, although their stability is pH-dependent, whereas vivianite is
82 favored under sustained anoxic, Fe(II)-rich conditions but may become unstable upon
83 oxidation, with implications for long-term P retention (Reddy et al., 1999).

84 Although many potential P compounds have been proposed to form in wetland systems, direct
85 identification of solid-phase P species is rare. Sequential extraction and thermodynamic
86 modeling provide indirect constraints but often cannot unambiguously differentiate between
87 sorbed P and distinct mineral phases. In addition, these bulk indirect methods largely ignore
88 the complex heterogeneity in soils and the presence of many P-bearing host phases spatially
89 separated by a few millimeters. Because the extracted P fractions are operational rather than
90 mineralogically defined, interpretation of P species remains ambiguous. For example, NaOH-
91 extractable P may include a mixture of organic P, Fe- and Al-associated inorganic P, while
92 HCl-extractable P can represent a range of P minerals, like Ca–P and vivianite, with differing
93 crystallinity and solubility (Hupfer et al., 2009). Although selective Fe(II)-based extraction
94 methods have been developed to estimate vivianite (Rothe et al., 2016; Wang et al., 2021;



95 Haasler et al. 2025), they are not phase-specific because the extractant dissolves Fe(II) from
96 different mineral phases, making unequivocal identification of vivianite difficult.

97 P K-edge X-ray absorption near-edge structure (XANES) spectroscopy overcomes the
98 limitations of indirect measurements of P speciation by directly measuring the molecular-scale
99 coordination environment of P. This permits resolving major P species, including Ca-P,
100 vivianite, and Fe(III)- or Al-associated P, within heterogeneous solids (Prietz et al., 2013).
101 When combined with micro-focused X-ray fluorescence (μ -XRF) mapping, elemental
102 distributions of P can be spatially constrained prior to targeted spectroscopic interrogation of
103 relevant hotspots (Langner et al., 2013).

104 Reliable predictions of P mobilization following peatland rewetting is essential for restoration
105 management, yet current regulatory models, including the Danish EPA approach, rely mainly
106 on bulk geochemical proxies and do not account for P speciation. Building on the RSC model
107 (Florea et al., 2024) and recent mineralogical evidence for Fe(II)-associated P formation in
108 neutral to alkaline soils (Florea et al., 2026), the present study applies bulk XANES and μ -XRF
109 coupled to μ -XANES to directly characterize P speciation in oxic and anoxic peat soils. By
110 combining synchrotron-based spectroscopic analyses with complementary chemical
111 measurements, we aim to identify the retention mechanisms controlling the fate of P mobilized
112 under anoxic conditions, including re-sorption to reactive mineral surfaces and precipitation as
113 secondary phases.

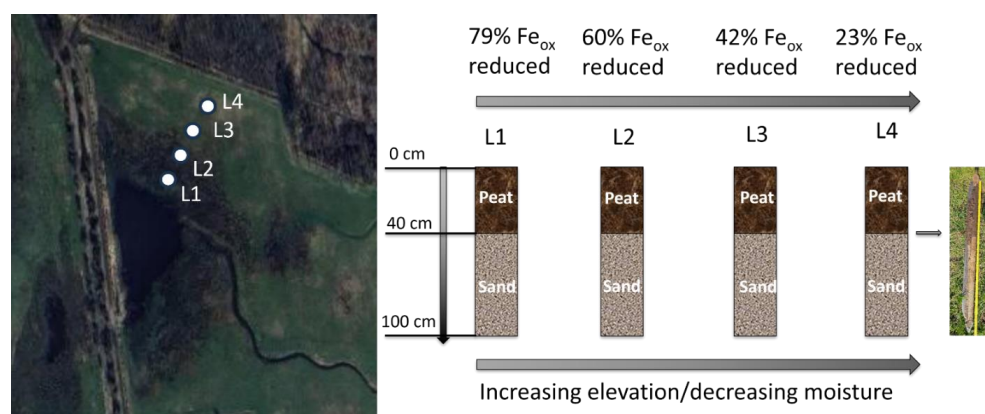
114 **2. Material and methods**

115 **2.1. Soil sampling**

116 The Løvenborg site, Zealand (55°41'15.2" N, 11°35'22.4" E) was selected as a representative
117 peatland site with neutral pH conditions and elevated Ca concentration, promoting P
118 precipitation under anoxic conditions (Florea et al., 2026). Sampling was performed along a



119 moisture-gradient transect to capture spatial variability in hydrological conditions (Figure 1).
 120 Undisturbed soil cores were collected using an Eijkelkamp cylindrical soil corer (45 mm
 121 diameter) equipped with a sampler liner tube.
 122 The moisture transect consisted of four sampling points extending from the wettest location
 123 (L1) to the driest (L4), with 10 m spacing between points. Soil samples were collected from a
 124 depth of 0–40 cm, corresponding to the thickness of the peat layer at this site. Beneath the peat
 125 layer, the subsoil was represented by a sand layer. The site had been rewetted prior to sampling,
 126 and groundwater levels fluctuated seasonally from near or above the soil surface during winter
 127 to approximately 30 cm below the soil surface during summer. The soil at Løvenborg is
 128 classified as a sapric Histosol according to the IUSS Working Group WRB (2022),
 129 characterized by a high degree of organic matter decomposition, dark coloration, and limited
 130 preservation of plant structures (Figure 1).



131 **Figure 1: Sampling transect, moisture gradients, soil profile and peat thickness from Løvenborg.**
 132 **Distance between sampling points was 10 meters. The extent of Fe(III) reduction of the Fe_{ox} pool**
 133 **varied from 23% to 79%. Samples were collected in November 2024.**

135 Immediately after collection, soil samples were packed in airtight plastic bags, transported to
 136 the laboratory, and stored at 2 °C until further processing. All subsequent handling of moist



137 soil samples was conducted at 20 °C in a Coy anoxic chamber maintained under an atmosphere
138 of 95% nitrogen and 5% hydrogen to prevent oxidation of Fe(II) and other oxygen-sensitive
139 elements.

