

**STABLE CARBON AND HYDROGEN ISOTOPIC COMPOSITIONS AND ABUNDANCES OF ANGIOSPERM BIOMARKERS IN OILS AND SOURCE ROCKS FROM THE DEEPWATER PORTION OF THE KUTEI BASIN, INDONESIA**

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The Kutei Basin is a Tertiary depocenter in central Indonesia which has recently produced hydrocarbons in the deepwater. The reservoir rock is a Miocene sand, which is several kilometers thick throughout parts of the basin. The coaly type source rocks of a majority of the petroleum systems in the basin are profoundly dominated by land plant remains, attributed to the rapid growth of tropical plants on the island of Borneo, as well as the rapid accumulation of detritus from the River Mahakam and its tributaries (Curiale et al., 2005, and references therein).

Miocene-reservoired oils and coals of the Kutei Basin have been studied previously (Curiale et al., 2005 and Curiale et al., 2006). Both biomarker and stable carbon isotopic data of isoprenoids and *n*-alkanes have revealed that no bona fide and acceptable oil-source rock correlation can be made using these coals, and that multiple oil families are evident. Several explanations have been proposed to explain the lack of a correlation, including: i) coals are not sources of these oils; ii) oils consist of multiple accumulations; iii) relative low maturity of these coals prevents a correlation; iv) Kutei oils contain additional material (e.g. oleanenes) through migration-contamination, which also has an impact on traditional molecular maturity ratios.

The present study extends previous work on the Kutei Basin's complex petroleum systems addressing migration-induced compositional changes, maturity and/or source effects. Current understanding and preliminary findings suggest that all these processes have played major roles in the petroleum geochemistry of the Kutei Basin. A holistic approach is underway, involving stable carbon and hydrogen isotope measurements of several suspected and established age-diagnostic biomarkers mostly derived from higher plants, namely oleanenes, lupanes, bicadinane, land plant wax *n*-alkanes and cadalene present in 11 oils and 12 immature coaly source-rocks (Miocene and Eocene, 15 Ma to 36 Ma). In addition stable carbon isotopes of individual aromatics (alkylnaphthalenes, alkylphenanthrenes) and their abundance ratios (*cf.* van Aarssen et al., 1999), as well as stable hydrogen isotopes of isoprenoids and *n*-alkanes (e.g Dawson et al., 2005) are being determined to assess evidence

for multiple accumulations and maturity, respectively. An improved separation of the important higher plant components using a combination of molecular sieves and argentation liquid chromatography has been carried out in order to obtain  $\delta^{13}\text{C}$  and  $\delta\text{D}$  data of selected plant biomarkers (e.g. cadalene, norlupanes and bicadinanes). Quantitation of all the higher plant biomarker components by GC-MRM techniques using a polyethylene glycol column (*c.f.* Armanios et al., 1995; Nytoft et al., 2002) has been performed on the oils and source-rocks. It is suggested that two broadly distinct oil families exist, but both are rich in angiosperm biomarkers. Most oils are dominated by an usually high abundance of cadalane (Fig. 1), the source of cadalane is currently under investigation. The oils can be separated based on their oleanane, bicadinane, norlupane, bisnorlupane and taraxastane abundances (Curiale et al., 2005). Interestingly norlupanes and bisnorlupanes have been identified in high abundance in low-latitude oils and their abundance increases with decreasing latitude by about 10 fold. Stable carbon isotopes of pristane also separate into two distinct families, one family characterised by  $^{13}\text{C}$  depleted pristane and norlupane.

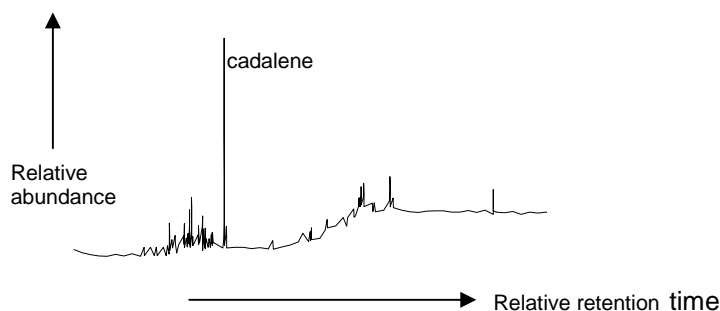


Figure. 1 GC-MS trace of an aromatic fraction of a Miocene oil from the Kutei Basin

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## **HYDROGEN AND CARBON ISOTOPE COMPOSITIONS OF N-ALKANES FROM LEAF WAXES IN MODERN ANGIOSPERMS AND GYMNOSPERMS: HOW DO THEY COMPARE?**

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Biomarker and stable isotopic signatures of higher plant leaf waxes are becoming increasingly popular in paleoclimate research (e.g., Schefuß et al., 2005; Pagani et al., 2006). Interpretation of results of this sort of studies, however, strongly depends on a thorough understanding of isotopic signatures from different plant types contributing to sedimentary organic matter. The purpose of this project is to investigate environmental factors that control stable isotopic composition of *n*-alkanes from modern angiosperms and gymnosperms growing under different climatic regimes. The project has two components. First, we sampled (approximately once a month) 3 angiosperm and 2 gymnosperm plants in one location in eastern Washington State, USA during the 2005 and 2006 growing seasons. Second, we are extending our work area by sampling (Fall 2006, Spring and Summer 2007) and analysing leaves from several angiosperm and gymnosperm species along a west-east climatic gradient in the Canadian Rocky Mountains. Data from the Fall 2006 campaign are not available yet but will be generated over the first half of 2007.

