

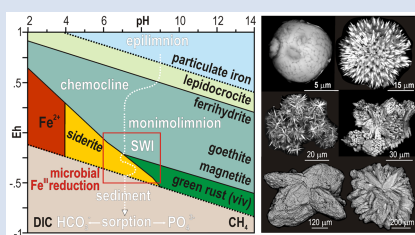
Authigenic minerals reflect microbial control on pore waters in a ferruginous analogue

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<https://doi.org/10.7185/geochemlet.2339>

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.

Received 4 September 2023 | Accepted 7 November 2023 | Published 6 December 2023

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 from the recrystallisation of ferric-ferrous iron (oxyhydr)oxides (Halevy *et al.*, 2017). Sulfides are also occasionally reported to occur, but only in minor quantities due to the scarcity of seawater sulfate at the time (Fakrae *et al.*, 2019). Although the Proterozoic Earth was an essentially microbial world, mineral phases precipitated by microbial biogeochemical cycling of iron, sulfur and carbon remain poorly constrained in terms of early diagenetic imprints prior to sediment lithification (Posth *et al.*, 2014). Characterising and identifying such mineral phases is therefore paramount in order to employ their signatures as recorders of past ferruginous environments and as tracers of microbial processes of the Earth's early oceans (Tosca *et al.*, 2019).

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 ($\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$), 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 (FeCO_3) and vivianite ($\text{Fe}_3[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$). Geomicrobiological investigations have shown that iron-, sulfur- and methane-related biogeochemical processes coexist in Lake Towuti sediments (Vuillemin *et al.*,

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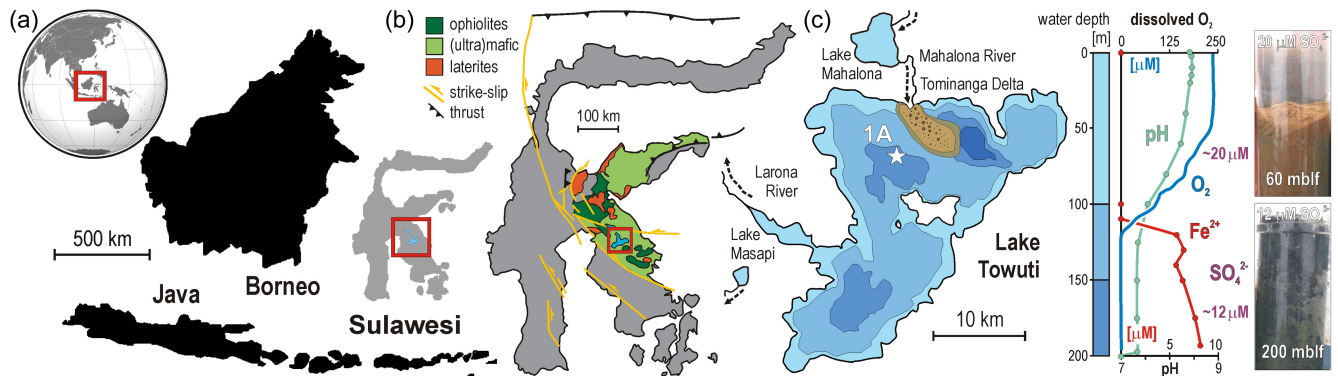


Figure 1 Site description of Lake Towuti. (a) World map displaying the location of Sulawesi Island, with close up on the Indonesia archipelago and location of the Malili Lake System. (b) Map of Sulawesi illustrating the (ultra)mafic and lateritic geology of the Malili Lake catchment. (c) Bathymetric map of Lake Towuti with position of drill site TDP-1A (156 m water depth), dissolved oxygen, iron, sulfate and pH profiles of Lake Towuti's water column (Bauer *et al.*, 2020), and gravity cores retrieved from 60 and 200 m water depth illustrating redox conditions at the water-sediment interface.

2016, 2018). Due to extremely low sulfate concentrations ($<20 \mu\text{M}$), 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 core profiles down to a basal age of about ~ 1 Ma (Russell *et al.*, 2020). Using transmitted light and scanning electron microscopy (SEM), we illustrate characteristic authigenic mineral phases, namely magnetite (Fe_3O_4), millerite (NiS), 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.