140 Within the anoxic chamber, each moist soil sample was gently homogenized by hand. A
141 representative subsample of approximately 20 g was removed and dried outside the glovebox
142 at 105 °C for 24 h to determine gravimetric soil water content. A second subsample of
143 approximately 20 g was oven-dried at 40 °C for six hours and sieved to <2 mm for subsequent
144 oxalate and citrate–bicarbonate–dithionite (CBD) extractions and analyses. Analysis of soluble
145 P (P_{Sol}) and HCl-extractable Fe(II) ($\text{Fe(II)}_{\text{HCl}}$) was performed on anoxic moist soil samples
146 (Florea et al., 2026).

147 **2.2. Soil characterization and solution analysis**

148 Soil solution was obtained from moist samples by centrifugation of 30 g soil into Chrom-Tech
149 50 mL PVDF Maxi-Spin 0.45 µm filter tubes (2,795 g; 0.45 µm filtration), and orthophosphate
150 (PO_4^{3-}), dissolved Fe(II), pH, electrical conductivity, and alkalinity determined following
151 standard procedures described in Florea et al. (2026) and detailed in the Supplementary
152 Information (Section S1.1). Orthophosphate and Fe(II) were quantified spectrophotometrically
153 using the molybdate-blue and 1,10-phenanthroline methods, respectively.

154 The extent of Fe(III) oxide reduction ($R_{\text{Fe(III)}}$) was calculated as the ratio of HCl-extractable
155 Fe(II) to oxalate-extractable Fe (Eq. 1), following established extraction protocols (Fadrus and
156 Maly, 1975; Lovley et al., 1987; Schoumans, 2000), while the residual sorption capacity was
157 calculated accordingly Eq. 2. Oxalate-extractable Al, Fe, and P (Al_{ox} , Fe_{ox} , and P_{ox}) were
158 measured by ICP-OES (Section S1.1).

$$159 \quad R_{\text{Fe(III)}} = (\text{Fe(II)}_{\text{HCl}} / \text{Fe}_{\text{ox}}) \times 100 \quad \text{Eq. 1}$$

$$160 \quad \text{RSC} = (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}) - \text{Fe(II)}_{\text{HCl}} \quad \text{Eq. 2}$$



161 The potential P release to solution, expressed as mobilized P (P_{mob}) was calculated according
162 to Eq. 3.

$$163 \quad P_{\text{mob}} = \text{Fe(II)}_{\text{HCl}} \times \frac{P_{\text{ox}}}{P_{\text{SC}}} \quad (\text{mmol kg}^{-1}) \quad \text{Eq. 3}$$

164 Total P (P_{T}), inorganic P (P_{inorg}), and P bound in soil organic matter ($P_{\text{org}} = P_{\text{T}} - P_{\text{inorg}}$) were
165 determined by hot acid digestion and blue-molybdate colorimetric analysis as described
166 previously in Florea et al., (2026). Total C and N were measured using an elemental analyzer,
167 and total elemental concentrations of Fe, Al, Ca, and Mg were determined by benchtop XRF
168 (detailed in Section S1). Dissolved cations, anions, and dissolved organic carbon (DOC) were
169 analyzed as described in Florea et al. (2026).

170 2.3. XANES data collection and analysis

171 Soil samples embedded in resin (sample preparation described Section S1.2) were analyzed at
172 the Lucia beamline (Vantelon et al. 2016) of the SOLEIL Synchrotron (Saint-Aubin, France)
173 using a combination of macro- and micro-focused X-ray techniques. Initially, macro-beam P
174 K-edge XANES measurements were collected on pellets using a $3 \times 2 \text{ mm}^2$ beam to identify
175 the average P speciation in each soil. The spectra were collected over an energy range of 2.13
176 to 2.21 keV, with an energy step of 0.2 eV around the edge and an acquisition time of 5 s/energy
177 step. This bulk analyses provided an overview of P speciation at the sample scale. Following
178 the macro-scale characterization, soil samples were subjected to μ -XRF mapping to obtain
179 high-resolution elemental distribution maps and to locate P hotspots. μ -XRF maps were
180 collected at 2.21 keV over areas of 1 mm^2 on resin-embedded soil thin sections in continuous
181 acquisition FlyScan mode using a focused beam of $3 \times 3 \text{ }\mu\text{m}^2$, with an equivalent pixel size of
182 $3 \text{ }\mu\text{m}$ and an acquisition time of 50 ms/pixel. The fluorescence spectra, collected from each
183 pixel of the map were normalized by the incident flux and corrected from the detector deadtime



184 value. Elemental maps were then extracted using fast XRF linear fit PYMCA software plugin
185 (Solé et al., 2007), that fitted the XRF spectra in each pixel of the map.
186 Twenty P hotspots from each sample were subsequently targeted for P K-edge μ -XANES
187 analyses to determine molecular-scale P speciation. μ -XANES spectra were collected in
188 continuous FlyScan acquisition mode over the energy range of 2.13 to 2.21 keV with energy
189 step of 0.2 eV and 500 ms/energy step. One to three spectra were collected in each spot
190 depending on signal to noise ratio and merged.
191 XANES spectra were processed according to standard procedures using Fastosh software
192 (Landrot and Fonda, 2025). The E_0 edge energy was chosen as the maximum of the first
193 derivative of the XANES spectrum. The background was subtracted from the spectra using
194 linear regression in the region before the edge and polynomial regression after the edge to
195 obtain a horizontal signal. Soil spectra were compared to a library of publicly available
196 reference P spectra that included organic P, various P-bearing minerals and sorbed P species
197 (Kim et al. 2015; Egger et al. 2015; Giguët-Covex et al. 2013).

198

199 **3. Results**

200 **3.1. Soil and solution properties**

201 Soil properties at the Løvenborg site (0–40 cm depth) were relatively homogeneous along the
202 moisture-gradient transect, with only moderate spatial variability among sampling points
203 (Table 1). Soil solution pH was consistently near-neutral to slightly alkaline, ranging from 6.8
204 to 7.2 across the four sampling points (L1–L4), and dry bulk density ranged between 310 kg
205 m^{-3} at L1 to 564 kg m^{-3} at L4.

