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## Anaerobic sulfur bacteria inducing carbonate lithification in modern- and possibly Precambrian microbial mats and stromatolites: The red-layer phenomenon

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Carbonate mineral formation in stromatolites and laminated microbial mats is still a subject of debate. Laminated structures found in sedimentary rocks of the Warrawoona Group, Western Australia (3.5 Ga) provide evidence of very early microbiallymediated carbonate layers. However, the microbial impact on the formation can rarely be proven since fossilized organisms and geochemical traces are missing. Recent studies performed in an environmental setting considered to be an analogue for the Archean could supply new evidence of participation of specific microorganisms, regarded as "living fossils". Photosynthetic sulfur bacteria are considered to be one of the oldest forms of life and are abundantly present in a microbial mat from the hypersaline Lagoa Vermelha, Brazil [1]. Studies on recent living and calcifying stromatolites, artificial anaerobic microbial mats and pure culture experiments show that purple sulfur bacteria may play an important role in the calcification process.

Living stromatolites from Lagoa Vermelha contain a distinct pattern of high Mg-calcite layers, embedded in a colour-striped microbial mat, similar to the "Farbstreifen-Sandwatt". Microsensor studies indicate that  $H_2S$  oxidation activity occurs in the absence of oxygen. Biogeochemical modelling suggests that microbes form elemental sulfur from anerobic  $H_2S$  oxidation, leading to a pH shift which induces the precipitation of carbonate minerals. Complete sulfide oxidation would lead to carbonate dissolution, however, studying the Lagoa Vermelha mats showed the opposite; formation of carbonates together with elemental sulfur. Molecular phylogenetic anal-

ysis of one bacterial strain from the microbial mat identified a bacterium related to *Ectothiorhodospira spp.*, capable of anaerobically oxidizing H<sub>2</sub>S to elemental sulfur (S°) according to:  $2 \text{ HS}^- + \text{HCO}_3^- \rightarrow 2 \text{ S}^\circ + \text{biomass} + 3 \text{ OH}^-$ 

Isolation of this organism together with experiments using an anoxic mini-chamber, allowed us to grow artificial sulfide oxidizing mats that could be studied by microsensors in the laboratory and model their activities. S-isotope analysis showed the possible pathway of sulfur in the microbial community, with participation of sulfate-reducing bacteria and sulfide-oxidizing bacteria. The same metabolism could be confirmed in both pure culture experiments and artificial microbial mats. We conclude that different metabolisms were active in the narrow chemical zoning of the microbial mat forming the carbonate layers. These findings expand our understanding of carbonate biomineralization and stromatolite formation in early anoxic ecosystems. In summary, even before the evolution of oxygenic photosynthesis, anaerobic sulfur bacteria may have contributed to the formation of bio-mediated carbonates resulting in the well-known lamination of microbial mats and stromatolite structures.

## References

[1] Vasconcelos et al. (2006) Sed Geol 185:175-183