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Chlorophyll derivatives as proxies of the marine photosynthetic production and succeeding biogeochemical processes

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Chlorophylls produced in the oceanic environment undergo potentially both abiotic and biotic decompositions. A majority of chlorophylls is to be destroyed through so-called Type II process that cleaves tetrapyrrole macrocycle oxidatively. A portion of chlorophylls, however, experiences the Type I process in which tetrapyrrole macrocycles are preserved intact with various degree of defunctionalization, hence surviving into sediments. These survived chlorophyll derivatives could be further altered chemically to be fossil porphyrins, red pigments extracted from sedimentary rock as old as the Proterozoic.

Although chlorophyll derivatives in marine sediments have been studied for almost a quarter century, our new HPLC method that excludes analytical artifacts revealed that major chlorophyll derivatives are pyropheophytins, cyclopheophorbide enols, chlorin carotenyl esters, and chlorin sterile esters. The chemical structures of these derivatives strongly suggest their formations through metabolic processes, not a simple abiotic product. In addition, derivatives of chlorophyll b, chlorophyll d, and bacteriochlorophyll a that should be derived from specific taxa are also commonly identified in marine surface sediments. These chlorophyll derivatives are thus potential proxies of not only photosynthetic productions but also metabolic, biochemical processes in the water column.

We pursue uses of these chlorophyll derivatives as proxies of water column biogeochemical processes by understanding taphonomy of chlorophylls. Here, we particularly focused in cyclopheophorbide enols which has turned out to be quantitatively most important after our new analytical method. I is thus important to elucidate the environment of it's formation and the organisms/processes concerned. We considered various analytical processes for the best method quantifying cyclopheophorbide enols from both water and sedimentary samples. We also determined physicochemical properties on hemi-synthesized cyclopheophorbide enols.

Keywords: chlorophyll derivatives, chlorophyll d, fossil porphyrin, cyclopheophorbide enols, marine photosynthetic production, biogeochemical processes