206 Total C and N contents were relatively high and showed limited variability, ranging from 27.4
207 to 28.4 mass % for C and from 1.9 to 2.3 mass % for N. Total Ca and Mg contents were



208 elevated, with Ca_T ranging from 785 to 1045 mmol kg^{-1} and Mg_T from 21 to 35 mmol kg^{-1} .
 209 Total Fe and Al contents were also high, with Fe_T between 445 and 620 mmol kg^{-1} and Al_T
 210 between 535 and 730 mmol kg^{-1} , while total P (P_T) contents ranged from 31.3 to 38.2 mmol
 211 kg^{-1} . The P_{inorg} content varied between 11.1 – 16.9 mmol kg^{-1} , and the P_{org} between 20.2 – 22.2
 212 mmol kg^{-1} . These results revealed a P_{org} fraction between 56 – 65 % of P_T .
 213 Oxalate-extractable iron (Fe_{ox}) and aluminum (Al_{ox}) contents were high across all samples,
 214 with Fe_{ox} ranging from 188 to 227 mmol kg^{-1} and Al_{ox} from 35.7 to 46.4 mmol kg^{-1} . Oxalate-
 215 extractable phosphorus (P_{ox}) varied between 12.7 and 17.8 mmol kg^{-1} .
 216 The subsoil sand layer composition (Table 2) showed low contents of Al_{ox} , Fe_{ox} and P_{ox} . Soil
 217 solution composition at the Løvenborg site reflected near-neutral to alkaline, ion-rich
 218 conditions across the moisture-gradient transect (Table 3) (Florea et al., 2026).

219

220 **Table 1: Properties of all soil sampling points from Løvenborg moisture transect. Samples were**
 221 **collected in November 2024. Adapted from Florea et al., (2026)**

Løvenborg collection depth 0-40 cm					
Measurement	Unit	L1	L2	L3	L4
pH ^a	in soil solution	7.1	7.2	6.9	6.8
Dry ρ ^b	kg m^{-3}	310	416	509	564
TC ^c	mass %	28.4	27.4	27.6	28.1
TN ^c	mass %	2.3	1.9	2.2	2.1
Mg_T^c	mmol kg^{-1}	21	25	28	35
Ca_T^c	mmol kg^{-1}	1045	906	905	785



Al_T^c	mmol kg^{-1}	535	730	620	575
Fe_T^c	mmol kg^{-1}	620	498	522	445
P_T^c	mmol kg^{-1}	35.5	38.2	31.3	34.4
$\text{P}_{\text{inorg}}^d$	mmol kg^{-1}	13.3	16.9	11.1	13.8
P_{org}^e	mmol kg^{-1}	22.2	21.3	20.2	20.6
Al_{ox}^f	mmol kg^{-1}	35.7	45.3	44.5	46.4
Fe_{ox}^f	mmol kg^{-1}	188.7	227.6	216.3	203.6

222 P_{ox}^f mmol kg^{-1} 15.4 17.8 12.7 16.3
 a - pH has been determined in soil solution

223 b – Bulk density

224 c – Total carbon (C), nitrogen (N), manganese (Mg), calcium (Ca), aluminum (Al), iron (Fe) and phosphorus (P)

225 d – Total inorganic P

226 e – Total organic P

227 f – Oxalate extractable Al, Fe and P

228

229 **Table 2: Sand layer proprieties, reported by Florea et al., (2026)**

	pH^a	Dry ρ_b^b kg m^{-3}	Texture ^c	Al_{ox}^d mmol kg^{-1}	Fe_{ox}^d mmol kg^{-1}	P_{ox}^d mmol kg^{-1}
Løvenborg Sand layer			Sand – 92%			
	7	1520	Clay – 4%	4	18	0.8
			Silt – 4%			

230 a - pH has been determined in soil solution.

231 b – Bulk density.

232 c – Texture of the sand layer



233 ^d – Oxalate extractable Al, Fe and P.

234

235 Soil solution pH ranged from 6.8 to 7.0, electrical conductivity was up to 4.9 mS cm⁻¹, and
 236 alkalinity, expressed as bicarbonate (HCO₃⁻), ranged from 830 to 930 µM. Major ion
 237 concentrations were elevated, with Cl ranging from 1290 to 1430 µM and Na from 204 to 297
 238 µM. Calcium concentrations were high throughout the transect (582 – 732 µM), with
 239 corresponding Mg concentrations of 42–100 µM, confirming Ca-rich conditions in soil
 240 solution. Dissolved Fe occurred predominantly as Fe(II) species, with concentrations between
 241 274 and 380 µM, indicating active reductive conditions. Sulfate concentrations varied from 29
 242 to 167 µM, with the highest values observed at the driest sampling point, while nitrate
 243 concentrations remained below detection limit across all samples (6.5–8.8 µM). Dissolved
 244 organic carbon (DOC) concentrations were moderately high, ranging from 4 to 4.5 mM.

245

246 **Table 3: Soil solution composition from soil sampling points from and Løvenborg. Samples were**
 247 **collected in wintertime, on 5th of November 2024. Adapted from Florea et al., (2026)**

Løvenborg collection depth 0-40 cm

Measurement	Unit	L1	L2	L3	L4
pH	in soil solution	6.9	7	6.9	6.8
NO ₃ ⁻	µM	8.8	6.5	8.5	8.7
SO ₄ ²⁻	µM	29	32	49	167
Cl ⁻	µM	1290	1380	1430	1350
HCO ₃ ⁻	µM	920	930	870	830



Ca ²⁺	μM	582	732	681	641
Mg ²⁺	μM	67	100	59	42
K ⁺	μM	25	25	24	19
Na ⁺	μM	204	250	297	292
Fe ²⁺	μM	380	310	376	274
DOC	mM	4.5	4.2	4.5	4

3.2. Iron reduction and phosphorus dynamics

R_{Fe(III)} varied markedly along the moisture-gradient transect (Figure 1). The lowest degree of reduction was observed at the driest sampling point (L4) with R_{Fe(III)} of 23%. In contrast, progressively higher degrees of Fe(III) reduction were recorded at the wetter sampling points, with R_{Fe(III)} values of 42%, 60%, and 79% at L3, L2, and L1, respectively.

Despite the pronounced reduction of Fe(III) oxides at the sampling points, P concentrations in soil solution (P_{Sol}) remained below the detection limit (0.1 μM) in all Løvenborg soil samples. No elevation of dissolved P in pore water with increasing R_{Fe(III)}, was observed.

The P_{mob} was consistently much higher (Section S2.1) than the measured P_{Sol} concentrations across the transect samples. This discrepancy indicates that P_{mob} was effectively immobilized within the soil matrix rather than released to soil solution.

