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Applications of Laser Ablation Inductively Coupled Plasma Mass Spectrometry in Microbialites

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Abstract

Microbialites are critical for documenting early life on Earth and potential early life in other regions of the solar system. However, the criteria for identifying microbialites remain controversial. Trace element geochemistry provides two types of information that aid in the recognition of putative microbialites. First, as most microbialites are composed of authigenic precipitates, trace elements can be used to investigate the fluids involved in their formation, thereby helping to identify paleoenvironmental conditions. For example, rare earth elements (REEs) preserved in microbialites are highly useful in distinguishing depositional environments. Second, microorganisms utilize and accumulate significant quantities of elements, including many metals. The preservation of such elemental enrichments may offer valuable biomarkers. Although research in this field is relatively nascent, high-precision in situ measurements (now with spatial mapping) of metals in microbialites-using techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) have confirmed persistent enrichments of biologically significant metals in microbialites. Consequently, trace element studies are increasingly proving valuable for investigating microbialites. Provided that diagenetic effects and the extent to which specific precipitates represent microenvironments are considered, trace element signatures may yield critical insights into depositional environments and metabolic processes within biofilms.

Keywords

Microbialites; Trace elements; LA-ICP-MS

1. Introduction

The composition of rare earth elements (REEs) in modern seawater is correlated with oceanic regions and water depth, making REEs valuable tracers for water mass circulation. Modern seawater REE patterns are governed by multiple input sources and are also influenced by dissolved oxygen levels. Consequently, the REE signa-

tures preserved in ancient sedimentary rocks play a pivotal role in deciphering the origins of paleo-seawater REEs and reconstructing marine geochemical evolution. Notably, variations in the abundances of redox-sensitive elements, such as cerium (Ce) and europium (Eu), within sedimentary REE profiles provide critical insights into changes in paleo-seawater oxygenation. These variations not only serve as key indicators for understanding the long-term stratification of the water column but also offer a robust tool for testing hypotheses linking marine redox dynamics to biological radiations and extinction events.

Microbialites are primarily composed of carbonate minerals precipitated through microbially induced processes in ambient water. Major types include stromatolites and thrombolites. Stromatolites are microbial deposits characterized by laminated structures, whereas thrombolites exhibit macroscopically clotted textures. Unlike biomineralization associated with skeletal growth, the geochemical signatures of microbialites-formed via induced mineralization are considered unaffected by biological selective absorption effects. Consequently, their elemental compositions are thought to faithfully record the chemical characteristics of the ambient water environment (Li, 2023).

Microbialites are products of synergistic interactions between benthic microbial communities and their environments. Notably, since the Phanerozoic Eon, the proliferation and decline of microbialites have been closely linked to metazoan evolutionary events and environmental changes. During the Cambrian-Early Ordovician, microbialites thrived extensively in shallow marine settings and exhibited diversification in types and morphologies. A marked decline in microbialite abundance occurred from the Middle Ordovician onward, temporally correlating with the Great Ordovician Biodiversification Event (GOBE). Conversely, microbialites experienced a resurgence following the Permian mass extinction, likely associated with reduced metazoan activity. These patterns underscore the significance of microbialites in deciphering the coevolution of life and environments throughout Earth's history.

In recent years, geochemical studies of microbialites, particularly investigations into their rare earth element (REE) signatures, have emerged as a focal point in international paleoceanographic research. REEs in microbialites are regarded as one of the most reliable proxies for inheriting and preserving the compositional features of paleo-seawater REEs. These signatures have been employed to reconstruct depositional environments of Cambrian and Jurassic microbialites, investigate driving mechanisms of the Ordovician Biodiversification Event (Chen, 2020), and elucidate redox conditions of paleo-seawater linked to delayed biotic recovery in the Early Triassic. Microbialite research has thus provided novel approaches and insights for analyzing changes in paleo-marine chemistry and reconstructing paleoecological and paleoenvironmental contexts (Luo, 2001).

Furthermore, advancements in instrumental analytical techniques, notably the coupling of high-selectivity ion chromatography (IC) with high-sensitivity inductively

coupled plasma mass spectrometry (ICP-MS), have significantly enhanced REE analysis. The capability of these techniques for elemental speciation analysis has established them as critical tools in REE studies.

