# Paleoenvironmental reconstruction using resistant macromolecules in the Cretaceous terrestrial plant fossils and kerogens

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Resistant macromolecules (RMMs) composing living plant tissues are more refractory against microbial degradation and diagenesis, and are well preserved as major parts in plant fossils and plant-derived organic particles in sediment. Monomer compositions of the RMMs vary depending plant taxa, organs and physiological factors including growth conditions and stages, frequently affected by environmental change. Thus, the RMM analysis may serve as powerful technique for evaluating paleobotany, paleovegetation and paleoenvironment. In the present study, we analyzed plant fossils and kerogen from the Cretaceous sediments in Japan to examine applicability of the RMMs for reconstructing paleochemotaxonomy and paleoenvironment.

We analyzed 1) angiosperms and gymnosperms mesofossils collected from the Cretaceous Ashizawa Formation, Futaba Group, Fukushima, and 2) kerogens separated from the mudstones collected from the Cretaceous Albian Shuparogawa Formation, Maruyama Formation and Hikagenosawa Formation of the Yezo Group, Hokkaido, Japan. The mesofossils include fruits, flower, leaf, stem, seeds and woods (Takahashi et al., 2008). The kerogens are separated from the powdered rock samples by HCl and HF treatments (Sawada, 2006). The residues removed free compounds were hydrolyzed, and these released compounds were analyzed by GC-MS. Also, pyrolysis and thermochemolysis of plant fossils and kerogens by using GC-MS equipped Curie-point pyrolyzer. Additionally, statistical analysis was calculated using the SPSS software. We used hierarchical clustering to group fossils with similar lipid distributions among species or organs.

As main hydrolyzed products (ester-bound molecular units) from all fossils, $C_6$-$C_{28}$ *n*-alkanoic acids and $C_8$-$C_{28}$ *n*-alkanols were detected. Phenolic compounds released were much minor, especially in charred fossils. Carbon number distributions appears to be different between the organs; low $C_{18}/C_{16}$ ratios in cuticles (e.g. flowers, fruits and leaves) and high $C_{18}/C_{16}$ ratios in woods, which indicates those of cutin and suberin, respectively. Statistical analysis were calculated in lipid distribution for these released alkyl lipids from each fossils. Cluster analysis revealed recognizable patterns of distributions of released alkyl lipids. All woody fossils are present in a cluster excluded non-woody ones. Thus, we propose that the paleochemotaxonomy of plant fossil are possible by making a comprehensive evaluation for various *n*-alkyl lipid units bound in the RMMs.

The $C_{10}$-$C_{28}$ *n*-alkanoic acids and $C_{10}$-$C_{30}$ *n*-alkanols were detected in the kerogens from the sediments of the Yezo Group. More recently, the long chain (>$C_{20}$) *n*-alkanols released from plant-derived RMM by hydrolysis have been reported to be remarkably abundant in deciduous broadleaved angiosperms (e.g., Mueller et al., 2012). Indeed, it is found that the ratios of *n*-alkanols to *n*-alkanoic acids are significantly correlated with angiosperm/gymnosperm ratios recorded by terrestrial plant-derived terpenoid biomarkers. From these results, we propose that the proportions of long chain *n*-alkanols released from terrestrial plant-derived kerogens are applicable to reconstruct for paleovegetation.

 

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