Moreover, re-sorption to residual Fe(III)-oxides or Al-(hydr)oxides alone cannot account for the low dissolved P concentrations, according to the RSC model, which indicates limited sorption capacity under the prevailing geochemical conditions (Section S2.1). Together, these observations are consistent with the formation of secondary mineral phases as a dominant P immobilization pathway rather than simple adsorption to remaining metal oxide surfaces.



265 The close agreement between P_{ox} measured by the molybdate blue method ($P_{ox_molybdate}$)
266 (Wolf and Baker, 1990) and dissolved total P quantified by ICP–OES (P_{ox_ICP}) indicates that
267 dissolved P was predominantly present as inorganic phosphate. The $P_{ox_molybdate}$: P_{ox_ICP}
268 ratio averaged 1.08 ± 0.07 (mean $\pm$ SD), with individual values ranging from 0.98 to 1.14
269 (Florea et al., 2026, Table S2). This demonstrates that the oxalate-extractable P pool is
270 predominantly composed of inorganic P, though some sample-to-sample variability was
271 observed. Moreover, the difference between P_{ox} and P_{inorg} is very low between the samples,
272 suggesting that oxalate extracted mostly inorganic P which accounted for 35–44% of P_T that
273 can be mobilized during anoxic conditions.

274

275 **3.3. Macro XANES analysis**

276 The macro-beam measurements represent P speciation spatially averaged across several mm²
277 within each soil sample. Bulk P K-edge XANES spectra of the soil samples (L1–L4 under oxic
278 and anoxic conditions) are shown in Figure 2 together with reference compounds.

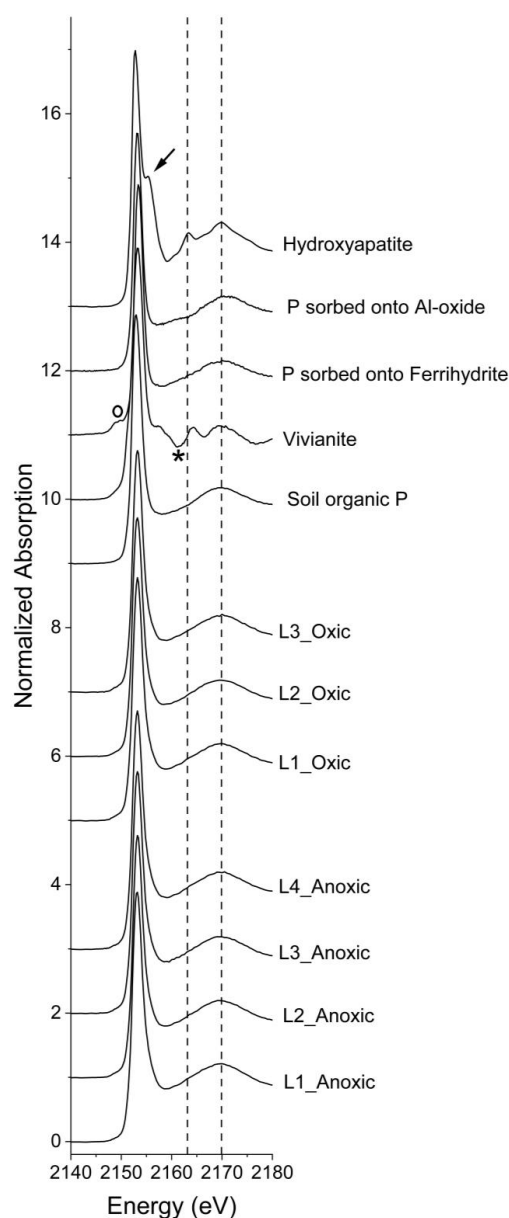
279 All spectra are characterized by a sharp and intense white line centered at ~2152–2153 eV. The
280 similarity of this feature under oxic and anoxic conditions indicates that the predominant
281 oxidation state and local phosphate coordination of P remained similar.

282 A subtle but reproducible pre-edge feature at ~2150 eV is present in several samples. Although
283 weak, this minor intensity occurs at an energy comparable to that observed for the P-sorbed
284 ferrihydrite reference and may indicate the presence of some ortho-P bound to Fe(III) oxides
285 (Figure S2). Under anoxic conditions, this pre-edge contribution was slightly attenuated,
286 although it remained detectable. The low amplitude of the pre-edge peak, combined with the
287 overall featureless character of the bulk spectra suggests that P bound to Fe(III) oxides are



288 present but do not dominate the bulk P pool, and no additional pre-edge structures indicative
289 of distinct reduced P species were apparent following redox treatment.

290 In the post-edge region (2160–2175 eV), the characteristic shoulder and oscillations diagnostic
291 of crystalline hydroxyapatite were not present in the bulk XANES data of the soil samples, nor
292 were distinct vivianite features (2164–2170 eV) resolved. These P-bearing phases were
293 specifically considered in the XANES analysis because they represent the expected minerals
294 of Ca-bound and Fe(II)-bound P under the geochemical conditions studied. Their absence in
295 the bulk spectra indicates that neither crystalline Ca–P phases nor vivianite dominates bulk P
296 speciation. Instead, the largely featureless spectra of both oxic and anoxic samples resembled
297 those of soil organic P (Figure S2), which is consistent with the high fraction of P_{org} (>50%)
298 measured in these peat soils.



299

300 **Figure 2: Bulk P K-edge XANES spectra for soil samples from the Løvenborg site. Spectra of oxic**
 301 **and anoxic samples are shown together with reference compounds representing hydroxyapatite,**
 302 **phosphate (P) sorbed onto aluminum (Al)-oxide, P sorbed onto ferrihydrite, vivianite and soil**
 303 **organic P. L1–L4 refer to the four sampling locations along the site transect. Dashed vertical lines**
 304 **indicate diagnostic post-edge features (2163–2170 eV). Arrows highlight the characteristic post-**
 305 **edge shoulder associated with hydroxyapatite, open circles mark subtle pre-edge features typical**
 306 **of iron (Fe(III))-bound phosphate, and asterisks denote a post-edge oscillation characteristic of**
 307 **vivianite.**



