

Intracellular detection of nickel-porphyrins moieties in a 1-Gyr old multicellular alga allows to track early phototrophy

M.C. Sforina^{1,*}, C.C. Loron¹, C.F. Demoulin¹, C. François², Y. Cornet¹, Y.J. Lara¹, D. Grolimund³, D. Ferreira Sanchez³, K. Medjoubi⁴, A. Somogyi⁴, A. Addad⁵, A. Fadel⁵, P. Compère⁶, D. Baudet⁷, J. J. Brocks⁸, E. J. Javaux¹

¹ Early Life Traces & Evolution-Astrobiology, UR Astrobiology, University of Liège, Belgium

² Commission for the Geological Map of the World, France

³ Paul Scherrer Institut, Swiss Light Source, Switzerland

⁴ Synchrotron Soleil, France

⁵ Unité Matériaux et Transformations, Université Lille 1, France

⁶ Functional and Evolutive Morphology, Department of Biology, Ecology and Evolution, UR FOCUS, and Center for Applied Research and Education in Microscopy, University of Liège, Belgium

⁷ Geodynamics & Mineral Resources Service, Royal Museum for Central Africa, Belgium

⁸ Research School of Earth Sciences, The Australian National University, Australia

The end of the Proterozoic has seen the transition between ecosystems with bacterial primary producers to ecosystems where primary producers are photosynthetic eukaryotes. The emergence of photosynthetic eukaryotes is an important step in the evolution of Life, leading to the complexification of trophic networks, making possible the emergence of animals and the colonization of land. Although this transition is observed in the Neoproterozoic biomarker record, few phototrophic organisms are unambiguously recognized in the fossil record. Therefore, the timing of the onset of eukaryotic photosynthesis and its evolution in the different groups of eukaryotes are still poorly understood.

We report bound Ni-tetrapyrrole moieties preserved *in-situ* within cells of *Arctacellularia tetragonala*, a ~1 Gyr-old multicellular eukaryote from the Mbuji-Mayi Supergroup (DR Congo). Tetrapyrroles (e.g. hemes, chlorophylls) are pivotal constituents of the cell metabolism. Whereas tetrapyrroles commonly degrade in the early phases of burial and diagenesis, they may transform into geoporphyrins. Geoporphyrins are common in bulk solvent extracts of Phanerozoic sedimentary rocks but exceedingly rare in the Precambrian. Current approaches do not allow association of the detected porphyrins to individual fossils. They can also not be performed on overmature rocks because even relatively mild thermal alteration around 200°C is incompatible with the preservation of free biomarkers.

Combining morphological, chemical and ultrastructural analyses with synchrotron-based X-ray Fluorescence and X-ray Absorption Spectroscopy, we identified the tetrapyrrole moieties as chlorophyll derivatives, and *A. tetragonala* as one of the earliest algae, part of the Archaeplastidae supergroup.

This new methodology, applicable to billion-of-year old, overmature rocks, provides new constraints on the evolution of phototrophy during the Precambrian and the diversification of primary producers in early ecosystems.

Mots-Clés : Organic-walled microfossils, Tetrapyrrole moieties, Photosynthetic eukaryotes, Ecosystem evolution, Precambrian