The initial 2005 *n*C<sub>27</sub>-alkane data from WA State show a clear separation between 2 gymnosperms and 2 angiosperms (Fig.1). From May to October,  $\delta$ D and  $\delta^{13}$ C values of common lilac and quaking aspen stayed within -166 and -182‰, and -31.6 to -32.7‰, respectively. However,  $\delta$ D and  $\delta^{13}$ C values of Scots pine and blue spruce were within -190 to -208‰ and -28.8 to -30.6‰, also without a major trend throughout the growing season. Similar to the other angiosperm species, European white birch was D-enriched ( $\delta$ D from -160 to -173‰) relative to gymnosperms. However,  $\delta^{13}$ C values of this species were more similar to those of Scots pine and blue spruce in May, but had a ca. 4‰ positive shift from May to October. Furthermore, birch underwent a significant increase in the proportion of *n*C<sub>31</sub>- vs. *n*C<sub>25</sub>-alkanes during the growing season. No other trees showed this trend.

Because all 5 plants experienced the same environmental conditions and were irrigated with the same water, we suggest that the observed isotopic variations derived from physiological differences among the species. Relative <sup>13</sup>C-enrichment and D-depletion of

Scots pine and blue spruce may have resulted from their lower stomatal conductance and greater water use efficiency in comparison with common lilac and quaking aspen. A higher stomatal conductance of birch in comparison with the other species under investigation led to a greater water stress of this plant during June-August 2005. Hence, the observed shift in the production of *n*-alkanes and the greatest  $\delta^{13}\text{C}$  response as well as its most D-enriched values.

Our first results already show that this study will have profound implications for interpreting  $\delta\text{D}$  and  $\delta^{13}\text{C}$  values of terrestrial plant *n*-alkanes in the sedimentary record. The initial results from WA State indicate that large fluctuations in relative humidity and temperature during a single growing season do not cause significant shifts in  $\delta\text{D}$  and  $\delta^{13}\text{C}$  values of *n*-alkanes. Second, large changes in  $\delta\text{D}$  (ca. 50‰) and  $\delta^{13}\text{C}$  (ca. 3.5‰) values of sedimentary *n*-alkanes may result not only from shifts in paleoclimatic variables (a common assumption) but also from changes in paleovegetation. Further results from the WA State in conjunction with results from the Canadian Rocky Mountains study will show how well  $\delta\text{D}$  and  $\delta^{13}\text{C}$  values of terrestrial plant *n*-alkanes reflect changes in environmental parameters, such as source water  $\delta\text{D}$  values, relative humidity, and soil moisture. This information will be crucial for investigating the levels and isotopic composition of atmospheric carbon dioxide as well as the state of paleohydrological cycle in the geologic past.

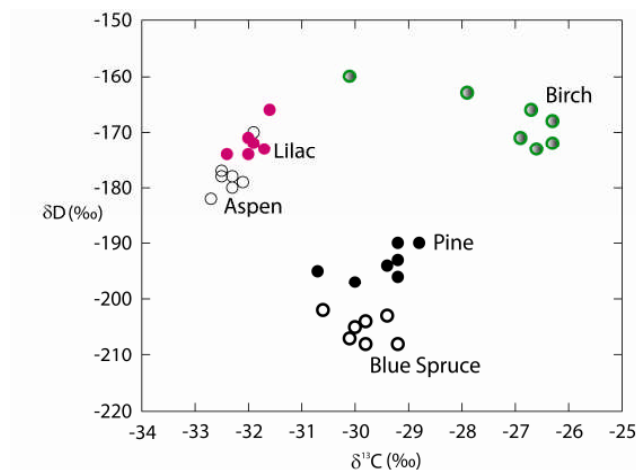


Figure 1. Carbon and hydrogen isotopic composition of leaf wax  $n\text{C}_{27}$  alkanes from angiosperm and gymnosperm trees in eastern Washington State, USA.