308

309 **3.4. Micro-XRF and μ -XAS analysis**

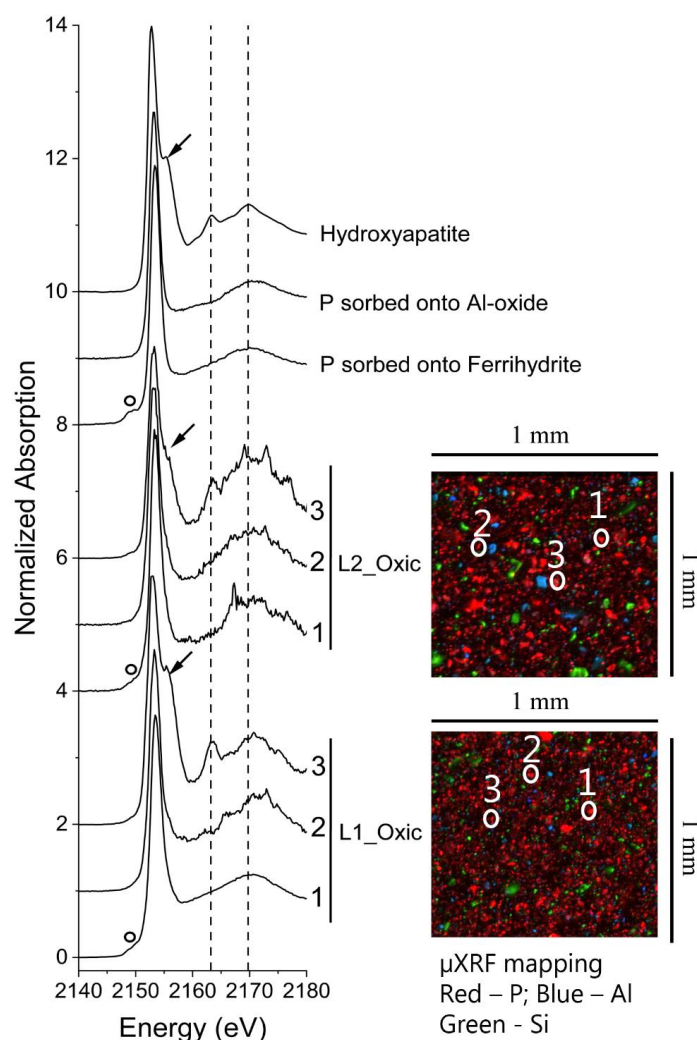
310 **3.4.1. Oxic samples**

311 The μ -XRF maps and P K-edge μ -XANES spectra collected from selected P hotspots within
312 the L1_Oxic and L2_Oxic samples are shown in Figure 3 together with reference spectra for P
313 sorbed onto ferrihydrite, P sorbed onto Al-oxide and hydroxyapatite. For L1_Oxic, the μ -XRF
314 maps revealed heterogeneous P distributions with varying spatial associations with Al and Si,
315 which demonstrates the high microscale geochemical heterogeneity within the peat matrix.
316 Furthermore, the μ -XANES data obtained from P hotspots resolved pronounced spatial
317 variability in P speciation for the oxic samples, with clear differences among P hotspots in the
318 pre-edge and post-edge regions. Some spectra exhibit a well-defined shoulder on the main
319 absorption peak (2154–2158 eV) and structured oscillations between ~2166 and 2172 eV,
320 which closely resembled the hydroxyapatite reference spectrum. In contrast, other P hotspots
321 displayed a broader and more dampened post-edge region, closely matching the spectrum of P
322 sorbed onto Al-oxide. Although resolvable pre-edge intensity indicated the presence of P-
323 Fe(III) bonding at some P hotspots, no distinct post-edge oscillations diagnostic of vivianite
324 were observed in any P hotspot, consistent with the oxic conditions of these samples (Figure
325 S3).

326 The L2_Oxic sample exhibited comparable microscale heterogeneity to L1_Oxic. μ -XRF
327 mapping showed spatially variable co-localization of P with Al-rich regions, and the μ -XANES
328 data similarly revealed hotspots with P speciation that resembled Ca-P environments in
329 addition to Fe- and Al-associated P environments. Although background noise was present in
330 some spectra, particularly in the post-edge region at higher X-ray energies, the diagnostic



331 features were sufficiently resolved to reliably distinguish Ca-P from Fe- and Al-bound P in the
332 L2_Oxic sample.



333

334 **Figure 3: μ -XANES spectra of oxic peat soil samples (L1_Oxic and L2_Oxic) compared with**
335 **reference compounds, including crystalline hydroxyapatite (Ca-P), phosphate (P) sorbed onto**
336 **aluminum (Al)-oxide, and P sorbed onto ferrihydrite. The dashed vertical lines indicate the post-**
337 **edge region 2163–2170 eV (2160–2175 eV) used for diagnostic phase comparison. Arrows**
338 **highlight the characteristic post-edge shoulder of hydroxyapatite, while open circles mark pre-**
339 **edge features associated with Fe-bound P environments. Right panels show corresponding μ -XRF**
340 **elemental maps of selected regions of interest for L1_Oxic and L2_Oxic samples, with P shown in**
341 **red, Al in blue, and Si in green. Numbered spots (1–3) indicate P hotspots selected for subsequent**
342 **μ -XAS analysis.**



343

344 **3.4.3. Anoxic samples**

345 μ -XRF maps and P K-edge μ -XANES data collected from selected P hotspots within L1–
346 L4_Anoxic are shown in Figure 4 together with reference spectra for vivianite, P sorbed onto
347 ferrihydrite, P sorbed onto Al-oxide, and hydroxyapatite. Across all anoxic samples, μ -XRF
348 mapping revealed highly heterogeneous P distributions, similar to those observed under oxic
349 conditions. Numerous P hotspots were identified that appeared to be co-located with Al,
350 consistent with a variety of different P-bearing phases, including Ca-P solids, vivianite and P-
351 bearing Al oxides. The μ -XANES data from selected hotspots from the four anoxic samples
352 are described below.

353 **L1_Anoxic**

354 For the L1_Anoxic sample (79% reduction state), the μ -XANES spectra of a variety of P
355 hotspots exhibited the structured shoulder between ~2166 and 2172 eV and pronounced
356 oscillations beyond 2168 eV of hydroxyapatite-type Ca–P coordination. The μ -XANES data
357 from other P hotspots on this sample matched more closely with the featureless spectrum of P
358 sorbed onto Al-oxide. Despite some variation in XANES features among different spots taken
359 for the L1_Anoxic sample, no diagnostic fingerprints for vivianite were observed in any
360 XANES spectrum collected from this sample. Thus, under anoxic conditions, the L1 sample is
361 best characterized by prominent Ca–P domains, the presence of P-bearing Al-oxides, and the
362 absence of substantial amounts of vivianite.

