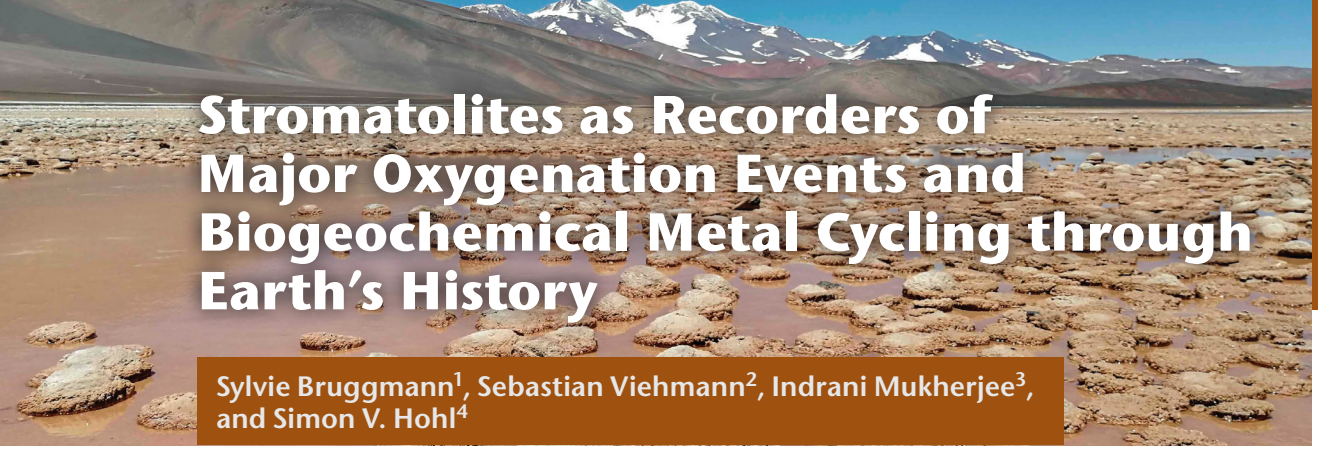

Stromatolites as Recorders of Major Oxygenation Events and Biogeochemical Metal Cycling through Earth's History

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Microbial carbonates are found throughout most of the geological record and have formed under varying atmospheric and hydrospheric conditions. Recent advancements in analytical techniques have enabled the use of novel, highly promising geochemical proxies, such as metals and their isotopes, to reconstruct ancient microbial habitats. Here, we review recent discoveries and the benefits of applying redox-sensitive and bioessential metal proxies in microbialites, aiming to reconstruct Earth's oxygenation and determine the availability of dissolved metals in past microbial habitats. These findings contribute to a better understanding of the evolution of microbial life and its ecological niches on Earth through time. Moreover, they offer a potential blueprint for the search for extra-terrestrial life, thereby informing ongoing and future planetary studies.

KEYWORDS: non-traditional stable isotopes; microbialites; redox evolution; bioessential metal cycling

INTRODUCTION

The ubiquitous occurrence of stromatolites and other microbialites throughout the geological record is remarkable, with evidence dating back at least 3.5 Ga and continuing to the present day (see Hofmann et al. 2026 this issue). Their resilience positions these unique bio-sedimentary structures as exceptional geochemical archives to investigate the co-evolution and interactions among Earth's atmosphere, hydrosphere, and biosphere. In particular, stromatolites formed within the photic zone of marine and lacustrine microbial habitats are capable of recording environmental changes during critical transitions in Earth's history, such as the Great Oxidation Event (GOE) in the early Paleoproterozoic, the Neoproterozoic Oxygenation Event (NOE) in the late Proterozoic, the Phanerozoic mass extinctions, and Cenozoic evaporation events (e.g., Anbar et al. 2007). Like other sedimentary deposits, the primary composition of stromatolites can be affected by detrital aluminosilicates or altered by post-depositional fluid–rock interactions during diagenesis or metamorphism. However, when authigenic carbonates formed in microbial mats remain free of detrital input, they resemble prime geochemical archives that directly mirror the chemistry of the fluids from which they formed (e.g., Webb and Kamber 2000). This chemical signature within ancient microbial mats provides insights into past environmental conditions, including redox conditions and the availability of dissolved metals, reflecting both regional influences and microscale heterogeneity (e.g., Viehmann et al. 2019).