2. Trace elements and microbialites

Various chemo-biomarker studies have been conducted on ancient and well-documented microbialites. In well-preserved specimens, carbon isotopes are utilized to distinguish microbial from non-microbial components in limestones. However, diagenetic alteration often compromises preservation, particularly in Precambrian stromatolitic carbonates, rendering such signatures unreliable. Sulfur isotopes also hold potential as organic biomarkers in modern and ancient rocks. Nevertheless, preservation challenges frequently invalidate their utility, especially in older Archean strata that have typically undergone at least low-grade metamorphism.

The concentration of transition metals in the biofilm usually decreases directly near the cells. Importantly, different microbial communities, including prokaryotes and eukaryotes, utilize various metals in different ways and with different fundamental proportions. Therefore, the accumulation of these elements in an unbalanced state with the surrounding environment may provide biomarkers, and the proportions of specific metals may provide information about the types of organisms involved. In addition, since the availability of certain elements varies in different redox states, the abundance of these metals in ancient hydrogen-containing precipitates may tell us a great deal about the evolution of the marine biogeochemical cycle (Chen, 2023).

The contents of trace elements preserved in microbialites may reflect four main sources (Fig. 1), namely:

(1) the biological enrichment of organic matter in the biofilm itself;

(2) the surrounding water body;

(3) the capture and binding of surrounding sediments, including hydroxides;

(4) young diagenetic fluids.

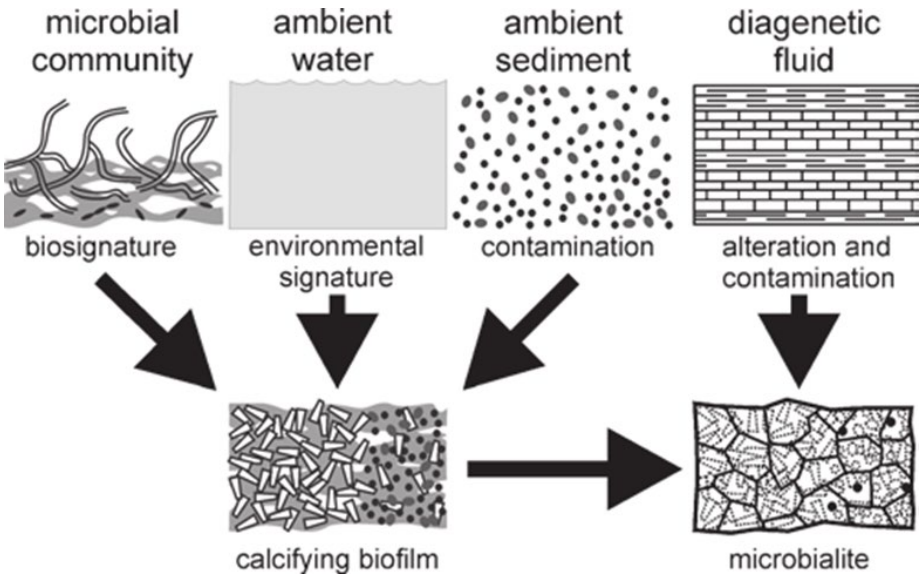

Fig. 1 Schematic diagram of potential sources of trace elements within microbial organisms.

3. Introduction of LA-ICP-MS

The use of lasers to extract substances for analysis from samples can be traced back to the early 1980s. Since then, lasers have not only been used to transfer the extracted substances to an ionization source or atomization source, but have also been used as an ion source themselves. Examples include laser ionization mass spectrometry and laser microprobe mass spectrometry techniques. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a new solid analysis technique.

