

Manganese carbonates linked to methane oxidation in ferruginous environments

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Manganese (Mn) carbonates (e.g. rhodochrosite, MnCO_3) with negative $\delta^{13}\text{C}$ compositions are widely distributed in the geologic record, and are generally assumed to represent the products of diagenetic reduction of precursor manganese oxides (e.g. MnO_2) with an organic carbon electron donor. This assumption underpins the utilization of sedimentary manganese enrichments (SMEs) as paleoredox proxies, given the strong oxidizing potential required to form manganese oxides. However, few studies have examined Mn mineral genesis in ferruginous environments where the methane cycle plays a prominent role in metal cycling. Here we present Mn, methane, and carbon isotope data from newly documented ferruginous lakes, whose strongly reducing water columns readily dissolve manganese oxides before they can reach sediments. At the chemocline of Brownie Lake in Minnesota, calcite dissolution coupled with methane oxidation creates a pulse of alkalinity within a substantial pool of dissolved Mn, triggering rhodochrosite saturation. The oxidation of methane also strongly shifts carbon isotope composition of dissolved inorganic carbon (DIC) to negative values, consistent with carbon isotope measurements reported from manganese carbonates in the rock record. Compositional maps of iron-manganese carbonates from Otter Lake, Michigan display pronounced crystal zoning with Mn concentrated in the crystal core, and coated with an iron rim. Together with previous reports of rhodochrosite from lake systems, these new data suggest that suboxic methane oxidation is a viable trigger for manganese carbonate precipitation that may mimic the isotopic signatures of diagenetic oxide reduction. If confirmed, this hypothesis suggests the utilization of carbonate-rich SMEs as an indicator of strongly oxidizing environments should be carefully re-evaluated.