Many metals are sensitive to oxidation–reduction changes and, depending on the redox conditions, either remain dissolved in ambient fluids or are bound to particles or sediment. Hence, the availability of many metals in dissolved form is directly linked to the oxygenation of the hydrosphere and atmosphere, both today and throughout Earth's history (Anbar 2008). Owing to microbially mediated mineralisation, microbial carbonates record the availability of dissolved bioessential elements. These elements can serve as macro-nutrients such as C, P, and N (see Thomazo et al. 2026 this issue), or act as metallic co-factors in enzymes, such as Fe, Mo, and V for N fixation; Fe, Ni, Co, and W for methanogenesis; or Zn, Mn, Mg, and Cu for oxygenic photosynthesis (e.g., Boden et al. 2021 and Toolkit). These competing metabolic processes emerged at different times in Earth's history and were directly governed by the availability of dissolved metals in the ambient ecosystem and thus, the interplay of Earth's oxygenation and geodynamic evolution.

It is highly plausible that the oxygenation of Earth's atmosphere and oceans and the availability of dissolved metals in ancient aqueous systems were directly coupled to microbial metabolic evolution(s), two fundamentally interconnected processes. Here, we highlight the utility of stromatolites and other microbialites as geochemical archives for investigating redox-sensitive and bioessential metals (and their stable-isotope signatures). These chemical records help track Earth's oxygenation events and metal availability for specific microbial metabolisms at different times throughout Earth's history.

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STROMATOLITES AS RECORDERS OF OXYGENATION

Redox-sensitive Metals in Stromatolites

Redox conditions, defined by the electrochemical gradient of the environment, strongly influence the solubility and the availability (due to mobility) of many metals in aqueous systems. Some metals, such as Cr, Cu, or Mo, are soluble, and thus available in seawater, mainly in their oxidised form (e.g., Anbar 2008). Locked in minerals of continental rocks, their mobilisation into aqueous systems relies at least partially on oxidative weathering of their host rocks (e.g., Anbar et al. 2007). In addition, the oxidation of some metals (e.g., Ce, Cr, Mo) can be catalysed by Mn- or Fe-oxides on micro- to macroscales, and thus, oxygen may not necessarily be present as free O_2 (Lyons et al. 2020 and references therein). Importantly, global changes in surface oxygenation result in distinct distribution patterns of metals such as V, Cr, Mn, Fe, Mo, Ce, and U in seawater, which are recorded in sediments including microbialites.

Many redox-sensitive metals, e.g., V, Cr, in addition to REE are elevated in modern microbialites compared with skeletal carbonates from the same environment (Webb and Kamber 2000). They can be directly incorporated into the carbonate crystal lattice in small quantities, e.g., Ce, Mo, and U (Kendall et al. 2017; Viehmann et al. 2019; Webb and Kamber 2000). Alternatively, they can accumulate in microbialites via sorption onto mineral surfaces, or in association with organic matter (OM; e.g., Webb and Kamber 2000; Martin et al. 2023). Here, we discuss four exemplary redox-sensitive metals: Ce, Cr, Mo, and U (FIG. 1). These metals have recently been used as powerful elemental or isotopic tracers to reconstruct Earth's oxygenation history using microbialites. Additional metals, some of which are also redox-sensitive, e.g., Fe, are discussed later (section "Bioessential Metals as Tracers for Metabolic Processes") due to their importance as bioessential metals.

Negative Ce anomalies in modern microbialites are characteristic of modern oxic seawater, an observation first reported 26 years ago (Webb and Kamber 2000). These anomalies arise from the oxidation of soluble Ce(III) to insoluble Ce(IV) on Mn oxide surfaces and a subsequent Ce removal from solution. In contrast, other REEs remain strictly trivalent. As a consequence, the ratio of Ce(III) to other REEs remaining in the solution is lower and the carbonate minerals forming in microbialites record the redox conditions of the precipitating fluid (Webb and Kamber 2000). The "Ce anomaly" allows the assessment of the relative enrichment/depletion in Ce compared with other REEs. A complication to this generally accepted behaviour is the occurrence of positive Ce anomalies as a

