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NITROGEN ISOTOPIC COMPOSITION OF BIOLOGICAL CHLOROPHYLLS AND THEIR DEPOSITIONAL DERIVATIVES IN GEOLOGICAL SEDIMENTS

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Chlorophylls are antenna pigments directly related to the photosynthetic processes of photoautotrophs. They and their depositional derivatives such as pheophytins and pyropheophytins are abundantly found in oceanic and lacustrine sediments (e.g. Keely and Maxwell, 1991). Therefore, they have widely and conventionally been used as definitive biomarkers of photoautotrophic activity in the aquatic surface environment (e.g. Sanger, 1998; Nakajima et al., 2003). Moreover, since chlorophylls contain hydrogen, carbon, and nitrogen, their isotopic compositions could record multiple information on the hydrologic and nutrient cycles in the environment where the photoautotrophs grow (e.g. Chikaraishi et al., 2005). Particularly, nitrogen isotopic composition of chlorophylls and their derivatives (including alkylporphyrins) is a potentially unique proxy for the reconstruction of nitrogen cycle in the geological past as well as modern aquatic environment. However, little information is available for the isotopic relationship among different chlorophyll species within a single photoautotroph, as well as for the isotopic modification associated with the structural change (e.g. chlorophyll to pheophytin) during depositional processes in the water column and sediments.

Here, we report nitrogen isotopic composition ($\delta^{15}N$) of chlorophylls *a*, *b*, *c*, and *d* in various photoautotrophs such as higher plant (*Quercus monglica*) and marine macroalgae (*Sargassum Filicinum*, *Gelidium japonica*), and of chlorophylls and their derivatives in a lake sediment (Lake Haruna, Japan). The chlorophylls and their derivatives were extracted and isolated by the improved procedure of Chikaraishi et al. (2005), and subsequently degraded to maleimides by chromic acid oxidation. Nitrogen isotopic composition of the maleimides was determined by gas chromatography/combustion/isotope-ratio mass spectrometry (GC/C/IRMS) with an analytical error (1σ) of less than ± 0.5‰.

Nitrogen isotopic composition of chlorophylls and their derivatives in the photoautotrophs and sediment was summarized in Table 1. Within a single photoautotroph, no substantial isotopic difference is observed between chlorophylls *a* and *b* for higher plant, chlorophylls *a* and *c* for brown alga, and chlorophylls *a* and *d* for red alga. It is consistent

with a theoretical consideration that no nitrogen isotopic discrimination could occur during chlorophyll biosynthetic pathway. Also, no substantial isotopic difference is observed between chlorophylls and their derivatives in the sediment. It suggests that the isotopic composition of chlorophylls is well preserved in their derivatives in the sediment.

Thus, we demonstrate no nitrogen isotopic fractionation between different structures of chlorophylls within a single photoautotroph and no nitrogen isotopic modification during depositional processes of chlorophylls in the water column and sediments, which provides indispensable background information for the interpretation of the isotopic signatures of chlorophylls and their derivatives in geological samples.

	Higher plant	Brown alga	Red alga	Sediment
	Q. mongolica	*S. filicinum*	*G. japonicum*	Lake Haruna
Chlorophyll *a*	+6.5	+3.2	+3.2	-4.1
Chlorophyll *b*	+6.2			-4.2
Chlorophyll *c*		+3.3		
Chlorophyll *d*			+3.4	
Pheophytin *a*				-3.9
Pheophytin *a'*				-4.4
Pheophytin *b*				-4.1
Pyropheophytin *a*				-4.0
Pyropheophytin *b*				-4.2
Sterylchlorinesters				-4.2

Table 1. Nitrogen isotopic composition of chlorophylls in higher plant (*Q. monglica*) and marine macroalgae (*S. Filicinum*, *G. japonica*), and of chlorophylls and their derivatives in a lake sediment (Lake Haruna, Japan)

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