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Exploring water column $MnCO_3$ formation in a manganese-enriched redox-stratified lake.

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Deposition of marine sedimentary manganese deposits (SME) increased significantly post-GOE (Great Oxidation Event) within oceans that are inferred to have been redox-stratified. Deposition of SME requires oxidizing conditions (E^0 of 1.5V for Mn^{2+} oxidation) to form Mn-oxides and reducing conditions to immobilize Mn^{2+} in carbonate minerals, a prevalent host of Mn in SME. Characterizing the pathways of $MnCO_3$ formation under redox-stratified conditions is key to reconstructing environmental states after the GOE. Specifically, it is uncertain whether Mn-oxides would be reduced to Mn^{2+} at a water-column redoxcline or be buried in anoxic sediments to undergo diagenetic transformation to $MnCO_3$. Steel Lake in north-central Minnesota is a unique “manganiferous” lake with oxygenated surface waters and high Mn/Fe ratios (~1500), resulting in high dissolved manganese (Mn) concentrations (100 μmol/L) in deep waters. Like other redox-stratified aquatic systems, abundant particulate Mn-oxides form above the redoxcline, resulting in high dissolved Mn within the redoxcline due to reductive dissolution of sinking Mn-oxides. The lake watershed overlays glacial till, sand, and calcareous-carbonate-rich sediments, producing waters of moderate alkalinity. The $\delta^{13}C_{DIC}$ values decrease across the redoxcline (-5.94‰ to -10.59‰, VPDB). These values, and increasing DIC concentrations with depth, are consistent with organic carbon remineralization at and below the redoxcline. Combined with the Mn^{2+} enhancement, we hypothesized that $MnCO_3$ could precipitate below the redoxcline.

Pink particulate material is routinely collected from filtered water at and below the redoxcline, which could be consistent with minerals such as rhodochrosite ($MnCO_3$). Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) of these precipitates signifies a Ca-Mn-Fe-rich phase surrounding calcareous and siliceous biogenic materials. Sediment trap samples were analyzed with X-ray absorption spectroscopy (XAS) and will be used to determine the oxidation state and mineralogy of this enriched Mn phase. X-ray diffraction and X-ray fluorescence data from surface sediments also indicate that carbonate minerals, such as calcite, are enriched in Mn and Fe. XAS of lake sediments will be used to determine if Mn-oxides are present in sediments. These results will provide insight into whether $MnCO_3$ minerals form via water-column precipitation instead of or in addition to sedimentary diagenetic formation.