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Spatial decoupling of iron oxidation and deposition in Precambrian oceans: A colloidal iron shuttle model inspired by a Pleistocene iron-rich rock from Milos, Greece

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Precambrian banded iron formations (BIFs) are critical archives of Earth's early biogeochemical cycles, yet the mechanisms of the iron transport and the precise locus of Fe-oxidation are still under debated. Traditional models often assume *in situ* oxidation of dissolved Fe(II) within the water column directly above depositional sites. This study provides a new perspective using unmetamorphosed Pleistocene iron-rich sedimentary rocks from Milos Island, Greece, which serve as a mineralogical analogue for BIFs. High-resolution scanning electron microscopic results reveal that Fe is predominantly hosted in hematite nanoparticles (0.1–0.75 μm) and their framboidal aggregates (6-22 μm). Mössbauer spectroscopy reveals that the hematite is poorly (hyperfine fields of 46.75-49.46 T) to mediumly (50.59-50.73 T) crystalline. Raman spectra further exhibit a prominent band shift at ca. 650 cm^{-1}, diagnostic of nanoscrystalline hematite. Both the morphology and sizes of the hematite particles are characteristic of typical aqueous colloids. Notably, energy dispersive X-ray spectroscopic mapping results demonstrate that carbonaceous materials are exclusively associated with hematite aggregates but absent from individual nanoparticles. These findings suggest that the Fe was likely transported as stable (oxy)hydroxide colloids, with organic matter and silica facilitating their subsequent aggregation and deposition. Based on the mineral genetic similarities between the studied samples and BIFs, this colloidal mechanism implies that Fe(III) nanoparticles in BIFs may reflect *ex situ* oxidation in distant regions rather than solely indigenous microbial processes at the depositional site, because colloids can migrate over significant distances. This colloidal iron shuttle model offers a refined framework for interpreting the spatial decoupling of redox processes in early Earth's biogeochemical cycles.