The working principle of a laser is based on stimulated emission and induced emission of light. Most laser ablation methods generally use solid-state lasers that operate in a pulsed mode. Since the birth of the first instrument, the complete dissolution of samples has been a prerequisite for the application of this technology. However, the LA-ICP-MS technology directly introduces solid samples into the system from the top or side of the ablation cell, replacing the nebulizing gas flow in the conventional method. This avoids the cumbersome and time-consuming wet chemical digestion process of samples in LA-ICP-MS, and greatly reduces the chance of toxic substances being exposed to the air. It also prevents the introduction of contaminants or the loss of volatile substances during sample preparation. Since solid sampling is adopted, the polyatomic interferences caused by water and acids are eliminated. The absence of solvents improves the sampling efficiency and greatly enhances the ability to test samples, especially those with low contents. Especially for very small or precious samples that cannot be damaged and cannot be analyzed by traditional sample dissolution methods, its superiority is even more prominent. LA-ICP-MS has the characteristics of in-situ, real-time, and rapid analysis, and has

become a new analytical and testing method for studying the composition and distribution characteristics of substances from a microscopic perspective. There are mainly two methods for collecting substances by laser ablation. The first is to perform a series of pulses at a fixed point, that is, single-point ablation. The second commonly used sampling technique is to perform a laser "grid vertex scan" across the surface of the sample, that is, line scan ablation. LA-ICP-MS has been widely applied in fields such as geoscience, materials science, environmental science, and life science.

4. Significance of trace elements in microbialites

4.1 Influence of microenvironment on the content of trace elements

Using trace element patterns to interpret sedimentary environments requires that the preserved element contents can represent those of the surrounding environment. However, microbialites represent microenvironments to varying degrees and may or may not reflect the same chemical composition of the surrounding water bodies when they were formed. Even the EPS sheaths of individual microorganisms can form diffusion gradients, isolating living cells from the surrounding chemical environment. In more complex biofilms and microbial mats, the diffusion pathways also become more extensive and complex with increasing depth. Decho suggested that differences in the types and distributions of EPS in biofilms establish "microdomains" with different physical and chemical properties. These microdomains regulate the pH value in various sedimentary environments as well as the concentrations of O_2, N and S compounds, and metals (nutrients and toxins). In more complex biofilms and microbial mats, the depth within the structure isolates various microenvironments, most notably in terms of differences in oxidation levels. In oxygenated benthic environments that are exposed, communities of facultative anaerobes and obligate anaerobes may occur within millimeters of the biofilm surface. Since microbial activities are increasingly confined to the pore spaces and holes (caves) within larger structures (such as large microbial communities or coral reefs), the fluids of submerged and restricted biofilms may evolve significantly from the ambient water bodies that reflect the broader sedimentary environment. In any case, the growth of microbialites (biologically induced or influenced precipitation) requires a continuous inflow of ambient water bodies into the microenvironment to provide sufficient ions for mineral growth. However, the extent to which this environment represents a microenvironment with an effective diffusion barrier may determine the degree to which the preserved geochemical surrogates reflect the chemistry of the water bodies in the "external" environment (Zhao, 2019).

In modern marine environments, microbial mediation of microenvironments has been well-documented. For instance, Nothdurft et al. documented the formation of brucite [$Mg(OH)_2$] in normal shallow marine microenvironments. Brucite typically precipitates in solutions with pH values exceeding 9, which are notably undersatu-

rated in shallow seawater. However, its precipitation occurs within microenvironments of abandoned spaces in living coral skeletons in modern reefs, driven by the chemical evolution of seawater in pore systems mediated by microbial endolithic activity. Despite frequent porewater exchange due to tidal and wave-driven water column dynamics, phototrophic organisms (cyanobacteria and filamentous green algae) within coral skeletons remove CO_2, thereby increasing the pH of semi-confined fluids in cavities. This process supports aragonite precipitation while reducing Ca^{2+} activity. Subsequent microbial degradation of organic matter (including ammonification) or utilization of HCO_3^-, potentially via cyanobacterial photosynthesis employing carbonic anhydrase, may further elevate pH by releasing excess OH^-. Regardless of the precise mechanism, brucite growth in these settings would not occur without extensive microbial modification of local hydrochemistry within the semi-confined cavities of coral skeletons, contrasting with ambient seawater conditions (McArthur et al., 1984).

