Authigenic minerals reflect microbial control on pore waters in a ferruginous analogue

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Abstract

Ferruginous conditions prevailed in the oceans through much of Earth’s history. However, minerals recording these conditions remain difficult to interpret in terms of biogeochemical processes prior to lithification. In Lake Towuti, Indonesia, ferruginous sediments are deposited under anoxic sulfate-poor conditions similar to the Proterozoic oceans, allowing the study of mineralogical (trans)formations during microbial diagenesis. Comprehensive pore water geochemistry, high resolution geochemical core profiles, and electron microscopy of authigenic minerals revealed in situ formation of magnetite, millerite, and abundant siderite and vivianite along a 100 m long sequence. Framboidal magnetites represent primary pelagic precipitates, whereas millerite, a sulfide mineral often overlooked under sulfate-poor conditions, shows acicular aggregates entangled with siderite and vivianite resulting from saturated pore waters and continuous growth during burial. These phases act as biosignatures of microbial iron and sulfate reduction, fermentation and methanogenesis, processes clearly traceable in pore water profiles. Variability in metal and organic substrates attests to environment driven processes, differentially sustaining microbial processes along the stratigraphy. Geochemical profiles resulting from microbial activity over 200 kyr after deposition provide constraints on the depth and age of mineral formation within ferruginous records.

Introduction

Ferruginous conditions (iron-rich, sulfate-poor) were widespread in the Archean and Proterozoic oceans and resulted in the deposition of ancient iron formations (Canfield et al., 2008). Precambrian iron formations are composed of diverse iron oxides and carbonates thought to have formed as primary pelagic precipitates, whereas millerite, a sulfide mineral often overlooked under sulfate-poor conditions, shows acicular aggregates entangled with siderite and vivianite resulting from saturated pore waters and continuous growth during burial. These phases act as biosignatures of microbial iron and sulfate reduction, fermentation and methanogenesis, processes clearly traceable in pore water profiles.

Modern analogues to Earth’s early oceans (Swanner et al., 2020) that allow the study of both modern pore water geochemistry and short term diagenetic evolution of ferruginous sediments are scarce. One such environment is the ferruginous sediments deposited in the Malili Lakes (Russell et al., 2016), a chain of five interconnected tectonic lakes hosted in variably weathered (ultra)mafic rocks on Sulawesi, Indonesia (Fig. 1a, b). Lateritic erosion of the catchment supplies considerable amounts of iron (oxyhydr)oxides, but little sulfate, to the lakes (Morlock et al., 2018). Lake Towuti (2.5° S, 121° E), with a maximum water depth of ca. 200 m, is presently oxygen depleted below 130 m depth (Fig. 1c) displaying a persistent monimolimnion wherein primary ferric iron phases, mostly ferrihydrite (Fe₃O₄ · 0.5H₂O), undergo reductive dissolution (Bauer et al., 2020). Subsequent sediment (trans)formation during early diagenesis (Vuillemin et al., 2019, 2020) precipitates secondary mineral phases, such as siderite (FeCO₃) and vivianite (Fe₃[PO₄]₂ · 8H₂O). Geomicrobiological investigations have shown that iron-, sulfur- and methane-related biogeochemical processes coexist in Lake Towuti sediments (Vuillemin et al., 2019).
Due to extremely low sulfate concentrations (<20 μM), sediment organic matter (OM) remineralisation proceeds mainly through methanogenesis (Friese et al., 2021). These sedimentary conditions make Lake Towuti a unique ferruginous analogue in which to study the evolution of pore water geochemistry under the influence of microbial reduction and mineral (trans)formations prior to sediment lithification (Vuillemin et al., 2023).

Here, we analyse one 100 m long sediment sequence to investigate the link between putative microbial processes and geochemical gradients under which authigenic minerals precipitate. We present detailed pore water geochemistry and high resolution geochemical gradients under which authigenic minerals precipitate during the evolution of pore water geochemistry (Vuillemin et al., 2023). Using transmitted light and scanning electron microscopy (SEM), we illustrate characteristic authigenic mineral phases, namely magnetite (Fe₃O₄), millerite (NiS), and siderite and vivianite, which occur in varying quantities throughout the stratigraphy. Together these data document the direct precipitation of successive phases from pore waters, highlight microbial processes of sediment remineralisation underlying reductive diagenesis, and allow us to establish mineral biosignatures in ferruginous records.

Results and Discussion

Authigenic mineral shapes and compositions can be employed to trace changes in redox controlled variations in water and pore fluid geochemistry associated with microbial processes in the upper sediment sequence. If mineral precipitation continues during burial, their signatures deviate from the stratigraphic context.