363 **L2_Anoxic**

364 For the L2_Anoxic sample (60% reduction state), the μ -XANES data varied substantially in
365 regions of interest separated by only a few mm. While several hotspots resembled P sorbed
366 onto Fe- and Al-(hydr)oxides, multiple hotspots exhibited a subtle but reproducible shoulder



367 in the 2164–2168 eV region characteristic of vivianite-like coordination. These features are
368 slightly less pronounced than the crystalline vivianite reference, which can be due to the
369 presence of multiple P-bearing phases in the same hotspot or a lower average crystallinity of
370 vivianite in the sample compared to the vivianite reference. In addition, the presence of Ca-P
371 solids was detected in some regions of the sample based on the characteristic post-edge
372 features.

373 **L3_Anoxic**

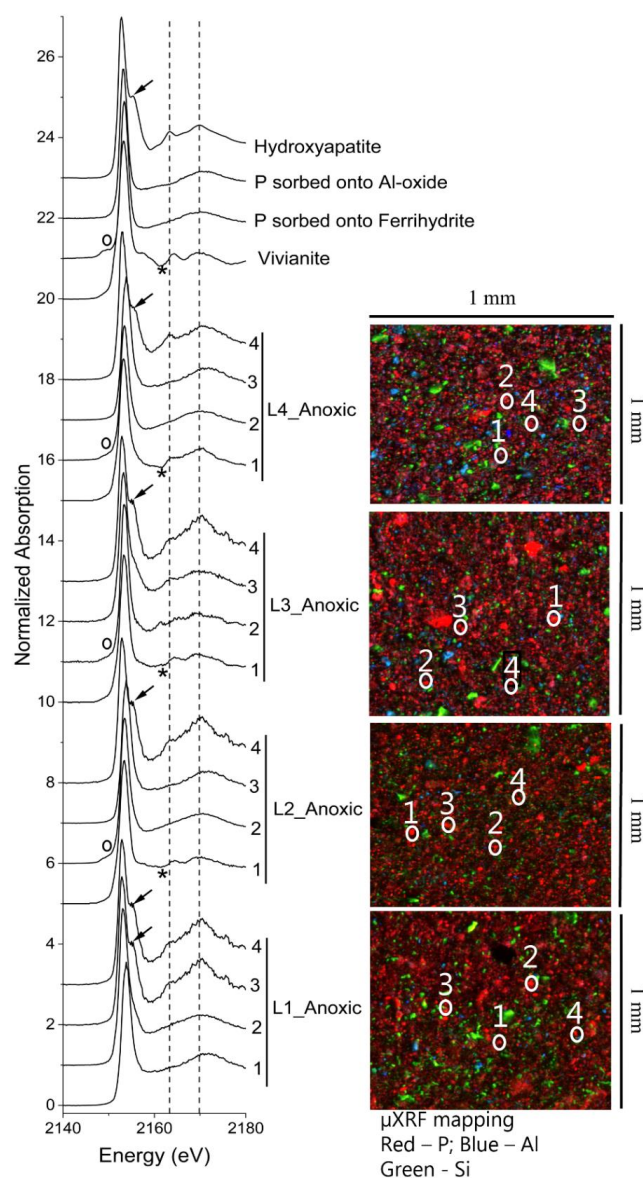
374 The μ -XANES data from targeted regions of the L3_Anoxic sample (42% reduction state)
375 consistently displayed vivianite-like post-edge shoulders in the diagnostic 2164–2168 eV
376 region. Additionally, the shoulder in the white line and pronounced post-edge features between
377 ~2166 and 2172 eV consistent with hydroxyapatite-type Ca-P coordination was observed in
378 other areas of the sample. These Ca-P domains are spatially distinct from Fe-associated
379 vivianite-like regions and indicate the presence of both types of P bonding environments,
380 though P sorbed to Fe- and Al-(hydr)oxides was also likely present based on key XANES
381 features (Figure 4).

382 **L4_Anoxic**

383 The μ -XANES data for the L4_Anoxic sample (23% reduction state) revealed well-defined
384 vivianite-like features in multiple hotspots, characterized by a pronounced shoulder at
385 approximately 2164 eV followed by a distinct decrease in absorption intensity and oscillation
386 shape in the 2164–2168 eV post-edge region. Compared to the L2_Anoxic sample, these
387 features indicative of vivianite were more consistently resolved. Similar to the other anoxic
388 samples, characteristic features indicative of Ca-P solids were also observed in several XANES
389 spectra, though some regions were also dominated by broad and generally featureless spectra
390 indicative of P sorbed to Fe- and Al oxides phases.



391 Collectively, μ -XANES demonstrated systematic microscale heterogeneity in P speciation
392 under anoxic conditions. While the L1_Anoxic spectra contained Al-associated P and Ca–P
393 signatures, vivianite phases emerged in the L2 sample and became more consistently resolved
394 in the L3 and L4 samples. Nevertheless, spectra resembling Ca–P solids were measured in every
395 anoxic (and oxic) sample. Importantly, both Ca–P and Fe(II)–P phases were unambiguously
396 resolved at the microscale despite not being detected in the corresponding bulk XANES
397 spectra. As already observed in soil studies, such as in Rivard et al. 2016 and Werner et al.
398 2017, this contrast reveals the importance of collecting both macro-beam XANES spectra to
399 determine the main P-bearing phases and micro-XANES spectra to characterize the
400 heterogeneity of the soil and determine the minor P-bearing phases, which is essential to obtain
401 a complete description of P speciation in such heterogeneous systems.