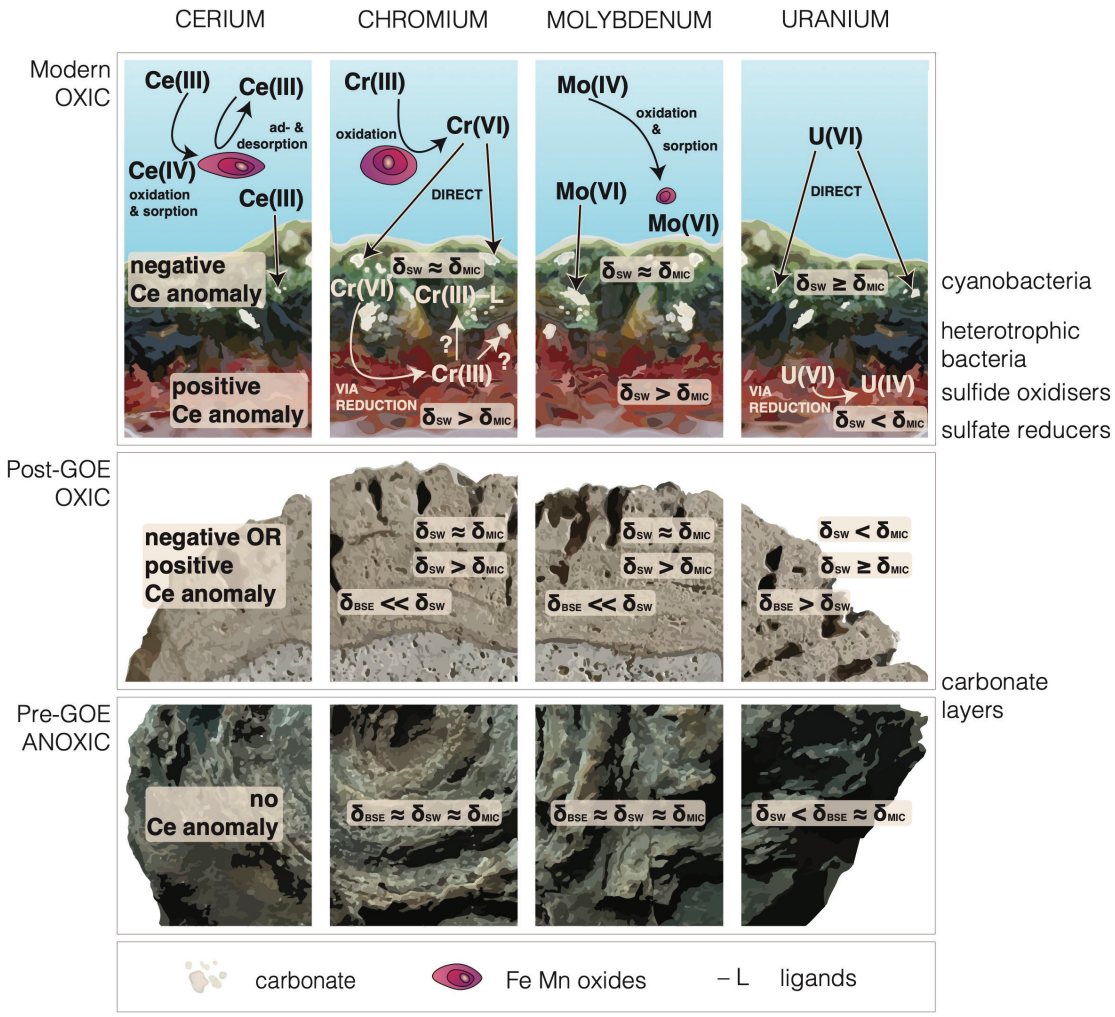

FIGURE 1 Simplified illustration of the accumulation of redox-sensitive metals and their isotopes in microbialites. The upper panel summarises redox changes and possible accumulation pathways of redox-sensitive metals from modern oxic water into carbonate forming in a microbial mat. Absolute isotope fractionation in δ values from ambient seawater (SW) recorded by microbialites (MIC) and relative to BSE in the two lower panels, showing expected values for oxic (post-GOE) and anoxic conditions (pre-GOE). Note that isotope compositions may deviate from the expected values for pre-GOE sedimentary rocks if oxygenation occurred.

result of biologically mediated Ce oxidation or breakdown of oxides under anoxic conditions that release Ce amongst other particle-reactive metals bound to the oxide surfaces back into solution. Recently conducted incubation experiments involving microbial secretion of Fe-chelating siderophores show that Ce(III) to Ce(IV) oxidation can occur even under strictly anoxic laboratory conditions (Kraemer and Bau 2022).

The incorporation of Cr into microbialites from oxic water, where Cr typically occurs as Cr(VI), remains speculative. Proposed pathways include a) direct incorporation of Cr(VI) from the precipitating fluid into carbonates; b) reduction of Cr (VI) to Cr(III) (e.g., via reduction by SRB), which is then trapped in the microbial mat by ligands; or c) incorporated as Cr(III) (e.g., Bruggmann et al. 2020; Uhlein et al. 2020). In line with the isotope fractionation of other metals, the lighter isotopes of Cr are preferentially reduced and removed to the sediment (Janssen et al. 2025 and references therein). Modern lacustrine and coastal microbialites show positive δ^{53}Cr values up to +1.07‰ (Bruggmann et al. 2020), close to average modern seawater (+1.04‰; Janssen et al. 2025). Thus, unlike skeletal carbonates, which are strongly affected by vital effects that lead to large Cr-isotope variations, microbialites appear to incorporate Cr from ambient fluids without isotope fractionation (Bruggmann et al. 2020).

