

HYDROGEN STABLE ISOTOPE RATIOS OF KEROGEN, BITUMEN, OIL, AND WATER IN HYDROUS PYROLYSIS

A. Schimmelmann¹, M. D. Lewan², and R. P. Wintsch¹

¹ Department of Geological Sciences, Indiana University, 1005 East 10th Street,
Bloomington, IN 47405-1403

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

INTRODUCTION

Diverse isotopic evidence has been mounting in favor of an active role of water in the chemical transformation of kerogen to bitumen, oil, and gas, and also as an agent promoting hydrogen isotopic exchange with organic hydrogen (e.g., Koepp, 1978; Schoell, 1981; Hoering, 1984; Stalker et al., 1998). At low temperatures, water-hydrogen exchanges quickly with isotopically labile organic hydrogen most of which is bound to organic nitrogen, sulfur, and oxygen (NSO-functional groups; Koepp, 1978; Schoell, 1981). In contrast, most carbon-bound hydrogen does not exchange with water at neutral pH, low temperature, and in the absence of a catalyst, thus conserving the D/H ratios of *n*-alkanes at temperatures well above 150°C (Hoering, 1984; Koepp, 1978). Some aromatic hydrogen and few alkyl hydrogen sites adjacent to branching and carbonyl positions may exchange with water-hydrogen at temperatures as low as 100°C (Alexander et al., 1982; Werstik and Ju, 1989), especially at low pH via carbonium ion mechanisms. At higher temperatures, extensive exchange between water-derived hydrogen and organic hydrogen is attributed to the quenching of free organic radical sites (Hoering, 1984; Lewan, 1997; Stalker et al., 1998). Thermodynamic calculations indicate that reactions of water with alkyl free radicals are highly favorable under experimental and natural maturation conditions (Lewan, 1997, p. 3714-3715).

The determination of meaningful D/H ratios in organic substrates needs to take into account the isotopically labile organic hydrogen that perpetually exchanges with ambient moisture. Only the low concentration of labile NSO-linked hydrogen in oil and bitumen warrants the use of δD of total organic hydrogen. In contrast, kerogens of low to moderate thermal maturity are more hydrophilic because they contain abundant NSO-functional groups that often contain labile hydrogen. In this study we control the isotopic composition of labile hydrogen in kerogen by dual equilibration with isotopic standard water vapors at 115°C, followed by a mass balance calculation to arrive at the isotopic composition of non-labile hydrogen in kerogen (Schimmelmann, 1991). To avoid semantic confusion about different types of exchangeable hydrogen, this study operationally defines "labile organic hydrogen" as the fraction of organic hydrogen that readily exchanges with water vapor at 115°C.

EXPERIMENTAL

We used four thermally immature source rocks that encompass different types of kerogen: Type-I (Mahogany Shale of the Eocene Green River Fm. in Utah), type-II (Clegg Creek Member of the Devonian-Mississippian New Albany Shale in Indiana), type-IIS (Senonian Ghareb Limestone from Jordan), and type-III (Paleocene lignite from Calvert Bluff Fm. of the Wilcox Gp. in Texas).

Hydrous pyrolyses were performed in stainless steel pipe reactors (pipe length 15.1cm, o.d. 1.9cm, internal volume ca. 25.5mL) that were loaded with 5.5 to 10g of rock chips (diameter 2mm to 7mm). The rock was submerged in 10 to 11ml of 0.093 molar aqueous ammonium chloride solution under nitrogen. Three isotopically different aqueous phases were

used with initial δD values of -110, +290, or +1260 per mil. After hydrous pyrolysis and cooling to room temperature, expelled oil or wax on the water surface was collected separately from the water phase. Bitumen was Soxhlet-extracted from dried and powdered rock. Kerogen was prepared by demineralization of bitumen-extracted powdered rock. The isotopic equilibration of aliquots of kerogen at 115°C in isotopic standard water vapors, the conversion of water and organic hydrogen to elemental hydrogen for mass-spectrometric analysis, and the calculation of δD values of non-labile hydrogen in kerogen were described by Schimmelmann (1991). We are aware that water will also continuously exchange with hydrogen in clay minerals and with exchangeable (labile) organic hydrogen.

