

REFRACTORY MACROMOLECULE AND BIOMARKER ANALYSES OF CRETACEOUS WOODY FRAGMENTS IN CENTRAL HOKKAIDO, JAPAN

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Land plant biomarkers have been frequently found as free compounds in ancient sediments and plant fossils, and can be useful as chemotaxonomic marker. However, such free biomarkers account for only a small fraction in plant organic fossil. The most part of plant fossil consists of refractory macromolecule, which is non-extractable with organic solvent, acid, and alkali. Refractory macromolecule survives decay more readily than free biomarker during diagenesis. Major sources of refractory macromolecules are thought to be plant biomacromolecule that were selectively *in situ* preserved. Refractory macromolecular and biomarker analyses were carried out for woody fossil fragments in Cretaceous sandstones of Oyubari area, central Hokkaido, in order to evaluate chemical state of organic molecules within the fossil and to obtain chemotaxonomic information from refractory macromolecule.

Fine to medium sandstones were collected from the outcrops of the Okusakainosawa sandstone and mudstone member of the Cretaceous (Albian) Shuparogawa Formation (Yezo Group), Tengunosawa of Oyubari area. The Shuparogawa Formation abundantly contained woody and coaly fossil fragments (Takashima *et al.*, 2004). Several larger fragments of woody macro fossil in rock samples were individually picked out. Rock samples were crushed to a fine powder. From the powder sample, woody fossil fragments were obtained by density centrifugation method (Sawada, 2006). Free lipids were ultrasonically extracted from the woody fragments with dichloromethane and methanol. The lipid extract was separated by silica gel column to four fractions. The residue after extraction was saponified with 1M KOH in methanol to obtain bound lipids. These fractions were analyzed by GC/MS.

The isomer ratios of C₂₉ steranes (20S/(20S+20R)) and C₃₂ hopanes (22S/(22S+22R)) averaged to be 0.45 and 0.58, respectively. Thus, maturity levels of the woody fossil fragments were arrived at the stage of late diagenesis to early catagenesis. Gymnospermous biomarkers such as diterpenoids (retene, abietane and pimarane etc.) could be identified as free compounds in all samples. However, there were no angiospermous biomarkers such as triterpanes (e.g., oleanane).

Organic molecules bound in macromolecules constituting woody fragments (with ester bonds), obtained by saponification, were mainly composed of short-chain (C₁₄ - C₁₈) fatty acids. Series of n-alkanols up to C₂₀ were also detected. From the distribution pattern,

these alkyl constituents might be originated from selectively-preserved refractory macromolecule such as cutin or suberin with ester bond. Meanwhile, other alkyl compounds (*e.g.* hydroxyl acid) that expected to be obtained as major hydrolysate from cutin or suberin within plant fossil fragments could not be detected. It suggests significant alteration or loss of these moieties during diagenesis. Nevertheless, even carbon-number predominance was observed in fatty acids and n-alkanols, which indicated that biological state may be preserved. Moreover, distribution patterns of fatty acids were found to be almost similar in all samples, while those of n-alkanol significantly varied.

Result of free biomarker analysis suggested all plant fragments were gymnosperms, which was concordant with palaeobotanical study in Hokkaido area (Nishida, 2005). Carbon number distribution patterns of fatty acids appears reasonable when compared with previous study for Cretaceous gymnosperm fossil (Almendros *et al.*, 1999). We suggest that can provide us chemotaxonomic information at the broad level of taxonomic groups, such as gymnosperm and angiosperm.

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