

Supplementary material

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

Supplementary Figures

Fig. S1

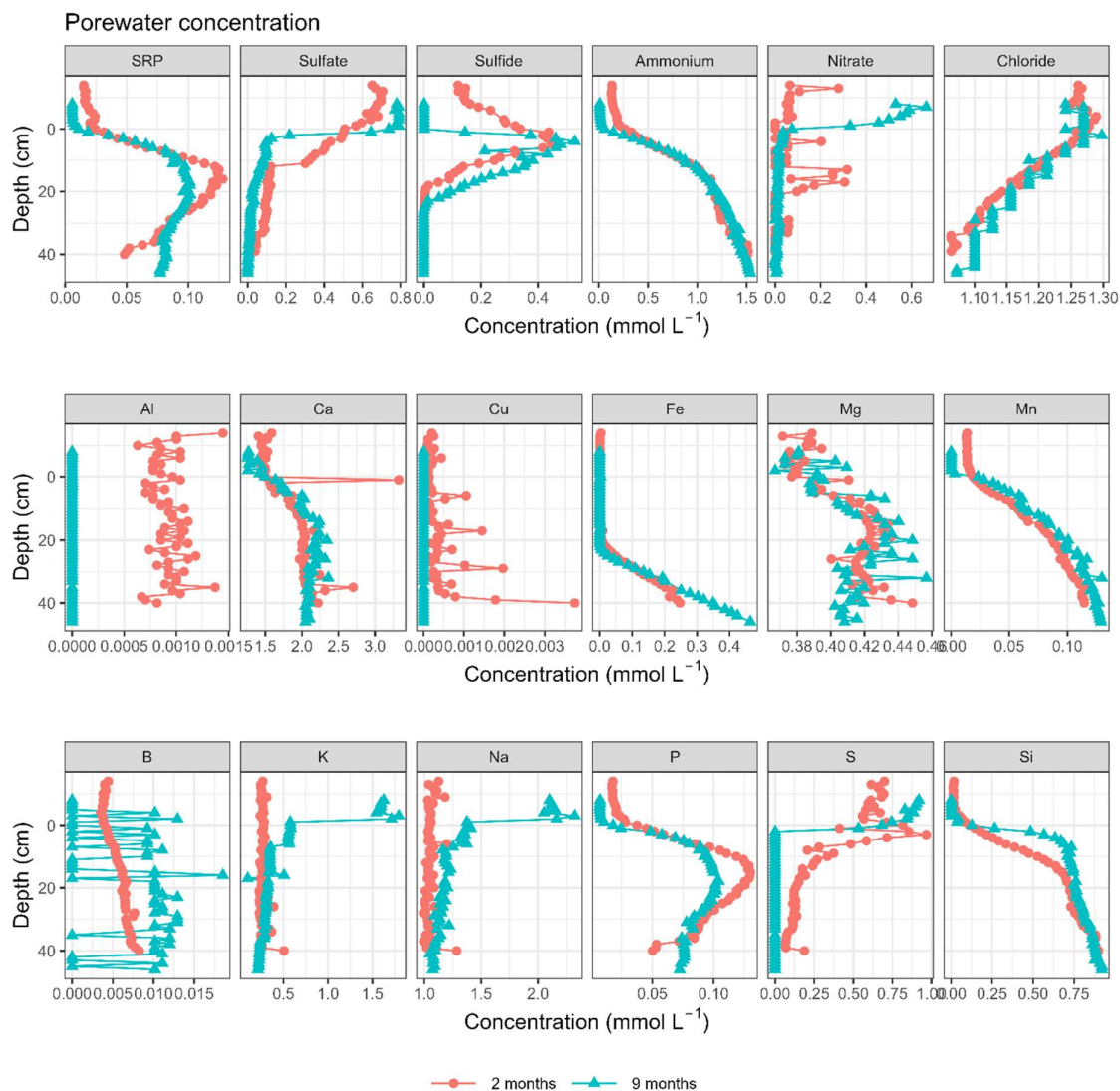


Fig. S1 Full porewater concentration profiles measured by the porewater peepers (PwP) at 2 months (PwP2m, red circles) and 9 months (PwP9m, blue triangles) after deployment in Lake Arendsee. Profiles show total element concentrations (P, Fe, Mn, S and Ca) and anion concentrations (SRP, ammonium, sulfate and sulfide) as a function of depth relative to the sediment–water interface (SWI, dashed line at 0 cm). The grey shading indicates sediment depth. These profiles complement the selected analytes shown in Fig. 4 of the main manuscript.