Methods

The Towuti Drilling Project (TDP) coring operations were carried out by the International Continental Scientific Drilling Program (ICDP) in spring-summer 2015, using the Deep Lakes Drilling System (Russell *et al.*, 2016). Hole TDP-1A (156 m water depth) was drilled with a contamination tracer to aid geomicrobiological sampling (Friese *et al.*, 2017). In the field, pristine core sections were transferred into an anaerobic chamber for pore water extraction, using Rhizon samplers for soft sediment, and an IODP-style titanium cylinder and hydraulic press for compact samples deeper than 10 m below lake floor (mblf). Alkalinity, pH, and Fe^{2+} , Mn^{2+} and PO_4^{3-} concentrations were determined *via* colorimetric titration, potentiometry and spectrophotometry, respectively. Dissolved inorganic carbon (DIC) was calculated by solving the carbonate system using the pH and alkalinity profiles and borehole temperatures. Major dissolved elements and volatile fatty acids (VFAs) were analysed by ion chromatography. Pore water trace metals were quantified by ICP-MS. Potential sulfate reduction rates (pSRRs) were determined by sediment incubation with radioactive $^{35}\text{SO}_4^{2-}$ (Friese *et al.*, 2021).

All cores from TDP site 1 were split and scanned at the National Lacustrine Core Facility (LacCore), described

macroscopically and microscopically to determine their stratigraphy and composition. A composite core was established based on visual alignment of lithologic features and magnetic susceptibility measurements (Russell *et al.*, 2020). The upper 100 m of the composite cores were scanned at 5 mm resolution on an XRF core scanner (ITRAX, Cox Ltd.) equipped with chromium and molybdenum X-ray tubes to resolve high atomic mass elements (Morlock *et al.*, 2021). The remainder of core TDP-1A was subsampled for heavy mineral extraction ($\geq 2.9 \text{ g cm}^{-3}$) *via* density and magnetic separation. Heavy mineral extracts were fixed onto SEM aluminium stubs and carbon coated ($\sim 20 \text{ nm}$ layer), using a Leica EM ACE600 high vacuum sputter coater. Morphological investigation and elemental point analyses were performed on a Zeiss Ultra 55 Plus field SEM and FEI Quanta 3D FEG, both coupled to energy dispersive X-ray spectrometres (EDX). All methods are detailed in the [Supplementary Information](#).

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 $12 \mu\text{M}$ 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 cmblf (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 millerites identified at 0.2 mblf and deeper suggest both pelagic

