

RELEASE OF BIOMARKERS FROM SULFUR-RICH KEROGENS DURING HYDROUS PYROLYSIS

Martin P. Koopmans^{1,3}, Jaap S. Sinninghe Damsté¹ and Michael D. Lewan²

¹Netherlands Institute for Sea Research, Department of Marine Biogeochemistry and Toxicology, P.O. Box 59, 1790 AB Den Burg, Netherlands

²U.S. Geological Survey, Box 25046, MS 977, Denver Federal Center, Denver, CO 80225, USA

³Present address: (i) University of Oslo, Department of Geology, P.O. Box 1047 Blindern, 0316 Oslo, Norway, and (ii) Saga Petroleum ASA, P.O. Box 490, 1301 Sandvika, Norway

Keywords: hydrous pyrolysis, generation of biomarkers, S-rich kerogen

INTRODUCTION

Hydrous pyrolysis is an established laboratory technique for the simulation of the natural maturation of kerogen. There has been some debate in the literature whether water plays a purely physical or maybe a chemical role during hydrous pyrolysis (*e.g.* Monthieux *et al.*, 1986; Lewan, 1992). This issue has recently been reviewed by Lewan (1997). Mass balance calculations have shown that CO₂ generated during hydrous pyrolysis derives O from the water added before the experiment (Lewan, 1992). Hydrothermal experiments with ethane and ethene showed that water was a source of H₂ (Seewald, 1994). In addition, experiments with kerogen and heavy water suggested that the deuterated alkanes generated were formed by reaction of alkyl radicals with heavy water-derived D (Hoering, 1984). Thus, the current understanding is that water acts as a source of H to quench thermally generated alkyl radicals, thereby both forming saturated hydrocarbons and inhibiting cross-linking reactions which may lead to the formation of an insoluble pyrobitumen.

The thermal degradation of kerogen has been characterised as a two step process (Lewan, 1992). First, kerogen is partially decomposed to a polar-rich bitumen, which at higher temperatures decomposes to yield free hydrocarbons as thermal stress increases. This sequence was also recognised in a study of a S-rich sample from the Monterey Formation (Baskin and Peters, 1992). However, these observations were based on bulk quantities (*i.e.* kerogen, bitumen, and free hydrocarbons), and a similar sequence based on molecular data using biomarkers has not been clearly established. Here, we describe results of thermal maturation experiments designed to follow the kerogen degradation pathway at a molecular level using a biomarker approach. In addition, we have investigated the role of water by performing experiments in the absence and presence of water.

EXPERIMENTAL

Hydrous and anhydrous pyrolysis experiments (200-360°C; 72 h) were carried out with two sedimentary rocks containing immature sulfur-rich organic matter. Detailed descriptions of the experimental procedures can be found elsewhere (Koopmans *et al.*, 1996, 1998). One sample is a claystone from the Gessoso-solfifera Formation (Upper Miocene, northern Italy), with a TOC content of 2.0 wt.%. Its mineral composition consists of quartz, smectite, illite, chlorite, and dolomite. The other sample is a limestone from the Ghareb Formation (Upper Cretaceous, Jordan), with a TOC content of 19.6 wt.%. Its mineral composition consists almost exclusively of calcite with only minor amounts (<10 wt.%) of quartz and apatite.

RESULTS

The extract of the claystone contains saturated hydrocarbons and organic sulfur compounds (OSC) with mainly normal and isoprenoid alkane skeletons. In addition, the extract comprises a polar fraction which contains molecular aggregates consisting of predominantly isoprenoid and cyclic alkane skeletons linked by S- and O-bonds (Koopmans *et al.*, 1996). The kerogen has been desulfurised and consists mainly of normal, isoprenoid and cyclic alkanes (Schaeffer *et al.*, 1995; Putschew *et al.*, 1998).

Hydrous pyrolysis of the claystone generates large amounts of saturated hydrocarbons and OSC from thermal degradation of the kerogen and the polar fraction (Koopmans *et al.*, 1996). We were able to follow the kerogen thermal degradation pathway at a molecular level by monitoring the speciation of several biomarkers. C₃₇ and C₃₈ alkenones, for example, were present in an S- and O-bound form in the kerogen of the unheated claystone, while their carbon skeletons were absent in the extract. After hydrous pyrolysis at gradually increasing temperatures, these carbon skeletons are first released into the polar fraction, and then as free hydrocarbons, OSC and saturated ketones (Fig. 1; Koopmans *et al.*, 1997).