A significant example of microbially mediated microenvironments leading to unexpected mineral precipitation in marine carbonates is the formation of low-magnesium calcite (LMC) within confined microbial boreholes in living coral skeletons. LMC is thermodynamically unfavorable for precipitation in marine carbonate systems due to seawater's high Mg:Ca ratio. Typically, LMC precipitates from freshwater (meteoric) environments characterized by lower Mg:Ca ratios and is thus considered preliminary evidence of meteoric diagenesis. In contrast, abiotic marine carbonates predominantly form as aragonite or high-magnesium calcite (HMC). In coral skeletons from the reef flat of Heron Reef, Great Barrier Reef, migrating coccoid cyanobacteria bore into skeletal aragonite at one end while backfilling the boreholes with LMC at the other end. The calcification process generates protons, enabling the utilization of HCO_3^- for photosynthesis, which is supplied by aragonite dissolution at the opposing borehole terminus. Crucially, the Mg:Ca ratio within the borehole microenvironment reflects that of the dissolving aragonite rather than ambient seawater, resulting in markedly lower ratios that favor calcite precipitation. The precipitation of borehole calcite represents a biologically controlled process, as it likely requires direct enzymatic activity from microorganisms. For instance, microbial ATP ases may actively transport Ca^{2+} to precipitation sites in exchange for protons, while carbonic anhydrase facilitates the conversion of HCO_3^- to CO_2 and H_2O, driving localized calcite formation. Regardless of the specific biochemical pathways, the dominance of calcite over aragonite directly reflects the non-marine Mg:Ca ratios of fluids within these highly confined microenvironments, despite their immersion in seawater (Li, 2023).

Another complexity associated with microenvironments involves the spatial proximity between precipitation and its "drivers" (i.e., alkalinity engines). In relatively confined settings, the localized saturation state for a given mineral, while microbially mediated, may allow abiotic mineral growth supported by a non-biological sub-

strate, even if the alkalinity-enhancing microbial communities are not immediately adjacent. Precipitates formed in this manner may be morphologically indistinguishable from abiotic cements. Such processes may occur in the interstitial spaces of clotted stromatolites or fenestrae of micritic stromatolites but have been demonstrated in abandoned intraskeletal voids of modern scleractinian corals. Aragonite cements are highly heterogeneously distributed, often nucleating on organic filaments but also growing epitaxially on exposed coral skeleton aragonite. The irregular distribution and volume of cements suggest they are not products of passive marine cementation. Instead, localized endolithic microbial communities and boring sponges elevate carbonate saturation indices within specific voids relative to others, enabling aragonite to nucleate either on microbial organic substrates or epitaxially on preexisting aragonite surfaces. Without such biological activity (e.g., alkalinity engines), cements might not precipitate at all. Consequently, in semi-confined environments, it may be impossible to distinguish between biologically influenced and inorganic mineralization as defined by Dupraz et al., depending on the scale of microenvironmental coupling (Stephen, 1999).

Therefore, microbialites represent mineral precipitation in a wide range of microenvironments, including: the encapsulation of EPS sheaths in open benthic environments; stratified microbial mats; the containment within semi-porous cavity systems; and highly restricted intra-rock environments. The extent to which the geochemistry of microbialites reflects the environmental water chemistry may vary accordingly. In the case of REEs, empirical evidence suggests that the fluids in the microenvironments of shallow Holocene reef caves have not evolved in terms of elemental ratios from the surrounding seawater. This also seems to be the case for the Devonian Renalcis, some of which grew in reef cave systems. Nevertheless, compared with eukaryotic skeletons and aragonite precipitated directly from water, the contents of rare earth elements in microbialites are very abundant, thus making them a particularly reliable marker of seawater. The theoretical, experimental, and empirical inconsistencies in the rare earth element distribution coefficients between fluids and carbonates indicate that it is currently not possible to calculate the elemental concentrations in ancient seawater based on the elemental concentrations of rare earth elements in ancient microbialites. However, the elemental ratios remain unchanged.