Molybdenum is thought to be incorporated directly into carbonates as an impurity (Kendall et al. 2017), including microbially mediated ones. In oxygenated seawater, isotopically light Mo is scavenged by Mn (and Fe) oxides, leaving isotopically heavier Mo available for precipitating carbonates (Kendall et al. 2017). Similarly, under euxinic conditions, i.e., both anoxic and sulfidic, thiomolybdates ($MoOS_3^{2-}$ or MoS_4^{2-}) or S-rich OM show preferential uptake of light isotopes, yet with smaller absolute fractionation factors (Kendall et al. 2017). Modern microbialites from the Bahamas Platform record δ^{98}Mo values in a narrower range (i.e., between +1.44‰ and +1.68‰), compared with other modern carbonates that reach seawater-like values of up to 2.36‰ (Thoby et al. 2019 and references therein). Thus far, the impact of OM degradation or of free H_2S generated by SRB on Mo isotope fractionation in microbialites remains unresolved (Eroglu et al. 2015).

Uranium can be directly incorporated into microbialite carbonates or, under suboxic or anoxic conditions, bound to OM (Viehmann et al. 2019; Martin et al. 2023). U is more soluble in its oxidised U(VI) state compared to its reduced forms. Biogenic carbonates typically record the seawater δ^{238}U value, with fractionation up to +0.2‰ commonly observed during U incorporation from the fluid into carbonates (see references in Martin et al. 2023). However, reduction of U in association with OM remineralisation seems to cause a shift in δ^{238}U values within a Holocene stromatolitic dome (Martin et al. 2023). Because U reduction favours heavy U isotopes, deeper stromatolite layers show higher and more variable δ^{238}U values (up to −0.15‰) and thus, larger offsets from seawater (≈ −0.37‰ in Shark Bay). This observation contrasts the seawater-like δ^{238}U values in surface layers of the same stromatolites, where reduction and subsequent U isotope fractionation have not yet occurred (Martin et al. 2023). Overall, modern marine microbialites from Shark Bay (Australia) record δ^{238}U values that are only slightly offset from seawater values.

Redox Evolution of the Earth Recorded by Metal Isotopes in Microbialites

The knowledge gained from modern microbial environments has been increasingly applied to extract information from the geological record, particularly for reconstructing the Precambrian redox evolution (Fig. 2). The oldest microbialites investigated for their Mo isotope compositions (Chobeni Formation, Pongola Supergroup, South Africa; 2.97 Ga) exhibit moderately elevated Mo isotope compositions relative to the bulk silicate Earth (BSE), reaching up to +0.32‰. As the same samples exhibit negative Ce anomalies, the authors suggested that Ce oxidation occurred locally, whereas global oxic Mo sinks, e.g., Mn oxides, were still limited at that time (Thoby et al. 2019). In contrast, Mo isotope compositions as high as +1.03‰ are detected in 2.93 Ga Ball Assemblage microbialites (Red Lake Greenstone Belt, Canada; Thoby et al. 2019). At this time, euxinic conditions were absent, and Fe and Mn oxides were abundant enough to oxidise Mo and remove isotopically light Mo, leaving the remaining dissolved Mo pool heavier. Further evidence of early oxygenation was recently found in microbialites of the 2.87 Ga Steep Rock Group, where negative Ce anomalies have been directly dated as evidence of oxygenic photosynthesis (Patry et al. 2025). The δ^{98}Mo values of only slightly younger microbialites from the same Group reach values up to +1.22‰ (Mosher Carbonate, Steep Rock Group, Canada; 2.80 Ga; Thoby et al. 2019). While no negative Ce anomaly was detected in the ~ 2.75 Ga Manjeri Formation of the Belingwe Greenstone Belt (Zimbabwe), slight fluctuations in redox conditions are indicated by δ^{238}U values, perhaps marking the onset of oxidative weathering (lowest value of -0.52‰; Martin et al. 2025). In contrast, microbialites from the 2.7 Ga Tumbiana Formation (Australia) show low U enrichment factors and unfractionated δ^{238}U values close to BSE (−0.36‰ to −0.29‰), indicating low atmospheric O_2 levels at this location (Brüske et al. 2020).

