Response to the Reviewers and Editor

Editor

We appreciate Editor's comments. Regarding their suggestions:

I do not have additional comments other than those raised by reviewers, except that I encourage you to check for repeatedly missing instances of using sub-/subscript for instance in H2S, CO2 or HCO3-, which you should also check again during proof stage.

We tracked all occurrences of these errors and corrected them.

Reviewer 1

Given the very widespread use of Fe, Mn and Fe/Mn as proxies for oxygen status in lake water, this article is timely and important. There are, however, two aspects by which the paper could be strengthened.

We appreciate the Referee's comments and their positive feedback; below, we answer their concerns and provide our proposed amendments to the text.

First, the paper uses the term geochemical focusing without defining the phrase or explaining how it differs from physical focusing mechanisms. A clear definition for the phrase, and discussion of how geochemical focusing ties in with the traditional hydrodynamic sorting concept would be extremely valuable.

This is a very good point; we now explain what we mean by geochemical focusing and that it is a different mode compared to hydrodynamic sorting, which is driven by particulate-matter movement in response to water-column dynamics. Now in the introduction we added the following passage, citing two fundamental papers.

"Geochemical focusing is a sequence of reductive dissolution, diffusion to overlying water and, after re-oxidation, lateral movement towards the deeper waters (Schaller and Wehrli, 1997). This contrasts with hydrodynamic sediment focusing, which is controlled by lake morphometry and physical phenomena such as wind velocity, wave action and bottom shear stress, leading to preferential movement of the finer sediment fraction towards the deepest points (Blais and Kalff, 1995)."

And

"Manganese shows spatial patterns similar to those of iron (Fig. 5 and 6). However, the majority of Mn lies between the deposition of calcium-dominated carbonates and Fe-bearing matter (Fig. A3). Opposite trends in Mn concentrations relative to organic and terrestrial matter suggest that geochemical focusing controls manganese concentrations in the sediments. This is further strengthened by the spatial variability of Mn/Ti ratios, with the highest values observed in the deepest parts of the lake, except for the lake outflow, where hydrodynamically induced lateral transport could play a more important role."

And

“Finally, below a depth of 14 m, the lakebed is primarily anoxic and is almost exclusively occupied by well-preserved laminated sediments. This demonstrates that oxygen conditions changing with the water depth control laminae preservation, providing evidence for the past extent of the hypolimnion. However, since wind stress and water column dynamics control mixing depth, the spatial variability of the sediments may also reflect mechanical sediment reworking, resuspension and resedimentation. Part of the relationships between detrital (Ti) and redox sensitive elements (Fe, Mn) could therefore be driven by transport processes, rather than geochemical focusing. Such sorting, however, would deposit finer fractions deeper in the lake, in contrast to coarser, detrital fractions, which are associated with erosive littoral zone and higher environment energy (Rowan et al., 1992). Then, Fe, Mn and Ti would covary, which is not a case in Lake Łazduny.”

Second, much is made of the distinction between laminated and homogeneous parts of the sediment. It seems to me that a convincing case can be made that this distinction arises purely from depth. The extraordinary scatter plots shown in figure 7 show a continuity of composition across the boundary between laminated and nonlaminated sediments, such that regression residuals would, I expect, show no distinction between laminated and unlaminated sediments. Could it not simply be that both element composition and sediment structure of consequences of depth, rather than composition being a consequence of lamination? I think the paper would be strengthened if these issues are elaborated more fully.

We fully agree with the Referee, and it was our goal to show this distinction as the Reviewer raised it. We see that we were not clear enough in this regard. Laminations (or their lack), their preservation as well as chemical composition are, clearly, function of depth. We tried to emphasize that the presence of lamination, while distinguishing sediment types, is still dependent on the water depth and water column dynamics. Throughout the text, we now tried to form more verbose connections, while retaining the results section.

“This demonstrates that oxygen conditions changing with the water depth control laminae preservation, providing evidence for the past extent of the hypolimnion.”

