Experimental controls on D/H and ^{13}C/^{12}C ratios of kerogen, bitumen and oil during hydrous pyrolysis

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Abstract

Large isotopic transfers between water-derived hydrogen and organic hydrogen occurred during hydrous pyrolysis experiments of immature source rocks, in spite of only small changes in organic ^{13}C/^{12}C. Experiments at 330 °C over 72 h using chips or powder containing kerogen types I and III identify the rock/water ratio as a main factor affecting $\Delta\delta D$ for water and organic hydrogen. Our data suggest that larger rock permeability and smaller rock grain size increase the H-isotopic transfer between water-derived hydrogen and thermally maturing organic matter. Increasing hydrostatic pressure may have a similar effect, but the evidence remains inconclusive. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Hydrous pyrolysis has become a successful laboratory method to simulate thermal maturation of source rocks in a pressure reactor (Lewan, 1993, 1997, 1998; Andresen et al., 1995; Michels et al., 1995). Under appropriate conditions, source rock chips that are submerged under water expel an oil phase that collects on the water surface and shows surprising similarity to natural petroleum (Lewan, 1997). δD values of natural hydrocarbons have been used for exploration and paleoenvironmental reconstruction. However, we now recognize that hydrogen from water chemically participates in the thermal maturation of organic matter (Siskin and Katritzky, 1991; Price, 1994; Seewald et al., 1998), and becomes part of organic hydrogen (Hoering, 1984; Lewan, 1993, 1997; Seewald, 1994; Stalker et al., 1995, 1998; Junk and Catallo, 1997; Seewald et al., 1998; ACS, 1999; Schimmelmann et al., 1999; Leif and Simoneit, 2000). This challenges us to re-evaluate experimentally the utility of D/H ratios in thermally matured fossil fuels and formation waters for exploration and paleoenvironmental reconstructions. The presence of excess water in thermal maturation of sedimentary organic matter also fosters the phase separation between oil and bitumen, which is a prerequisite for oil migration, and thus affects the overall hydrogen and carbon isotope distribution among organic phases like kerogen, bitumen, and oil.

The influence of higher temperature and longer reaction time in hydrous pyrolysis experiments resulting in increased hydrogen isotopic transfer between water-derived hydrogen and organic hydrogen pools was documented by Schimmelmann et al. (1999) for four different source rocks. The present study explores the roles

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of water/rock ratio, grain size, and pressure at constant temperature and time. We avoid the word 'exchange' in describing the hydrogen isotope transfer between water-derived hydrogen and organic hydrogen, because the term 'exchange' fails to address the addition of hydrogen from inorganic sources to organic free radicals in quenching reactions, nor does it apply to the saturation of alkene groups. The broader term 'isotopic transfer' is better suited to account for the analytically determined net D-enrichment of organic hydrogen pools when in contact with hot, D-enriched water.

2. Methods

Compositions of two thermally immature source rocks utilized in this study are given in Table 1. All waters used in the hydrous pyrolysis experiments for this study had a starting δD value of $+1260$ per mil. The experimental conditions of the various thermal maturation experiments were a constant 330 °C for 72 h, but differed in pressure and loads (Table 2). Seven

"GC"-labeled experiments were performed in cylindrical gold-cells (length 10 cm, i.d. 5 mm, headspace filled with argon) that were loaded with powdered rock (diameter 50 μm) and water, sealed by arc-welding, placed in the bore of a hydrothermal pressure vessel, and heated with a thermal accuracy of ±7 °C. Two "SS"-labeled experiments were run in stainless steel reactors (Schimmelmann et al., 1999) and used 2–7 mm diameter rock chips that were submerged under water, with nitrogen filling the headspace. The thermal accuracy of "SS"-experiments was ±1 °C. The weights of all loaded GC and SS reactor vessels before and after heating were unchanged to exclude the possibility of material loss due to leakage.

The "SS"-experiments yielded expelled oil that could be sampled from the surface of the water phase after hydrous pyrolysis. In the case of lignite, the expelled oil was waxy and solidified at room temperature. The recovered rock chips were dried and powdered in a ball mill. The extraction of rock powder with chloroform yielded bitumen. The "GC"-hydrous pyrolysis experiments in narrow gold cells at higher pressures required rock powder and smaller

Table 1
Characterization of immature source rock starting material

Kerogen type	Rock unit name, location, age; reference	TOC[a]	Kerogen		Bitumen	
		wt.%	$\delta D_{nonlabile}$[b]	$\delta^{13}C_{PDB}$	δD	$\delta^{13}C_{PDB}$
I	Mahogany Shale, Green River Fm., Utah, Eocene; Ruble et al., 1995	15.23	−150	−30.33	−224	−31.32
III	Lignite from the Calvert Bluff Fm., Wilcox Group, Texas, Paleocene; Breyer, 1997	58.0	−130	−26.42	−145	−28.16

[a] TOC = total organic carbon.
[b] $\delta D_{nonlabile}$ = δD value of organic hydrogen in kerogen that does not exchange with water vapor at 115 °C (further details in Schimmelmann et al., 1999).