In ~1 Ga stromatolites from the Paranoá Group (Brazil), negative Ce anomalies and low Mn concentrations reflect carbonate buildups under somewhat oxic conditions at the stromatolite–seawater interface (Viehmann et al. 2019). In contrast, positive Ce anomalies are recorded in anoxic environments due to the dissolution of Fe and Mn oxides and subsequent enrichment of Ce (along with Fe and Mn) in solution and ultimately, in the precipitate. Such concentration patterns were observed in stromatolites from the same location as above, indicating carbonate formation in a different microenvironment within the microbial mat under anoxic conditions (Viehmann et al. 2019).

In <1 Ga microbialites, U and Cr isotope values have been suggested to record ambient seawater values or microbial metal reduction. Promising data are found in microbialites from the 0.72 Ga Andrée Land Group (Greenland), yielding δ^{53}Cr values up to +0.43‰, thus higher than BSE (Bruggmann et al. 2020). These values overlap with presumably abiotically formed sedimentary carbonate rocks of the same age and confirm that the conditions during their formation were indeed oxic (Bruggmann et al. 2020). Marine stromatolitic cements from the Cryogenian (≈ 0.65 Ga) Balcanoona Reef complex (Australia) show δ^{238}U values of around −0.23‰, a value possibly representative of Cryogenian seawater. However, this value overlaps with global riverine inputs (−0.3‰ to 0.0‰), and closely resembles both modern average seawater and the δ^{238}U value of BSE (−0.29‰ ± 0.03‰; Hood et al. 2016 and references therein). In contrast, lower Cambrian stromatolites from the ≈ 0.52 Ga Jaíba Member (Brazil) display strongly negative δ^{53}Cr values (down to −0.69‰), well below BSE (−0.12‰ ± 0.10‰; Janssen et al. 2025). These low values may result from a combination of biotic and abiotic Cr reduction, leading to the preferential incorporation of isotopically light Cr into microbialites (Uhlein et al. 2020).

Overall, metal concentrations and their isotopes, such as those discussed above, provide insights into local and global redox conditions. In Precambrian environments, such information is often complicated, with locally oxygenated environments co-existing under overall anoxic conditions.

Mild oxidation in microenvironments may require more than one isotope system to detect the presence of oxygen, depending on the redox potential of the metal proxy.

BIOESSENTIAL METALS AS TRACERS FOR METABOLIC PROCESSES

Roles of Bioessential Metals in Stromatolites During Earth's History

Bioessential metals can be utilised by microbial primary producers in enzymes (TABLE 1). These enzymes catalyse metabolic processes directly related to P acquisition, C or N fixation, or environmental adaptation such as defence against viral attacks. Enzymes need co-factors, i.e., specific metal ions such as Fe, Zn, or Co, which serve as active chemical sites that catalyse reactions (breaking bonds or transferring electrons). However, the availability of dissolved metals in an ecosystem varies between different environments and throughout Earth's history, as summarised above. The metallome includes the entirety of metals in a cell. Zooming out from this microscale, the total availability of dissolved metals in a microbial habitat defines which metals can be utilised for microbial metabolism. The interplay between environmental metal availability (the microbialite metallome) and the evolution of new enzymes that utilise these metals allows for the tracing of certain metabolic processes back in deep time (e.g., Hohl et al. 2025 and Life in Stone).

The last three decades have yielded a vast amount of metal data from microbial carbonates from diverse aqueous environments spanning over 3.5 billion years. Metal enrichments in authigenic carbonates formed in microbial environments allow the assessment of habitat-specific metal availability and potential metabolic pathways (Stüeken et al. 2022) and can be paired with microbiome analyses (16S rRNA; see Iniesto et al. 2026 this issue). Additionally, big data approaches enable analysis of the metallome of microbial habitats over extended periods, allowing determination of metal availability in individual paleoenvironments (marine shelf, lagoonal restricted, lacustrine) over time (Fogret et al. 2024).

Key events in metallome evolution include the early Archean, where the activity of Fe^{2+}-oxidising photoferrotrophs transformed the aqueous Fe pool by harnessing Fe^{2+} as an electron donor for anoxygenic photosynthesis using Fe-S proteins. Based on molecular clock analyses, the last ancestor of oxygenic phototrophs presumably evolved shortly after the emergence of cyanobacteria, using the Mn_4CaO_5 cluster in the Photosystem II protein (Jabłonska and Tawfik 2021). The availability of these metals may have created transient O_2 "whiffs," as observed in 2.87 Ga stromatolites of the Steep Rock Group (Patry et al. 2025), although pervasive oxygenation was not achieved until after the GOE. In Archean stromatolites, Ni was crucial to sustain fermentation via methanogenesis, as Ni-rich [NiFe]-hydrogenases and methyl-CoM reductase (mcr) are required for methane (CH_4) production (e.g., Hohl et al. 2025 and references therein). Post-GOE, oxidative weathering of a progressively more evolved silicate crust depleted oceanic Ni (the "Ni famine"; Konhauser et al. 2009), starving methanogens and favouring aerobic metabolic pathways that used newly abundant O_2-soluble metals (Mo, Cu; Anbar 2008).