“The chemical composition of the surface sediments of Lake Łazduny varies with lithological type and water depth. Spatial variability and GAMs (Fig. 7) indicate progressing differences between the sediments occupying different water depths, which in turn results in differentiation of homogenous and laminated sediments (Fig. A4).”

“The spatial diversity of the sediment lithology in Lake Łazduny corresponds to the average extent of hypoxic and anoxic conditions. Sediment structure therefore reflects the properties and dynamics of the water column. Geochemical composition records changing conditions more directly, whereas lamination is a secondary effect, preserved only when there are no disturbances (Zolitschka et al., 2015). This resembles Lake Suminko, where Tylmann et al. (2012)

demonstrated that the spatial extent of the varved sediments mirrors the extent of the monimolimnion."

Some specific points of greater or lesser significance

Line 12. A more specific word than Numerous would strengthen this statement

We agree, but given it is the opening of an Abstract, we feel we're either about to provide a concrete number (without a reference, given it is an abstract) or drop the soft numeration totally. Therefore, we removed "numerous".

Line 24. By "deposition" do you mean "formation"?

Yes, corrected.

Lines 68 and 69. This surprises me. In the few lakes where I have done a similar investigation I found maximum manganese (up to 25%) to be in shallow sediment under fully oxygenated water and presumably migrated laterally from deeper oxygen depleted water. Are you seeing hints of this at the SE end of the lake?

Yes, indeed, the SE-most core has some elevated Mn concentrations as well. Lateral migration towards the outlet could be in play. The paragraph regarding the XRF-derived elemental maps now includes more information, after adding Fe/Ti and Mn/Ti maps as suggested by the second referee.

"Furthermore, redox-sensitive iron (Fe_{clr}) and manganese (Mn_{clr}) showed enrichment in the deepest, anoxic parts of the lake, with an overall pattern opposite to that of sulfur. Si_{clr}, Fe_{clr}, and Mn_{clr} exhibited a sharp increase with depth and the spatial extent of anoxia. After controlling for detrital input, Fe/Ti and Mn/Ti ratios suggest that the highest deposition of both metals is confined mostly to the deepest parts of the lake. Manganese departs from this pattern slightly, also showing elevated values close to the lake outlet."

And also:

"Therefore, we interpret Fe and Mn concentrations as diagnostic of at least partially redox-dependent processes. Furthermore, the spatial variability of Fe/Ti and Mn/Ti (Fig. 4) indicates that both redox-sensitive metals are enriched in the deepest parts of the basin even after accounting for detrital input, arguing against detrital delivery as the main control on their distribution. We argue that the influence of hydrodynamic focusing, in which particulate matter is being transported, plays a less important role in Lake Łazduny, where the littoral zone is limited except in the northern part. This does not exclude the process but rather limits its magnitude. Our monitoring data, especially the depth of the oxycline and spatial Mn patterns, suggest a strong link between lake turnover, hypolimnetic oxygenation, and Mn burial in sediments."

Line 76. I'm sure there is a simple explanation, but at the location you give I find your lake but with the name Jezioro Błękitne. I looked on Google Earth simply because I struggle to believe that any lake in this temperate landscape could be endorheic. There must be out flowing water because 1) the landscape has a positive water balance, and 2) the lake is not hypersaline. And, your map Figure 1 shows an outflow stream! I think the word endorheic is being misapplied here.

This is an error on our side; we meant to type exorheic (open) lake. Thank you for catching it. Indeed, the lake has an outflow. It is now corrected in the text. Regarding the Błękitne/Łazduny conundrum, numerous map services use "Błękitne" as the name, and it is formally recognized as a second name of the lake (coming from its clear waters). However, Łazduny is recognized as the formal name.

Line 264. How can you rule out enrichment of organically associated Fe in deep water resulting from abiotic hydrodynamic size sorting? This would then correlate with biogenic silica, also enriched in deep water due to hydrodynamic sorting.

