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Diagenetic siderites and vivianites in ferruginous sediment from Lake Towuti, Indonesia.

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Lake Towuti is a deep tectonic basin surrounded by ultramafic rocks and lateritic soils. Its geographic position in central Indonesia and relatively great age (estimated $>$500 ky) makes the lake a prime location to record paleoclimatic changes in the tropical Western Pacific warm pool in its sedimentary sequence. It was therefore chosen as a drilling target by the International Continental Drilling Program (ICDP). Ultramafic rocks and lateritic soils eroded from the catchment supply Lake Towuti with little sulfate but considerable amounts of iron oxyhydroxides/oxides. In the monimolimnion, bottom water anoxia allows for microbially-mediated iron reduction. The extreme scarcity of sulfate and nitrate/nitrite in Lake Towuti's anoxic bottom water represents conditions analogous to those of the Archean Ocean. Nevertheless, Lake Towuti may mix on occasion, resulting in transient oxygenation of its bottom water, which could profoundly change paleoclimatic and microbiological proxies. These geochemical conditions, which are relatively rare on the modern Earth, make Lake Towuti an ideal site to study iron mineral formation and diagenesis under conditions relevant to the early Earth.

In May to July 2015, the ICDP Towuti Drilling Project recovered a total $>$1000 m of sediment cores from three sites, including a 114 m long core dedicated to geomicrobiological studies. Siderite ($FeCO_3$) was recovered from 50 distinct layers and investigated to assess authigenesis. Vivianite ($Fe_2[PO_4]_2 \cdot 8H_2O$) was found in 5 different horizons and the crystals handpicked. SEM and TEM imaging showed that siderites exist as both micritic phases and mosaic monocrystals, developing strong twinings and aggregation in deeper samples. Elemental mapping revealed Mn/Fe zonations with Mn enrichment in the center of the minerals, implying mineral formation and growth under variable pore water chemistry. Green rust ($Fe_6[OH]_{12} \cdot [CO_3 \cdot 2H_2O]$) and magnetite ($Fe_3O_4$) were observed in association within individual siderite specimens, suggesting multiple and variable diagenetic pathways and potential oxidative overprinting. The presence/absence of siderite and vivianite may reflect dynamics at the paleo water–sediment interface, and ensuing variability in the relative burial of ferric iron, phosphorus, and organic matter and subsequent diagenetic processes in the sediment. Notably, we observe siderite-rich intervals that are entirely devoid of vivianite. These siderites display heavy $\delta^{13}C$ but light $\delta^{56}Fe$ compositions. In contrast, siderites, which are less abundant in vivianite-containing intervals, display persistent light $\delta^{13}C$ and $\delta^{56}Fe$ compositions.