402

403 **Figure 4: μ-XANES analysis of anoxic peat soil samples (L1_Anoxic to L4_Anoxic) compared**
 404 **with reference compounds representing hydroxyapatite, P sorbed onto Al-oxide, P sorbed onto**
 405 **ferrihydrite and vivianite. Dashed vertical lines indicate the diagnostic post-edge region (2163–**
 406 **2170 eV). Arrows highlight the characteristic post-edge shoulder associated with hydroxyapatite.**
 407 **Open circles mark subtle pre-edge features typical of Fe-bound phosphate environments, while**
 408 **asterisks denote the post-edge oscillations characteristic of vivianite. Right panels show**
 409 **corresponding μ-XRF elemental maps of selected regions of interest, with phosphorus (P) shown**
 410 **in red, aluminum (Al) in blue, and silicon (Si) in green. Numbered spots (1–4) indicate P hotspots**
 411 **selected for subsequent μ-XANES analysis.**

412



413 **4. Discussion**

414 The results of this study demonstrate that Fe(III) reduction and P mobilization can become
415 decoupled in neutral, Ca-rich peat soils. Rather than being controlled by a single dominant
416 retention pathway, P dynamics appear to result from the interplay of Fe-, Al-, and Ca-associated
417 processes operating at different spatial scales. The following sections discuss the mechanisms
418 responsible for maintaining low dissolved P concentrations despite extensive reductive Fe
419 transformation.

420 **4.1. Decoupling of Fe(III) reduction and dissolved P release in alkaline peat soils**

421 The Løvenborg transect is characterized by near-neutral pH, high alkalinity, elevated solution
422 Ca^{2+} concentrations, and relatively high contents of Fe and Al in both total and oxalate-
423 extractable fractions. Such conditions define a chemically buffered peat system in which both
424 Fe- and Ca-mediated P retention pathways are thermodynamically feasible, as commonly
425 reported for Fe–P and Ca–P systems in soils and sediments (Reddy et al., 1999).

426 High Fe_{ox} contents ($189\text{--}228 \text{ mmol kg}^{-1}$) relative to P_{ox} ($12.7\text{--}18.5 \text{ mmol kg}^{-1}$) indicate a large
427 reactive Fe pool with substantial capacity for P sorption, surface complexation, and potential
428 co-precipitation. Simultaneously, elevated Ca_{T} ($785\text{--}1045 \text{ mmol kg}^{-1}$) and solution Ca^{2+} (582--
429 $732 \text{ }\mu\text{M}$) reflect high Ca availability under bicarbonate-buffered conditions. Elevated $\text{Fe(II)}_{\text{HCl}}$
430 and dissolved Fe^{2+} concentrations ($274\text{--}380 \text{ }\mu\text{M}$) indicate active reductive processes along the
431 moisture gradient, thus, the system combines: i) abundant reducible Fe(III) (hydr)oxides, ii)
432 high dissolved Fe^{2+} under anoxia, and iii) Ca-rich, near-neutral porewater chemistry.

433 A key observation is the pronounced Fe(III) reduction along the transect—up to ~79% of the
434 Fe_{ox} pool at the wettest location, without detectable concentration of P_{Sol} in porewater. The
435 calculated P_{mob} values exceed measured P_{Sol} concentrations, which remained below the
436 detection limit ($0.1 \text{ }\mu\text{M}$) (Section S3), indicating that P released during reductive dissolution



437 did not accumulate in solution but was rapidly re-immobilized within the soil matrix. Although
438 residual or re-precipitated Fe(III) and Al (hydr)oxide surfaces may provide sorption capacity
439 even under reducing conditions (Florea et al., 2024), the XAS data provided clear evidence that
440 Ca-P and vivianite-type solids formed, which is discussed further in the subsequent sections.

441 **4.2. Microscale heterogeneity: coexistence of Al-P, Fe-P, Ca-P and vivianite**

442 Macro-beam P K-edge XANES revealed negligible differences between oxic and anoxic
443 samples, with the bulk spectra dominated by organic and Fe/Al-associated P and no signature
444 of crystalline vivianite or hydroxyapatite. This result suggests that redox-driven
445 transformations involved only a relatively small reactive P fraction, whereas the majority of
446 the bulk P pool remained unchanged. Therefore, the vivianite-like and Ca-P phases identified
447 by μ -XANES are interpreted as localized microscale retention mechanisms rather than
448 dominant bulk P containing solids.

449 In contrast to the macro spectra, μ -XRF and μ -XANES analyses showed pronounced
450 microscale heterogeneity. Both oxic and anoxic samples contained discrete domains
451 characterized by Fe(III)-associated P, Al-associated P, and, notably, apatite-like Ca-P
452 coordination. The identification of Ca-P phases represents a key finding of this study, as these
453 phases were neither detected by bulk XRD nor predicted by equilibrium saturation calculations
454 used in Florea et al. (2026).

455 Ca-P signatures occur as spatially discrete microsites rather than pervasive bulk phases, which
456 explains their absence using bulk characterization methods. Potential external sources of Ca-
457 P appear unlikely because mineral P fertilizers are not documented at the site and typically
458 dissolve rapidly rather than persist as discrete Ca-P phases (Chien et al., 2011; Shigaki et al.
459 2006) and aeolian inputs are likely negligible for this area. Instead, the subsoil and groundwater
460 represent plausible Ca sources, particularly given the high groundwater pH (~8–8.5) at the



461 study site. Upward groundwater flow from underlying calcareous deposits can provide an
462 important source of Ca^{2+} to peat soils (Glaser et al., 1996). The sandy subsoil composition
463 (Table 2) further supports the interpretation of groundwater as a potential source of dissolved
464 Ca and mineral-derived constituents.

465 For anoxic samples, μ -XANES spectra exhibited features consistent with Fe(II)–P
466 coordination, with lower amplitude and less well-defined structure compared to crystalline
467 reference spectra. This may reflect lower abundance, reduced crystallinity, or heterogeneous
468 distribution of Fe(II)–P phases, which is consistent with XRD analysis of the soil samples
469 (Florea et al., 2026). While these results do not provide clear evidence for widespread vivianite
470 precipitation as the dominant immobilization pathway, they are consistent with localized
471 Fe(II)–P formation where dissolved Fe^{2+} and P concentrations locally exceed saturation
472 thresholds. The μ -XANES data therefore demonstrate that P retention in Løvenborg peat
473 operates through coexisting microscale mechanisms rather than a single bulk-scale control.

474 **4.3. Mechanistic interpretation and implications for P immobilization in neutral anoxic** 475 **peat soils**

476 Integrating soil chemical characteristics, Fe(III) reduction data, and XANES results support a
477 conceptual model in which reductive dissolution of Fe(III) (hydr)oxides initially releases
478 sorbed P into the porewater. However, the mobilized P is not released to solution but is rapidly
479 re-immobilized through Fe- and Ca-associated sequestration pathways. The overall
480 consequence of these coupled processes is internal redistribution and stabilization of P rather
481 than net mobilization to the soil solution.