Table 2
Experimental conditions of hydrous pyrolysis experiments in gold cells (GC-numbers) and stainless steel reactors (SS-numbers)

Experiment No.	Kerogen type	Pressure (MPa)	Rock		Water load (g)	Rock:water weight ratio
			Diameter	Load (g)		
GC-1	I	50	<50 μm	0.484	0.15	3.23
GC-2	I	50	<50 μm	0.475	0.15	3.17
GC-3	I	400	<50 μm	0.626	0.15	4.17
GC-4	I	400	<50 μm	0.983	0.15	6.55
GC-5	III	54	<50 μm	0.133	0.15	0.89
GC-6	III	400	<50 μm	0.228	0.15	1.52
GC-7	III	400	<50 μm	0.487	0.15	3.25
SS-1	I	~13[a]	2–7 mm	10.0	10.0	1.00
SS-2	III	~13[a]	2–7 mm	5.5	11.0	0.50

[a] Vapor pressure at 330 °C.

amounts of water. "GC"-experiments, therefore, neither allowed sampling of an expelled oil phase nor the direct sampling of a residual water phase. Instead, after the piercing of gold cells, we inserted the cells individually in Pyrex side arms attached to small 6 mm o.d. Pyrex U-tubes that were cooled externally with liquid nitrogen and connected to a vacuum line. Water and a volatile hydrocarbon fraction from each gold cell were thus freeze-dried into a U-tube. The U-tubes were finally sealed at both ends with a micro-torch and the contents allowed to warm to room temperature. A sharp phase separation resulted for water and the supernatant liquid, clear hydrocarbons. One side of each U-tube was opened and custom-made narrow-bore Pyrex capillaries were used to selectively subsample the water phase for D/H determination. The dry rock powder was extracted with chloroform to yield bitumen which includes hydrocarbons that would have been expelled as oil in the presence of a large excess of water during hydrous pyrolysis. Extracted bitumen from "GC"-experiments is, therefore, the approximate equivalent of 'bitumen + oil' from "SS"-experiments.

Kerogens were prepared from chloroform-extracted rock powder using the HF/BF$_3$-method (Robl and Davis, 1993). Our earlier study (Schimmelmann et al., 1999) had used the conventional HCl/HF kerogen preparation method. To document the isotopic comparability of both methods, we prepared pairs of kerogens from rocks using both methods. Analytical procedures, including additional heavy-liquid demineralization of kerogens, isotopic equilibration of labile (e.g. exchangeable with water vapor at 115 °C) hydrogen in kerogens to arrive at δD values of nonlabile hydrogen in kerogen, combustion of organic substrates to yield CO$_2$ and water, reduction of water to H$_2$ gas, and the stable isotope mass-spectrometry followed the description by Schimmelmann et al. (1999).

We report our hydrogen isotopic data according to Coplen's (1996) guidelines relative to Vienna standard mean ocean water VSMOW (zero per mil) and normalized to standard light arctic precipitation SLAP (-428 per mil). Mass-spectrometric results in customary δ-notation have a precision of ± 1.5 per mil for δD within the range of natural abundance, and ± 0.05 per mil for $\delta^{13}C_{PDB}$ values. We caution that the accuracy deteriorated to an estimated ± 15 per mil for δD values above $+1000$ per mil, due to uncertainty in the extrapolation of the VSMOW–SLAP-based calibration without additional absolute standards with strong D-enrichment.

3. Results

Our analytical results derive from two thermally immature source rocks prior to artificial thermal maturation (Table 1) and from 9 hydrous pyrolysis experiments at 330 °C for 72 hours (Table 2).

3.1. Small variance of $^{13}C/^{12}C$ ratios

Carbon stable isotope ratios of kerogen, bitumen and oil show relatively minor variance as a response to thermal maturation. The δ^{13}C results in Table 3 underscore the well-known isotopic disproportionation of sedimentary organic carbon during thermal maturation into ^{13}C-depleted low-molecular hydrocarbon compounds and relatively ^{13}C-enriched remaining kerogen, as documented from anhydrous pyrolysis (Sackett, 1978; Peters et al., 1981; Arneth and Matzigkeit, 1986; reviewed by Whiticar, 1996), hydrous pyrolysis (Andresen et al., 1995; Everlien et al., 1995), and in particular from hydrous

