Experimental investigations of the kinetics of bitumen generation

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Petroleum generation is a two-step reaction: (1) the thermal decomposition of kerogen to form bitumen, and (2) decomposition of bitumen to oil and gas. Even through bitumen has long been recognized as the intermediate product in the formation of petroleum, we lack knowledge of many aspects of its chemical composition and generation kinetics. To better understand the reaction mechanism by which bitumen is generated from kerogen, the kinetic parameters for its generation have been determined through a series of hydrous pyrolysis experiments using both the New Albany Shale (Devonian, Type II) and the Menillite Shale, (Oligocene, Type IIS).

Bitumen generated from the New Albany Shale can be chemically distinguished from the expelled oil based on the proportion of saturates, aromatics and polar compounds, with the bitumen phase being enriched in NSOs (resins + asphaltenes) and aromatics relative to the expelled oil. With increasing reaction progress, the relative amount of the saturate fraction remains unchanged, while the amounts of aromatics, resins and asphaltenes all show a progressive increase. The isotopic composition of the saturate, aromatic and NSO fractions also remains relatively constant with increasing reaction progress, which is evidence against the cleavage of carbon-carbon bonds during bitumen generation.

Under our experimental conditions, bitumen generation can be modeled as a pseudo-first order reaction. The activation energy for the generation of bitumen from the New Albany Shale is higher than that reported in previous studies, and is within the range of energies for carbon bond cleavage (~>30 kcal/mol). C-C bond cleavage is inconsistent with the isotopic evidence, indicating that this activation energy more likely reflects the disruption of other bond types, such as hydrogen bonds or other weak non-covalent bonds. Kerogen may be viewed as a structured fluid, so that polymer theory rather than aqueous chemistry may be more apporpriate for modeling bitumen generation, through the incorporation of mechanisms such as disentanglement. By comparing the kinetic parameters for the New Albany Shale to those for the Menillite Shale, the role of kerogen composition, specifically the presence of sulfur, will be determined for this intermediate reaction.

Source, age and taxon-specificity of biomarker parameters tested on a large diverse oil set

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The interrelationships between biomarker parameters were tested using a set of 100 oil samples in order to observe correlations to source-rock age, depositional environment and lithology. Parameters tested include ratios built on C_{26} to C_{30} steranes, diasteranes, mono- and triaromatic steroids, highly branched isoprenoids, distributions of hopanes, gammacerane, oleanane, and plant diterpanes and the tetracyclicpolyprenoid (TPP). Many of these parameters have not been systematically tested previously using oil sets, some only with rock sets, including the occurrence and abundance triaromatic-23,24-dimethylcholesteroids and 4,23,24-trimethylcholesteroids, which are likely taxon specific for haptophytes and dinoflagellates (Figure 1). Trends among the various C_{27}-C_{28}-C_{29} steroids discriminate on the basis of geologic age, lithology and depositional environment of the source rock. Many parameters will be discussed.

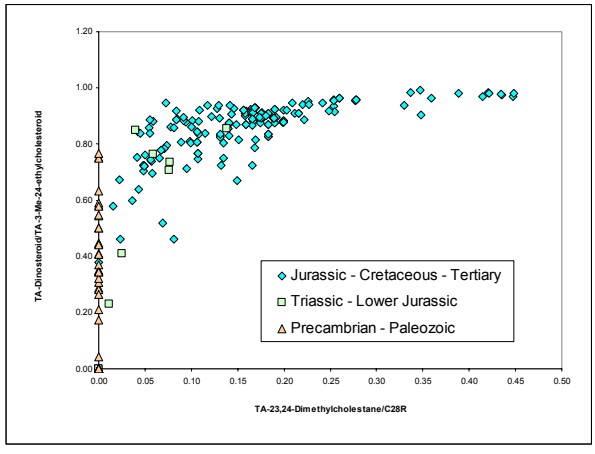

Figure 1. The plot of triaromatic-23,24-dimethylcholesteroids (TA-DMD) versus 4,23,24-trimethylcholesteroids (TA-Dinos) occurrrence in oils shows the former to be more restricted to oils of Triassic and younger source than the latter.