During the Proterozoic, rising O_2 levels, the diversification of eukaryotes, and the emergence of early metazoans intensified competition for dissolved metals as nutrients. Microorganisms evolved advanced strategies, such as the

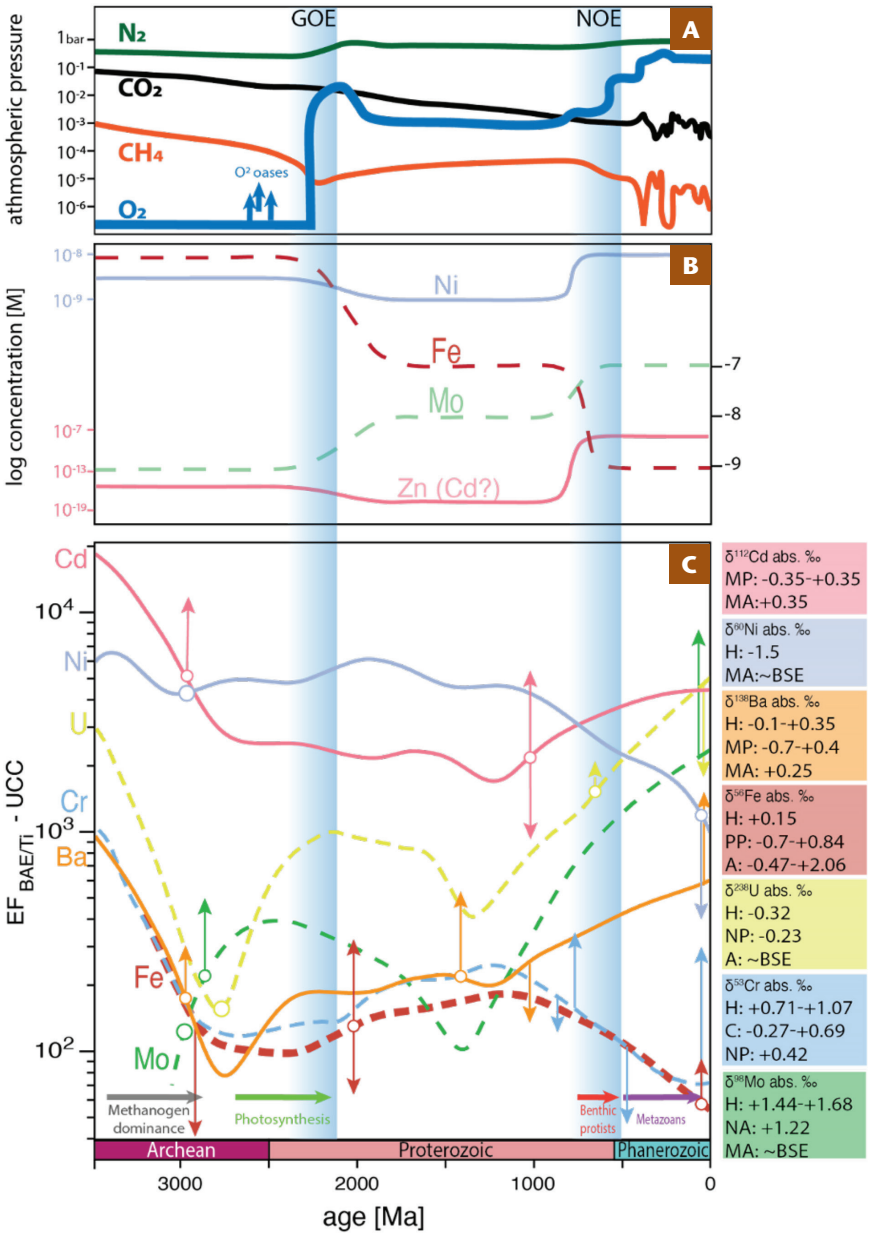

FIGURE 2 Evolution of critical chemical compounds in the atmosphere, hydrosphere, and geo-biosphere. (**A**) Atmospheric pressure of major gases indicating the positions of the GOE and NOE. AFTER CATLING (2020). (**B**) Predicted dissolved metal concentrations in the hydrosphere showing corresponding nutrient availability based on the redox state of the oceans. AFTER ANBAR (2008). (**C**) Compilation of enrichment factors of metals in microbialites relative to upper continental crust (UCC) and selected metal isotopes. Enrichment factors (EF) of bioavailable elements (BAE) relative to Ti indicate progressive redox-sensitive enrichments (U, Mo) or depletions (Cr, Fe) following the GOE and NOE, and utilisation of Cd, Ni in microbial biomass as metallic co-factors or EPS related micro-barites (Ba). Magnitude and direction of metal isotope fractionation from BSE in microbialites are presented as arrows (including BSE = arrow above/below circle; away from BSE = arrow without circle; or no fractionation from BSE = plain circle). Boxes on the right show published absolute isotope values of stromatolites (in ‰) of the Holocene (H), Cambrian (C), Neoproterozoic (NP), Mesoproterozoic (MP), Paleoproterozoic (PP), Neoarchean (NA), and Mesoarchean (MA).

Table 1 METAL CO-FACTORS IN SOME MICROBIALITE-FORMING MICROORGANISMS.

Metal	Metabolism	Key Enzymes	Role in Microbialites and Potential Isotope Fractionation
Fe	Anoxygenic photosynthesis	Fe-S proteins (pscA)	Photoferrotrophs (e.g., *Chlorobium*) drive Fe^{2+} oxidation, creating Fe-rich laminae; strong negative Fe isotope fractionation in microbialites from Proterozoic on (von Blanckenburg et al. 2008)
Mg	Oxygenic photosynthesis	RuBisCO (Mg^{2+}-dependent)	Cyanobacteria (e.g., *Microcoleus*) fix CO_2, alkalinising water and inducing $CaCO_3$ nucleation; no microbial Mg isotope fractionation (Hu et al. 2023)
Ni	Methanogenesis	Methyl-CoM reductase (mcrA, Ni) [NiFe]-hydrogenase(mcr)	Methanogens (e.g., *Methanosarcina*) produce CH_4, creating pore spaces in mats; large negative Ni isotope fractionation (Hohl et al. 2025)
