

Hydrothermal braunite synthesized under simulated diagenesis of manganese oxides with reduced manganese: Implications for the ancient manganese cycle

KAITLIN KOSHURBA AND JENA E. JOHNSON

University of Michigan

Presenting Author: kaitkosh@umich.edu

Manganese containing minerals are effective paleo-redox proxies due to this transition metal's ability to exist in a wide range of valence states and its high redox potential. Reduced manganese (Mn^{2+}) is soluble and only undergoes low-level mineralization (<1 wt %) in carbonate rocks when substituting for Ca^{2+} . This metal is only deposited in considerable quantities in its oxidized forms (Mn^{3+} and Mn^{4+}) as insoluble (oxyhydr)oxides, and reduced manganese generally requires oxygen or O_2 -related species to form these oxides. Therefore, manganese enrichments are usually inferred to indicate the interaction between Mn^{2+} and oxygen.

Braunite [$Mn^{2+}Mn^{3+}_6O_8(SiO_4)$], a partially oxidized manganese silicate, is a pervasive component of Paleoproterozoic and Neoproterozoic sedimentary manganese deposits, which are typically associated with fluxes in global oxygen. Braunite's sedimentary textures suggest that this mineral is a product of diagenesis; however, like many diagenetic minerals, the precursor precipitates and post-depositional processes that lead to braunite's mineralization are poorly constrained. Understanding braunite's mineralization process should illuminate the depositional and biogeochemical history of braunite-containing manganese enrichments and enhance our paleoenvironmental interpretations of these deposits. We hypothesized that the requisite conditions for braunite mineralization involve the deposition of a manganese oxide precursor mineral that subsequently undergoes diagenetic reactions with aqueous silica and Mn^{2+} present in sedimentary porewaters. We tested this idea by synthesizing a Mn^{3+} -oxide, feitknechtite ($MnOOH$), and conducted experiments aging this synthetic mineral at diagenetic temperatures in a siliceous solution including and omitting aqueous Mn^{2+} . At the end of the aging period, we identified braunite had formed in solutions containing both aqueous silica and Mn^{2+} . In siliceous solutions that lacked reduced manganese, we identified the precipitate as manganite ($MnOOH$) a polymorph of our experimental precursor. The transformation of precursor manganese oxides to form braunite upholds this mineral's capability to be used as an indicator for manganese oxidation, and thus most likely implies oxygenation or dynamic oxygen levels during precursor mineral deposition. Our results further demonstrate the importance of reduced manganese, and thus reducing porewaters, for braunite mineralization to occur.