We agree that we cannot, and we clearly didn't explore this venue as much as we could. We now rephrased this part as follows:

"Feorg is correlated with biogenic silica, consistent with its organic provenance, as Fe is an important nutrient and a constituent of diatom cells (Hutchins and Bruland, 1998). BSi, resulting mainly from the deposition of redox-resistant diatom valves (Smol and Stoermer, 2010), follows the expected pattern of hydrodynamic focusing, with the highest concentrations in the deepest areas. As diatom frustules often undergo hydrodynamic sorting and transport (Anderson, 1990), the same process could control Feorg, leading to its elevated concentrations in the deepest parts of the lake."

Reviewer 2

This study addresses the interpretation of Fe and Mn as redox proxies in lakes, which is a challenging topic in paleolimnology with implication to modern limnology, lake management and water quality. The dataset is extensive and the integration of modern limnology with sediment geochemistry is a novel approach. The study is based on state-of-the-art methods and is well-written. The paper demonstrates that geochemical focusing associated with seasonal oxygen dynamics can produce substantial enrichment of Fe and Mn in deeper basin sediments and links this to the pre-required conditions for varve preservation, reinforcing the need for spatial context when interpreting paleoredox indicators.

Overall, I don't have major comments, and I think the paper is sound and relevant. I'm sure this will be an important contribution that will guide others to conduct similar studies in other lakes. There are, however, still a few aspects that should be discussed in more detail in order to strengthen the major findings.

Thank you for your encouragement and constructive comments. Below we address your concerns, and provide our proposed amendments to the text.

1. **Building on the Anonymous Referee #1's second major point, I wonder whether the observed relationships between the geochemical composition of the sediments and sediment structure (homogeneous vs laminated) are better explained by depositional environment than by oxygenation alone. The Ti_clr distribution suggests strong spatial differences in terrigenous sediment delivery, with the littoral zone receiving substantially more detrital material than the deepest central area of the lake. This could affect sedimentological process such as reworked sediments and/or erosion due to a more energetic sediment influx, which might prevent the preservation of laminations at the littoral zone. So, the transition from homogeneous to laminated sediments may reflect not only changing oxygen conditions but also changing hydrodynamic energy and detrital sediment influx distribution. Because depth, oxygenation, Ti abundance, sediment structure, and Fe-Mn concentrations all covary, the current dataset does not fully disentangle these controls. I encourage the authors to discuss more explicitly whether laminated sediments and Fe-Mn enrichment may represent parallel responses to depositional setting rather than a direct oxygen-driven relationship. Perhaps, adding Fe/Ti and Mn/Ti plots to Figure 3 and Figure 7 might help.**

Indeed, we did not fully explore the fact that hydrodynamic energy and, therefore, for example, the transport of Ti and other detrital phases could explain some of our findings. One way we approached this control was to include water depth in the PCA (Fig. S03), but it was not stressed as much as it could be. We have now amended Figures 4, 7 and S04 with Fe/Ti as well as Mn/Ti (XRF) maps and plots, respectively. We also put additional emphasis on this in the text, starting in the results and discussion:

"Furthermore, redox-sensitive iron (Fe_{clr}) and manganese (Mn_{clr}) showed enrichment in the deepest, anoxic parts of the lake, with an overall pattern opposite to that of sulfur. Si_{clr}, Fe_{clr}, and Mn_{clr} exhibited a sharp increase with depth and the spatial extent of anoxia. After controlling for detrital input, Fe/Ti and Mn/Ti ratios suggest that the highest deposition of both metals is confined mostly to the deepest parts of the lake. Manganese departs from this pattern slightly, also showing elevated values close to the lake outlet."

And

"Manganese shows spatial patterns similar to those of iron (Fig. 5 and 6). However, the majority of Mn lies between the deposition of calcium-dominated carbonates and Fe-bearing matter (Fig. A3). Opposite trends in Mn concentrations relative to organic and terrestrial matter suggest that geochemical focusing controls manganese concentrations in the sediments. This is further strengthened by the spatial variability of Mn/Ti ratios, with the highest values observed in the deepest parts of the lake, except for the lake outflow, where hydrodynamically induced lateral transport could play a more important role."