482 Thermodynamic calculations using Visual MINTEQ (Section S3) indicate that pore waters
483 under reducing conditions are strongly supersaturated with respect to vivianite (saturation
484 index = 3.2–4.2), whereas Ca–P phases (hydroxyapatite) are only weakly to moderately



485 supersaturated (saturation index = 0.03–1.5) (Table 4). However, positive saturation indices
486 alone do not guarantee mineral precipitation, as nucleation and crystal growth kinetics also
487 exert strong controls on mineral formation (Emerson and Widmer, 1978).

488 Vivianite generally forms more readily than Ca–P minerals because it can nucleate at lower
489 supersaturation, whereas Ca–P precipitation typically requires higher supersaturation and is
490 subject to stronger kinetic constraints (Wang and Nancollas, 2008; Reynaud et al., 2022).
491 Consequently, thermodynamic supersaturation does not necessarily result in immediate
492 mineral precipitation, particularly for Ca–P phases. This distinction is important for
493 interpreting our results. Although porewater calculations indicated supersaturation with respect
494 to both vivianite and Ca–P minerals (Table 4), vivianite was detected by XRD, Mössbauer
495 spectroscopy (Florea et al., 2026), and μ -XAS, whereas Ca–P phases were observed only at
496 localized microscale hotspots. These observations suggest that kinetic limitations may restrict
497 the extent of Ca–P precipitation despite favorable thermodynamic conditions.

498 **Table 4: Saturation index calculated for vivianite and hydroxyapatite using Minteq and the soil**
499 **solution parameters given in Table 3.**

Løvenborg collection depth 0-40 cm				
Saturation index	L1	L2	L3	L4
Vivianite	4.2	4	3.7	3.2
Ca-P (hydroxyapatite)	0.09	1.5	0.7	0.03

500
501 An important unresolved question concerns the temporal separation of Ca–P and Fe(II)–P
502 formation. Ca–P precipitation may be favored during drier spring–summer periods, when
503 evaporation and upward water movement concentrate Ca^{2+} in near-surface porewaters,
504 particularly under alkaline groundwater influence. In contrast, vivianite forms during wetter



505 autumn–winter periods, when reducing conditions promote Fe(II) accumulation. A related
506 question concerns the fate of Fe(II) produced during reductive dissolution. Dissolved Fe²⁺
507 concentrations remain relatively moderate, and only a small fraction of the reduced Fe is
508 incorporated into vivianite. A substantial fraction may instead be retained by sorption to or
509 complexation with organic matter, which can buffer dissolved Fe²⁺ concentrations and
510 influence Fe–P mineral formation (O’Connell et al., 2015).

511 Upon seasonal oxidation, Fe(II) is rapidly oxidized to Fe(III), destabilizing vivianite and
512 shifting saturation indices toward undersaturation. The relatively fast destabilization of
513 vivianite due to Fe(II) oxidation likely explains the absence of vivianite signatures in oxic bulk
514 spectra. Under these conditions, P may be redistributed through sorption onto newly formed
515 Fe(III) (hydr)oxides and, where Ca–P supersaturation persists, localized Ca–P precipitation. In
516 addition, oxidation of pre-existing vivianite may promote its transformation toward more
517 oxidized Fe–P phases, potentially contributing to continued P retention under fluctuating redox
518 conditions. However, Ca–P precipitation is likely constrained by slow precipitation kinetics
519 and high DOC concentrations, which can inhibit mineral nucleation despite favorable
520 thermodynamic conditions (Cao et al., 2007).

521 Together, these results demonstrate that extensive Fe(III) reduction does not necessarily result
522 in P release when efficient retention mechanisms are present. Despite substantial Fe(III)
523 reduction, dissolved P concentrations remain low due to rapid re-immobilization via sorption
524 and precipitation pathways. Although most P in peat soils is stored as organic P and is largely
525 unaffected by seasonal redox dynamics, peat degradation over longer time spans increases the
526 inorganic P pool that participates in these redox-controlled processes. Consequently, risk
527 assessment approaches that rely primarily on Fe:P ratios, redox indicators, bicarbonate-
528 dithionite or oxalate-extractable Fe pools, including the Danish and German models (Forsmann
529 & Kjærsgaard, 2014; Zak et al., 2010), and related geochemical screening frameworks



530 developed for rewetted peatlands (Smolders et al., 2017), may overestimate P release and
531 export in geochemical settings where efficient re-immobilization via Ca–P precipitation,
532 vivianite formation, or sorption rapidly buffers dissolved P concentrations.

533

534

535 **5. Conclusions**

536 Overall, the Løvenborg fen peatland represents a redox-active but strongly P-buffered system.
537 Although soils are rich in P and Fe(III) reduction is substantial, P is not mobilized to solution;
538 instead, it remains retained in the soils via microscale precipitation and sorption processes.
539 Bulk P speciation at the scale of several millimeters was generally similar across redox
540 treatments, whereas microscale analyses on hotspots revealed the coexistence of vivianite, Ca–
541 P and Fe/Al (hydr)oxide-associated P phases. These findings demonstrate that P dynamics in
542 neutral peat soils are controlled by mineral-scale heterogeneity and coupled Fe–Ca
543 geochemistry rather than by a simple redox-driven P release paradigm.

544

545 **Data availability**

546 The data underlying the findings of this study are available at Zenodo at:
547 [10.5281/zenodo.22826799](https://doi.org/10.5281/zenodo.22826799)

548

549 **Author contribution**

550 AFF conceptualized the study, designed and conducted the experiments, performed the data
551 analysis and interpretation, and prepared the original manuscript. DHZ contributed to the



552 conceptualization and methodology of the study, interpretation of the results, and supervision.
553 CvG contributed to the X-ray absorption spectroscopy methodology, data analysis, and
554 interpretation of the spectroscopic results. CR contributed to the X-ray absorption spectroscopy
555 measurements, data analysis, and interpretation of the spectroscopic results. HCBH contributed
556 to the conceptualization and methodology of the study, interpretation of the results,
557 supervision, and project administration. AFF prepared the original manuscript, and all authors
558 contributed to reviewing and editing the manuscript.

559

560 **Competing interests**

561 The authors declare that they have no conflict of interest.

562

563 **Disclaimer**

564 The views and interpretations expressed in this article are those of the authors and do not
565 necessarily reflect those of their affiliated institutions.

566

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