Table 3
Analytical results from hydrous pyrolysis experiments in gold cells (GC) and stainless steel reactors (SS)[a]

Experiment No.	Water δD_{final}	Kerogen		Bitumen		Oil	
		$\delta D_{nonlabile}$[b]	$\delta^{13}C_{PDB}$	δD	$\delta^{13}C_{PDB}$	δD	$\delta^{13}C_{PDB}$
GC-1	848	*331*	*−29.65*	240[c]	−30.66	n.d.[d]	n.d.[d]
GC-2	815	*337*	*−29.68*	241[c]	−30.64	n.d.[d]	n.d.[d]
GC-3	879	*278*	*−30.16*	195[c]	−30.79	n.d.[d]	n.d.[d]
GC-4	669	*218*	*−30.03*	124[c]	−30.77	n.d.[d]	n.d.[d]
GC-5	875	*554*	*−25.94*	371[c]	−27.24	n.d.[d]	n.d.[d]
GC-6	735	*448*	*−26.01*	322[c]	−27.13	n.d.[d]	n.d.[d]
GC-7	n.d.	*295*	*−25.97*	195[c]	−27.39	n.d.[d]	n.d.[d]
SS-1	1108	387, *382*	−29.56, *−29.53*	246	−30.48	269	−31.30
SS-2	998	607, *611*	−26.09, *−26.08*	451	−27.04	319	−27.11

[a] Data in bold italic print indicate that the Robl and Davis (1993) BF$_3$- method was used for the preparation of kerogens.
[b] $\delta D_{nonlabile}$ = δD value of organic hydrogen in kerogen that does not exchange with water vapor at 115 °C.
[c] Extracted bitumen contains the non-volatile oil fraction.
[d] Oil was not recovered as an expelled, separate phase following hydrous pyrolysis in gold cells.

pyrolysis of a Green River Fm. shale sample similar to the one used in this study (Collister et al., 1992).

3.2. Rock/water ratio

Hydrous pyrolysis reactors are closed systems where the magnitude of isotopic shifts depends in part on the relative sizes of the participating hydrogen pools. The rock/water ratio is thus an influential parameter because it determines the mass ratio of inorganic and organic hydrogen. During thermal maturation of source rocks, water with a starting δD value of $+1260$ per mil is transferring deuterium to organic matter that has starting δD values ranging from -224 to -130 per mil (Table 1). This hydrogen isotopic transfer increases $\delta D_{organic}$ values from originally negative to positive values and at the same time decreases δD_{water} values (Table 3). Experiments GC-1 and GC-2 with similar rock/water ratios and otherwise identical experimental parameters indicate good reproducibility of δD values (Fig. 1). The paired experiments GC-3 and GC-4 for Green River Fm. shale, and experiments GC-6 and GC-7 for lignite were all performed at a pressure of 400 MPa and differ only in their rock/water ratios (Table 2). Each pair shows organic hydrogen isotopic differences that are directly attributable to, and consistent with increasing rock/water ratios (Fig. 1). Shifts in δD_{water} values during hydrous pyrolysis experiments at low rock/water ratios up to 1.52 in Fig. 1 are much larger for the organic-hydrogen-rich lignite (dotted line with steeper slope) with abundant D-depleted organic hydrogen than for the relatively mineral-rich Green River Fm. shale (solid line with smaller slope) containing less abundant organic hydrogen. Shifts in δD from experiments GC-5, SS-1, and SS-2, however, not only reflect changes in rock/water ratio (Fig. 1), but are additionally affected by differences in pressure and grain size (Table 2). A linear relationship between δD values of kerogens and bitumens is apparent in Fig. 3, regardless of experimental differences. The rock/water ratio is the key factor determining δD values of the two organic phases that are immobile during hydrous pyrolysis experiments. δD Values of immature, unreacted source rocks fall on or near the regression line, in spite of the fact that they were not used in the linear regression. Data for untreated kerogen and bitumen reflect, essentially, infinite rock/water ratios. The δD_{water} value for experiment GC-3 is abnormally high in comparison with other gold cell data and likely reflects an analytical error, but still agrees qualitatively with our observation of a strong rock/water influence (Fig. 1). Experiment GC-3, however, will not be considered further when investigating other, more subtle experimental influences on D/H shifts.