RESULTS

Waters with strong initial D-enrichment transfer deuterium to organic phases over time, whereas water with an initial δD value of -110 per mil receives organic deuterium. In effect, the directions of isotopic shifts for organic hydrogen in kerogen, bitumen, and oil are opposite to the respective shifts observed for water, depending on the starting δD value of water. Our isotopic choices for water as the dominant hydrogen pool determine the directions of isotopic exchange for all minor, organic hydrogen pools. The converging patterns of isotopic changes of waters and the associated type-II kerogen, bitumen, and oil from 330°C hydrous pyrolysis experiments are shown in Figure 1.

Our D/H data permit a mass balance approach to estimate the fraction of organic hydrogen in kerogen, bitumen, and oil that is derived from water in hydrous pyrolysis experiments. Our calculations are based on hydrous pyrolysis experiments with starting δD values for water of -110 and + 1260 per mil. We cannot discriminate between added hydrogen and hydrogen that was exchanged at temperatures above 115°C, but the calculations are not affected by the presence of labile hydrogen in kerogen. Details of underlying assumptions and algorithms are presented elsewhere (Schimmelmann et al., in review). The percentage P (Table 1) reflects the estimated abundance of water-derived hydrogen in bitumen and oil, and in non-labile organic hydrogen in Kerogen. The isotopic influence of water-hydrogen on type-II kerogen and associated bitumen and oil from New Albany Shale increases over time at 330°C, and with increasing temperature over 72 hours (Table 1a). The four types of source rocks used in this study differ in their content of potentially reactive and exchangeable hydrogen, and therefore in their P values and in their ability to shift δD values of water (Table 1b).

DISCUSSION

Many chemical and physical processes affecting the hydrogen isotopic balance between reactants and phases occur simultaneously and continuously during hydrous pyrolysis of immature source rocks in contact with water. Some bitumen is already present in immature source rocks prior to hydrous pyrolysis, but significant amounts are generated from the kerogen with increasing temperature, along with low-molecular weight compounds (Lewan, 1997). With increasing temperature, the water-saturated bitumen partially decomposes into an immiscible hydrophobic oil that is expelled from the rock (Lewan, 1997). Our D/H data represent time-series of snapshots of this dynamic system of water, kerogen, bitumen, and oil.

Our P values in Table 1b show that hydrogen in type-I kerogen and its associated bitumen and expelled wax is the most isotopically conservative, i.e. with the lowest P values, whereas hydrogen is least isotopically conservative in type-IIS kerogen and its associated bitumen and expelled oil. The decrease in P values in the order of kerogen-types IIS > II \approx III > I can be interpreted in terms of basic chemical structural differences. The strongly aliphatic

type-I kerogen (Tissot and Welte, 1984; Horsfield et al., 1994) has a large isotopically conservative pool of hydrogen in its mostly *n*-alkyl linkages, and can thus be expected to generate the smallest number of free radicals during hydrous pyrolysis and to express the smallest *P* values for kerogen, bitumen, and oil. Type-II kerogen is expected to contain a more branching molecular carbon structure, with larger propensity toward generation of free radical sites and consequently larger *P* values. A similar increase in *P* in type-III kerogen may be the result of a larger abundance of oxygen in lignite, which favors the formation of free radicals. Type-IIS kerogen would form even more free radicals under the same thermal conditions because it contains labile S-S and C-S bonds with low activation energy (Tomic et al., 1995; Lewan, 1998).

CONCLUSIONS

Immature source rocks containing different types of kerogen were heated in hydrous pyrolysis experiments. D/H ratios were monitored in isolated kerogen, extracted bitumen, expelled oil, and ambient water. The isotopic transfer of hydrogen between water and organic hydrogen increases with higher temperature and longer duration of hydrous pyrolysis, via exchange and/or addition, resulting in a convergence of δD values of water and of organic hydrogen. Isotopic mass-balance calculations suggest that, depending on temperature, time, and source rock type, between 35 and 75% of carbon-bound hydrogen is ultimately derived from water-hydrogen. Organic hydrogen in kerogen, bitumen and oil/wax from source rocks containing different types of kerogen rank from least to most isotopically conservative in the order IIS < II \approx III < I, which is consistent with models of chemical reactivity in kerogens through maturation.

