P386-TH

ORIGIN AND FATE OF CARBOXYLIC ACIDS IN CRUDE OILS AS REFLECTED IN THEIR STABLE CARBON ISOTOPIC COMPOSITION

Christian HALLMANN, Kliti GRICE and Ben VAN AARSSEN

Centre for Applied Organic Geochemistry, Curtin University of Technology, GPO Box U1987, Perth 6845, Western Australia

Carboxylic acids were found to be present in minor to moderate amounts in a large number of oils (eg. Rodrigues et al., 2000). Although they have been characterised in previous studies, their origin and fate after the expulsion of petroleum from its source rock have been under explored. The interaction of petroleum with water, which occurs during expulsion, migration, and reservoir residence, can lead to the dissolution of carboxylic acids of low-molecular-weight (Borgund and Barth, 1993). Consequently, acetic acid is commonly found as a constituent of water in reservoirs. Oil-water interaction can in theory lead to the generation of carboxylic acids *de novo*, through oxidation of hydrocarbons. Helgeson et al. (1993) suggested that hydrocarbons and formation waters in petroleum reservoirs are often in metastable equilibrium, and Seewald (2001) proposed that the composition of acids, produced by abiotic oxidation processes from alkanes, can be predicted quantitatively and results in an excess of acetic acid. Life in the deep subsurface can be fuelled by the availability of short-chain carboxylic acids such as acetic acid (Wellsbury et al., 1997). On the other hand, biodegradation of hydrocarbons also produces biogenic acids as secondary metabolites. While a number of acidic metabolites were detected during *in-vitro* biodegradation experiments (e.g. Wilkes et al., 2003), only few studies have detected acids likely to be of biological origin in crude oils (Aitken et al., 2004). By combining the application of organic geochemistry with metabolomics to biodegraded oil reserves, significant improvements in understanding the controls on the deep biosphere can be achieved.

The stable carbon isotopic composition of carboxylic acids released from the kerogen, as well as those formed by abiotic oxidation processes should be similar to that of *n*-alkanes as they are related by oxidation and decarboxylation processes. Biogenic acids, however, are anticipated to be characterised by slightly lighter carbon isotopic signatures since they either originate from cell-wall lipids or the modification of petroleum hydrocarbons by methylation or fumarate-addition (Rios-Hernandez et al., 2003), the latter leading to succinyl-derivates.

Carboxylic acids in petroleum are not routinely analysed due to the laborious workup procedures and generally low abundances. A rapid and reproducible small-scale method was recently developed within our group, allowing for the efficient analysis of carboxylic acids in larger sample sets and preventing the loss of volatile fatty acids.

This presentation focuses on the quantitative distribution of carboxylic acids and their hydrocarbon counterparts, as well as their stable carbon isotopic signatures in a range of oils that have experienced varying degrees of subsurface biological alteration. Biodegradation, abiotic oxidation, and water-washing processes can thus be identified.

REFERENCES

Rodrigues, D., Koike, L., de Reis, F., Alves, H., Chang, H., Trindade, L., and Marsaioli, A. 2000. Carboxylic acids of marine evaporitic oils from Sergipe-Alagoas Basin, Brazil. *Organic Geochemistry* **31**, 1209-1222.

Borgund, A., and Barth, T. 1993. Migration behaviour of petroleum-associated short-chain organic acids. *Organic Geochemistry* **20**, 1019-1025.

Helgeson, H., Knox, A., Owens, C., and Shock, E. 1993. Petroleum, oil field waters, and authigenic mineral assemblages: Are they in metastable equilibrium in hydrocarbon reservoirs? *GCA* **57**, 3295-3339.

Seewald, J. 2001. Model for the origin of carboxylic acids in basinal brines. *GCA* **65**, 3779-3789.

Wellsbury, P., Goodman, K., Barth, T., Cragg, B., Barness, S., and Parkes, J. 1997. Deep marine biosphere fuelled by increasing organic matter availability during burial and heating. *Nature* **388**, 573-576.

Wilkes, H., Kuehner, S., Bolm, C., Fischer, T., Classen, A., Widdel, F., Rabus, R. 2003. Formation of *n*-alkane- and cycloalkane-derived organic acids during anaerobic growth of a denitrifying bacterium with crude oil. *Organic Geochemistry* **34**, 1313-1323.

Aitken, C., Jones, D., and Larter, S. 2004. Anaerobic hydrocarbon biodegradation in deep subsurface oil reservoirs. *Nature* **231**, 291-294.

Rios-Hernandez, L., Gieg, L., and Suflita, J. 2003. Biodegradation of an alicyclic hydrocarbon by a sulfate-reducing enrichment from a gas condensate-contaminated aquifer. *Applied and Environmental Microbiology* **69(1)**, 434-443.