In contrast to D/H ratios, carbon isotope ratios for each source rock type show only small and nonsystematic shifts over increasing rock/water ratios (Table 3).
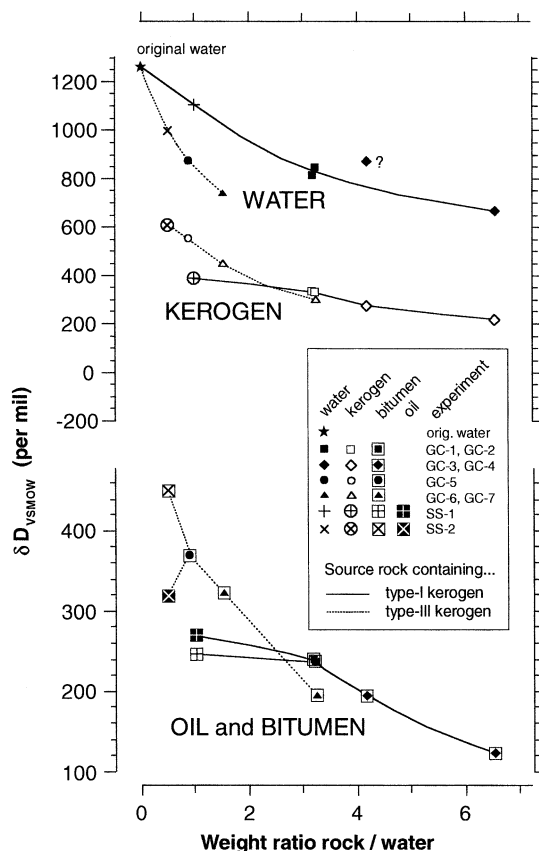

Fig. 1. Hydrogen isotope data from hydrous pyrolysis experiments at 330 °C for 72 h, utilizing thermally immature source rocks that contain kerogen types-I and-III. All waters had an initial δD value of $+1260$ per mil. With decreasing rock/water ratio the organic hydrogen pools tend to receive more deuterium from water via isotopic transfer. SS-1 and SS-2 sampled supernatant oil separate from extracted bitumen, whereas experiments in gold cells yielded only one combined 'bitumen' phase upon extraction. We caution that in many experiments the rock/water ratio is not the only variable influencing D/H ratios (see Table 2).

3.3. Grain size, permeability, and pressure

Experiments SS-1 and SS-2 utilized rock chips, whereas all gold cell experiments used rock powder. SS-1 using dense, mineral rich Green River Fm. shale with a rock/water ratio of 1.0 is the only experiment that does not fit the pattern from water-rich to rock-rich experiments in Fig. 2, but plots where one expects a rock/water ratio of 3. SS-2 using permeable lignite chips fits the pattern in Fig. 2 regardless of grain size. A general pattern of decreasing hydrogen isotopic differences $\Delta\delta D_{water-organic}$ with increasing pressure is suggested in Fig. 3. We caution, however, that the experiments also varied slightly in their rock/water ratios and used different grain sizes of source rocks (Table 2). In the case
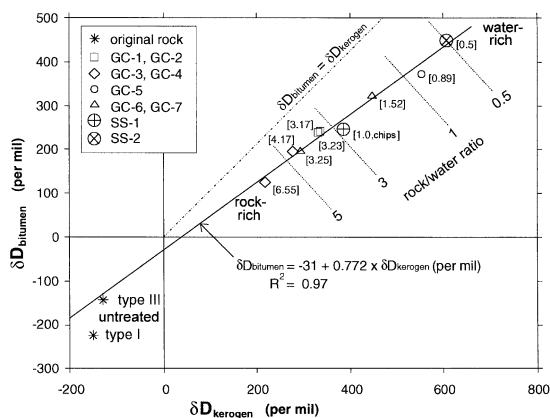
Fig. 2. δD Values of kerogens and bitumens of the 9 hydrous pyrolysis experiments define a linear regression line, with $R^2 = 0.97$. δD Values from immature, unreacted source rocks fall on or near the regression line, in spite of the fact that they were not used in the linear regression. Numbers in brackets indicate experimental rock/water ratios; untreated kerogen and bitumen reflect essentially infinite rock/water ratios.
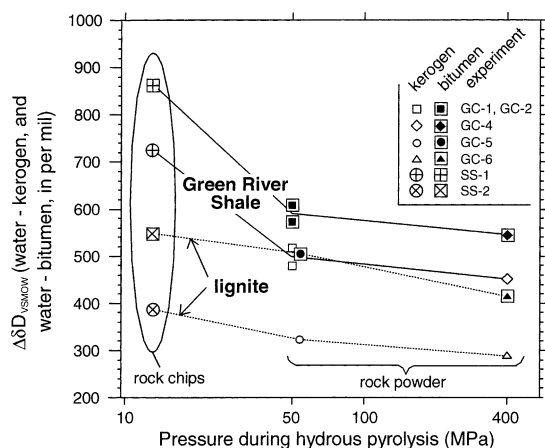

