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# Fe(II) Oxidation in a Simulated Precambrian Upwelling Zone Produces Fe(II,III)-Silicates That Transform Into Green Rust

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Iron- and silica-rich sedimentary deposits known as Banded Iron Formations (BIFs) record Archean and Paleoproterozoic seawater chemistry, but our reconstructions are hindered by an incomplete understanding of what the initial precipitate and deposited sediment were. Typically, the oxidation of upwelled aqueous Fe(II) in the near-surface ocean are thought to produce BIF precursor phases. Experimental simulations replicating Fe(II) oxidation in upwelling zones are needed to resolve the identity of primary BIF minerals and the mechanisms of their formation and transformation before we can accurately interpret the BIF record. However, traditional batch experiments where Fe(II) is depleted cannot replicate the persistently Fe(II)- and Si-rich waters of a Precambrian upwelling zone. To more accurately mimic this Precambrian environment, we designed a continuous flow reactor to maintain high dissolved Fe(II) and Si levels in synthetic seawater during Fe(II) oxidation. We characterized both the earliest-forming precipitates as well as phases that were aged in the presence and absence of dissolved trace oxygen ($O_2$). Here we show that partial Fe(II) oxidation in a consistently ferruginous system initially produces Fe(II,III)-silicates, which then transform into green rust via Fe(II)-catalyzed recrystallization. Our results demonstrate that mixed-valence Fe-silicates can be original products of $O_2$-mediated iron oxidation. Furthermore, the initial phases formed in seawater can undergo substantial mineralogical and compositional changes within hours after precipitation, such as our observations of secondary green rust. Reconstructions of ancient ocean chemistry based on BIFs must therefore account for potential initial Fe(II,III) silicates that are subject to recrystallization during particle export, resulting in multiple iron phases reaching the seafloor.