



## Sources and transformation processes of pheopigments in Lake Haruna, Japan

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Depositional derivatives of chlorophyll *a* (Chl *a*), such as pheophytin *a* (Phe *a*), pyropheophytin *a* (PPhe *a*) and steryl chlorin esters (SCEs), have been widely and conventionally used as direct indicators of algal activity in the aquatic environments. However, few studies have studied their detailed sources and transformation processes based on molecular isotopic evidences. Particularly, the SCEs may represent a wide diversity of sources including biotic modifications by zooplankton, because they are produced during the grazing processes of zooplankton. In this study, we estimated the sources and transformation processes of pheopigments in the sediments from Lake Haruna, Japan, based on carbon ( $\delta^{13}\text{C}$ ) and hydrogen isotopic compositions ( $\delta\text{D}$ ) of phytol and sterols as side chains of pheopigments.

A domain of the phytol from Chl *a* in the  $\delta^{13}\text{C}$ - $\delta\text{D}$  diagram is very close to that of phytols from both Phe *a* and phytoplankton. In contrast, the phytol from PPhe *a* is plotted on a mixing line between phytols from phytoplankton and terrestrial C3 plants. The carbon and hydrogen isotopic compositions of algal sterols (e.g. cholest-5-en-3 $\beta$ -ol and 24-methycholesta-5,22-dien-3 $\beta$ -ol) from SCEs are very close to those of phytoplankton sterols, whereas those of multiple-source sterols (e.g. 24-ethylcholest-5-en-3 $\beta$ -ol) from SCEs are between those of phytoplankton and terrestrial C3 plant sterols. These isotopic signatures strongly suggest that the phytol from Phe *a* and algal sterols from SCEs are attributable ( $\sim 100\%$ ) to those of phytoplankton, whereas the phytol from PPhe *a* and multiple-source sterols from SCEs are derived from both phytoplankton and terrestrial plants. Our results suggest that the terrestrially derived phytol and sterols could contribute when PPhe *a* and SCEs are produced by the grazing processes.