Fig. S2

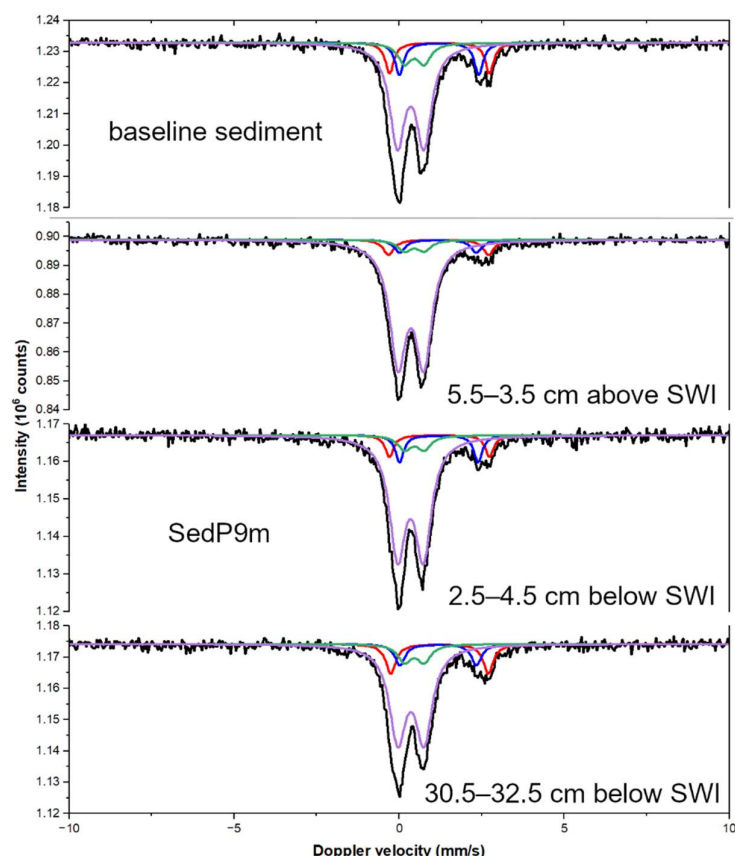


Fig. S2 ^{57}Fe Mössbauer spectra measured at 295 K for the baseline sediment and three selected chambers of SedP9m: 5.5–3.5 cm above the SWI (top), 2.5–4.5 cm below the SWI (chamber 3), and 30.5–32.5 cm below the SWI (chamber 10). Black lines show experimental data; coloured lines show fitted components corresponding to vivianite site B (red), vivianite site A (blue), oxidized vivianite/Fe(III) (green), and FeS/FeSO₄ phases (violet). The fitted Mössbauer parameters (isomer shift IS, quadrupole splitting QS, linewidth Γ , and spectral contributions) are listed in Table 2 of the main manuscript. The forced contribution of oxidized vivianite (30 % of total vivianite signal) is described in the Supplementary Discussion below.

Supplementary Discussion

Mössbauer spectroscopy: interpretation and accuracy of vivianite quantification

The Mössbauer spectra of the different sediment samples measured at room temperature (295 K) show similar features, consisting of a superposition of multiple doublets typical of paramagnetic Fe species, with differences in relative intensities between samples. Specifically, each spectrum consists of a superposition of an intense narrower doublet and two less intense wider doublets.

The intense doublet shows isomer shift (IS) and quadrupole splitting (QS) values in the ranges $0.34\text{--}0.36\text{ mm}\cdot\text{s}^{-1}$ and $0.78\text{--}0.80\text{ mm}\cdot\text{s}^{-1}$, respectively, typical of Fe^{3+} or low-spin Fe^{2+} minerals. These values are consistent with sulfidic iron species, most likely iron monosulfide or iron sulfate species. The high linewidth value of this doublet suggests a distribution of IS and/or QS values, accounting for differences in purity, size and speciation of these FeS minerals. In particular, these could also be attributed to FeSO₄ minerals, similar

to ferricopiapite (Dyar et al., 2013), which could be a result of mineral oxidation during sample preparation.

The less intense and wider pair of doublets, both with IS values in the range 1.18–1.22 mm·s⁻¹ and QS values of 2.26–2.36 mm·s⁻¹ and 2.95–3.03 mm·s⁻¹, respectively, are typical of Fe²⁺ minerals and consistent with vivianite Mössbauer parameters reported in the literature (Murad and Cashion, 2004; Prot, 2021). These two doublets correspond to the two distinct Fe crystallographic sites in vivianite (site I and site II), which theoretically occur in a 1:2 ratio. However, deviations from this ratio are expected when performing room-temperature Mössbauer spectroscopy on naturally occurring vivianite, as a result of thermal effects, Fe-for-metal substitution (e.g., Mn), particle size effects, partial vivianite oxidation, and the lower accuracy of quantification at room temperature (Murad and Cashion, 2004).

To provide consistency across samples, a doublet for oxidized vivianite representing approximately 30 % of the total vivianite signal was forced during fitting, following the approach of Prot (2021). This was done coherently with the known oxygen exposure of the samples prior to measurement. This preparation likely also affected iron sulfide phases, but their oxidation product (FeSO₄) gives a similar Mössbauer signal (Dyar et al., 2013) and these phases were collectively fitted.

The Fe-vivianite content appears to decrease from 34 % in the baseline and deeper chambers of the peeper, down to 19 % above the SWI. Conversely, FeS/FeSO₄ minerals increased from 65 % to 82 %. These changes support the transformation of vivianite into FeS/FeSO₄ with proximity to the SWI, consistent with a process of sulfide-driven vivianite dissolution followed by FeS re-precipitation.

As discussed in the main manuscript, the vivianite-P values derived from these spectra should be treated with caution. The quantification relies on several assumptions: (1) a fixed 30 % oxidized vivianite contribution, (2) the stoichiometry of pure vivianite (Fe:P = 3:2), and (3) a fixed Mn correction factor from SEM-EDS. Each of these assumptions introduces uncertainty, and small errors in spectral contribution can propagate into relatively large errors in absolute vivianite-P values. The Mössbauer-derived vivianite-P estimates are therefore best interpreted as indicative of the direction and approximate magnitude of change, rather than precise quantitative values.

Supplementary References

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Murad, E. and Cashion, J.: Mössbauer Spectroscopy of Environmental Materials and Their Industrial Utilization, Springer US, Boston, MA, <https://doi.org/10.1007/978-1-4419-9040-2>, 2004.

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