And also

"Therefore, we interpret Fe and Mn concentrations as diagnostic of at least partially redox-dependent processes. Furthermore, the spatial variability of Fe/Ti and Mn/Ti (Fig. 4) indicates that both redox-sensitive metals are enriched in the deepest parts of the basin even after accounting for detrital input, arguing against detrital delivery as the main control on their distribution. We argue that the influence of hydrodynamic focusing, in which particulate matter is being transported, plays a less important role in Lake Łazduny, where the littoral zone is limited except in the northern part. This does not exclude the process but rather limits its magnitude. Our monitoring data, especially the depth of the oxycline and spatial Mn patterns, suggest a strong link between lake turnover, hypolimnetic oxygenation, and Mn burial in sediments."

And

"The lowest concentrations were associated with homogeneous sediments, while the highest were associated with laminated sediments. Similarly, Fe/Ti and Mn/Ti ratios followed patterns of both µXRF-derived and total concentrations based on sequential extraction, showing clear enrichment in the sediments from the deeper parts of the basin."

And

"Finally, below a depth of 14 m, the lakebed is primarily anoxic and is almost exclusively occupied by well-preserved laminated sediments. This demonstrates that oxygen conditions changing with the water depth control laminae preservation, providing evidence for the past extent of the hypolimnion. However, since wind stress and water column dynamics control mixing depth, the spatial variability of the sediments may also reflect mechanical sediment reworking, resuspension and resedimentation. Part of the relationships between detrital (Ti) and redox sensitive elements (Fe, Mn) could therefore be driven by transport processes, rather than geochemical focusing. Such sorting, however, would deposit finer fractions deeper in the lake, in contrast to coarser, detrital fractions, which are associated with erosive littoral zone and higher environment energy (Rowan et al., 1992). Then, Fe, Mn and Ti would covary, which is not a case in Lake Łazduny."

2. **It would be useful to provide more information on the composition and microfacies of the varves. Line 229-231 *"Sedimentation in Lake Łazduny follows the well-described pattern observed in other lakes with varved sediments (Zolitschka et al., 2015) with diagnostic calcite laminations (Tylmann et al., 2013a). During the warm season, increased primary production and higher water temperatures influence the epilimnetic pH and carbon budget, steering carbonate precipitation (Dean and Megard, 1993)".* This statement is not well-supported by element distribution across the lake (Fig. 3). The location of laminated sediments is associated with elevated biogenic Si rather than elevated Ca concentrations.**

The way we phrased it could certainly be improved. What we meant is that in Lake Łazduny, calcite layers are one of the diagnostic layers, marking a clear varve year beginning – this, compared to other Polish lowland lakes, is a characteristic. However, truthfully, biogenic silica and diatoms specifically do form a layer underlying calcite lamina – which can be seen under the microscope. Furthermore, not part of this study – but in the cores we observed thick (up to 1 cm) diatom layers intercalated between normal laminations. Therefore, if even though Ca is relatively less enriched in the deepest points, it is season-specific and forms a lamina, the same is true for Si and diatom frustules. Additionally, we do agree that the Ca deposition is elevated in the shallower water depths, partially because of the *Chara* that are growing in the photic zone of the lake. However, even though there is more Ca in the shallow waters, it cannot form laminations due to water dynamics and bioturbation.

Please see, for example:

"Furthermore, Charophyta meadows in the lake reside close to the shoreline, providing an additional source of algal organic matter and inducing calcite (CaCO3) precipitation. This could explain higher TIC concentrations in the shallow lake zones rather than in the lake's deepest points."

We have now rephrased the passage to take BSi into account.

"Sedimentation in Lake Łazduny follows the well-described pattern observed in other lakes with varved sediments (Zolitschka et al., 2015), with diagnostic calcite laminae forming in the warm season (Tylmann et al., 2013a). Most calcite laminae are preceded by the deposition of diatom frustules, which in places produce distinct, macroscopically visible layers. During the warm season, increased primary production and higher water temperatures influence the epilimnetic pH and carbon budget, steering carbonate precipitation (Dean and Megard, 1993)."

Other minor comments:

I think Figure 7 legend should read as "water depth" instead of "sediment depth"

We agree; it now reads "water depth".