Molecular evidence of the earliest photosynthetic life and the biogeochemical cycles in the Archean

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We report molecular and molecular-isotopic evidence of photosynthesis in the late Archean. We isolated maleimides[Λ], derivatives of ancient chlorophylls (or bacteriochlorophylls), from organic-rich dolostones/shales of the upper Archean (the Klein Naute Fm., Transvaal Supergroup, South Africa, 2.52 Ga), sampled from an AGDP core drilled on the Campbellrand-Malmani platform in South Africa. The structure of a maleimide obtained therein retained the *neo*-pentyl group that is known as a unique structure of bacteriochlorophyll *c*-*e* of green sulfur bacteria. Green sulfur bacteria are anoxigenic phototrophs with a photosystem similar to the Photosystem I of oxygenic phototrophs such as cyanobacteria. We will discuss both the evolutionary and paleoenvironmental significance of the appearrence of green sulfur bacteria prior to the Great Oxidation Event. We also discuss the nitrogen cycle at that time based on molecular-specific nitrogen isotopic analyses of these maleimides.

[Λ]The tetrapyrrole units of chloropigments are long preserved in the form of alkylporphyrinin within sediments and sedimentary rocks. Maleimides (1*H*-pyrrole-2,5-diones) can be obtained as oxidation products of kerogenous organic residues of geological samples, which are presumed as derivatives of alkylporphyrins that have been bound to the sedimentary macromolecules. Stable nitrogen isotopic signatures of these porphyrins and maleimides are thus a valuable proxy for the reconstruction of past aquatic nitrogen cycles. Recently, We have developed various practical approaches for nitrogen isotopic analyses of sedimentary porphyrins as well as maleimides derived from kerogen-bounded tetrapyrroles.