Fig. 3. The isotopic differences $\Delta\delta D$ between δD values of the final waters and the δD values of organic hydrogen pools after hydrous pyrolyses of Green River Fm. shale and lignite containing types-I and III kerogens, respectively. All waters had an initial δD value of $+1260$ per mil. The pressure is plotted on a logarithmic scale. Experiments at 13 MPa in stainless steel reactors utilized rock chips, whereas experiments at higher pressures in gold cells used powdered rock. Lines are drawn to guide the eye. We caution that in many experiments pressure is not the only variable influencing $\Delta\delta D$ (see Table 2).

of lignite, the $\Delta\delta D_{\text{water-organic}}$ values in Fig. 3 plot in an almost linear fashion over the logarithmic pressure regardless of grain size, suggesting that high porosity and presence of fissures in lignite limits the significance of grain size. In contrast, Green River Fm. shale rock chips (at 13 MPa) plot with much larger $\Delta\delta D_{\text{water-organic}}$ values when compared against Green River Fm. shale

powder (at 50 MPa). Larger grain size of the denser and less permeable shale may be responsible for retardation of isotopic transfer due to slower transportation or diffusion of water through rock chips.

3.4. Isotopic influence from the method of kerogen preparation

The two methods of wet-chemical kerogen preparation (HCl/HF or BF_3) do not result in significant carbon isotopic differences between pairs of kerogens. The hydrogen isotopic diffrences are 4–5 per mil and nonsystematic. Five other pairs of kerogens from shales, which are not part of this study, showed even smaller hydrogen isotopic differences of up to 3 per mil. The BF_3-method (Robl and Davis, 1993) operates at room temperature and has the advantage of minimizing chemical degradation of kerogen, in contrast to conventional demineralization in hot, concentrated acids. Additional advantages are apparent in the speed and safety of the BF_3 method, and in a lower ash content of kerogens when compared with the HCl/HF method.

4. Discussion

4.1. Comparability of results from experiments in steel and gold reactors

The spatial limitation of experiments in small gold cells prevented us from conducting specific pairs of experiments in gold cell and carburized stainless steel reactors, to test for surface-catalytic artifacts while keeping all other experimental variables constant. The isotopic variance observed in our experiments can be attributed to distinct experimental conditions and gives no evidence for catalytic influence of either gold or carburized stainless steel surfaces in the process of artificial thermal maturation. This interpretation is supported by kinetic results from hydrous pyrolysis experiments that indicate the direct comparability of data from gold-cell reactors and from carburized stainless steel reactors (Knauss et al., 1997).

4.2. Hydrogen isotopic transfer in artificial maturation

Isotopic transfer between water-derived hydrogen and organic hydrogen under conditions of artificial thermal maturation of organic matter was observed in several studies using D_2O (Hoering, 1984; Stalker et al., 1995, 1998; Lewan, 1997; Leif and Simoneit, 2000) and deuterium-enriched waters (Schimmelmann et al., 1999). the activated transition states during reaction of organic matter, via radical and/or ionic mechanisms, offer a window of opportunity for water-derived hydrogen to covalently bond with organic carbon. Even in the

absence of reactions involving carbon-carbon bond breaking, some carbon-bound hydrogen is isotopically exchangeable with water-derived hydrogen. For example, some hydrogen in condensed and substituted aromatic systems is exchangeable at elevated temperature, and most N-, O-, and S-bound organic hydrogen is exchangeable with water-hydrogen even at room temperature in contact with water vapor (see Schimmelmann et al., 1999). In contrast, exchange experiments of aliphatic and low-molecular aromatic compounds in D_2O in absence of organic-chemical reactions suggested that most hydrogen in hydrocarbons exchanges very slowly at 200–240 °C and that measurable δD shifts are not to be expected in less than 10^8 years for uncatalyzed exchange under natural conditions (Koepp, 1978; Yeh and Epstein, 1981; Schoell 1984).

The hydrogen isotopic changes during artificial maturation experiments depend on the mass ratios of the available hydrogen pools, which are controlled by the initial ratio of rock to water (Fig. 1). For example, the isotopic shift $\Delta\delta D_{water} = \delta D_{original\ water} - \delta D_{final\ water}$ is smallest in stainless steel reactors (experiments SS-1 and SS-2) where more water was loaded relative to rock, whereas $\Delta\delta D_{organic}$ values are smallest in gold cell reactors in experiments where rock was in contact with relatively little water. In the latter case, the $\Delta\delta D_{water}$ is large because some ^1H from D-depleted organic functional groups (–OH, –COOH, –NH$_2$, etc.) is transferred from organic matter and from hydrogen-containing minerals in source rock to water. The isotopic consequences of a chosen rock/water ratio are merely reflecting the overall isotopic mass balance in a closed system and are not constraining chemical reactions during thermal maturation. Lewan (1997) has shown that the rock/water ratio has no effect on the extent of chemical reaction during hydrous pyrolysis, as measured by expelled oil generation.