In order to elucidate the role of water during hydrous pyrolysis, we also conducted experiments in the absence of water (anhydrous pyrolysis). For the claystone, the results are quite dramatic. While hydrous pyrolysis generates large amounts of normal, isoprenoid and cyclic alkanes, anhydrous pyrolysis does not generate these compounds (Fig. 2). For the limestone, normal, isoprenoid and cyclic alkanes are generated in comparable amounts during hydrous and anhydrous pyrolysis, although during anhydrous pyrolysis destruction of alkanes at high temperatures seems to occur at an earlier stage (Fig. 2). In addition, desulfurisation of the polar fraction of the claystone heated at 200°C by anhydrous pyrolysis does not release any biomarkers, in contrast to hydrous pyrolysis. This strongly suggests that anhydrous pyrolysis is not capable of converting S-bound biomarkers in the polar fraction to free biomarkers.

DISCUSSION

Our results suggest that the presence of water and the mineral matrix play an important role in the generation of biomarkers from S-rich kerogens (cf. Fig. 2). Quantitative experimental studies by Huizinga *et al.* (1987a,b) showed that mineral matrix effects on hydrocarbon generation from powdered mixtures of kerogen and minerals were more extreme under anhydrous than hydrous pyrolysis, especially when smectite was the employed mineral. In addition, they found evidence that the combined effect of smectite and a high organic S content leads to increased degradation of bitumen generated from the kerogen. Thus, the combination of smectite and a high organic S content for the claystone in our study may explain the large differences observed between the claystone and the limestone.

The actual mechanism and reactions responsible for smectite inhibiting the generation of biomarkers under anhydrous conditions and not under hydrous conditions remain to be determined. The greater availability of clay mineral interlayers to bitumen under anhydrous pyrolysis may be important, because under anhydrous pyrolysis these interlayers are probably less hydrated than under hydrous pyrolysis. Huizinga *et al.* (1987a) showed that adsorption of the polar constituents of bitumen to smectite was enhanced during anhydrous pyrolysis. For our experiments, this would imply that the polar fraction of the claystone, which contains abundant S-bound biomarkers, would be adsorbed to these clay minerals during anhydrous pyrolysis. Once inside the clay mineral interlayers, the high contact area of mineral surface to organic matter may favor cross-linking reactions that form an insoluble pyrobitumen rather than cracking reactions that form free hydrocarbons. This is supported by our desulfurisation experiments, which showed that S-bound biomarkers in the claystone were destructed during anhydrous at 200°C.

Thus, during anhydrous pyrolysis, the biomarker thermal generation sequence described above, *i.e.* (i) bound moiety in the kerogen, (ii) bound moiety in the polar fraction, (iii) free biomarker, is hindered because no biomarkers are generated from the polar fraction. This explains the differences in the amounts of S-bound biomarkers during hydrous and anhydrous pyrolysis of the claystone, and consequently also the differences in generation of free biomarkers (i) between hydrous and anhydrous pyrolysis of the claystone, and (ii) between anhydrous pyrolysis of the claystone and the limestone.

CONCLUSIONS

Our experiments show that the thermal degradation of kerogen to bitumen to free biomarkers can be monitored on a molecular level. Water is essential in releasing biomarkers from S-rich kerogens, especially when clay minerals are present. The exact chemical role that water plays, however, remains to be determined.

ACKNOWLEDGEMENTS

The Natural Resources Authority of Jordan is gratefully acknowledged for their assistance in helping the authors collect a sample of the Ghareb Formation from the El Lajjun quarry. Analytical assistance was provided by F. Carson, M. Dekker, W.I.C. Rijpstra and Dr W.G. Pool.

REFERENCES

- Baskin, D.K. and Peters, K.E., 1992, Early generation characteristics of a sulfur-rich Monterey kerogen: AAPG Bulletin, v. 76, pp. 1-13.
- Hoering, T.C., 1984, Thermal reactions of kerogen with added water, heavy water and pure organic substances: Organic Geochemistry, v. 5, pp. 267-278.
- Huizinga, B.J., Tannenbaum, E. and Kaplan, I.R., 1987a, The role of minerals in the thermal alteration of organic matter - III. Generation of bitumen in laboratory experiments: Organic Geochemistry, v. 11, pp. 591-604.

