

Biomarker evidence for an unique prokaryotic microbial mat ecosystem in a epicontinental sea on the Mesoproterozoic (1.45~1.30Gyr) North China Craton

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Mesoproterozoic marine paleoenvironment has drawn much more attention [1, 2]. Microbial mats may be very important for Proterozoic marine ecosystem [3].

The Mesoproterozoic Hongshuizhuang Formation (HSZF; ca. 1.45Myr) and the Xiamaling Formation (XMLF; ca. 1.4~1.3Myr), predominantly composed of organic-rich shale with TOC content up to 12% and 19%, and with biggest thickness up to 80m and 500m, respectively, developed in a north epicontinental sea on the North China Craton (NCC). The medium-maturated (H/C atomic ratio = 0.9 ~ 1.2) HSZF and XMLF shales present excellent preservation of biomarkers.

The results show: 1) Steranes diagnostic for eukaryotes are below the detection limit. 2) The saturates are predominately composed of mono- and bi-methyl substituted mid-chain methyl groups. 3) Aryl-isoprenoid hydrocarbons derived from green and purple sulfur bacteria were not detectable in the HSZF and XMLF shales.

Thus, the biomarker assembly of HSZF and XMLF suggests that organic-rich shales were deposited in a unique ecosystem where benthic microbial mats well developed, in which cyanobacteria were the primary production, while eukaryotes and phototrophic green and purple sulfur bacteria were all biogeochemically restricted. It is suggested that this kind of ecosystem might have been developed worldwide and maintained for an extended period during Mesoproterozoic.

- [1] Anbar & Knoll (2002) *Science* **297**, 1137–1142.
[2] Johnston *et al.* (2009) *PNAS* **106**, 16925–16929.
[3] Pierson *et al.* (1992) in *The Proterozoic Biosphere*, pp.245–347.

Investigating an amorphous precursor pathway to calcification: Implications for high magnesium carbonates

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With the realization that many calcified skeletons form by processes involving a precursor phase of amorphous calcium carbonate (ACC), a new paradigm for mineralization is emerging. There is evidence the Mg content in biogenic ACC is regulated by carboxylated (acidic) proteins and other macromolecules, but the physical basis for such a process is not well understood. In vitro experiments recently found that ACC compositions express a systematic relationship to the chemistry of carboxyl-rich biomolecules [1]. Molecules with a strong affinity for binding Ca compared to Mg promote the formation of Mg-enriched ACC products that are compositionally equivalent to high Mg-calcites and dolomite. Insights from this study raise the question of whether mineralization by a pathway involving this reactive intermediate could explain why some carbonates often contain higher Mg contents than are possible by classical crystal growth processes in the laboratory. Because this process is well documented in calcifying organisms, we hypothesize that high Mg carbonates in sedimentary environments can also be formed by non-classical pathways involving the transformation of ACC to the final crystalline products.

In new work, we are investigating the fates of high Mg ACC through asking two vital questions: (1) What are the process(es) by which some calcites can form with Mg contents that approximate a dolomitic composition? (2) How is the cation ordering to form a true dolomite structure obtained? To answer these questions we are conducting *in vitro* precipitation experiments, with a range of solution Mg/Ca ratios, small molecules and environmentally relevant particles at 20–40°C. Preliminary findings show the resulting precipitates are similar to the products reported in laboratory studies of microbially induced dolomites, which also form poorly crystalline aggregates. Structural analysis by XRD show precipitates are calcites of MgCa(CO₃) composition, and not dolomites because they lack characteristic cation ordering. These results support the model of an alternative pathway for obtaining high Mg carbonates of dolomite composition, not possible in conditions where classical crystal growth processes dominate.

- [1] Wang *et al.* (2009) *PNAS* **106**, 21511–21516.