Pore water geochemical evolution and mineral precipitation. Reducible iron oxides in sediments originate from lateritic weathering of Towuti’s (ultra)mafic catchment (Morlock et al., 2018) and authigenic oxidation of ferrous iron in the water column (Sheppard et al., 2019). Consequently, alternating red and green sediments reflect variations in the composition, abundance and changes in iron oxidation state through time (Russell et al., 2020). During settling when the water column is stratified, particulate iron undergoes partial reductive dissolution in the monimolimnion (Bauer et al., 2020), precipitating pelagic framboidal magnetites (Fig. 2a). Currently bottom waters contain ca. 20 to 12 μM sulfate (Vuillemin et al., 2016), promoting sulfate reduction rates (SRR) that are highest at the sediment water interface (SWI) and drastically drop within the upper 20 cm blf (Fig. 3a). In contrast to euxinic conditions under which Fe sulfides (e.g., mackinawite) act as the primary Ni-hosting phases (Mansor et al., 2019), iron sulfides were not observed. Under the present ferruginous conditions, sulfate reduction with organic carbon as the reductant produces sulfide that reacts with nickel (Fig. 4) and precipitates millerite (NiS). The habits of millerite identified at 0.2 m blf and deeper suggest both pelagic
precipitation and post-depositional growth at the SWI and in shallow sediments during active sulfate reduction (Fig. 2b).

Due to stratification in ferruginous Lake Towuti, the main terminal electron acceptors (i.e. $O_2$, $NO_3^-$, $SO_4^{2-}$) are rapidly depleted in the sediment (Figs. 1, 3a), which implies that anaerobic OM degradation should proceed via mineral ferric iron and $CO_3^{2-}$ reduction. Reductive dissolution of hydrous ferric oxides (e.g., ferrihydrite) continues in shallow sediments releasing substantial amounts of $Fe^{2+}$ (278 μM) to the pore water (Fig. 3a).

Below 50 cmblf, because goethite and magnetite represent the main reducible ferric phases remaining in sediments (Figs. 2a, S-1), fermentation is preferentially performed over microbial respiration of less reactive substances (Friese et al., 2021). Nevertheless, steadily increasing metal concentrations in pore water (Mn, As, Co) suggests that Fe reduction concomitant with fermentation (Fig. 3a) continues at slow rates, promoting the dissolution of less reactive ferric-ferrous phases during burial.

From 1 to 10 mbf, pore water $NH_4^+$, $PO_4^{3-}$ and VFA concentrations provide concomitant evidence of microbial OM degradation (Fig. 3a). Between 30 cmblf and 5 mbf, formate, lactate, acetate and butyrate concentrations vary with metabolic production and consumption (i.e. acidogenesis, acetogenesis). Below
5 mblf, persistently low VFA concentrations (<20 μM) indicate complete remineralisation to methane (Friese et al., 2021) accompanied by a decrease in microbial uptake of PO₄³⁻. Such stepwise fermentation and steady increase in DIC define the depth at which pore waters reach siderite saturation (Vuillemin et al., 2019). The pore water pH (7.1–7.5) implies that this biogenic DIC reacts in the form of HCO₃⁻ with dissolved Fe²⁺ to consistently precipitate siderite between 50 cmblf and 5 mblf.
of the SWI produces HS\textsuperscript{−} concentrations (served as such in the sediment (Fig. 2a). Even at low sulfate concentrations, which are inherent to microbial growth and methanogenesis lasting 200 kyr after deposition. These precipitation stages, which are observed at the onset of vivianite precipitation (Fig. 2d) after siderite (Vuillemin et al., 2020). Ca\textsuperscript{2+} and Mg\textsuperscript{2+} concentrations drop around 15 mblf, suggesting that PO\textsubscript{4}\textsuperscript{3−} supplies CO\textsubscript{3}\textsuperscript{2−} for precipitation with Fe\textsuperscript{2+} and Mn\textsuperscript{2+} available in pore water (Fig. 3).

Pore water geochemical profiles in Lake Towuti’s upper sediment column stem from microbial activity and dissolution—precipitation of specific mineral phases (Figs. 2, 3). We observe a characteristic succession of authigenic mineral precipitation as a function of chemical equilibration of ferruginous pore waters (Jiang and Tosca, 2019) during anaerobic respiration of terminal electron acceptors and sediment OM remineralisation. Namely, magnetite, millerite, siderite, and vivianite represent biosignatures of microbial iron and sulfate reduction, fermentation and methanogenesis lasting 200 kyr after deposition.

Geochemical gradient and continuous mineral overgrowth. Based on the geochemical gradient that developed in Lake Towuti’s upper 25 m of sediment (Fig. 3a) and pH-Eh stability fields for authigenic minerals (Figs. 2, 3), we estimated that the initial environments of formation for magnetite, millerite, siderite, and vivianite correspond to the monomilomamion, SWI, shallow (<1–5 mblf) and deep sediments (>15 mblf), respectively. These precipitation stages, which are inherent to microbial processes, can overlap according to the geochemical gradient that develops in anoxic waters and sediments (Fig. 3a, b).