Equal rates of deuterium transfer from water to either kerogen or bitumen during hydrous pyrolysis would result in a slope of one for the regression line in Fig. 2. Instead, the slope of 0.77 ($n = 9$; $R^2 = 0.97$) suggests that for every four deuterium atoms added to kerogen, only approximately three D atoms enter bitumen during hydrous pyrolysis. It is intriguing that kerogens and bitumens from untreated source rocks falls near the regression line, in spite of the fact that the data were not used in the linear regression. More data from different source rocks are needed.

By plotting not the δD values of kerogen or bitumen, but instead the difference $\Delta\delta D_{water-organic}$ between δD values of water and δD values of kerogen or bitumen (Fig. 3), we reduce the influence of the rock/water ratio in our attempt to identify additional experimental controls that influence hydrogen isotopic transfer. Fig. 3 suggests that increasing pressure enhances the rate of isotopic transfer between inorganic and organic hydrogen.

Increased pressure may force more D-enriched H_2O into the bitumen-soaked pore space of the less compressible rock matrix, thus increasing the ratio of water-hydrogen versus organic hydrogen within the source rock, and resulting in a net increase in deuterium transfer to organic hydrogen. A major effect of hydrostatic pressure enhancing the rate of diffusion through micropore systems was noted by Noor et al. (1986). Higher pressure also increases the solubility of water in bitumen, similar to the situation between water and silicate and basaltic melts where the partial molar volume of dissolved H_2O is smaller than the molar volume of free H_2O (Yoder, 1979; Pineau et al., 1998). Hydrostatic pressure has long been recognized as a factor in the thermal maturation of organic matter (Landais et al., 1994; Michels et al., 1994, 1995), although possibly of limited influence (Knauss et al., 1997). Higher pressure in hydrous pyrolysis of Woodford Shale (containing type-II kerogen; Landais et al., 1994; Michels et al., 1994, 1995) was reported to reduce and retard the chemical maturation of kerogen and polar compounds, which seems to contradict our interpretation of isotopic results from type-I and-III source rocks. However, the Woodford Shale studies do not give assurance that intergranular and headspace within sealed gold cells under hydrous pyrolysis conditions were sufficiently small relative to the available volume of liquid water to ensure that rock, organic matter and water experienced hydrostatic fluid pressure rather than grain-supported lithostatic pressure. Lithostatic pressure would not be conveyed to organic matter and fluid phases and would thus improperly test for the influence of fluid pressure on the kinetics of organic reactions in the presence of water. Our gold cell experiments used sufficient water to arrive at the described hydrostatic pressures of up to 400 MPa. We caution that our data presented in Fig. 3 are no proof for fluid pressure as an important control on hydrogen isotopic transfer, because our experiments do not maintain a constant rock/water ratio and thus cannot dismiss the claim that part or all of the observed $\Delta\delta D$ variance is caused by factors other than pressure. Further investigations are required.

The SS-2 results from rock chips of highly permeable lignite (containing type-III kerogen) compare well with results from gold cell experiments (GC-5, GC-6, GC-7) that used powdered lignite (Figs. 2 and 3). We suggest that the natural permeability of chips of lignite via fissures is so large that powdering to particle sizes below 50 μm does not greatly enhance isotopic transfer kinetics in our experiments. In contrast, chips (SS-1) and powder (GC-1, GC-2, GC-4) of the less permeable Green River Fm. shale show a large difference. SS-1 is also the only experiment that does not plot in Fig. 2 according to its experimental rock/water ratio of one, but indicates an effective rock/water ratio of about 3. There seems to be significantly less isotopic transfer

between inorganic and organic hydrogen phases in experiment SS-1 when the less permeable Green River Fm. shale (containing type-I kerogen) is used in 2–7 mm chips, in comparison with experiments GC-1, GC-2, and GC-4 that used powdered shale. The hypothesized effect of grain size for less permeable rock cannot be quantitatively separated from that of increasing pressure, but we feel that the observed strong isotopic differences across the small range of 13 MPa for SS to 50 MPa for GC experiments (Fig. 3) are unlikely caused by pressure when raising the pressure further to 400 MPa does not result in large isotopic changes. The $\Delta\delta D$ offset between lignite and shale-derived data in Fig. 3 is in part due to the more aliphatic, less reactive character of type-I kerogen in the Green River Fm. relative to more aromatic type-III kerogen from lignite.

