

Carbon isotopic ratios of sterols in steryl chlorin esters in Lake Baikal sediment

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Steryl chlorin esters (SCEs) are bio-transformed components of chlorophyll *a* esterified with algal sterols, which are widely observed in marine and lacustrine sediments. SCEs have strong stability against diagenesis in sediments for millions of years (Soma et al., 2001). Because of these properties, SCEs would be used as a biomarker to represent paleoproductivities. Their carbon isotopic compositions provide the useful information about carbon cycles. To determine the utility of sterol in SCEs as a carbon isotope surrogate for phytoplankton, the carbon isotopic ratios of SCEs in the surface sediment recovered from southern basin in Lake Baikal were measured.

The SCEs fractions were collected by HPLC. Their fractions were saponified by methanolic KOH (5wt% H₂O) for 4.5h at 75°C. Prior to GC analysis free sterols were acetylated. The carbon isotopic ratios of acetylated sterols were measured by GC/C/IRMS.

Detected sterols in SCEs were mainly cholest-5-en-3 β -ol, 24-methylcholesta-5,22-E-dien-3 β -ol, 24-ethylcholesta-5-en-3 β -ol. The carbon isotopic ratios of total sterols in SCEs from Lake Baikal sediments were $-32.3 \pm 0.4\%$ and it was depleted in ¹³C by -5.2% relative to that of phytoplankton in Lake Baikal (Yoshii et al., 1999). The observed depletions of $\delta^{13}\text{C}$ in sterols relative to biomass, eukaryotic algae, are reported 5 to 8 ‰ (Schouten et al. 1998). Therefore, the carbon isotopic ratios of sterols in SCEs should be useful to infer the algal activity in the Lake Baikal.

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$\delta^{13}\text{C}$ and δD evidence for two series of PAH formation in the natural environments

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Polycyclic aromatic hydrocarbons (PAHs) have been found in extraterrestrial materials including meteorites, as well as in terrestrial samples such as geological sediments and automobile exhausts. Compound-specific carbon isotope analysis of PAHs has been provided information on their sources and formation mechanisms.

Naraoka et al. (2000) determined $\delta^{13}\text{C}$ values of individual PAHs from carbonaceous chondrites, where more condensed PAHs are more depleted in ¹³C ranging from -8 to -26% (relative to PDB) as the H/C ratio decreases. This relatively large isotopic fractionation could occur during cyclization and/or carbon addition under the kinetic control. Furthermore, two reaction pathways of “pyrene series” and “fluoranthene series” are distinguished. “Pyrene series” is more depleted in ¹³C relative to “fluoranthene series” at the same H/C ratio, although pyrene and fluoranthene are structural isomers (C₁₆H₁₀) each other.

On the other hand, the $\delta^{13}\text{C}$ variation of PAHs from automobile exhausts (-23 to -27%) is generally smaller than that of carbonaceous chondrites. Okuda et al. (2003) revealed from the exhaust samples that more condensed PAHs are more enriched in ¹³C as the H/C ratio decreases. The $\delta^{13}\text{C}$ signature of PAHs in automobile exhausts can be explained by an isotopic thermodynamic equilibrium under high temperature condition, where ¹³C-enrichment is favored in more condensed carbon structure. “Pyrene series” and “fluoranthene series” are also recognized in automobile exhaust samples. However, “pyrene series” is more enriched in ¹³C relative to “fluoranthene series” at the same H/C ratio, which is the opposite isotopic trend compared to PAHs in carbonaceous chondrites.

Compound-specific hydrogen isotopic compositions also revealed a different isotope signature between pyrene and fluoranthene. Pyrene is more enriched in D than fluoranthene in carbonaceous chondrites. The δD trend is opposite to $\delta^{13}\text{C}$ trend. While pyrene is more depleted in ¹³C, but more enriched in D relative to fluoranthene. Isotope exchange experiments of hydrogen in PAHs show that pyrene can exchange its hydrogen with water faster than fluoranthene (Oba and Naraoka, in this volume). These $\delta^{13}\text{C}$ and δD signatures clearly indicate the two distinctive reaction pathways (“pyrene series” and “fluoranthene series”) for the PAH formation in the natural environments.

References

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