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## CARBON ISOTOPIC COMPOSITIONS OF VOLATILE FATTY ACIDS AS PROXIES FOR BIOGEOCHEMICAL PROCESSES IN GAS HYDRATE BEARING SEDIMENTS

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In recent decades, our understanding of biogeochemical processes has benefited enormously from the information encoded in the stable carbon isotopic composition of organic molecules. For low-molecular-weight metabolites,  $\delta^{13}\text{C}$  values are routinely acquired for methane and used to examine details of its production and consumption. Similarly, the carbon isotopic composition of acetate, a ubiquitous intermediate in anaerobic metabolism, is affected by its sinks and sources. However, systematic information on the isotopic composition of acetate and other water-soluble metabolites in natural environments is rare due to analytical obstacles (for references see Heuer et al, 2006). Only the recent development of a new technique for online isotope-ratio-monitoring liquid chromatography/mass spectrometry (irm-LC/MS) (Krummen et al., 2004) has set the stage for routine carbon isotopic analysis of dissolved volatile fatty acids (VFAs). A first systematic irm-LC/MS survey of VFAs in a wide range of natural sediments and sediment incubations has revealed a large variability in the carbon isotopic compositions of acetate, propionate and butyrate with  $\delta^{13}\text{C}$  values ranging from -5‰ to -85‰ vs VPDB (Heuer et al., 2006). Incubation experiments suggest a systematic link between the carbon isotopic composition of the investigated VFAs and the dominant-carbon transforming processes of the sediments, i.e. fermentation, methanogenesis and homoacetogenesis. These latest findings underline the potential of  $\delta^{13}\text{C}$  values of acetate and other VFAs as powerful indicators of biogeochemical processes predominating *in situ* in natural sediments.

In this presentation, we will examine the role of acetate in gas hydrate-bearing sediments. Based on  $\delta^{13}\text{C}$ -values of methane, a large fraction of the methane in marine gas hydrates is thought to result from biogenic sources. However, only little is known about methanogenic processes in the deep marine biosphere, deep pore-water profiles of the potential methane precursor acetate are rare (e.g. Egeberg and Barth, 1998; Wellsbury et al. 2000), and  $\delta^{13}\text{C}$  values of acetate have not been reported for this type of environment, yet. We will show results from carbon isotopic investigations of gas hydrate bearing sediments at the Cascadia Margin, NE Pacific, which were drilled during Integrated Ocean Drilling

Program Expedition 311. We find both concentrations and isotopic compositions of acetate to change with sediment depth (Fig 1). Acetate concentrations rise from  $<5 \mu\text{M}$  at the sediment-water interface to  $670 \mu\text{M}$  at 250 meters below seafloor.  $\delta^{13}\text{C}$  values of acetate increase from  $-35$  to  $-17\text{‰}$  vs VPDB. Given uniform  $\delta^{13}\text{C}$  values of dissolved organic carbon (DOC) close to  $-23\text{‰}$ , the low values of acetate in the top 130 m of the sediment column require either partial production of acetate from a  $^{13}\text{C}$ -depleted pool of precursors such as biomass from methanotrophs or partial production of acetate by  $\text{CO}_2$  reduction (homoacetogenesis). Accordingly, a change in the precursor pool below 130 mbsf or an increasing importance of acetoclastic methanogenesis are plausible processes explaining the increase of  $\delta^{13}\text{C}$  of acetate with depth. The feasibility of the latter process, flow of acetate to methane, is supported by thermodynamic calculations.

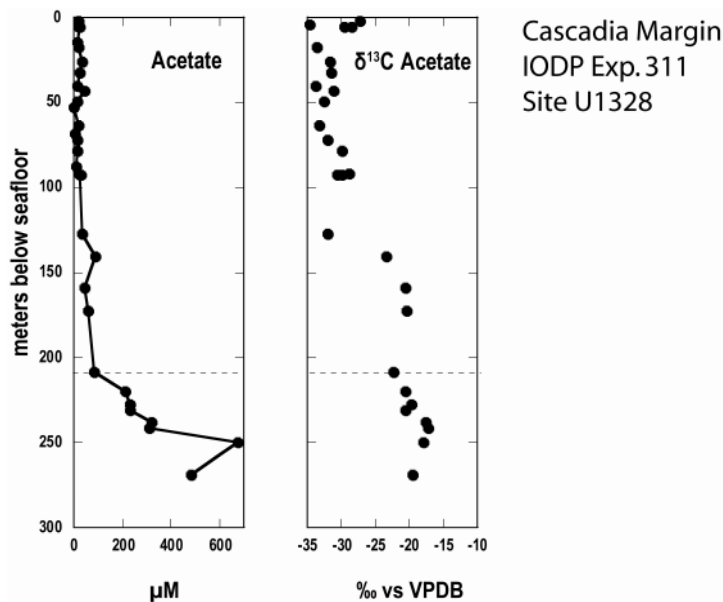


Figure 1. Analysis of pore-water acetate by irm-LC/MS yields quantitative and carbon isotopic data for samples obtained from gas-hydrate bearing sediments at the Cascadia margin, NE Pacific. The dashed line indicates the depth of the bottom simulating reflector and is assumed to represent the base of the gas hydrate stability field.

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