4.3. Relevance of hydrogen isotopic results from hydrous pyrolysis for natural maturation

Extrapolation of our results from hydrous pyrolysis experiments to naturally maturing organic matter allows us to predict that the D/H ratios in organic fractions will become increasingly shifted in the direction of the isotopic composition of ambient formation waters. Marine source rocks would originally contain marine-derived formation waters with δD values close to zero per mil, whereas terrigenous source rocks would likely be in contact with somewhat D-depleted formation waters, depending on local meteoric and hydrologic conditions. In most cases the water would be significantly D-enriched relative to typically D-depleted organic hydrogen in sediments (Schoell, 1984). Isotopic
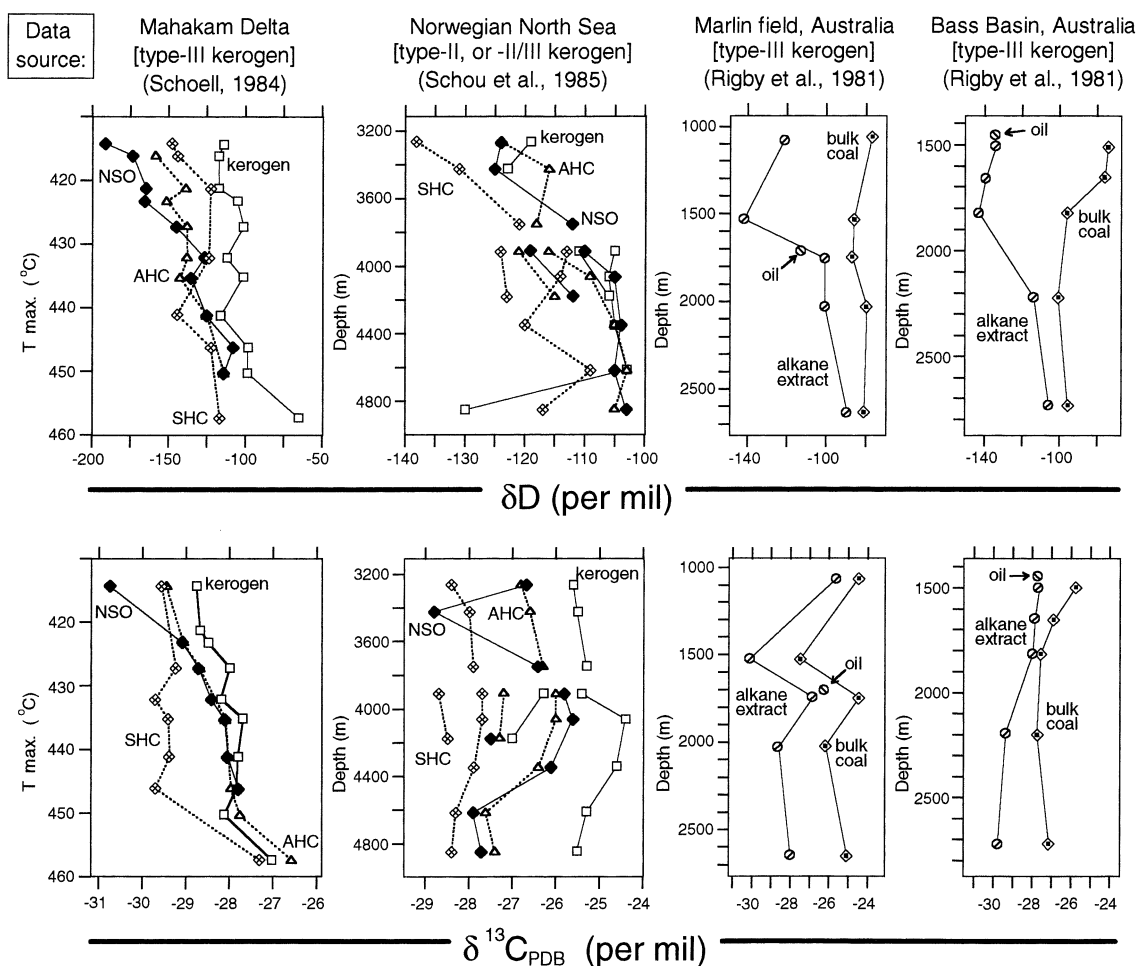

Fig. 4. Comparative overview of hydrogen and carbon isotope ratios in organic fractions from natural maturational sequences. Top row: δD values of kerogen, saturated hydrocarbons (SHC), aromatic hydrocarbons (AHC), and nitrogen- sulfur-, and oxygen-containing extractable compounds (NSO) show a strong general trend towards less negative δD values with increasing thermal maturity, or depth. Data on bulk coal are an exception, possibly because untreated bulk coal contains a significant amount of mineral hydrogen which influences bulk δD values. Bottom row: trends of $\delta^{13}C$ values over increasing thermal maturity strongly vary among the cited studies.