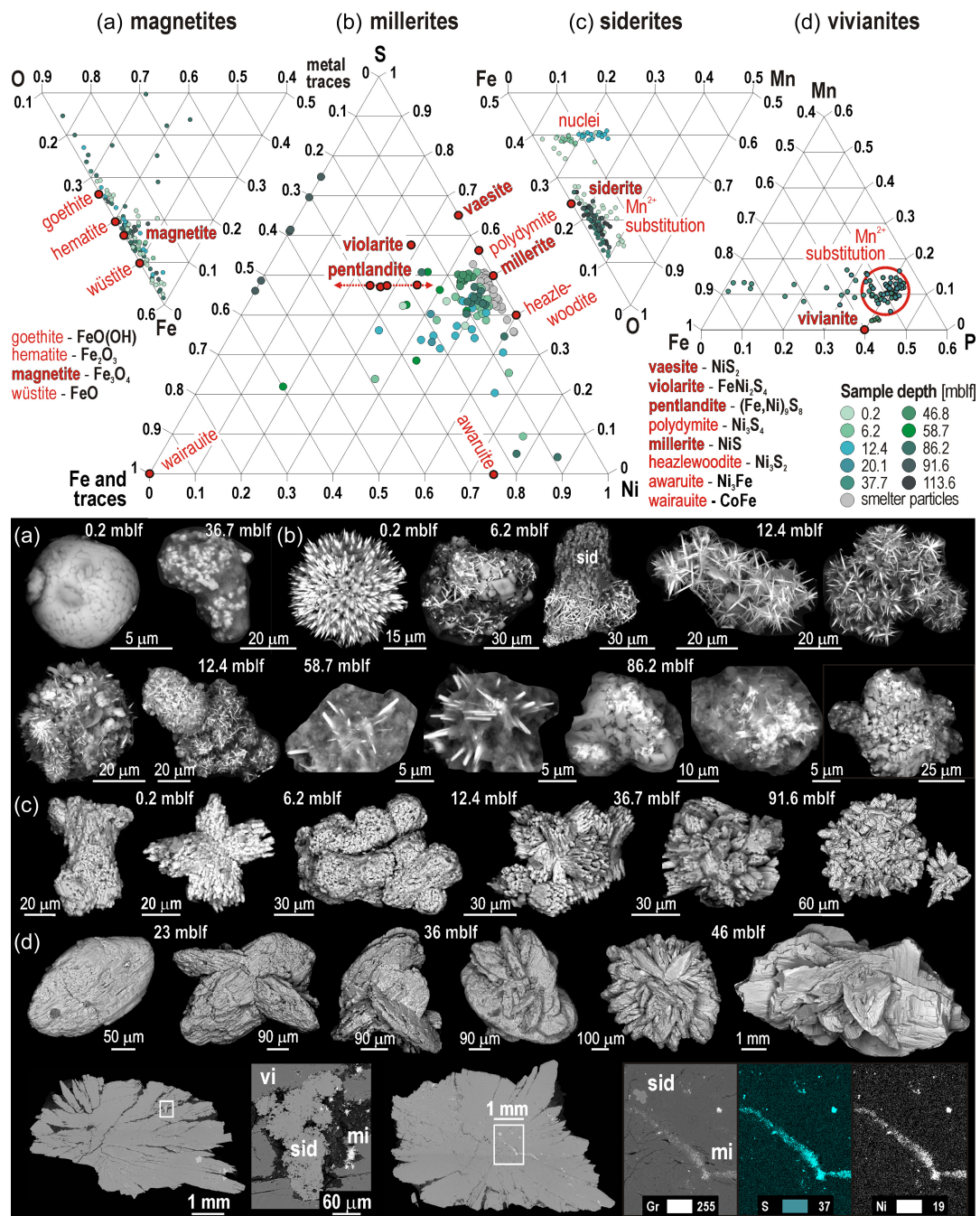


Figure 2 EDX point analyses and SEM images of diagenetic minerals. **(Top)** Ternary plots show: **(a)** magnetites and coextracted iron oxides (goethite, wüstite), **(b)** millerites with incorporation of Fe²⁺ traces, **(c)** siderites and **(d)** vivianites with substitution of Mn²⁺ for Fe²⁺. Smelter particles represent airborne contaminants from the nearby mine. **(Bottom)** **(a)** Magnetites in framboidal habits; **(b)** millerites in acicular spherules and aggregates, sometimes entangled and overgrown by siderites; **(c)** siderites aggregating into twins and mosaic monocrystals; and **(d)** vivianites in tabular habit developing into rosettes. The crystal section shows inclusions of millerite and siderite.

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.* O₂, NO₃⁻, SO₄²⁻) are rapidly depleted in the sediment (Figs. 1, 3a), which implies that anaerobic OM degradation should proceed *via* mineral ferric iron and CO₃²⁻ reduction. Reductive dissolution of hydrous ferric oxides (*e.g.*, ferrihydrite) continues in shallow sediments releasing substantial amounts of Fe²⁺ (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 cmblf, pore water NH₄⁺, PO₄³⁻ and VFA concentrations provide concomitant evidence of microbial OM degradation (Fig. 3a). Between 30 cmblf and 5 cmblf, formate, lactate, acetate and butyrate concentrations vary with metabolic production and consumption (*i.e.* acidogenesis, acetogenesis). Below

