Could negative carbonate carbon isotope excursions be a primary signal in ferruginous environments?

CHAD WITTKOP[1], ELIZABETH D. SWANNER[2], NICHOLAS LAMBRECHT[3], ASHLEY GRENGS[1], AND SERGEI KATSEV[3]

[1] Minnesota State University, Department of Chemistry & Geology, Mankato, MN, USA, chad.wittkop@mnsu.edu
[2] Iowa State University, Department of Geological & Atmospheric Sciences, Ames, IA
[3] Large Lakes Observatory, University of Minnesota, Duluth, MN

The negative $\delta^{13}C$ compositions of manganese (Mn) carbonates (e.g. rhodochrosite, $MnCO_3$) are widely assumed to represent the products of diagenetic reduction of precursor Mn-oxides (e.g. MnO_2) coupled with organic carbon oxidation. While this pathway for Mn-carbonate genesis is viable in many environments, the strongly reducing water columns postulated in most Archean and early Proterozoic settings would inhibit deposition of precursor Mn-oxides. Methane (CH_4) oxidation offers an alternative pathway to Mn-carbonate precipitation in ferruginous settings, where it would also generate negative carbonate $\delta^{13}C$, but proceed in weakly oxidizing environments where Mn would remain reduced and dissolved.

To evaluate the role of CH_4 oxidation in Mn-carbonate genesis we examined Mn and carbon cycling in ferruginous Brownie Lake, Minnesota. Here dissolved Mn accumulates at and below a shallow chemocline where waters rapidly transition from oxic to ferruginous, with deep waters significantly enriched in dissolved iron and CH_4. Field monitoring identifies a zone of CH_4 oxidation initiating at the base of the chemocline in suboxic conditions and coinciding with a transition from calcite saturation to Mn-carbonate saturation. Reactive transport modeling of this zone suggests calcite dissolution plays a key role in buffering CO_2 addition from CH_4 oxidation, and dissolving calcite crystals provide nucleation sites for Mn-carbonates. Elemental mapping of Ca-Mn-Fe carbonates from lake sediments supports these findings, and documentation of carbonate particulate phases from ferruginous field sites is currently underway. Scaling these analogs to marine pH consistent with Archean-Proterozoic conditions generates additional Mn-carbonate mineral saturation. This model may also extend to some well-preserved examples of Precambrian Fe-carbonates.