The prospect of water-hydrogen becoming available to maturing organic matter may pleasantly revise estimates of oil and gas potentials in sedimentary basins, but its potential D/H isotopic implications may force isotope geochemists to rethink their interpretation of D/H ratios in maturing fossil fuels and associated formation waters. The unresolved controversy about substituting long geologic time in natural maturation with higher temperature in artificial maturation, however, advises to caution when extrapolating our specific isotopic findings from hydrous pyrolysis to D/H ratios in fossil fuels.

ACKNOWLEDGEMENTS

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research with grant #31203-AC2, to the U.S. Geological Survey under Energy Resources Project 51564, and to NATO Collaborative Research Programme grant 971381.

REFERENCES

- Alexander, R., Kagi, R. I., and Larcher, A. V., 1982, Clay catalysis of aromatic hydrogen-exchange reactions, *Geochim. Cosmochim. Acta* 46: 219-222.
- Hoering, T. C., 1984, Thermal reactions of kerogen with added water, heavy water and pure organic substances, *Org. Geochem.* 5: 267-278.
- Horsfield, B., Curry, D. J., Bohacs, K., Litke, R., Rullkötter, J., Schenk, H. J., Radke, M., Schaefer, R. G., Carroll, A. R., Isaksen, G., and Witte, E. G., 1994, Organic geochemistry of freshwater and alkaline lacustrine sediments in the Green River Formation of the Washakie Basin, Wyoming, U.S.A., *Org. Geochem.* 22: 415-440.
- Koepp, M., 1978, D/H isotope exchange reaction between petroleum and water: A contributory determinant for D/H-isotope ratios in crude oils? In *Short papers of the Fourth International Conference, Geochronology, Cosmochronology, Isotope Geology.* (ed R.

- E. Zartman), *USGS Open-File Report 78-701*: 221-222. Reston VA, US Geological Survey.
- Lewan, M. D., 1997, Experiments on the role of water in petroleum formation, *Geochim. Cosmochim. Acta* **61**: 3691-3723.
- Lewan, M. D., 1998, Sulphur-radical control on petroleum formation rates, *Nature* **391**: 164-166.
- Schimmelmann, A., 1991, Determination of the concentration and stable isotopic composition of non-exchangeable hydrogen in organic matter, *Anal. Chem.* **63**: 2456-2459.
- Schimmelmann, A., Lewan, M. D., and Wintsch, R. P., (in review), D/H isotope ratios of kerogen, bitumen, oil, and water in hydrous pyrolysis of source rocks containing kerogen types-I, -II, -IIS, and -III, submitted to *Geochim. Cosmochim. Acta*.
- Schoell, M., 1981, D/H-Isotopenverhältnisse in organischen Substanzen, Erdölen und Erdgasen. *BMFT Forschungsbericht T 81-204*, 1-79, Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany.
- Stalker, L., Larter, S. R., and Farrimond, P., 1998, Biomarker binding into kerogens: evidence from hydrous pyrolysis using heavy water (D₂O), *Org. Geochem.* **28**: 239-253.
- Tissot, B. P., and Welte, D. H., 1984, *Petroleum Formation and Occurrence*. Springer-Verlag.
- Tomic, J., Behar, F., Vandembroucke, M., and Tang, Y., 1995, Artificial maturation of Monterey kerogen (Type II-S) in a closed system and comparison with Type II kerogen: implications on the fate of sulfur, *Org. Geochem.* **23**: 647-660.
- Werstiuk, N. H., and Ju, C., 1989, Protium-deuterium exchange of benzo-substituted heterocycles in neutral D₂O at elevated temperatures, *Can. J. Chem.* **67**: 812-815.