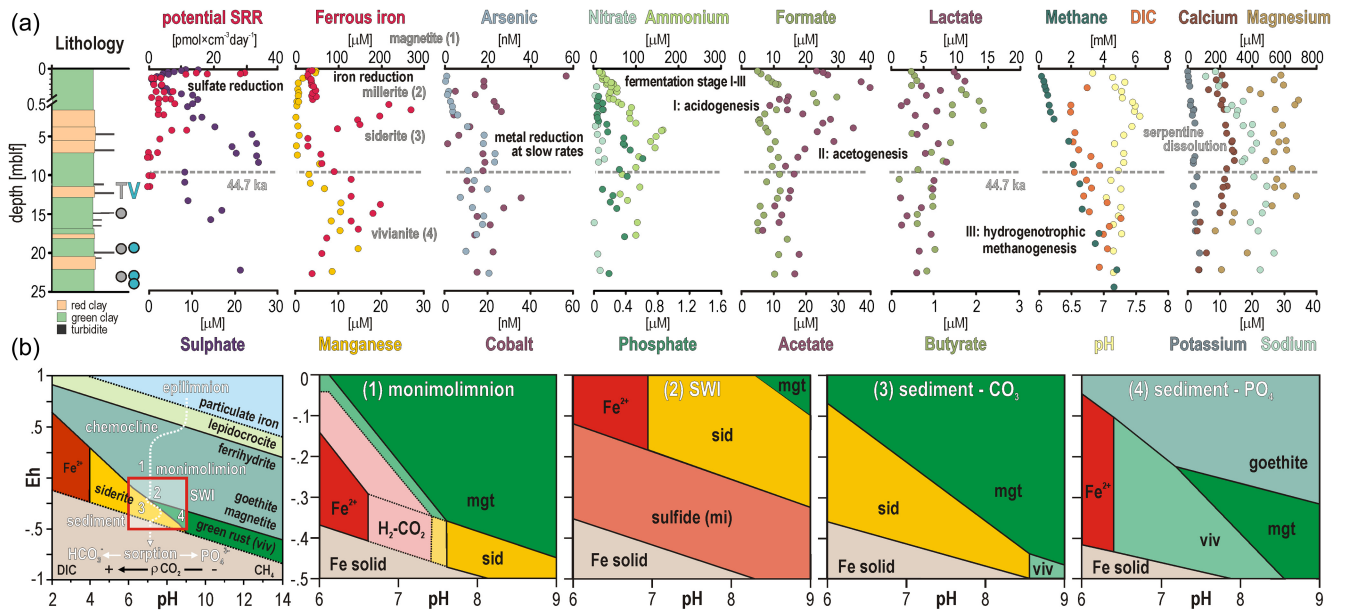


Figure 3 Depth profiles for pore water geochemistry and stability diagrams for Fe-bearing phases. (a) Lithology of Lake Towuti's upper 25 mblf including tephra (T) and vivianites (V); potential sulfate reduction rates (SRR); pore water concentrations for sulfate, ferrous iron, manganese, arsenic, cobalt, nitrate, ammonium, phosphate, formate, acetate, lactate, butyrate, methane, dissolved inorganic carbon (DIC), pore water pH, calcium, magnesium, potassium and sodium. Data points represent averaged triplicates (reproducibility <5 %). The dotted line signifies the base of the ¹⁴C ages, i.e. 44.7 ka (Russell et al., 2020). (b) Stability diagram tracing the measured pH and decreasing Eh during sedimentation and burial, successively focusing on conditions (red square) observed during *in vitro* microbial Fe³⁺ reduction (Maher et al., 2003) corresponding to (1) the monimolimnion (Roh et al., 2003), (2) sediment water interface (SWI) wherein millerite replaces pyrite (Craw and Bowell, 2014), (3) shallow and (4) deep sediments under carbonate- (Zachara et al., 2002) and phosphate-saturated conditions (Morton and Edwards, 2005), respectively.

