

## ***Interactive comment on “Organic matter mineralization and trace element post-depositional redistribution in Western Siberia thermokarst lake sediments” by S. Audry et al.***

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General comments There is a large difference in pH between Shirokoe (around 3.5) and the two other lakes (5.1 and 5.6). What is regulating pH? This must be explained in the text. I do not believe DOC regulates the pH, because the DOC concentration is almost the same in all three lakes. The low pH in Shirokoe suggest a strong acid not a weak. Furthermore, why is the sulphate concentration so high in lake Shirokoe? This is only briefly discussed in the text. It appears to me that the low pH and high sulphate originates from pyrite weathering. Is this likely? This is a fundamental question. Is pyrite, or mono sulphides, present in the original peat or soil (bedrock?), or is it

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weathering of secondary sulphides formed in lakes? This could also explain temporary changes in the sulphate concentration. When the groundwater table is low, sulphides are oxidized by oxygen and high sulfate concentrations are obtained when the ground water is rising. Furthermore, it is well known that a suite of trace elements can be found in pyrite. The trace metal pattern in primary sulphides can thus be used as a fingerprint for trace metal distribution.

We agree that pyrite weathering could play a role in controlling pH and sulfate concentration of the water column. Pyrite content in the peat soils and/or bedrock surrounding the three thermokarst lakes was not determined. However, it has been reported that pyrite can be present in peat soils in fairly significant amounts (Dellwig et al., *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 167, 359-379, 2001). Therefore, high sulfate concentrations and low pH exhibited by Lake Shirokoe's water column compared to the two other lakes could be partially explained by strong pyrite weathering and the associated production of sulfuric acid in relation to higher pyrite weathering due to stronger lixiviation of the surrounding peat compared to the two other lakes. However, the concentration of H<sub>2</sub>SO<sub>4</sub> in Lake Shirokoe's water column alone cannot explain the low pH. Additional pH regulation is likely to be related to the concentration and the nature of DOC.

We agree that DOC concentration is almost the same in all three lakes. However, Pokrovsky et al. (*Biogeosciences*, 8, 565-583, 2011) clearly shown a decrease in the relative proportion of low molecular weight <1 kDa (1 kDa~1 nm) OC concentration along with a decrease in the concentration of total dissolved (<0.45 μm) OC in the course of lake maturation. This decrease was accompanied by an increase in the small size organic ligands and a simultaneous decrease in the proportion of large-size organic (humic) complexes of allochthonous (soil) origin. Therefore, a change in the nature, rather than a change in the total concentration, could partially explain the pH increase observed in the course of the lake maturation.

We suggested in the original manuscript that secondary (authigenic) sulfides form in

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the sediments of Lake Shirokoe and that these could partially be oxidized due to the influence of groundwater lateral fluxes, shallow near-surface run-off and shallow water table. However, oxidation of these secondary phases can hardly contribute to the observed high-sulfate and low-pH water column of Lake Shirokoe as: (i) porewater sulfate concentration decreases below detection limit towards the water-sediment interface (Fig. 7) and (ii) diffusive transport (Table 4) indicates that Lake Shirokoe's sediments are a sink (and not a source) of dissolved sulfate for the water column. The potential influence of pyrite weathering on pH and sulfate concentration of the water column is now discussed in the Section 5.3 (page 15, lines 472-492) of the revised manuscript according to the above argumentation. The geochemistry of other trace elements (trivalent and tetravalent elements, REEs, anions such as Mo, W, Ge, V) was also studied but will make the subject of another manuscript.

The oxidation of ammonium is strongly pH dependent (slow oxidation at low pH). This means that ammonium can migrate up into the water column from the sediment especially in lake Shirokoe. The authors should briefly discuss the significance of slow nitrification in relation to slow oxidation of ammonium at low pH, although ammonium was not measured.

We agree. The significance of slow nitrification in relation to slow oxidation of ammonium at low pH is briefly discussed in Section 5.2 (page 14, lines 431-433) in the revised manuscript.

The nitrogen species in the free water column should be displayed in table 1.

N-species data are not available for the water column of the three lakes

Detailed comments Page 8848, line 22. tremendous necessity. . . better with important "Tremendous" has been changed for "important" as suggested.

Page 8850, line 16. Table 1 does not show a change of DOC from 120 to 7 mg/l

We agree. We should not have mentioned Table 1 here.

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Page 8857, line 17. Is the dissolved nitrate shown in any figure?

Yes. Bottom water and porewater nitrate concentrations are shown in Figure 7.

Page 8858, line 20. Any explanation for the removal of Mn(II)?

As we stated in the manuscript: "there is no evidence of redox control on Mn chemistry" in Lake Shirokoe. This is supported by the nearly constant porewater Mn concentration within the first 5 cm of sediments ( $\sim 0.65 \mu\text{M}$ ; see Fig. 7). Therefore, the slightly higher dissolved Mn concentration in the bottom water ( $0.89 \mu\text{M}$ ; Fig. 7) compared to the first porewater sample at 1 cm depth below the water-sediment interface ( $0.63 \mu\text{M}$ ) might be due to adsorption of dissolved Mn onto mineral and/or organic particles. However, we thought that we do not have sufficient data to make our case and decided not to include any contention about that matter as it would have been too much speculative.

Page 8864, line 8. In the water column? No Figure is showing this. First it is stated Co and Ni are correlated with Fe. . . Cobalt is also likely to. . .?? Rephrase.

Water column results are shown in Pokrovsky et al., 2011 (Biogeosciences, 8, 565–583, 2011). We used these results to support our case regarding Co and Ni redox behaviors in the sediments. To avoid any ambiguity, we rephrased this portion of the text as follows: "Pokrovsky et al., (2011) showed that in the water column of the three thermokarst lakes, Co and Ni are correlated with Fe and likely to be adsorbed and/or coprecipitated with Mn oxyhydroxides."

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