Table 1. Calculated percentage (*P*) of the amount of water-derived hydrogen in the total hydrogen of bitumen and oil, and in the non-labile hydrogen of kerogen, after hydrous pyrolysis experiments in waters with starting δD values of -110 and +1260 per mil. The $\Delta\delta D$ of water is the difference between the final δD values and the starting δD values in water, in per mil.

Hydrous Pyrolysis Experimental Conditions			Kerogen	Bitumen	Oil	$\Delta\delta D$ of Water (per mil)	
Kerogen Type	Temp. (°C)	Time (h)	<i>P</i> (%)	<i>P</i> (%)	<i>P</i> (%)	[starting δD values:]	
						[-110]	[+1260]
a) variations in temperature and time							
II	310	72	47.1	53.1	36.1	10	-115
II	330	12	42.6	48.3	33.9	9	-82
II	330	36	56.6	58.4	43.3	8	-91
II	330	72	61.7	61.9	50.3	11	-104
II	330	144	66.0	70.2	57.7	9	-111
II	350	72	74.5	73.1	58.9	14	-140
b) variations in source rock							
I	330	72	44.4	34.9	39.6	4	-152
II	330	72	61.7	61.9	50.3	11	-104
IIS	330	72	69.7	69.9	68.4	15	-186
III	330	72	69.5	56.9	44.6	22	-262

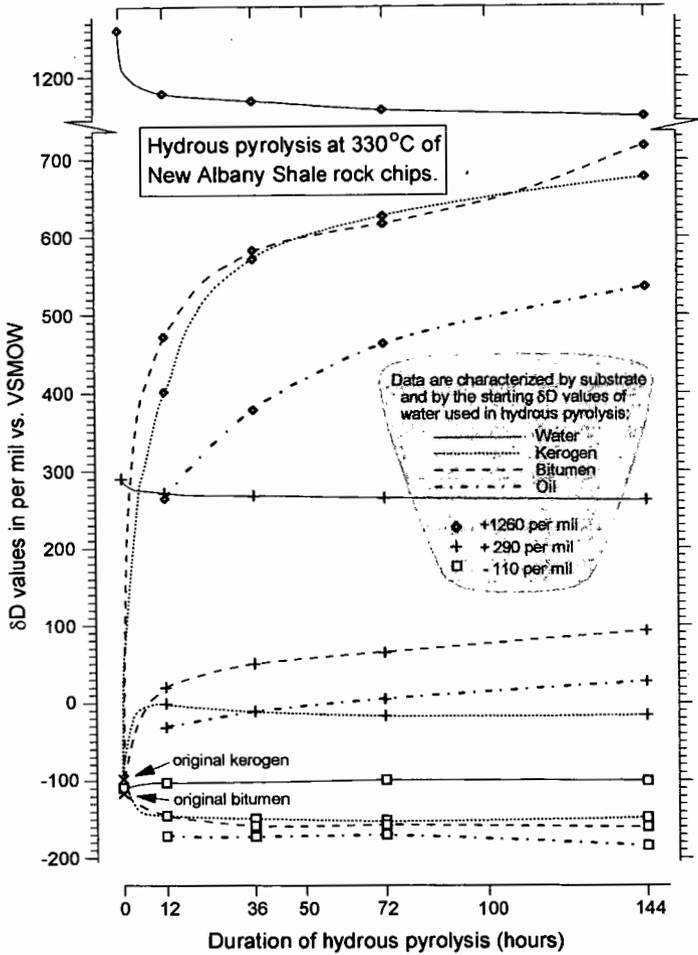


Fig. 1: D/H results from water, kerogen (non-labile hydrogen), bitumen, and oil from hydrous pyrolysis experiments, at 330°C of New Albany Shale. Three isotopically different waters were used, resulting in distinctly converging isotopic shifts of water and organic phases over time for each type of water used, due to isotopic hydrogen transfer between inorganic and organic hydrogen. Connecting lines are drawn to guide the eye. No oil was available before hydrous pyrolysis.