Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.15839

Isotope signatures of siderites spanning 1 Ma of depositional historyin ferruginous Lake Towuti.

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Lake Towuti is a deep tectonic basin surrounded by ultramafic rocks and lateritic soils whose weathering supplies considerable amounts of iron (oxyhydr)oxides. Under stratified conditions, particulate iron dissolves in the monimolimnion following microbial reduction of ferric iron with minor sulfate reduction, turning these anoxic bottom waters into a potential ferruginous analog of the early oceans. Lake Towuti's relatively great age makes its mineralogy a prime recorder of depositional redox processes and microbial diagenesis. Siderites ($FeCO_3$) and vivianites ($Fe_2[PO_4]_2 \times 8H_2O$) were recovered from distinct layers along a 1 Ma sediment archive. SEM/TEM imaging documented diagenetic growth of siderites from micritic phases into twins and aggregates, forming spherules of mosaic monocrystals with increasing burial depth. Continuous growth of vivianite crystals proceeded from tabular to rosette habits, forming large nodules in the sediment. Mineral inclusions, consisting of framboidal magnetite (Fe_3O_4) and millerite (NiS), indicated microbial reduction of iron and sulfate antecedent to the formation of siderite and vivianite. Pore water profiles showed that magnetite, millerite, siderite, and vivianite precipitated successively in soft sediments as pore waters gradually saturated during microbial remineralization of organic matter and reduction of electron acceptors. Analysis of oxygen, iron, and carbon isotope compositions of siderites allowed disentangling depositional and diagenetic signals in terms of past redox conditions and ensuing relative burial of ferric iron and organic matter. Siderite $\delta^{18}O$ signatures reflected in-lake hydrological conditions, e.g. enhanced lake evaporation during the Last Glacial Maximum. Low negative $\delta^{56}Fe$ values recorded periods of water column stratification and oxygenation events, with minor partitioning of Fe isotopes after deposition. In contrast, negative $\delta^{56}Fe$ values measured on vivianites pointed to diagenetic dissolution of ferric/ferrous phases and incorporation of kinetically fractionated light Fe^{2+} into the crystals. Siderite $\delta^{13}C$ signatures reflected incorporation of biogenic HCO_3^- produced during sediment organic matter remineralization, whereas positive $\delta^{13}C$ excursions indicating increased biogenic production of methane following mass balance. While the morphologies, inclusions and isotope compositions of siderite grains traced microbial reducing processes, overgrowth on siderite nuclei during ~1 Ma of burial partially attenuated the depositional signal inherited from paleolake bottom waters to integrate microbial diagenesis prior to lithification.