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Siderite precipitation from a carbonate green-rust precursor in ferruginous Canyon Lake

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Siderite ($FeCO_3$) is an important component of Precambrian iron formations (IFs), and is frequently reported in the sediments of modern ferruginous lakes [1]. The mineral is generally interpreted as diagenetic, resulting from reduction of primary iron oxides coupled to organic carbon oxidation. While this diagenetic pathway satisfactorily explains both the carbon isotope composition and textures observed in many siderite occurrences, some examples are not consistent with this interpretation, and a direct precipitation pathway for siderite has long been suspected. To evaluate this possibility, we examined Fe- and Mn-phases in water column particulates and sediments from ferruginous Canyon Lake in Michigan, USA.

Anoxically-preserved sediment trap and sediment samples analyzed by both XANES and EXFAS techniques show that short-range ordered Fe-oxides in the upper water column begin a conversion to carbonate green rust (GR) in the deep ferruginous water column. Manganese phases remain largely reduced in the water column. Surface sediment samples contain a mixture of GR and a reduced-Mn phase. In a zone about 60-cm below the lake floor, both GR and rhodochrosite were indicated by XANES, and siderite is indicated by X-ray diffraction and scanning electron microscopy. Porewater dissolved inorganic carbon ranges from 4.2 to 8.0 mM in the sediments.

The detection of co-existing rhodochrosite and GR in sediment samples suggests that kinetics may favor Mn-carbonate precipitation before siderite, even if the latter is more thermodynamically favored. Rhodochrosite crystals would also provide nucleation sites for siderite, which helps explain the widespread observation of Mn-enriched siderites (manganosiderite) in IFs. In contrast to other recently-documented siderite occurrences, we observed no evidence of a significant Fe-oxide reservoir entering the sediments, and the micritic siderite crystals in Canyon Lake are more similar in size and occurrence to siderite varves [e.g. 1] and well-preserved carbonate IFs than the large crystal aggregates observed in Lake Towuti [2]. Our work demonstrates a viable, direct carbonate precipitation pathway for siderite in ferruginous environments, and offers further evidence for the importance of GR as a precursor in IF genesis.

[1] Swanner *et al.* (2020) *Earth Sci. Rev.* **211**, 103430. [2] Vuillemin *et al.* (2019) *Geology* **47**: 540-544.