4.2 Utilize trace elements to reconstruct the sedimentary environment

REEs geochemistry has also been used to constrain the sedimentary environment of some of the oldest known stromatolites, which are from the early Archean of the North Pole Dome area in the Pilbara Craton, Western Australia. Lowe and Walter first described the oldest known stromatolites there. However, the biogenic origin of these structures soon became a controversial issue. Subsequently, in the succession of the 3.43 Ga Strelley Pool Formation, a large number of better-preserved stromatolites were discovered from a slightly higher succession sequence. Hofmann et al.

provided a convincing argument for the biogenic origin based on morphology and sedimentary environment. However, Lindsay et al. questioned their interpretation and argued that these structures were hydrothermal precipitates and were unlikely to be of biogenic origin. Van Kranendonk et al. tested this hypothesis and demonstrated that the structures had a seawater-like REEs pattern, with LREE (Light Rare Earth Elements) depletion, a superchondritic Y/Ho ratio and a positive LaN anomaly, as well as associated granular carbonate sediments showing identifiable sedimentary structures. As expected in the anoxic Archean seawater, the samples lacked a negative CeN anomaly. Compared with the definite hydrothermal precipitates of the nearby associated Panarama volcano, its REEs pattern was very different from that of hydrothermal origin. Therefore, based on REEs geochemistry, the hypothesis of hydrothermal precipitate structures was refuted.

Seawater-like REEs patterns have been found in Precambrian and Phanerozoic marine carbonates. Subsequently, Allwood et al. documented the accreted stromatolites formed in the Strelley Pool Formation and showed that their morphology changed with the change of the sedimentary environment in a way that was completely consistent with the stromatolites produced by benthic biofilms (Liu, 2008).

Based on the REEs preserved in microbialites, some studies have been able to distinguish different water masses and/or differences in local sediment inputs. Kamber and Webb found that the stromatolites from the deeper environment at the edge of the Campbellrand carbonate platform in the late Archean (2.52 Ga) of South Africa have an REESn pattern, which reflects that the open seawater has a greater LREE depletion. Compared with the stromatolites formed on the top of the shallow platform, the EuN anomaly is more developed, and the mixing of lagoon waters and continental waters is more common. Nothdurft et al. were able to clearly distinguish the REEs characteristics of the open sea preserved by Devonian calcareous microorganisms. These characteristics come from the isolated platform reefs on the Lennard Shelf in the Canning Basin, Western Australia, and the runoff-rich waters soaking on the continental margin reefs. Similar patterns have also been found in the Holocene microbialites in the Vanuatu coral reefs. In this case, the microbialites in the Urélapa Reef off the coast of Espiritu Santo and the Tasmaloum Reef on the edge of the volcanic island show trends of increasing REE concentrations, increasing positive EuN anomalies, and decreasing Y/Ho ratios from offshore to onshore. This trend is consistent with the increase in runoff pollution from the weathered volcanic rocks of Espiritu Santo. In a certain special case, Frimmel showed that the REEs geochemistry of the Neoproterozoic cap carbonates (including stromatolites) in southwestern and central Africa changes systematically with the approach of the interpreted paleoshoreline. During the Neoproterozoic period, cap carbonates were widely deposited directly on glacial sediments, which may be caused by an initial pulse of high alkalinity resulting from the chemical weathering of fine-grained bedrock in a high-CO_2 atmosphere during the deglaciation period, although there are other in-

terpretations. The relatively flat REEsN pattern, lacking a well-developed LaN anomaly and a superchondritic Y/Ho ratio, was found in the nearshore environment. It does not reflect the direct pollution of the incorporated siliciclastic materials but is interpreted as the incorporation of nearshore colloids with a high concentration of shale-like REEs distribution. The farther offshore, the LREE depletion, positive LaN anomaly, and superchondritic Y/Ho ratio make the pattern more like that of seawater. Although the carbonates of the Roch Pina Formation cannot rule out an isolated, hydrothermally influenced lake, Frimmel interpreted the carbonates he analyzed as nearshore marine marginal stromatolite reefs (Luke, 2004).

