The role of a pan-eukaryotic chlorophyll catabolism during the late Proterozoic global oxygenation: a hypothesis

*柏山 祐一郎[1]
*Yuichiro Kashiyama[1]

1. 福井工業大学大学院工学研究科応用理工学専攻
1. Graduate School of Engineering, Fukui University of Technology

The energy used in the modern Earth's biosphere is largely dependent on solar radiation coming through the mechanism of photosynthesis that carried by various phototrophic organisms. In all modern mechanisms of photosynthesis, chlorophylls, efficient photosensitizers, serve as central and indispensable factors, by which photon energy is converted to chemical potential in organic molecules. Among such mechanisms, one of the most important aspects is found in oxygenic photosynthesis, where water molecules, ubiquitous and the most abundant molecule in the biosphere, is recruited as a terminal electron donor of the photosynthetic electron transport chain. The emergence of oxygenic photosynthesis and, moreover, its becoming predominant in the primary production must have been a major innovation in Earth's history, which must have drastically increased photosynthetic production (and the energy flux) from the sun to the Earth's biosphere.

The use of water in photosynthesis, however, inevitably generates molecular oxygen. Importantly, molecular oxygen is rather incompatible with chlorophyll-based lives; the molecular oxygen (triplet oxygen) is efficiently photosensitized by chlorophylls, resulting in generation of highly cytotoxic reactive species called "singlet oxygen" (i.e., phototoxicity of chlorophylls). It has been studied that elaborated mechanisms present within modern oxygenic phototrophs that protect cellular components against the phototoxicity. However, the phototoxicity of chlorophylls is a potential obstacle in biological interactions that comprise energy flow in the biosphere after the photosynthetic inflow toward higher levels of the food web. Namely, chlorophylls can be potential phototoxins in the food of the primary consumers because such "elaborated mechanisms against the phototoxicity" must be disrupted when the phototrophs were consumed and digested by the heterotrophs.

In the modern aquatic ecosystem, it has been evident in recent studies that microbial eukaryotes comprise majority of the primary consumer who directly preys on microbial phototrophs through phagocytosis, algae, thereby called algivorous protists (protists denote unicellular eukaryotes). The present work is based on a latest discovery that the algivorous protists generally catabolize chlorophylls contained in the dietary algae into non-phototoxic $13^2,17^3$-cyclopheophorbide enols (CPEs) along with their phagocytotic digestion. Therefore, this CPE catabolism is a key biochemical process that allows massive consumption of the aquatic primary producers in the modern oceans. Furthermore, because CPE catabolism occurs so ubiquitously among nearly all major phylogenetic assemblages (i.e., supergroups), CPE catabolism must have already been present in common ancestors of the extant eukaryotes, even possibly in the last eukaryotic common ancestor (LECA).

Such protistan algivory should indeed have played an even more important role in the earlier periods before emergence of metazoan planktons in the Proterozoic. Partial pressure of molecular oxygen in the atmosphere is thought have been highly suppressed long after the earliest Proterozoic Great Oxidation Event until it rapidly rose up close to the modern level immediately following the end of the last Snowball Earth event in the late Proterozoic. This "Last Oxygenation Event (LOE)" was probably attributed to a

massive photosynthetic production by oxygenic phototrophs, by cyanobacteria and/or eukaryotic microalgae, together with efficient export production and sequestration of hence produced reduced carbons into the sediment. Interestingly, the appearance of CPE catabolism among the modern lineages of eukaryote predates the timing of the LOE, indicating that algivorous protists were already present during LOE and played an important role in the biogeochemical cycle responsible for accumulation of molecular oxygen into atmosphere through massive consumption of otherwise phototoxic algal producers.

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