- Huizinga, B.J., Tannenbaum, E. and Kaplan, I.R., 1987b, The role of minerals in the thermal alteration of organic matter - IV. Generation of *n*-alkanes, acyclic isoprenoids, and alkenes in laboratory experiments: *Geochimica et Cosmochimica Acta*, v. 51, pp. 1083-1097.
- Koopmans, M.P., de Leeuw, J.W., Lewan, M.D. and Sinninghe Damsté, J.S., 1996, Impact of dia- and catagenesis on sulphur and oxygen sequestration of biomarkers as revealed by artificial maturation of an immature sedimentary rock: *Organic Geochemistry*, v. 25, pp. 391-426.
- Koopmans, M.P., Schaeffer-Reiss, C., de Leeuw, J.W., Lewan, M.D., Maxwell, J.R., Schaeffer, P. and Sinninghe Damsté, J.S., 1997, Sulphur and oxygen sequestration of *n*-C₃₇ and *n*-C₃₈ unsaturated ketones in an immature kerogen and the release of their carbon skeletons during early stages of thermal maturation: *Geochimica et Cosmochimica Acta*, v. 61, pp. 2397-2408.
- Koopmans, M.P., Rijpstra, W.I.C., de Leeuw, J.W., Lewan, M.D. and Sinninghe Damsté, J.S., 1998, Artificial maturation of an immature sulphur- and organic matter-rich limestone from the Ghareb Formation, Jordan: *Organic Geochemistry*, v. 28, pp. 503-521.
- Lewan, M. D., 1992, Water as a source of hydrogen and oxygen in petroleum formation by hydrous pyrolysis: *ACS, Div. Fuel Chemistry Preprints*, v. 37, No. 4, pp. 1643-1649.
- Lewan, M.D., 1997, Experiments on the role of water in petroleum formation: *Geochimica et Cosmochimica Acta*, v. 61, pp. 3691-3723.
- Monthieux, M., Landais, P. and Durand, B., 1986, Comparison between extracts from natural and artificial maturation series of Mahakam delta coals: in Leythaeuser, D. and Rullkötter J., eds., *Advances in Organic Geochemistry 1985*; *Organic Geochemistry*, v. 10, pp. 299-311.
- Putschew, A., Schaeffer-Reiss, C., Schaeffer, P., Koopmans, M.P., de Leeuw, J.W., Lewan, M.D., Sinninghe Damsté, J.S. and Maxwell, J.R., 1998, Abundance and distribution of sulfur- and oxygen-bound components in a sulfur-rich kerogen during simulated maturation by hydrous pyrolysis: *Organic Geochemistry*, in press.
- Schaeffer, P., Harrison, W.N., Keely, B.J. and Maxwell, J.R., 1995, Product distributions from chemical degradation of kerogens from a marl from a Miocene evaporitic sequence (Vena del Gesso, N. Italy): *Organic Geochemistry*, v. 23, pp. 541-554.
- Seewald, J.S., 1994, Evidence for metastable equilibrium between hydrocarbons under hydrothermal conditions: *Nature*, v. 370, pp. 285-287.

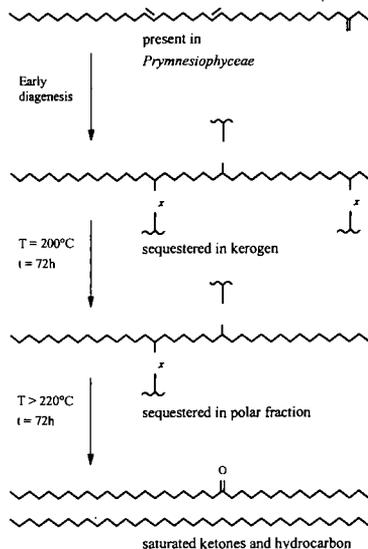


Fig. 1. Biomarker thermal generation sequence for C_{38} alkenone.

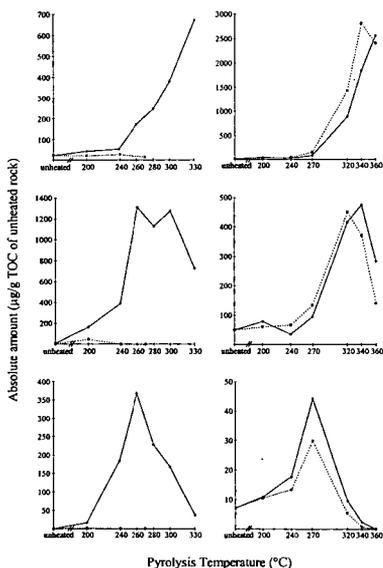


Fig. 2. Generation profiles of (a) octadecane, (b) phytane and (c) (20R)-5 α -24-ethylcholestane for the claystone and (d-f) limestone from hydrous (solid line) and anhydrous pyrolysis (stippled line) for 72 h. Anhydrous pyrolysis of the claystone does not generate biomarkers.