5. Application of LA-ICP-MS in microbialites

In addition to identifiable fossils, the desire to accurately determine the biogenic origin of geological materials is driving active research in many disciplines. One of the key target materials is the purportedly microbially originated limestones (i.e., microbialites). It is now possible to infer with certainty the hydrogen-bearing nature of carbonate sediments. That is, even many samples of great geological age have been shown to preserve several aspects of the water chemistry in which they precipitated. The most prominent property in this regard is the relative abundances of rare earth elements and yttrium (REY), as their relative abundances in seawater are highly specific. Only certain groundwaters have similar REY patterns, but most suspected microbial carbonates have recognizable gross morphologies and occur in specific environments, such as coral reefs or carbonate platforms, and are thus easily distinguishable from groundwater precipitates.Unfortunately, the issue of determining whether a carbonate rock is a strictly abiogenic precipitate or formed under biological influence is more complex. In well-preserved microbial carbonates (many of which represent stromatolites in Precambrian rocks), there may be structural properties that are only compatible with the capture and binding of active sediments. However, discrete fossilized microorganisms are rarely preserved. In some Holocene microbialites, the patterns of accretion and growth actually preclude the preservation of microorganisms. Therefore, the presence of microfossils cannot be used as a necessary criterion for interpreting biogenic origin. In some well-preserved samples, there may be molecular evidence from organic compounds (i.e., biomarkers) that can be used to infer the organisms that formed a specific community. In samples that have experienced temperatures exceeding the stability of these molecules, reduced carbon may still be retained, and this carbon has been shown to exhibit the expected light isotopic composition characteristic of biogenic origin. Similarly, the sulfur isotopic composition of pre-diagenetic pyrite may indicate the presence of sulfate-reducing bacteria, especially when combined with a 33S depletion. However, many Precambrian carbonates, especially the oldest known ones, have been silicified, recrystallized, and/or deformed to the extent that microstructures are lost or ambiguous, reduced carbon has been lost, and isotopic signa-

tures are obscured. Unless other more reliable chemical and isotopic fingerprints are developed, it will be impossible to determine the origin of the oldest carbonates on Earth, and the empirical progress in understanding the emergence of life on Earth for the first time will slow down.

6. Conclusions

The correct interpretation of microbialites is of great significance for understanding the temporal evolution of early life and the Earth system. However, just like common biosedimentary structures, microbialites are formed by complex systems, which represent a continuum of processes with different contributions from biological, physical, and chemical components. Therefore, their identification and interpretation can be challenging. Trace element geochemistry has been proven to be a valuable tool for evaluating and assessing established microbialites.The contents of trace elements in microbialites represent multiple sources, including:

(1)elements that are intentionally or accidentally enriched through biological processes within biofilms or microbial mats;

(2) elements that passively accumulate from the surrounding fluid environment;

(3) elements related to the capture and binding of particulate matter or sediments;

(4) elements intruded from diagenetic fluids. The first source of elements, that is, those enriched through biological processes, can serve as biomarkers. Recognizing the unbalanced behavior of these elements may even potentially serve as biomarkers for putative microbialites from extraterrestrial sources.

If the nature of the microbial community is better constrained, and the activity of specific metals in microbial metabolism is known, the enrichment of certain elements may provide direct evidence of the types of biological communities, organisms, or metabolic patterns present in a given microbial mat or biofilm. If the element contents more reflect the surrounding water bodies in the sedimentary environment, they may contribute to the interpretation of these environments, including the identification of different water bodies, and may record the changes in marine chemistry over time.

In conclusion, the analysis of trace element geochemistry of microbialites has a promising prospect. New analytical techniques, such as LA-ICP-MS with spatial mapping, are breaking new ground in determining element abundances at extremely low concentrations, in challenging materials, and at extremely small spatial scales, which is particularly relevant to geomicrobiology research. Combining this type of research with other geochemical techniques (such as stable isotope studies) as well as fundamental sedimentology and stratigraphy can lead to a more skillful reconstruction of paleosedimentary and paleogeographic environments. However, there is still much room for documenting biomarkers and environmental markers in modern and well-defined ancient microbialites to refine the interpretation, review procedures, and analytical methods. As our basic understanding of microbialites as

records of biological communities and geochemical environments improves, the analysis will provide crucial new data for our understanding of the biogeochemical evolution of the Earth.

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