transfer between water-derived hydrogen and organic hydrogen will therefore shift organic hydrogen towards less negative δD values. Oil contains the highest concentration of aliphatic, isotopically non-exchangeable hydrogen (Koepp, 1978; Schoell, 1984). Indeed, Yeh and Epstein (1981) found a tentative correlation between δD values of 114 petroleum samples with latitude, but not with maturity. δD values of total hydrocarbons in light oils from marine source rocks tend to be less negative than those of non-marine origin (Shen, 1995). Likewise, the δD values of oils from Northeastern Brazil were found to be mainly related to δD_{water} values in the paleoenvironments in which the primary producers lived, but were not related to thermal maturation, biodegradation, or distance of the secondary migration (Santos Neto and Hayes, 1999). With increasing thermal maturity the hydrogen isotopic fate of immobile kerogen and bitumen is likely more complicated than that of oil, namely that the concentration of water-derived hydrogen in immobile phases may increase and will cause relative isotopic differences between phases or compound classes to decrease.

Our predictions are supported by several published coal and petroleum δD datasets across thermal maturation gradients (Fig. 4). Schoell's (1984) δD values from Mahakam Delta type-III kerogen, associated saturated hydrocarbon extract (SHC), aromatic hydrocarbon extract (AHC) and nitrogen-, sulfur-, and oxygen-containing extractable heterocomponents (NSO) all exhibit overall trends towards less negative δD values with increasing thermal maturity. Kerogen, AHC, and NSO also become isotopically more similar to each other, whereas the chemically less reactive (isotopically more conservative) SHC largely parallels the isotopic trends of kerogen. δD values of kerogen and extracts from the Norwegian North Sea also exhibit overall trends towards less negative δD and smaller $\Delta\delta D_{kerogen-bitumen}$ values with increasing thermal maturity (Schou et al., 1985). Likewise, extracts from Australian coals become more D-enriched over depth (Rigby et al., 1981). The extracts from coals isotopically agree well with associated oils, but δD values of the bulk coal are likely compromised by contamination from mineral hydrogen. Interestingly, the offshore coals and their extracts were found to be more D-enriched than their onshore counterparts, and the authors speculated that this was the result of hydrogen isotopic exchange between water and organic hydrogen in coal.

We agree with Schoell (1984) that climatic and biotic changes affecting the isotopic character of the original biomass may have contributed to D/H variability in geological settings over depth and time, but such influences are typically oscillatory in nature and rarely manifest themselves in long-term trends as depicted in Fig. 4. The loss of thermogenic [13]C- and D-depleted methane and other low-molecular hydrocarbons undoubtedly contributed to some observed isotopic trends in the residual organic matter, in particular in case of the Mahakam Delta data (Schoell, 1984), but the absence of a parallel ^{13}C-enrichment over depth in the other records in Fig. 4 suggests that thermogenic loss of hydrocarbons cannot adequately explain the observed D/H trends. Instead, the long-term trends towards D-enrichment coinciding with increasing thermal maturity are likely caused by isotopic transfer of relatively D-enriched, water-derived hydrogen during thermal-maturation reactions, as simulated in our hydrous pyrolysis experiments.

5. Conclusions

1. After temperature and time (Schimmelmann et al., 1999), the rock/water ratio is the third most important experimental control on the hydrogen isotopic transfer in hydrous pyrolysis.

2. Less deuterium uptake by organic matter in Green River Fm. shale than by organic matter in lignite may be attributed to the significantly smaller permeability of the denser shale when compared against the lignite with high microporosity and presence of fissures. An underlying mechanism may be the larger diffusive barrier for water in the bitumen-impregnated shale, especially when the shale is used in the form of chips rather than as a fine powder. An additional factor is likely the more aliphatic, less reactive character of type-I kerogen in the Green River Fm. relative to more aromatic type-III kerogen.

3. Inconclusive evidence suggests that higher hydrostatic pressure may cause increased hydrogen isotopic transfer. Additional experiments are needed.

4. In contrast to hydrogen, the organic carbon disproportionates isotopically during hydrous pyrolysis to kerogen, bitumen, and oil, expressing isotopic shifts of up to ca. 1 per mil, with no obvious dependence on pressure, grain size, or rock/water ratio. Thermogenic gas was not considered in this study.

5. Extrapolation of hydrous pyrolysis-derived isotopic results to natural thermal maturation predicts that D/H ratios in coal, kerogen, extracted bitumen, and to a lesser degree in oil, will be increasingly altered with rising thermal maturity by transfer of deuterium from ambient formation waters. Published D/H stratigraphic profiles confirm the expected ΔδD across maturational gradients for kerogen, oil fractions, and extracts. In the same stratigraphic profiles, carbon isotope ratios of the organic fractions follow different patterns that cannot be correlated uniformly with ΔδD or increasing thermal maturity.

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