Trace elements diagenesis associated with Fe-Mn Nodules formation in the sediments of limed lakes

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Thousands of boreal lakes have been limed in Scandinavia since the 1980's to counteract the effect of acidification, representing one of the largest lake geoengineering efforts to date. However, the geochemical legacy of such lake manipulations is poorly studied. Here, we measured the concentrations of alkali earth metals (Ca, Mg, Ba), metals (Mn, Fe, Al, Co, Cd, Pb), metalloids (As, Mo) and phosphorus (P) in 165 surface sediment samples from 17 limed lakes, as well as in sediment cores and porewater samples from two lakes with the highest sedimentary Fe and Mn. Our results indicate that the increase in pH at the sediment-water interface (SWI) of limed lakes has triggered Mn (oxy)hydroxide precipitation, yielding to the widespread formation of ferromanganese nodules. These nodules are enriched in trace elements, reaching for example 11500, 908 and 40 µg/g for Ba, Mo and As, respectively. Intense redox cycling of Fe and Mn at the SWI has redistributed trace elements in the sediment column. Thermodynamic modeling suggests that at the SWI: i) Ba, Co, Mo and Pb partitioned with Mn (oxy)hydroxides, ii) As and P partitioned with Fe (oxy)hydroxides and iii) Cd was was predominantly bound to organic matter. At depth and under sulfidic conditions, modelling points to trace elements being redistributed with sulfides. In contrast, P is either re-adsorbed onto Al oxides after the reductive dissolution of Fe(oxy)hydroxides, or precipitated as discrete $MnHPO_{4(s)}$ phases (saturation index = ± 0.1). We conclude that the diagenetic redistribution and partitioning of trace elements onto Fe-Mn nodules, rather than direct inputs of trace elements from liming, has elevated trace element burden in the sediments.