

## Compositions of molecules bound in terrestrial plant-derived kerogens from Cretaceous sediments, Hokkaido, Japan

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Organic particle derived from terrestrial higher plant is usually contained in ancient sediment. The terrestrial plant-derived organic particle is mainly composed of resistant macromolecules such as cutin and suberin polymers and well preserved biochemical and taxonomic information for living plant. Our research group proposed that molecular compositions of the resistant macromolecule in plant fossil could be useful as chemotaxonomic indicator (Ikeda et al., submitted). In the present study, we applied this chemotaxonomic indicator to terrestrial plant-derived organic matter (kerogen) collected from Cretaceous sedimentary sequence to examine applicability of this indicator for reconstructing paleovegetation, and moreover, terrestrial paleoenvironmental variations.

We analyzed mudstones and sandstones collected from the Lower Cretaceous Albian Shuparogawa Formation, Maruyama Formation and Hikagenosawa Formation of the Yezo Group in the Tengunosawa route, Oyubari, Hokkaido, Japan. These formations are turbidite sediments that carbonized plant fragments are abundantly contained. Kerogens were separated from the powder rock samples as reported by Sawada (2006, *Island Arc* 15, 517-536). The kerogens were extracted with methanol and dichloromethane, and were subsequently refluxed under high temperature to remove free compounds completely. Finally, the residues were saponified by KOH/methanol to obtain ester-bound compounds. GC-MS analysis was performed for identification and quantification of compounds. Also, we observed the kerogens with fluorescent light microscope.

Fluorescent light microscopic observation of kerogens shows that the kerogens from all sediments are mainly composed of wood and non-fluorescent amorphous organic matter (NFA), and contain plant cuticle as minor component. This indicates that all kerogens used are originated from terrestrial higher plant tissues. As saponified products (ester-bound molecular units) from all kerogens, C14-C18 n-alkanoic acids (fatty acids) are mainly detected, and C10-C24 n-alkanols are identified. There are predominance of even carbon numbers of fatty acids and n-alkanols released from kerogens, and these released compounds are presumably originated from monomers of cutin and suberin polyesters in resistant macromolecules of the kerogens. The C18/C16 ratios of fatty acids released from kerogens significantly vary from the Shuparogawa to Hikagenosawa Formation in the Tengunosawa route. Previous study (Ikeda et al., submitted) suggested that the C18/C16 ratios of the bound fatty acids obtained after saponification varied depending on relative abundances of woody / herbaceous fossils. It is found that the variations of the C18/C16 released fatty acid ratios are almost synchronous to those of angiosperm / gymnosperm ratios recorded by terrestrial higher plant biomarkers (Nakamura et al., submitted). In the Cretaceous flora, it is presumed that the woody and herbaceous plants were mainly composed of gymnosperm and angiosperm, respectively. Thus, the synchronous variations between the C18/C16 released fatty acid ratios and biomarker angiosperm / gymnosperm ratios suggest that these organic geochemical data showed the variations of paleovegetation for angiosperm-dominant grassland / gymnosperm-dominant forest in the Cretaceous paleo-Hokkaido areas. From these insights, we propose that the C18/C16 ratio of fatty acid released from kerogen can be useful as paleovegetation indicator. In addition, C18 ratios in n-alkanols bound in kerogen have potential as paleovegetation indicator.

**Keywords:** terrestrial plant-derived kerogen, bound molecule, paleovegetation indicator, terrestrial paleoenvironment, Yezo Group, Cretaceous