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Assessing Triassic carbonate microbialites as proxies for paleo-seawater trace element composition – two case studies from the Dolomites (northern Italy) compared.

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Marine microbial carbonates are widely used as archives of the trace element composition of seawater. The precipitation of microbialites should not involve "vital effects" fractionation, since it is induced by microbial activity and/or by the presence of biofilm and extracellular polymeric substances. Microbialites are expected to preserve a faithful record of the seawater REE+Y composition.

Microbialites from the Triassic of the Dolomites (Northern Italy) were analyzed for their trace element composition by using both LA-ICP-MS with spot sizes from 75 to 100 μm, and an electron microprobe with spot sizes of ca. 2 μm. A set of samples from the upper Anisian Latemar platform comprise microbialites characterized by clotted peloidal (thrombolitic) fabric. These are associated with primary aragonitic fossils, which have been completely replaced by calcite. Abundant marine radiaxial fibrous cements occlude all but the largest pores. Marine cements, along with microbialites, consist of low-Mg calcite.
Microbialites with thrombolitic fabrics were also sampled from the lower Carnian patch-reefs of the Cortina d'Ampezzo Basin. In this case, aragonitic shells and skeletons of sponges and corals retained their original mineralogy and ultrastructure and microbialites have a high-Mg calcite mineralogy (8-10 molar% $MgCO_3$). The marine carbonate minerals in this lower Carnian case study are thus better preserved than in the upper Anisian Latemar platform, and it could be expected that they retained the Carnian seawater trace element signature. Marine cements are scarce while most pores are filled by siderite or ferrous calcite early burial cements.

Marine cements and most microbialites from the upper Anisian Latemar platform show seawater-like shale-normalized REE+Y patterns, despite having been altered to low-Mg calcite. Microbialites in the lower Carnian of the Cortina d'Ampezzo Basin mostly yield REE+Y patterns that differ from seawater REE+Y, and rather resemble those of burial Fe-rich cements. Given the exceptional preservation of these samples, this divergence from an expected marine REE+Y pattern could hardly be explained by diagenetic alteration.
Petrographic observations show that microbialites of both case studies were initially highly porous. However, while the porosity of late Anisian microbialites was filled by marine cements soon after deposition, the micron-scale pores of early Carnian microbialites were filled during early burial by Fe-rich cements. The intermixing of microbial carbonate and early burial Fe-rich cement occurs at such a small scale, that even the spatial resolution of electron microprobes is often insufficient to analyze microbial carbonates and pore-filling cements separately.

When analyzing trace element contents of fossil microbialites, it is mostly the pore-filling cements that are analyzed. Only if the pore-filling phase is a marine cement, does the trace element content of microbialites have the potential to faithfully record the chemical composition of seawater. In such instances, however, mm-scale rims or crusts of marine cements are commonly also present and should be preferred for trace element analyses.