

## Syntheses of organic matter and Fe-oxides by aerobic Fe-oxidizing bacteria in a deep ocean ~3.45 Ga ago

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Previous researchers have postulated that anaerobic photoautotrophic Fe-oxidizing bacteria (FeOB) played a major role in the Fe geochemical cycle (especially in the formations of banded iron formations) in Archean. However, no fossil evidence for FeOB has been found in rocks older than ~2.4 Ga. Here we report the morphological, chemical, mineralogical, and isotopic characteristics of the remnants of microbial mats in the Marble Bar Chert/Jasper (MBC) in East Pilbara, Western Australia. We interpret that the mats were developed mostly by aerobic chemolithotrophic FeOB on a 2,000 m-deep ocean-floor during the influence of low-temperature submarine hydrothermal fluids at ~3.45 Ga. We will further discuss implications of our findings on the chemical and biological evolutions of the early Earth.

The major findings and their interpretations from this study include: (a) The intricate nano-scale features of the interface between the OM-rich layers and the underlying minerals suggest that the microbial mats were biochemically bonded to the minerals, rather than simply settling on the minerals; (b) The  $\delta^{13}\text{C}$  values (-35 to -21‰) of the kerogens suggest that the kerogens were composed with two populations of primary producers: one that utilized  $\text{CO}_2$  via the Calvin-Benson cycle for C-fixation (e.g., cyanobacteria, FeOB, sulfide-OB) and the other involved in the  $\text{CH}_4$  related cycle (e.g., methanogens, methanotrophs); (c) Sub-nano- to nano-scale (<0.5 nm – 100  $\mu\text{m}$ ) morphologies and chemistries of organic matter (OM) and associated Fe-oxides (mostly hematite) in the MBC closely resemble those of modern aerobic chemolithotrophic FeOB; (d) The close association of nano-crystals of barite with the “microfossils” of FeOB suggests the local production of  $\text{SO}_4$  by sulfide-OB; and (e) The  $\delta^{34}\text{S}$  values (-4 to +1‰) of pyrite crystals in the benthic mats suggest the activity of sulfate-reducing bacteria (SRB).

Based on the above data we suggest that: (1) Microbial mats in the MBC developed at the interface between  $\text{CO}_2$ - and  $\text{O}_2$ -rich bottom ocean water and the underlying unconsolidated cherts which were invaded by low-temperature,  $\text{Fe}^{2+}$ - and  $\text{H}_2\text{S}$ -bearing hydrothermal fluids; (2) Although oxygenic photoautotrophs (cyanobacteria) had evolved by ~3.45 Ga, the involvement of cyanobacteria in the formation of benthic mats in the MBC is unlikely. This is because cyanobacteria could not have been active in the deep (dark) ocean, and the remnants of cyanobacteria in the photic zone could not have accumulated on the deep seafloor (>2,000m) with widely variable thickness in centimeter to meter scales; and (3) The microbial mats were comprised of various autotrophs (primary producers) and heterotrophs. The primary producers were mostly aerobic chemolithotrophic FeOB with minor sulfide-oxidizing bacteria (sulfide-OB) and methanotrophs, and the heterotrophs were mostly Fe-reducing bacteria (FeRB), sulfate-reducing bacteria (SRB), and methanogens. They imply that the global oceans and the atmosphere were already fully oxidized at ~3.45 Ga and the diverse microbial world had evolved by ~3.5 Ga. Our findings of the presence of negative- and positive Ce anomalies and the Y/Ho ratios (up to ~120) of the host cherts also support these implications.