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The significance of chemical kinetics and structural markers in source rock kerogens and related asphaltenes

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Asphaltenes can be considered as the soluble fragments of respective kerogens and appear to be equivalent to labile part of source rock kerogens. They represent the macromolecular fraction in source rock bitumen as well as in oil reservoirs. Asphaltenes have been utilized in petroleum exploration to give information about bulk petroleum formation characteristics of their related deep seated source rocks, especially in areas where this source rocks have not been drilled or are inappropriate.

Here we study asphaltenes from reservoir oils, from source rock bitumen as well as their related source rock kerogens in order to enhance the application and the limitations of petroleum asphaltenes to predict the characteristics of related source rocks. More than 50 source rock and oil samples from a natural laboratory - the Duvernay Formation (WCSB) Petroleum system - have been studied systematically using bulk petroleum kinetics, open system pygc and - last but not least - closed system artificial maturation experiments.

Predicting the bulk petroleum formation for geological heating rates shows that the transformation behavior of asphaltenes and source rock kerogens is quite similar, in spite of the fact, that the onset of the main petroleum formation phase from the source rock asphaltenes was predicted to start earlier than for the related kerogens.

The differences were even more significant when studying the molecular composition of hydrocarbons formed from the different asphaltene types and their related kerogens. The aromaticity of products formed from source rock asphaltenes and kerogens was very high, while products formed from reservoir oil asphaltenes were low in aromaticity and fit very well with the composition of natural oils. In addition facies indicators such as the 1.2.3.4-TMB/ (n-C11+n-C12) ratio are very similar when comparing petroleum asphaltenes and natural formed products. Last but not least it can also be observed that the gas formed from source rock asphaltenes is much drier relative to products formed from source rock kerogens.

Interestingly some of those observations indicate that products formed from asphaltenes are very close to natural petroleum characteristics and may help to bridge the compositional differences between petroleum artificially formed from kerogens and the petroleum formed in nature.

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Thermodynamic and carbon isotopic constraints on the origin of unusual bitumens in the uranium deposits of Athabasca (Saskatchewan, Canada)

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The presence of unusual bitumen-like material in the unconformity-type uranium deposits of Athabasca raises the question of the origin of this material as well as of its role in the formation of the uranium deposits. Based on similar carbon isotope compositions for the bulk bitumen and graphite present in basement faults, a genetic relationship has been proposed in which bitumen-forming hydrocarbons would have been produced through hydrothermal alteration of graphite [1]. Recent ion microprobe measurements on individual bitumen particles reveal large microscale variations in δ^{13} C values within a single bitumen particle, whereas those values in the graphite appear to be homogeneous [2]. Such variations are in contradiction with a graphite-derived bitumen scenario.

Thermodynamic calculations have been carried out to evaluate the importance of hydrocarbon generation by hydrothermal alteration of graphite, for which a general reaction can be written as

 $n \operatorname{C}_{\operatorname{graphite}} + (m/2) \operatorname{H}_2 \operatorname{O}_{(l)} = \operatorname{C}_n \operatorname{H}_{m(l)} + (m/4) \operatorname{O}_{2(g)}$, (1)where $H_2O_{(l)}$, $C_nH_{m(l)}$ and $O_{2(g)}$ represent liquid water, a given liquid hydrocarbon species and oxygen gas, respectively. Values of the equilibrium constant $(K_{(1)})$ for reaction (1) have been calculated using thermodynamic properties taken from the literature [3] for representative series of hydrocarbons at the temperature and pressure conditions of the unconformity, which allowed to calculate the activities of the liquid hydrocarbons produced by reaction (1) as a function of oxygen fugacity. In accord with the carbon isotope results, the calculations indicate that hydrocarbon liquids cannot be produced by hydrothermal alteration of graphite under geologically relevant oxygen fugacity values. The possibility of an abiotic Fischer-Tropsch-type synthesis for these unusual hydrocarbons is discussed based on the carbon isotope measurements and further thermodynamic considerations [4].

References

- [1] Landais et al. (1993) CJES 30, 743-753.
- [2] Sangély et al. (2004) GCA (this volume).
- [3] Helgeson et al. (1998) GCA 62, 985-1081.
- [4] Zolotov and Shock (1999) JGR 104, 14033-14049.