Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.36533

Missing manganese in Banded Iron Formations: Untangling pre-oxidation Archean iron deposition

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The Archean Earth was strikingly different from the modern due to the absence of oxygen until after the 2.45 Ga Global Oxidation Event (GOE). Earth's anoxic atmosphere coincided with a reducing ocean, generating the accumulation of aqueous metals such as iron (Fe^{2+}) and manganese (Mn^{2+}). Predating the evolution of silica-biomineralizing organisms, the Archean ocean would have contained silica at or near saturation concentrations. This markedly different oceanic chemistry led to the deposition of Banded Iron Formations (BIFs), which are iron- and silica-rich layered deposits unique to the Precambrian ocean. With a poor fossil record prior to 2 Ga, BIFs illuminate metal (bio)geochemical cycling on the Early Earth. Despite the enrichment of Mn in the Archean Ocean, pre-GOE BIFs contain markedly low Mn concentrations. Hypothesized initial progenitors of BIFs include phases with oxidized iron, such as iron oxides and green rust, which would likely involve iron redox cycling and exclude reduced Mn^{2+}. However, an emerging view proposes that the iron silicate greenalite [$Fe^{2+}_3Si_2O_5(OH)_4$] was the precursor phase of BIFs. It is unknown whether greenalite incorporates aqueous manganese during its formation, but this behavior could indicate the plausibility of the original greenalite hypothesis. We synthesized greenalite at high pH and under reducing conditions in synthetic seawater solutions containing variable aqueous Mn and dissolved inorganic carbon concentrations to assess whether Mn would be incorporated into the silicate's structure. Our experiments yielded a Mn-free greenalite under all conditions and demonstrated that Mn was excluded from the final mineral assemblage under most Mn^{2+} concentrations, consistent with the BIF record. Our findings suggest that greenalite, formed without O_2 or other redox activity, is a viable precursor mineral to generate Banded Iron Formations. Archean BIFs formed entirely by ferrous greenalite would support a sharp, rather than gradual, rise in oxygen around the GOE.