Mn	Oxygenic photosynthesis	Photosystem II (Mn_4CaO_5 cluster)	Cyanobacteria release O_2, oxidising Mn^{2+} to Mn^{4+} in microbialite layers
V	Alternative N_2 fixation	Vanadium nitrogenase (vnf)	Diazotrophs (e.g., *Azotobacter*) fix N_2 in Mo-poor microbialite systems
Mo	Nitrogen fixation	Mo-nitrogenase (nifDK)	Cyanobacteria (e.g., Rivularia) dominate nitrogen fixation in Mo-rich coastal microbialites; strong positive Mo isotope fractionation from Proterozoic onwards (Thoby et al. 2019)
Co	Vitamin B_{12} synthesis	Cobalamin-dependent enzymes	SRB (e.g., *Desulfovibrio*) produce B_{12}, supporting heterotrophs in mats
Cu	Denitrification	Nitrous oxide reductase (nosZ)	Aerobic-anaerobic interfaces (e.g., *Pseudomonas*) reduce N_2O, altering local pH
Zn/Cd	CO_2 hydration	Zn/Cd-carbonic anhydrase (CA)	Cd substitutes in Zn-limited oceans; strong Cd isotope fractionation associated with microbialites (Viehmann et al. 2019; Hohl et al. 2026)

production of siderophores, metal-scavenging molecules, to exploit scarce Fe^{3+} and other metals such as Zn and Cu. This period presumably also saw the emergence of Cd-dependent carbonic anhydrases, enabling efficient CO_2 hydration for photosynthesis in Zn-poor oceans, where Cd often substituted for Zn (Viehmann et al. 2019; Hohl et al. 2024a). These adaptations illustrate a co-evolutionary race for metals, with microbialites potentially recording shifts in metal availability (e.g., Cd/Zn ratios) and the retreat of metals into extreme environments during the Phanerozoic as eukaryotes and metazoans reshaped biogeochemical cycles (Peters et al. 2019). The availability and limitations of bioessential metals in microbial habitats with extreme and rapidly changing environmental conditions, such as during the Badenian Salinity Crisis (~14 Ma), have been reported in microbialites of the Oberpullendorf Basin in Austria (Viehmann et al. 2023). Metal enrichments in microbialites relative to the BSE expressed with increased enrichment factor (EF) values (see general overview in Fig. 2) together with seawater-like REE signatures are characteristic of a marine transgression into a microbial ecosystem. In contrast, marine regression and restriction may result in a decrease in EFs, likely related to the interplay between microbial consumption and incorporation into carbonates (Viehmann et al. 2023).

