

## Morphological record of oxygenic photosynthesis in conical stromatolites

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Conical stromatolites are thought to be robust indicators of the presence of photosynthetic and phototactic microbes in aquatic environments as early as 3.5 billion years ago. However, phototaxis alone cannot explain the presence of thickened, often disrupted, curled and contorted laminae in the crests of many Mesoproterozoic, Paleoproterozoic, and some Archean conical stromatolites.

Our laboratory experiments with cone-building cyanobacteria demonstrate that cyanobacterial production of oxygen in the tips of modern conical aggregates creates contorted laminae and sub-millimeter to millimeter-scale scale enmeshed bubbles. Similarly sized fossil bubbles and contorted laminae are unambiguously present only in the crestral zones of some conical stromatolites ~ 2.7 billion years or younger. This implies not only that cyanobacteria built Proterozoic conical stromatolites, but also that fossil bubbles may constrain the timing of the evolution of oxygenic photosynthesis.

## High reactivity of nano-sized iron oxides in microbial reduction

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Microbial iron reduction is considered to be a significant subsurface process. The rate-limiting bioavailability of the insoluble iron oxyhydroxides is yet a topic for debate. Surface area and mineral structure are recognized as crucial parameters for microbial reduction rates of bulk, macroaggregate minerals. However, a significant fraction of iron oxide minerals in the subsurface is present as nanosized particles. We therefore studied the role of nanosized and colloidal iron hydroxides in microbial iron reduction. In batch growth experiments with *Geobacter sulfurreducens*, synthesized nanoparticles of different ferric iron minerals were added as electron acceptors. This led to strongly increased iron reduction rates. The respective bulk, macroaggregate iron phases were reduced up to two orders of magnitude slower. The increased reactivity was not only due to the large surface areas of the nanosized minerals, but also due to a higher reactivity per unit surface. We hypothesize that this is attributed to the unique properties of the nanosized iron particles, namely their high surface energies, and specific surface topographical features. The high reactivity of synthetic nanosized iron hydroxides was also confirmed by a column experiment on a larger scale including flow conditions inside porous media. Additionally, naturally precipitated, nanosized iron hydroxide colloids from a column containing material from a topsoil horizon showed a similarly high reactivity as synthetic iron hydroxide colloids did. Furthermore, a 60-fold enhancement of reduction rates of bulk ferrihydrite was observed when nanosized particles were added, implying an important role of nanosized iron oxides in the electron transfer to bulk iron minerals.

In summary, nanosized iron hydroxides serve as superior electron acceptors in microbial iron reduction and contrast the current knowledge on the low reactivity of bulk, macroaggregate iron hydroxides.