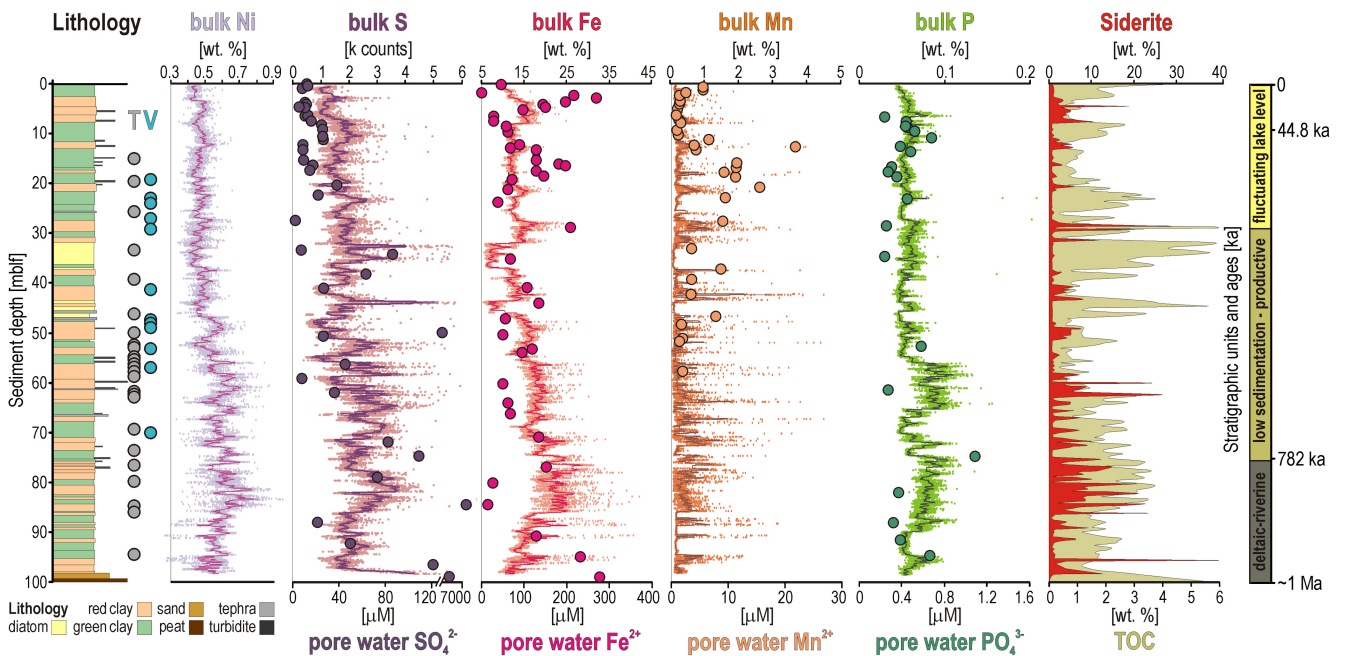


Figure 4 Depth profiles for bulk sediment, and pore water geochemistry. (Left to right) Stratigraphy of site TDP-1A with tephra (T) and vivianites (V); XRF core scanning profiles for Ni, S, Fe, Mn and P in bulk sediment overlain by pore water concentrations for SO₄²⁻, Fe²⁺, Mn²⁺ and PO₄³⁻; siderite concentration based on coulometry; total organic carbon (TOC). XRF core scanning profiles represent point analyses with moving averages at 5 mm and 2 cm resolution, respectively. Data points represent averaged triplicates (reproducibility <5 %).

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 de-

limit 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 cmlf and 5 mblf



(Table S-1), whereas CO₂ fixation *via* hydrogenotrophic methanogenesis subsequently reduces DIC activity in pore waters (Fig. 3b).

The increasing pore water Na⁺, Ca²⁺ and Mg²⁺ concentrations with depth (Fig. 3) indicate that (ultra)mafic sheet silicates (*e.g.*, serpentine) partially dissolve after burial (Table S-1). Ca²⁺ and Mg²⁺ concentrations are predicted to decrease the solubility of PO₄³⁻ in ferruginous solutions (Kubeneck *et al.*, 2023), thereby influencing pore water chemical equilibrium. Their presence in pore water could exert control over the onset of vivianite precipitation (Fig. 2d) after siderite (Vuillemin *et al.*, 2020). Ca²⁺ and Mg²⁺ concentrations drop around 15 mblf, suggesting that PO₄³⁻ supplants CO₃²⁻ for precipitation with Fe²⁺ and Mn²⁺ 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 (Fig. 3b), we estimated that the initial environments of formation for magnetite, millerite, siderite and vivianite correspond to the monimolimnion, 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⁻ in pore water which preferentially reacts with Ni²⁺ over Fe²⁺ 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 millerites 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 (Benning and Waychunas, 2008). As demonstrated for redox (trans)formation of green rust (Halevy *et al.*, 2017), pore water solutions become saturated with ferrous colloids (Moens *et al.*, 2021) that react with either carbonate 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 Fe²⁺, Mn²⁺ and Mg²⁺ 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 Fe²⁺, siderites substitute Mn²⁺ in their initial growth phase, while later forming vivianites have an overall manganoan composition substituting both Mn²⁺ and Mg²⁺ (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.* Ni²⁺, Mn²⁺, Fe²⁺, CO₃²⁻, HS⁻, PO₄³⁻). 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 reddish clays 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 94/3-1), SNSF grants to AV (P2GEP2_148621) and HV (20FI21_153054/1, 200021_153053/1). AP and LGB acknowledge financial support from the Helmholtz Recruiting Initiative (I-044-16-01) for access to the Potsdam Imaging and Spectral Analyses (PISA) facility.

Editor: Andreas Kappler



Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2339>.



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Cite this letter as: Vuillemin, A., Morlock, M., Paskin, A., Benning, L.G., Henny, C., Kallmeyer, J., Russell, J.M., Vogel, H. (2023) Authigenic minerals reflect microbial control on pore waters in a ferruginous analogue. *Geochem. Persp. Lett.* 28, 20–26. <https://doi.org/10.7185/geochemlet.2339>

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