Bioessential Metal Isotopes in Microbialites

In the last decade, isotope analyses of bioessential metals in microbialites have emerged as powerful geochemical proxies for testing nutrient utilisation (e.g., Hohl et al. 2025). Cultivation experiments have laid the foundation for a better understanding of truly biological over non-biological kinetic mineral adsorption or incorporation-related isotope fractionation. As a result, a variety of bioessential metal-isotope systems have been tested in modern and ancient microbialites to assess their potential as biomarkers of metallome evolution. For example, Holocene microbialites from Lagoa Salgada (Brazil) show large variation in Mg isotope compositions, driven by environmental conditions; i.e., changes in lagoonal restriction relative to the open ocean result in variable Mg fluxes. As a result, Mg co-precipitation in carbonates at EPS nucleation sites does not record direct cellular control over the observed $\delta^{26}Mg$ fractionation (Hu et al. 2023). In contrast, in the same microbialites, high $\delta^{13}C$ and low $\delta^{60}Ni$ values were detected and directly linked to pronounced methanogenic activity (Hohl et al. 2025). Microbial carbonates precipitated in the presence of methanogens record a light C and heavy Ni isotope-depleted pool in semi-enclosed porewater systems that underwent degassing of ^{12}C-enriched methane, while light Ni isotopes were preferentially utilised by methanogens. While this Holocene-restricted environment records strong Ni isotope fractionation, no such fractionation was reported in Archean stromatolites of the Pongola Supergroup (South Africa; Hohl et al. 2024a), arguing either for the absence of significant methanogenic activity or for high dissolved Ni concentrations in Archean oceans as predicted by Konhauser et al. (2009). However, positively fractionated $\delta^{114}Cd$ values above the BSE in the same microbialites suggest the utilisation of Cd as a co-factor in carbonic anhydrase, hinting at early photosynthesis (Hohl et al. 2024a). Extensive Cd isotope fractionation away from crustal values was also observed in Proterozoic microbial habitats, where Rayleigh-type fractionation and co-variation with redox-sensitive metals suggest Cd cycling linked to variable redox levels within an ancient microbial mat (Viehmann et al. 2019). Iron isotopes may offer an additional means of tracing layer-specific redox conditions within microbial habitats and distinguishing between oxygenic photosynthesisers and Fe-oxidising chemolithotrophs. Modern microbial mats containing cyanobacteria produce high levels of O_2, resulting in quantitative oxidation of ferrous Fe and $\delta^{56}Fe$ values matching those of the dissolved Fe source (von Blanckenburg et al. 2008). In contrast, the higher $\delta^{56}Fe$ values in Precambrian stromatolites indicate lower oxidation levels, attributable to localised Fe-photoferrotrophy via Fe-S enzymes. Finally, the role of Ba isotope fractionation in past microbial environments has been explored, with research suggesting that EPS serve as a nucleation site for micro-barites enriched in isotopically light Ba. Hohl et al. (2024b) show that microbial carbonates precipitating in sulfate-rich microbial habitats therefore record heavier Ba isotopic compositions. These results validate the use of Ba isotope compositions as an indirect paleoproductivity proxy and tracer for SRB in shallow water microbial ecosystems through the geological history.

CONCLUSIONS AND PERSPECTIVES

The application of metals and their novel stable isotope systems enables identification of nutrient cycling in modern and ancient microbial ecosystems at millimetre to centimetre scales. In particular, authigenic carbonates that compose stromatolites and other microbialites are unique archives for tracing the co-evolution of redox conditions and the availability of bioessential metals within microbial habitats, which paved the way for metabolic evolution on Earth. In addition, microbialite research provides unique insights into the evolution of early metazoans alongside microbial habitats for which efficient recycling of bioessential metals, such as those in enzymatic co-factors, was key. By combining geochemical data with high-resolution petrographic and textural characterisation, microbialites can be used to reconstruct both modern and ancient microbial ecosystems. This potential extends beyond Earth: microbialites may also serve as powerful analogues for extra-terrestrial biosignatures (see Perspective), positioning their study at the interface of geochemistry and astrobiology. To fully exploit this potential, expanding existing databases and further exploring novel, highly promising geochemical proxies for microbialites are priorities. Doing so will not only enhance our understanding of life's evolution on Earth but also provide a blueprint for exploring habitable environments on other planets.

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