In Lake Towuti, some framboidal magnetites form as pelagic precipitates in the chemocline (Fig. 1c) during periods of water column stratification (Bauer et al., 2020) and are preserved as such in the sediment (Fig. 2a). Even at low sulfate concentrations (<20 μM), microbial sulfate reduction in the vicinity of the SWI produces HS\textsuperscript{−} in pore water which preferentially reacts with Ni\textsuperscript{2+} over Fe\textsuperscript{3+} to form millerite, incorporating minor Fe and trace metals (Figs. 2b, S-2 and S-3). The spherical habits fused into acicular aggregates of authigenic millerite originating from microbial sulfate reduction appear in places with early siderite phases, or fully overgrown by siderite (Figs. 2b, S-3). Furthermore, millerite aggregates within siderite-rich zones (Fig. S-4) suggest increased millerite precipitation during deeper mixing phases and oxygenation of the sediment water interface, sulfate reduction taking place predominantly around the redox front within the upper few centimetres of the sediment column (Fig. S-5).

Crystallisation of successive phases from pore waters and the entangled habits that we observe (Fig. 2) reveal a certain degree of Ostwald ripening where smaller precursor crystals dissolve and re-precipitate allowing larger crystal nuclei to further grow over time of burial (Fleming and Waychunas, 2008). As demonstrated for redox (trans)formation of green rust (Haley et al., 2017), pore water solutions become saturated with ferrous colloids (Moens et al., 2021) that react with either carbonic or phosphate ions over time to form siderite monocrystals (Vuillemin et al., 2019) and vivianite nodules (Vuillemin et al., 2020). Siderite SEM images document diagenetic growth from micritic phases into twins and aggregates, forming spherules of mosaic monocrystals (Fig. 2c) promoted by saturated pore water conditions during burial (Table S-1). Similarly, vivianite SEM images reveal crystal growth from tabular habits into rosettes (Fig. 2d), forming macroscopic crystals due to diagenetic diffusion during burial, indicating that vivianite constitutes an important sink for Fe\textsuperscript{2+}, Mn\textsuperscript{2+} and Mg\textsuperscript{2+} in pore waters that reached saturation in specific sedimentary layers. Millerite and siderite inclusions identified in a vivianite crystal cross section suggest that these phases precipitated first (Fig. 2d). Finally, EDX results (Figs. 2, S-2) show that magnetites have minor trace metal concentrations, millerites incorporate some Fe\textsuperscript{2+}, siderites substitute Mn\textsuperscript{2+} in their initial growth phase, while later forming vivianites have an overall manganese composition substituting both Mn\textsuperscript{2+} and Mg\textsuperscript{2+} (Kubeneck et al., 2023).

Mineral biosignatures in their recent and ancient stratigraphic context. The mineralogy of Lake Towuti presents an alternation of dark green to reddish-grey clays, considered to reflect detrital iron fluxes to the lake, stratification regimes, and redox conditions at the SWI (Russell et al., 2016, 2020). Variations in the burial of ferric iron and OM, their availability as substrates and the pore water geochemistry (Fig. 4) ensuing microbial breakdown, can imprint different mineral biosignatures during early diagenesis (Morlock et al., 2021). Each of these minerals, whether forming in the water column, near surface sediments or from pore waters, acts as a discrete sink for selective solutes (i.e. Ni\textsuperscript{2+}, Mn\textsuperscript{2+}, Fe\textsuperscript{2+}, CO\textsubscript{3}\textsuperscript{2−}, HS\textsuperscript{−}, PO\textsubscript{4}\textsuperscript{3−}). Pore water profiles thereby provide constraints on the depth of formation and age difference with the stratigraphy. Yet their abundance along the stratigraphic record results from past depositional modes and redox biogeochemistry.

Iron inflows deposited under oxygenated conditions formed red clay beds containing abundant, but poorly reactive, detrital magnetites and diagenetic siderites (Vuillemin et al., 2023). Millerites were also found in red clays in which slightly more sulfate was available for microbial reduction at the time of deposition (i.e. ~20 μM). These magnetites and millerites were progressively overgrown by diagenetic siderite during burial. While framboidal magnetites and spherical millerites represented pelagic precipitates forming under stratified conditions, vivianites nucleated from diffusive pore waters in greenish clays. To conclude, we could show that millerite precipitates in ferruginous anoxic waters and shallow sediments at sulfate levels relevant to sulfur cycling in Earth’s early oceans (Farquhar et al., 2010). Whereas vivianite preservation over a geologic scale is compromised, continuous precipitation of siderite from saturated pore waters forms spheroids that can coalesce into lithified bands like those documented in ancient red beds.

Acknowledgements

The financial, logistic and administrative support of the International Continental Scientific Drilling Program (ICDP), U.S. National Science Foundation (NSF), German Research Foundation (DFG), Swiss National Science Foundation (SNSF), PT Vale Indonesia, Ministry of Research, Education, and Higher Technology of Indonesia (RISTEK), U.S. National Lacustrine Core Repository, DOSECC Exploration Services, and GFZ German Research Centre for Geosciences is acknowledged. This study was financed through DFG grants of the ICDP priority program to JK (KA 2293/8-1) and AV (VU 94/1-1, VU 94/1-1). Similarly, vivianite

Editor: Andreas Kappler